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FAKULTET ZA FIZIČKU HEMIJU

Danica V. Bajuk-Bogdanović

ISPITIVANJE STABILNOSTI
12-VOLFRAMFOSFORNE,
12-VOLFRAMSILICIJUMOVE I
12-MOLIBDENFOSFORNE KISELINE U
RASTVORIMA

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Danica V. Bajuk-Bogdanović

INVESTIGATION OF STABILITY OF
12-TUNGSTOPHOSPHORIC,
12-TUNGSTOSILICIC AND
12-MOLYBDOPHOSPHORIC ACID
IN SOLUTIONS

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Mentor

Redovni profesor, dr Ivanka Holclajtner-Antunović

Univerzitet u Beogradu - Fakultet za fizičku hemiju

Članovi komisije

Vanredni profesor, dr Gordana Ćirić-Marjanović

Univerzitet u Beogradu - Fakultet za fizičku hemiju

Redovni profesor, dr Vesna Kuntić

Univerzitet u Beogradu - Farmaceutski fakultet

Docent, dr Snežana Uskoković-Marković

Univerzitet u Beogradu - Farmaceutski fakultet

Datum odbrane:

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Ispitivanje stabilnosti 12-volframfosforne, 12-volframsilicijumove i 12-molibdenfosforne kiseline u rastvorima

Rezime:

12-volframfosforna (WPA), 12-volframsilicijumova (WSiA) i 12-molibdenfosforna kiselina (MoPA) su heteropoli kiseline (HPK) koje pripadaju velikoj klasi jedinjenja koja se nazivaju polioksometalati. U osnovi struktura ovih kiselina je Keggin-ov anjon (KA) čija se hidrolitička stabilnost razlikuje od kiseline do kiseline, što je utvrđeno ULj, IC, ramanskom i ^{31}P NMR spektroskopijom. Najmanje je stabilna MoPA, kod koje roditeljska Keggin-ova struktura u razblaženim rastvorima ($2 \cdot 10^{-5} \text{ mol dm}^{-3}$) nije prisutna čak ni pri $\text{pH} < 1,0$, a u koncentrovanim rastvorima ($5 \cdot 10^{-2} \text{ mol dm}^{-3}$) egzistira samo pri $\text{pH} < 1,0$. WPA je stabilnija, i kod nje je roditeljski anjon prisutan pri $\text{pH} < 1,0$ u razblaženim, odnosno $\text{pH} < 1,5$ u koncentrovanim rastvorima. Najstabilnija je WSiA, kod koje je KA prisutan u razblaženim vodenim rastvorima do $\text{pH} = 8,5$ odnosno do $\text{pH} = 6,4$ u koncentrovanim rastvorima.

Korišćenje 50 % metanola kao rastvarača dovodi do stabilizacije KA u ovim kiselinama, tako da se u slučaju MoPA javlja sve do $\text{pH} = 3,5$ i u razblaženim i u koncentrovanim rastvorima. Za WPA u koncentrovanim rastvorima oblast pH u kojoj se javlja KA se proširuje do $\text{pH} = 2,5$, a u razblaženim čak i do $\text{pH} = 7,0$. Najstabilnija WSiA se dodatno stabilise u prisustvu metanola, pa se KA javlja sve do $\text{pH} = 11,5$ u razblaženim, odnosno $\text{pH} = 7,8$ u koncentrovanim rastvorima.

Proces dekompozicije WPA je delimično reverzibilan, a za vodene rastvore je potvrđena vremenska stabilnost u toku jedne godine. Prilikom upotrebe pufera za podešavanje pH vrednosti rastvora HPK, mora se voditi računa o mogućoj interakciji HPK sa puferom, kao što je to slučaj pri primeni TRIS pufera.

Dobijeni rezultati se mogu iskoristiti za utvrđivanje oblika HPK prisutnih u različitim sistemima. U slučaju polianilin - WPA mikro/nanostruktura KA je dominantno prisutna vrsta, ali se identifikuju i male količine Dawson-ovog i monolakunarnog KA. WPA i WSiA u inkubacionom medijumu (uz prisustvo enzima Na^+/K^+ -ATPaze i ATP), u obliku monolakunarnog KA, inhibiraju dejstvo enzima Na^+/K^+ -ATPaze, što je od značaja za različite biohemijske procese.

Ključne reči: heteropoli kiseline, solvolitička stabilnost, pH vrednost, ULj, IC, ramanska i ^{31}P NMR spektroskopija

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Title:

Investigation of stability of 12-tungstophosphoric, 12-tungstosilicic and 12-molybdophosphoric acid in solutions

Abstract:

Heteropoly acids (HPA): 12-tungstophosphoric (WPA), 12-tungstosilicic (WSiA) and 12-molibdophosphoric acid (MoPA) belong to the polyoxometalates, the huge and important class of compounds. The main structure of those acids is Keggin anion (KA). The hydrolytic stability of KA differs between acids, and that is confirmed by UV, IR, Raman and ^{31}P NMR spectroscopy. The less stable is MoPA, where parent Keggin structure in diluted solutions ($2 \cdot 10^{-5} \text{ mol dm}^{-3}$) not exists even on $\text{pH} < 1.0$, while in concentrated solutions ($5 \cdot 10^{-2} \text{ mol dm}^{-3}$) exists only if $\text{pH} < 1.0$. WPA is more stable; the parent Keggin anion is stable at $\text{pH} < 1.0$ in diluted, and $\text{pH} < 1.5$ in concentrated WPA solutions. The highest stability has WSiA, where KA remains *in toto* up to pH 8.5 and 6.4, in diluted and concentrated solutions, respectively.

The addition of methanol to the HPA solutions (50 % (v/v)) leads to KA stabilization for the investigated acids. As the result, KA remains stable up to pH 3.5 for both diluted and concentrated MoPA solutions. In presence of methanol, WPA structure remains stable till pH 2.5 in concentrated, and even to pH 7.0 in diluted solutions. In case of WSiA, the KA structure is present up to pH 11.5 and 7.8, in diluted and concentrated solutions, respectively.

The WPA decomposition process is partly reversible. Further, we confirmed the stability of the water solutions during the period of one year. In the case of buffer using, it is necessary to take into consideration the possible interactions of HPA with buffer's components (TRIS buffer was tested as an example).

The results can be used to determine the form of HPA present in different systems. In the case of polyaniline - WPA micro/nanostructures, KA is dominantly present species, while the traces of Dawson and monolacunar KA were identified by using IR spectroscopy. WPA and WSiA in the incubation medium (in the presence of commercial enzyme and its substrate-ATP) form monolacunary Keggin anion and exhibit concentration-dependent inhibitory effect on the activity of Na^+/K^+ -ATPase. This is important for different biochemical processes.

Keywords: heteropoly acids, solvolytic stability, pH values, UV, IR, Raman and NMR spectroscopy

Scientific field: Physical Chemistry

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1. UVODNI DEO

1.1. UVOD

12-volframfosforna (WPA), 12-volframsilicijumova (WSiA) i 12-molibdenfosforna kiselina (MoPA) su heteropoli kiseline (HPK) koje pripadaju velikoj klasi jedinjenja koja se nazivaju polioksometalati (POM).

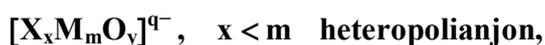
Polioksometalati su hemijski veoma raznoliki, jer u njihov sastav ulazi veliki broj elemenata, a takođe imaju i “organsku” - strukturnu različitost, te se u ovom smislu može reći da oblast ove grupe jedinjenja leži između neorganske i organske hemije.

Premda se POM ispituju od tridesetih godina XIX veka, tek u poslednjih pedesetak godina eksperimentalne tehnike omogućavaju da se potpunije sagleda raspon struktura i reaktivnosti ovih jedinjenja. Mnoga ključna pitanja koja se tiču sastava, veličine i strukture, inkorporacije metala, mehanizama sinteza i reaktivnosti, su ostala nedovoljno objašnjena do danas.

Postoje dve vrste POM koji se razlikuju po svom hemijskom sastavu: *izopoliokso-metalati* i *heteropoliokso-metalati*. Anjoni ovih jedinjenja mogu biti predstavljeni opštim formulama:



i



gde je M adendni atom, a X heteroatom, koji se naziva i centralni, ukoliko je u centru polianjona. Često je razlika između ove dve vrste polioksometalata formalna, posebno u slučajevima kada postoji više različitih adendnih atoma.

U grupu heteropoli anjona (HPA) spadaju jedinjenja veoma različita po svojim strukturama i sastavima. Prema opštoj definiciji, HPA su oksoanjoni sastavljeni od dva ili više elemenata u pozitivnim oksidacionim stanjima, od kojih je jedan iz grupe V, Nb, Ta, Mo, W, a drugi nemetal srednje elektronegativnosti ili prelazni metal.

Međutim, za većinu primena, definicija HPA može biti pojednostavljena, i po njoj se oksoanjoni sastoje od 4 do 18 atoma W, Mo i V i jednog ili dva heteroatoma iz grupe: P^{5+} , As^{5+} , Si^{4+} , Ge^{4+} , B^{3+} ili iz grupe prelaznih metala. *Rosenheim* [1] je predložio ime “**heteropolikiseline**” za ovu klasu jedinjenja, koja su do tada opisivana kao mešane, duple kiseline.

Najznačajnija podklasa HPA je grupa heterododekametalata, sa opštom formulom $X^nM_{12}O_{40}^{(8-n)-}$, čiji članovi imaju takozvanu *Keggin*-ovu strukturu [2].

Heteropoli kiseline su jake kiseline, sastavljene od HPA i protona. Osobine HPK u čvrstom stanju su vrlo dobro proučene, dok njihove osobine u rastvorima nisu dovoljno dobro objašnjene uprkos brojnim publikacijama. Ponašanje ovih jedinjenja u rastvorima je značajno sa aspekta njihovog formiranja i razgradnje, što je veoma važno za njihovu biomedicinsku i katalitičku primenu.

Postoji veliki broj publikacija koje govore o biomedicinskoj primeni POM. Ova jedinjenja su generalno netoksična za normalne ćelije, te pokazuju antiviralnu, antitumorsku, antibakterijsku i antikoagulantnu aktivnost [3]. Međutim, mnogi polioksometalati su termodinamički i kinetički nestabilni u vodi pri fiziološkim uslovima i mikromolarnim koncentracijama, te degradiraju u smešu manjih hemijskih vrsta. To je razlog koji ograničava njihovu primenu u medicini. Naime, pitanje koje se nameće u svim biohemijskim-biomedicinskim ispitivanjima je, da li početni, aktivni oblik ovih jedinjenja, ostaje isti u organizmu, na mestu dejstva. Uglavnom se u literaturi navodi roditeljski oblik heteropoli anjona kao aktivan, a da to nije potkrepljeno dokazima. U cilju što potpunijeg objašnjenja mehanizma farmakološkog delovanja HPK, potrebno je identifikovati stvarno prisutnu molekulsku vrstu pri različitim koncentracijama HPK i različitim uslovima sredine, a posebno pod fiziološkim uslovima.

Poslednjih tridesetak godina HPK, pored biohemijske i biomedicinske primene, bude veliki interes istraživača na polju katalize. Njihove kiselo-bazne i oksido-redukcione osobine se široko upotrebljavaju u homogenoj i heterogenoj katalizi. Heteropoli jedinjenja koja imaju *Keggin*-ovu strukturu su najviše ispitivana, zato što poseduju relativno visoku termičku stabilnost i visoku kiselost. Ova jedinjenja se mogu koristiti direktno kao "balk" materijali (u masi) ili se mogu deponovati na različite nosače. Iz više razloga, kao što su efikasnost, povećanje broja dostupnih aktivnih mesta (HPK imaju malu specifičnu površinu od 1 - 10 m²g⁻¹, te je važno povećati specifičnu površinu, odnosno broj dostupnih kiselih centara), cena itd., nanošenje na različite nosače je više zastupljeno. Polianjoni se deponuju na podloge iz rastvora u odgovarajućim rastvaračima, tako što se heterogena smeša rastvor - nosač meša do isparavanja rastvarača. Tipično se ovakvi katalizatori pripremaju

impregnacijom iz vodenog rastvora ili rastvora odgovarajuće HPK u smeši alkohol/voda. U ovakvim katalizatorima HPK su kao nanočestice raspoređene na površini supstrata. Oni se intenzivno proučavaju i nalaze primenu u mnogim reakcijama [4]. U cilju razumevanja prirode i osobina finalnog čvrstog materijala, neophodno je dobro poznavati osobine polianjona u rastvorima. Takođe, poboljšavanje katalitičkih svojstava ovih jedinjenja, kao i utvrđivanje mehanizma katalitičkih procesa, je moguće samo uz identifikaciju oblika HPK prisutnog u katalitičkoj reakciji.

Prema tome, i u slučajevima medicinske primene, kao i primene u industriji kao efikasnih katalizatora, strukturna stabilnost ovih jedinjenja pri različitim eksperimentalnim uslovima je veoma značajna.

1.2. PREDMET I CILJ RADA

Predmet ove Doktorske disertacije je solvolitička stabilnost HPK iz grupe heterododekametallata u rastvorima pri različitim uslovima sredine.

U Disertaciji su ispitivane tri heteropoli kiseline:

12-volframfosforna (WPA),

12-volframsilicijumova (WSiA) i

12-molibdenfosforna (MoPA).

Cilj ove Doktorske disertacije je praćenje solvolitičke stabilnosti WPA, WSiA i MoPA u vodenim rastvorima, kao i u smešama vode i metanola, spektroskopskim metodama (ULJ/Vid, IC, ramanskom i ³¹P NMR spektroskopijom). Ideja rada je da se identifikuju molekulske vrste prisutne pri različitim pH vrednostima rastvora, sa posebnim akcentom na fiziološke uslove. Takođe će se pratiti vremenska stabilnost pojedinih molekulskih formi, kao i reverzibilnost procesa transformacije odgovarajućih oblika, prisutnih pri određenim eksperimentalnim uslovima. Posvetiće se pažnja i primeni dobijenih rezultata u identifikaciji aktivnih oblika u mikro/nanostrukturnom sistemu polianilin - WPA, kao potencijalnom katalizatoru. Takođe će biti utvrđen oblik HPK koji je prisutan u reakciji inhibicije aktivnosti Na⁺/K⁺-ATPaze.

2. LITERATURNI PREGLED

2.1. ISTORIJSKI PREGLED

Hemija polioksometalata počela je da se razvija 1826. godine kada je *Berzelius* [5] opisao žuti talog, koji je nastao kada je amonijum-molibdat dodat fosfornoj kiselini, a koji je danas poznat kao 12-amonijum molibdofosfat, $[\text{NH}_4]_3[\text{PMo}_{12}\text{O}_{40}]$. To je otvorilo potpuno novo područje neorganske hemije. *Svanberg* i *Struve* su 1848. godine uveli ova jedinjenja u analitičku hemiju, kao reagense za određivanje fosfora [6]. Heteropoli molibdati Cr^{3+} i Fe^{3+} su opisani od strane *Struve*-a 1854. godine kao "dvojne soli" [7]. Godine 1862. *Marignac* uočava dva strukturalna izomera $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ čime je započela i strukturalna karakterizacija polioksometalata [8]. Već 1908. godine bilo je poznato oko 750 heteropoli jedinjenja.

Međutim, strukturalna polioksometalata ostaje nepoznata čak jedan vek nakon njihovog otkrića. *Werner*, *Miolati* i *Pizzighelli*, *Rosenheim*, kao i *Pauling*, su predložili strukturalnu zasnovanu na povezanim metal-kiseoničnim poliedrima. Prvi pokušaj razumevanja strukturalne HPA potiče od *Werner*-a koji je pokušao da objasni strukturalnu HPA iz 12:1 serije¹, na osnovu koordinacione teorije [9]. *Miolati* i *Pizzighelli* su 1908. godine dali svoju hipotezu o strukturali [10], a dalje ju je razvio *Rosenheim*, koji je sistematski ispitivao HPA u toku prvih 35 godina XX veka [11].

Prema *Miolati-Rosenheim*-ovoj teoriji 12-molibdofosforna kiselina je derivat hipotetičke kiseline $\text{H}_7[\text{PO}_6]$ u kojoj su kiseonikovi atomi zamenjeni Mo_2O_7 grupama. Ova hipoteza, koja je imala veliki doprinos u rasvetljavanju ovog veoma konfuznog polja, usled nepostojanja odgovarajuće analitičke metode, važila je sve do kasnih 1920-tih godina. Tada *Pauling* predlaže da se princip uglavnom zasnovan na jonskim radijusima i strukturalama jonskih kristala primeni i na HPA [12]. Ova ideja je odbačena, jer nije uzimala u obzir vezivanje MO_6 oktaedara preko ivica.

Nekoliko godina nakon *Pauling*-ove ideje, 1933. godine *Keggin* je rešio strukturalu $\text{H}_3[\text{PW}_{12}\text{O}_{40}] \cdot 5\text{H}_2\text{O}$, rendgenskom difrakcijom na prahu. Ova strukturala, koja je dobila ime po njemu, sastoji se od 12 povezanih oktaedara, čiji centar zauzima tetraedarski koordinisan heteroatom [13]. Njegove rezultate su potvrdili *Bradley* i *Illingworth* 1936. godine, ispitivanjem 29 hidrata volframfosforne kiseline [14]. Njihovi rezultati su bili bazirani na rendgenskoj difrakciji na prahu, a potvrđeni su i

¹ Prvi broj predstavlja broj adendnih, a drugi broj heteroatoma u HPA

eksperimentima na monokristalu, čije su rezultate objavili *Brown* i saradnici 1977. godine [15].

Ilustrovano na primeru WPA, evolucija teorija o sastavu i strukturi HPA je išla od formule $H_7[P(W_2O_7)_6]$ prema *Miolati-Rosenheim*-ovoj, preko $H_3[PO_4W_{12}O_{18}(OH)_{36}]$ po *Pauling*-ovoj teoriji, do konačne *Keggin*-ove formule $H_3[P(W_3O_{10})_4]$, koja se često piše i kao $H_3PW_{12}O_{40}$.

Strukturu drugog široko rasprostranjenog oblika, iz serije 6:1, takozvanog *Anderson*-ovog heteropoli anjona, otkrio je *Evans* difrakcijom rendgenskih zraka na monokristalu $[Te^{6+}Mo_6O_{24}]^{6-}$ soli, 1948. godine [16]. Ova struktura se u literaturi često sreće pod nazivom *Anderson-Evans*-ova struktura.

1953. godine *Dawson* objavljuje novu strukturu iz serije 18:2, $[P_2W_{18}O_{62}]^{6-}$, koja se danas često označava kao *Wells-Dawson*-ova [17]. Ova struktura je predstavljena kao blisko povezana sa *Keggin*-ovom. 1968. godine, *Dexter* i *Silverton* objavljuju strukturu $[Ce^{4+}Mo_{12}O_{42}]^{8-}$ i pokazuju da se veliki Ce heteroatom u CeO_{12} nalazi u centru ikosaedra [18].

Ranih sedamdesetih godina hemija polioksometalata doživljava veliki procvat. Ovaj period je povezan sa intenzivnim radom mnogih grupa, posebno onih koje predvode *Souchay* (Francuska), *Ripan* (Rumunija), *Spitsyn* (Rusija) i *Baker* (USA) [19]. U periodu od 1980.-1990. godine broj grupa koje se bave ovom tematikom raste paralelno sa širenjem polja primene polioksometalata. Tako su 1995. godine bile publikovane strukture oko 180 polioksometalata.

Primene modernih tehnika karakterizacije doprinele su boljem razumevanju struktura i osobina polioksometalata. Međutim, postoje još mnoga nerešena pitanja koja se tiču strukturnih principa, mehanizama sinteza i reaktivnosti polioksometalata.

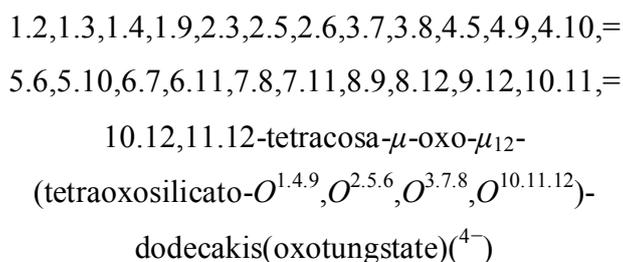
2.2. TERMINOLOGIJA I NOMENKLATURA

U upotrebi su različita generička imena za oksokiseline i oksoanijone. Zbog njihovog velikog broja teško je definisati nedvosmislenu i konzistentnu terminologiju. Za kisele oblike, polikiseline, koriste se izrazi *polioksokiseline* (uključujući heteropolikiseline i izopolikiseline), a za oksoanijone, termini *polianjoni*, *polioksoanjoni* i *poliokso-metalati* (uključujući heteropoli anijone i izopolianjone). Pored ovih, za polianjone ili polikiseline koriste se izrazi kao što su metal-kiseonični klaster jon, metal-oksadni molekul i dr.

Nekiseonični elementi u unutrašnjosti polianjona se nazivaju *heteroatomima*, a u nekim slučajevima *centralni*, a oni na perifernim delovima *adendni* ili *poliatomi*.

Nomenklatura heteropoli jedinjenja u literaturi nije usaglašena. Na primer, za $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ javljaju se (u literaturi na engleskom jeziku) imena “*silicotungstate*”, “*tungstosilicate*”, “*silicododecatungstate*”, “*dodecatungstosilicate*” ili “*12-tungsto-silicate*”.

Vrlo detaljnu i sistematičnu nomenklaturu polianjona razvili su *Y. Jeannin* i *M. Fournier*, 1987. godine [20]. Ona koristi sistem obeležavanja atoma metala, a u nekim slučajevima i atoma kiseonika, radi spečavanja dvoznačnosti. Na primer, za pomenuti $[\text{SiW}_{12}\text{O}_{40}]^{4-}$, T_d simetrije, ime bi glasilo:



Dobijeno ime je, kao što se vidi, vrlo dugačko i komplikovano, pa se praktično nikad ne upotrebljava u rutinskom radu.

U najvećem broju slučajeva primenu nalazi samo relativno mali broj dobro poznatih tipova POM, tako da se u literaturi koriste uglavnom samo trivijalna imena.

U ovom radu je prihvaćena nomenklatura koja HPA tretira kao kvazi koordinacione komplekse [2]. Heteroatom se posmatra kao centralni atom kompleksa, a adendni atomi kao ligandi. U formulama HPA, heteroatomima se pišu pre adendnih, a kontra joni pre heteroatoma. Na primer, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ je 12-volframosilikat,

$H_4[SiW_{12}O_{40}]$ je 12-volframsilicijumova kiselina, a $Na_4[SiW_{12}O_{40}]$ natrijum 12-volframosilikat.

2.3. STRUKTURNE KARAKTERISTIKE HETEROPOLIANJONA

HPA sadrži veliki broj atoma kiseonika, ponekad atome vodonika, te atome najmanje dva druga elementa u pozitivnim oksidacionim stanjima. Struktura HPA je sastavljena od diskretnih fragmenata, metal-oksidnih struktura, određenih veličina i oblika. Ovi kompleksi predstavljaju termodinamički relativno stabilne aranžmane i za njih je karakteristično da zadržavaju svoje identitete, u vodenim i nevodenim rastvorima, isto kao i u jonskim kristalima.

Tipično, heteropoli kompleksi sadrže u velikom atomskom odnosu jednu vrstu atoma u pozitivnom oksidacionom stanju - **adendni** atom i u mnogo manjem odnosu drugu vrstu (ili vrste) atoma, takođe u pozitivnom oksidacionom stanju – **heteroatom** (heteroatom).

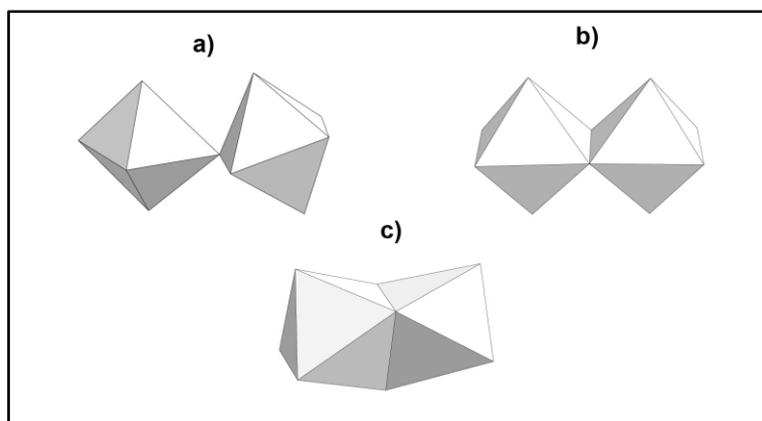
Opšta formula HPA je $[X_xM_mO_y]^{q-}$, $x < m$, gde je M adendni atom, a X heteroatom. W, Mo i V su adendni atomi u velikom broju HPA. Nekoliko drugih elemenata, iako manje uobičajeno, mogu takođe igrati ulogu adendnog atoma. To su, na primer, Nb^{5+} , Ta^{5+} , Re^{7+} , I^{7+} . Preko 60 drugih elemenata, uključujući najveći deo nemetala i prelaznih metala, mogu funkcionisati kao heteroatom.

Osnovna izgrađivačka jedinica HPA je oktaedar, koji je izgrađen od adendnog atoma metala okruženog sa 6 atoma kiseonika. Na slici 1. su shematski prikazani mogući načini vezivanja oktaedara. Najpovoljnije povezivanje dva oktaedra određeno je odbijanjima između atoma u centrima oktaedara, koje je najmanje pri vezivanju oktaedara preko temena ili ivica, dok je povezivanje preko stranica termodinamički nepovoljno.

Da bi jedan atom mogao biti adendni, on mora da menja svoju koordinaciju sa kiseonikom, od 4 na 6, pri polimerizaciji u rastvoru i pri zakišeljavanju i da ima veliko pozitivno naelektrisanje i radijus unutar opsega radijusa pogodnih za oktaedarsko vezivanje sa kiseonikom. Pogodnost atoma za ulogu adendnog atoma raste ako je moguće da formira dvostruku vezu sa terminalnim (nedeljenim) atomima kiseonika (koji se obično označavaju kao O_d) u njihovim MO_6 oktaedarima, preko $p\pi-d\pi$

interakcije. Formiranje heteropoli kompleksa obuhvata polimerizaciju adendnih poliedara oko heteroatoma pri zakišeljavanju rastvora.

Adendni atomi se ne nalaze u centrima svojih oktaedara, već su pomereni prema O_d atomima kiseonika. Dva faktora koja igraju ulogu u ovoj distorziji adendnih oktaedara su: formiranje dvostruke veze između adendnih atoma (označenih sa M) i O_d atoma, te veća polarizibilnost O_d atoma u odnosu na adendne atome. Visoko naelektrisani M atomi proizvode jaku jon-indukovani dipol privlačnu interakciju sa susednim O_d atomom u njihovom oktaedru. Pošto su spoljašnji atomi kiseonika najpolarizibilniji u odnosu na adendne atome kompleksa, oni vrše najjaču interakciju, dok ostali atomi kiseonika postaju unutrašnji ili premošćujući.



Slika 1. Vezivanje MO_6 oktaedara preko a) temena, b) ivica i c) stranica

Većina tipičnih adendnih atoma (W, Mo, V) formira dvostruku vezu sa spoljašnjim atomima kiseonika. Dva faktora koja utiču na pokretanje adendnih atoma prema O_d atomima su čvrsto povezana. Što dvostruka veza više skraćuje M- O_d rastojanje, veća je polarizacija i jače je privlačenje jon-indukovani dipol. Što je veće približavanje M atoma prema O_d atomima, kraća je i jača dvostruka veza. Na primer, razlike u W-O rastojanjima između unutrašnjih i perifernih atoma kiseonika su od 0,07 do 0,1 nm.

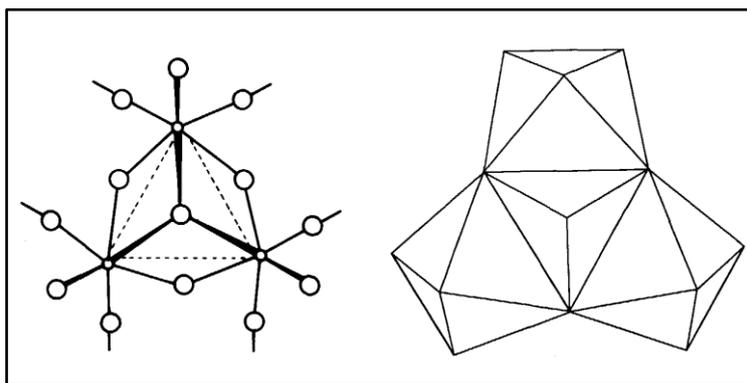
Prema tome, tipični heteropoli kompleksi imaju spoljašnji sloj kiseonikovih atoma koji su izuzetno jako polarizovani prema unutrašnjosti kompleksa. Ispod ovog sloja je sloj adendnih atoma, koji su jako privučeni slojem spoljašnjih atoma kiseonika i koji sami jako privlače spoljašnji sloj atoma kiseonika. Ova kombinacija dovodi do

formiranja omotača ispod kojeg je šupljina, tako da unutar izomornih heteropoli kompleksa često može biti različit heteroatom.

Velika polarizibilnost atoma kiseonika prema unutrašnjosti kompleksa dovodi do toga da je spoljašnjost kompleksa relativno pozitivna, tako da je veza sa atomima vodonika ekstremno slaba, pa su HPK jake kiseline, sa pKa od 0-2.

Polimerizacija adendnih vrsta zahteva mehanizam koji uključuje vezivanje protona na atome kiseonika. Zbog polarizacije spoljašnjeg sloja atoma kiseonika, mnogo je verovatnije postojanje malih diskretnih heteropoli kompleksa nego nerastvornog čvrstog matriksa velikih dimenzija [19].

Za adendne oktaedre u HPA, značajana je podstruktura u vidu M_3O_{13} grupa, slika 2. Ove grupe se formiraju povezivanjem tri oktaedra preko zajedničkih ivica, a kao rezultat se javlja deljenje atoma kiseonika između tri atoma metala.

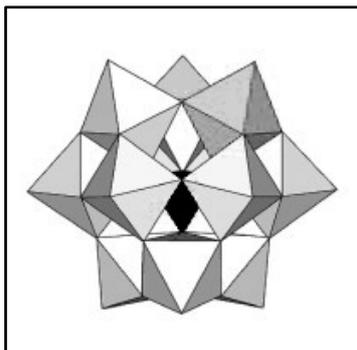
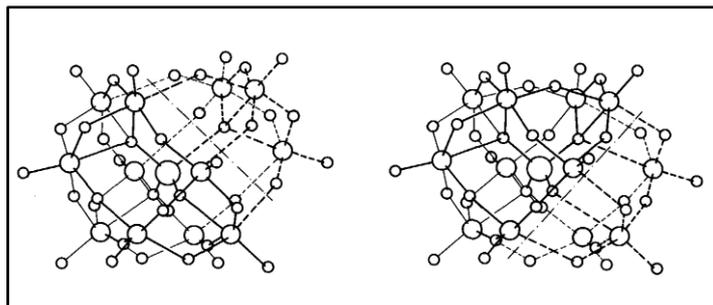


Slika 2. Povezivanje MO_6 oktaedara u M_3O_{13} grupe

Osnovne HPA strukture se mogu svrstati u tri grupe, prema koordinacionom broju heteroatoma. Prvoj grupi pripadaju HPA serije 1:12 i 2:18 sa tetraedarski koordinisanim heteroatomima, kao i njihovi redukovani, delimično hidrolizovani ili supstituisani derivati. Drugu grupu čine anjoni 1:6 serije sa oktaedarski, a treću sa ikosaedarski koordinisanim heteroatomima [21].

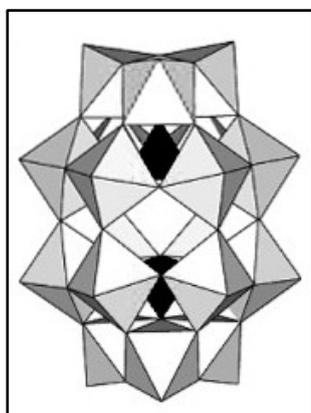
Sferne strukture iz prve grupe se nazivaju *planarne strukture* (lat. *plenarius* pun, kompletan) a njihovi degradirani derivati *lakunarne strukture* (lat. *lacuna* šupljina, praznina). Planarne strukture mogu biti sa jednim (*Keggin*-ova struktura) ili sa dva centralna tetraedra (*Dawson*-ova struktura).

HPA, sa opštom formulom $X^nM_{12}O_{40}^{(8-n)-}$ imaju takozvanu *Keggin*-ovu strukturu, i izgrađeni su od četiri M_3O_{13} grupe koje su povezane tako da oktaedri iz različitih jedinica dele samo temena, a ne stranice, kako je tačno prvi put 1933. godine opisao *Keggin*. U središtu ove strukture nalazi se tetraedarski koordinisan heteroatom, slika 3.

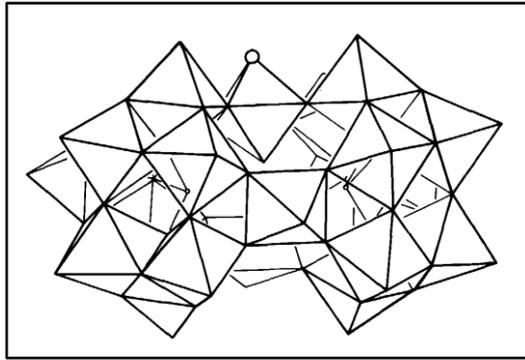
Slika 3. *Keggin*-ov anjon

Slika 4. $X^nM_9O_{31}^{(8-n)-}$ struktura izvedena iz *Keggin*-ove strukture, levo: uklanjanjem 3 atoma metala iz jedne M_3O_{13} grupe (*A-tip*), desno: uklanjanjem 3 atoma metala iz susednih grupa (*B-tip*)

Struktura $X^nM_9O_{34}^{(8-n)-}$ se može posmatrati kao da je izvedena iz *Keggin*-ove strukture uklanjanjem 3 atoma metala iz jedne M_3O_{13} (*A-tip*) ili uklanjanjem 3 susedna adendna atoma iz susednih grupa (*B-tip*), slika 4. Iz dve ovakve jedinice *B* tipa, mogu se formirati anjoni iz *Dawson*-ove serije, koji imaju molekulsku formulu $X^n_2M_{18}O_{62}^{(2n-16)-}$, slika 5.

Slika 5. *Dawson*-ov anjon

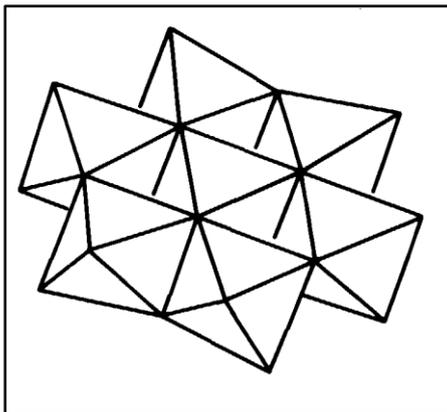
Još jedna interesantna struktura je opisana formulom $X^n_2W_{21}O_{71}^{(2n-16)-}$, a koja se može formirati iz lakunarnih oblika XW_{11} pri zakišeljavanju, bez viška volframa. Ova jedinjenja se sastoje od najverovatnije dve XW_9 jedinice, kombinovanjem 3 atoma volframa u kvadratno-piramidalnoj koordinaciji, slika 6.



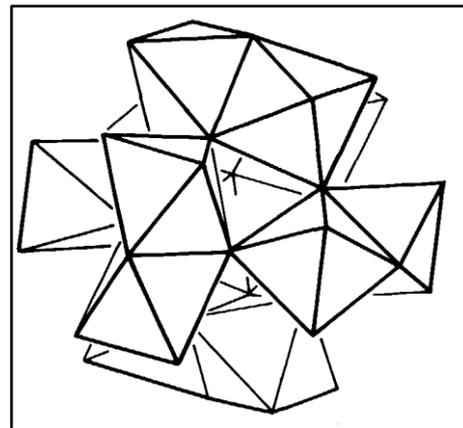
Slika 6. $X^n_2W_{21}O_{71}^{(2n-16)-}$ anjon

U većini slučajeva heteroatom je tetraedarski koordinisan. Međutim, u slučaju *Anderson-ove* serije, $X^nM_6O_{24}^{(12-n)-}$ (slika 7.) i *Dexter-Silverton-ove* serije, $X^nM_{12}O_{42}^{(12-n)-}$ (slika 8.), heteroatom je oktaedarski, odnosno ikosaedarski koordinisan.

Anderson-ova struktura je ravna struktura sastavljena od 6 oktaedara povezanih u prsten oko sedmog oktaedra u centru. U slučaju *Dexter-Silverton-ove* serije, X je lantanoid sa ikosaedarskom koordinacijom u centru strukture.



Slika 7. Anjon *Anderson-ove* serije



Slika 8. Anjon *Dexter-Silverton-ove* serije

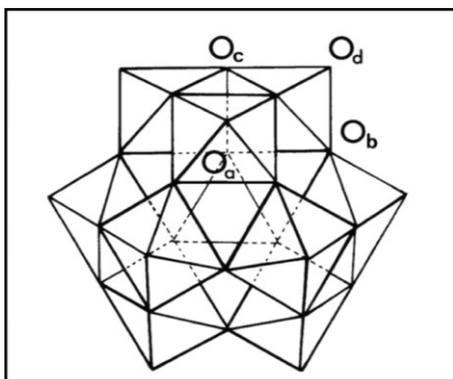
Pored pomenutih, postoji još veliki broj veoma različitih struktura.

2.3.1. Struktura *Keggin*-ovog anjona i lakunarnog *Keggin*-ovog anjona

Izolovani *Keggin*-ov anjon (KA) je izgrađen od XO_4 tetraedra (simetrije T_d), koji je okružen sa 12 MO_6 oktaedara (simetrije C_s), koji formiraju 4 povezane M_3O_{13} jedinice (simetrije C_{3s}).

Postoje 4 tipa atoma kiseonika u KA, slika 9. :

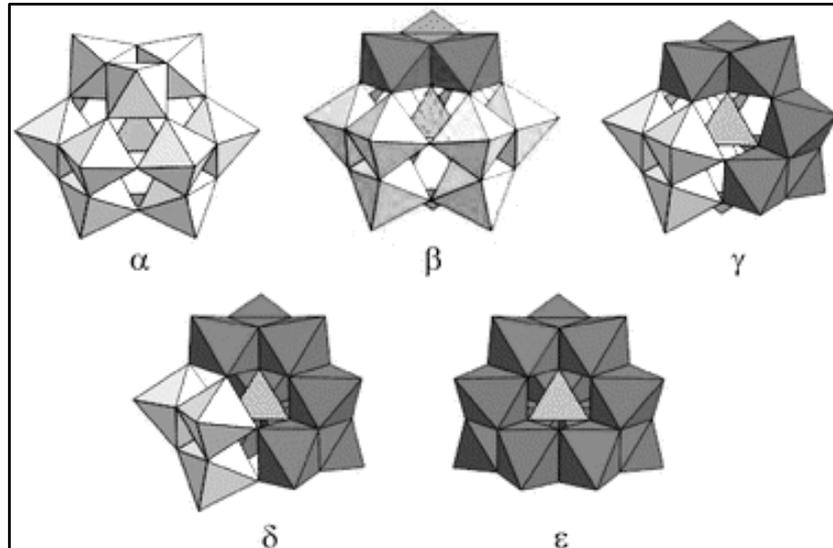
- 4 O_a atoma (simetrije C_{3v}), koji povezuju XO_4 tetraedar sa 3 oktaedra u M_3O_{13} grupi
- 12 O_b atoma (simetrije C_s) u M-O-M mostovima između dve različite M_3O_{13} grupe (koje dele ivice) – *intertrijadni kiseonici*,
- 12 O_c atoma (simetrije C_s) u M-O-M mostovima unutar jedne M_3O_{13} grupe (koje dele temena) – *intratrijadni kiseonici*
- 12 O_d atoma (simetrije C_s) na terminalnim pozicijama, koji nisu deljeni između oktaedara [22].



Slika 9. Četiri različita tipa atoma kiseonika u *Keggin*-ovom anjonu

Ovako opisana struktura ima T_d simetriju i predstavlja α izomer. Ostali izomeri *Keggin*-ove strukture nastaju rotiranjem jedne ili više M_3O_{10} jedinica za ugao od 60° . Iako teorijski može postojati 5 izomera, slika 10., najznačajniji su α i β izomeri. Koji će od ova dva izomera biti dobijen pri sintezi zavisi od metoda sinteze, pri čemu su od značaja temperatura i redosled dodavanja kiseline i heteroatoma. β izomer prelazi u α izomer pod uticajem zagrevanja ili dužeg stajanja. Ova transformacija zavisi od heteroatoma, tako da je u slučaju Si, β izomer stabilan duži vremenski period, dok se u slučaju P proces izomerizacije odvija u toku nekoliko dana na sobnoj temperaturi. Drugi izomeri su najverovatnije suviše nestabilni u rastvorima da bi se izolovali.

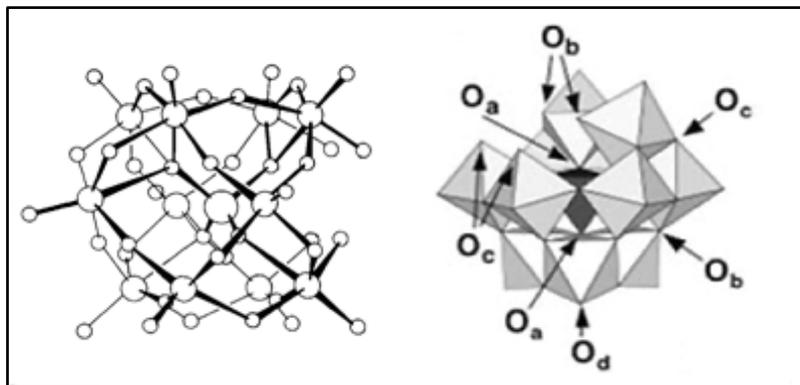
Internuklearno rastojanje između dva W atoma kod β izomera je kraće od onog kod α izomera, a uglovi W-O-W su manji, što može biti razlog manjoj stabilnosti β izomera [2].



Slika 10. Izomeri Keggin-ove strukture

Upšteno govoreći, što je veći broj zajedničkih ivica između oktaedra, stabilnost je manja, a ovaj efekat je čak jači ukoliko oktaedri dele stranice, što je posledica elektrostatičkog odbijanja adendnih atoma metala. Prema tome, *Keggin*-ova struktura u kojoj oktaedri različitih grupa dele samo uglove, odnosno α izomer, je najstabilnija.

Udaljavanjem jedne MO jedinice iz KA nastaje monolakunarni KA, slika 11.



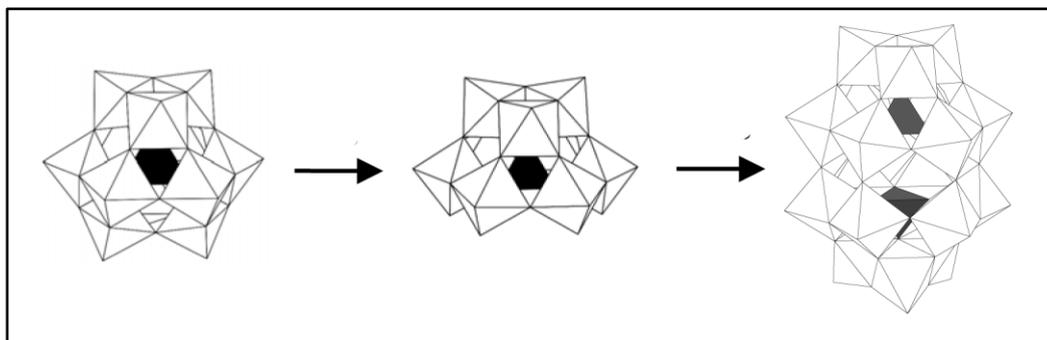
Slika 11. Monolakunarni Keggin-ov anjon

Na ovaj način dva O_b i dva O_c atoma postaju terminalni, a O_a atom postaje dostupan za interakciju. Ovih pet atoma kiseonika formiraju pentadendatni otvor u lakunarnom HPA i predstavljaju najaktivnije atome kiseonika u molekulu za građenje hemijskih veza.

2.3.2. Struktura Dawson-ovog anjona i lakunarnog Dawson-ovog anjona

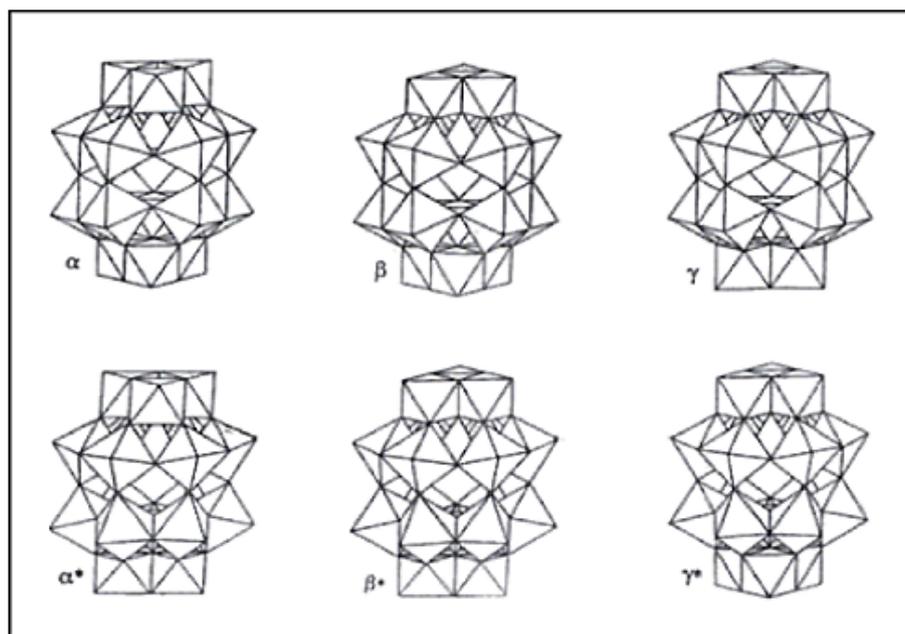
Kejrmann je prvi put opisao sintezu volframfosforovog jedinjenja *Wells–Dawson*-tipa, 1892. godine [23]. Međutim, kristalografsko ispitivanje strukture objavio je *Dawson* 60 godina kasnije [17].

Opšta formula HPA *Wells–Dawson*-ovog tipa je $[(X^{n+})_2M_{18}O_{62}]^{(16-2n)-}$, gde je X^{n+} centralni atom koji može biti P(V), As(V), S(VI), okružen omotačem od adendnih atoma M, koji su najčešće volfram (VI) ili molibden (VI) ili njihova smeša. Može se smatrati da se ova struktura formira od 2 trolakunarna *Keggin*-ova anjona, $X^nM_9O_{34}^{(8-n)-}$, slika 12. i najčešće se naziva *Dawson*-ov anjon (DA).



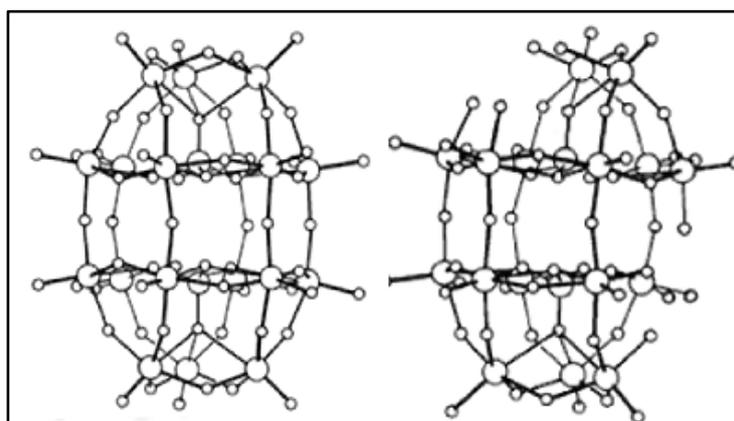
Slika 12. Shematski prikaz nastajanja DA: uklanjanjem 3 MO jedinice iz KA nastaje trolakunarni KA, a spajanjem dva ovakva anjona DA

Struktura poznata kao α izomer, sadrži dve identične "polu-jedinice" sa centralnim atomima okruženim sa 9 oktaedarskih jedinica, koje su povezane preko atoma kiseonika. Izomeri ove strukture nastaju pri rotaciji polu-jedinica za $\pi/3$ oko X-X ose, slika 13.



Slika 13. Izomeri Dawson-ove strukture

Slično i kod mnogih drugih HPA i *Wells-Dawson*-ovom strukturom je moguće hemijski manipulirati da bi se napravila šupljina, slika 14. Uklanjanjem 6 WO_6 jedinica iz $[(X^{n+})_2M_{18}O_{62}]^{(16-2n)-}$ anjona dobija se struktura sa 12 atoma M. Ove lakunarne vrste se dobijaju degradacijom DA u kontrolisanoj baznoj sredini (nije publikovana direktna sinteza). Šupljine u lakunarnim anjonima mogu se popunjavati sa različitim elementima kao što su Mo, V i drugi metali, lantanidi i itd.



Slika 14. Dawson-ov anjon (levo) i lakunarni Dawson-ov anjon (desno)

2.3.3. Kristalna struktura heteropoli jedinjenja

U opštem slučaju, čvrste HPK i njihove soli formiraju jonske kristale. Često između HPA postoje velike šupljine u koje se smeštaju velike količine kristalizacione vode (više od trideset molekula po Keggin-ovoj jedinici), kao i kontra joni. Ovi molekuli vode su povezani vodoničnim vezama i mogu se lako i reverzibilno uklanjati iz čvrstih heteropoli jedinjenja (HPJ), zagrevanjem na 100 - 150 °C. Kristalna struktura HPJ zavisi od stepena hidratacije, na primer, WPA pokazuje promenu u kristalnoj strukturi sa gubitkom hidratacione vode, tabela 1.

Tabela 1. Kristalna struktura različitih hidrata 12-volframfosforne kiseline

Hidrat	Kristalni sistem
$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$	Kubna
$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 21\text{H}_2\text{O}$	Ortorombična
$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$	Triklinična
$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$	Kubna

Proces hidratacije/dehidratacije je često povezan sa promenom zapremine jedinične ćelije kristala. Pored vode i mnogi polarni organski molekuli, kao što su alkoholi, ketoni, etri, amini, sulfoksidi, itd., mogu ulaziti i izlaziti iz strukture što može imati veliki značaj u heterogenoj katalizi sa čvrstim HPJ.

Kristali HPJ obično imaju vrlo nisku energiju rešetke. Naelektrisanje na velikim HPA je delokalizovano preko velikog broja atoma, čime je u velikoj meri umanjena elektrostatička interakcija. Spoljašnjost tipičnog HPA sadrži kiseonike koji su jako polarizovani prema adendnim atomima i stoga nepolarizabilni u drugim pravcima. Ovim kiseonicima nedostaje mogućnost formiranja vodoničnih veza normalne jačine. Kao rezultat, HPA su slabo solvatisani u rastvorima i kristalna struktura HPJ je često prilično pokretna, za razliku od krute mreže metalnih oksida ili zeolita. Ova njihova strukturalna fleksibilnost ima veliki značaj pri primeni ovih jedinjenja kao čvrstih katalizatora.

Prema specijalnoj strukturalnoj klasifikaciji koja prepoznaje značaj strukturalne fleksibilnosti HPJ, a koja je široko prihvaćena u heterogenoj katalizi sa POM, razlikujemo **primarnu** (strukturalna polioksanijona), **sekundarnu** (kristalna strukturalna) i

tercijarnu strukturu (tekstura čvrstog jedinjenja, na primer veličina čestice, poroznost, veličina površine, raspodela protona itd).

Oblik HPA *Dawson*-ovog tipa nije sferan kao kod *Keggin*-ovog tipa i njegova sekundarna struktura je manje uređena, što su *Baronetti* i saradnici [24] zaključili iz rezultata rendgenske difrakcije i IC spektroskopije. I 24- i 2- hidratni oblik, imaju molekule vode između jedinica primarne strukture. Delimični gubitak vode dovodi do povećavanja neuređenosti sekundarne strukture. Gubitak poslednja dva molekula vode dovodi do formiranja anhidrovane faze u kojoj je primarna struktura očuvana.

2.4. OSOBINE HETEROPOLIANJONA

Fizičke osobine HPA su u priličnoj meri nezavisne od njihovog sastava, tako da su slične unutar jedne klase anjona, na primer onih sa *Keggin*-ovom strukturom. Razlike unutar jedne klase su u velikoj meri povezane sa različitim adendnim atomima, dok u opštem slučaju heteroatom ima manji uticaj.

2.4.1. Rastvorljivost

Značajna karakteristika HPA je njihova rastvorljivost. Rastvorljivost zavisi od vrste kontraiona i rastvarača. Protonovane forme svih članova *Keggin*-ove i *Dawson*-ove serije su rastvorne u vodi, u nižim alkoholima i acetonu. U višim alkoholima, rastvorljivost takođe može biti vrlo dobra, posebno pri povišenim temperaturama. Na primer, WPA u 2-etilheksanolu na 80 °C je rastvorna u količini od 100 gdm⁻³. Uopšteno govoreći, HPK su veoma dobro rastvorne u rastvaračima koji imaju kiseonik u svom molekulu, a nisu rastvorne u nepolarnim rastvaračima, kao što su npr. benzen, hloroform i ugljen disulfid. Npr., rastvorljivost H₄SiMo₁₂O₄₀·8H₂O u vodi je 88, u etil acetatu 86, a u dietiletru 85 % (w/w), na 25 °C [25].

Rastvorljivost soli HPK je veoma zavisna od vrste katjona i naelektrisanja HPA. Litijumove i natrijumove soli relativno slabo naelektrisanih KA su vrlo rastvorne (u rangi kgdm⁻³), dok su kalijumove, rubidijumove, cezijumove i amonijačne soli praktično nerastvorne. Uopšteno govoreći, soli HPA sa većim katjonima su manje rastvorne. Međutim, zabeležena je i zavisnost rastvorljivosti od ukupnog naelektrisanja

HPA. Npr., u slučaju $PV_nMo_{(12-n)}O_{40}^{(3+n)-}$, kalijumove soli sa različitim n se mogu dobiti selektivnom kristalizacijom iz vodenih rastvora, zahvaljujući progresivno boljoj rastvorljivosti soli sa povećanjem n [26, 27].

Rastvorljivost u dietiletru i etil acetatu je poseban slučaj, jer HPA mogu formirati komplekse sa ovim rastvaračima. Kada se vrlo kiselim vodenom rastvoru HPA dobijenom posle sinteze doda etar, formiraju se tri sloja. U trećem se nalazi protonovani etar, HPA i voda. Ovo je vrlo koncentrovana faza sa gustinom oko $2,5 \text{ gcm}^{-3}$, što se koristi kao metod za separaciju i prečišćavanje HPA.²

Rastvorljivost HPA se može objasniti imajući u vidu njihove druge osobine. Naime, HPA su veliki simetrični anjoni sa malom gustinom naelektrisanja. Ovo ih čini veoma "mekanim" jonima koji imaju jaku interakciju sa drugim "mekanim" jonima. Ova mekoća ih čini lako rastvornim u organskim rastvaračima, koji obično nisu pogodni za rastvaranje neorganskih soli [25].

2.4.2. Solvolitička stabilnost rastvora heteropolianjona

U vodenim rastvorima su najstabilniji HPA sa heteroatomom čija je valencija 4. Tako su heteropoli kiseline sa Si i Ge kao centralnim atomom mnogo otpornije prema alkalnoj hidrolizi od onih koje sadrže P, dok kiseline sa As i B uopšte nisu stabilne u vodenim rastvorima. Međutim, uloga pH vrednosti rastvora je od presudnog značaja, pa su i "stabilne" kiseline stabilne samo u kiseloj sredini. Takođe i koncentracija rastvora igra značajnu ulogu, jer pri nižim koncentracijama i stabilnost postaje manja.

Uprkos intenzivnim ispitivanjima stabilnosti i reakcionih puteva HPK *Keggin*-ovog tipa u rastvorima, dobijeni rezultati i zaključci u literaturi su često zbunjujući i nesaglasni, iako su dobijeni pod sličnim eksperimentalnim uslovima.

Kepert i Kyle su ispitivali hidrolitičku transformaciju KA sa Si, P ili B kao centralnim atomom i W kao adendnim atomom. Našli su da se razlaganje 12-volframsilikata odvija kroz tri stepena sa $[SiW_{11}O_{39}]^{8-}$ i $[SiW_9O_{34}]^{10-}$ kao intermedijernim vrstama [28, 29]. *Kyle* je takođe pratio hidrolizu $[PW_{12}O_{34}]^{9-}$, kao

² Ova metoda je korišćena pri sintezama HPK u ovom radu

jednog od intermedijera pri razlaganju $[\text{PW}_{12}\text{O}_{40}]^{3-}$ [30]. Kinetiku formiranja i razgradnje 12-molibdofosfata pratili su *Kircher i Crouch* [31].

Rob van Veen sa saradnicima [32] je pratio formiranje molibdofosfata. Vodeni rastvor koji je sadržavao smešu natrijum-molibdata i natrijum-fosfata je zakišljen sa koncentrovanom HCl i formiranje molibdofosfatnih anjona je praćeno sa ^{31}P NMR spektroskopijom, kao metodom koja je veoma pogodna za identifikaciju molibdofosfatnih vrsta u rastvoru. Rezultati su potvrđeni i ramanskom spektroskopijom, kao i diferencijalnom pulsnom polarografijom.

Prema *Pope*-u [2] razgradnja WPA pri dodatku NaOH ide do fosfata i volframata, uz fomiranje nekoliko intermedijera, $[\text{P}_2\text{W}_{21}\text{O}_{71}]^{6-}$, $[\text{PW}_{11}\text{O}_{39}]^{7-}$, $[\text{P}_2\text{W}_{19}\text{O}_{67}]^{10-}$ i $[\text{PW}_9\text{O}_{34}]^{9-}$. *Detusheva* i saradnici [33] su identifikovali proizvode razlaganja WPA u toku titracije sa NaOH, uz pomoć NMR, IC i Ramanske spektroskopije kao $[\text{P}_2\text{W}_{21}\text{O}_{71}]^{6-}$, $[\text{PW}_{11}\text{O}_{39}]^{7-}$, $[\text{PW}_9\text{O}_{34}]^{9-}$, $[\text{PW}_{12}\text{O}_{42}]^{7-}$ i WO_4^{2-} . Takođe, ^{31}P NMR spektroskopijom *Toufaily* sa saradnicima [34] je našao da se $[\text{PW}_{12}\text{O}_{40}]^{3-}$ javlja na $\text{pH} < 2$, $[\text{P}_2\text{W}_{21}\text{O}_{71}]^{6-}$ između $\text{pH} 2$ i 3 , $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ između $\text{pH} 2$ i $4,5$, a $[\text{PW}_{11}\text{O}_{39}]^{7-}$ na $\text{pH} \geq 2$.

McGarvey i Moffat [35] su pratili glavne vrste prisutne u rastvorima WPA i MoPA kao funkciju pH , NMR i IC spektroskopijom. Oni su našli da se sa porastom pH vrednosti *Keggin*-ovi anjoni ovih kiselina, preko lakunarnih formi, razlažu do fosfata i volframata, odnosno fosfata i molibdata. Prema njihovim rezultatima monolakunarni KA u rastvoru WPA postoji u pH oblasti od $2 - 8$, dok su ispod ove pH vrednosti prisutni uz dominantan KA i drugi fosfovolframati.

Jürgensen i Moffat [36] su proučavali stabilnost $[\text{PW}_{12}\text{O}_{40}]^{3-}$, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ i $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ primenom tečne hromatografije i našli da su 12-volframofosfati manje stabilni od 12-volframosilikata, ali da su mnogo stabilniji i od molibdofosfata i od molibdosilikata. Takođe su zaključili da je 95 % WPA razloženo na $\text{pH} 6,8$. Međutim, oni u svojim eksperimentima nisu pratili razlaganje do kraja i nisu registrovali intermedijere koji se javljaju u reakciji dekompozicije.

WPA je ispitivana u širokom opsegu pH od $1 - 12$ korišćenjem tečne hromatografije kombinovane sa IC, ULj-Vid, ^{31}P NMR spektroskopijom i spektroskopijom sa induktivno spregnutom plazmom (ISP). Praćeno je razlaganje WPA

u vodenim rastvorima pri čemu je nađeno da se na $\text{pH} < 8$ dekompozicija odvija udaljavanjem $\text{W}=\text{O}$ jedinica, a da iznad ove pH vrednosti dolazi do potpune razgradnje do fosfata. Autori su takođe pratili i uticaj dodatka organskog rastvarača (etanola i acetona) na stabilnost WPA [37].

Smith i Patrick su primenili ^{31}P i ^{183}W NMR spektroskopiju za detaljno ispitivanje WPA i WSiA. Oni su našli da je razlaganje WPA mnogo kompleksnije nego u slučaju WSiA. Takođe su zaključili da su ^{183}W NMR spektri vrlo kompleksni za analizu pri nižim pH zbog velikog broja pikova koji se preklapaju, dok je identifikacija pomoću ^{31}P NMR spektara otežana zbog varijacije hemijskih pomaka sa pH vrednošću, kao posledica promene jonske jačine rastvora [38, 39, 40].

Na osnovu rezultata pomenutih istraživanja može se zaključiti da hidrolitička stabilnost HPK zavisi od strukture anjona, prirode heteroatoma i adendnih atoma, kao i uslova sredine. Generalno je prihvaćen stav da je većina HPK sa W ili Mo u strukturi stabilna u kiseljoj sredini. Sa porastom pH vrednosti na kompleksan način dolazi do transformacije u smešu neorganskih produkata, dok u alkalnoj sredini dolazi do potpune razgradnje. Međutim, rezultati nisu uvek konzistentni u pogledu identiteta molekulskih vrsta i oblasti pH u kojima se one javljaju.

Iako pH vrednost rastvora igra veliku ulogu u stabilnosti HPA, ona nije jedina koja utiče na stabilnost. Naime, često se ignoriše činjenica da POM nisu savršeni kompleksi i da pri razblaživanju dolazi do degradacije u manje kondenzovane vrste. Ova nepovoljnost može biti minimizovana korišćenjem smeša vode i organskih rastvarača, koji dovode do stabilizacije polaznih vrsta zbog kinetičkih ili/i termodinamičkih efekata. Ova stabilizacija je praćena polarografskim metodama, elektronskom apsorpcijom ili NMR spektroskopijom. Npr. MoPA je stabilna u 50 % metanolu do koncentracije $10^{-3} \text{ mol dm}^{-3}$, dok u vodenim rastvorima razlaganje počinje već pri koncentracijama manjim od $10^{-1} \text{ mol dm}^{-3}$ (slobodni fosfat je detektovan pomoću ^{31}P NMR spektroskopije čak i pri ovoj koncentraciji). Na isti način, upotreba voda-dioksan rastvarača omogućava dobijanje i proučavanje 12-molibdoarsenata koji je nestabilan u vodi [41].

Kao i anjoni *Keggin*-ovog tipa, tako i dvoatomske polioksoanjonske strukture pokazuju nestabilnost u rastvorima. *Dawson*-ov anjon $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ se u vodenim rastvorima razlaže na $\text{H}_x\text{PMo}_{12}\text{O}_{40}^{(3-x)-}$, pentamolibdofosfat $\text{H}_x\text{P}_2\text{Mo}_5\text{O}_{23}^{(6-x)-}$ i

heptamolibdat $\text{Mo}_7\text{O}_{24}^{6-}$ ili molibdat MoO_4^{2-} zavisno od kiselosti sredine [42]. U organskim rastvaračima dolazi do stabilizacije i, kako su pokazali *Valle* i saradnici, heteropoli struktura ostaje nepromenjena 24 sata na sobnoj temperaturi i pri grejanju na 50 °C i ne menja se nakon isparavanja rastvarača [43].

2.4.3. Termička stabilnost

Jedna od osnovnih osobina HPK i njihovih soli je da formiraju veći broj kristalohidrata, koji su jasno definisani i stabilni u određenim temperaturnim oblastima. Stabilnost pojedinih oblika zavisi od temperature i relativne vlažnosti okoline.

West i *Audrieth* su publikovali jedno od prvih ispitivanja termičke stabilnosti HPK sa W ili Mo kao adendnim i P ili Si kao centralnim atomom primenom diferencijalne termijske analize (DTA). Našli su da svaka od ispitivanih kiselina ima jedan endotermni pik na $T \leq 300$ °C i jedan egzotermni na $T \geq 360$ °C. Autori su uočili da se $\text{H}_8[\text{W}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$ razlaže na 50 °C, a da u slučaju kada se u centru $\text{W}_{12}\text{O}_{40}$ anjona nalazi Si^{4+} ili P^{5+} temperatura razlaganja raste na oko 400 ili 500 °C, respektivno [44].

U tabeli 2. dati su rezultati diferencijalne skanirajuće kalorimetrije (DSK) analize [45] za tri kiseline koje su predmet ove teze.

Tabela 2. Položaji pikova DSK krivih za MoPA, WPA i SiWA [45]

Uzorak	Endotermni proces Temperatura / °C				Egzotermni proces Temperatura / °C
	T ₁	T ₂	T ₃	T ₄	T ₅
MoPA	45,9	90,9	120,3	133,9	444,3
WSiA	79,7	203,4			545,2
WPA	73,6	189,7			612,1

Kod sve tri kiseline se javlja nekoliko endotermnih pikova koji odgovaraju gubitku vode iz polazne strukture HPK i jedan egzotermni pik koji odgovara termičkoj dekompoziciji HPK i formiranju bronzi.

Prema rezultatima termijskih analiza, prelazi između različitih hidrata i fazni prelazi, za WPA se mogu predstaviti sledećom shemom [46]:

WPA-29 (28-31 °C) → **WPA-21** (35-42 °C) → **WPA-14/6** (60 °C) → **6-WPA** (175-230 °C) → **O-WPA** (410-440 °C) → **D-WPA** (580-620 °C) → **bronz**a **PW₈O₂₆**

Iz sheme se vidi da se prelazi između viših hidrata odvijaju na relativno bliskim temperaturama. Inače, ove promene su reverzibilne ili delimično reverzibilne i stajanjem na sobnoj temperaturi, pri relativno visokoj vlažnosti vazduha, od heksahidrata može se dobiti viši hidrat³. O-WPA je anhidrovana faza i u njoj su prisutna tri protona. Daljim zagrevanjem gubi se još jedan molekul vode, koji se formira od protona i terminalnih atoma kiseonika iz KA, i nastaje ogoljen anjon D-WPA. *Keggin*-ova struktura ostaje nenarušena do 580 - 620 °C, kada dolazi do čvrsto-čvrsto rekristalizacije i formiranja bronzne PW₈O₂₆.

Baronetti i saradnici [24] su kalcinovanjem na vazduhu pri 300 °C, 400 °C i 600 °C ispitivali termičku stabilnost kiseline *Dawson*-ovog tipa pomoću difrakcije X – zraka i pokazali da dehidratirana kiselina zadržava svoju strukturu i pri kalcinaciji na 600 °C. Prema rezultatima termogravimetrijske analize (TGA) gubitak vode se odvijao u dva stepena :



2.4.4. Kiselost

HPK su dobro poznate kao jake *Brønsted*-ove kiseline, ali tek u skorije vreme je njihova kiselost kvantitativno okarakterisana i upoređena sa kiselošću uobičajenih mineralnih kiselina.

Objavljen je veliki broj radova koji se odnose na kiselost HPK u rastvorima. Međutim, podaci za konstante disocijacije HPK su uglavnom vrlo okvirni, jer su polianjoni nestabilni u rastvorima.

Konstante disocijacije za različite HPK u vodenim rastvorima su date u tabeli 3. u obliku $pK_i = -\log K_i$, gde je K_i konstanta disocijacije. Radi poređenja, u istoj tabeli su date konstante disocijacije za H₃PO₄. U praćenim HPK prva tri protona se disosuju potpuno, a ostali protoni stepenasto sa porastom pH vrednosti. Može se zapaziti da se vrednosti konstanti disocijacije za HPK između sebe mnogo ne razlikuju, za razliku od konstanti disocijacije za neorganske kiseline kod kojih su razlike mnogo veće. Iz

³ O ovoj činjenici treba voditi računa pri pravljenju rastvora određenih koncentracija, odnosno uzorke odgrejane do heksahidrata treba do merenja čuvati u eksikatoru sa silikagelom ili drugim odgovarajućim sredstvom za sušenje.

podataka u tabeli može se videti da su sve ispitivane kiseline mnogo jače od H_3PO_4 [47].

Razlika u kiselosti između HPK i tipičnih neorganskih kiselina može se objasniti u okvirima elektrostatičke teorije, uzimajući u obzir veličinu i naelektrisanje anjona. Pošto su HPA veći nego anjoni neorganskih kiselina, veza između protona i HPA je slabija, odnosno konstanta disocijacije je veća nego kod neorganskih kiselina. Sa druge strane, visok stepen delokalizacije naelektrisanja na anjonu dovodi do nižeg efektivnog naelektrisanja na njegovim baznim proton akceptorskim centrima i slabijeg privlačenja protona i anjona. Kao rezultat ovoga, $H_{8-n}XM_{12}O_{40}$ su mnogo jače kiseline od $H_{8-n}XO_4$ [48].

Tabela 3. Konstante disocijacije HPK i H_3PO_4 u vodenim rastvorima na 25 °C [47]

	$H_5PMo_{10}V_2O_{40}$	$H_6PMo_9V_3O_{40}$	$H_7PV_{12}O_{36}$	$H_8NbMo_{12}O_{42}$	$H_8CeMo_{12}O_{42}$	$H_8UMo_{12}O_{42}$	H_3PO_4
pK_1							2,12
pK_2							7,20
pK_3							11,9
pK_4	1,16	1,25	3,4	3,24			
pK_5	2,4	1,62	4,9	3,43	2,12		
pK_6		2,00	6,4	3,64	1,98	2,13	
pK_7			7,9	4,28	2,99	3,02	
pK_8				5,73	4,16	4,31	

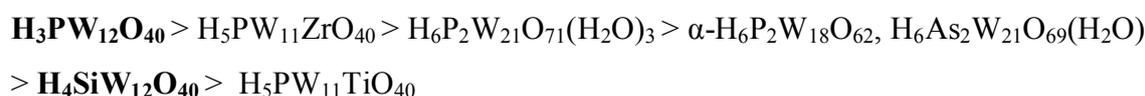
Nevodeni i mešoviti rastvarači pokazuju različite efekte na konstante disocijacije HPK. Šta više, HPK su značajno stabilnije u organskim rastvaračima. U tabeli 4. [47], date su konstante disocijacije različitih HPK i nekih neorganskih kiselina u sirćetnoj kiselini, acetonitrilu, acetonu i etanolu.

Na osnovu vrednosti iz tablice 4. može se zaključiti da su HPK mnogo jače od uobičajenih mineralnih kiselina, čak i od vrlo jakih kiselina kao što su CF_3SO_3H i $HClO_4$. Ova činjenica je od osnovnog značaja za primenu HPK u kiseloj katalizi. Podaci u tabeli takođe pokazuju da kiselost HPK u acetonitrilu, acetonu, etanolu ne varira značajno sa promenom sastava i strukture HPK.

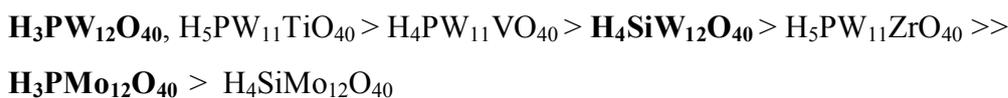
Tabela 4. Konstante disocijacije HPK i nekih neorganskih kiselina u različitim rastvaračima na 25 °C [47]

HPK	HOAc	CH ₃ CN			(CH ₃) ₂ CO			C ₂ H ₅ OH		
	pK ₁	pK ₁	pK ₂	pK ₃	pK ₁	pK ₂	pK ₃	pK ₁	pK ₂	pK ₃
H ₆ P ₂ W ₂₁ O ₇₁ (H ₂ O) ₃	4,66	1,8	5,6	7,6						
H ₆ P ₂ W ₁₈ O ₆₂	4,39	1,8	5,7	7,7						
H ₆ P ₂ Mo ₁₈ O ₆₂	4,36	2,0	6,0	8,0						
H ₃ PMo ₁₂ O ₄₀	4,68				2,0	3,6	5,3	1,8	3,4	5,3
H ₄ SiW ₁₂ O ₄₀	4,87	1,9	5,9	7,9	2,0	3,6	5,3	2,0	4,0	6,3
H ₃ PW ₁₂ O ₄₀	4,70	1,7	5,3	7,2	1,6	3,0	4,1	1,6	3,0	4,1
H ₅ PW ₁₁ TiO ₄₀	5,32	2,0	6,0	7,9	1,7	3,2	4,2			
H ₅ PW ₁₁ ZrO ₄₀	5,45	1,8	5,5	7,5	2,0	3,4	5,2			
H ₃ PW ₁₁ ThO ₃₉	5,48									
CF ₃ SO ₃ H	4,97	5,5			2,7					
HNO ₃					3,6			3,6		
HClO ₄	4,87									
HBr	5,60									
H ₂ SO ₄	7,00									
HCl	8,40							4,0		

Redosledi jačine kiselosti HPK se razlikuju u svakom pojedinom rastvaraču. Tako, u CH₃CN, kiselost HPK sa adendnim W se menja u sledećem nizu [47]:



U acetonu redosled kiselosti HPK je [47]:



Iako sastav HPK ima mali uticaj na njihovu kiselost, ovaj efekat se ipak može uočiti. Kiselost se smanjuje sa redukcijom HPK i zamenom Mo ili W atoma sa V i/ili zamenom centralnog atoma P sa Si.

Mnogo jasnija zavisnost kiselosti od sastava i strukture HPK se uočava u slučaju rastvora u sirćetnoj kiselini. Za HPK sa W kiselost se menja na sledeći način:



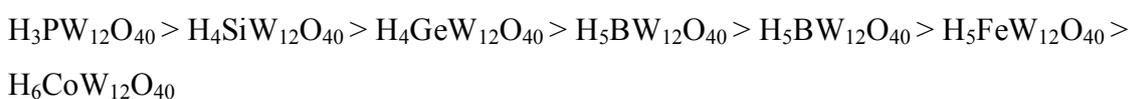
Za HPK *Keggin*-ovog tipa konstante disocijacije u acetonu se smanjuju u seriji:



Zamena W(VI) sa Mo(VI) nema uticaj na vrednost konstanti disocijacije, dok zamena W sa Ti(IV), Zr(IV) ili Th(IV) dovodi do smanjenja konstanti disocijacije.

Na kiselost rastvora utiče stepen disocijacije kiseline kao i bazičnost rastvarača. Tako na primer, u manje polarnoj sirćetnoj kiselini sve HPK su relativno slabe monobazne kiseline. U polarnijim rastvaračima kao što su CH_3CN , $(\text{CH}_3)_2\text{CO}$ i $\text{C}_2\text{H}_5\text{OH}$, HPK sa *Keggin*-ovom strukturom su potpuno disosovane u prvom koraku i delimično u drugom. Kiseline, kao što su $\text{H}_3\text{PW}_{12}\text{O}_{40}$ i $\text{H}_5\text{PW}_{11}\text{TiO}_{40}$ su u acetonu potpuno disosovane u prvom i drugom i delimično u trećem koraku.

Merenjem *Hammett*-ove kiselinske funkcije H_0 indikatorskom metodom, za seriju razblaženih rastvora HPK *Keggin*-ovog tipa, u acetonitrilu pri istoj koncentraciji protona, nađeno je da kiselost opada u sledećem nizu [47]:



Ovaj niz je u saglasnosti sa teorijski predviđenim povećanjem jačine kiseline sa smanjenjem naelektrisanja anjona.

H_0 vrednosti su takođe određene i za vodene rastvore $\text{H}_6\text{P}_2\text{W}_{21}\text{O}_{71}$. Pri istim molarnim koncentracijama ova kiselina je mnogo jača od $\text{H}_3\text{PW}_{12}\text{O}_{40}$, ali pri istoj koncentraciji protona njihove kiselosti su vrlo slične [49, 50].

Kiselost je najvažnija karakteristika HPA. Jačina HPK je mnogo veća od odgovarajuće slobodne kiseline heteroatoma. Centralni atom ima najveću ulogu u kiselosti HPA, a ukupno naelektrisanje anjona je mnogo značajnije od tipa adendnog atoma. U vodenim rastvorima svi protoni u HPK su potpuno disosovani.

Čvrste HPK su prave *Brønsted*-ove kiseline i dosta su jače od standardnih čvrstih kiselina, kao što su $\text{SiO}_2\text{-Al}_2\text{O}_3$.

2.4.5. Lakunarni heteropolianjoni

Ranije pomenuti lakunarni heteropolianjoni, nastali alkalnom disocijacijom HPA, formiraju posebnu kategoriju. Njihove osobine se razlikuju od osobina kompletnih HPA:

- Nisu prave kiseline
- Nisu rastvorni u organskim rastvaračima
- Imaju puferski kapacitet
- Stabilni su u uskom opsegu pH vrednosti.

Pored ovog odlikuje ih niži stepen simetrije, veća gustina naelektrisanja, kao i veća reaktivnost u odnosu na roditeljski oblik.

Značajna razlika između ovih jedinjenja i kompletnih (planarnih) HPA je njihova sposobnost da koordinišu katjone. Oni mogu igrati ulogu domaćina za različite metalne katjone. Stabilnost ovakvih kompleksa zavisi i od HPA i od metalnih katjona, pri čemu su molibdenovi HPA manje stabilni od volframovih. Precizna struktura ovakvih kompleksa je nepoznata, iz razloga što su šupljine ili metalom ispunjene šupljine slučajno orjentisane u HPA kristalima, pa je vrlo komplikovano određivanje njihove strukture pomoću rendgenske difrakcije. Ovi kompleksi su u opštem slučaju stabilni na pH od 4 do 8, dok u kiselijim sredinama gube metalni jon i lakunarni ligandi prelaze u polazni *Keggin*-ov ili *Dawson*-ov anjon [25].

2.4.6. Toksičnost

Heteropoli jedinjenja nisu štetna za zdravlje ljudi i ne predstavljaju opasnost po okolinu, izuzev ako su u njihovom sastavu prisutni toksični metali. Pri fiziološkim uslovima HPA su u velikoj meri razloženi, a volframova jedinjenja kao što su WO_4^{2-} imaju nisku toksičnost u poređenju sa jedinjenjima drugih teških metala. Ovo je posledica toga što su oksoanioni u molekulskom obliku vrlo rastvorni u vodi i vrlo brzo se izlučuju preko urina [51]. W, Mo i V su u nekom stepenu toksični, ali ni jedan od njih ne dovodi do hroničnog trovanja, jer se ne akumuliraju u organizmu. Od tri pomenuta elementa, V je najopasniji, verovatno zbog visokog oksidacionog potencijala. Pri industrijskoj primeni ovih jedinjenja nije zabeležena njihova škodljivost po zdravlje i bezbednost ljudi [25].

Pri primenama POM u biomedicini, glavna prepreka je njihova neorganska priroda, usled čega je izražena njihova toksičnost *in vivo* [52]. Iz tog razloga, sintetišu se novi POM modifikovani tako da uzrokuju manju ćelijsku toksičnost, dok je zadržana zahtevana biološka aktivnost. Tako, otkad je sintetizovan od strane *Klemperer*-a [53] 1978. prvi POM modifikovan sa organskim polianjonom, a koji se vezuje kovalentno za organskometalnu grupu $[(\text{CpTi})\text{PW}_{11}\text{O}_{39}]^{4-}$, sintetizovan je i veliki broj organsko-metalno-supstituisanih heteropolianjona, supstitucijom metala, kao i organskom derivatizacijom [54-57]. *Kuntić* i saradnici [58] su ispitivali ćelijsku toksičnost

jedinjenja volframfosforne kiseline sa aminokiselinama, alaninom i glicinom, i došli do zaključka da postoji smanjenje toksičnog delovanja na ćelije u modifikovanim HPK.

2.5. OPŠTI PRINCIPI SINTEZA POLIOKSOMETALATA U VODENIM RASTVORIMA

Najjednostavniji metod za sintezu heteropolioksometalata (HPOM) sastoji se u zakišeljavanju smeše vodenih rastvora oksometalata i pogodnog oblika heteroatoma, konvencionalnim neorganskim kiselinama kao što su hlorovodonična, sumporna, azotna itd. Poželjno je koristiti alkalne soli oksometalata rastvorljive u vodi, kao što su $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ili $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ koje su komercijalno dostupne. Takođe je i za heteroatome pogodno birati rastvorna jedinjenja, posebno oksokiseline (H_3PO_4 , H_3AsO_4) ili alkalne soli (Na_2SiO_3).

Faktori koji se moraju uzeti u obzir pri sintezama su:

- **Molekulski odnos M/X**, koji je generalno blizak stehiometrijskom odnosu, ali u nekim slučajevima je neophodan višak heteroatoma.
- **Temperatura**; neke vrste se dobijaju u metastabilnom stanju i tada je pažljiva kontrola temperature neophodna.
- **Konačna pH vrednost**; svaki HPOM ima region pH u kome je stabilan, ili bar u kome je njegov udeo u smeši sa nekoliko HPOM najveći.
- **Priroda rastvarača**; u nekim slučajevima stabilnost je poboljšana dodatkom rastvarača kao što su alkohol, dioksan ili acetonitril u vodeni rastvor.
- **Priroda kontra jona**; POM su polianjoni koji reaguju manje ili više sa katjonima u rastvoru. Kao rezultat, formiranje pojedinih vrsta je kontrolisano katjonima prisutnim u rastvorima.

Izolovanje HPK u čvrstom stanju ima veliki značaj za njihovu identifikaciju i strukturnu karakterizaciju. Dodavanje alkalnih, amonijumovih, tetraalkilamonijumovih ili guanidinijevih hlorida, bromida ili nitrata rastvoru HPK dovodi do taloženja heteropoli soli. Međutim, u rastvoru su često prisutne različite vrste, pa je njihovo razdvajanje moguće jedino ako postoje velike razlike u proizvodima rastvorljivosti. Ukoliko je kiselina stabilna moguće je njeno izolovanje ekstrakcijom pomoću etra [59].

Nedostatak ovog klasičnog postupka je mali prinos i veliki gubici, tako da se za sinteze koriste i druge metode, kao što je elektromembranska sinteza [60] ili jonska izmena [61].

2.6. PRIMENA POLIOKSOMETALATA

Primena POM je zasnovana na njihovim jedinstvenim osobinama, kao što su veličina, masa, sposobnost prenosa i “skladištenja” elektrona i protona, termička stabilnost, te visoka Brønsted-ova kiselost odgovarajućih kiselina.

POM nalaze primenu u različitim oblastima hemije. Jedna od najstarijih primena je u analitičkoj i kliničkoj hemiji. Primenjuju se za detekciju, odvajanje i određivanje mnogih supstanci, što je zasnovano na osobinama kao što su velika molekulska masa, elektrohemijska aktivnost i mogućnost redukcije, te mogućnost da veliki broj elemenata može biti inkorporiran u njihovu strukturu. Prva i verovatno najrasprostranjenija je primena u analitičkoj hemiji za određivanje P i Si. Postoji veliki broj elemenata, kao što su Ti, Zr, Hf, Th, Nd, Ce, Sb, čije je analitičko određivanje zasnovano na formiranju heteropolimolibdata [62].

Sposobost POM da koagulišu proteine i talože organske molekule čini ih vrlo pogodnim za kvantitativno određivanje farmaceutika i bioloških uzoraka. Reakcije taloženja su uglavnom zasnovane na elektrostatičkoj interakciji između POM i katjonskih centara na biomolekulima [63].

Zbog visokog stepena hidratacije i prisustva kiselih protona HPK su dobri protonski provodnici. Na visoku protonsku provodljivost HPK skrenuli su pažnju 1979. godine japanski naučnici *Nakamura* i *Ogino* sa saradnicima [64, 65]. Sa vrednostima provodljivosti od $\kappa = (1-100) \cdot 10^{-3} \text{ Scm}^{-1}$ na sobnoj temperaturi svrstavaju se u superjonske protonske provodnike. Zbog ove osobine HPJ postaju interesantna kao obećavajući materijali, potencijalno pogodni za izradu različitih elektrohemijskih uređaja, na primer, membrana u H_2/O_2 gorivnim baterijama, jon selektivnih membrana, senzora, a zbog njihovih oksido-redukcionih osobina i elektrohromnih displeja [66, 67].

Dva polja u kome POM nalaze najveću primenu su kataliza i medicina.

2.6.1. Primena polioksometalata u medicini

Iz godine u godinu u literaturi se beleži sve veći broj potencijalnih primena u humanoj medicini.

Antiviralna aktivnost

Grupa istraživača u Parizu predvođena *Chermann*-om primetila je inhibitorni efekat "supernatanta ćelijske kulture" na murin leukemija i sarkoma viruse. Ovaj "supernatant" se dobija u proceduri pri kojoj se dodaje silicijumvolframova kiselina [68]. Posle ovog otkrića oni su nastavili sistematsko ispitivanje uticaja WSiA kao i drugih POM [69-72]. Pojava HIV virusa je intenzivirala ispitivanja potencijalnih antivirusnih lekova, a među njima i POM [73-77].

Antitumorska aktivnost

Prve rezultate o antitumorskoj aktivnosti POM *in vivo* je publikovao *Mukherjee* [78]. Smeša WPA, MoPA i kofeina je davana pacijentu obolelom od karcinoma crevnog trakta. Smeša je rastvorana u vodenom rastvoru natrijum-laktata ili natrijum-bikarbonata i u obliku injekcija davana pacijentu u toku 6 dana. Nakon primene ove smeše zabeležen je prestanak rasta tumora.

Yamase i saradnici opisuju heptamolibdate kao nove antitumor supstance koje za 80% usporavaju rast metilholantren-indukovanog tumora i adenokarcinoma, a takođe pokazuju značajnu antitumorsku aktivnost prema humanom karcinomu dojke implantiranom u laboratorijske miševе. Njihovi rezultati su takođe pokazali da struktura $[\text{Mo}_7\text{O}_{24}]^{6-}$ igra veliku ulogu u antitumorskoj aktivnosti [79, 80].

Posle ovoga, različiti tipovi POM sa različitim metalima, kao što su Mo, V ili W, okarakterisani su i proučavani sa aspekta antitumorske aktivnosti. Pažnja se posvećuje korelaciji citotoksičnosti jedinjenja sa redukcionim potencijalom metalnog jona. U nekoliko serija vrlo sličnih jedinjenja je nađeno da vrednosti IC_{50}^4 imaju isti redosled kao i redukcionim potencijali; veći redukcionim potencijal, veća citotoksičnost [81]. Međutim, ovo ipak ne može biti generalizovano. Struktura i sastav takođe igraju značajnu ulogu u aktivnosti. Biomedicinsko ispitivanje POM koji sadrže amino

⁴ IC_{50} je mera toksičnosti POM. To je efektivna koncentracija koja odgovara 50%-tnoj inhibiciji ćelijskog rasta

kiseline ili peptide je fokusirano na nalaženje POM koji bi pokazivali dobru antitumorsku aktivnost uz poboljšanje kliničke bezbednosti primene [82].

Antibakterijska aktivnost

Najšire korišćena grupa antibiotičkih lekova, β -laktamski antibiotici, kao što su penicilini i cefalosporini, onemogućavaju formiranje ćelijskog zida u bakteriji. Porast otpornosti bakterija prema lekovima predstavlja veliki problem u medicini. Naime, mnoge bakterije proizvode enzime, β -laktamaze, koje hidrolizuju β -laktamski prsten antibiotika i čine ga neaktivnim. Iz tog razloga leku se dodaju inhibitori β -laktamaze (npr. klavulonska kiselina). *Tajima* je 1993. publikovao efekat smeše volframata i fosfata u kombinaciji sa β -laktamskim antibioticima [83]. On je otkrio pojačanje antibakterijskog efekta leka na soj bakterija meticilin-resistant *Staphylococcus aureus* i nazvao ga *faktor T*, koji je kasnije identifikovao kao monolakunarni $[PW_{11}O_{39}]^{7-}$ [84]. Istraživanje je prošireno na više od 70 POM u kombinaciji sa β -laktamskim antibioticima [85, 86].

2.6.2. Primena polioksometalata u katalizi

Između svih ostalih primena POM, primena u katalizi je najznačajnija. Od svih patentiranih primena POM preko 80 % je vezano za katalizu [87].

Sistematsko ispitivanje počinje početkom sedamdesetih godina prošlog veka. Većina pionirskih radova iz tog doba potiče iz Japana (*Izumi, Misono, Ono, Otake, Yoneda* i njihovi saradnici) i Rusije (*Matveev* i saradnici). Uspešna industrijska primena u periodu od 70-tih i 80-tih godina prošlog veka dovodi do ekspanzije novih istraživanja na tom polju. Prvi komercijalni proces zasnovan na POM je hidratacija propena do 2-propanola iz 1972. godine.

I danas postoji veliki broj istraživanja i vrlo je verovatno da će ih biti i u budućnosti, zahvaljujući brojnim prednostima koje POM imaju kao katalizatori. Naime, katalizatori zasnovani na POM imaju veću aktivnost nego poznati tradicionalni katalizatori, upotrebom ovih katalizatora često je moguće postići višu selektivnost, a takođe su i ekološki pogodni. Najznačajnije prednosti su njihova multifunkcionalnost i strukturna mobilnost.

Zahvaljujućim svojim jedinstvenim osobinama HPJ obećavaju kao kiseli, redoks i bifunkcionalni (kiseli i redoks) katalizatori. Sa jedne strane, HPK imaju vrlo jaku *Brønsted*-ovu kiselost, a sa druge su vrlo efikasni oksidansi, koji pokazuju brzu reverzibilnu multielektronsku redoks transformaciju. Njihove kiselo-bazne i oksido-redukционе osobine variraju sa hemijskim sastavom. Čvrsta HPJ imaju diskretnu jonsku strukturu sastavljenu od HPA i kontra katjona, slično mrežastoj strukturi metalnih oksida ili zeolita. Struktura često ostaje očuvana pri supstituciji ili oksidaciji/redukciji i pokazuje visoku protonsku provodljivost i »pseudotečnu fazu«. Povrh svega, mnoga HPJ imaju vrlo dobru rastvorljivost u polarnim rastvaračima i prilično visoku termičku stabilnost u čvrstom stanju.

Katalitičke reakcije se mogu sprovoditi i u homogenim i heterogenim (gas-čvrsto stanje, tečno-čvrsto stanje ili dvofaznim tečno-tečnim) sistemima.

Postoje tri tipa heterogene katalize: 1) površinski, 2) balk (u masi) tip I-pseudotečni i 3) balk tip II, kao što je prikazano u tabeli 5. [88].

Tabela 5. Tri tipa heterogene katalize HPJ [88]

Tip	Opis	Primer
Površinski	<ul style="list-style-type: none">• Uobičajeni tip katalize u kome se reakcija odvija na dvodimenzionalnoj površini čvrstog katalizatora;• brzina reakcije proporcionalna veličini površine	Oksidacija aldehida i CO
Balk tip I-pseudotečni	<ul style="list-style-type: none">• Reaktanti su apsorbirani u interpolianjonski prostor i tu reaguju, a produkti se odatle desorbiraju;• reakciono polje postaje trodimenzionalno, kao kod tečnosti;• brzina reakcije proporcionalna zapremini katalizatora	Dehidracija alkohola na niskoj temperaturi
Balk tip II	<ul style="list-style-type: none">• Reakcija se uglavnom odigrava na površini, ali učestvuje cela zapremina katalizatora zahvaljujući brzim migracijama protona i elektrona;• brzina reakcije proporcionalna zapremini katalizatora u idealnom slučaju	Oksidativna dehidrogenacija i oksidacija H ₂

Lakunarna HPJ modifikovana pomoću prelaznih metala takođe nalaze svoju primenu kao katalizatori. Tako se lakunarni $K_7PW_{11}O_{39}$ modifikovan sa viškom $MnCl_2$ pokazao kao efikasan i selektivan katalizator za oksidehidrogenizaciju propana [90]. Lakunarni metal-supstituisani POM pokazuju elektrokatalitičku aktivnost na površinama elektroda [91].

Međutim, pored svih prednosti HPJ kao čvrstih katalizatora, mora se istaći jedan nedostatak. Naime, HPJ imaju malu specifičnu površinu od $1-10\text{ m}^2\text{g}^{-1}$. Iz ovog razloga je važno povećati specifičnu površinu, odnosno broj dostupnih kiselih centara. Ovo se može ostvariti nanošenjem HPJ na površinu nosača sa većom specifičnom površinom. Kao nosač se najviše upotrebljava SiO_2 , a takođe se koriste i $SiO_2-Al_2O_3$, Al_2O_3 , TiO_2 , ugljenik, gline, heteropoli soli i drugi jonoizmenjivi materijali [4, 89].

2.7. METODE ISPITIVANJA HETEROPOLI JEDINJENJA

Zbog kompleksnih sastava i struktura, kao i nestabilnosti, za analizu POM preporučljivo je kombinovati različite eksperimentalne metode i tehnike. Pogodna metoda mora imati mogućnost razlikovanja sličnih formulacija, kao što su na primer $P_2W_{17}O_{61}^{10-}$ i $P_2W_{68}O_{62}^{6-}$ i preciznost određivanja heteroelemenata koji su prisutni u manjoj koncentraciji (< 1 do 2 %). Takođe, na izbor metode utiče i agregatno stanje ispitivanog uzorka, odnosno da li se ispituju čvrsti (kristalni) uzorci ili rastvori.

Zbog velikog stepena hidratacije HPJ, termijska analiza se najčešće koristi u analizi kristalnih uzoraka. Termijskom analizom dolazi se do informacija o temperaturama na kojima dolazi do faznih transformacija HPJ [44, 45].

Elektrohemijske tehnike nalaze primenu u karakterizaciji redoks osobina POM. Na primer, ciklična voltometrija može dati informacije o reduktibilnosti i stabilnosti redukovanih oblika [92, 93]. Za ispitivanja različitih izomera najviše se koriste polarografija i ciklična voltometrija [94], dok se polarografske tehnike takođe koriste za određivanje Mo i W u POM [95, 96].

Sa dostupnošću instrumenata sa velikom rezolucijom, atomska emisijska spektroskopija sa induktivno spregnutom plazmom (ISP-AES), može biti iskorišćena za analizu POM. Prednost ove metode je relativno jednostavna priprema uzorka, brzina, posebno u slučaju istovremene analize više elemenata, kao i velika preciznost i tačnost

pri pažljivoj pripremi standarda, te odsustvo fizičkih interferencija. Ograničenje ove metode je povezano sa potencijalnim interferencijama elemenata; međutim, kako za svaki element postoji više linija, pogodnim odabirom linije spektralne interferencije se mogu izbeći ili minimizovati [97].

Spektroskopske metode nalaze veliku primenu u ispitivanju POM, pa tako vrlo uspešno mogu da se primene i za određivanje strukture HPJ u tečnom i čvrstom stanju. Najšire se primenjuju ultraljubičasta/vidljiva (ULj/Vid), infracrvena (IC), ramanska i nuklearna magnetno rezonantna (NMR) spektroskopija.

2.7.1. ULj/Vid spektroskopija

ULj/Vid apsorpcioni spektri se koriste i u strukturalnoj i kvantitativnoj analizi HPJ. Mogu se primeniti u ispitivanju vrlo razblaženih rastvora (od 10^{-3} do 10^{-5} moldm⁻³) u rastvaračima koji su dovoljno transparentni u ispitivanoj spektralnoj oblasti.

HPA jako apsorbuju u ULj oblasti između 180 i 270 nm, što je rezultat $p\pi - d\pi$ prelaza u M-O vezi. Na ULj spektar mogu uticati: struktura kompleksa, katjoni i supstituišući elementi. HPA sa Keggin-ovom strukturom pokazuju dve jake apsorpcione trake. Trake oko 200 i 260 nm odgovaraju $O_d \rightarrow M$, odnosno $O_b/O_c \rightarrow M$ prenosu naelektrisanja, respektivno [98].

Za WPA sa KA maksimum trake se nalazi na 264 nm. Za druge volframfosfatne anjone položaj maksimuma trake se hipsohromno pomera sa smanjenjem odnosa W/P. Maksimumi apsorpcionih traka vodenih rastvora različitih volframfosfatnih anjone dati su tabeli 6. [37].

Tabela 6. Položaji maksimuma traka u ULj spektrima vodenih rastvora različitih volframfosfatnih anjona [37]

Anjon	λ_{\max} / nm
$[PW_{12}O_{40}]^{3-}$	264
$[P_2W_{21}O_{71}]^{6-}$	257
$[P_2W_{19}O_{67}]^{10-}$	253
$[P_2W_{18}O_{62}]^{6-}$	250
$[PW_{11}O_{39}]^{7-}$	244
$[PW_9O_{34}]^{9-}$	249
PO_4^{3-}	< 200

Kvantitativna ispitivanja apsorpcionih spektara polioksometalata u različitim organskim sredinama su pokazala da postoje regioni u spektrima u kojima se ispoljavaju različiti efekti organskog rastvarača. Tako su *Hill i Bouchard* našli da su u oblasti većih energija u blizini maksimuma apsorpcije, promene u spektrima od rastvarača do rastvarača umerene do slabe. Sa druge strane, u oblasti nižih energija, krilo trake je veoma osetljivo na vrstu rastvarača. Takođe su našli da su apsorpcioni koeficijenti u nekoliko organskih rastvarača za WPA slični i za oko 30 % viši nego u vodi, dok se položaji maksimuma veoma malo razlikuju od rastvarača do rastvača [99].

Za WSiA, *Fournier* i saradnici su našli da se talasna dužina menja od 261 nm za vodu (najpolarniji ispitivani rastvarač) do 263,5 nm za dihlormetan (najmanje polaran) [41].

ULj/Vid spektri su posebno značajni za ispitivanja redoks osobina HPA, pošto redukovani oblici HPA vrlo intenzivno apsorbuju. Moguće je razlikovati jednoelektronski i dvoelektronski redukovane HPK. U kinetičkim ispitivanjima redoks osobina se gotovo uvek koristi ova metoda. *Barteau* i saradnici su pokazali da se ivica apsorpcione trake može dovesti u vezu sa redoks osobinama HPA. Tako HPA sa većom oksidacionom snagom imaju ivicu apsorpcione trake na većim talasnim dužinama [100].

ULj/Vid spektroskopija se vrlo često koristi za određivanje koncentracije HPK kao katalizatora u katalitičkim merenjima, merenjem apsorpcije maksimuma apsorpcione trake [101]. Ultraljubičasta apsorpcija molibdenovih HPA može biti iskorišćena za određivanje sadržaja P ili Si u uzorku, jer dodatak Mo u višku u kiseli rastvor koji sadrži P ili Si dovodi do formiranja HPK *in situ*, što se može pratiti pomoću ULj spektara.

2.7.2. Vibraciona spektroskopija

Infracrvena spektroskopija je najčešće korišćena tehnika za karakterizaciju HPJ, zbog jasno definisanih 5 ili 6 traka koje odgovaraju *Keggin*-ovoj strukturi. Vrlo često ova metoda se koristi za dokazivanje prisustva ove strukture u različitim sistemima, na primer u katalitičkim merenjima.

Jedno od prvih, ako ne i prvo, ispitivanje heteropoli jedinjenja ovom metodom potiče od *Sharpless*-a i *Munday*-a, koji su ispitivali amonijumove soli 12-volfram- i 12-

molibdofosforne, volframorne, volfram- i molibdensilicijumove, volfram- i molibdenarsenove, molibdomanganove i molibdotitanove kiseline, tehnikom KBr pastile, te predložili asignaciju traka [102]. Detaljno ispitivanje molibdovanadofosforne kiseline i njenih natrijumovih i amonijumovih soli, tehnikom suspenzije u Nujol-u dali su *Tsigdinos* i *Hallada* 1968. godine [103]. Od 1968. god. izašao je veliki broj publikacija sa IC spektrima ovih jedinjenja, između kojih se po citiranosti ističe francuska grupa (*R. Thouvenot, C. Rocchiccioli-Deltcheff, P. Souchaz, R. Frank, M. Fournier*).

Vibracioni spektri HPK se mogu posmatrati kao doprinos POM anjona (primarna struktura) i kristalizacione vode i hidratizanih protona (sekundarna struktura).

Izolovani KA ima, kao što je pomenuto, T_d simetriju i njegovi normalni vibracioni modovi mogu biti predstavljeni kao:

$$\Gamma_{\text{vib}} = 9A_1 + 4A_2 + 13E + 16F_1 + 22F_2$$

od kojih su F_2 modovi aktivni i u ramanskim i IC spektrima, dok su A_1 i E modovi samo ramanski aktivni. Iako su mešanja između vibracija XO_4 tetraedara i MO_6 oktaedara neizbežna, trake u spektrima se obično označavaju kao vibracije grupa. Strogo govoreći, ovo bi važno samo za $M=O_d$ istežuću vibraciju. Doprinosi različitih tipova istežućih modova su [104]:

$$\Gamma_{X-O} = A_1 + F_2$$

$$\Gamma_{M-O_a} = A_1 + E + F_1 + 2F_2$$

$$\Gamma_{M-O_b} = A_1 + A_2 + 2E + 3F_1 + 3F_2$$

$$\Gamma_{M-O_c} = A_1 + A_2 + 2E + 13F_1 + 3F_2$$

$$\Gamma_{M-O_d} = A_1 + E + F_1 + 2F_2$$

Simetrične i asimetrične vibracije različitih vrsta M-O veza se javljaju u sledećim spektralnim oblastima:

- M- O_d veze od 1000-960 cm^{-1}
- M- O_b -M mostovi 890-850 cm^{-1}
- M- O_c -M mostovi 800-760 cm^{-1} .

Vibracioni mod XO_4 je gotovo nezavistan od drugih modova za $X = P$, ali u slučaju $X = Si, Ge, B$, itd. dolazi do mešanja sa drugim vibracionim modovima. Istežuće vibracije Si-O, Ge-O i P-O na 930, 830 i 1080 cm^{-1} u KA, respektivno, pokazuju više

vrednosti frekvencija nego jednostavni XO_4^{n-} anjon, ukazujući na izraženiji π karakter X-O veze u *Keggin*-ovom anjonu [105].

Glavne trake koje se javljaju u IC spektrima WSiA, WPA i MoPA date su tabeli 7. [22, 104].

Tabela 7. Glavne trake koje se javljaju u IC spektrima *Keggin*-ovih anjona WSiA, WPA i MoPA [22, 104, 107]

	$SiW_{12}O_{40}^{4-}$	$PW_{12}O_{40}^{3-}$	$PMo_{12}O_{40}^{3-}$	Asignacija
Talasni brojevi/ cm ⁻¹ i intenziteti traka		1080 j	1070 j	$\nu_{as}(P-O_a)$
	1020 sr			
	982 j	985 j	965 j	$\nu_{as}(M-O_d)$
	930 vj			$\nu_{as}(Si-O_a)$
	885 sr	887 j	870 j	$\nu_{as}(M-O_b-M)$
	792vj	807 vj	790 vj	$\nu_{as}(M-O_c-M)$
		598 sr	598 sr	$\delta_{as}(O_aXO_a)$
	558 r			
	535 j	525 j	500 sr	
	515 sl			
	480 r	480 j	460 j	
	415 j	425 j	410 j	
[vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame], M = W ili Mo, X = P ili Si v- istežuća, δ -deformaciona, s-simetrična, as-asimetrična vibracija				

Talasni brojevi pojedinih vibracija variraju u zavisnosti od rastvarača, stepena hidratacije čvrstih HPK i od veličine katjona u odgovarajućoj soli. *Rocchiccioli-Deltcheff* i saradnici su ispitujući veliki broj jedinjenja sa *Keggin*-ovom strukturom uočili da je u većini slučajeva anjon-anjon interakcija elektrostatičkog tipa odgovorna za povećanje frekvencija istežućih M-O_d vibracija $\nu(M-O_d)$. Ova interakcija je povezana sa veličinom katjona, tako da što je katjon manji, viša je frekvencija M-O_d vibracije. Ova interakcija nestaje u slučaju kada je kontra jon dovoljno velik da drži polianjone na rastojanju. Minimalno rastojanje od 0,6 nm između O_d kiseonika susednih polianjona je potrebno za zanemarivanje ove interakcije [107].

Pomoću vibracione spektroskopije se mogu pratiti izomeri *Keggin*-ove strukture. Vibracioni spektri svih α izomera različitih volframovih i molibdenovih anjona su slični, jer imaju identičnu strukturu. Sa druge strane, strukturna homogenost β izomera nije tako očigledna. Kada se posmatraju anjoni u celini, α - izomer ima T_d simetriju, a β - izomer C_{3v} simetriju, tako da se očekuje da vibracioni spektri α -izomera budu mnogo

složeniji od spektara β -izomera (svaki F_2 mod T_d grupe dovodi do dva A_1+E moda u C_{3v} grupi i neki zabranjeni simetrični modovi postaju dozvoljeni). Kako se ovo cepanje ne uočava u spektrima β -izomera, očigledno da klasični pristup ne može adekvatno da se primeni u slučaju ove grupe jedinjenja. *Thouvenot* i saradnici su predložili koncept po kome su M_3O_6 grupe povezane sa O_b atomima, po kojem pošto su M_3O_6 grupe slične u obe strukture moraju davati i slične spektre koji se onda razlikuju samo u oblasti karakterističnoj za "interligandne" vibracije [108].

C. Rocchiccioli-Deltcheff i *M. Fournier* su pratili efekat dehidratacije na vibracije u Keggin-ovom anjonu kod WPA i MoPA i našli da je $M-O_b-M$ asimetrična istežuća vibracija $\nu_{as}(M-O_b-M)$ osetljiva na stepen hidratacije. Pri dehidrataciji dolazi do smanjenja talasnog broja ove vibracije za oko 20 cm^{-1} [109].

Distorzija KA i narušavanje njegove tetraedarske simetrije dovodi do ukidanja trostruke degeneracije, F_2 modovi postaju razdvojeni i posledično, nove trake se javljaju u spektrima.

Kao što je pomenuto, lakunarni KA ima defektnu strukturu kojoj nedostaju jedan atom metala i jedan terminalni kiseonik. U opštem slučaju, kod ovih anjona dolazi do cepanja trake X-O vibracije, koje je posledica promene simetrije, jer KA ima T_d simetriju, dok lakunarni anjon ima C_s simetriju. Ova promena simetrije dovodi do ukidanja degeneracije i pojave novih traka. Za lakunarni KA se očekuju 147 normalna moda, i kako poseduje C_s simetriju, sve trake su i IC i ramanski aktivne. Pošto se u spektrima uočava samo oko 15-20 traka, svaka od njih potiče od nekoliko preklopljenih modova. Prema izračunavanju za KA označene su grupne frekvencije: trake između 1000 i 900 cm^{-1} su povezane sa istežućim $M - O_d$ vibracijama, a dve široke trake između 900 i 800 cm^{-1} sa $M-O_c-M$ i $M-O_b-M$ istežućim vibracijama. U oblasti nižih energija od 600 do 300 cm^{-1} nalazi se nekoliko traka povezanih sa savijajućim $M-O_c-M$ i $M-O_b-M$ i $O-Si-O$ vibracijama [110].

Korelacija IC i ramanskih spektara lakunarnih anjona sa spektrima KA potvrđuje hipotezu o defektnoj Keggin-ovoj strukturi. U slučaju $SiW_{11}O_{39}^{8-}$ anjona, dolazi do promene simetrije anjona od T_d simetrije u $SiW_{12}O_{40}^{4-}$ do C_s u $SiW_{11}O_{39}^{8-}$, što dovodi do širenja, ali ne i do očekivanog cepanja traka. IC spektri Mo i W anjona se razlikuju u oblasti istežućih $M-O_c-M$ vibracija. U slučaju $SiMo_{11}O_{39}^{8-}$ uočava se široka traka oko 740 cm^{-1} , a kod $SiW_{11}O_{39}^{8-}$ dve razdvojene trake na 797 i 725 cm^{-1} . U $SiMo_{11}O_{39}^{8-}$

uglovi svih Mo-O_c-Mo mostova su jednaki, ali manji nego u SiW₁₁O₃₉⁸⁻, što odgovara brznoj evoluciji SiMo₁₁O₃₉⁸⁻ u vodenim rastvorima (do smanjenja frekvencije istežuće M-O-M vibracije dolazi usled smanjenja ugla u M-O_c-M vezi, a u opštem slučaju smanjenje frekvencije istežuće vibracije se interpretira kao slabljenje kohezije između anjona). Sa druge strane u SiW₁₁O₃₉⁸⁻ samo mostovi koji su u susedstvu šupljine imaju drugačije uglove (traka na 725 cm⁻¹), dok su ostali isti kao i u SiW₁₂O₄₀⁴⁻ (traka na 797 cm⁻¹). Ovo ukazuje da su strukture sa Mo manje krute od odgovarajućih struktura sa W. U PM₁₂O₄₀³⁻ anjonu traka v₃ vibracije (F₂) je jasno odvojena od drugih u spektru. U PM₁₁O₃₉⁷⁻ ova traka se cepa na dve komponente, kod PMo₁₁O₃₉⁷⁻ na 1060 i 1010 cm⁻¹, a kod PW₁₁O₃₉⁷⁻ na 1085 i 1040 cm⁻¹, kao posledica smanjenja simetrije [130].

Trake karakteristične za IC spektre monolakunarne strukture PW₁₁O₃₉⁷⁻ su, prema literaturnim podacima, na 1100, 1046, 958, 904, 812 i 742 cm⁻¹ [111]. Međutim, podaci u literaturi nisu usaglašeni, tako da se javljaju i drugačije vrednosti. U tabeli 8. su sumirani položaji i asignacije traka u IC spektrima XW₁₁O₃₉ⁿ⁻ [105, 130].

Ramanska spektroskopija je osetljiva na: 1) broj različitih WO_x jedinica u strukturi, što se reflektuje brojem simetričnih traka u oblasti viših talasnih brojeva; 2) stepen distorzije pojedine WO_x strukture, koji se odražava pomeranjem trake simetrične istežuće trake u odnosu na traku idealne strukture; 3) prisustvo polivolframatih veza W-O-W. Nedostatak ove metode je mnogo veća osetljivost za vrste sa W-O vezom višeg reda, na primer W_d=O u odnosu na W-O [112].

Tabela 8. Glavne trake koje se javljaju u IC spektrima monolakunarnih Keggin-ovih anjona WSiA, WPA i MoPA [130]

Anjon	α-SiW ₁₁ O ₃₉ ⁸⁻	α-PW ₁₁ O ₃₉ ⁷⁻	α-PMo ₁₁ O ₃₉ ⁷⁻	Asignacija
Talasni broj/ cm ⁻¹	885	1085 1040	1060 1010	v _{as} (X-O _a)
	952	950	930 900	v _{as} (M-O _d)
	870	900 860	860	v _{as} (M-O _b -M)
	797 725	810 725	790 742	v _{as} (M-O _c -M)
M=W ili Mo, X=P ili Si; v _{as} - asimetrična istežuća vibracija				

Glavne trake koje se javljaju u ramanskim spektrima Keggin-ovih anjona WSiA, WPA i MoPA date su tabeli 9. [104, 22].

Tabela 9. Glavne trake koje se javljaju u ramanskim spektrima Keggin-ovih anjona WSiA, WPA i MoPA [22, 104, 107]

	SiW ₁₂ O ₄₀ ⁴⁻	PW ₁₂ O ₄₀ ³⁻	PMo ₁₂ O ₄₀ ³⁻	Asignacija
Talasni brojevi/ cm ⁻¹ i intenziteti traka	1016 vs			
	998 vj	1011 vj	997 vj	v _s (M-O _d)
	981 sr	996 sl	981 sr	v _{as} (M-O _d)
		981 sr	978 sr	v _s (P-O _a)
	935 sl			v _s (Si-O _a)
	915 sl	925 sl	900 sl	v _{as} (M-O _b -M)
	893 sl	900 sl	870 sl	
	553 sl	536 sl	605 sr	v _s (M-O-M)
	536 sl	522 sl		δ _{as} (O _a XO _a)
	371 sl	372 sl	374 sl	v _s (M-O _a)
	331 sl	337 vs	350 vs	
	220 j	217 j	248 j	
[vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame], M= W ili Mo, X= P ili Si; v- istežuća, δ-deformaciona, s-simetrična, as-asimetrična vibracija				

U slučaju monolakunarnih anjona trake koje odgovaraju v_s(M-O_d) i v_{as}(M-O_d) vibraciji se nalaze na 979 i 964 cm⁻¹ za PW₁₁O₃₉⁷⁻, odnosno na 963 i 948 cm⁻¹ za PMo₁₁O₃₉⁷⁻ [105]. U slučaju monolakunarnog SiW₁₁O₃₉⁸⁻ (čvrsti K₈SiW₁₁O₃₉) u ramanskom spektru se javljaju trake na 996, 973, 950, 923 cm⁻¹, koje se pripisuju v_s(W-O_d) vibraciji, zatim na oko 865 cm⁻¹ pridružena v_{as}(W-O_b-W) i na 805 cm⁻¹, v_{as}(W-O_c-W) vibraciji. Takođe se javljaju trake savijajućih vibracija na 524 cm⁻¹ (δ(W-O_b-W), δ(W-O_c-W)) i na oko 380 cm⁻¹ (δ(W-O_b-W), δ(W-O_c-W), δ(O-Si-O)) [110].

IC spektar α-P₂W₁₈O₆₂⁶⁻ je vrlo sličan onom kod roditeljskog Keggin-ovog oblika. I u ovom slučaju vibracije PO₄ tetraedra se posmatraju nezavisno od ostatka anjona. Trake na 960, 912 i 780 cm⁻¹ se pripisuju skeletnim vibracijama, i to traka na 960 cm⁻¹ W-O_d asimetričnoj istežućoj vibraciji, na 912 cm⁻¹ vibracijama "inter", a na 780 cm⁻¹ "intra" W-O-W mostova. Razlike u talasnim brojevima odgovarajućih vibracija kod α-PW₁₂O₄₀³⁻ i P₂W₁₈O₆₂⁶⁻ se mogu objasniti razlikama u uglovima između mostova u ove dve strukture (što je veći ugao veći je i talasni broj). Simetrična (993 cm⁻¹ u ramanskom spektru) i asimetrična W-O_d vibracija se javljaju na nižim

talasnim brojevima nego kod KA. Ovo odgovara slabljenju W-O_d veze sa njenim produženjem, kao što pokazuju kristalografska merenja.

Na istežuće vibracije u PO₄ tetraedru veliki uticaj ima simetrija polianjona. U α-P₂W₁₈O₆₂⁶⁻ svaki PO₄ tetraedar ima lokalnu simetriju C_{3v}, a celina od dva tetraedra u njemu D_{3h} simetriju. U IC spektrima ovog Dawson-ovog anjona, javljaju se trake na 1090 cm⁻¹ (jaka), 1022 cm⁻¹ (slaba) i oko 975 cm⁻¹ (rame). Prve dve trake proizilaze iz ν₃ (F₂) vibracije (1080 cm⁻¹ u Keggin-ovom anjonu). Treća vibraciona traka potiče iz IC neaktivnog moda ν₁ (A₁) (993 cm⁻¹ u ramanskom spektru KA) i uočava se kao rame na jakoj traci ν_{as}(W-O_d). U ramanskom spektru uočavaju se samo dve trake, slabog intenziteta na oko 1022 cm⁻¹ i srednjeg na oko 979 cm⁻¹ [113, 114].

Prema Valle i Briand [43] trake u IC spektrima P₂Mo₁₈O₆₂⁶⁻ su na 1075 (ν_{as} (P-O)), 1001 – 985 (ν_{as} (Mo-O)), 938 (ν_{as} (Mo-O_b-Mo)), 905 (δ(O-P-O)) i 865 – 761 (ν_{as} (Mo-O_c-Mo)) cm⁻¹.

Vibracioni spektri različitih poliookso -volframata i -molibdata su slični i u slučaju njihovog javljanja u smešama teško je izvršiti jednoznačnu identifikaciju samo na osnovu vibracionih spektara. Kao ilustracija u tabeli 10. su date trake u IC spektrima različitih volframfosfata [115].

Tabela 10. Trake koje se javljaju u IC spektrima različitih volframfosfata [115]

	Talasni broj/ cm ⁻¹									
	ν _{as} (P-O)			ν _{as} (W-O)		ν _{as} (W-O-W)				
K ₆ P ₂ W ₂₁ O ₇₁	1095	1085	1030	972	940	890	790	750	700	670
K ₇ P ₂ W ₂₀ O ₇₀	1090	1078	1020	955	925	860	795	748	660	
K ₁₄ P ₂ W ₂₀ O ₇₂	1080		1025	940		890	855	755	640	
K ₁₄ P ₂ W ₁₉ O ₆₉	1075	1065	1025	960		888	825	770	750	715
K ₇ PW ₁₁ O ₃₉	1085		1040	950		900	865	810	725	
A ₃ α-K ₉ PW ₉ O ₃₄	1056		1002	932	909	815	728			
A ₃ β-K ₉ PW ₉ O ₃₄	1054		1008	935	918	845	828	755		
A ₃ α-Na ₉ PW ₉ O ₃₄	1058		1015	937		886	820	763		
ν _{as} - asimetrična istežuća vibracija										

2.7.3. NMR spektroskopija

Iako bi teorijski u slučaju POM mogle biti primenjene ¹H, ¹¹B, ¹⁷O, ²⁷Al, ²⁹Si, ³¹P, ⁵¹V, ⁷¹Ga, ⁷⁷Se, ⁹⁵Mo, ⁹⁵Nb, ¹⁸³W, ¹²⁵Te i ¹⁹⁵Pt NMR spektroskopija, samo mali broj POM koji sadrže ove elemente je ispitivan NMR spektroskopijom.

U slučaju ^{31}P NMR hemijski pomak daje značajne informacije o strukturi i sastavu ovih materijala, dok ^{17}O NMR spektroskopija daje informacije o prirodi vezivanja kiseonikovih atoma. Ograničavajuća okolnost pri primeni ^{17}O NMR spektroskopije je niska prirodna zastupljenost ovog jezgra (0,04%) tako da je potrebno obogaćivanje uzorka ovim jezgrom. Međutim, sa savremenim instrumentima sa povećanom osetljivošću moguće je dobiti spektre sa zadovoljavajućim odnosom signal/šum u razumnom vremenskom periodu. Primena ^{29}Si NMR spektroskopije je takođe publikovana, ali zbog niske osetljivosti u poređenju sa ^{31}P NMR spektroskopijom, veoma malo se koristi. ^{183}W jezgro ima spin 1/2 i ^{183}W NMR spektri su sastavljeni od vrlo uskih linija, što ovu tehniku čini vrlo značajnom za objašnjavanje struktura, jer su hemijski pomaci veoma osetljivi na elektronske i strukturne promene. I ovi spektri se teže dobijaju, takođe zbog niže osetljivosti, pa se tek razvojem moćnijih instrumenata intenzivira njihova primena [116].

^{95}Mo NMR spektroskopija nije primenjiva za HPJ, jer ^{95}Mo ima spin 5/2 te predstavlja kvadrupol, zbog toga se spektri mogu dobiti samo kod monomernih ili najviše dimernih molibdenovih jedinjenja.

^{31}P NMR spektroskopija

^{31}P NMR spektroskopija može biti iskorišćena za identifikaciju pojedinih oblika molibdofosfata i volframofosfata i u rastvorima i u čvrstom stanju (^{31}P MAS NMR). Hemijski pomaci u slučaju različitih molibdofosfata i volframofosfata su u opsegu većem od 10 ppm (u poređenju sa manje od 0,5 ppm za ^1H NMR), što je čini veoma pogodnom metodom za identifikaciju pojedinih oblika čak i u smešama.

Anjon $\text{PW}_{12}\text{O}_{40}^{3-}$ može biti lako identifikovan po piku na -14,5 ppm, a $\text{PMo}_{12}\text{O}_{40}^{3-}$ po piku na -3,2 ppm (prema 85 % H_3PO_4). Za vodeni rastvor α/β $\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ javljaju se hemijski pomaci na -12,3, -11,6 i -10,8 ppm [24]. Prisustvo drugih anjona takođe se može utvrditi na osnovu hemijskih pomaka, koji su dati u tabelama 11. i 12. napravljenim prema literaturnim podacima [32, 37, 40, 118, 119].

Tabela 11. ^{31}P NMR hemijski pomaci za različite molibdofosfate i fosfate

[32, 106, 118, 119]

Molibdofosfat/ fosfat	Hemijski pomak/ ppm		
	Prema ref. [32]	Prema ref. [119]	Prema ref. [106, 118]
$\text{PMo}_{12}\text{O}_{40}^{3-}$	-3,2		-3,2
$\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$	-2,4		-2,53
$\text{H}_x\text{P}_2\text{Mo}_5\text{O}_{23}^{(6-x)-}$, $x = 0 - 2$	2,0 (za $x = 0$)	2,35 (za $x = 0$) 1,94 (za $x = 1$) 1,86 (za $x = 2$)	
$[\text{PMo}_9\text{O}_{31}(\text{OH})_3]^{6-}$	-1,1 (srednje pH) do 0,9 (niže pH)		
$\alpha\text{-A-H}_x\text{PMo}_9\text{O}_{31}(\text{OH})_3^{(6-x)-}$, $x = 2 - 3$			Od -1,15 do -1,00
$\alpha\text{-B-H}_x\text{PMo}_9\text{O}_{31}(\text{OH})_3^{(6-x)-}$, $x = 2 - 3$			Od 0,47 do 0,08
$\alpha\text{-H}_x\text{PMo}_{11}\text{O}_{39}^{(7-x)-}$, $x = 2 - 3$	od -0,6 (više pH) do -1,14 (niže pH)		Od -0,78 do -1,2
$\text{PMo}_6\text{O}_{25}^{9-}$	od 0,5 (više pH) do 0,17 (niže pH)		
$[\text{PMo}_{10}\text{O}_{34}]^{3-}$	-0,33		
H_3PO_4		0,48	
H_2PO_4^-		0,86	
HPO_4^{2-}		3,58	

Tabela 12. ^{31}P NMR hemijski pomaci za različite volframofosfate i fosfate [37, 40]

Volframofosfat/ fosfat	Hemijski pomak/ ppm	
	Prema ref. [40]	Prema ref. [37]
$\text{PW}_{12}\text{O}_{40}^{3-}$	-14,50	-14,7
$\text{P}_2\text{W}_{21}\text{O}_{71}^{6-}$	-13,17	-12,6
$\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$	-12,30	-11,2
$\text{P}_2\text{W}_{19}\text{O}_{67}^{10-}$		-9,4
$\text{P}_2\text{W}_{20}\text{O}_{70}^{10-}$	-12,40	
$\text{PW}_{11}\text{O}_{39}^{7-}$	-10,15	-9,8
$\text{P}_2\text{W}_5\text{O}_{23}^{6-}$	-1,65	
$\text{P}_2\text{W}_{19}\text{O}_{69}^{14-}$	-9,02	
$\text{PW}_9\text{O}_{34}^{9-}$		-7,6
H_3PO_4	0,68	
H_2PO_4^-	3,31	
HPO_4^{2-}	3,32	
PO_4^{3-}		0,1

^{31}P NMR spektroskopija može biti iskorišćena i za identifikovanje i razlikovanje α i β izomera, što je ilustrovano u tabeli 13. [120]. U slučaju α izomera Dawson-ovog anjona $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ koji ima dva identična atoma fosfora, u ^{31}P NMR spektru se uočava samo jedan pik.

Tabela 13. Hemijski pomaci za α i β izomere volframofosfata [120]

Volframofosfat	Hemijski pomak/ ppm
$\alpha\text{-PW}_{12}\text{O}_{40}^{3-}$	-14,6
$\beta\text{-PW}_{12}\text{O}_{40}^{3-}$	-13,7
$\alpha\text{-PW}_{11}\text{O}_{39}^{7-}$	-10,2
$\beta\text{-PW}_{11}\text{O}_{39}^{7-}$	-8,6
A- $\alpha\text{-PW}_9\text{O}_{34}^{9-}$	-5,1
A- $\beta\text{-PW}_9\text{O}_{34}^{9-}$	-3,2
$\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}^{6-}$	-12,4
$\beta\text{-P}_2\text{W}_{18}\text{O}_{62}^{6-}$	-11,6

Sa druge strane kod β izomera ovog anjona pokazuje se mala razlika u hemijskim pomacima za njegova dva atoma fosfora. Prema tome, pojava samo jednog ili dva identična pika zavisi od toga da li su dva atoma fosfora sa jednakim okruženjem ili ne. Važno je pomenuti da je hemijski pomak PW_9 polu-anjona praktično konstantan i neosetljiv na promene koje se mogu odvijati u drugom polu-anjonu (šupljina ili supstitucija). NMR spektri α_1 - i $\alpha_2\text{-LiK}_9\text{P}_2\text{W}_{17}\text{O}_{61}$, $\text{K}_6\text{P}_2\text{W}_{17}\text{MoO}_{62}$ i $\text{K}_8\text{H}_2\text{P}_2\text{W}_{17}\text{ZnO}_{62}$ veoma dobro ilustruju ovu činjenicu. U ovim slučajevima u jednom polu-anjonu se dešava udaljavanje ili supstitucija jednog atoma W, tako da polu-anjoni postaju različiti i uočavaju se dva pika istog intenziteta. U svakom paru ovih pikova, hemijski pomak više vrednosti ostaje praktično nepromenjen i jednak vrednosti koja se uočava kod $\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}^{6-}$. Ova vrednost odgovara A-tipu PW_9 polu-anjona, dok niža vrednost odgovara atomu fosfora u drugom polu-anjonu koji je izmenjen [117].

3. EKSPERIMENTALNI DEO

3.1. PRIPREMA UZORAKA

3.1.1. Sinteze kiselina i PANI-WPA

Spisak reagenasa:

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (Merck, Nemačka)

80 % H_3PO_4 (Merck)

HCl (Merck)

$(\text{C}_2\text{H}_5)_2\text{O}$ (Merck)

$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (Merck)

$\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (Merck)

NaOH (Centrohem, Srbija)

HCl (Merck).

CH_3OH (Merck)

Anilin (Centrohem)

$(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Centrohem)

Sinteza 12-volframfosforne kiseline (WPA):

50 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ je rastvoreno u 50 cm³ tople destilovane vode. U ovaj rastvor, uz neprestano mešanje, polako je dodata smeša 5 cm³ 80 % H_3PO_4 i 40 cm³ koncentrovane HCl. Rastvor je ostavljen da se slegne talog, koji odvojen dekantovanjem rastvora. Zatim, talogu je dodato 60 cm³ tople vode. Rastvoreni talog je prenešen u levak za odvajanje i dodato mu je 20 cm³ HCl i 35 cm³ etra $(\text{C}_2\text{H}_5)_2\text{O}$. Intenzivno je mučkano, uz povremeno otvaranje slavine. U levku za odvajanje nakon nekog vremena uočene su tri faze. Gornja faza je etar zasićen vodom, srednja faza je vodeni sloj i donja faza je voda zasićena etrom i polikiselinom [121].

Slobodna kiselina koja nastaje na ovaj način sa etrom daje proizvod u obliku teških uljanih kapi, koje se talože na dnu levka za odvajanje. Ovaj sloj je odvojen i ostavljen da iskristališe. Transparentni, bezbojni kristali su izvađeni iz matičnog rastvora, rastvoreni u malo destilovane vode i ostavljeni da ponovo iskristališu.

Da bi dobili heksahidrat $\text{WPA} \cdot 6\text{H}_2\text{O}$, koji je stabilan i pogodan za odmeravanje, kristali izvađeni iz matičnog rastvora su prosušeni na vazduhu, a zatim odgrevani na 80 °C desetak minuta.

Sinteza 12-molibdenfosforne kiseline (MoPA):

U 30 cm³ mlake destilovane vode rastvoreno je 20 g Na₂MoO₄·2H₂O. Ovom rastvoru je polako dodavana smeša od 0,48 cm³ 80 % H₃PO₄ i 20 cm³ koncentrovane HCl, koje su prethodno pomešane. Pri tome se talože heteropolianjoni. Posle dekantovanja u talog je dodato 20 cm³ vode. Rastvor je prenesen u levak za odvajanje i dodato mu je 9 cm³ HCl i 14 cm³ etra, pri čemu su nastale tri faze.

Posle odvajanja donje faze i kristalizacije na sobnoj temperaturi dobijeni se žuti transparentni kristali MoPA. Kristali izvađeni iz matičnog rastvora, rastvoreni u malo destilovane vode i ostavljeni da ponovo iskristališu.

Da bi dobili heksahidrat MoPA·6H₂O, kristali izvađeni iz matičnog rastvora su prosušeni na vazduhu, a zatim odgrevani na 60 °C desetak minuta.

Priprema 12-volframsilicijumove kiseline (WSiA):

12-volframsilicijumova kiselina H₄SiW₁₂O₄₀ je rastvorena u maloj količini destilovane vode i ostavljena da iskristališe. Pre odmeravanja, kristali izvađeni iz matičnog rastvora prosušeni su na vazduhu, a zatim odgrevani na 80 °C desetak minuta, da bi dobili heksahidrat WSiA·6H₂O.

Sinteza PANI-WPA :

Sinteza je započeta dobijanjem rastvora anilin/anilinijum 12-volframofosfata, tako što su vodeni rastvori (30 cm³) WPA (1,86 g WPA·6H₂O) i anilina (1,86 g, 0,02 mol) pomešani pri 20 °C i dodata im je destilovana voda do ukupne zapreme od 100 cm³. Ovom rastvoru je dodato 100 cm³ vodenog rastvora amonijum peroksidisulfata (NH₄)₂S₂O₈ (APS) (5,705 g, 0,025 mol) uz konstantno mešanje. Reakcija je praćena merenjem temperature i pH vrednosti smeše. Nakon stajanja 24 h na 20 °C, talog PANI-WPA je odvojen filtriranjem, ispran nekoliko puta sa vodenim i etanolnim rastvorom sumporne kiseline (5·10⁻³ M) i dietiletom, a zatim sušen na vakumu na 60 °C, 3 h. U svakom eksperimentu koncentracije anilina (0,1 M) i APS (0,125 M) su održavane konstantnim, dok se menjao polazni maseni odnos WPA·6H₂O / anilin: 0,2; 0,25; 0,5 i 1.

3.1.2. Priprema uzoraka za merenja

U eksperimentima su korišćene dve koncentracije rastvora HPK: 5·10⁻² moldm⁻³ i 2·10⁻⁵ moldm⁻³. Rastvori više koncentracije su pravljani odmeravanjem odgovarajuće

mase heksahidrata kiselina, tabela 14., i rastvaranjem u odgovarajućem rastvaraču. Rastvori niže koncentracije su dobijeni razblaživanjem rastvora koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$.

Tabela 14. Skraćeno ime, molekulska formula i masa ispitivanih uzoraka

Skraćeno ime	WPA	MoPA	WSiA
Molekulska formula	$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$	$\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$	$\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$
Molekulska masa	2988,27	1933,34	2986,38
Potrebna masa u g za 50 ml rastvora konc. $5 \cdot 10^{-2} \text{ mol dm}^{-3}$	7,4707	4,8334	7,4695

Za pravljenje rastvora korišćena je destilovana voda i metanol (*Merck*), kao i njihove smeše. Za podešavanje pH vrednosti korišćen je 5M rastvor NaOH i koncentrovana HCl, da bi promena zapremine polaznog rastvora bila zanemarljivo mala. Merenje pH vrednosti je vršeno pH-metrom Testo 206-pH1, uz kalibraciju sa ftalatnim (pH = 4) i fosfatnim (pH = 7) puferom (*BAKER ANALYZED Reagent, J.T.Baker*).

Inkubaciona smeša, u kojoj su utvrđivani strukturni oblici WPA i WSiA u reakciji inhibicije Na^+/K^+ -ATPaze sastavljena je od 50 mmol dm^{-3} TRIS-HCl pufera (pH 7,4) (*Sigma Chemicals Co., Nemačka*); 100 mmol dm^{-3} NaCl (*Merck, Nemačka*); 20 mmol dm^{-3} KCl (*Merck*); 5 mmol dm^{-3} MgCl_2 (*Sigma Chemicals Co.*). U ovaj rastvor se dodaje 290 mg/L komercijalne Na^+/K^+ -ATPaze izolovane iz cerebralnog korteksa svinje (*Sigma Chemicals Co.*) i 2 mmol/L ATP (*Sigma Chemicals Co.*).

Količina od 5 cm^3 rastvora korišćenih u eksperimentu pripremana je prema shemi datoj u tabeli 15.

Tabela 15. Shema pripremanja rastvora korišćenih za utvrđivanje strukturnih oblika WPA i WSiA u reakciji inhibicije Na^+/K^+ -ATPaze

	Zapremine rastvora/ cm^3					
	Inkubac. smeša	20 mM ATP	enzim	voda	$1 \times 10^{-2} \text{ M}$ WPA	$1 \times 10^{-2} \text{ M}$ WSiA
Rastvor 1	1,25	0,5	0,625	2,625		
Rastvor 2	1,25	0,5	0,625	2,125	0,5	
Rastvor 3	1,25	0,5	0,625	2,125		0,5

3.2. METODE ISPITIVANJA I INSTRUMENTI

3.2.1. ULj/Vid spektroskopija

ULj/Vid spektri rastvora koncentracije $2 \cdot 10^{-5} \text{ mol dm}^{-3}$ su dobijeni pomoću **Cintra 10e (GBS) spektrofotometra**. Rastvori su snimani u kvarcnim kivetama sa dužinom optičkog puta od 10 mm. Kao referentni rastvor je korišćen čist rastvarač.

3.2.2. Infracrvena spektroskopija

IC spektri su snimani na instrumentu **Thermo Nicolet 6700**, tehnikom KBr pastile. Spektri su snimani u opsegu od $4000 - 400 \text{ cm}^{-1}$, sa 64 skana po spektru i pri rezoluciji od 2 cm^{-1} . Za pripremu pastile korišćeno je 150 mg prethodno stopljenog i spraćenog KBr u koji je dodavano 2 mg uzorka. Nakon homogenizovanja dobijeni prah je presovan u pastilu uz vakumiranje kalupa. Uzorci kiselina za IC merenja su dobijani uparavanjem 1 cm^3 rastvora koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$, u sušnici na temperaturi od $80 \text{ }^\circ\text{C}$. Pre pripreme pastila, uzorci su čuvani u eksikatoru nad silikagelom.

3.2.3. Ramanska spektroskopija

Ramanski spektri su snimani na instrumentu **DXR Raman Microscope, Thermo Scientific**.

Spektri rastvora heteropoli kiselina koncentracija $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ su snimani pomoću eksterne sonde sa optičkim vlaknom (PN 840-187100) korišćenjem diodnog lasera visoke snage (780 nm). Rastvori su konstantno mešani na magnetnoj mešalici u staklenim čašama. U rastvore je dodavan 5M rastvor NaOH u kapima, do postizanja željene pH vrednosti koja je kontrolisana pH metrom, a zatim je sniman ramanski spektar. U isti rastvor dodavane su nove količine rastvora NaOH do sledećih potrebnih pH vrednosti i snimani su spektri.

Čvrsti uzorci su dobijeni uparavanjem alikvota rastvora izabраниh pH vrednosti. Uziman je po 1 mL rastvora koji je uparavan u sušnici na $80 \text{ }^\circ\text{C}$. Spektri su snimani korišćenjem diodnog lasera (zeleni, 532 nm, čvrsto stanje).

Uslovi pod kojima su snimani spektri su dati u tabeli 16.

Tabela 16. Uslovi pri kojima su snimani ramanski spektri rastvora i čvrstih uzoraka

	Spektri rastvora		Spektri čvrstih uzoraka		
	poglavlja 4.1-4.3	poglavlje 5.2.	poglavlja 4.1-4.3	poglavlje 5.1.	poglavlje 5.2.
Talasna dužina ekscitacione linije lasera/ nm	780	780	532	532	532
Snaga lasera/ mW	150	150	10 (2 u poglavlju 4.2.)	0,1	5
Rešetka sa br. ureza/ mm	400	400	1800	900	900
Vreme ekspozicije/ s	5	60	10		10
Broj ponavljanja	20	5	10		10
Apertura/ μm	25 "slit"	50 "slit"	25 "pinhole"		50 "pinhole"

3.2.4. ^{31}P NMR spektri

NMR spektri su snimani sa **Bruker MSL 400 spektrometrom** pri frekvenciji magnetnog polja od 161,978 MHz, sa 2048 ponavljanja, dužinom pulsa od 9,0 μs i repeticionim vremenom od 500 ms, pri temperaturi od 25 °C. Zapremina uzorka je bila 2,5 cm^3 u cevčici prečnika 10 mm. Kao spoljašni standard korišćen je metilendifosfonat (MDP) sa hemijskim pomakom 17,05 ppm u odnosu na 85 % H_3PO_4 . Koncentracija WPA i MoPA u ovim merenjima je bila $5 \cdot 10^{-2} \text{ mol dm}^{-3}$.

4. REZULTATI I DISKUSIJA

4.1. ISPITIVANJE STABILNOSTI 12-VOLFRAMFOSFORNE KISELINE U RASTVORIMA

4.1.1. Vodeni rastvori 12-volframfosforne kiseline

Za ispitivanje stabilnosti WPA u vodenim rastvorima primenjene su ULj spektroskopija u slučaju veoma razblaženih rastvora (početne koncentracije $2 \cdot 10^{-5}$ moldm⁻³) a IC, ramanska i ³¹P NMR spektroskopija, korišćenjem koncentrovanih rastvora WPA (početne koncentracije $5 \cdot 10^{-2}$ moldm⁻³). Početna pH vrednost rastvora je pH = 3,5 za koncentraciju $2 \cdot 10^{-5}$ moldm⁻³ i pH = 1,0 za $5 \cdot 10^{-2}$ moldm⁻³.

ULj spektri rastvora WPA

U ULj oblasti elektromagnetnog zračenja elektronski spektri HPK sa *Keggin*-ovom strukturom pokazuju dve intenzivne apsorpcione trake, koje odgovaraju prelazima $O_d \rightarrow M$ i $O_b/O_c \rightarrow M$ [98]. Prateći promenu položaja i intenziteta trake na 265 nm koja odgovara prelazu $O_b/O_c \rightarrow M$ kod KA, može se steći uvid o narušavanju strukture KA. Preliminarna ispitivanja su pokazala da je optimalna koncentracija rastvora kiseline, sa kojom se dobijaju spektri odgovarajuće apsorpcije, $2 \cdot 10^{-5}$ moldm⁻³.

Na slici 15. su dati ULj spektri rastvora WPA polazne koncentracije⁵ $2 \cdot 10^{-5}$ moldm⁻³ na različitim pH vrednostima od 1,0 - 11,5, koje su postignute dodavanjem HCl i NaOH [122]. Apsorpciona traka sa maksimumom kod 265 nm, pri pH = 1,0, se hipsohromno pomera sa porastom pH vrednosti, na 259 nm pri pH = 2,0, i na 252,5 nm pri pH = 3,5, uz smanjenje intenziteta trake. Pri porastu pH do 7,0 maksimum trake ostaje na istom položaju. Daljim povećavanjem pH, intenzitet trake se dalje značajno smanjuje ukazujući na razlaganje nastalih vrsta. Ovi rezultati ukazuju na postojanje strukturno različitih oblika u pojedinim oblastima pH vrednosti: ispod pH = 2,0, između 3,5 i 7,0, i iznad 8,5, ali je teško identifikovati nastale produkte.

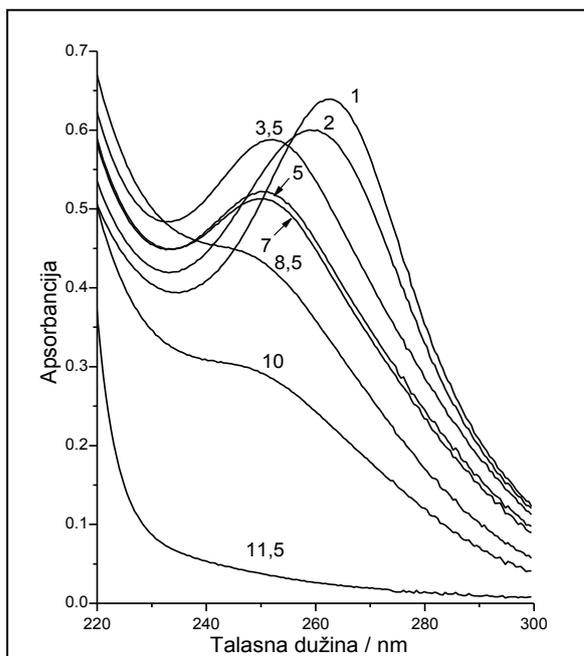
Očigledno je da pH vrednost igra veliku ulogu u stabilnosti WPA. Sve promene u ULj spektrima rastvora WPA pri različitim pH vrednostima, mogu se dovesti u vezu

⁵ ova koncentracija se neznatno menja usled dodatka HCl i NaOH prilikom podešavanja pH

sa promenama u strukturi HPK, ali je teško izvesti zaključak o prirodi nastale promene i identifikovati nastale produkte.

Iako se primenom ULj spektroskopije može steći samo grubi uvid u promene u sistemu, bez preciznog identifikovanja prisutnih molekulskih vrsta, njena primena je ipak opravdana, jer na vrlo brz i lak način možemo pratiti promene u rastvorima veoma niskih koncentracija HPK, koje su od interesa za ispitivanje biološke aktivnosti ovih jedinjenja.

Očigledno je da u vodenom rastvoru WPA, pri niskoj koncentraciji, WPA nije prisutna u obliku KA, ali da se zakišeljavanjem ovog rastvora sa HCl do pH = 1,0, može dobiti roditeljski anjon.



Slika 15. ULj spektri rastvora WPA polazne koncentracije $2 \cdot 10^{-5} \text{ mol dm}^{-3}$, na različitim pH vrednostima. Osnovni rastvor ima pH 3,5, kiseliji i bazniji rastvori su dobijeni dodatkom HCl, odnosno NaOH. Brojevi na slici predstavljaju pH vrednosti.

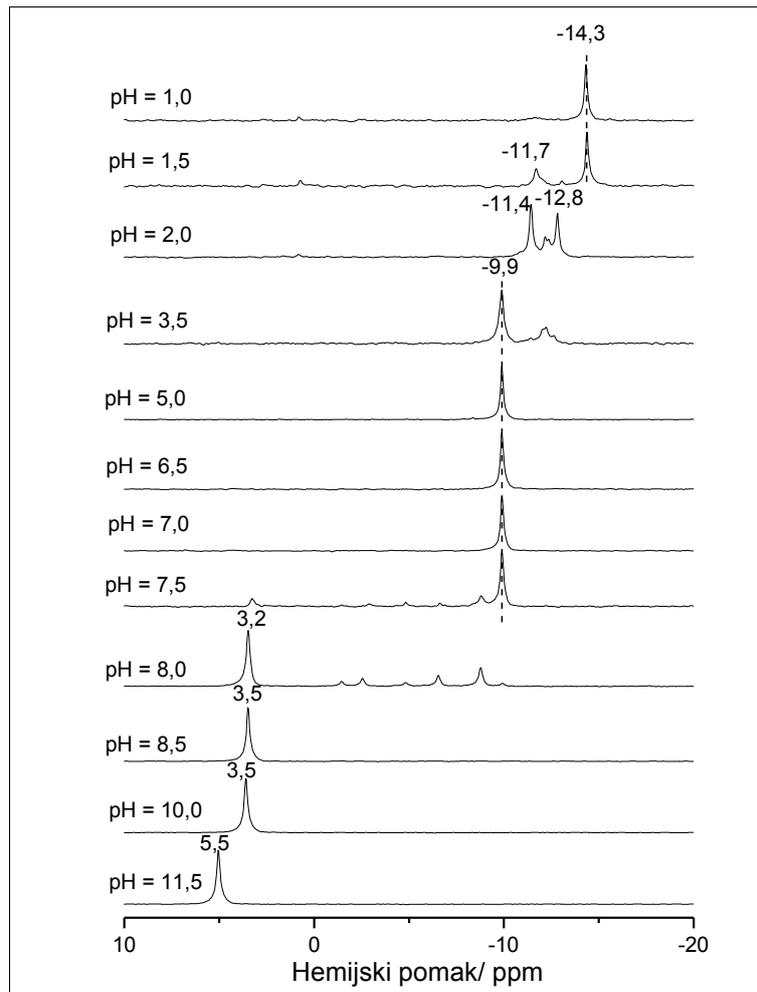
³¹P NMR i ramanski spektri rastvora WPA

³¹P NMR spektri rastvora WPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u pH oblasti od 1,0 do 11,5 su dati na slici 16. [122], a hemijski pomaci u tabeli 17. Vrednosti hemijskih pomaka iz literature [37, 40] korišćene su za identifikaciju pojedinih jona formiranih u rastvoru. Roditeljski $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anjon može biti lako identifikovan na osnovu pika na $-14,3 \text{ ppm}$. Ovaj anjon je dominantan pri pH = 1,0 i 1,5. Nekoliko pikova na oko -12 ppm se javlja pri pH = 1,5 i 2,0. Ovi pikovi se mogu pripisati

⁶ ova koncentracija se neznatno menja usled dodatka NaOH prilikom podešavanja pH

strukturama sa dva atoma fosfora iz *Dawson*-ove serije, kao što su $[\text{P}_2\text{W}_{21}\text{O}_{71}]^{6-}$, $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ i $[\text{P}_2\text{W}_{20}\text{O}_{70}]^{10-}$.

Sa daljim povećanjem pH, pri pH = 3,5 pikovi na pozicijama oko -12 ppm ostaju u spektru, ali njihov intenzitet opada, dok pik na oko -9.9 ppm, koji odgovara lakunarnom KA $[\text{PW}_{11}\text{O}_{39}]^{7-}$ postaje dominantan. Ovaj pik ostaje jedini u spektrima sve do pH = 7,0.



Slika 16. ^{31}P NMR spektri vodenih rastvora WPA početne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ na različitim pH vrednostima

Analiza spektara jasno ukazuje na kompleksnu šemu hidrolitičkog razlaganja KA u kiseljoj sredini. Prvi stepen dekompozicije nije uklanjanje W-O jedinice, odnosno nastajanje monolakunarnog anjona, kako su ranije prepostavili *McGarvey* i *Moffat* [35]. Dobijeni rezultati pokazuju da se u prvoj fazi razlaganja KA formiraju anjoni *Dawson*-ove serije, a da se zatim iz njih pri daljem porastu pH vrednosti formira

monolakunarni KA u oblasti pH od 3,5 do 7,0. Ovaj rezultat je u saglasnosti sa zaključcima *Smith*-a i *Patrick*-a [40]. U ovom opsegu pH vrednosti monolakunarni oblik je jedina vrsta prisutna u rastvoru. Na pH = 7,5 pored ovog oblika koji je dominantan javlja se i drugi oblik. Prema *Himeno* i saradnicima, β izomer lakunarnog KA uvek koegzistira sa α izomerom [120], tako da se pik na -8,8 ppm može pripisati β -[PW₁₁O₃₉]⁷⁻.

Promena pH od 7,5 do 8,0 dovodi do potpunog razlaganja [PW₁₁O₃₉]⁷⁻ anjona i u spektru se uočava porast intenziteta drugih signala. Pojavljuje se pik na -6,6 ppm koji odgovara trolakunarnom [PW₉O₃₄]⁹⁻. Najintenzivniji signali u spektrima pri pH \geq 8,0 odgovaraju fosfatnim anjonima.

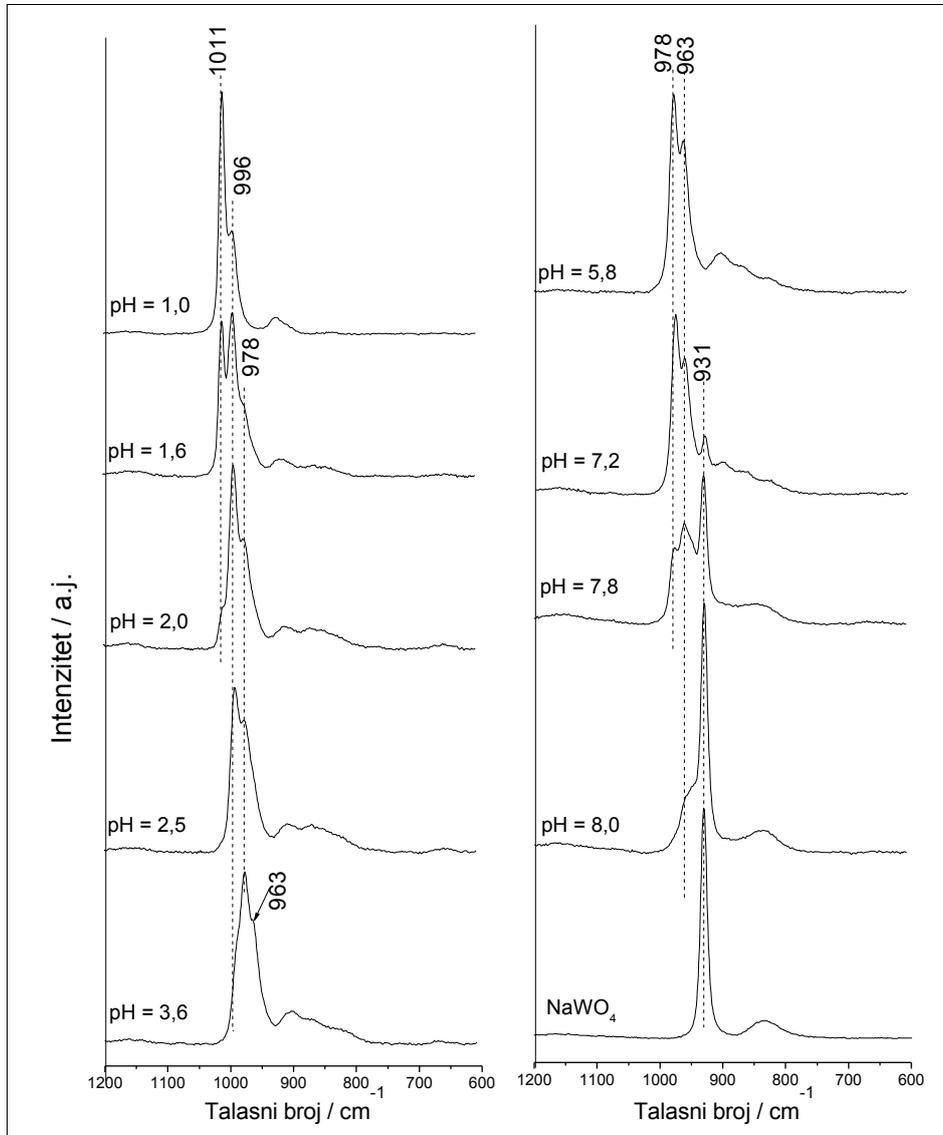
U alkalnim rastvorim sa pH > 7,5, prema ³¹P NMR spektrima, dolazi do potpune degradacije polivolframata do volframatnih i fosfatnih aniona. Pikovi sa različitim vrednostima hemijskih pomaka odgovaraju fosfatnim anjonima, [H₂PO₄]⁻, [HPO₄]²⁻ i [PO₄]³⁻ (tabela 17.).

Tabela 17. Hemijski pomaci u ³¹P NMR spektrima vodenih rastvora WPA početne koncentracije 5 · 10⁻² moldm⁻³ pri različitim pH vrednostima

Hemijski pomak/ ppm	pH											Anjon	
	1,0	1,5	2,0	3,5	5,0	6,5	7,0	7,5	8,0	8,5	10,0		11,5
-14,3	-14,4												[PW ₁₂ O ₄₀] ³⁻ Dawson-ov tip
		-12,8											
	-11,7	-11,4											α-[PW ₁₁ O ₃₉] ⁷⁻ β-[PW ₁₁ O ₃₉] ⁷⁻
			-9,9	-9,9	-9,9	-9,9	-9,9	-8,8	-8,8				
									-6,6				[PW ₉ O ₃₄] ⁹⁻ fosfatni anjoni
								3,2	3,5	3,5	3,6		
												5,5	

Za rastvore istih polaznih koncentracija (5 · 10⁻² moldm⁻³) snimljeni su ramanski spektri u oblasti talasnih brojeva od 1200 - 600 cm⁻¹. Spektri su dati na slici 17., a talasni brojevi i intenziteti traka u tabeli 18. U spektru osnovnog rastvora WPA uočavaju se dve trake na 1012 i 996 cm⁻¹. Prva traka odgovara $\nu_s(M-O_d)$, a druga

$\nu_{as}(M-O_d)$ i $\nu_s(P-O_a)$ vibraciji⁷ [104, 107]. Na pH = 1,6 traka na 995 cm^{-1} postaje intenzivnija od prve i pojavljuje se traka na 978 cm^{-1} .



Slika 17. Ramanski spektri vodenih rastvora WPA početne koncentracije $5 \cdot 10^{-2}\text{ mol dm}^{-3}$ na različitim pH vrednostima

Traka na 978 cm^{-1} koja se javlja na pH = 1,6 potiče od DA što je u skladu sa NMR spektrima. Prema C. Rocchiccioli-Deltcheff i saradnicima [114] u ramanskom spektru DA uočavaju se slaba traka 1022 cm^{-1} i traka srednjeg intenziteta na oko 979 cm^{-1} . Pošto se na pH = 1,6 DA javlja u smeši sa KA, njegova slaba traka na 1022 cm^{-1}

⁷ Druga traka, koja se inače u spektru uočava kao dublet, ovde nije razložena, jer je snimanje spektra vršeno pri rezoluciji koja ne omogućava njihovo razlaganje.

se preklapila sa krilom jake trake KA na 1011cm^{-1} , tako da se jasno uočava samo traka na 978cm^{-1} . Na $\text{pH} = 3,6$ pojavljuje se nova traka (ovde tek vidljiva kao rame) na 963cm^{-1} , što ukazuje na pojavu nove strukture.

Tabela 18. Talasni brojevi i intenziteti traka u ramanskim spektrima vodenih rastvora početne koncentracije $5 \cdot 10^{-2}\text{mol dm}^{-3}$ pri različitim pH vrednostima i Na_2WO_4

Talasni brojevi/ i intenziteti traka cm^{-1}	pH											Na_2WO_4
	1,0	1,6	2,0	2,5	3,0	3,6	5,8	7,2	7,8	8,0		
	1011	1011sr	1011sl									
	vj											
	996	995 sr	994 j	992 sr								
	sr	978 r	979 sr	978 sr	979 sr	978 sr	978 j	978 sr	976 s			
						963r	963 sr	964 sr	961sr	960r		
								931 vs	931 sr	931 j	931 j	
					902 vs	902 vs	903 vs	905 vs				
									845 vs	836 vs	836 vs	
	vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame											

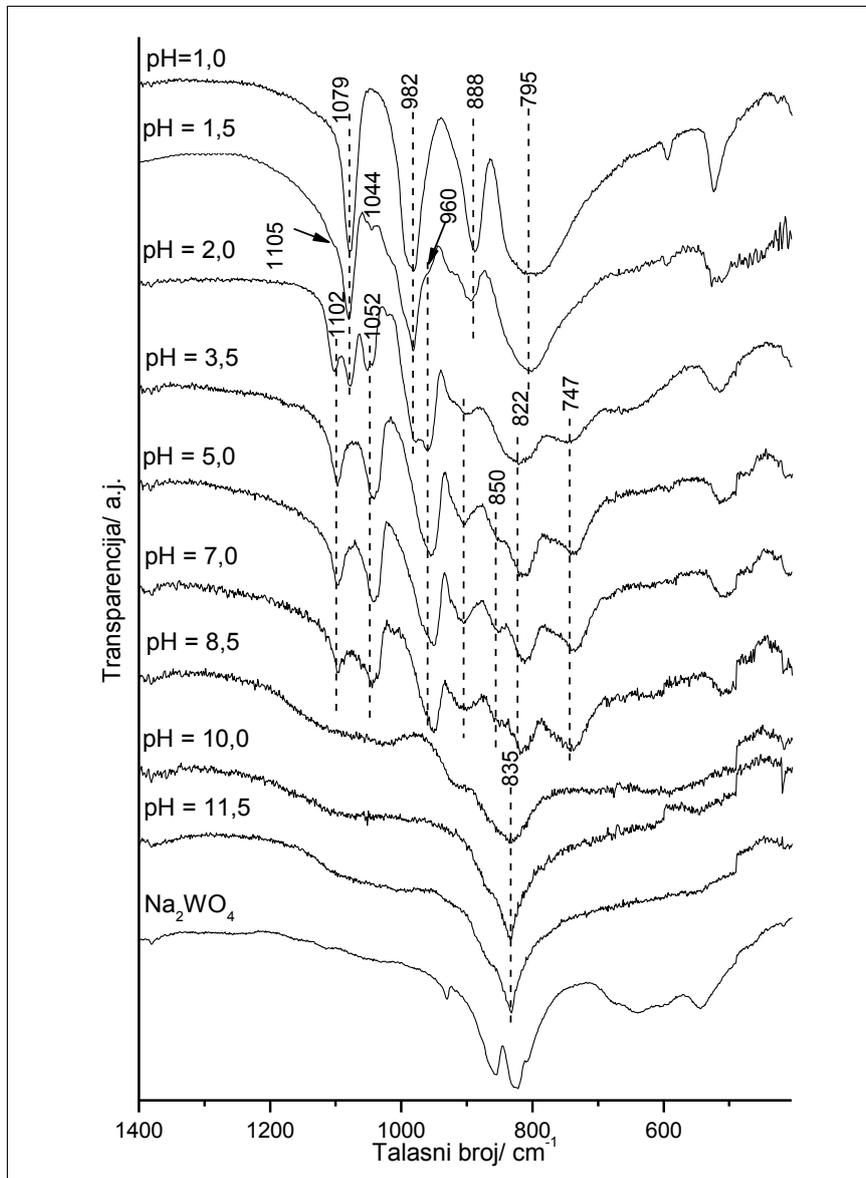
Iz ovoga proizilazi da je polazni, Keggin-ov oblik anjona, kao jedina vrsta prisutan samo do $\text{pH} \sim 1,5$, a da se na višim pH vrednostima uz njega javlja i drugi oblik koji egzistira do $\text{pH} \sim 3$, pri čemu se do $\text{pH} \sim 2$ javljaju paralelno oba oblika. Počevši od $\text{pH} = 3,6$ pa do $\text{pH} = 7,8$ u spektrima su prisutne trake na oko 978 i 963cm^{-1} , koje potiču od $\nu_s(\text{M-O}_d)$ i $\nu_{as}(\text{M-O}_d)$ vibracije monolakunarnog KA⁸ [105]. Spektri na $\text{pH} = 7,2$ i $7,8$ se razlikuju po intenzitetu traka, i na višem pH druga traka postaje intenzivnija. Prema podacima u literaturi, za $[\text{PW}_9\text{O}_{34}]^{9-}$ je karakteristična jaka traka na 966cm^{-1} i slabije trake na oko 898 i 851cm^{-1} [123, 124], tako da se ovaj anjon može identifikovati u uskoj pH oblasti neposredno pre potpune dekompozicije do volframata. Traka koja odgovara WO_4^{2-} , na 931cm^{-1} , počinje da se javlja na $\text{pH} = 6,9$, a na $\text{pH} > 8,0$ to je jedini volframov anjon prisutan u rastvoru.

IC i ramanski spektri čvrstih uzoraka

Dodatne informacije o promenama struktura WPA sa promenom kiselosti u koncentrovanim rastvorima, kao i o eventualnom uticaju uparavanja rastvora, dobijene

⁸ prema ³¹P NMR spektrima, uz α -izomer monolakunarnog KA javlja se i β -izomer, ali se na osnovu vibracionih spektara, zbog velike sličnosti spektara oni teško mogu razlikovati, pogotovo u smeši [108].

su analizom IC i ramanskih spektara suvih ostataka rastvora početne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ pri različitim pH vrednostima. Na slici 18. su dati IC spektri suvih ostataka u oblasti traka karakterističnih za KA, dok su u tabeli 19. prikazani položaji i intenziteti traka [125]. Spektar Na_2WO_4 je dat radi poređenja.



Slika 18. IC spektri suvih ostataka rastvora WPA početne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ na različitim pH vrednostima. Spektar Na_2WO_4 je dat radi poređenja

U spektru uparenog rastvora na $\text{pH} = 1,0$ uočavaju se trake na 1079, 982, 888, 795, 596 i 523 cm^{-1} . Prve četiri potiču od istežućih asimetričnih P-O_a, W-O_d, W-O_b-W i W-O_c-W vibracija, respektivno, a poslednje dve od deformacionih asimetričnih

O_a-P-O_a vibracija [107]. Spektar je identičan spektru čvrste WPA izvađene iz matičnog rastvora, iz čega proizilazi zaključak da rastvaranje u vodi i uparavanje rastvora na 80 °C nema uticaja na krutu mrežu WPA.

Tabela 19. Talasni brojevi i intenziteti traka u IC spektrima suvih ostataka rastvora WPA početne koncentracije $5 \cdot 10^{-2} \text{ moldm}^{-3}$ na različitim pH vrednostima

	pH										
	1,0	1,5	2,0	3,5	5,0	7,0	8,5	10,0	11,5	Na ₂ WO ₄	
Talasni brojevi/ cm ⁻¹ i intenziteti traka		1105 r	1102 sr 1090 sl	1097 sr	1096 sr	1097 sr					
	1079 j	1079 vj 1044 sl	1078 j 1052 sr	1042 sr	1042 sr	1044 sr					
	982 vj	982 vj 960 r	980 j 960 j	956 j	951 j	950 j					
	888 j	920 r 890 sr	920 r 902 sl	903 sl 850 r	905 sl 852 r	900 sl 850 r	910 r				
	795 vj,š	800 vj,š	821 j,š 747 sl,š 664 sl,š	816 j,š 742 sr,š	812 sr 730 sr,š	819 sr 742 sr,š		835 j,š	835 j,š	835 j,š	860 r 855 j
	593 sl 523 sr	594 sr 520 sr	514 sl	515sl,š	504 sl,š	513 sl,š					822 j
	vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame										

Može se primetiti da se već na pH = 1,5, pored traka povezanih sa KA javljaju i druge trake. Ranije je pomenuto (poglavlje 2.7.2) da su istežuće vibracije u PO₄ tetraedru ekstremno osetljive na simetriju polinjona. U spektru se uočava cepanje trake koja odgovara ovoj vibraciji što ukazuje na postojanje struktura sa simetrijom nižom od T_d simetrije KA. Takve strukture su monolakunarna, PW₁₁O₃₉⁷⁻ koja pripada C_s simetrijskoj grupi i strukture sa po dva atoma P (*Dawson-ove*), na primer P₂W₁₈O₆₂⁶⁻ sa C_{3v} simetrijom. Na pH = 2,0 se uočavaju trake na 1102, 1090, 1078, 1052, 1020, 980, 960, 920, 902, 821, 747, 664 i 514 cm⁻¹. Trake koje su karakteristične za monolakunarnu strukturu su, prema literaturnim podacima, na 1100, 1046, 958, 904, 812 i 742 cm⁻¹ [111], a za *Dawson-ovu* strukturu na oko 1090, 1020, 950, 910, 780 cm⁻¹ [113]. Prema tome, trake na pH = 2,0 odgovaraju trakama KA (1078, 980 cm⁻¹), ali je evidentno prisustvo novih traka koje bi se mogle pripisati monolakunarnom KA (1102, 1052, 960 cm⁻¹) ili DA (1090, 1020 cm⁻¹). Međutim, zbog preklapanja širokih traka u IC spektrima ovih vrsta, ne može se jednoznačno utvrditi koje su vrste prisutne pri ovoj pH vrednosti.

U opsegu od pH 3,5 do 7,0 spektri su vrlo slični, sa manje traka nego u spektrima na pH = 2,0 i to na 1097, 1042, 956, 903, 816, 742 cm^{-1} , koje odgovaraju spektru monolakunarnog KA. Na višim pH vrednostima u spektrima se uočavaju samo trake koje potiču od volframata i fosfata⁹ (slika 18.).

U toku snimanja ramanskih spektara rastvora, iz rastvora na onim pH u čijim spektrima je primećena promena u odnosu na prethodnu podešenu pH vrednost, uzimani su alikvoti i uparavani na 80 °C. Na slici 19. su dati ramanski spektri suvih ostataka ovih rastvora WPA, u oblasti od 1200 - 50 cm^{-1} , a u tabeli 20. talasni brojevi i intenziteti traka [126].

Tabela 20. Tal. br. i intenziteti traka u ramanskim spektrima suvih ostataka vodenih rastvora WPA početne konc. $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ pri različitim pH vrednostima i Na_2WO_4

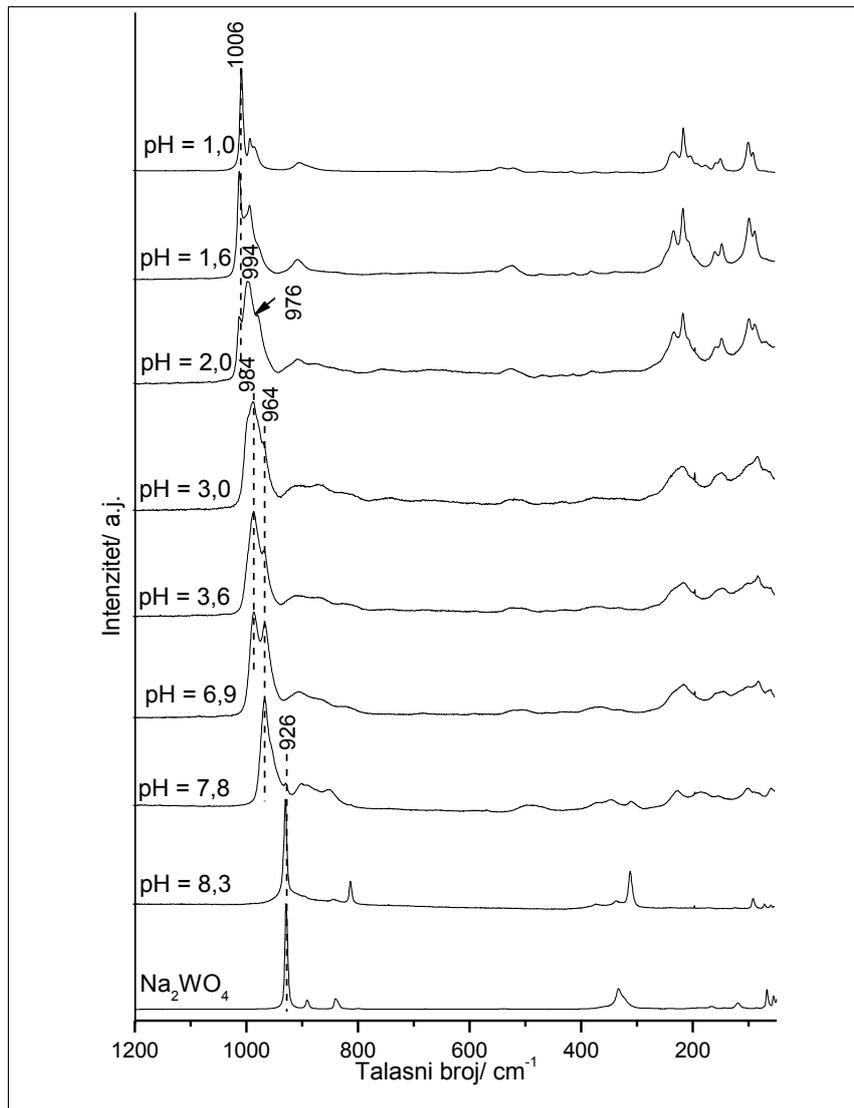
	pH								Na_2WO_4	
	1,0	1,6	2,0	3,0	3,6	6,9	7,8	8,3		
Talasni brojevi/ cm^{-1} i intenziteti traka	1006 vj	1010 vj	1010 sr							
	991 sr	991sr	994 vj	995 r						
	984 sl	980 r	976 sr	985 j	984 j	983 j				
				967 r	966 sr	964 j	964 j			
							926 sl	926 j		
	903 sl,š	900 sl,š	904 sl,š		903 sl	902 sl	899 sl			929 j
			865 sl,š							891 sl
								810 sl		839 sl
	520 sl,š	520 sl,š	520 sl,š	517 sl,š	520 sl					
							309 sl	309 sr		334 sr
	232 sl	232 sl	230 sl				224 sl			
	214 sr	215 sr	215 sr	217 sl	214 sl	214 sl	193 sl			
	200 sl	194 sl	194 sl	194 sl	194 sl	194 sl				
	175 sl	158 sl	157 sl							
	148 sl	145 sl	145 sl	145 sl	146 sl	142 sl				
98 sr	96 sl	96 sl		98 sl	98 sl	89 sl	89 sl			
89 sl	86 sl	86 sl	81sl	81 sl	80 sl				66 sl	

vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame

Pri pH = 1,0, u spektru se uočavaju trake na 1006, 991 i 984 cm^{-1} . Kao što je pomenuto u slučaju ramanskih spektara rastvora, prva traka odgovara $\nu_s(\text{M-O}_d)$, a druge dve $\nu_{as}(\text{M-O}_d)$ i $\nu_s(\text{P-O}_a)$ vibracijama¹⁰.

⁹ Za P-O vibraciju u PO_4^{3-} anjonu je karakteristična široka traka od 1110-1000 cm^{-1} , Table II, *IRSCOT, IR structural correlation tables and data cards, Heyden & Son Limited*

¹⁰ trake su ovde razdvojene zbog snimanja sa većom rezolucijom



Slika 19. Ramanski spektri suvih ostataka vodenih rastvora WPA početne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ na različitim pH vrednostima i Na_2WO_4

Do pH = 2,0 sve tri trake su prisutne u spektru, ali sa promenjenim odnosom intenziteta, intenzitet $\nu_s(\text{M-O}_d)$ vibracije slabi, a intenzitet druge dve vibracije raste. Počevši od pH = 3,0 u spektru se uočavaju trake monolakunarnog KA, a na pH = 7,8 jaka traka na 962 cm^{-1} karakteristična za $[\text{PW}_9\text{O}_{34}]^{9-}$. Traka volframata na oko 930 cm^{-1} se javlja kao slaba traka već od pH = 7,8, da bi već sa malom promenom pH do 8,3 ona postala intenzivna. Poredeći ramanske spektre rastvora i uparenih uzoraka dolazi se do zaključka da su spektri na odgovarajućim pH vrlo slični, odnosno da se brzim uparavanjem male zapremine rastvora ne menja struktura komponenata rastvora.

Međutim, zbog mogućnosti snimanja ramanskih spektara čvrstih uzoraka sa većom rezolucijom može se izvršiti preciznija identifikacija.

Ako analiziramo IC i ramanske spektre suvih ostataka uzoraka u oblasti pH od oko 3,5 do 7,0 vidimo da je prema obe metode, u ovoj oblasti, dominantan oblik koji u IC spektrima ima trake na 1097 i 1046 cm^{-1} , a u ramanskim 984 i 966 cm^{-1} , odnosno monolakunarni KA.

Takođe pri pH oko 8,5 sa obe metode je potvrđen nestanak *Keggin*-ove strukture i nastanak volframata. Prema ramanskim spektrima razlaganje monolakunarnog KA do volframata ne ide direktno, nego postoji intermedijerni trolakunarni anjon sa trakom na 964 cm^{-1} u ramanskom spektru.

Iz svih prikazanih rezultata sledi zaključak da je WPA hidrolitički veoma nestabilna i u razblaženim i u koncentrovanim vodenim rastvorima. U razblaženim rastvorima koncentracije $2 \cdot 10^{-5} \text{ mol dm}^{-3}$ WPA nije u obliku KA, ali se zakišeljavanjem rastvora do pH = 1,0 vraća u roditeljski oblik. U koncentrovanim rastvorima, sa koncentracijom $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ WPA je u obliku KA. Vrlo mala promena pH vrednosti dovodi do narušavanja strukture.

Oblast pH vrednosti od početne do pH = 3,5 je oblast vrlo složenih ravnoteža između roditeljskog KA, *Dawson*-ovih struktura i monolakunarne *Keggin*-ove strukture. Između pH = 3,5 i 7 je oblast u kojoj je dominantna monolakunarna struktura. Iznad ove pH vrednosti, u alkalnoj sredini, počinje narušavanje lakunarne strukture, iz koje daljim gubitkom WO jedinica, preko trolakunarnog KA, nastaju volframatni i fosfatni anjoni.

4.1.2. Metanol/vodeni rastvori 12-volframfosforne kiseline

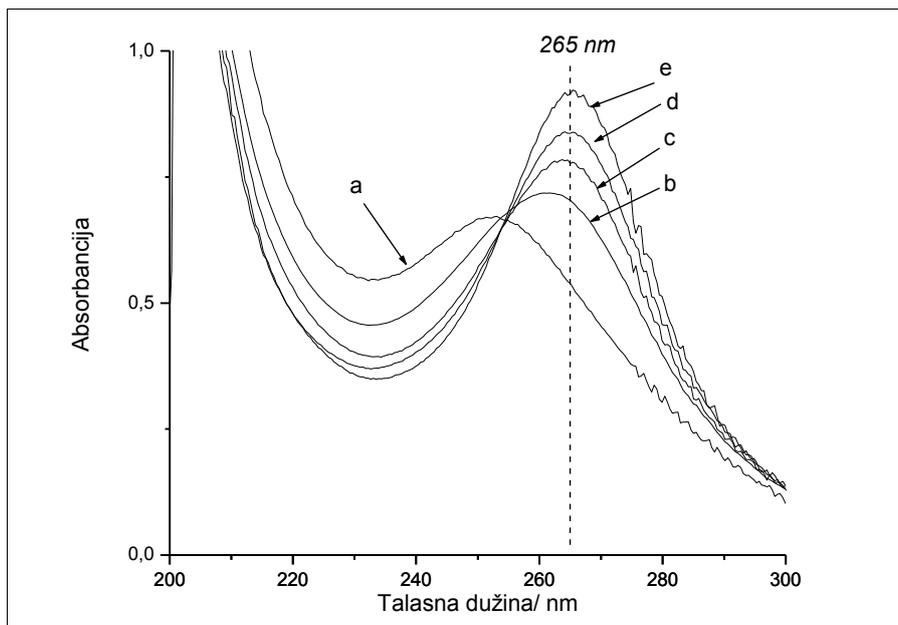
Pošto u literaturi ne postoje detaljne studije o osobinama WPA u organskim rastvaračima, kao ni u smešama organski rastvarač/voda, kao model sistem za praćenje solvolitičke stabilnosti WPA, izabran je rastvor WPA u metanol/vodenom rastvaraču. U cilju identifikacije prisutnih molekulskih vrsta pri različitim pH vrednostima, te uticaja dodatka metanola na stabilnost WPA primenjene su iste metode kao i u slučaju rastvora u vodi [126].

Direktno poređenje pH vrednosti u vodi i smeši voda/metanol je ograničeno. Skala pH vrednosti organskih rastvarača zavisi od konstante autoprotolize K_{ap} , tako je

na primer, za etanol skala od 0 - 19,5, a za metanol 0 - 16,7. Vrednost K_{ap} zavisi i od udela metanola u binarnoj smeši sa vodom, tako da je za 20 % (w/w) metanol 14,055, za 28 % - 14,067, a za 50 % - 14,097, za 80 % - 14,218, a za 90 % - 14,845 [127]. Prema tome, izmerene pH vrednosti u rastvorima sa manjim udelom metanola mogu biti direktno poređene sa onima u vodenim rastvorima, jer je odstupanje zanemarljivo malo. Sa druge strane, date pH vrednosti u rastvorima sa većim udelom metanola, mogu biti uzete samo okvirno.

ULj spektri rastvora WPA

Sa slike 20. na kojoj su dati ULj spektri WPA koncentracije $2 \cdot 10^{-5} \text{ mol dm}^{-3}$ u rastvaračima sa različim udelima metanola, se vidi da se traka na 265 nm karakteristična za KA javlja u rastvorima kada je udeo metanola 50 % (v/v) i veći.

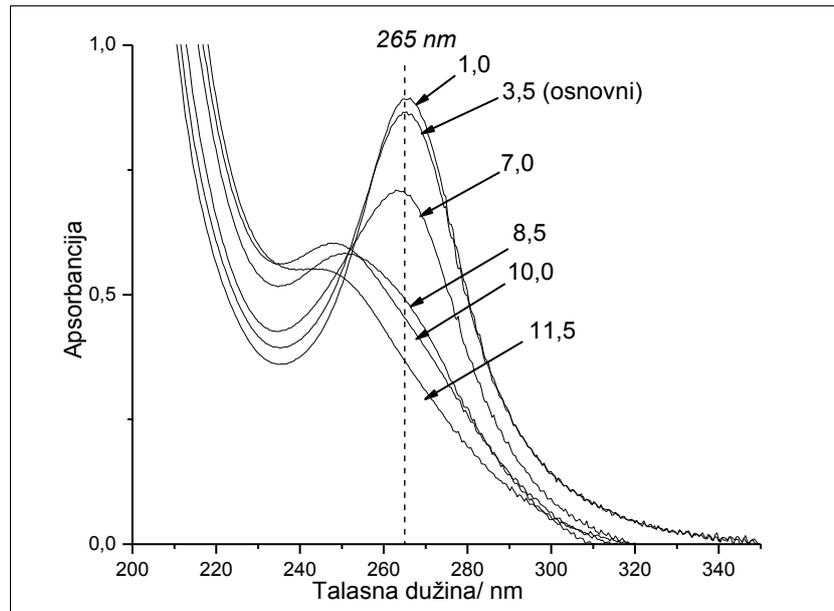


Slika 20. ULj spektri WPA koncentracije $2 \cdot 10^{-5} \text{ mol dm}^{-3}$ u smešama metanol/voda sa različitim udelom metanola: a) 0 %, b) 25 %, c) 50 %, d) 75 % i e) 100 % (v/v)

Intenzitet trake se smanjuje sa porastom udela metanola u rastvaraču, jer je molarni apsorpcioni koeficijent na talasnoj dužini maksimuma trake (λ_{\max}) u organskim rastvaračima za oko 30 % viši nego u vodenim rastvorima, dok se λ_{\max} samo neznatno razlikuju [99].

Za rastvor sa udelom metanola 25 % maksimum trake je hipsohromno pomeren na 252,5 nm usled dekompozicije KA. Prema tome, minimalni udeo metanola u rastvaraču potreban da bi u razblaženim rastvorima WPA bila u obliku roditeljskog anjona je 50 % .

Na slici 21. su dati ULj spektri metanol/vodenog rastvora WPA sa polaznim udelom metanola 50 % ¹¹, u opsegu pH vrednosti od 1,0 - 11,5.



Slika 21. ULj spektri rastvora WPA početne koncentracije $2 \cdot 10^{-5} \text{ moldm}^{-3}$ u rastvaraču sa polaznim udelom metanola 50 %, na različitim pH vrednostima.

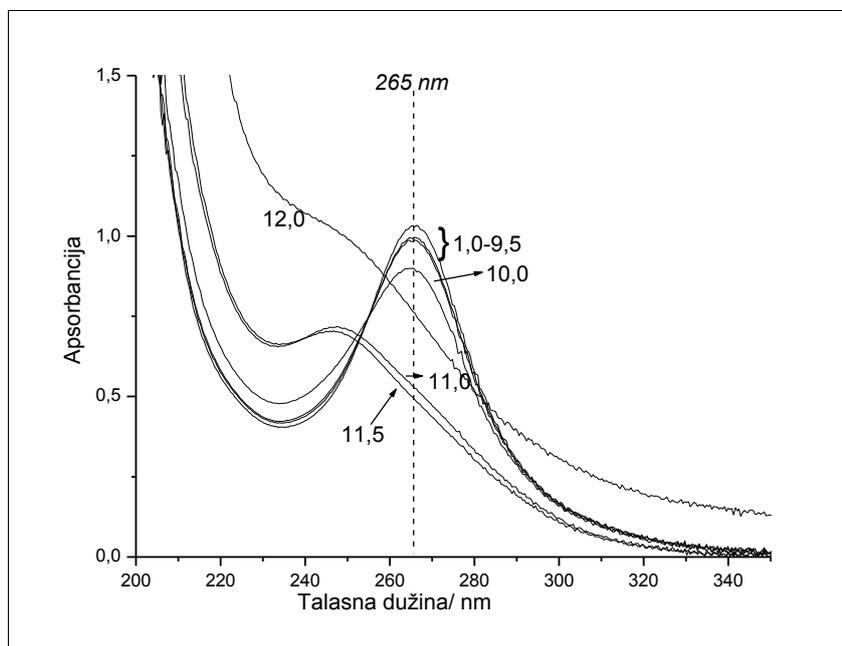
Vidi se da apsorpciona traka sa maksimumom kod 265 nm ostaje u spektru počev od pH = 1,0 sve do pH = 7,0, pri čemu opadanje intenziteta potiče od razblaženja rastvora dodavanjem NaOH. U alkalnijim rastvorima dolazi do pomeranja maksimuma trake ka nižim talasnim dužinama od 252 - 248 nm, što odgovara različitim molekulskim vrstama formiranim od roditeljskog KA WPA [37].

Ovi rezultati ukazuju na stabilizaciju *Keggin*-ove strukture u odnosu na vodene rastvore, gde je prisustvo KA potvrđeno samo na pH = 1,0.

¹¹ ova koncentracija metanola se neznatno menja usled dodatka NaOH prilikom podešavanja pH

Značaj ovih rezultata je u tome što pokazuju mogućnost dobijanja WPA u obliku KA u širem opsegu kiselosti, čak i u razblaženim rastvorima uz pogodan odabir ko-rastvarača.

Kada se WPA rastvori u čistom metanolu, dolazi do proširenja oblasti u kojoj egzistira KA do pH = 10,0, kao što se vidi na slici 22. Maksimum trake je na 265 nm u oblasti pH vrednosti od 1,0 do 10,0. Na pH = 11,0 i 11,5 maksimum trake je na 248 nm, a čak i na pH = 12,0 ova traka je prisutna kao rame. Za razliku od vodenih rastvora, u ovom slučaju, je čak i u izrazito alkalnoj sredini, pri pH = 10,0, prisutna polivolframatna struktura.



Slika 22. UV spektri rastvora WPA početne koncentracije $2 \cdot 10^{-5} \text{ mol dm}^{-3}$ u metanolu (sa polaznim udelom metanola 100 %) na različitim pH vrednostima.

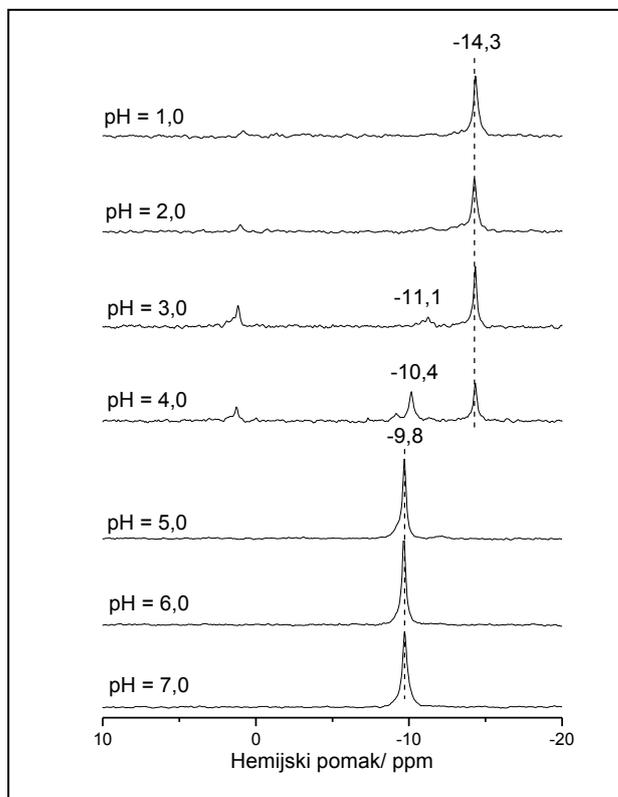
³¹P NMR i ramanski spektri metanol/vodenih rastvora WPA

³¹P NMR spektri rastvora WPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u metanol/vodenom rastvaraču sa 50 % metanola¹² u pH oblasti od 1,0 to 7,0 su dati na slici 23., a hemijski pomaci su sumirani u tabeli 21.

Roditeljski KA sa pikom na -14.3 ppm se javlja kao dominantan do pH = 4,0, ali se od pH > 3,0 počinju javljati i novi pikovi. Na pH > 5,0 u spektrima je prisutan

¹² ova koncentracija metanola se neznatno menja usled dodatka NaOH prilikom podešavanja pH

signal na $-9,8$ ppm, karakterističan za monolakunarni KA. Rastvor na $\text{pH} = 7,0$ je zamućen i dalje dodavanje NaOH dovodi do izdvajanja taloga.



Slika 23. ^{31}P NMR spektri rastvora WPA početne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 50 %, na različitim pH vrednostima

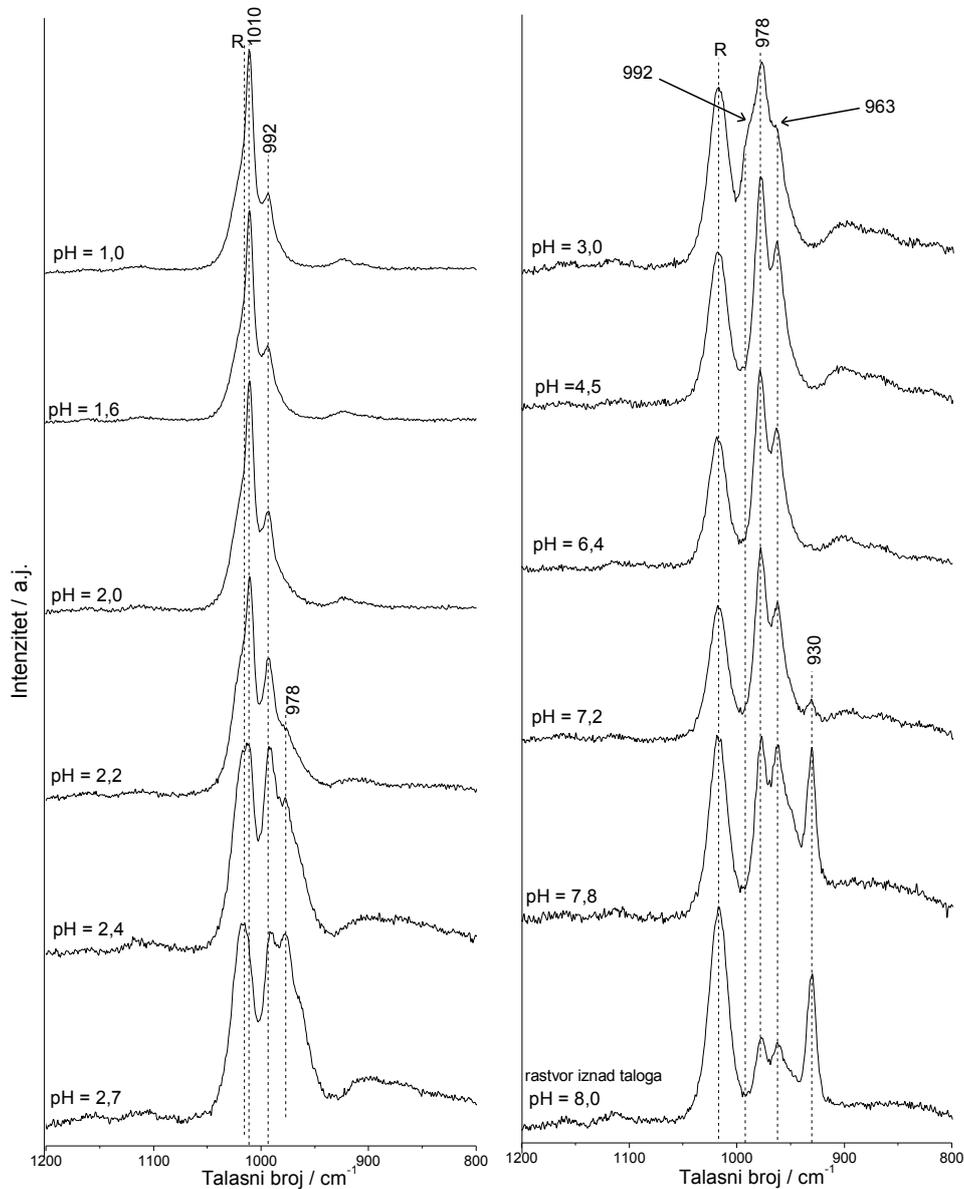
Tabela 21. Hemijski pomaci u ^{31}P NMR spektrima rastvora WPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 50 %, na različitim pH vrednostima

Hemijski pomak /ppm	pH							Anjon
	1,0	2,0	3,0	4,0	5,0	6,0	7,0	
-14,3	-14,3	-14,3	-14,3	-14,3				$[\text{PW}_{12}\text{O}_{40}]^{3-}$
		-11,1						Dawson-ov tip
			-10,2	-9,8	-9,8	-9,8	-9,8	$[\text{PW}_{11}\text{O}_{39}]^{7-}$

Ramanski spektri su snimani za rastvore sa tri različita odnosa metanol/voda, pri različitim pH vrednostima u oblasti od $1200 - 600 \text{ cm}^{-1}$, a rezultati su prikazani na slikama 24. - 26. i tabelama 22. i 23. Traka istežuće C-O vibracije rastvarača je obeležena sa R.

Prema ramanskim spektrima rastvora sa polaznim udelom metanola u rastvaraču 25 % (v/v) (slika 24., tabela 22.), trake KA na 1010 i 992 cm^{-1} se javljaju do $\text{pH} = 2,2$,

ali se na ovom pH pojavljuje i traka na 978 cm^{-1} u vidu ramena, koja kao što je pomenuto u prethodnom poglavlju potiče od vibracija u DA.



Slika 24. Ramanski spektri rastvora WPA polazne konc. $5 \cdot 10^{-2}\text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 25 %, na različitim pH vrednostima (R-rastvarač)

Počev od $\text{pH} = 3,0$ u spektru se pojavljuje i traka na 963 cm^{-1} pomoću koje uz traku na 978 cm^{-1} , možemo identifikovati monolakunarni KA. Kao i kod vodenih rastvora, izjednačavanje intenziteta ove dve trake na $\text{pH} = 7,8$ (u slučaju

monolakunarnog KA traka na 978 cm^{-1} je jača od one na 963 cm^{-1}) ukazuje na pojavu trolakunarnog anjona.

Tabela 22. Tal. br.i intenziteti traka u ramanskim spektrima rastvora WPA polazne konc. $5 \cdot 10^{-2}\text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 25 %

		pH											
		1,0	1,6	2,0	2,2	2,4	2,7	3,0	4,5	6,4	7,2	7,8	8,0*
Talasni brojevi/ cm^{-1} i intenziteti traka	1010	1010	1010	1010									
	vj	j	j	j									
	992	992	992	992	992	992	992	992					
	sl	sl	sl	sr	sr	sr	r						
				978 r	978	978	978	978	978	978	978	978	978
					sr	sr	sr	sr	sr	sr	sr	sr	sl
								965	963	963	963	962	963
								sl	sl	sl	sl	sr	sl
												931	930
												sr	sr

vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame; *rastvor iznad taloga

Počevši od $\text{pH} = 7,2$ u spektrima se uočava traka volframata na 930 cm^{-1} , čiji intenzitet očekivano raste sa povećanjem pH vrednosti, međutim dalje dodavanje rastvora NaOH dovodi do pojave taloga. Prve količine nastalog taloga se brzo rastvaraju, ali iznad $\text{pH} = 8,0$ talog se počinje izdvajati. Iz ovog razloga, spektar na $\text{pH} = 8,0$ je snimljen za rastvor iznad taloga nakon izbistravanja, i u njemu se pored trake volframata uočavaju i trake lakunarnih anjona.

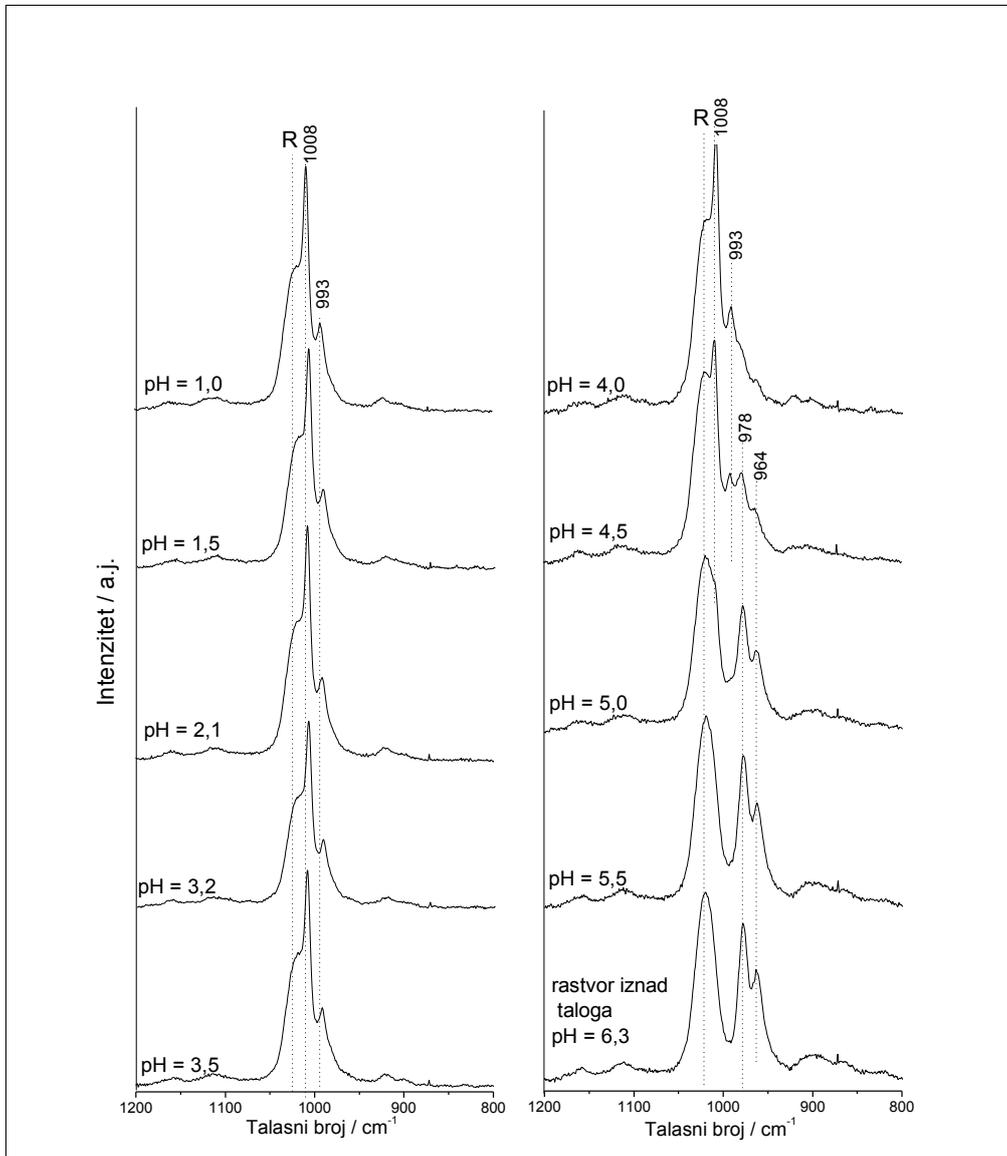
Prema ramanskim spektrima rastvora sa udelom metanola u rastvaraču 50 % (slika 25., Tabela 23.), trake KA na 1008 i 993 cm^{-1} se javljaju do $\text{pH} = 4,5$, kada se uz njih javljaju trake karakteristične za monolakunarni KA.

Tabela 23. Tal. br. i intenz. traka u ramanskim spektrima rastvora WPA polazne konc. $5 \cdot 10^{-2}\text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 50 %

		pH										
		1,0	1,5	1,8	2,1	3,2	3,5	4,0	4,5	5,0	5,5	6,3*
Talasni br./ cm^{-1} i int. traka	1008	1008	1008	1008	1008	1008	1008	1008	1009	1009		
	j	j	j	j	j	j	j	sr	r			
	993	992	992	991	992	992	992	991				
	sl	sl	sl	sl	sl	sl	sl	sl				
								978	978	978	978	978
								r	sl	sr	sr	sr
								978	964	964	963	963
								r	vs	sl	sl	sl

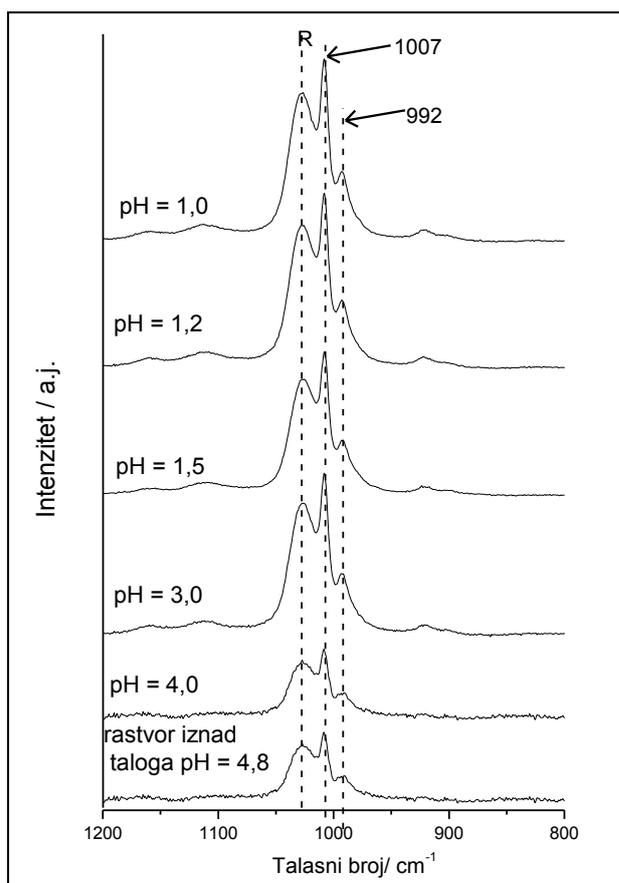
vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame; *rastvor iznad taloga

Od pH = 5,0, u potpunoj saglasnosti sa rezultatima ^{31}P NMR spektroskopije, u rastvoru je prisutan monolakunarni KA. Ovaj anjon ostaje u rastvoru i na pH = 6,3 kada se primećuju prvi znaci zamućivanja rastvora.



Slika 25. Ramanski spektri rastvora WPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 50 %, na različitim pH vrednostima (R-rastvarač)

Kod 75 % metanolnog rastvora, slika 26., do taloženja dolazi već na pH = 4,8, a na pH < 4,8 vrednosti u spektrima su prisutne samo trake KA.



Slika 26. Ramanski spektri rastvora WPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 75 %, na različitim pH vrednostima (R-rastvarač)

Može se uočiti da se talasni broj $\nu_s(\text{M-O}_d)$ vibracije neznatno pomera ka nižim talasnim brojevima sa rastom udela metanola (1012, 1010, 1008, 1007 cm^{-1} , za 0, 25, 50 i 75 % metanola, respektivno), što je indikacija slabe interakcije KA i rastvarača.

IC i Ramanski spektri čvrstih uzoraka

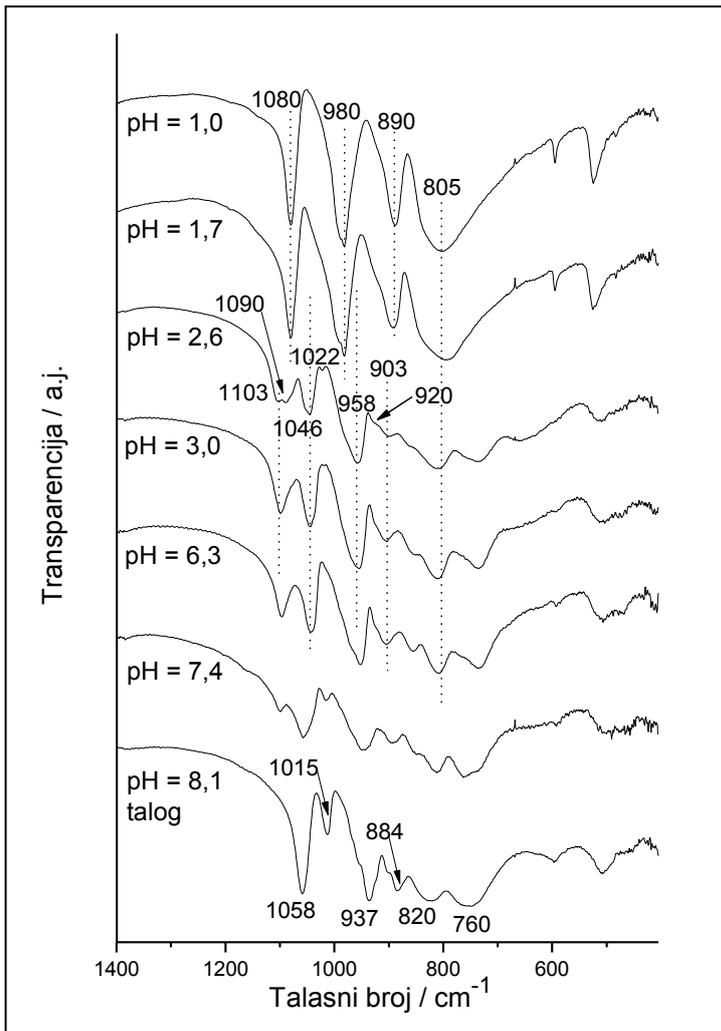
Iz rastvora na pH vrednostima na kojima su uočene promene u ramanskim spektrima tečnih uzoraka uzimani su alikvoti koji su uparavani i zatim su snimljeni IC i ramanski spektri suvih ostataka, radi detaljnije analize.

Na slikama 27., 28. i 29. su dati IC spektri suvih ostataka rastvora WPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$, sa 25, 50 i 75 % metanola u rastvaraču, respektivno.

Četiri trake karakteristične za krutu mrežu KA se uočavaju u spektrima uparenih rastvora pri svim ispitivanim odnosima metanol/voda, na pH oko 1 i podudaraju se sa trakama u čvrstoj WPA, kao i u slučaju uparenih vodenih rastvora WPA. Dok se u slučaju vodenih rastvora prve promene u spektru dešavaju već pri $\text{pH} > 1,5$ u metanol/vodenim rastvorima te promene se dešavaju pri $\text{pH} > 2,5$ za rastvor sa

25 % metanola, pri $\text{pH} > 3,5$ za 50 % i $\text{pH} > 4,5$ za rastvor sa 75 % metanola. U svim spektrima dolazi do cepanja trake P-O_a vibracije na dve trake oko 1100 i 1050 cm^{-1} , što odgovara, kao što je pomenuto u slučaju vodenih rastvora, monolakunarnom KA.

U spektrima rastvora sa 25 % metanola (slika 27., tabela 24.) KA je stabilan do $\text{pH} = 2,5$. U uskoj oblasti pH od 2,5 do 3,0, trake na oko 1090, 1022, 958 i 920 cm^{-1} , ukazuju na prisustvo struktura sa dva atoma P [113].



Slika 27. IC spektri suvih ostataka rastvora WPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 25 %, na različitim pH vrednostima

Sa porastom pH do 6,3 u spektrima su prisutne trake na 1100, 1045, 955, 903, 812 i 738 cm^{-1} , koje su karakteristične za monolakunarni KA. Ovaj anjon je jedina vrsta prisutna u rastvoru sve dok pH ne pređe 7,0, kada dolazi do njegovog razlaganja do trolakunarnog $\text{PW}_9\text{O}_{34}^{9-}$ koji počinje da se taloži u rastvoru, ali se pri ovoj pH brzo rastvara. Daljim dodavanjem NaOH, pri $\text{pH} > 8,0$ ovaj anjon počine da se izdvaja kao

talog i može se identifikovati na osnovu traka na 1058, 1015, 937, 884, 820 i 760 cm^{-1} registrovanih u snimljenom ramanskom spektru taloga [115].

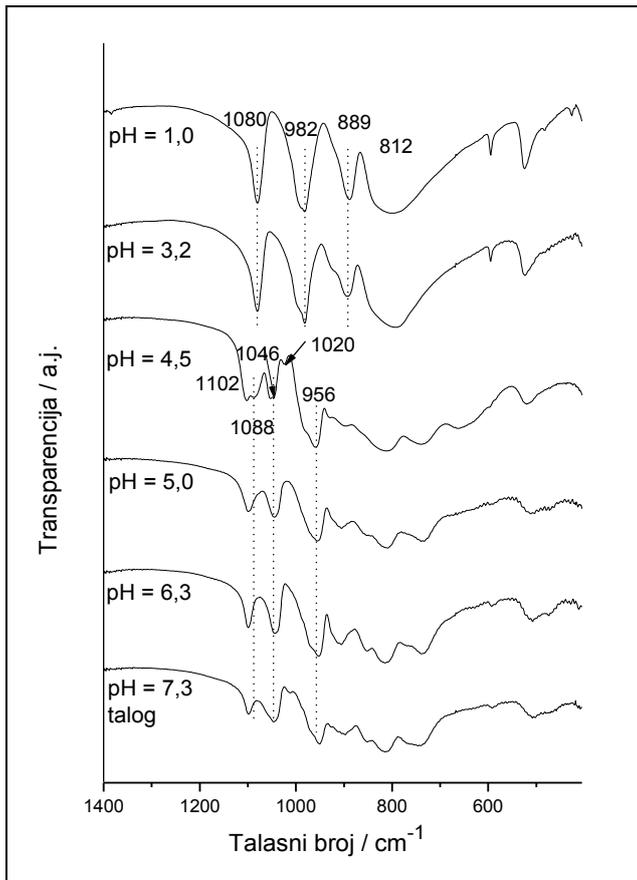
Tabela 24. Talasni brojevi i intenziteti traka u IC spektrima suvih ostataka rastvora WPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 25 %, na različitim pH vrednostima

		pH							
		1,0	1,7	2,6	3,0	6,3	7,4	8,1(talog)	
Talasni brojevi/ cm^{-1} i intenziteti traka				1103 sl 1090 sl	1100 sr	1097 sr	1100 sl		
	1080 vj	1080 vj					1056 vj	1058 j	
				1046 sr 1022 vs	1045 sr	1043 j	1015 sl	1015 sr	
	990 r 980 vj	990 r 980 vj				970 r 952 j		955 r 937 vj	
				920 vs 903 sl	903 sl	905 sl	893 sl, š	903 vs 884 sl	
	887 j	887 j							
	805 j,š	805 j,š		861sl 811 sr 738 sr	855 sl 812 sr,š 738 sr	855 sl,š 812 sr,š 738 sr,š	850 sl, š 815 sr,š 750 sr, š	820 sr 760 sr 597 sl	
	594 sl 524 sr	594 sl 524 sr		516 sl	516 sl	510 sl	490 sl,š	505 sl	
	vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame								

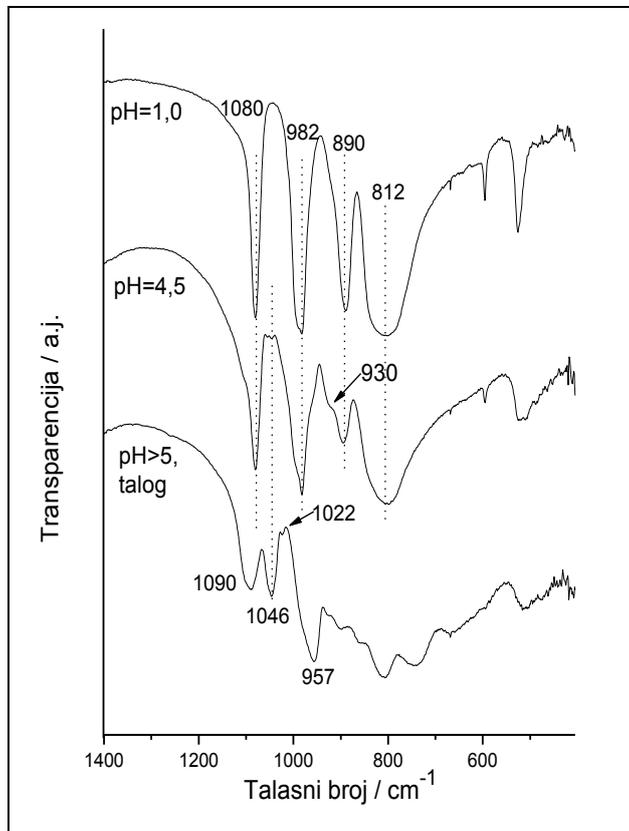
Taloženje $\text{Na}_9\text{PW}_9\text{O}_{34}$ alkalizacijom rastvora WPA u 25 % metanolu do pH= 8,1 pomoću NaOH, može biti iskorišćeno kao jednostavan i brz način sinteze ovog lakunarnog oblika.

U rastvorima sa udelom metanola 50 % oblast pH u kojoj je stabilan KA se proširuje do pH = 4,5. Promene u spektrima prema slici 28. i tabeli 25., su slične onima kod rastvora u 25 % metanolu. Spektar pri pH = 4,5 je vrlo sličan spektru na pH = 2,6 u slučaju manje koncentracije metanola. Monolakunarni anjon je stabilan do pH = 6,3. Daljim dodavanjem NaOH počinje da se izdvaja talog koji se prema IC spektru sastoji od $\text{PW}_{11}\text{O}_{39}^{7-}$ i tragova $\text{PW}_9\text{O}_{34}^{9-}$.

U rastvoru sa još većim udelom metanola, 75 %, IC spektri dati na slici 29. ukazuju na prisustvo KA, uz tragove monolakunarnog anjona, do pH = 4,5. U ovom rastvoru formiranje taloga započinje već na pH > 3,0, ali se brzo rastvara do pH > 5,0 kada počinje da se izdvaja. Ovaj talog se sastoji uglavnom od $\text{PW}_{11}\text{O}_{39}^{7-}$ uz prisustvo tragova $\text{PW}_9\text{O}_{34}^{9-}$ i $\text{PW}_{12}\text{O}_{40}^{3-}$.



Slika 28. IC spektri suvih ostataka rastvora WPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 50 %, na različitim pH vrednostima



Slika 29. IC spektri suvih ostataka rastvora WPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 75 %, na različitim pH vrednostima

Tabela 25. Talasni brojevi i intenziteti traka u IC spektrima suvih ostataka rastvora WPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udjelom metanola 50 % i 75 %, na različitim pH vrednostima

Udeo metanola		50%					75%		
pH	1,0	3,2	4,5	5,0	6,3	7,3(talog)	1,0	4,5	5,0(talog)
Talasni brojevi/ cm^{-1} i intenziteti traka			1103 j	1100 j	1100 j	1100 j			1090 j, š
	1080 vj	1080 vj	1085 j	1045 j	1045 j	1045 j	1080 vj	1080 vj	
			1050 j					1046 vsl	1046 j
			1023 sl			1013 sl			1022 sl
	990 r	990r			970 r		990 r	990 r	
	980 vj	980 vj	985 r				980 vj	980 vj	
				958 j	955 vj	955 vj			957 vj
			924 r	931 sl				930 r	930 sl
				899 sl,š	905 sr	905 sr	905 sr		900 sl
	887 j	882 j						890 j	
			854 sl	854 sl	854 sl			860 sl	
805 j,š	800 j,š	814 sr,š	809 j	809 j	809 j		812 vj,š	812 vj,š	
		736 s,š	736sr	736 sr	736sr			742 sl,š	
594 sl	594 sl						594 sl	594 sl	
524 sr	524 sr						524 sr	522 sr,š	
								515 sl,š	

vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame

Na slikama 30., 31. i 32. su dati ramanski spektri suvih ostataka rastvora WPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ sa 25, 50 i 75 % metanola u rastvaraču, respektivno, na različitim pH vrednostima.

Kako se alkalizacija rastvora sprovodi dodavanjem NaOH, dolazi do stvaranja rastvorne soli $\text{Na}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$. Na taj način mogu se objasniti male razlike u spektrima KA, posebno na niskim talasnim brojevima, u oblasti vibracija rešetke. Takođe, $\nu_s(\text{W-O}_d)$ vibracija je osetljiva na zamenu katjona, tako da se u slučaju H^+ nalazi na 1007 cm^{-1} , a kada je katjon Na^+ na $1012,5 \text{ cm}^{-1}$ [107].

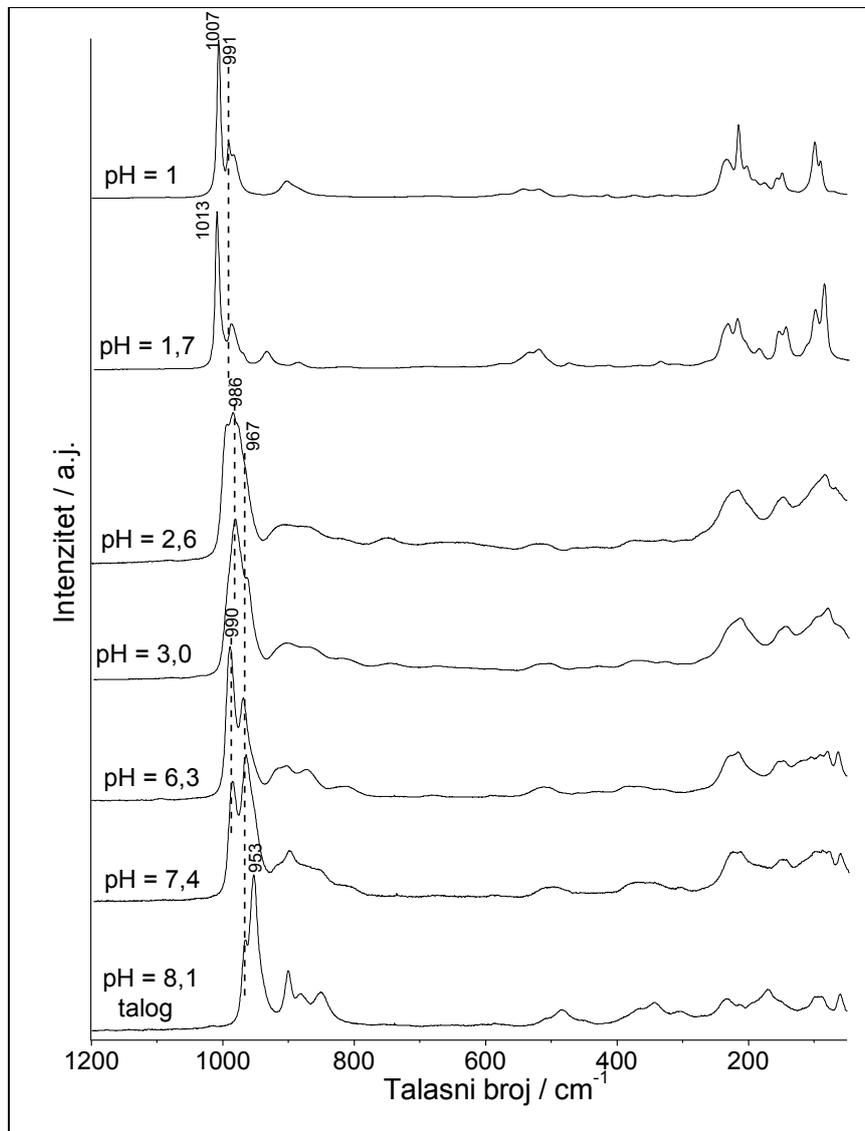
Ramanski spektri na slici 30. i tabeli 26. potvrđuju prisustvo KA u rastvorima sa 25% metanola do $\text{pH} = 1,7$. Trake na $986, 967, 904, 870, 510$ i 217 cm^{-1} ukazuju da je lakunarni oblik dominantan od $\text{pH} = 3,0$ do $6,3$.

U alkalnijim rastvorima formira se trolakunarni oblik $\text{PW}_9\text{O}_{34}^{9-}$ sa trakom istežuće simetrične vibracije na 965 cm^{-1} . Na $\text{pH} = 8,1$ formira se talog $\text{Na}_9\text{PW}_9\text{O}_{34}$. Ovi rezultati su u potpunoj saglasnosti sa rezultatima dobijenim iz IC spektara.

Čvrsti uzorci dobijeni iz rastvora sa 50 % metanola imaju u ramanskim spektrima, koji su dati na slici 31., pri $\text{pH} = 4,5$ široku intenzivnu traku između 990 i 960 cm^{-1} u oblasti W-O vibracija, što ukazuje na prisustvo novih komponenti koje su

uočene i u IC spektrima. Na pH = 5,0 spektar sadrži trake karakteristične za monolakunarni anion, koji se na pH = 6,5 izdvaja kao talog.

U rastvorima sa 75 % metanola, prema ramanskim spektrima suvih ostataka prikazanim na slici 32., KA je stabilan do pH = 4,5, kada počinje zamućivanje rastvora. Sa spektra na ovoj pH vrednosti jasno je da KA ostaje očuvan, ali se u spektru uočavaju odstupanja od osnovnog spektra, što ukazuje na prisutvo i drugih vrsta u rastvorima. Dalji dodatak NaOH i porast pH dovodi do taloženja $[\text{PW}_{11}\text{O}_{39}]^{7-}$.

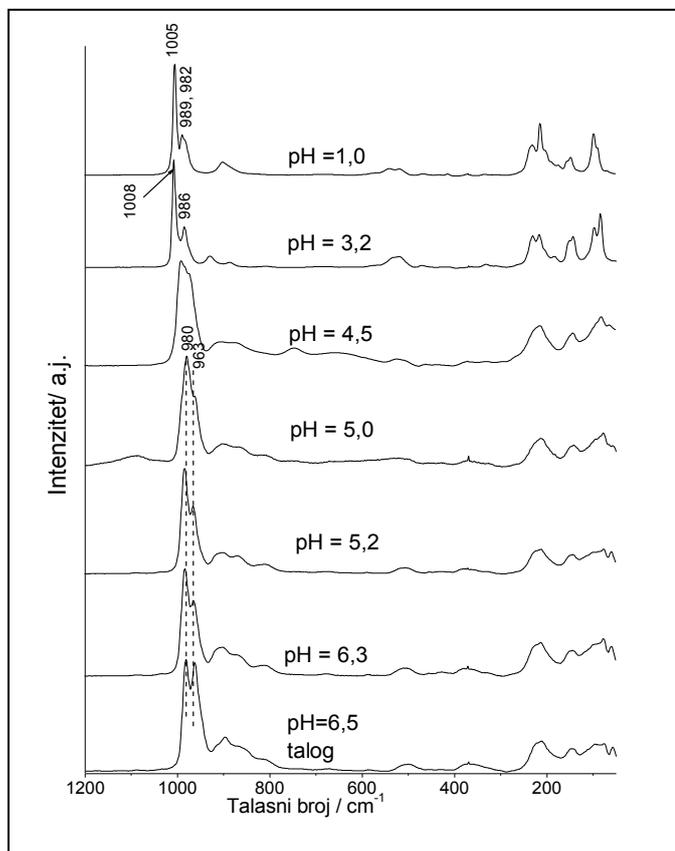


Slika 30. Ramanski spektri suvih ostataka rastvora WPA polazne konc. $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 25 %, na različitim pH vrednostima

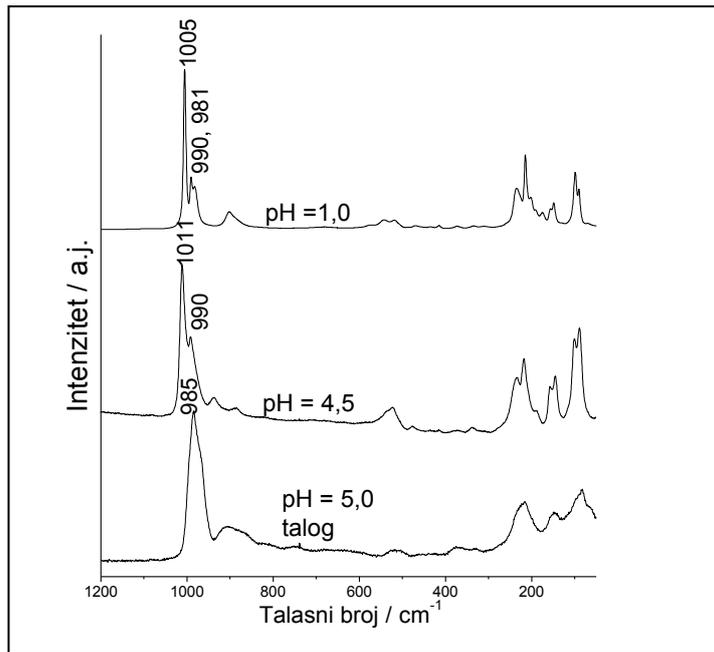
Tabela 26. Talasni brojevi i intenziteti traka u ramanskim spektrima suvih ostataka rastvora WPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 25 %, pri različitim pH vrednostima

Talasni brojevi / cm^{-1} i intenziteti traka	pH						
	1,0	1,7	2,6	3,0	6,3	7,4	8,1 talog
1007 vj	1013 vj						
991 j	991 j	990 r			990 vj	990 j	
983 r		986 vj	986 vj	986 vj			
		970 r	967 r	967 r	969 j	968 vj	966 j
	937 sr						953 vj
903 sr		907 sr	904 sr	904 sr	903 sr	903 sr	901 j
	889 sl	886 sl					880 sr
			870 sl	870 sl	875 sr		
543 sl	538 sl						852 sr
520 sl	523 sr		510 sl	510 sl			488 sl
							344 sl
234 sr	235 sr						234 sl
216 j	220 j	217 j	216 j	216 j	217 j	217 j	
							172 sl
156 sl	156 sr						
149 sr	148 sr	147 sr	146 sr	146 sr	146 sr	149 sr	
100 j	102 sr						
90 sl	88 j	84 j	83 j	83 j	80 sl	81 sl	90 sl

vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame



Slika 31. Ramanski spektri suvih ostataka rastvora WPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 50 %, na različitim pH vrednostima



Slika 32. Ramanski spektri suvih ostataka rastvora WPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 75 %, na različitim pH vrednostima

Tabela 27. Tal. br.i inten. traka u ramanskim spektrima suvih ostat. rastvora WPA pol. konc. $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 50 % i 75 %

Udeo metanola	50 %							75 %				
	pH	1,0	3,2	4,5	5,0	5,2	6,3	6,5 (talog)	1,0	4,5	5,0 (talog)	
Talasni brojevi / cm^{-1} i intenziteti traka		1005 j	1008 j						1005j	1011 j		
		989 sr	986 sr	990 j					990 sr	990 sr		
		982 r		982 r	980 j	980 j	982 j	982 j	981 sr		985 j	
				965 r	963 sr	963 sr	963 sr	961 j			965 r	
			930 sl							937 sl		
		902 sl		909 vs	904 sl	902 sl		915 r	915 sl	903 sl	909vs	900 sl,š
			885 vsl					899 sr	897 sr			
				872 vs							888vs	
					863 sl	866 sl	862 sl,š	862 sl,š				
				846 vs								
					809 sl	810 sl	810 sl,š	810 sl,š				
		542 vs	542 vs							544vs	540 r	
		517 vs	517 vs	517 vs						519vs	520vs	520 sl,š
							505 sl,š	505 sl,š				
						365 sl,š	365 sl,š					
	231 sl	231 sl							235 sr	234 sl		
						223 sr	223 sr					
	213 sr	216 sl	216 sl	212sl	213 sl	209 sr	209 sr		213 j	217 sl	220 sl, š	
	155 sl	153 sl							157 sl	156 sl		
	147 sl	147 sl	143 sl	143 sl	141 sl	145 sl	145 sl		150 sl	143 sl	145 sr,š	
	98 sr	99 sl		94 sl	97 sl	96 sl	96 sl		99 sr	99 sr		
	90 sl	85 sr	81 sl	80 sl	79 sl	76 sl	76 sl		90 sl	88 sr	80 sr	

vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame

Poredeći spektre rastvora i odgovarajuće spektre suvih ostataka, zaključujemo da su rezultati saglasni u pogledu opsega pH vrednosti u kojima se javlja lakunarni KA. Međutim, postoje razlike između spektara na nižim pH vrednostima, koje su posledica bolje rezolucije prilikom snimanja spektara suvih uzoraka, a verovatno i da prilikom snimanja spektara rastvora nije bilo dovoljno vremena da se u rastvoru postigne potpuna ravnoteža.

Iz rezultata svih primenjenih metoda sledi zaključak da u metanol/vodenim rastvorima WPA dolazi do njene stabilizacije i u razblaženim i u koncentrovanim rastvorima u odnosu na vodene rastvore. U razblaženim rastvorima sa udelom metanola $\geq 50\%$ koncentracije $2 \cdot 10^{-5} \text{ mol dm}^{-3}$ WPA je u obliku KA, za razliku od vodenih rastvora kod kojih dolazi do razlaganja KA. U koncentrovanim rastvorima, sa koncentracijom $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ WPA je takođe u obliku KA i njegovo prisustvo u rastvorima pri porastu pH vrednosti zavisi od udela metanola u rastvaraču. Takođe, od ovog udela zavisi i pri kojoj kiselosti rastvora će doći do izdvajanja taloga, kao i sastav taloga. Sa druge strane, očigledno je da koncentracija rastvora igra veliku ulogu u ponašanju WPA u rastvorima, te da se rezultati dobijeni za razblažene rastvore ne mogu primeniti u slučaju koncentrovanih rastvora i obrnuto. U tabeli 28. su sumirani rezultati dobijeni za rastvore WPA sa različitim koncentracijama i udelima metanola.

Tabela 28. Karakteristike rastvora WPA pri različitim udelima metanola

Koncentracija WPA / mol dm^{-3}	$2 \cdot 10^{-5}$			$5 \cdot 10^{-2}$			
	0	50	100	0	25	50	75
Udeo metanola/ (v/v)%	0	50	100	0	25	50	75
Prisustvo KA do pH	< 1	< 7	< 10	< 2	< 2,5	< 2,5	< 4,5
Stvaranje taloga pri pH	Nema taloga			> 8	> 6,5	> 4,5	
Sastav taloga					$\text{Na}_9\text{PW}_9\text{O}_{34}$	$\text{Na}_7\text{PW}_{11}\text{O}_{39}$	$\text{Na}_7\text{PW}_{11}\text{O}_{39}$

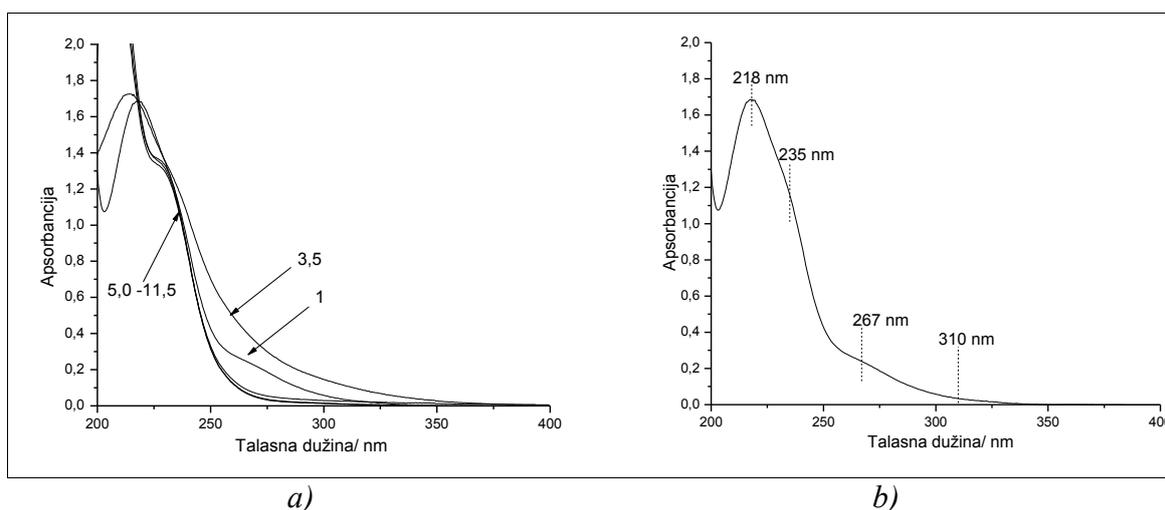
4.2. ISPITIVANJE STABILNOSTI 12-MOLIBDENFOSFORNE KISELINE U RASTVORIMA

4.2.1. Vodeni rastvori 12-molibdenfosforne kiseline

Za ispitivanje stabilnosti MoPA u vodenim rastvorima, korištene su iste koncentracije i metode kao i u slučaju WPA. Početna pH vrednost rastvora je pH= 3,5 za koncentraciju $2 \cdot 10^{-5} \text{ mol dm}^{-3}$ i pH = 1,0 za $5 \cdot 10^{-2} \text{ mol dm}^{-3}$.

ULj spektri vodenog rastvora MoPA

Na slici 33. a) su dati ULj spektri rastvora MoPA pri pH od 1,0 do 11,5 i b) samo na pH= 1,0 [128].



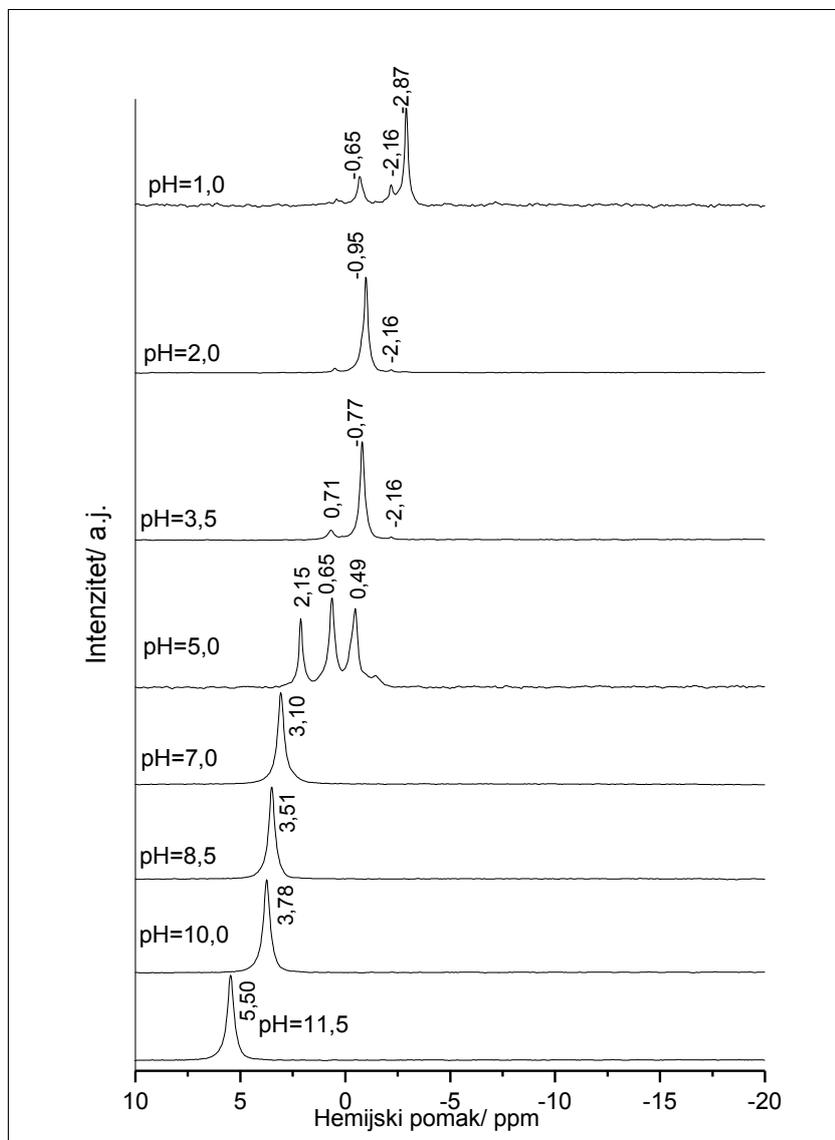
Slika 33. a) ULj spektri rastvora MoPA polazne koncentracije $2 \cdot 10^{-5} \text{ mol dm}^{-3}$, na različitim pH vrednostima, b) ULj spektar na pH = 1,0

Dodavanjem HCl postignuta je pH = 1,0 a pH više od 3,5 dodavanjem NaOH u osnovni rastvor MoPA. Može se primetiti da je spektar osnovnog rastvora različit od onog na pH = 1,0, odnosno da se pri pH = 3,5 javlja apsorpciona traka sa maksimumom na 214 nm i ramenom na 230 nm, dok je na pH = 1,0 maksimum trake na 218 nm, sa ramenima na 235 i 267 nm. Kako je za Keggina-ovu strukturu MoPA karakteristična apsorpciona traka na oko 300 nm [129, 131], očigledno je da u razblaženim vodenim rastvorima dolazi do hidrolize KA, i da zakiseljavanjem rastvora do pH = 1,0 ne dolazi

do njegove regeneracije, kao što je slučaj sa WPA. Spektri od pH = 5,0 do 11,5 su vrlo slični, sa ramenom na 230 nm. Prema ovome, može se zaključiti, da u razblaženom rastvoru koncentracije $2 \cdot 10^{-5} \text{ mol dm}^{-3}$, MoPA nije u obliku KA čak ni kada se pH podesi na pH = 1,0, te da se razlaganje KA odvija u kiseljoj sredini pri pH < 5,0.

^{31}P NMR i ramanski spektri vodenog rastvora MoPA

^{31}P -NMR spektri i hemijski pomaci za rastvore MoPA na različitim pH vrednostima su prikazani na slici 34. i u tabeli 29. [128].



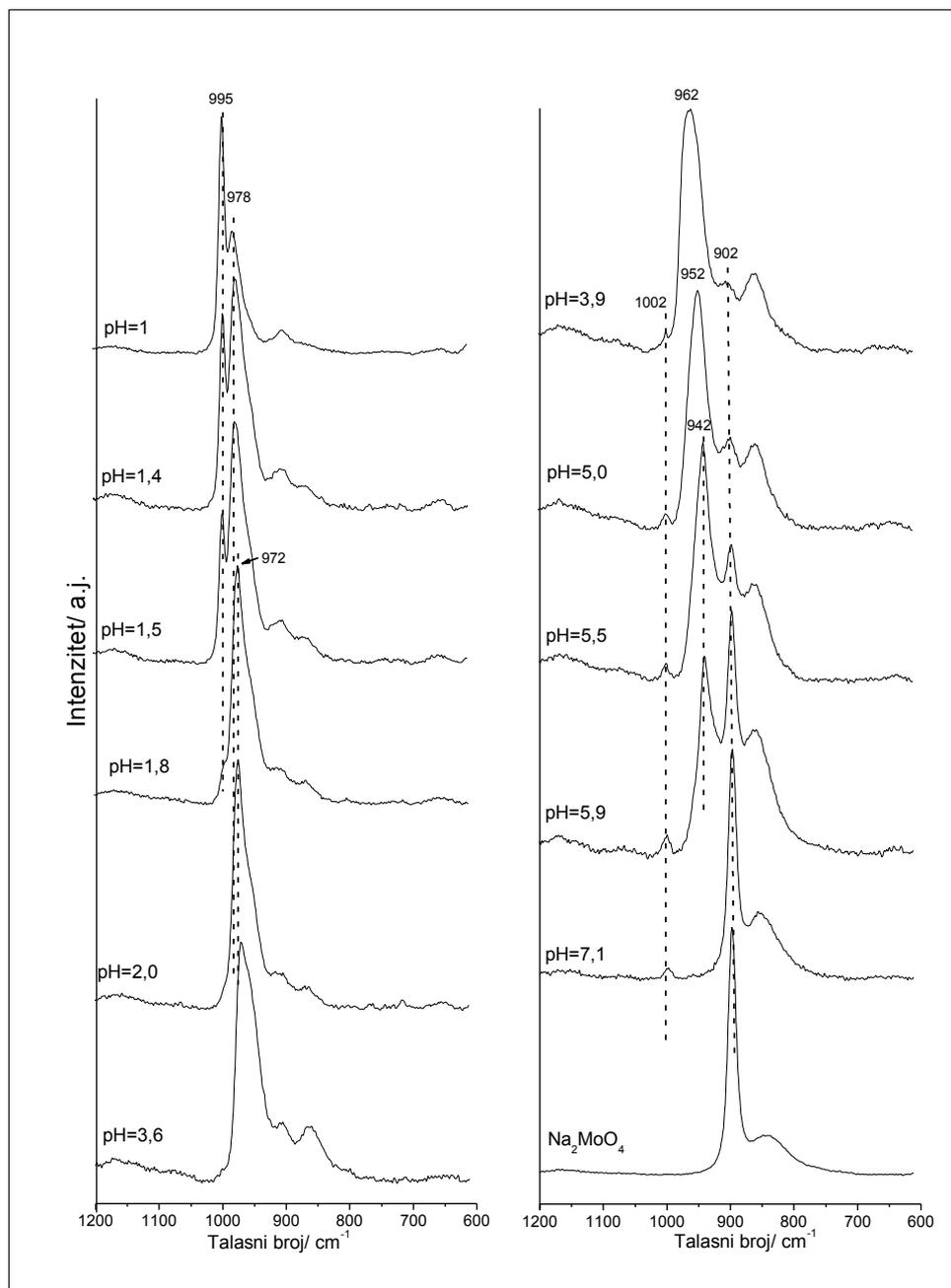
Slika 34. ^{31}P NMR spektri vodenih rastvora MoPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ pri različitim pH vrednostima

Pojedine vrste su identifikovane prema literaturnim podacima [32,118,119]. Na pH = 1,0, uočava se intenzivan pik na -2,87 ppm koji se pripisuje $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, a već na pH = 2,0 ovaj signal nestaje iz spektra. Pik malog intenziteta na -2,16 ppm odgovara $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ i ostaje i na pH = 2,0 i 3,5, ali sa još slabijim intenzitetom. Pik koji se javlja na pH = 1,0, sa hemijskim pomakom na -0,65 može biti pripisan monolakunarnom $[\text{PMo}_{11}\text{O}_{39}]^{7-}$ anjonu. Prisustvo ovih drugih vrsta pored roditeljskog KA, već u osnovnom rastvoru, ukazuje na veliku nestabilnost MoPA i u koncentrovanim vodenim rastvorima. Najintenzivniji pik u rastvorima pri pH = 2,0 (na -0,95 ppm) i pri pH = 3,5 (na -0,77 ppm), odgovara lakunarnom $[\text{PMo}_{11}\text{O}_{39}]^{7-}$ anjonu, koji je dominantan pri ovim pH vrednostima. Pored pika monolakunarnog KA i DA na pH = 3,5 se javlja i pik na 0,71 koji se može pripisati heksalakunarnom $[\text{PMo}_6\text{O}_{25}]^{6-}$ anjonu. U rastvoru na pH = 5,0, intenzitet pika koji potiče od monolakunarnog jona na -0,49 ppm je nešto slabiji, a intenzivni signali na 0,65 i 2,15 ppm odgovaraju produktima degradacije, $[\text{PMo}_6\text{O}_{25}]^{6-}$ i fosfatnom jonu, respektivno. Razlike između pomaka koji se uočavaju za $[\text{PMo}_{11}\text{O}_{39}]^{7-}$ pri nižim i višim pH vrednostima od -0,95 do -0,49 ppm, mogu biti objašnjene ekstenzivnom protonacijom lakunarnog KA [32]. U spektrima rastvorima sa pH > 5, pikovi odgovaraju fosfatnim jonima. Moffat i saradnici pik na oko 2 ppm koji se javlja u molibdo-fosfatnim sistemima između pH 5 i 7 označavaju kao $[\text{P}_2\text{Mo}_5\text{O}_{23}]^{7-}$ [35], tako da postoji verovatnoća da se i ovaj anjon javlja na pH = 5,0 u smeši sa mono i heksalakunarnim KA.

Tabela 29. Hemijski pomaci u ^{31}P NMR spektrima vodenih rastvora MoPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ pri različitim pH vrednostima

	pH								Anjon
	1,0	2,0	3,5	5,0	7,0	8,5	10,0	11,5	
Hemijski pomak/ ppm					3,10	3,51	3,78	5,50	Fosfatni anjoni
				2,15					
			0,71	0,65					
		-0,65	-0,95	-0,77	-0,49				$[\text{PMo}_6\text{O}_{25}]^{9-}$
		-2,16	-2,16	-2,16					$[\text{PMo}_{11}\text{O}_{39}]^{7-}$
		-2,87							$[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$
								$[\text{PMo}_{12}\text{O}_{40}]^{3-}$	

Na slici 35. dati su ramanski spektri rastvora MoPA na različitim pH vrednostima, a u tabeli 30., talasni brojevi i intenziteti traka. U spektru na pH = 1,0, uočavaju se 3 trake, vrlo jaka na 995 cm^{-1} ($\nu_s(M=O_d)$), srednja na 978 cm^{-1} ($\nu_{as}(M=O_d)$) i $\nu_s(P-O_d)$ nerazložene zbog slabije rezolucije) i slaba na 903 cm^{-1} ($\nu_{as}(M-O_b-M)$), koje odgovaraju vibracijama u KA [104, 107].



Slika 35. Ramanski spektri vodenih rastvora MoPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ na različitim pH vrednostima.

Prema NMR spektrima Dawson-ov anjon $[P_2Mo_{18}O_{62}]^{6-}$ se javlja pri pH 1,0 - 3,5, ali je prisutan u mnogo manjoj koncentraciji od KA. Prema literaturnim podacima, karakteristične trake u ramanskom spektru ovog anjona su na 979 i 715 cm^{-1} [42]. Međutim, prva traka se preklapa sa najintenzivnijom trakom KA, a druga se javlja sa vrlo slabim intenzitetom, tako da se prisustvo DA ne može pouzdano potvrditi na osnovu ramanskih spektara.

Tabela 30. Položaj maksimuma traka u ramanskim spektrima vodenih rastvora MoPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ pri različitim pH vrednostima i Na_2MoO_4

	pH												Na_2MoO_4	
	1,0	1,4	1,5	1,8	2,0	3,0	3,6	3,9	4,5	5,0	5,5	5,9		7,1
Talasni brojevi / cm^{-1} i intenziteti traka								1002	1002	1002	1002	1002	1002	
								sl	sl	sl	sl	sl	sl	
	995	995	995	995										
	vj	sr	sr	vsl										
	978	977	977	975	975	975	972	962	962					
	sr	j	vj	vj	vj	vj	vj	j	j					
				957	957	957	957			952				
				r	r	r	r			j				
											942	942		
											j	sr		
903	907	907	907	907	907	907								
sl	sl	sl	sl	sl	sl	sl								
							902	902	902	897	897	897	897	
							sl	sl	sr	sr	j	j	j	
	867	867	867	867	867	867	862	862	862	862	862	862	862	
	sl	sl	sl	sl	sl	sr	sr	sr	sr	sl	sl	sl	sl	

vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame

Trake na 995, 978 i 903 cm^{-1} ostaju u spektrima do pH = 1,8, ali sa promenom u intenzitetima prve dve trake. Naime, intenzitet prve trake opada, a druge raste, tako da je na pH = 1,8 prva traka vrlo slaba, a javlja se nova traka na 957 cm^{-1} , u vidu ramena na traci na 975 cm^{-1} . Prema ovome, razlaganje KA započinje već sa prvim dodavanjem NaOH, odnosno već i pri minimalnoj promeni pH vrednosti.

Identifikacija novonastalih vrsta je otežana zbog činjenice da je izuzetno teško dobiti rastvor u kome bi $[PMo_{11}O_{39}]^{7-}$ bio jedina ramanski aktivna vrsta, tako da se podaci u literaturi odnose na spektar uzorka u kome je on dominirajuća vrsta.

Na spektrima od pH = 2,0 do pH = 3,6 se u spektrima uočava asimetrična traka na 975 cm^{-1} sa ramenom na 957 cm^{-1} , što je prema podacima iz literature [32]

karakteristično za lakunarni KA. Takođe i na $\text{pH} < 2,0$, porast intenziteta trake na oko 975 cm^{-1} , mogao bi da ukazuje na istovremeno prisustvo KA i lakunarnog KA.

Već od $\text{pH} = 3,9$ u spektrima se javlja traka vibracije $\nu_3(T_2)$ u PO_4^{3-} anjonu na 1002 cm^{-1} [132], što ukazuje da već u kiseloj sredini dolazi do degradacije KA i oslobađanje fosfata.

U intervalu od $\text{pH} = 3,9$ do $4,5$, u spektru je naintenzivnija traka na 962 cm^{-1} . Prema *Rob van Veen*-u i saradnicima [32], položaj najintenzivnije trake u ramanskom spektru monolakunarnog KA zavisi od pH sredine, tako da se pri $\text{pH} = 2,5$ nalazi na 970 cm^{-1} , a pri $3,4$ na 963 cm^{-1} . U skladu sa ovim lakunarni KA je prisutan pri $\text{pH} < 4,5$.

Prema NMR spektrima pri $\text{pH} = 5,0$, u rastvoru se javlja smeša monolakunarnog i heksalakunarnog anjona, a moguće i $[\text{P}_2\text{Mo}_5\text{O}_{23}]^{7-}$. Najintenzivnije trake ovih molibdofosfata se javljaju na međusobno vrlo bliskim talasnim brojevima [32], tako da ih je veoma teško pouzdano identifikovati u smeši.

Za $[\text{PMo}_6\text{O}_{25}]^{9-}$ je karakteristična intenzivna traka na 942 cm^{-1} [32], koja se uočava pri $\text{pH} = 5,5$.

U neutralnoj sredini u spektru ostaju samo trake molibdata na 897 i 862 cm^{-1} i traka fosfata na 1002 cm^{-1} .

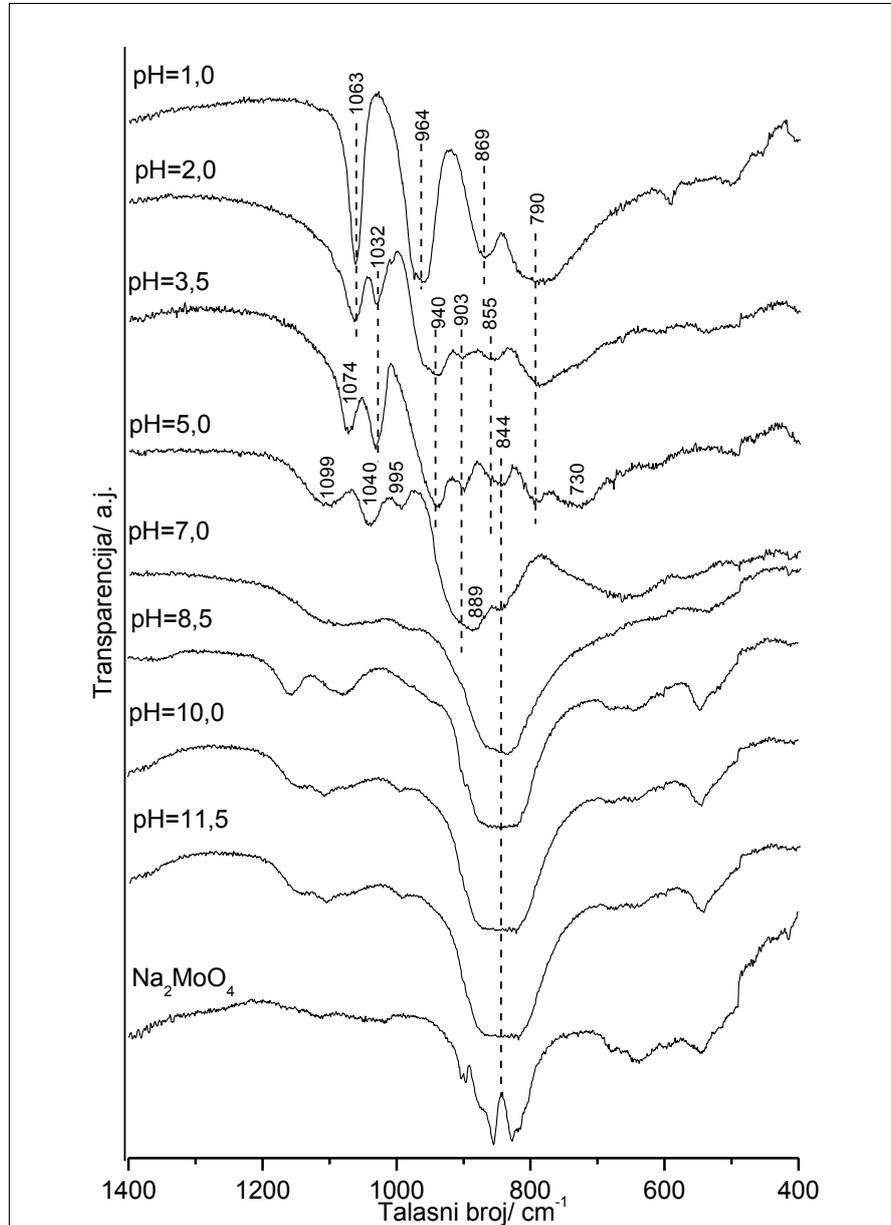
IC i Ramanski spektri suvih ostataka vodenih rastvora MoPA

Na slici 36. su dati IC spektri suvih ostataka za rastvore MoPA različitih pH u oblasti karakterističnih traka za KA, dok su u tabeli 31. prikazani položaji i intenziteti traka [128]. Spektar Na_2MoO_4 je dat radi poređenja.

Može se uočiti da samo spektar suvog ostatka rastvora na $\text{pH} = 1,0$ odgovara spektru čvrste MoPA sa trakama na 1063 ($\nu_{as}(\text{P-O}_a)$), 964 ($\nu_{as}(\text{M=O}_d)$), 869 ($\nu_{as}(\text{M-O}_b\text{-M})$), 790 ($\nu_{as}(\text{M-O}_c\text{-M})$) i 592 i 504 cm^{-1} ($\delta_{as}(\text{O}_a\text{PO}_a)$) [104].

Promene u spektrima su vidljive već pri $\text{pH} = 2$, tj. traka P–O vibracije se cepa na dve trake na 1065 i 1032 cm^{-1} zbog narušavanja visoko simetrične strukture KA. Spektri na $\text{pH} 2,0$ i $3,5$ su kompleksni i identifikacija vrsta zastupljenih u manjoj količini je vrlo otežana zbog velike širine traka pojedinih vrsta. Najintenzivnije trake koje se uočavaju pri $\text{pH} = 2,0$ na 1065 , 1032 , 940 , 903 , 855 i 789 cm^{-1} odgovaraju $[\text{PMo}_{11}\text{O}_{39}]^{7-}$ anjonu [35] koji je dominantna vrsta pri ovoj pH vrednosti. Pri $\text{pH} = 3,5$

traka na 1065 cm^{-1} se pomera na 1074 cm^{-1} verovatno zbog preklapanja sa trakom fosfata koji nastaju kao produkti razlaganja.



Slika 36. IC spektri suvih ostataka vodenih rastvora MoPA polazne koncentracije $5 \cdot 10^{-2}\text{ moldm}^{-3}$ na različitim pH vrednostima

Pri $\text{pH} \geq 5,0$, očigledan je početak dekompozicije MoPA do molibdata i fosfata. Molibdati imaju široku traku od $800 - 900\text{ cm}^{-1}$, dok je za P-O istežuću vibraciju u PO_4^{3-} anjonu karakteristična traka od $1020 - 960\text{ cm}^{-1}$, a za savijajuću od $1160 - 1100\text{ cm}^{-1}$ [133].

Prema spektrima rastvora (NMR i ramanskim) pri pH = 5,0 javlja se $[\text{PMo}_6\text{O}_{25}]^{9-}$ anjon, ali u literaturi nije nađen IC spektar ovog anjona. Traka na 989 cm^{-1} koja se javlja pri ovoj pH vrednosti verovatno potiče od ovog anjona. U spektrima suvih ostataka rastvora pri $\text{pH} \geq 7,0$ prisutne su samo trake molibdata i fosfata.

Prema tome, IC spektri potvrđuju da u alkalnim rastvorima dolazi do potpunog razlaganja polioksometalatne strukture MoPA.

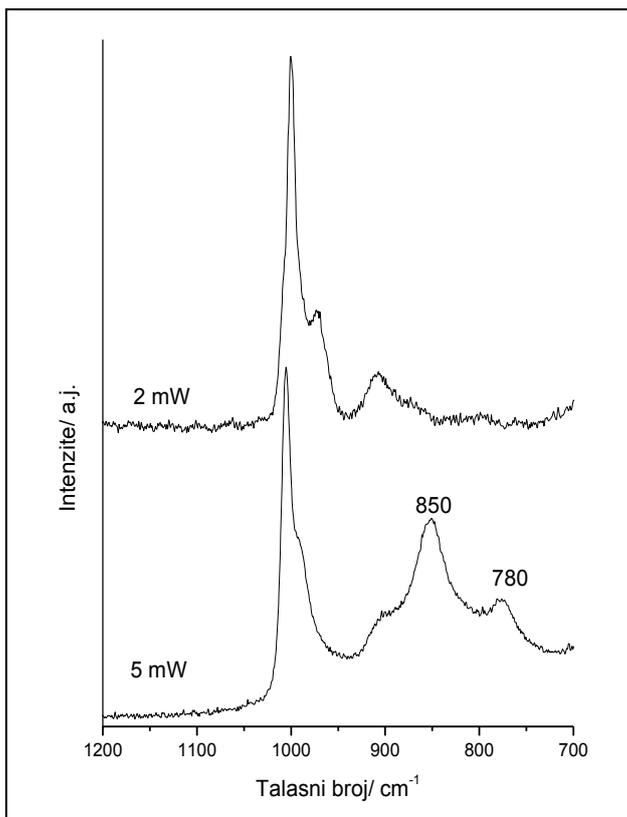
Tabela 31. Talasni brojevi i intenziteti traka u IC spektrima suvih ostataka rastvora MoPA polazne koncentracije $5 \cdot 10^{-2}\text{ moldm}^{-3}$, na različitim pH vrednostima

	pH							Na ₂ MoO ₄	
	1,0	2,0	3,5	5,0	7,0	8,5	10,0		11,5
Talasni brojevi/ cm^{-1} i intenziteti traka				1099 sr	1095 sl,š	1155 sr	1157 sl	1155 sl	
			1074 j			1079 sr	1107 sl	1107 sl	
	1063 j	1065 j 1032 sr	1033 j	1040 j 995 sr	983 r		995 sl	995 sl	
	964 vj	940 sl,š 903 vsl	938 sr 901 sl			940 r			902 sl 880 r
	869 j			889 vj,š					
		855 vsl,š	855 r 844 sl	844 r	844 sl	844 vj,š	845 vj,š	843 vj,š	855 vj 827 vj
	790 vj,š	789 sr,š	797 sl 726 sl						
				660 sr,š					
	592 sl					675 sl 645 sl	674 sl 643 sl	674 sl 650 sl	680 sl 640 sl
	504 sl				536 sl	546 sr	545 sr	544 sr	547 sl

vj -vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame

Prema literaturnim podacima postoje razlike u ramanskim spektrima MoPA, snimljenim pri različitim eksitacionim snagama lasera. Pri višoj snazi lasera uočavaju se trake na 850 i 820 cm^{-1} , koje ne postoje pri nižim snagama [134]. Traci na 850 cm^{-1} odgovara istežuća Mo-O-Mo vibracija u monokliničnom, a na 820 cm^{-1} u ortorombičnom MoO₃ [135]. Spektri snimljeni pri višim snagama lasera dokazuju razlaganje MoPA u čvrstom stanju i formiranje molibden trioksida. Poznato je da se početak dekompozicije MoPA odvija na temperaturama višim od $350\text{ }^\circ\text{C}$, pa je razlog

ovih razlika u spektrima zagrevanje uzorka laserskim snopom. Na slici 37. je dat uporedni prikaz spektara MoPA snimljenih pri snagama 2 i 5 mW. Pored traka koje potiču od MoPA, na spektru dobijenom pri snazi 5 mW uočavaju se trake na 850 i 780 cm^{-1} , koje odgovaraju istežućim vibracijama Mo-O veza u monokliničnom MoO_3 . Iz ovog razloga je neophodno voditi računa o snagama lasera sa kojima se snimaju spektri MoPA da bi se izbeglo termičko razlaganje KA. Stoga su spektri suvih ostataka rastvora MoPA na različitim pH su snimljeni pri snazi lasera od 2 mW.



Slika 37. Ramanski spektri suvog ostataka vodenog rastvora MoPA koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ na $\text{pH} = 1,0$ snimljeni sa različitim snagama lasera

Na slici 38. su dati ramanski spektri suvih ostataka za rastvore MoPA različitih pH i Na_2MoO_4 , dok su u tabeli 32. prikazani položaji i intenziteti traka.

Spektar na $\text{pH} = 1,0$, ima najintenzivnije trake na 990 (ν_s ($M=O_d$)), 980 (ν_{as} ($M=O_d$), ν_s ($P-O_d$)), 880 (ν_{as} ($M-O_b-M$)), 605 (ν_s ($M-O-M$)), 240 cm^{-1} (ν_s ($P-O_d$)), koje odgovaraju trakama $\text{PMo}_{12}\text{O}_{40}^{3-}$ [22]. U spektrima do $\text{pH} = 2,0$ nema velikih promena, izuzev u oblasti vibracija rešetke (ispod 200 cm^{-1}), što je posledica dodavanja NaOH, odnosno nastajanja rastvorne soli $\text{Na}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$. Takođe je evidentan porast intenziteta trake na 980 cm^{-1} i njen mali batohromni pomeraj do 971 cm^{-1} , što ukazuje na prisustvo smeše KA i lakunarnog KA.

Tabela 32. Talasni brojevi i intenziteti traka u ramanskim spektrima suvih ostataka rastvora MoPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$, na različitim pH vrednostima

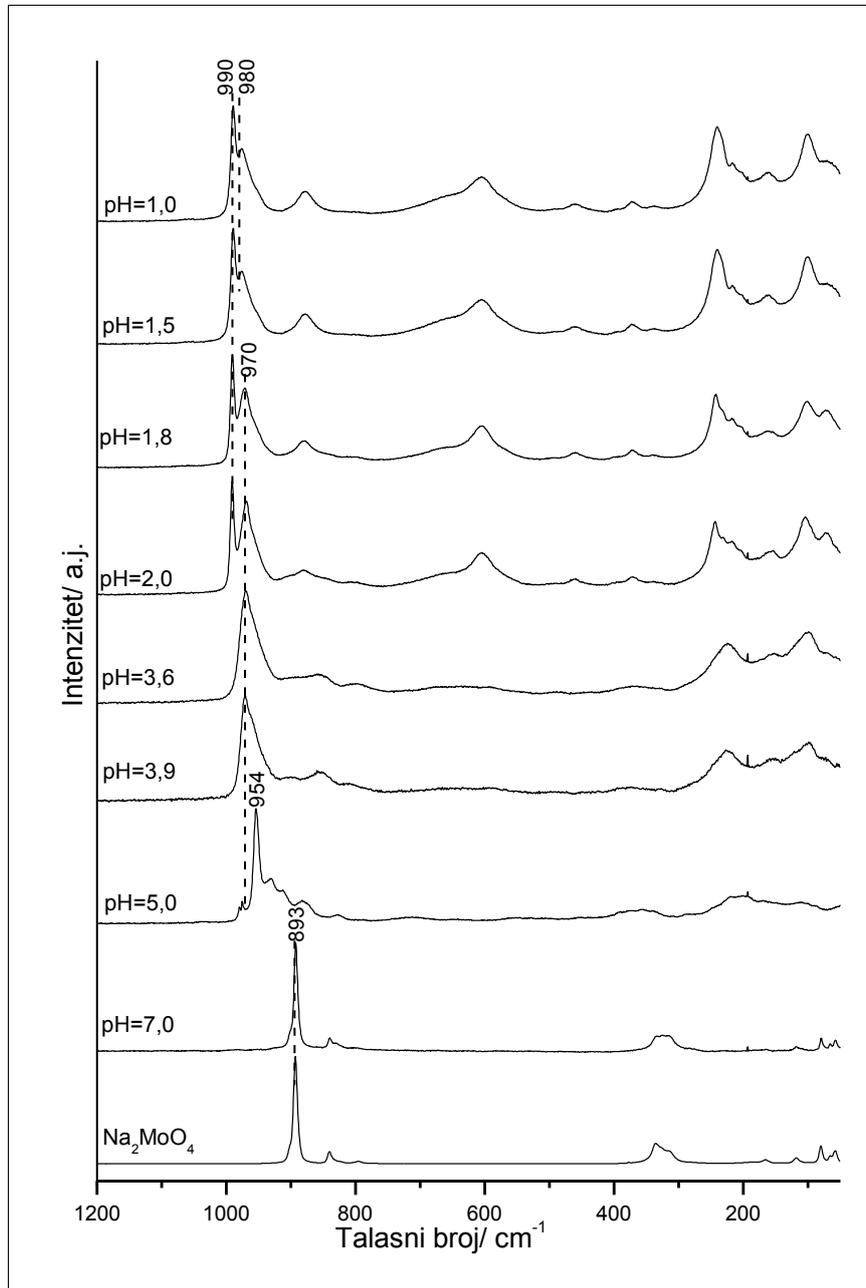
	pH							Na ₂ MoO ₄	
	1,0	1,5	1,8	2,0	3,6	3,9	5,0		7,1
Talasni brojevi / cm ⁻¹ i intenziteti traka	990 vj 980 j	990 vj 980 j	991 vj 971 j	991 vj 970 j	970 j	971 j	980 sl		
					950 r	950 r	954 vj 930 sr 912 sr 883 sl	893 vj	893 vj
	880 sr	880 sr	878 sr,š	881 sl,š					
					860 sl,š	860 sr			
					800 sl,š		827 sl	840 sl	840 sl
							712 sl,š		
	650 r 605sr,š	650 r 605sr,š	650 r 604 sr	650 r 605sr,š					
	465sl,š	465sl,š	460 sl	460 sl,š					
	373 sl	373 sl	371sl	371 sl,š					
	336 sl	336 sl					350sl,š	327sr,š	336 sr 311 r
	240 j	240 j	242 sr	243 sr 233 sr 220 sr	225sr,š	227sr,š			
	217 sl	217 sl	218 sl				200 sl,š		
	162 sl	162 sl	163 sl	156 sr	153sl,š	150sl,š		166 sl 119 sl	166 sl 118 sl
	100 sr	100 sr	100 sr	105 sr	99 sr,š	99 sr,š	114 sl,š		
								80 sl	80 sl

vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame

Za razliku od spektara rastvora kod kojih već na pH = 2,0 nema trake $\nu_s (M=O_d)$ vibracije roditeljskog anjona, ona je ovde vrlo intenzivna, što ukazuje da je pri procesu dehidratacije došlo do delimične regeneracije KA.

Na pH = 3,6 i 3,9 su kao i u slučaju ramanskih spektara rastvora prisutne trake lakunarnog KA (970 cm⁻¹ sa ramenom na 950 cm⁻¹). Na pH = 5,0 najintenzivnija je traka na 954 cm⁻¹, koja je, kao što je pomenuto, karakteristična za [PMo₆O₂₅]⁹⁻ [32],

ali se javlja i traka koja potiče od monolakunarnog KA. U neutralnoj sredini u spektru ostaju samo trake na 893, 840, 327, 166, 119 i 80 cm^{-1} , koje odgovaraju spektru $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$.



Slika 38. Ramanski spektri suvih ostataka vodenih rastvora MoPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ na različitim pH vrednostima

Za razliku od spektara rastvora, gde se traka fosfata uočavala u spektrima na svim ispitivanim pH vrednostima počevši od $\text{pH} = 3,9$, traka fosfata na 1002 cm^{-1} se u ovom slučaju ne javlja. Ovo je posledica toga što je praškasti uzorak sa nehomogenim rasporedom slobodnih fosfata u uzorku sniman sa mikroramanskim spektrometrom, gde je oblast obuhvaćena snimanjem mikronske veličine, tako da se fosfat nije nalazio u snimanoj oblasti iako je najverovatnije prisutan u uzorku.

Generalno, pošto je razlaganje MoPA potpuno već u kiseloj sredini može se zaključiti da je ova HPK izuzetno hidrolitički nestabilna. Shema razlaganja je slična onoj kod WPA, ali do dekompozicije dolazi pri nižim pH vrednostima. Do razlaganja KA dolazi već i pri najmanjoj promeni pH vrednosti uz nastajanje lakunarnog KA kao dominantanog oblika do $\text{pH} = 3,5$, dok je pri $\text{pH} = 5,0$ prisutan $[\text{PMo}_6\text{O}_{25}]^{9-}$. Slobodni fosfati se detektuju u ramanskim spektarima rastvora već pri $\text{pH} > 3,9$, a slobodni molibdati pri $\text{pH} > 5,0$.

4.2.2. Metanol/ vodeni rastvori 12- molibdenfosforne kiseline

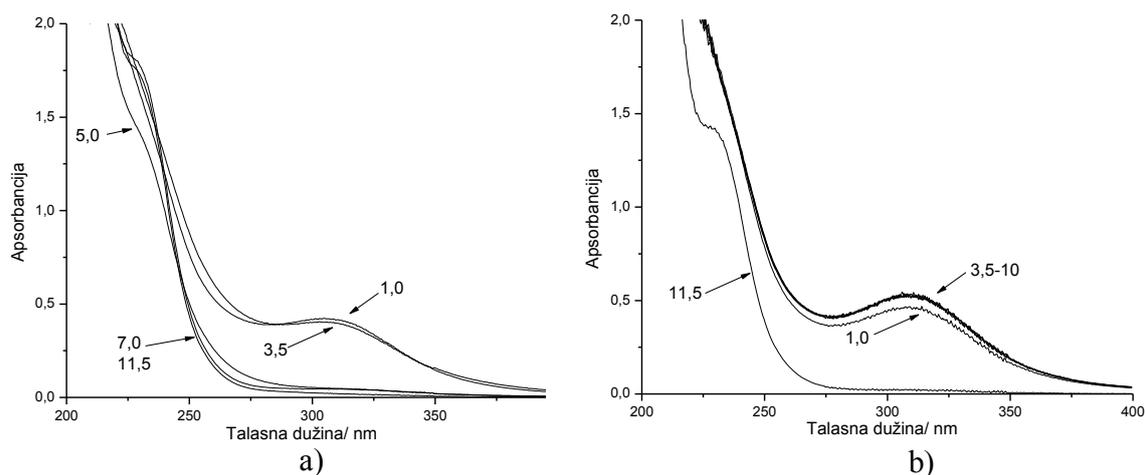
Ispitivanje hidrolitičke stabilnosti MoPA je pokazalo da je reč o veoma nestabilnoj HPK. Pošto je u slučaju WPA dokazana stabilizacija u prisustvu organskog rastvarača, cilj nam je bio da proverimo da li bi se po očekivanoj analogiji isto ponašala i MoPA u metanol/vodenom rastvaraču. Za razliku od vodenih rastvora koji ostaju žuti u dužem vremenskom intervalu, metanol/vodeni rastvori menjaju boju od žute do zelene, verovatno zbog stvaranja "heteropoli plavog" usled brze i reverzibilne redukcije Mo^{VI} do Mo^{V} . Zbog ovog su neposredno pre svakog eksperimenta pripremani sveži rastvori.

ULj spektri metanol/vodenih rastvora MoPA

Na slici 39. su dati ULj spektri rastvora MoPA početne koncentracije $2 \cdot 10^{-5} \text{ mol dm}^{-3}$ pri pH od 1,0 do do 11,5 u rastvaraču sa polaznom koncentracijom metanola 50 % i 100 %. Dodavanjem HCl postignuta je $\text{pH} = 1,0$, a pH više od 3,5 kolika je pH polaznog rastvora, dodavanjem NaOH, kao i u slučaju vodenih rastvora.

Može se primetiti da su spektri osnovnog rastvora i spektar na $\text{pH} = 1,0$ skoro identični. U spektru se javlja traka sa maksimumom na oko 310 nm, koja odgovara KA

[129, 131]. Rame na 230 nm se javlja od pH = 5,0. Spektri na pH > 7,0 su vrlo slični ovima na pH = 5,0, takođe sa ramenom na 230 nm. Traku na 214 nm koja postoji u vodenom rastvoru, ovde nije moguće pratiti zbog intenzivne apsorpcije metanola u ovoj oblasti. Prema tome, dodatak metanola dovodi do stabilizacije KA, tako da je i u razblaženom rastvoru KA prisutan do pH = 3,5.



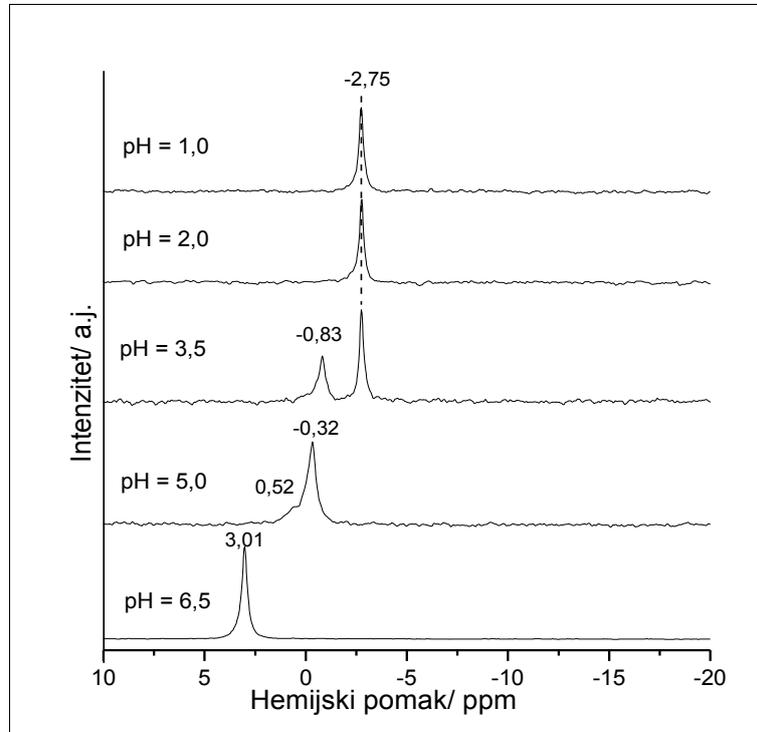
Slika 39. ULj spektri rastvora MoPA početne konc. $2 \cdot 10^{-5} \text{ mol dm}^{-3}$ na različitim pH vrednostima u rastvaraču sa polaznim udelom metanola: a) 50 %; b) 100 %

U slučaju upotrebe čistog metanola, spektri od pH 1,0 do 10,0 su gotovo identični, sa trakom na 310 nm, a tek u spektru na pH 11,5 se ova traka gubi te ostaje samo rame na 230 nm. Ovo ukazuje na izuzetnu stabilizaciju KA u odnosu na vodeni rastvor, jer je roditeljski anjon prisutan čak i u alkalnoj sredini.

Ramanski i ^{31}P NMR spektri metanol/vodenog rastvora MoPA

Sa ^{31}P -NMR spektra prikazanih na slici 40. i iz hemijskih pomaka datih u tabeli 33., očigledno je da je kod rastvora MoPA u 50 % metanolu shema razlaganja mnogo jednostavnija nego u slučaju vodenih rastvora. Na pH = 1,0, uočava se intenzivan pik na $-2,75 \text{ ppm}$, koji odgovara $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, i koji ostaje u spektrima sve do pH = 3,5 kada se uz njega javlja i pik lakunarnog $[\text{PMo}_{11}\text{O}_{39}]^{7-}$ anjona, na $-0,83$. Lakunarni anjon je dominantan na pH = 5,0 (sa hemijskim pomakom pomećenim na $-0,32 \text{ ppm}$, jer hemijski pomak zavisi od protonacije anjona, kao što je pomenuto u poglavlju 4.2.1.), ali se uz njega javlja i $[\text{PMo}_6\text{O}_{25}]^{9-}$, koji se identifikuje po piku na $0,52 \text{ ppm}$ [32]. Na

pH = 6,5, rastvor više nije bistar i u spektru se javlja samo signal koji potiče od fosfatnog anjona. Dalje dodavanje NaOH dovodi do izdvajanja taloga.

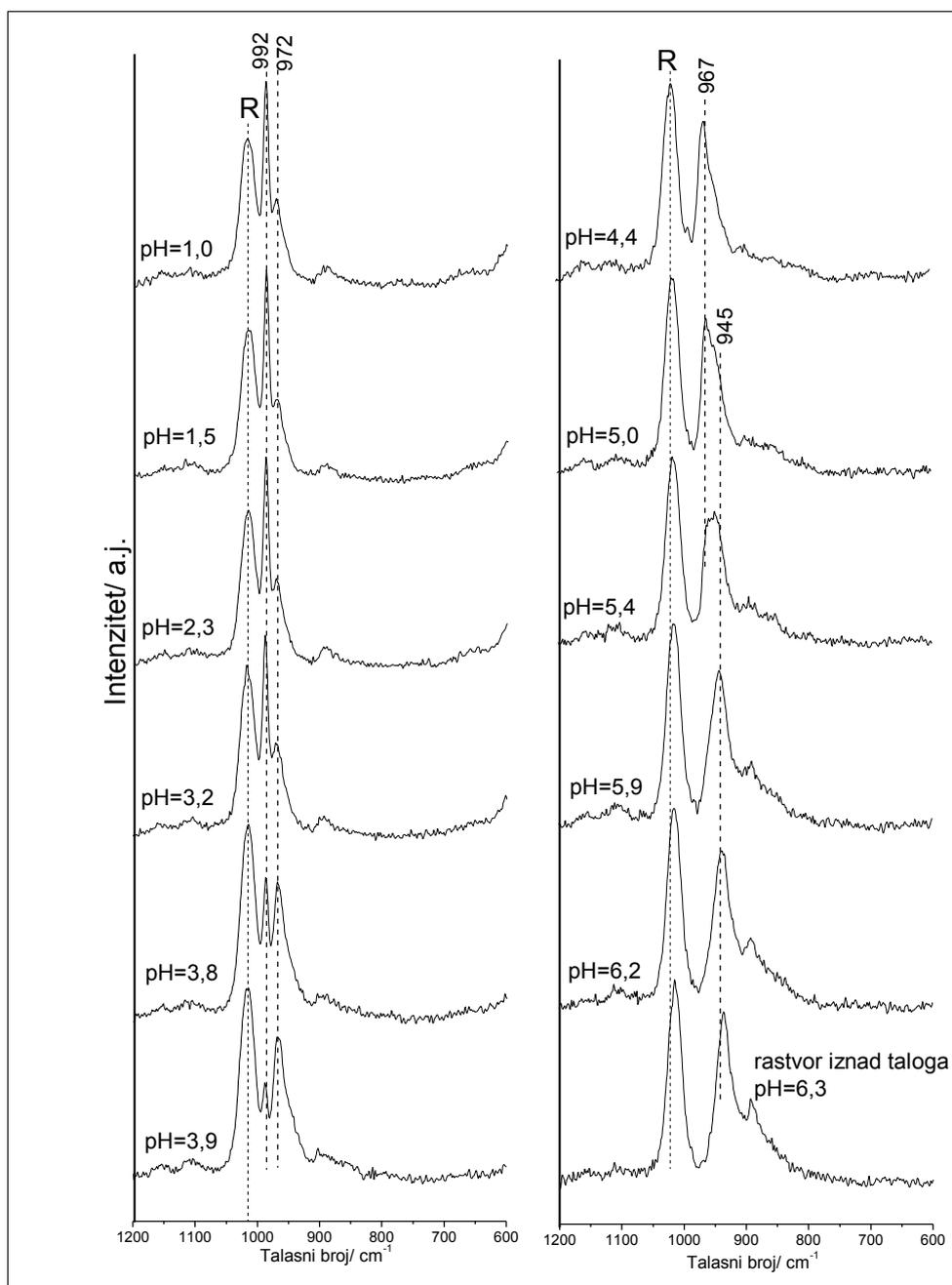


Slika 40. ^{31}P NMR spektri rastvora MoPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 50%

Tabela 33. Hemijski pomaci u ^{31}P NMR spektrima rastvora MoPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 50% na različitim pH vrednostima

	pH					Anjon
	1,0	2,0	3,5	5,0	6,5	
H _i pomak/ ppm					3,01	Fosfatni anjon
				0,52		$[\text{PMo}_6\text{O}_{25}]^{9-}$
			-0,83	-0,32		$[\text{PMo}_{11}\text{O}_{39}]^{7-}$
	-2,75	-2,75	-2,75			$[\text{PMo}_{12}\text{O}_{40}]^{3-}$

Na slici 41. dati su ramanski spektri rastvora MoPA u 50 % metanolu na različitim pH vrednostima, a talasni brojevi i intenziteti traka su sumirani u tabeli 34.



Slika 41. Ramanski spektri rastvora MoPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 50% na različitim pH vrednostima (R-traka rastvarača)

Na spektrima traka istežuće C-O vibracije metanola na 1017 cm^{-1} je označena sa R. Na pH oko 1, uočavaju se trake istežućih vibracija: vrlo jaka na 992 cm^{-1} (ν_s ($M=O_d$)), srednja na 974 (ν_{as} ($M=O_d$), ν_s ($P-O_d$)), nerazložene zbog slabije rezolucije spektra) i slaba na 895 (ν_{as} ($M-O_b$ - M)) cm^{-1} koje odgovaraju vibracijama u KA. Ove

trake u spektrima vodenih rastvora su prisutne do $\text{pH} = 1,8$, dok u slučaju smeše metanol/vode oblast u kojoj postoji KA se proširuje do $\text{pH} = 3,9$. Spektre su sa gotovo nepromenjenim odnosom intenziteta sve do $\text{pH} = 3,2$ kada intenzitet prve trake počinje da slabi, dok se u slučaju vodenih rastvora promene u spektrima dešavaju pri $\text{pH} < 1$. Sa porastom pH , raste intenzitet druge trake i ona se postepeno batohromno pomera do 970 cm^{-1} , što ukazuje na stvaranje monolakunarnog KA.

Tabela 34. Položaj maksimuma traka u ramanskim spektrima rastvora MoPA polazne konc. $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola 50 %

		pH											
		1,0	1,5	2,3	3,2	3,8	3,9	4,4	5,0	5,4	5,9	6,2	6,3*
Talasn. br. / cm^{-1} i inten. traka	992	992	992	992	992	992							
	vj	vj	vj	vj	sr	sr							
	974	974	974	974	972	970 j	967	967	967 j				
	sl	sl	sl	sl	sr		j	j					
							950	950	945	945	942	941 j	
							r	r	j,š	j	j		
	895	895	895	895	895	895	895	895	895	895	898	898	
	sl, š	sl, š	sl, š	sl, š	sl, š	sl, š	sl, š	sl, š	sl, š	sl, š	sr	sr	

vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame; *rastvor iznad taloga

Od $\text{pH} = 4,4$ do $\text{pH} = 5$ u spektru se uočava traka na 967 cm^{-1} karakteristična za lakunarni KA, sa ramenom na oko 950 cm^{-1} . Intenzitet ramena postepeno raste tako da se na $\text{pH} = 5,4$ izjednačava sa intenzitetom trake na 967 cm^{-1} . Kako je za $[\text{PMo}_6\text{O}_{25}]^{9-}$ karakteristična traka na oko 950 cm^{-1} , pri ovoj pH vrednosti u rastvoru se, u skladu sa NMR spektrima nalazi smeša ova dva oblika. Pri $\text{pH} > 5,9$ heksalakunarni anjon je jedina vrsta prisutna u rastvoru. U ovom slučaju nije moguće pratiti stvaranje fosfata, jer se njihova traka na 1002 cm^{-1} nalazi u oblasti u kojoj je i jaka i široka traka rastvarača.

Između rezultata NMR i ramanske spektroskopije postoje određena mala neslaganja u pogledu oblasti pH u kojoj je prisutan neki anjon. Prema NMR spektrima, na $\text{pH} = 3,5$ je prisutan i lakunarni uz KA, dok se prema ramanskim spektrima on počinje stvarati pri $\text{pH} = 3,8$. Ovo se može objasniti velikom nestabilnošću pojedinih molbdofosfata u rastvorima. Naime, snimanjem ramanskog spektra pomoću eksterne sonde, maksimalno je skraćeno vreme od podešavanja pH do snimanja spektra, a takođe je i samo snimanje oko 10 puta kraće nego u slučaju NMR spektara. Zbog ovoga, pri

snimanju ^{31}P NMR spektara dolazi do dalje razgradnje anjona formiranih na datoj pH vrednosti.

Iz rezultata ramanske i ^{31}P NMR spektroskopije može se zaključiti da je u koncentrovanom metanol/vodenom rastvoru MoPA prisutna u obliku KA, bez prisustva drugih vrsta koje se javljaju u slučaju vodenih rastvora. Pri promeni pH do pH = 3,2, on ostaje jedina vrsta prisutna u rastvoru. Dekompozicija KA se odvija najverovatnije bez formiranja DA, preko monolakunarne $[\text{PMo}_{11}\text{O}_{39}]^{7-}$ i heksalakunarne $[\text{PMo}_6\text{O}_{25}]^{9-}$ forme.

IC i Ramanski spektri suvih ostataka metanol/vodenih rastvora MoPA

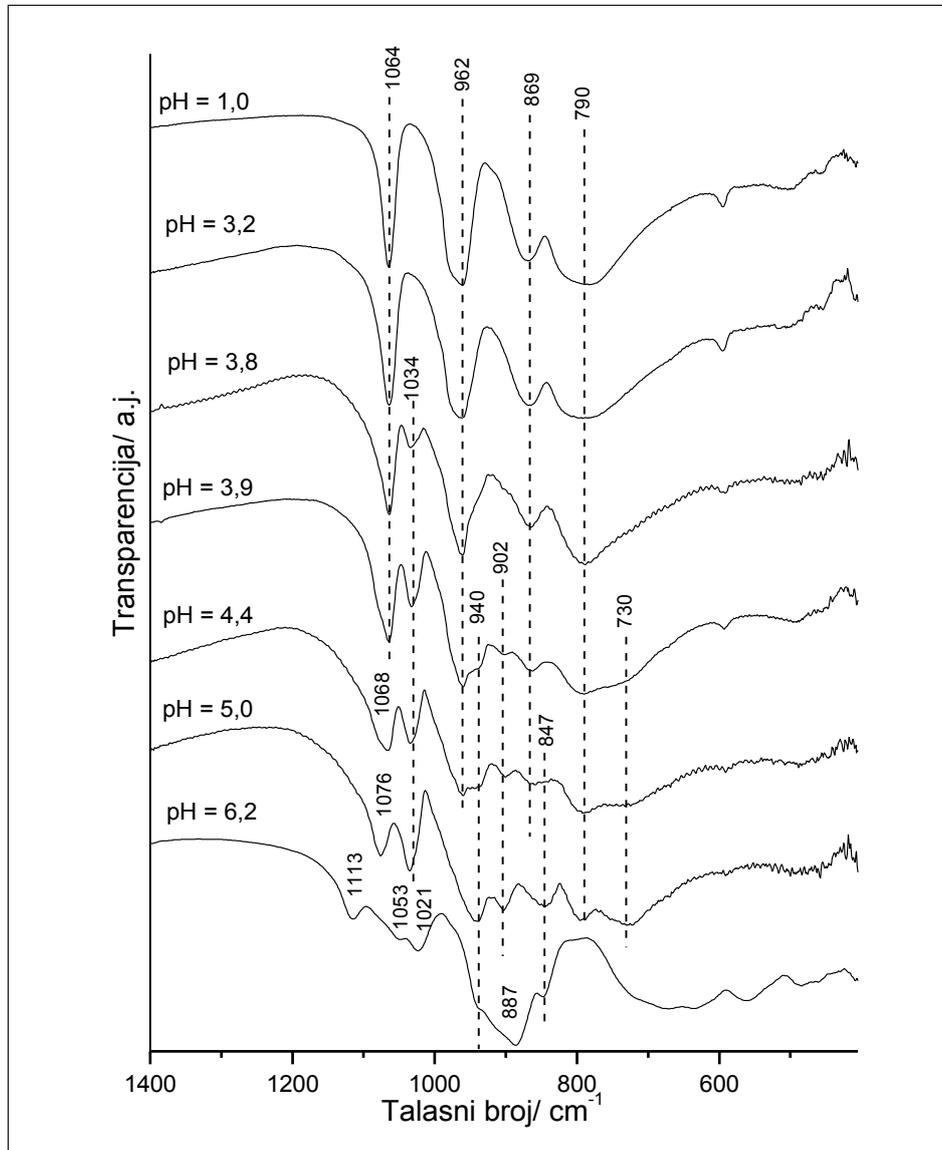
Na slici 42. su dati IC spektri suvih ostataka za rastvore MoPA u 50 % metanolu na različitim pH u oblasti karakterističnih traka za krutu mrežu KA, dok su u tabeli 35. prikazani položaji i intenziteti traka.

Tabela 35. Tal. br. i intenz. traka u IC spektrima suvih ostataka rastvora MoPA polazne konc. $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa početnom konc. metanola 50 %

	pH						
	1,0	3,2	3,8	3,9	4,4	5,0	6,2
Talasni brojevi / cm^{-1} i intenziteti traka						1076 j	1113 sr
	1064 j	1064 j	1064 j	1064 j	1068 j		1053 sl
			1034 sl	1034 sr	1035 j	1035 j	1021 sr
	962 vj	962 vj	961 vj	960 vj 940 r 902 sl	960 j 940 r 902 sl	962 r 940 sr 903 sr	936 sl
							887 j,š
	869 j	869 j	865 j	864 sr	860 sl 845 vs	845 sr	847 sr
	790 vj,š	790 vj,š	788 vj,š	790 vj,š 730 sl	791 sr,š 730 sl	795 sr 730 sr	
	592 sl	592 sl	592 sl	593 sl			
							565 sl
	504 vsl	504 vsl					

vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame

Može se uočiti da spektar suvog ostatka rastvora na pH = 1,0 odgovara spektru čvrste MoPA. Za razliku od vodenih rastvora u kojima promene u spektrima počinju već pri pH = 2,0, u ovom slučaju i na pH = 3,2, u spektru su prisutne samo trake KA.



Slika 42. IC spektri suvih ostataka rastvora MoPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa početnom koncentracijom metanola 50 %, na različitim pH vrednostima.

Cepanje trake P–O vibracije na dve trake na 1064 i 1038 cm^{-1} započinje pri pH = 3,8, zbog stvaranja monolakunarnog KA. Ova promena se kod vodenih rastvora dešava već pri pH = 2,0. Do pH = 5,0 trake koje su karakteristične za lakunarni KA

ostaju u spektrima, ali se javljaju i neke nove slabije trake verovatno zbog vrsta koje su zastupljene u manjoj meri u smeši. Takođe, kao i kod vodenih rastvora, dolazi do postepenog pomeranja trake P-O_a vibracije zbog preklapanja sa trakom P-O vibracije fosfata oslobođenih u procesu razlaganja. Na spektru pri pH = 6,2 uočavaju se trake na 1115, 1053, 1022, 936, 885 i 847 cm⁻¹. Ovaj spektar odgovara spektru vodenih rastvora pri pH = 5,0, sem u oblasti P-O vibracija, koji je pripisan [PMo₆O₂₅]⁹⁻ anjonu.

Na slici 43. su dati ramanski spektri suvih ostataka, dok su u tabeli 36. prikazani položaji i intenziteti traka.

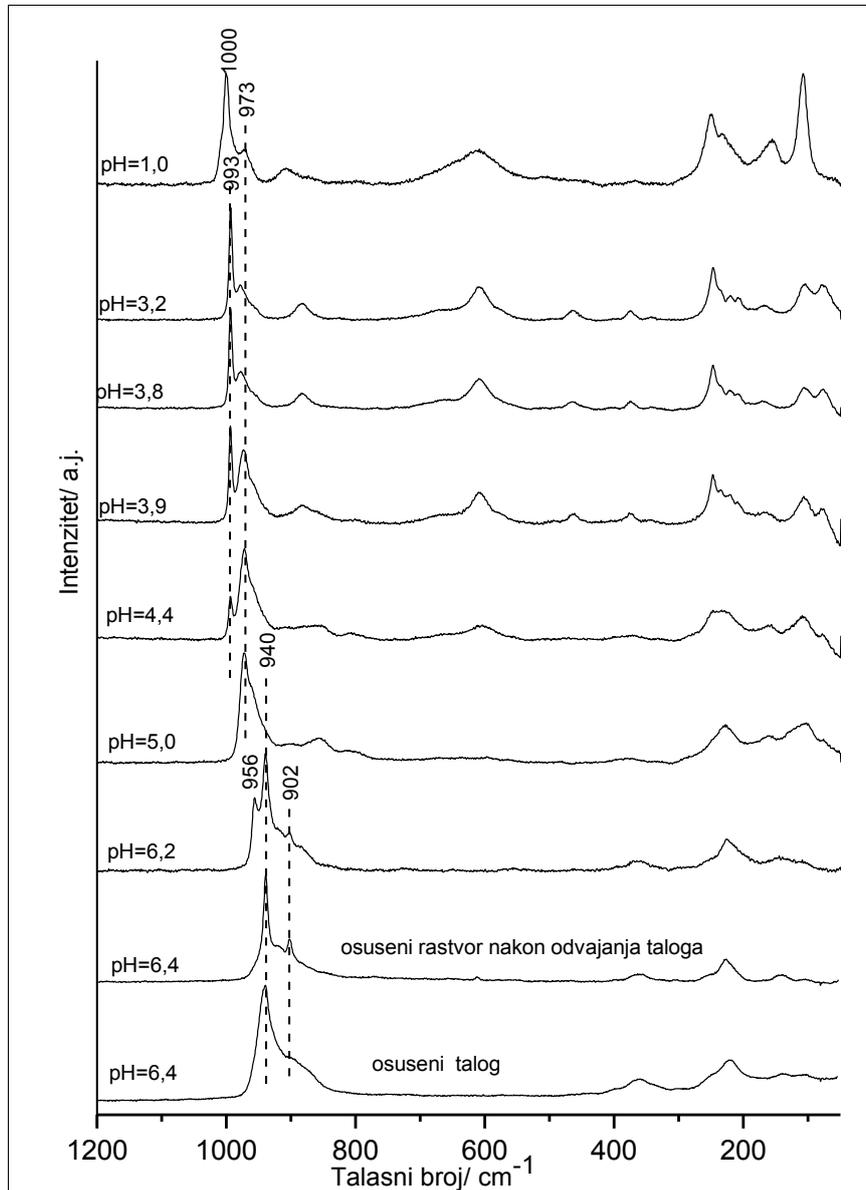
Tabela 36. Talasni brojevi i intenziteti traka u ramanskim spektrima suvih ostataka rastvora MoPA polazne koncentracije 5 · 10⁻² moldm⁻³ u rastvaraču sa početnom koncentracijom metanola 50 %, na različitim pH vrednostima

	pH									
	1,0	3,2	3,8	3,9	4,4	5,0	6,2	6,4*	6,4 [#]	
Talasni brojevi / cm ⁻¹ i intenziteti traka	1000 vj	993 vj	993 vj	993 vj	993 sr					
	973 sr	978 sr	978 sr	972 j	972 j	972 j				
				960 r	960 r	960 r	956 sr			
							940 vj	940 vj	940 vj	
							895 vsl			
	907 sr						902 sl	902 sr	902sr,š	
		882 sr	884 sr	882 sr						
					860 sl,š	856 sl				
					806 sl					
	609 j	611 sr	609 sr	610 sr	604 sl					
		465 sl	465 sl	462 sl						
		375 sl	374 sl	377 sl						
							365 sl	365 sl	365 sl	
250 j	247 j	247 j	247 j							
233 sr	235 vsl	235 vsl	235 sl	234 sr						
	220 sl	221 sl	220 sl			228 sr	226 sr	226 sr	226 sr	
	209 sl	209 sl	209 sl							
	168 sl	168 sl	168 sl							
155 sr					157 sl	159 sl				
108 vj	104 sr	106 sr	107 sr	109 sr	103 sr					
	80 sr	76 sr	76 sr	78 sl						

vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame;* osušeni rastvor nakon odvajanja taloga, [#] osušeni talog

U spektru na pH = 1,0 uočava se da je traka asimetrične istežuće Mo-O_d vibracije šira i pomerena ka višim talasnim brojevima u odnosu na spektar čvrste MoPA. Ovo se može objasniti promenama nastalim usled reakcije MoPA sa metanolom, koja rezultuje kidanjem O_d...H...O_c vodonične veze, protonacijom metanola

i formiranjem $O_d \dots (CH_3OH)_n H^+ \dots O_c$ vodonične veze. Promena u jačini vodonične veze dovodi do promene u jačini Mo-O_d veze, pa samim tim i do promena u položaju trake njene istežuće vibracije.



Slika 43. Ramanski spektri suvih ostataka rastvora MoPA polazne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa početnom koncentracijom metanola 50 %, na različitim pH vrednostima

U spektrima do pH = 3,8 nema velikih promena, sem u oblasti vibracija rešetke, zbog stvaranja natrijumove soli. Na pH = 3,9 u spektru se uočava batohromni pomeraj

trake sa 978 na 972 cm^{-1} i pojava ramena na 960 cm^{-1} , ali traka karakteristična za KA na 993 cm^{-1} ostaje čak i na $\text{pH} = 4,4$ sa oslabljenim intenzitetom. Iz ovih rezultata je jasno da se do ove pH vrednosti u rastvoru nalaze istovremeno MoPA u obliku KA i monolakunarnog KA.

Do potpunog nestanka KA dolazi na $\text{pH} = 5,0$, kada je prisutan monolakunarni KA, sa karakterističnom trakom na 972 cm^{-1} . Na $\text{pH} = 6,2$ javljaju se trake na 956 i 940 cm^{-1} karakteristične za monolakunarni KA (po analogiji sa vodenim rastvorima, kod kojih se talasni broj karakteristične vibracije za lakunarni anjon smanjuje sa porastom pH) i za $[\text{PMo}_6\text{O}_{25}]^{9-}$ [32]. Kada se odvoji talog od rastvora, u spektru suvog ostatka i u osušenom talogu nestaje traka na 956 cm^{-1} , a ostaje samo traka na 940 cm^{-1} . Prema tome, $\text{Na}_9[\text{PMo}_6\text{O}_{25}]$ počinje da se taloži kada se dodavanjem NaOH nagradi tolika količina ovog jedinjenja da se prekorači njegov proizvod rastvorljivosti u smeši metanol/voda.

Postoje male razlike između ramanskih spektara rastvora i uparenih uzoraka na istim pH vrednostima, što ukazuje na reverzibilnost reakcije razlaganja i delimičnu regeneraciju polaznog anjona. Na primer, na $\text{pH} = 3,8$ u spektru rastvora se uočava promena u spektru KA, ali se ona ne primećuje u spektru uparenog uzorka; na $\text{pH} = 4,4$ u rastvorima nema više KA, ali prema spektrima uparenih uzoraka dolazi do njegove delimične regeneracije. Takođe se uočava da se na $\text{pH} = 6,2$ pri uparavanju regeneriše monolakunarni KA.

Generalno, može se zaključiti da se primenom smeše metanol/voda može poboljšati solvolitička stabilnost MoPA i u koncentrovanim rastvorima. Razlaganje MoPA počinje oko $\text{pH}=3,0$, preko $[\text{PMo}_{11}\text{O}_{39}]^{7-}$, do $[\text{PMo}_6\text{O}_{25}]^{9-}$ koji se taloži pri $\text{pH} > 6,3$. Kako su molibdofosfati veoma nestabilni u rastvorima, utvrđivanje preciznih granica pH vrednosti u okviru kojih se javljaju pojedini oblici je veoma otežano. Karakteristike rastvora MoPA u vodi i u 50 % metanolu sumirane su u tabeli 37.

Tabela 37. Karakteristike rastvora MoPA u vodi i u 50 % metanolu

Koncentracija MoPA /mol dm^{-3}	$2 \cdot 10^{-5}$			$5 \cdot 10^{-2}$	
Udeo metanola/ (v/v)%	0	50	100	0	50
Prisustvo KA do pH	-	< 3,5	< 10	< 1	< 3,5
Stvaranje taloga pri pH				> 6,2	
Sastav taloga	Nema taloga			$\text{Na}_9\text{PMo}_6\text{O}_{25}$	

4.3. ISPITIVANJE STABILNOSTI 12-VOLFRAMSILICIJUMOVE KISELINE U RASTVORIMA

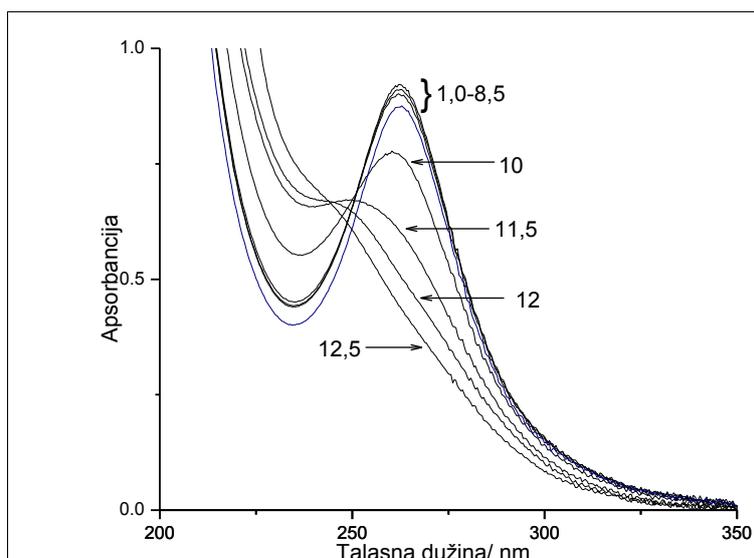
4.3.1. Vodeni rastvori 12- volframsilicijumove kiseline

Za ispitivanje stabilnosti WSiA u vodenim rastvorima, kao i u slučaju prethodne dve HPK, primenjene su iste metode (sem NMR) i korišćene iste koncentracije rastvora. Početna pH vrednost rastvora je pH = 3,5 za koncentraciju $2 \cdot 10^{-5} \text{ mol dm}^{-3}$ i pH = 1,0 za $5 \cdot 10^{-2} \text{ mol dm}^{-3}$.

UV spektri vodenog rastvora WSiA

Na slici 44. su dati ULj spektri rastvora WSiA pri pH od 1,0 do 12,5 [128]. Dodavanjem HCl postignuta je pH = 1,0 a pH više od 3,5 dodavanjem NaOH u osnovni rastvor WSiA.

Maksimum apsorpcione trake, koji odgovara prenosu naelektrisanja u W-O-W vezama, se nalazi na 262 nm sve do pH 8,5, a na pH = 10,0 se neznatno pomera na 261 nm. Na pH = 11,5 traka se pomera na 252 nm. Prema ovim spektrima u slučaju WSiA, u razblaženim vodenim rastvorima KA ostaje očuvan i u alkalnoj sredini za razliku od WPA i MoPA.



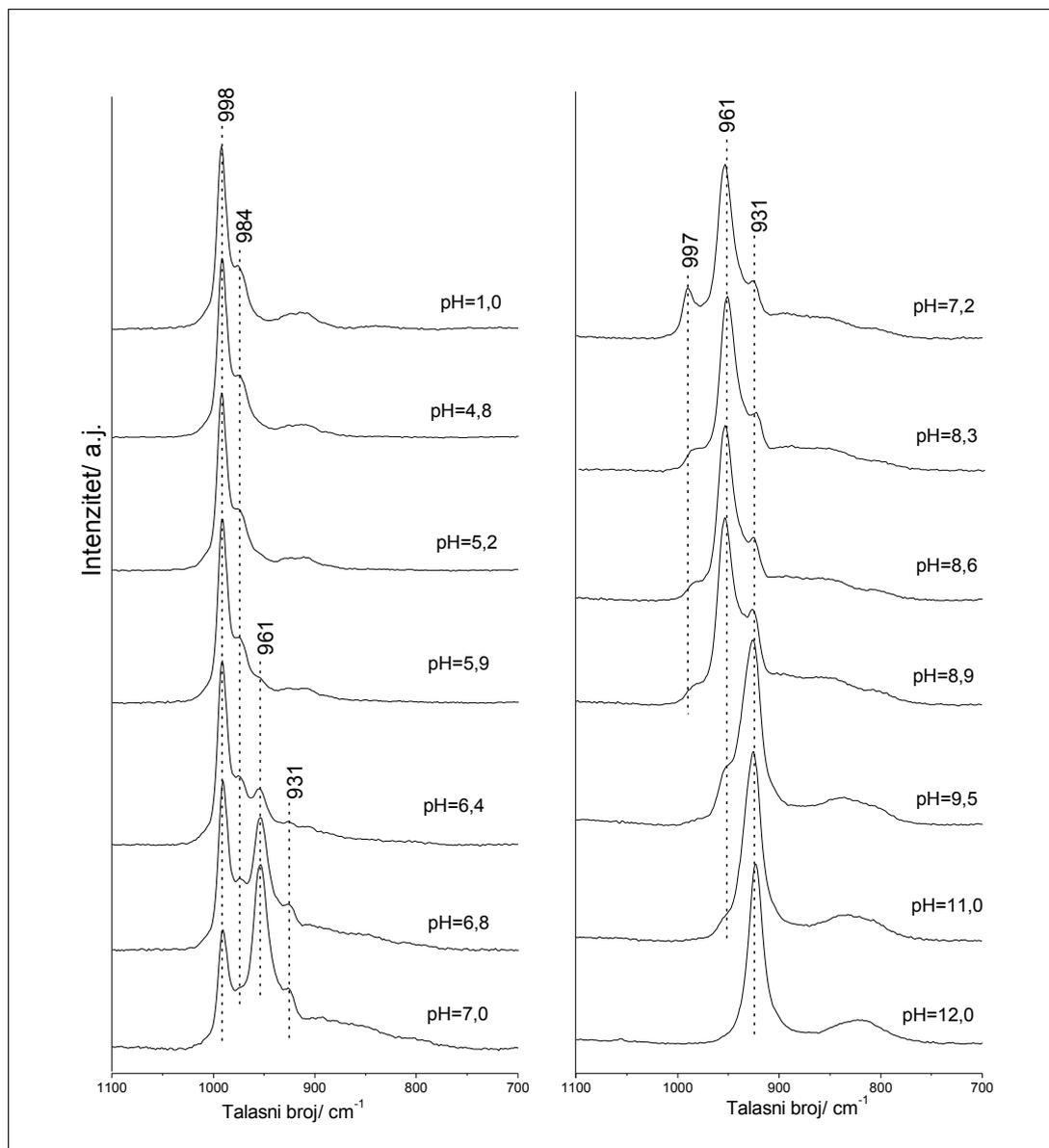
Slika 44. ULj spektri vodenih rastvora WSiA početne koncentracije $2 \cdot 10^{-5} \text{ mol dm}^{-3}$ na različitim pH vrednostima

Ramanski spektri vodenog rastvora WSiA

Na slici 45. dati su ramanski spektri rastvora WSiA na različitim pH koje su postignute dodavanjem NaOH u osnovni rastvor, a u tabeli 38. su položaji i intenziteti traka.

Na pH = 1,0 se uočavaju: jaka traka na 998 cm^{-1} ($\nu_s (M=O_d)$), srednja na 984 ($\nu_{as} (M=O_d)$) i dve slabe trake na 936 ($\nu_s (Si=O_d)$) i na 916 ($\nu_{as} (M-O_b-M)$) cm^{-1} , karakteristične za KA [22, 107]. Ovaj anjon prema ramanskim spektrima ostaje u rastvorima kao jedini silikovolframata sve do pH = 5,9. Pojava trake na oko 961 cm^{-1} pri pH = 6,4 ukazuje na početak hidrolize KA. Za monolakunarni anjon u rastvorima je karakteristična jaka traka na oko 960 cm^{-1} , koja se javlja uz slabiju traku na 995 cm^{-1} [110, 130] koja postoji i u spektru KA, zbog čega je nemoguće samo na osnovu ramanskih spektara utvrditi da li je prisutan monolakunarni KA ili smeša monolakunarnog i KA.

Porast pH vrednosti dovodi do porasta intenziteta trake na 961 cm^{-1} , a smanjenja intenziteta trake na 998 cm^{-1} , što ukazuje da je u alkalnoj sredini dominantan lakunarni oblik nastao degradacijom KA. Od pH = 8,9 u rastvorima se javljaju veće količine volframata, što se vidi iz porasta intenziteta trake na 931 cm^{-1} koja je karakteristična za njih. Spektar na pH = 12,0 je identičan spektru rastvora natrijum volframata.



Slika 45. Ramanski spektri vodenih rastvora WSiA početne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ na različitim pH vrednostima

Prema ovim rezultatima, KA je potpuno očuvan u koncentrovanim vodenim rastvorima WSiA čak i u neutralnoj sredini, a volframosilikatna struktura je potpuno razorena tek u alkalnoj sredini pri $\text{pH} > 9,0$.

Tabela 38. Položaj maksimuma traka u ramanskim spektrima vodenih rastvora WSiA početne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ pri različitim pH vrednostima

		pH													
		1,0	4,8	5,2	5,9	6,4	6,8	7,0	7,2	8,3	8,6	8,9	9,5	11,0	12,0
Talasni br. /cm ⁻¹ i inten. traka		998	998	998	998	998	997	997	997	997	997	997			
		vj	vj	vj	vj	vj	j	j	sr	sl	vsl	vsl			
		984	984	984	984	984	984								
		sr	sr	sr	sr	sr	sr								
					961	961	961	961	961	961	961	961	961	961	961
					sl	sr	vj	vj	vj	vj	vj	vj	r	r	
		936	936	936	936	931	931	931	931	931	931	931	931	931	931
		sl	sl	sl	sl	sl	sl	sl	sl	sl	sl	sr	vj	vj	vj
		916	916	916	916	911									
		sl	sl	sl	sl	sl									
							841	841	841	841	841				
							sl,š	sl,š	sl,š	sl,š	sl,š				
												829	829	829	
												sl	sl	sl	

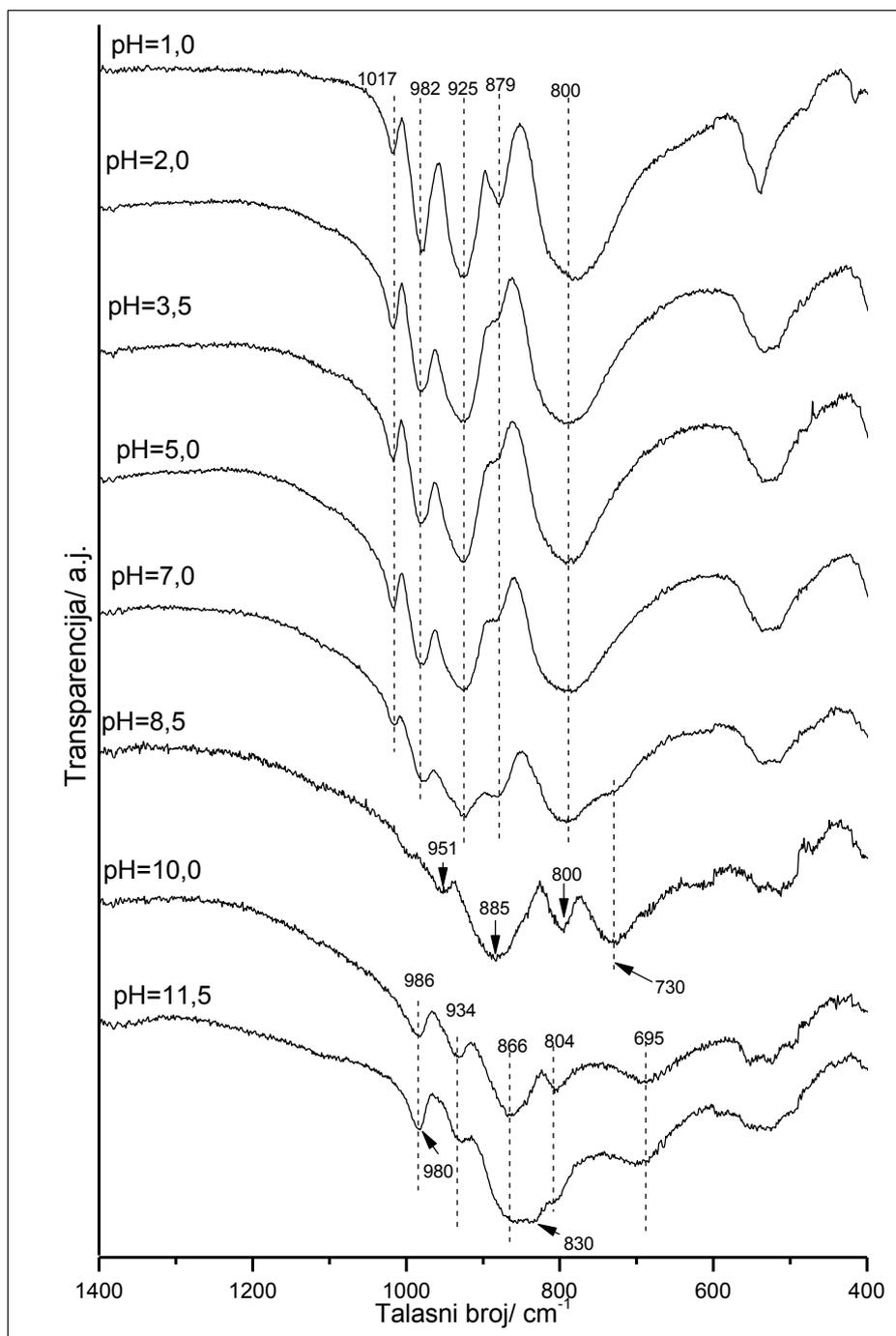
vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame

IC i Ramanski spektri suvih ostataka vodenih rastvora WSiA

Dodatne informacije o promenama strukture WSiA sa promenom kiselosti u koncentrovanim rastvorima mogu se dobiti uparavanjem rastvora kiseline različitih pH vrednosti i snimanjem njihovih IC i ramanskih spektara.

Na slici 46. su dati IC spektri suvih ostataka za rastvore WSiA različitih pH u oblasti karakterističnih traka za KA, dok su u tabeli 39. prikazani položaji i intenziteti traka.

Može se zapaziti da spektar suvog ostatka rastvora na pH = 1,0, odgovara spektru čvrste WSiA sa karakterističnim trakama za KA na 1017, 982 ($\nu_{as}(M=O_d)$), 925 ($\nu_{as}(Si-O_a)$), 879 ($\nu_{as}(M-O_b-M)$), 800 ($\nu_{as}(M-O_c-M)$) i 538 cm⁻¹ ($\delta_{as}(O_aPO_a)$) [22], te da su sve ove trake prisutne u spektrima do pH = 7,0, kada se javljaju male promene, u vidu slabljenja intenziteta traka i pojave slabe trake na 730 cm⁻¹. Međutim, u alkalnim rastvorima dolazi do promena u spektrima. Na pH = 8,5 javljaju se trake na 951, 885, 870, koje odgovaraju $\nu_{as}(M=O_d)$, $\nu_{as}(Si-O_a)$ i $\nu_{as}(M-O_b-M)$ vibraciji, respektivno i trake $\nu_{as}(M-O_c-M)$ vibracije na 800 i 730 cm⁻¹ u monolakunarnom SiW₁₁O₃₉⁸⁻ anjonu [105, 130].



Slika 46. IC spektri suvih ostataka rastvora WSiA početne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ na različitim pH vrednostima

Od pH 8,5 do pH 10 dolazi do novih promena u spektru i pojave traka na 896, 934, 866, 804 i 695 cm^{-1} , koje se mogu pripisati vibracijama u trolakunarnom $\text{SiW}_9\text{O}_{39}^{10-}$ anjonu [136]. Sve ove trake ostaju u spektru i na pH = 11,5, ali se javlja i

traka volframata na oko 830 cm^{-1} , a raste intenzitet trake na oko 980 cm^{-1} , usled doprinosa vibracije slobodnog silikata¹³.

Tabela 39. Talasni brojevi i intenziteti traka u IC spektrima suvih ostataka rastvora WSiA početne koncentracije $5 \cdot 10^{-2}\text{ mol dm}^{-3}$ na različitim pH vrednostima

	pH							
	1,0	2,0	3,5	5,0	7,0	8,5	10,0	11,5
Talasni brojevi / cm^{-1} i intenziteti traka	1017 sl	1017 sr	1016 sr	1016 sr	1018 sl			
	982 j	980 j	980 j	980 j	980 sl		986 sl	983 sl
					951 sl,š	951sl		
	925 vj	924 vj	926 vj	925 vj	923 sr		934 sl	927 r
	879 sl	880 r	880 r	880 r	880 sl	885 j,š		
						870 r	866 j,š	860 j,š
								830 r
	800 vj,š	800 vj,š	800 vj,š	800 vj,š	800 vj,š	795 sr	804 sl	
					730 sl,š	730 j,š		
	538 sr	535 sr,š	535 sr,š	535 sr,š	535 sr,š	530 sr,š	695 sl,š	700 sl,š
	373 sr	383 sr	380 sr	380 sr	375 sr		530 sr,š	530 sl,š
						360 sl	365 sl	365 sl
334 sr	335 sl	335 sl	335 sl	335 sl		325 sl	324 sl	
							321 sl	

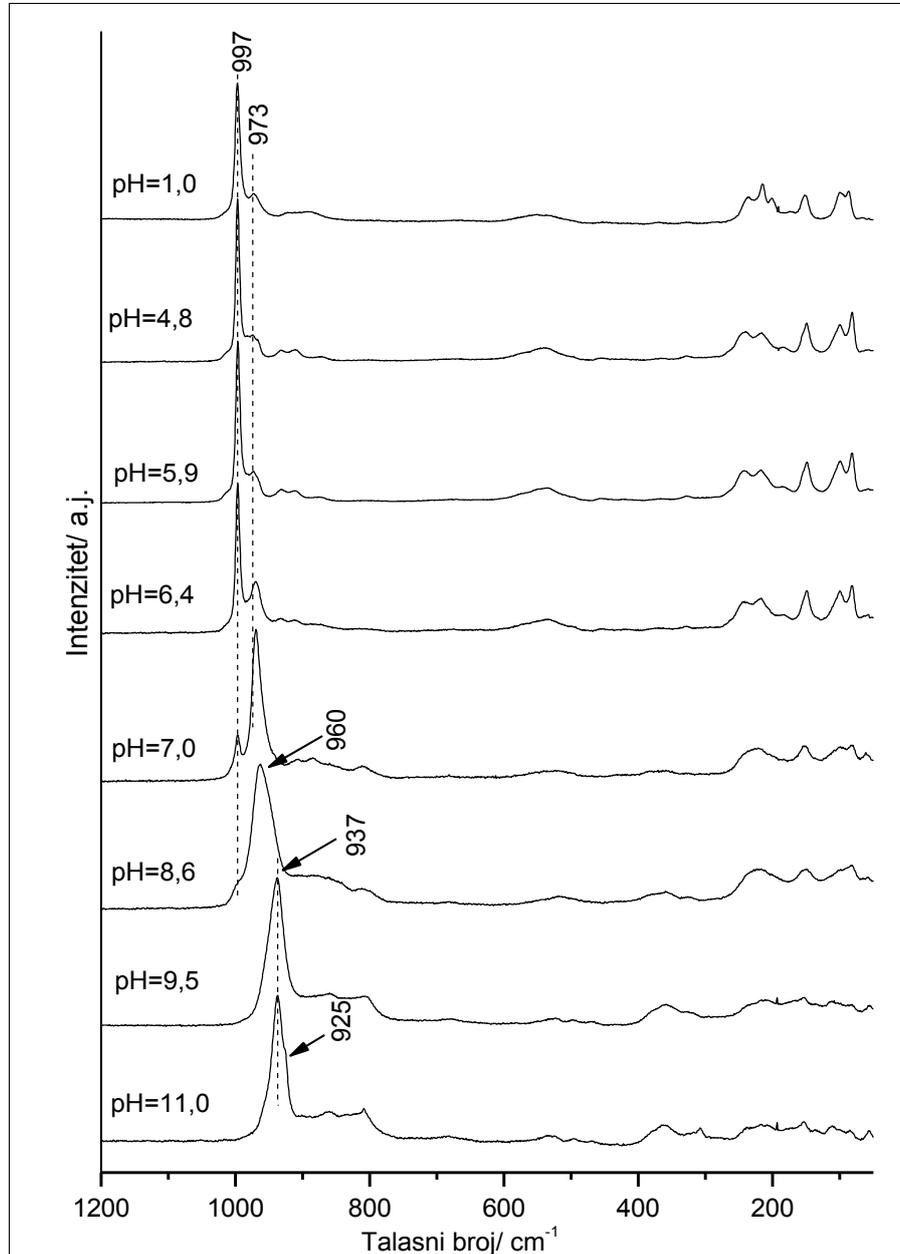
vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame

Ramanski spektri dati na slici 47. i tabeli 40. potvrđuju rezultate dobijene na osnovu IC spektara. Spektri koji se dobijaju za suve ostatke rastvora do $\text{pH} = 6,4$ su vrlo slični, sa najintenzivnijim trakama na $997 (\nu_s (M=O_d))$, $973 (\nu_{as} (M=O_d))$ i $214 (\nu_s (W-O_a))\text{ cm}^{-1}$. Male razlike koje se javljaju u spektrima na niskim talasnim brojevima potiču od zamene katjona, odnosno građenja rastvorne soli $\text{Na}_x\text{H}_{4-x}\text{SiW}_{12}\text{O}_{40}$ usled dodavanja NaOH. Prema spektrima rastvora pri ovoj pH vrednosti prisutan je i lakunarni KA, međutim u spektrima osušenih uzoraka možemo videti samo trake KA, što ukazuje da dolazi do regeneracije KA pri uparavanju do određene pH.

Trake karakteristične za KA su prisutne do $\text{pH} = 7,0$, ali dolazi do promene odnosa intenziteta traka na 997 i 974 cm^{-1} . Za čvrstu so sa monolakunarnom *Keggin*-ovom strukturom karakteristične su trake na 996 i 973 cm^{-1} [110], isto kao i u KA, ali je traka na 973 cm^{-1} kod monolakunarnog anjona najintenzivnija u spektru. Ove trake su prisutne u spektrima do $\text{pH} = 8,6$, sa tim da je na ovoj pH traka vrlo široka sa

¹³ Table IX, *IRSCOT, IR structural correlation tables and data cards*, Heyden & Son Limited

maksimumom na oko 960 cm^{-1} što ukazuje na prisustvo smeše monolakunarnog i (prema IC spektrima) trolakunarnog KA.



Slika 47. Ramanski spektri suvih ostataka rastvora WSiA početne koncentracije $5 \cdot 10^{-2}\text{ mol dm}^{-3}$ na različitim pH vrednostima

Spektri na pH=9,5 i 11,0 su slični, sa najintenzivnijom trakom na 937 cm^{-1} , ali se na pH=11,0 javlja i traka volframata (kao rame) na 925 cm^{-1} . U literaturi nema

podataka za ramanske spektre trolakunarnog $\text{SiW}_9\text{O}_{39}^{10-}$, ali se u skladu sa IC spektrima traka na 937 cm^{-1} može pripisati vibraciji u ovom anjonu.

Tabela 40. Talasni brojevi i intenziteti traka u ramanskim spektrima suvih ostataka rastvora WSiA početne koncentracije $5 \cdot 10^{-2}\text{ mol dm}^{-3}$ na različitim pH vrednostima

	pH							
	1,0	4,8	5,9	6,4	7,0	8,6	9,5	11,0
Talasni brojevi / cm^{-1} i intenziteti traka	997 vj	997 vj	997 vj	997 vj	997 sr	995 r		
	973 sr	974 sr 931 sl	974 sr 931 sl	974 j 931 sl	970 vj	960 vj,š		937 vj 925 r
	922 sl							
	891 sl	910 sl	910 sl	910 sl	908 sl 885 sl			
		870 sl	870 sl	870 sl		877 sl,š 812 sl	861 sr 808 sr	861 sr 808 sr
							682 sl	682 sl
	551 sl,š	541 sl,š	541 sl,š	541 sl,š	531 sl, š	514 sl	521 sl	521 sl
							500 sl	500 sl
							466 sl	466 sl
							360 sr	360 sr
							324 sr	308 sr
	235 sl	241 sr	241 sr	241 sr				
	214 sr	217 sr	217 sr	217 sr	228 sr,š	228 sr,š	218 sl	218 sl
	201 sl							
		185 sl	185 sl	185 sl				
	151 sr	150 sr	150 sr	150 sr	154 sr	154 sr	152 sl	152 sl
	100 sr	100 sr	100 sr	100 sr	99 sr	99 sr	110 sl	110 sl
87 sr	83 sr	83 sr	83 sr	83 sr	83 sr	88 sl	88 sl	

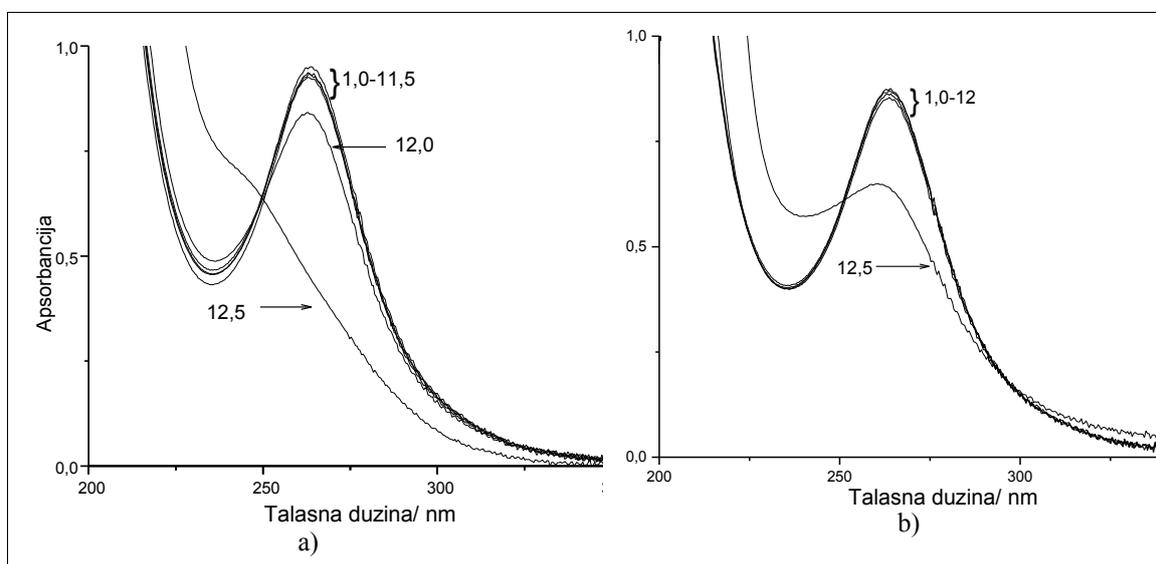
vj-vrlo jaka, j-jaka, sr-srednja, sl-slaba, vs-vrlo slaba, š-široka, r-rame

Prema svim ovim rezultatima može se zaključiti da su vodeni rastvori WSiA hidrolitički stabilniji od rastvora ostale dve ispitivane kiseline. Kiselina postoji u obliku KA pri $\text{pH} < 7,0$. U neutralnoj sredini je prisutna smeša KA i monolakunarnog KA. U oblasti pH od 7,0 do 8,9 u rastvoru je prisutan monolakunarni KA. Pri $\text{pH} > 8,9$ nastaje trolakunarni oblik koji je prisutan čak i na $\text{pH} = 11,0$.

4.3.2. Metanol/vodeni rastvori 12-volframsilicijumove kiseline

ULj spektri metanol/vodenih rastvora WSiA

ULj spektri metanol/vodenih rastvora WSiA su snimljeni za rastvore istih koncentracija i na isti način podešenih pH vrednosti, kao i u prethodnim eksperimentima. Na slici 48. prikazani su spektri WSiA u rastvaraču sa polaznom koncentracijom metanola 50 % i 100 %. Sa spektara se vidi da se povećanjem udela metanola razblaženi rastvori koji su i u vodenom rastvoru relativno stabilni, dodatno stabilišu, tako da je u čistom metanolu KA stabilan sve do pH = 12,0.

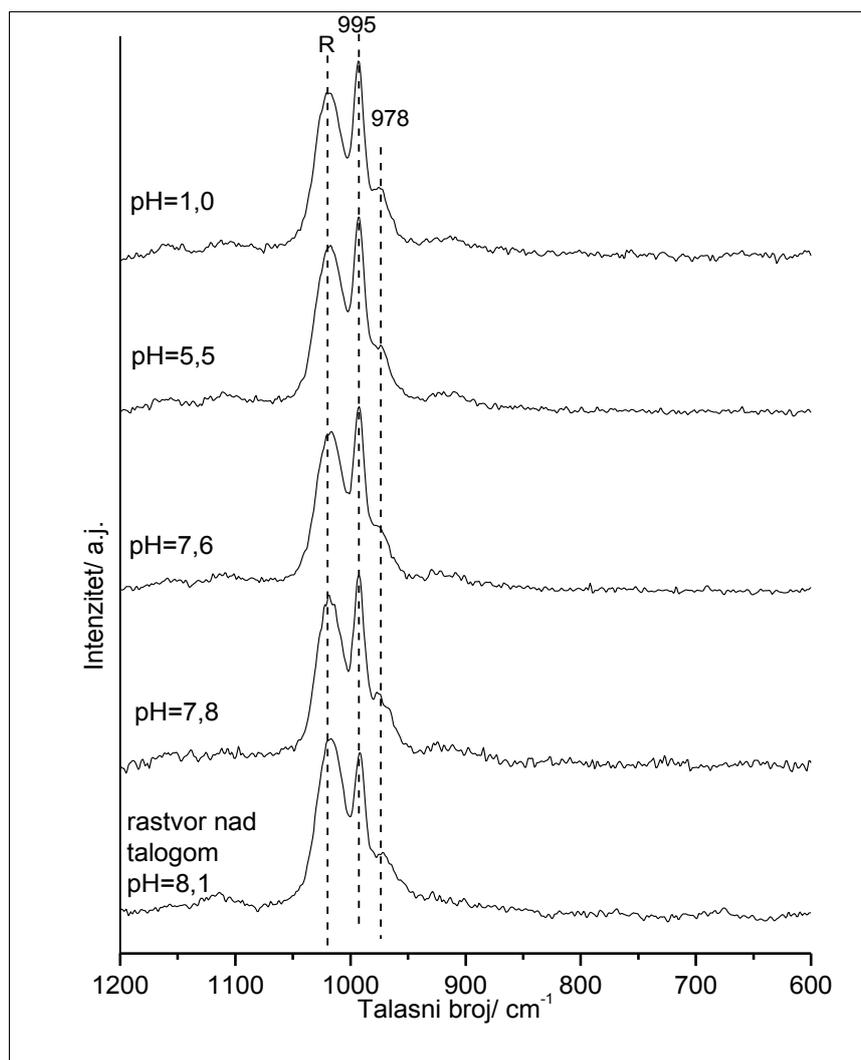


Slika 48. ULj spektri rastvora WSiA početne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa polaznim udelom metanola a) 50 %; b) 100 %

Ramanski spektri metanol/vodenih rastvora WSiA

Na slici 49. dati su ramanski spektri rastvora WSiA rastvorene u 50 % metanolu na različitim pH. Sa spektara je očigledno da se Keggin-ova struktura u rastvoru zadržava sve do pH = 8,1 kada započinje taloženje.

Prema tome, dodatak metanola dovodi do očekivane stabilizacije KA u koncentrovanim rastvorima WSiA, tako da je do taloženja pri pH > 8,0 ostaje potpuno očuvan.

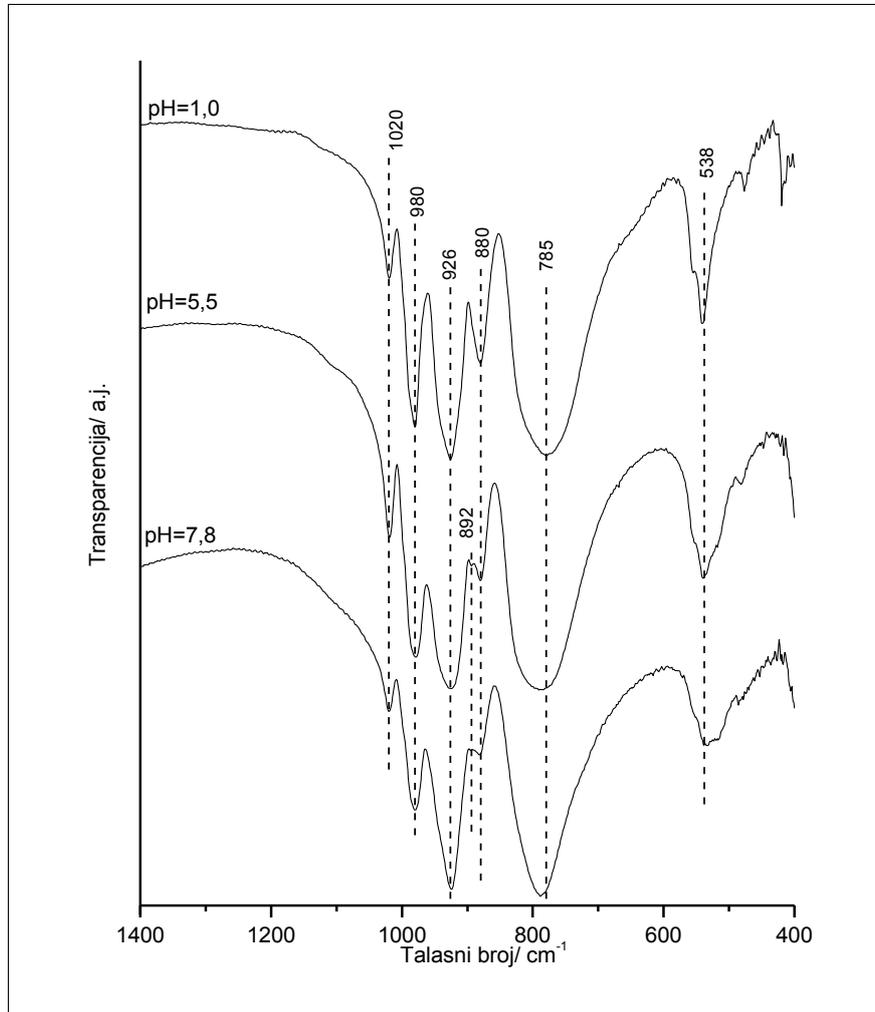


Slika 49. Ramanski spektri rastvora WSiA početne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa početnom koncentracijom metanola 50 %, na različitim pH vrednostima. R-traka rastvarača

IC i Ramanski spektri suvih ostataka metanol/vodenih rastvora WSiA

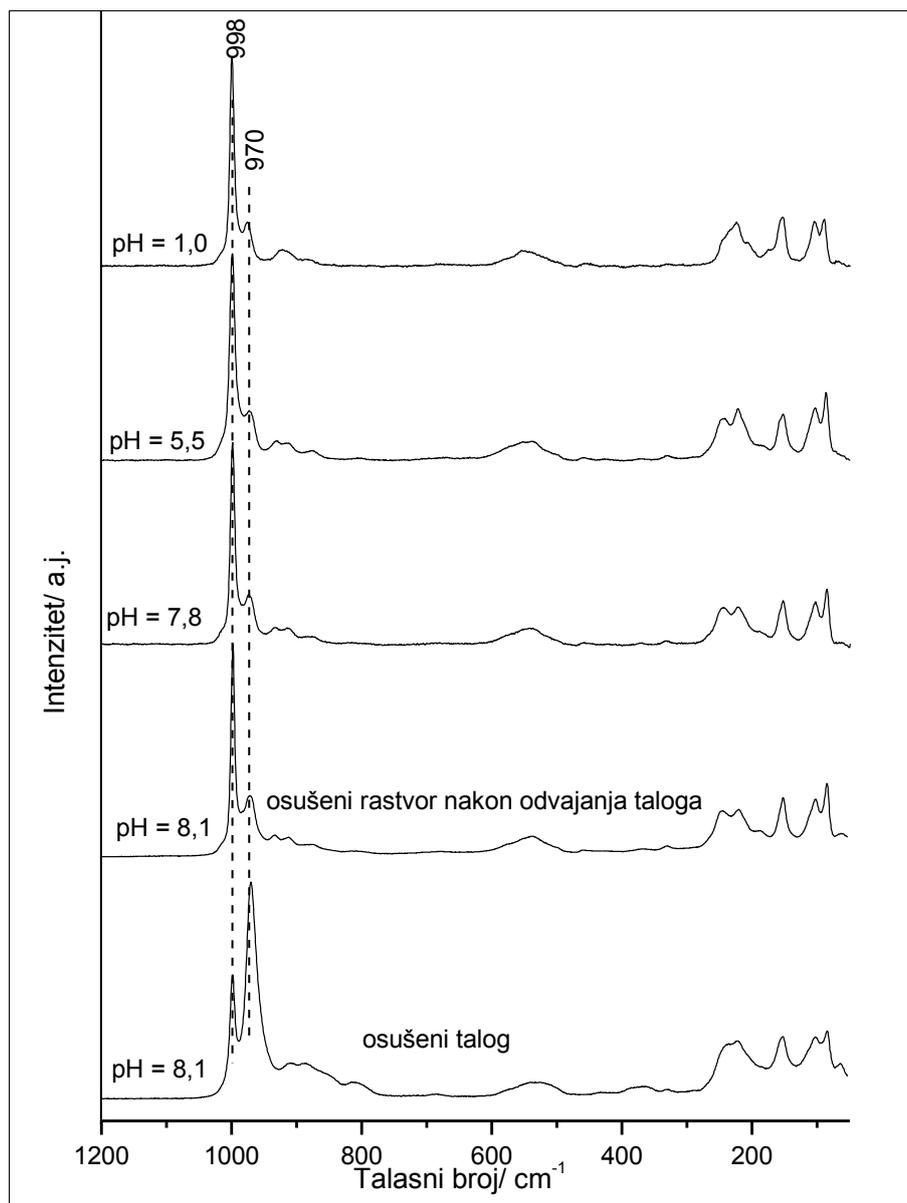
Sa slike 50. na kojoj su dati spektri suvih ostataka može se zapaziti da spektar na $\text{pH} = 1,0$ odgovara spektru čvrste WSiA sa karakterističnim trakama za KA na 1020, 980 ($\nu_{as} (M=O_d)$), 926 ($\nu_{as} (Si-O_a)$), 880 ($\nu_{as} (M-O_b-M)$), 785 ($\nu_{as} (M-O_c-M)$) i 538 cm^{-1} ($\delta_{as} (O_aPO_w)$) [104]. Spektri na $\text{pH} = 5,5$ i $7,8$ su slični spektru na $\text{pH}=1$, ali dolazi do pojave nove trake na 982 cm^{-1} . Prema Rocchiccioli-Deltcheff i saradnicima [107], zamena vodonika sa alkalnim metalom u $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ dovodi do povećanja talasnog

broja ν_{as} (*M-O_b-M*) vibracije sa 880 na 894 cm^{-1} . Prema tome, može se zaključiti da je u uparenom rastvoru pored WSiA bila i so $\text{Na}_4\text{SiW}_{12}\text{O}_{40}$, nastala usled dodatka NaOH.



Slika 50. IC spektri suvih ostataka rastvora WSiA početne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa početnom koncentracijom metanola 50 %, na različitim pH vrednostima

Ovo potvrđuju i ramanski spektri na ovim pH vrednostima dati na slici 51., jer su u svim spektrima prisutne trake karakteristične za KA na 998 i 970 cm^{-1} . U spektru taloga dolazi do porasta intenziteta trake na 970 cm^{-1} , koja je karakteristična za monolakunarni KA. Očigledno je da je $\text{Na}_8\text{SiW}_{11}\text{O}_{39}$ manje rastvoran od $\text{Na}_4\text{SiW}_{12}\text{O}_{40}$ u smeši metanol/voda i da se zbog toga izdvaja u vidu taloga.



Slika 51. Ramanski spektri suvih ostataka rastvora WSiA početne koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ u rastvaraču sa početnom koncentracijom metanola 50 %, na različitim pH vrednostima

Prema tome, rastvaranje WSiA u metanol/vodenom rastvaraču dovodi do toga da KA ostaje očuvan i u slabo alkalnoj sredini do pH = 8,1. U tabeli 41. sumirane su karakteristike rastvora WSiA u vodi i 50 % metanolu.

Tabela 41. Karakteristike rastvora WSiA u vodi i 50 % metanolu

Koncentracija WSiA /mol dm^{-3}	$2 \cdot 10^{-5}$			$5 \cdot 10^{-2}$	
Udeo metanola/ (v/v)%	0	50	100	0	50
Prisustvo KA do pH	8,5	11,5	12,0	6,4	7,8
Stvaranje taloga pri pH					8,1
Sastav taloga	Nema taloga				$\text{Na}_8\text{SiW}_{11}\text{O}_{39}$

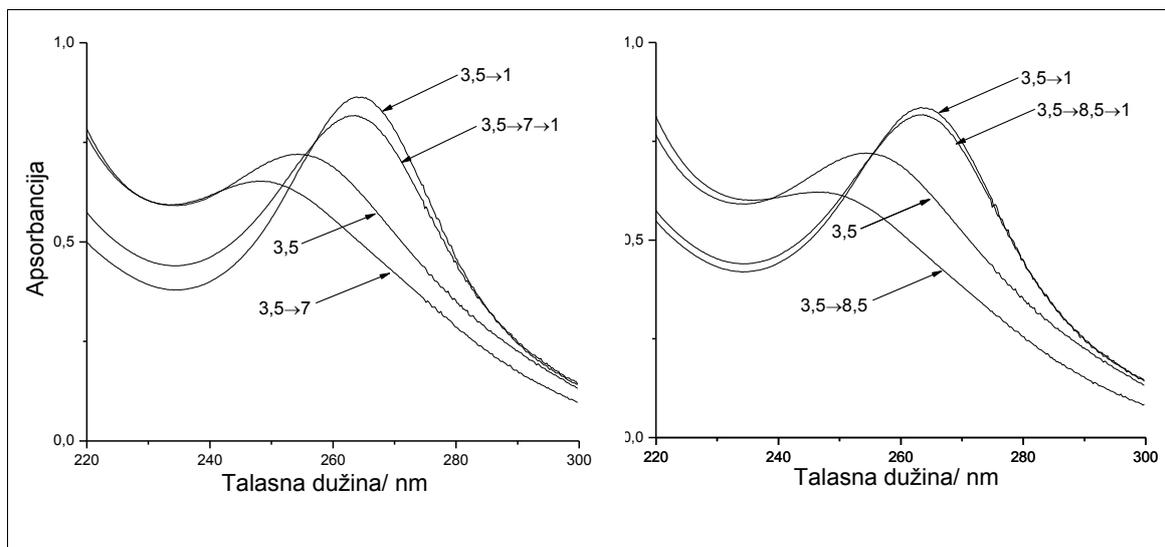
4.4. REVERZIBILNOST RAZLAGANJA KEGGIN-OVOG ANJONA U VODENIM RASTVORIMA

Identifikacija vrsta prisutnih u rastvorima WPA je iskorišćena za praćenje reverzibilnosti procesa dekompozicije sa promenom kiselosti rastvora. Dodavanjem NaOH u rastvor WPA čiji je pH zavisno od koncentracije kiseline podešen sa HCl na pH = 1,0 ($2 \cdot 10^{-5}$ mol dm^{-3}) ili je već bio 1,0 ($5 \cdot 10^{-2}$ mol dm^{-3}), pH je promenjena od pH = 1,0 do pH 7,0 i 8,5, a onda dodavanjem HCl vraćena na pH = 1,0.

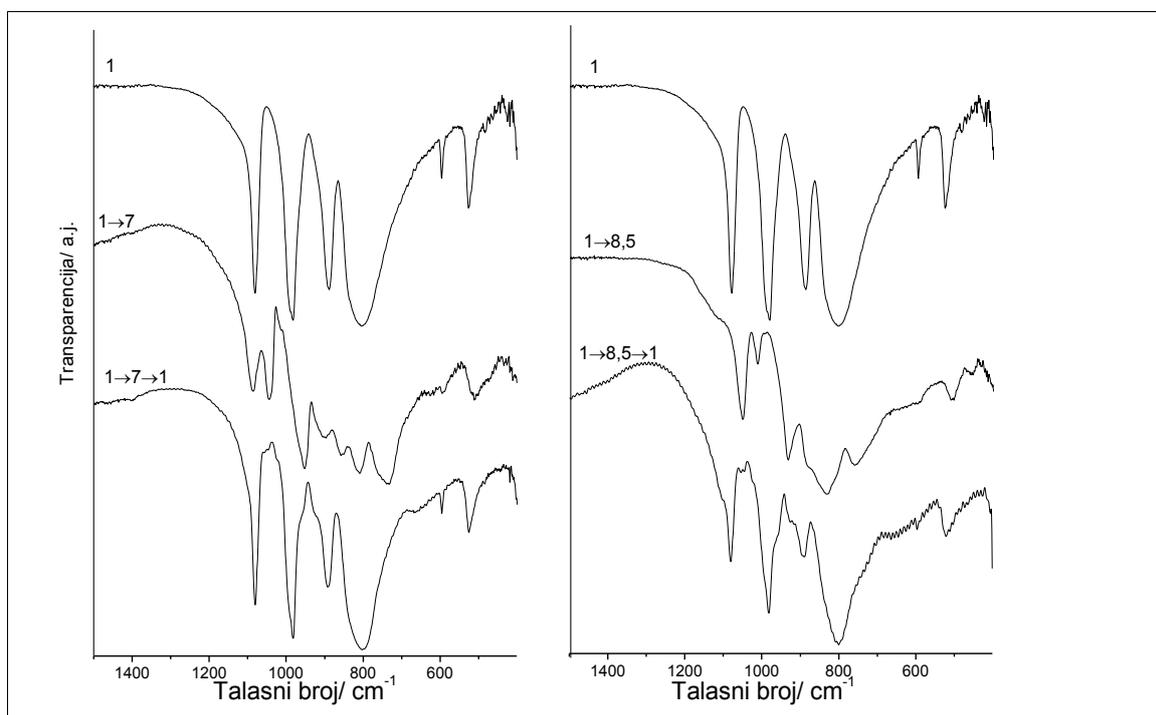
Polazni vodeni rastvor WPA koncentracije $2 \cdot 10^{-5}$ mol dm^{-3} čija je pH vrednost pH = 3,5 ima maksimum apsorpcione trake na 252,5 nm, a kada mu se doda HCl do pH = 1,0 maksimum se pomera na položaj karakterističan za KA (263 nm), kao što je pokazano u poglavlju 4.1.1. Na slici 52. upoređeni su ULj spektri vodenih rastvora, kod kojih je pH vrednost menjana od polazne do pH = 1,0, sa spektrima kod kojih je dodavanjem NaOH najpre postignuta pH vrednost 7,0 ili 8,5, a zatim zakišeljavanjem sa HCl pH vrednost podešena na pH = 1,0. Uočava se pomeranje apsorpcione trake ka manjim talasnim dužinama sa porastom pH vrednosti rastvora, ali se vraćanjem pH na pH = 1,0 ova traka ponovo javlja na položaju koji je karakterističan za KA.

Na slici 53. je upoređen IC spektar suvog ostataka rastvora koncentracije $5 \cdot 10^{-2}$ mol dm^{-3} i pH = 1,0 sa spektrima kod kojih je pH vrednost promenjena od pH = 1,0 do pH = 7,0 ili 8,5, a onda dodavanjem HCl vraćena na pH = 1,0.

Sa slike se može zaključiti da se KA regeneriše gotovo potpuno kada se pH vrati sa 7,0 na 1,0 dok u slučaju pH = 8,5, reverzibilnost nije potpuna.

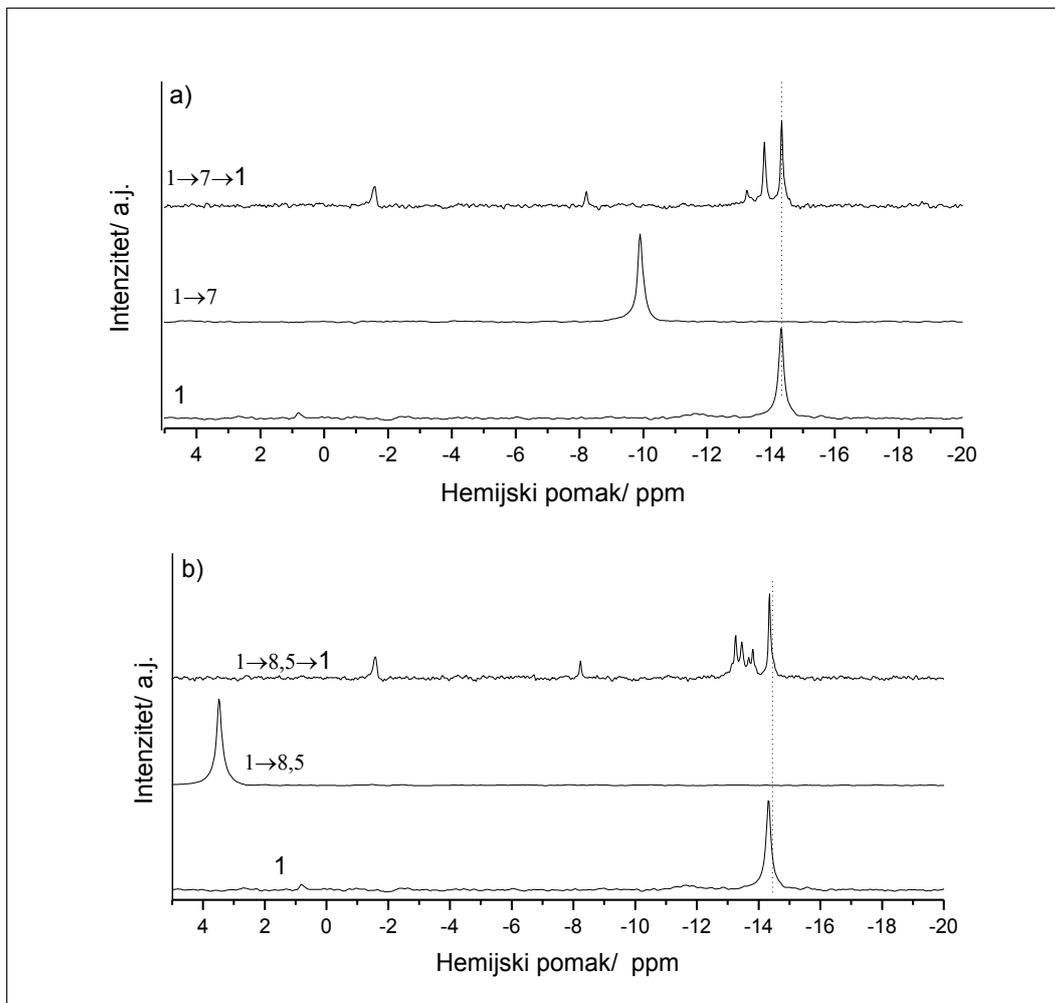


Slika 52. Praćenje reverzibilnosti razlaganja KA u rastvorima WPA pomoću ULj spektroskopije: levo promena pH vrednosti od 7,0 do 1,0; desno od 8,5 do 1,0



Slika 53. Praćenje reverzibilnosti razlaganja KA u rastvorima WPA pomoću IC spektroskopije: levo promena pH vrednosti od 7,0 do 1,0; desno od 8,5 do 1,0

^{31}P NMR spektri rastvora istih koncentracija i pH vrednosti menjanih na isti način kao i za rastvore koji su uparavani za snimanje IC spektara, dati su na slici 54. Pik na $-14,3$ ppm, karakterističan za KA je dominantan, ali se javljaju i drugi pikovi na oko -13 ppm koji ukazuju na prisustvo vrsta iz Dawson-ove serije.

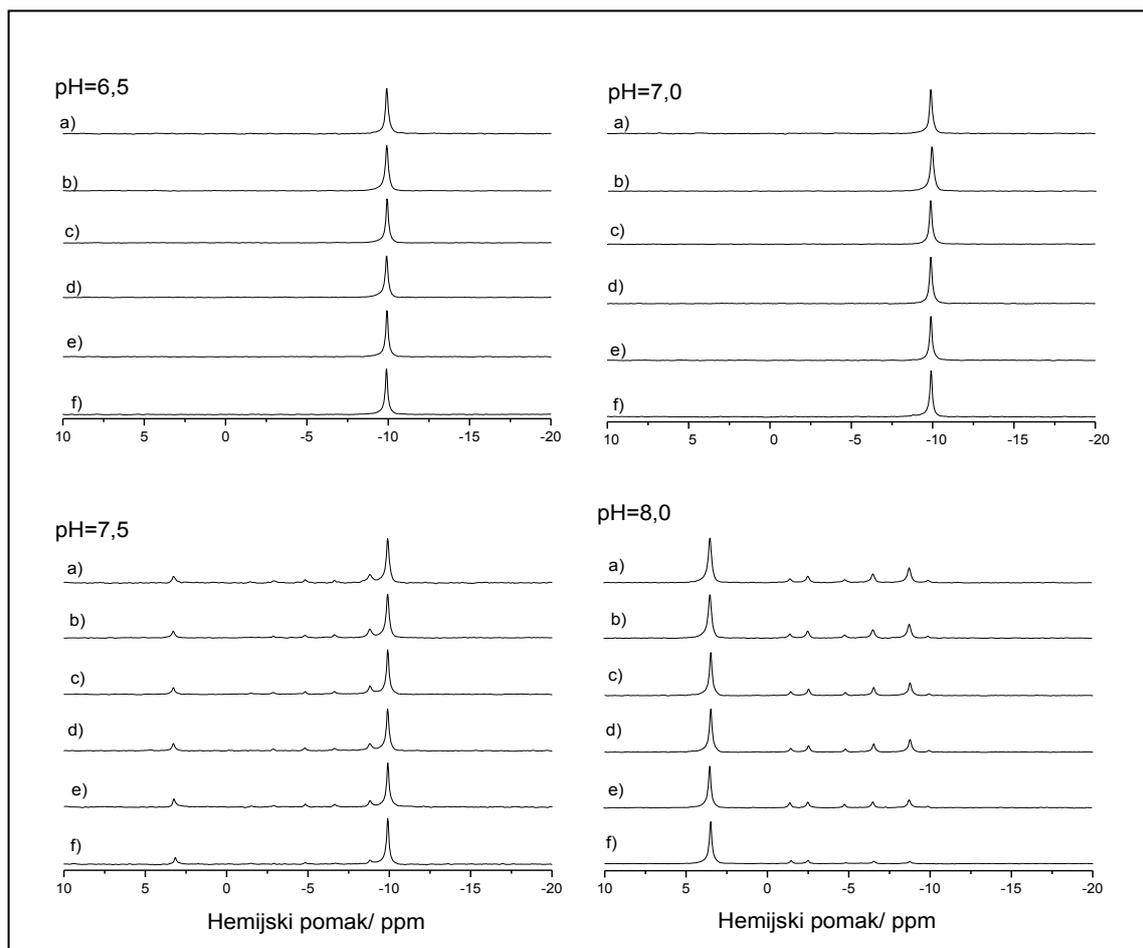


Slika 54. Praćenje reverzibilnosti razlaganja KA u rastvorima WPA pomoću ^{31}P NMR spektroskopije: a) promena pH vrednosti od 7,0 do 1,0; b) od 8,5 do 1,0

Prema tome, može se zaključiti da je pri višim koncentracijama reverzibilnost procesa dekompozicije nepotpuna.

4.5. VREMENSKA STABILNOST VODENIH RASTVORA WPA

Oblast pH vrednosti između 6,5 i 8,0 je veoma bitna za biomedicinska ispitivanja, tako da je korisno razmatrati uticaj vremena proteklog od momenta rastvaranja na stabilnost rastvora WPA pri ovim pH vrednostima.



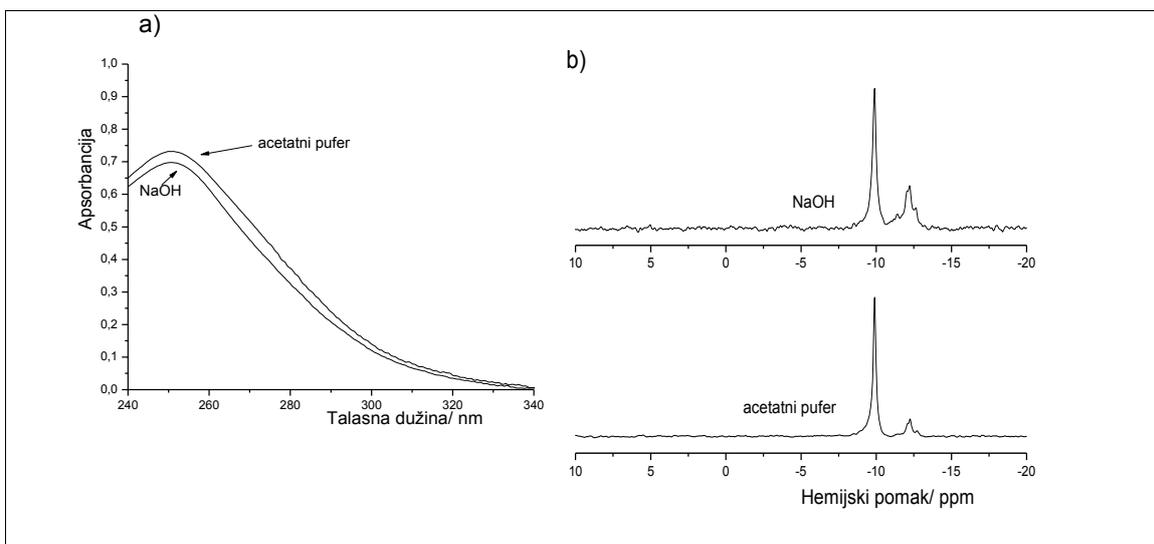
Slika 55. Praćenje stabilnosti rastvora WPA na pH = 6,5, 7,0, 7,5 i 8,0 u toku vremena pomoću ^{31}P NMR spektrometrije. Spektri su snimani: a) neposredno nakon pripreme rastvora, b) nakon 2 sata, c) 24 sata, d) 7 dana, e) 30 dana i f) godinu dana

Sa svih spektara se jasno uočava da su rastvori ovih pH vrednosti stabilni u toku vremena u kojem su praćeni.

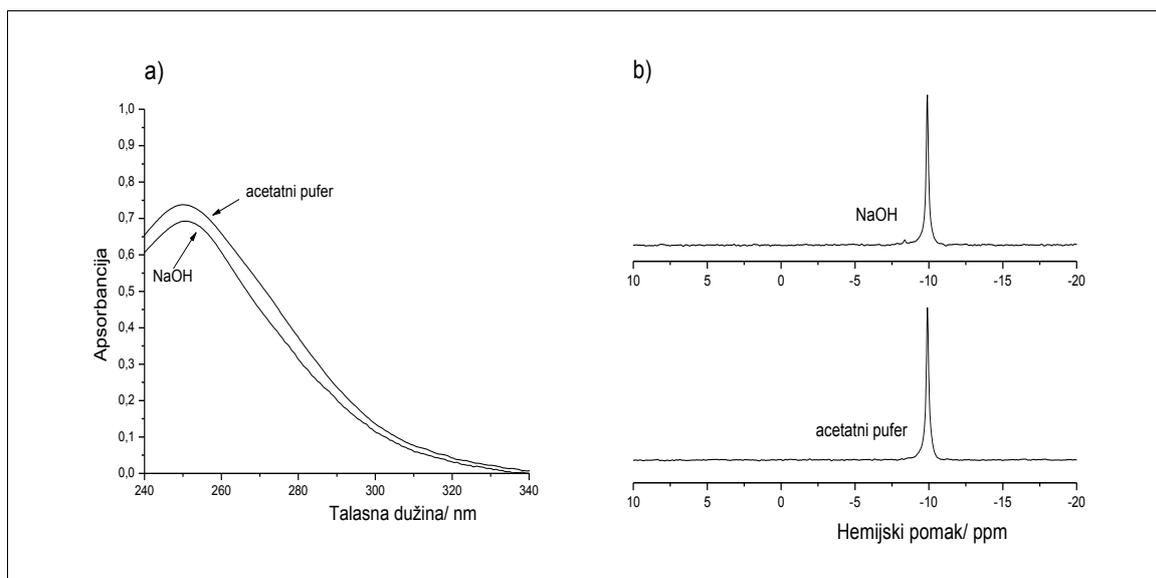
4.6. RASTVORI HETEROPOLI KISELINA U PUFERSKIM SISTEMIMA

U *in vitro* eksperimentima, u kojima se HPJ koriste kao biohemijski agensi, pH vrednosti se obično podešavaju upotrebom različitih pufera. U ovakvim vrstama ispitivanja za fiziološke pH vrednosti najčešće se upotrebljavaju TRIS (tris(hidroksimetil)aminometan, HCl) i fosfatni pufer. Za pH vrednosti niže od fizioloških koristi se acetatni pufer. Upotreba fosfatnog pufera u slučaju WPA nije pogodna, jer dolazi do njegove interakcije sa WPA, odnosno razgradnje KA.

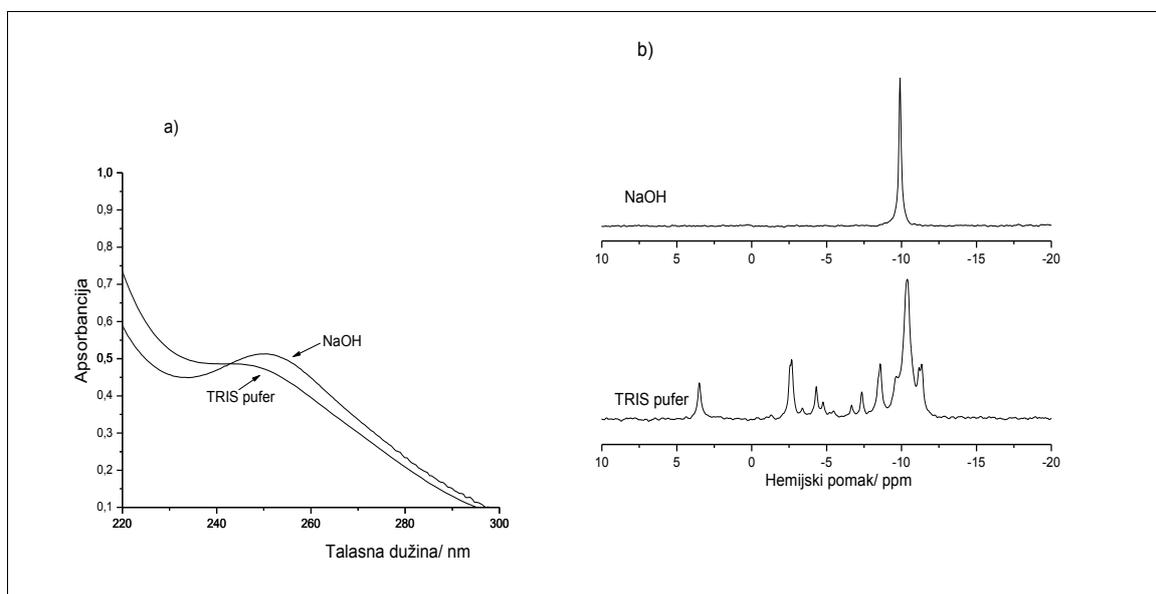
Na slici 56. i 57. dati su ULj i ^{31}P NMR spektri vodenih rastvora WPA puferovanih sa acetatnim, a na slici 58. sa TRIS puferom. Podešene pH vrednosti u slučaju acetatnog pufera su 3,5 i 5,0, a u slučaju TRIS pufera pH = 7,0. Spektri puferovanih rastvora su poređeni sa spektrima rastvora čije su pH vrednosti podešavane sa NaOH. Koncentracije rastvora su, kao i u do sada opisanim eksperimentima, u slučaju ULj spektara $2 \cdot 10^{-5} \text{ mol dm}^{-3}$, a kod ^{31}P NMR spektara $5 \cdot 10^{-2} \text{ mol dm}^{-3}$.



Slika 56. a) ULj spektri rastvora WPA koncentracije $2 \cdot 10^{-5} \text{ mol dm}^{-3}$, b) ^{31}P NMR spektri rastvora WPA koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ na pH = 3,5 u acetatnom puferu. Radi poređenja dati su i spektri rastvora iste kiseline čija je pH podešena dodavanjem NaOH



Slika 57. a) ULj spektri rastvora WPA koncentracije $2 \cdot 10^{-5} \text{ mol dm}^{-3}$, b) ^{31}P NMR spektri rastvora WPA koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ na $\text{pH} = 5,0$ u acetatnom puferu. Radi poređenja dati su i spektri rastvora iste kiseline čija je pH podešena dodavanjem NaOH



Slika 58. a) ULj spektri rastvora WPA koncentracije $2 \cdot 10^{-5} \text{ mol dm}^{-3}$, b) ^{31}P NMR spektri rastvora WPA koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ na $\text{pH} = 7,0$ u TRIS puferu. Radi poređenja dati su i spektri rastvora iste kiseline čija je pH podešena dodavanjem NaOH

Sa ovih slika može se uočiti da su u slučaju primene acetatnog pufera ULj i ^{31}P NMR spektri gotovo identični onima koji se dobijaju za rastvore čija je pH podešena dodavanjem NaOH. Prema tome, može se zaključiti da ne dolazi do reakcije WPA sa komponentama acetatnog pufera, odnosno da je njegova upotreba za podešavanje pH vrednosti pogodna.

Međutim, poređenjem ^{31}P NMR spektra rastvora WPA u TRIS puferu sa spektrom rastvora čija je pH podešena dodavanjem NaOH na istu pH vrednost, može se zaključiti da se u slučaju primene TRIS pufera, uz dominantan lakunarni KA, formiraju i drugi polivolframofosfati.

Dobijeni rezultati ukazuju da u biohemijskim primenama POM odabir pufera mora biti veoma pažljiv, jer može imati uticaj na biohemijski efekat i na njegovo tumačenje.

4.7. PRIMENA REZULTATA ISPITIVANJA STABILNOSTI HETEROPOLIKISELINA PRI FORMIRANJU PANI - WPA I U REAKCIJI INHIBICIJE Na^+/K^+ - ATPaze

4.7.1. Identifikacija volframfosfatnih struktura ugrađenih u PANI matriks pri oksidativnoj polimerizaciji anilina u prisustvu WPA

Polianilin (PANI) je poslednjih godina jedan od najinteresantnijih i najviše proučavanih provodnih polimera. Posедуje vrlo specifične osobine kao što su: električna provodljivost poluprovodničkog ili metalnog ranga, veliki broj oksidoredukcionih i kiselo-baznih stanja, kao i elektrohromizam.

Dopiranjem PANI provodljivost se može povećati od 10^{-10} - 10^{-7} Scm^{-1} , koliko je provodljivost nedopiranog PANI, koji je izolator, do provodljivosti većih od 10 Scm^{-1} , odnosno provodljivosti metalnog ranga. Dopiranje može biti protonsko i anjonsko. Pri hemijskoj i elektrohemijskoj polimerizaciji dopanti su najčešće kiseline, organske i neorganske.

Polimerne kiseline se takođe mogu ugraditi kao dopanti u provodne polimere u toku sinteze, na taj način što se monomer anilin rastvara u velikoj količini polikiseline, a zatim se vrši oksidativna polimerizacija anilina [137].

PANI se najčešće dobija oksidacijom anilina u kiseloj vodenoj sredini uz prisustvo APS (amonijum peroksidisulfata) kao oksidanta. Indukcioni period (temperatura reakcione smeše se ne menja), koji je tipičan za reakciju ovog tipa, je praćen egzotermnom polimerizacijom. Pokazano je da mnoga organska i neorganska jedinjenja ubrzavaju proces oksidacije, posebno skraćivanjem indukcionog perioda. Obrnut efekat, usporavanje oksidacije anilina, je zapaženo u slučaju kao što je dodatak 1,3-fenilendiamina. Međutim, Stejskal i saradnici [138] su našli da prisustvo volframata takođe produžava period indukcije u oksidaciji anilina. Prema tome, HPK igraju specifičnu ulogu u sintezi PANI, jer produžavaju indukcioni period nekoliko puta, čak i kada su dodate u veoma malim količinama. Ova činjenica može biti iskorišćena za poboljšavanje površinske polimerizacije anilina, jer je zapaženo da debljina PANI filma na površini uronjenoj u reakcionu smešu raste kada joj se dodaju volframati.

PANI kombinovani sa volframovim HPK se upotrebljavaju kao katalizatori u organskim reakcijama, kao jonski izmenjivači i provodni kompoziti. HPK mogu protonovati PANI. Pošto su HPK veoma dobri protonski provodnici koji se primenjuju u gorivim ćelijama, njihovo kombinovanje sa provodnim polimerima može biti od potencijalne koristi.

PANI-WPA može biti dobijen hemijskom ili elektrohemijском oksidativnom polimerizacijom anilina u prisustvu WPA, ili protonacijom PANI baze sa ovom kiselinom.

Sinteza PANI-WPA

G. Ćirić-Marjanović i saradnici su sintetisali mikro/nano strukturalni PANI, oksidativnom polimerizacijom anilina, bez nosača (external-template-free) u vodenom rastvoru WPA, uz korišćenje APS kao oksidanta. Oksidacija je počinjala u blago kiselom sredini sa $\text{pH} = 5,4 - 5,9$, zavisno od polaznog masenog odnosa WPA/anilin. U tabeli 42. su sumirani uslovi sinteze za sve sintetisane uzorke [139].

U toku oksidacije anilina sa APS, kada se molekuli anilina spajaju u polimerni lanac, atomi vodonika iz amino grupa anilina i iz *para*-pozicije benzenovog prstena se oslobađaju u vidu protona usled čega dolazi do porasta kiselosti reakcione smeše. Profil pH vrednosti snimljen tokom polimerizacije, slika 59., ukazuje na moguće strukturne promene u WPA. Za utvrđivanje oblika WPA u konačnom proizvodu iskorišćeni su ramanski i IC spektri PANI - WPA i rezultati koji su dobijeni u poglavlju 4.1. ove teze.

Tabela 42. Uslovi sinteze [139].

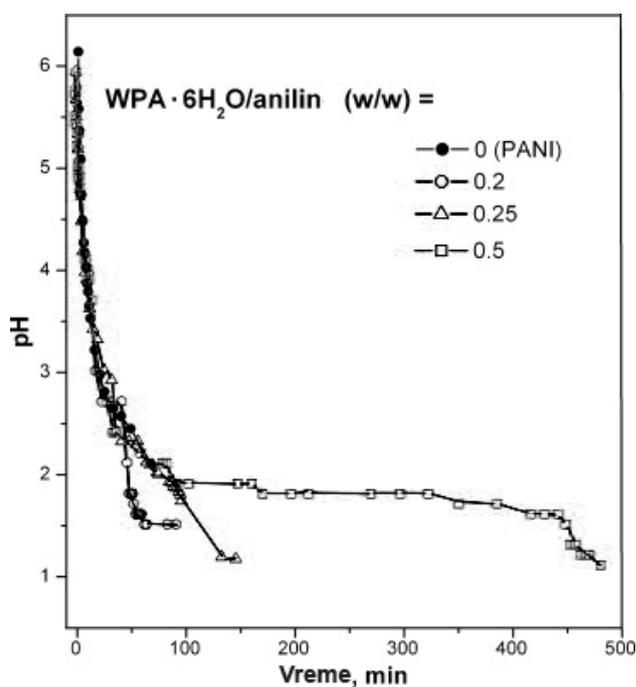
Polazni maseni odnos WPA: anilin	Koncentracija WPA [mol \cdot dm $^{-3}$]	Vreme polim. [h]	pH. rastvora monom ^a	Polazna pH ^b	Konačna pH
0	0	2	8,4	6,2	1,1
0,2	$6,2 \cdot 10^{-4}$	2	6,1	5,9	1,4
0,25	$7,8 \cdot 10^{-4}$	3	6,0	5,9	1,1
0,5	$1,6 \cdot 10^{-3}$	24	5,8	5,7	1,2
1	$3,1 \cdot 10^{-3}$	24	5,5	5,4	1,1

^a rastvor anilin/anilinijum 12-volframofosfata pre dodavanja APS;

^b pH vrednost merena neposredno po mešanju rastvora anilin/anilinijum WPA i APS

IC i ramanski spektri PANI-WPA

Na slici 60. su dati IC spektri PANI - WPA uzoraka sintetisanih pri različitim masenim odnosima WPA \cdot 6H $_2$ O/anilin, nanostrukturnog PANI - sulfat/hidrogensulfat sintetisanog bez dodatka WPA, WPA \cdot 6H $_2$ O i oligomernog intermedijera sintetisanog pri polaznom masenom odnosu WPA \cdot 6H $_2$ O/anilin = 0,5, izolovanog pri kraćem vremenu polimerizacije ($t_{pol} = 4$ h) u odnosu na polimer koji je sintetisan sa $t_{pol} = 24$ h. Trake karakteristične za PANI emeraldinsku so se javljaju u IC spektrima svih uzoraka oko 1571, 1495, 1304, 1246, i 1148 cm $^{-1}$.



Slika 59. Promena pH vrednosti u toku oksidacije anilina (0,1 M) sa APS (0,125 M) u vodi pri različitim polaznim masenim odnosima WPA/anilin

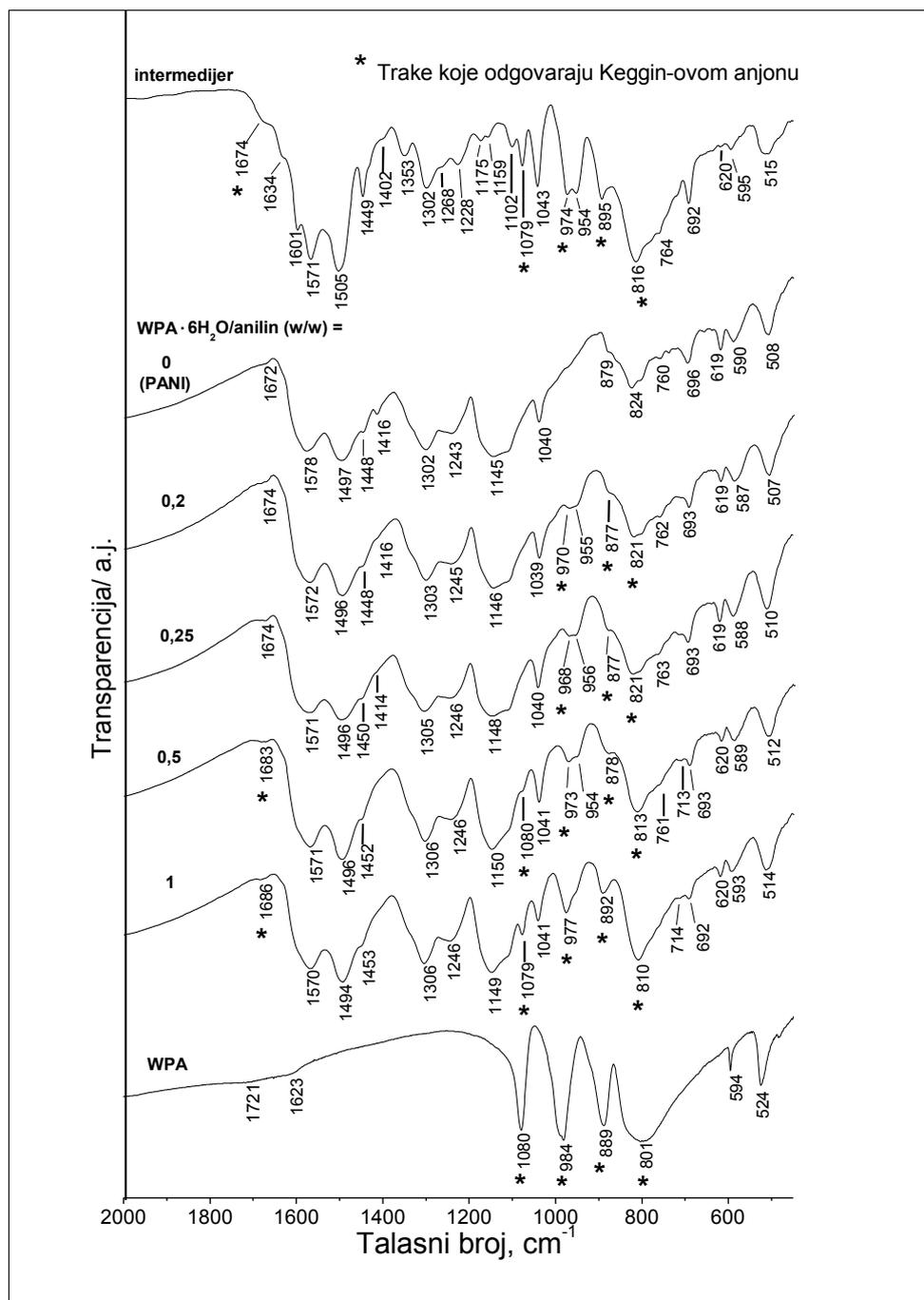
IC spektri potvrđuju da volframfosfatni anjon igra ulogu kontra jona u pozitivno naelektrisanom PANI matriksu. Traka karakteristična za $\nu_{as}(P-O_a)$ vibraciju u KA na 1080 cm^{-1} se javlja u spektrima svih uzoraka. Traka $\nu_{as}(W-O_b-W)$ vibracije oko 890 cm^{-1} se preklapa sa trakom $\gamma(C-H)$ vibracije 1,2,4-trisupstituiranog benzenovog prstena u razgranatoj PANI jedinici i moguće sa trakom hidrogensulfatnog jona. Sa druge strane, traka $\nu_{as}(W-O_c-W)$ vibracije na oko 810 cm^{-1} se meša sa $\gamma(C-H)$ vibracijom 1,4-disupstituiranog benzenovog prstena u linearnim PANI lancima.

Uz traku na oko 980 cm^{-1} , koja odgovara $\nu_{as}(W-O_d)$ vibraciji, javlja se rame na oko 955 cm^{-1} . Ova činjenica, prema rezultatima datim u poglavlju 4.1. ove teze ukazuje na prisustvo monolakunarnog *Keggin*-ovog i *Dawson*-ovog anjona koji se javljaju na $\text{pH} > 1$.

Kako je u polaznoj reakcionoj smeši koncentracija WPA varirala od $6 \cdot 10^{-4}$ do $3 \cdot 10^{-3}\text{ mol dm}^{-3}$, a pH se menjala od oko $\text{pH} = 6$ na početku procesa do pH oko 1, strukturni oblici WPA u toku reakcije polimerizacije se mogu posmatrati sa aspekta reverzibilnosti strukturnih promena WPA. Prema IC spektrima datim u poglavlju 4.4. KA se regeneriše gotovo potpuno kada se pH vrati sa $\text{pH} = 7$ na $\text{pH} = 1$, posebno u slučaju nižih koncentracija. Prema ovome, očekivano je da se u finalni materijal ugrađuje WPA uglavnom u obliku KA. Pored ovog anjona se u izvesnoj meri javljaju i druge volframofosfatne vrste, posebno pri polaznom masenom odnosu $\text{WPA} \cdot 6\text{H}_2\text{O}/\text{anilin} \leq 0,5$.

Trake koje odgovaraju KA u IC spektru oligomernog intermedijera¹⁴ na 1080 , 974 , 895 i 816 cm^{-1} imaju relativno veći intenzitet u poređenju sa odgovarajućim trakama u spektru PANI - WPA. Ovo je u saglasnosti sa značajno većim količinom W u intermedijeru, nego u finalnom PANI - WPA, što je utvrđeno ISP - OES (Induktivno spregnuta plazma - optička emisiona spektroskopija) merenjima [139]. Pored traka karakterističnih za KA u spektru intermedijera se javlja i traka na 954 cm^{-1} , koja postoji u spektrima monolakunarnog KA i DA. Pošto je pH na kraju sinteze 1,9, prema rezultatima u poglavlju 4.1.1. očekivano je prisustvo veće količine DA. Pored trake istežuće P-O vibracije na 1080 cm^{-1} koja se javlja u KA, javljaju se i trake na 1102 i 1043 cm^{-1} usled cepanja trake na 1080 cm^{-1} zbog prisustva monolakunarnog KA.

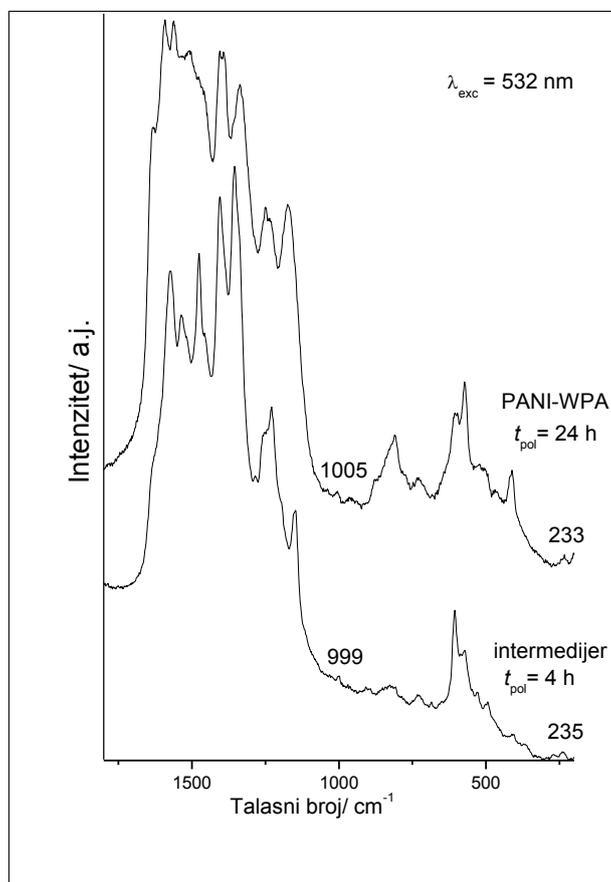
¹⁴ izolovanog u fazi reakcije pre stvaranja dugih lanaca PANI, nakon 4h



Slika 60. IC spektri PANI - WPA uzoraka sintetisanih pri različitim masenim odnosima WPA·6H₂O/anilin, nanostrukturnog PANI - sulfat/hidrogen sulfat, WPA·6H₂O i intermedijera

Na slici 61. su dati ramanski spektri intermedijera ($t_{\text{pol}} = 4$ h) i PANI - WPA ($t_{\text{pol}} = 24$ h) oba sintetisana sa polaznim masenim odnosom WPA·6H₂O/anilin = 0,5. Spektri su snimani korišćenjem veoma male snage lasera od 0,1 mW da bi se izbegla

degradacija uzorka. Detaljnu analizu ovih spektara dala je G. Ćirić-Marjanović sa saradnicima [139]. U spektru intermedijera uočavaju se trake volframofosfata na 999 i 235 cm^{-1} , a u spektru PANI - WPA na 1005 i 233 cm^{-1} .



Slika 61. Ramanski spektri intermedijera ($t_{pol} = 4$ h) i PANI - WPA ($t_{pol} = 24$ h) oba sintetisana sa polaznim masenim odnosom $\text{WPA} \cdot 6\text{H}_2\text{O}/\text{anilin} = 0,5$, $\lambda_{exc} = 532$ nm

Prema ramanskim spektrima datim u poglavlju 4.1.1., do $\text{pH} = 1,6$ najintenzivnija je traka na 1006 cm^{-1} , a na $\text{pH} = 2$ na 994 cm^{-1} . Kao što je rečeno, pH vrednost na kraju sinteze intermedijera je bila 1,9, a PANI - WPA 1,2, tako da su rezultati očekivani i potvrđuju da se u PANI - WPA, volframofosfat inkorporira uglavnom u obliku KA, dok u intermedijeru to nije slučaj.

4.7.2. Utvrđivanje aktivnog oblika 12-volframfosforne i 12-volframsilicijumove kiseline u reakciji inhibicije Na^+/K^+ -ATPaze

Na^+/K^+ -ATPaza pripada P-tipu ATPaza, koje koriste energiju adenozintrifosfata (ATP) za transport jona nasuprot elektrohemijuskog gradijenta. Na^+/K^+ -ATPaza je enzim u ćelijskoj membrani koji uspostavlja i održava visoku unutrašnju koncentraciju K^+ jona i nisku unutrašnju koncentraciju Na^+ jona, što je ključno za normalnu ćelijsku aktivnost većine životinjskih ćelija. Aktivnost ovih enzima je vrlo osetljiva na prisustvo nekih jona metala i organskih jedinjenja, posebno nekih lekova i pesticida [140, 141]. Novija istraživanja pokazuju da pored uloge u transportu jona, Na^+/K^+ -ATPaza interaguje sa susednim membranskim proteinima i tako učestvuje u prenosu signala do intracelularnih organela [142].

M. Čolović i saradnice su ispitivale *in vitro* efekat različitih koncentracija (u opsegu od 10^{-8} do 10^{-3} mol dm^{-3}) WSiA i WPA na aktivnost Na^+/K^+ -ATPaza i E-NTPDaza¹⁵ korišćenjem sinaptičke plazma membrane (SPM) pacova kao model sistema. Kao referentni sistem uzeta je komercijalno dostupna Na^+/K^+ -ATPaza izolovana iz cerebralnog korteksa (kore velikog mozga) svinje. Na^+/K^+ -ATPaza i E-NTPDaza su izabrane zbog njihove uloge u normalnom funkcionisanju većine ćelija eukariotskih organizama, kao i u razvoju različitih tumora [143], a sa druge strane poznatog uticaja POM na nukleotid-zavisne enzime [144], kao i njihove antitumorske aktivnosti [79-82]. Specifična aktivnost enzima praćena je pomoću ULj/Vid spektroskopije, merenjem koncentracija neorganskog fosfata Pi oslobođenog enzimskom hidrolizom ATP-a. Za obe ispitivane kiseline dokazano je da inhibiraju aktivnost Na^+/K^+ -ATPaze na koncentraciono zavisnan način. Takođe je pokazano da je sposobnost inhibicije enzima ispitivanih HPK i Na_2WO_4 sasvim različita. Pri koncentraciji $1 \cdot 10^{-5}$ mol dm^{-3} HPK inhibiraju i SPM i komercijalnu Na^+/K^+ -ATPaze više od 75 %, dok je aktivnost volframata pri istoj koncentraciji zanemariva. Takođe, ispitivane koncentracije WPA i WSiA pokazuju sličan inhibicioni potencijal prema ekto-ATPazama, dok 1mM Na_2WO_4 ne pokazuje takvu aktivnost [145].

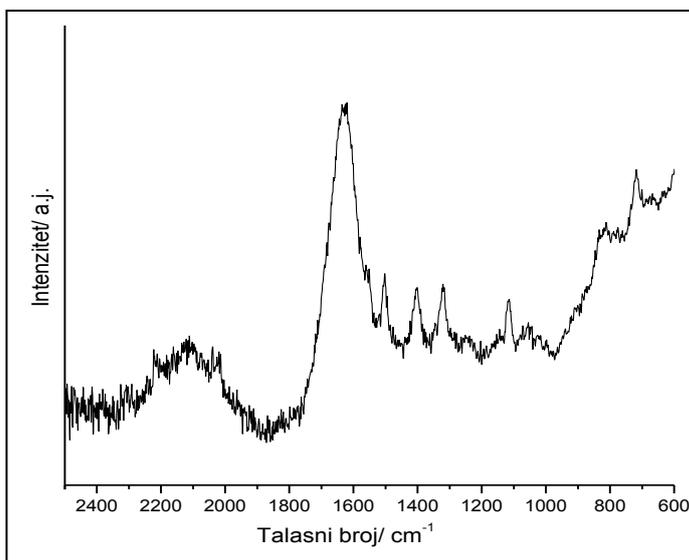
Aktivni oblici WPA i WSiA, kao i njihova stabilnost na fiziološkoj pH vrednosti u inkubacionom medijumu prilikom određivanja enzimske aktivnosti Na^+/K^+ -ATPaze,

¹⁵ ektonukleozid trifosfat difosfohidrolaza (ekto-ATPaza)

utvrđeni su pomoću IC i ramanske spektroskopije korišćenjem rezultata iz poglavlja 4.1.1 i 4.3.1 ove disertacije.

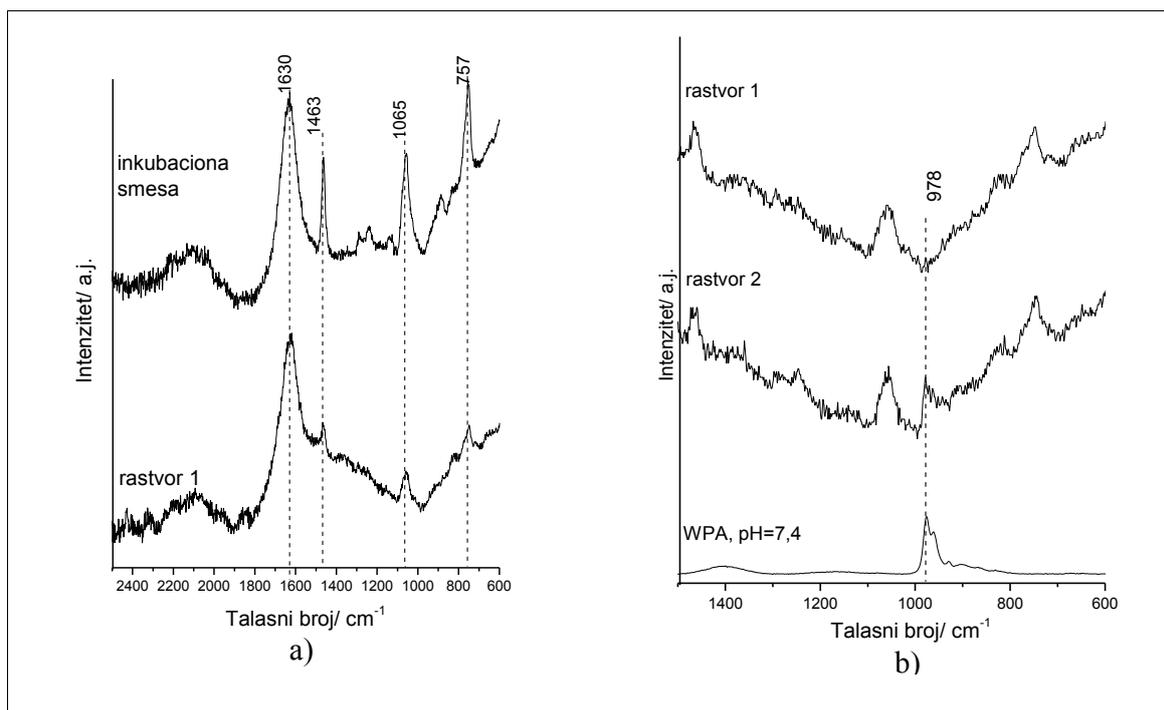
Ramanski spektri rastvora

Na slici 62. je prikazan ramanski spektar rastvora ATP koncentracije 20 mM, na kome se uočavaju trake na 1625, 1502, 1402, 1321, 1114 i 718 cm^{-1} . U spektru *rastvora 1*, slika 63. a), u kome u pomešani inkubaciona smeša, ATP, enzim i voda prisutne su trake na 1630, 1462, 1056, 755 cm^{-1} koje se javljaju i u samoj inkubacionoj smeši, a potiču od TRIS-HCl pufera [146]. Trake ATP slabijeg intenziteta se ne uočavaju (zbog deset puta manje koncentracije ATP u *rastvoru 1*), a najintenzivnija traka na 1625 cm^{-1} se preklapa sa trakom TRIS-HCl pufera.



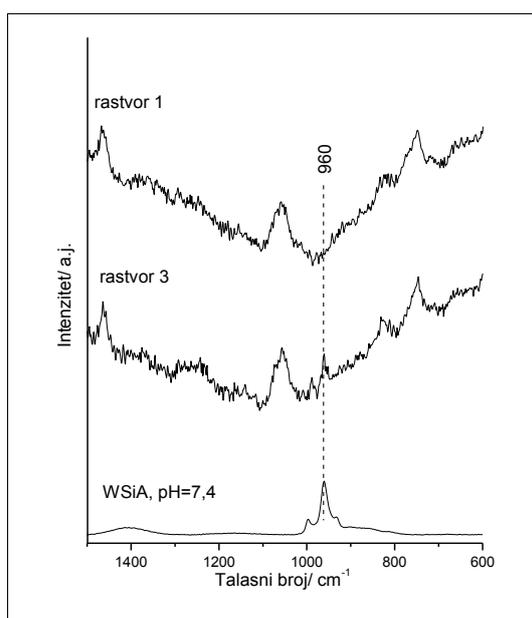
Slika 62. Ramanski spektar
20 mM ATP, $\lambda_{exc}=780 \text{ nm}$

U spektru *rastvora 2*, koji uz komponente *rastvora 1* sadrži i WPA, datom na slici 63. b), se pored traka inkubacione smeše, javlja i nova traka na 978 cm^{-1} . Prema rezultatima u poglavlju 4.1.1, jasno je da je u ovom sistemu struktura WPA narušena i da se WPA nalazi u obliku lakunarnog KA, koji se javlja i u vodenim rastvorima pri pH oko 7. Radi poređenja na slici 63. je dat i spektar vodenog rastvora WPA na pH = 7,4, koja je podešena dodavanjem NaOH.



Slika 63. Ramanski spektri a) inkubacione smеше i rastvora 1 (inkubaciona smeša + ATP + enzim + voda; b) rastvora 1, rastvora 2 (inkubaciona smeša + ATP + enzim + WPA + voda) i vodenog rastvora WPA na pH = 7,4 (dodat NaOH), $\lambda_{exc}=780$ nm

Slično, i u spektru *rastvora 3*, kao što se vidi na slici 64., koji uz komponente *rastvora 1* sadrži i WSiA, se pored traka inkubacione smеше, javljaju i trake na 997 i 960 cm^{-1} koje se javljaju i u vodenim rastvorima pri pH = 7,4.

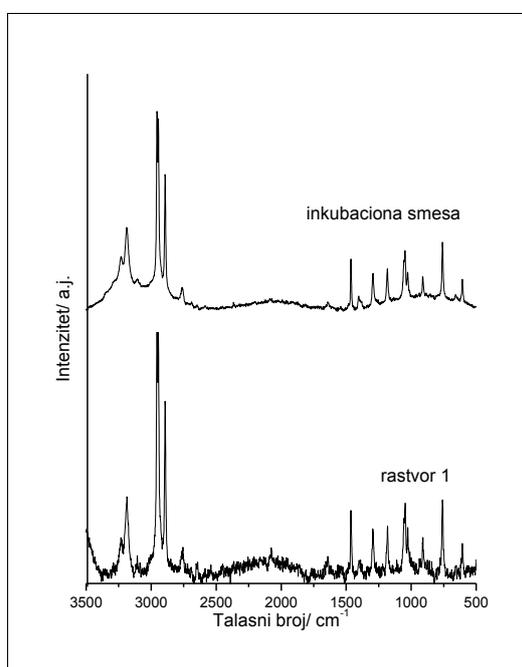


Slika 64. Ramanski spektri rastvora 1 (ink. smeša + ATP + enzim + voda), rastvora 3 (ink. smeša + ATP + enzim + WSiA + voda) i vodenog rastvora WSiA na pH = 7,4 (dodat NaOH), $\lambda_{exc}=780$ nm

Intenzivnija traka odgovara lakunarnom KA, a manje intenzivna je karakteristična za KA. Prema tome, jasno je da je i u ovom sistemu struktura HPK narušena i da se WSiA nalazi u obliku monolakunarnog KA, kao dominantne vrste, ali je za razliku od WPA prisutan u manjoj meri i nedegradiran KA.

Ramanski spektri suvih ostataka

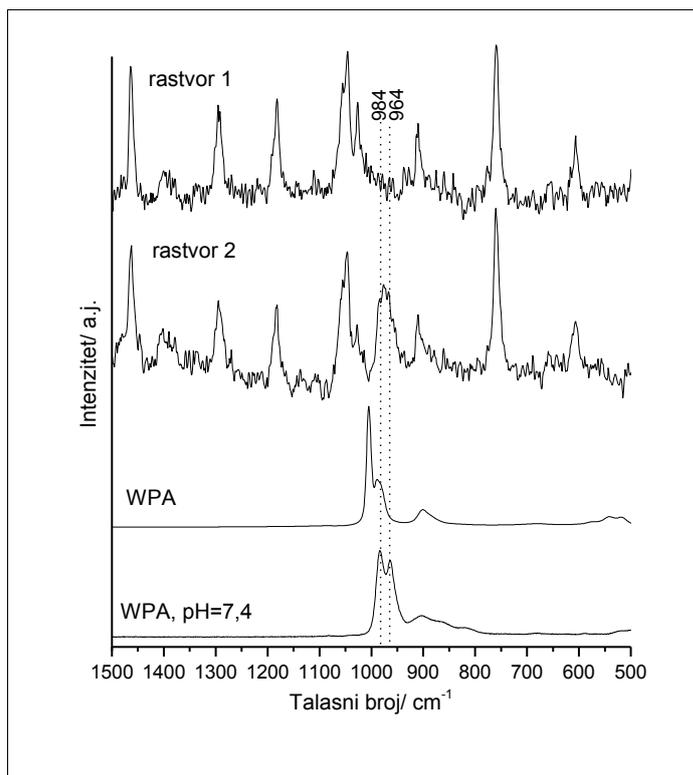
Na slici 65. se vidi da su u spektru suvog ostatka *rastvora 1*, prisutne trake koje postoje i u inkubacionoj smeši, a koje prema podacima u literaturi potiču od TRIS–HCl pufera [148].



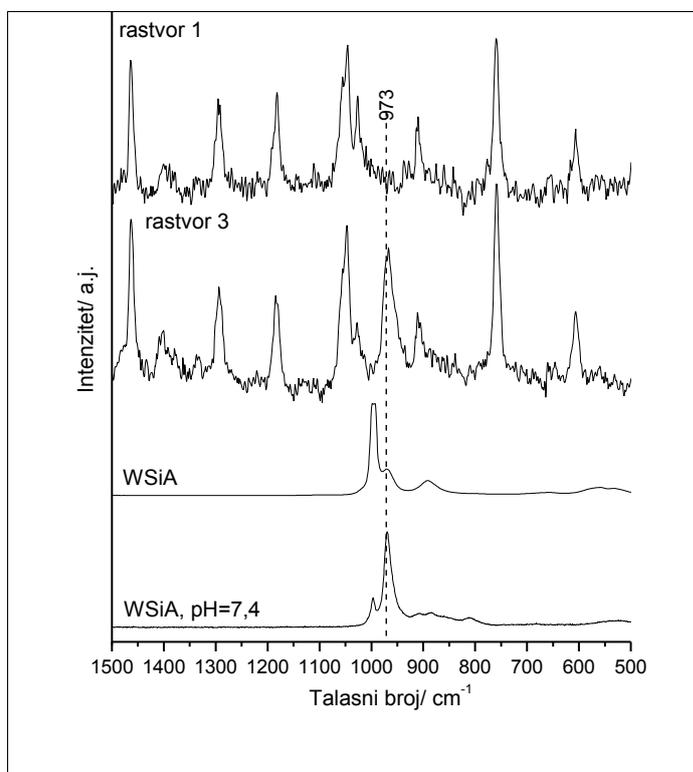
Slika 65. Ramanski spektri suvih ostataka inkubacione smeše i rastvora 1 (inkubaciona smeša + ATP + enzim + voda), $\lambda_{exc}=532\text{ nm}$

Sa slike 66. je očigledno da se u spektru suvog ostataka *rastvora 2*, pored traka inkubacione smeše, javlju i dve nove trake na 984 i 964 cm⁻¹, koje su karakteristične za monolakunarni KA.

I u slučaju WSiA u spektrima suvog ostataka *rastvora 3*, slika 67., se pored traka inkubacione smeše, uočava i pojava nove trake na 973 cm⁻¹, koja je karakteristična za lakunarni KA WSiA.



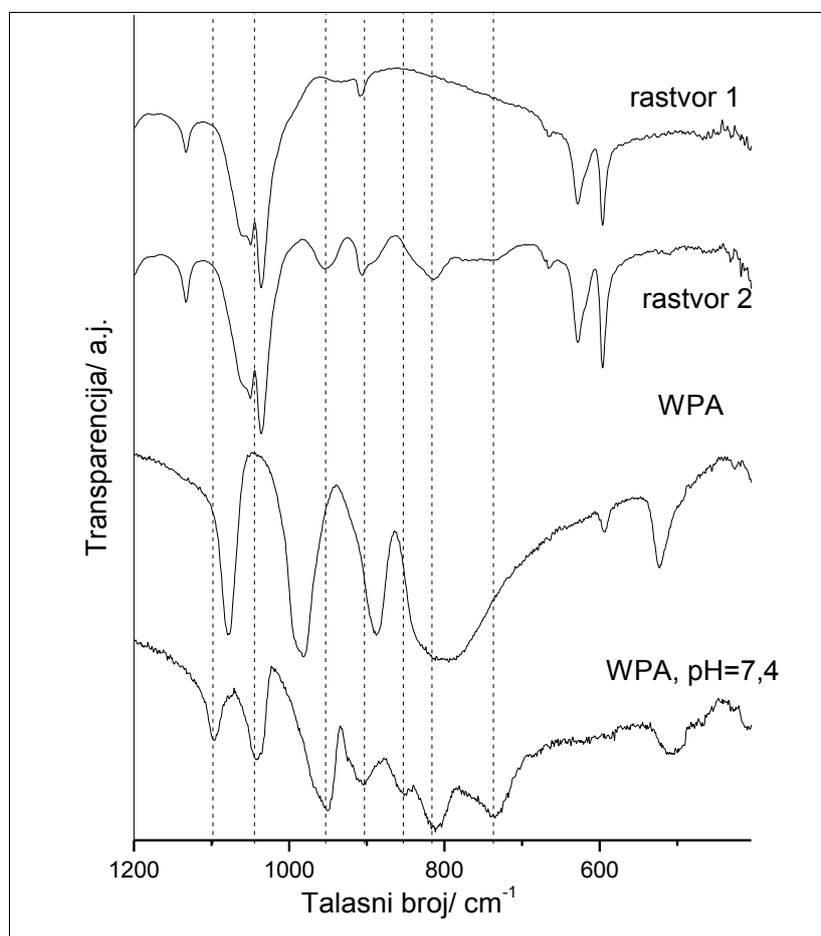
Slika 66. Ramanski spektri suvih ostataka rastvora 1 (inkubaciona smeša + ATP + enzim + voda), rastvora 2 (inkubaciona smeša + ATP + enzim + WPA + voda), čvrste WPA i suvog ostatka vodenog rastvora WPA na pH = 7,4 (dodat NaOH), $\lambda_{exc}=532$ nm



Slika 67. Ramanski spektri suvih ostataka rastvora 1 (ink. smeša + ATP + enzim + voda), rastvora 3 (ink. smeša + ATP + enzim + WSiA + voda), čvrste WSiA i suvog ostatka vodenog rastvora WSiA na pH = 7,4 (dodat NaOH), $\lambda_{exc}=532$ nm

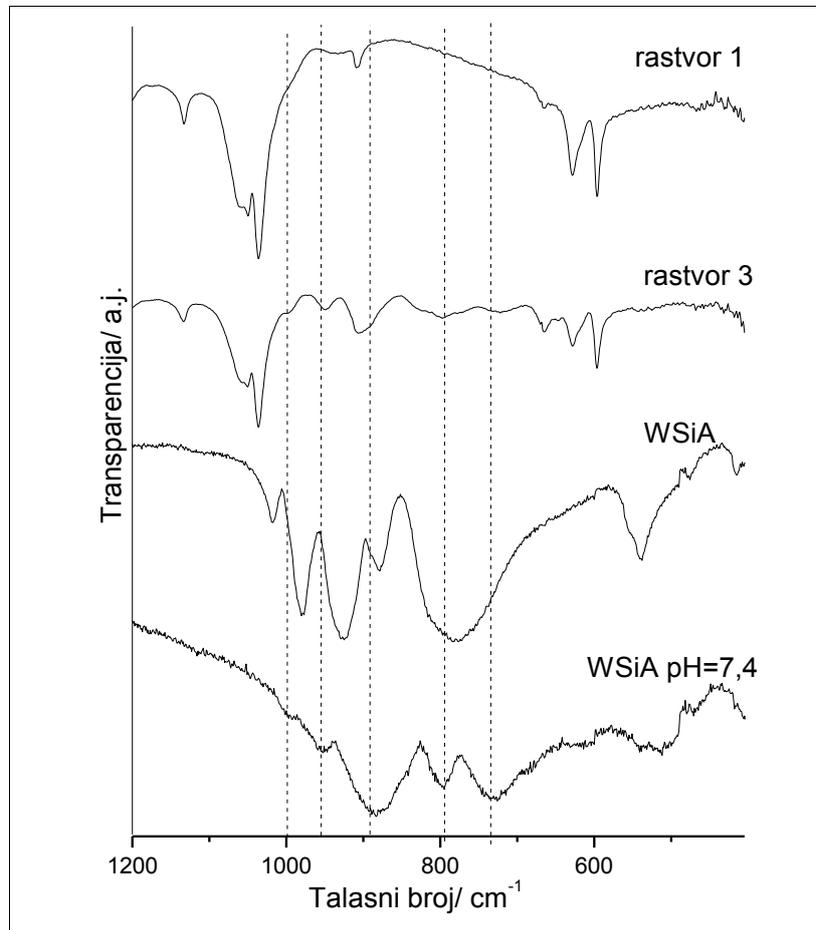
IC spektri suvih ostataka

Na slici 68. se vidi da su u IC spektru suvog ostatka *rastvora 1*, prisutne trake na 1133, 1035, 903, 629 i 599 cm^{-1} koje potiču od TRIS - HCl pufera [148]. Trake ATP se ne uočavaju zbog male koncentracije u *rastvoru 1*. U spektru suvog ostatka *rastvora 2*, pored traka inkubacione smeše, odnosno TRIS-HCl pufera, javljaju se i nove trake. Traka na 953 cm^{-1} odgovara W-O_d vibraciji, traka na 903 cm^{-1} W-O_b-W, a trake na 816 i 740 cm^{-1} W-O_c-W vibraciji u monolakunarnom KA WPA, $\text{PW}_{11}\text{O}_{39}^{7-}$. Trake P-O vibracije koje se u lakunarnom anjonu javljaju na 1100 i 1045 cm^{-1} se ne uočavaju u spektrima suvih ostataka zbog preklapanja sa trakama *rastvora 1*.



Slika 68. IC spektri suvih ostataka *rastvora 1* (inkubaciona smeša + ATP + enzim + voda), *rastvora 2* (inkubaciona smeša + ATP + enzim + WPA + voda), čvrste WPA i suvog ostatka vodenog *rastvora WPA* na $\text{pH} = 7,4$ (dodat NaOH)

U slučaju WSiA, kao što se vidi sa slike 69. u spektru *rastvora 3*. javljaju se nove trake koje ne postoje u spektru *rastvora 1*, na 996, 952, 890, 792 i 725 cm^{-1} , a koje odgovaraju vibracijama u monolakunarnom KA WSiA, $[\text{SiW}_{11}\text{O}_{39}]^{8-}$.



Slika 69. IC spektri suvih ostataka *rastvora 1* (inkubaciona smeša + ATP + enzim + voda), *rastvora 3* (inkubaciona smeša + ATP + enzim + WSiA + voda), čvrste WSiA i suvog ostatka vodenog rastvora WSiA na $\text{pH} = 7,4$ (dodat NaOH)

Na osnovu ovih rezultata može se zaključiti da su WPA i WSiA u inkubacionom medijumu uz prisustvo ATP i komercijalnog enzima u obliku monolakunarnog KA. Prema tome, $[\text{PW}_{11}\text{O}_{39}]^{7-}$ i $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ su oblici koji predstavljaju aktivne vrste u procesu inhibicije aktivnosti Na^+/K^+ -ATPaze.

5. ZAKLJUČAK

Za analizu solvolitičke stabilnosti WPA, MoPA i SiWA korišćene su ULj/Vid, IC, ramanska i ^{31}P NMR spektroskopija. Rezultati su pokazali da se kombinovanjem ovih metoda može uspešno pratiti stabilnost ispitivanih HPK. Izvedeni su sledeći zaključci:

- WPA je hidrolitički veoma nestabilna i u razblaženim i u koncentrovanim vodenim rastvorima. U razblaženim rastvorima pri koncentraciji od $2 \cdot 10^{-5} \text{ mol dm}^{-3}$ WPA nije u obliku KA, ali se zakišeljavanjem rastvora do $\text{pH} = 1,0$ vraća u KA.
- U koncentrovanim rastvorima, sa koncentracijom $5 \cdot 10^{-2} \text{ mol dm}^{-3}$, WPA je u obliku KA. Promena pH vrednosti dovodi do narušavanja ove strukture tako da je KA prisutan do $\text{pH} < 1,5$. Oblast pH vrednosti od 1,5 do 3,5 je oblast vrlo složenih ravnoteža između KA, Dawson-ovih struktura i monolakunarnog KA. Između pH 3,5 i 7,0 je oblast u kojoj je dominantna monolakunarna struktura. Iznad ove pH vrednosti, u alkalnoj sredini, počinje narušavanje lakunarne strukture, iz koje daljim gubitkom WO jedinica, preko trolakunarnog KA, nastaju volframatni i fosfatni anjoni.
- U metanol/vodenim rastvorima WPA dolazi do stabilizacije KA i u razblaženim i u koncentrovanim rastvorima. U razblaženim rastvorima sa udelom metanola $\geq 50\%$ (v/v) WPA je u obliku KA. Oblast do koje je prisutan KA zavisi od udela metanola u rastvaraču. Pri polaznom udelu metanola 50 % KA prisutan do $\text{pH} = 7,0$, a pri polaznom udelu metanola 100% do $\text{pH} < 10,0$. U koncentrovanim rastvorima, WPA je takođe u obliku KA i njegovo prisustvo u rastvorima pri porastu pH vrednosti takođe zavisi od udela metanola u rastvaraču. Takođe, od ovog udela zavisi i pri kojoj kiselosti rastvora će doći do izdvajanja taloga, kao i sastav taloga.
- Koncentracija rastvora igra veliku ulogu u stabilnosti WPA u rastvorima, tako da su različite oblasti stabilnosti pojedinih molekulskih vrsta u razblaženim i koncentrovanim rastvorima.
- MoPA je izuzetno hidrolitički nestabilna, nestabilnija od WPA. Shema razlaganja je slična onoj kod WPA, ali do dekompozicije dolazi pri nižim pH vrednostima. U razblaženim rastvorima KA nije prisutan čak ni na $\text{pH} < 1,0$. U koncentrovanim rastvorima do razlaganja KA dolazi već i pri najmanjoj promeni pH vrednosti uz nastajanje lakunarnog KA kao dominantnog oblika do $\text{pH} = 3,5$, dok je pri $\text{pH} =$

5,0 prisutan heksalakunarni oblik $[\text{PMo}_6\text{O}_{25}]^{9-}$. Slobodni fosfati se detektuju u ramanskim spektrima rastvora već pri $\text{pH} > 3,9$, a slobodni molibdati pri $\text{pH} > 5,0$.

- Dodatak metanola dovodi do izuzetne stabilizacije razblaženih rastvora MoPA, tako da je KA stabilan do $\text{pH} = 3,5$ kada je udeo metanola 50 %, a u čistom metanolu čak i u alkalnoj sredini pri $\text{pH} < 10,0$.
- U mešanom metanol/vodenom rastvaraču se poboljšava solvolitička stabilnost MoPA i u koncentrovanim rastvorima. Razlaganje MoPA počinje oko $\text{pH} = 3,5$, najverovatnije bez formiranja *Dawson*-ovih struktura, preko monolakunarne $[\text{PMo}_{11}\text{O}_{39}]^{7-}$ i heksalakunarne $[\text{PMo}_6\text{O}_{25}]^{9-}$ forme, koja se taloži pri $\text{pH} > 6,3$ u vidu soli $\text{Na}_9\text{PMo}_6\text{O}_{25}$. Kako su molbdofosfati veoma nestabilni u rastvorima, utvrđivanje preciznih granica pH vrednosti u okviru kojih se javljaju pojedini oblici, je veoma otežano.
- Vodeni rastvori WSiA su hidrolitički stabilniji od rastvora WPA i naročito MoPA. Kiselina postoji u obliku KA pri $\text{pH} < 8,5$ u razblaženim, odnosno $\text{pH} < 6,4$ u koncentrovanim rastvorima. Hidroliza se odvija preko monolakunarnog oblika koji je stabilan do $\text{pH} = 8,9$ i trolakunarnog oblika koji je prisutan čak i na $\text{pH} = 11,0$, do volframata i silikata.
- Dodatak metanola dovodi do stabilizacije KA u rastvorima WSiA, tako da je u razblaženim rastvorima prisutan pri $\text{pH} > 11,5$ a u koncentrovanim pri $\text{pH} > 7,8$. Pri $\text{pH} = 8,1$ počinje taloženje $\text{Na}_8\text{SiW}_{11}\text{O}_{39}$.
- Reverzibilnost procesa dekompozicije pri vraćanju pH sa 7,0 i 8,5 zakišeljavanjem do $\text{pH} = 1,0$ je potpuna pri nižim koncentracijama ($2 \cdot 10^{-5} \text{ mol dm}^{-3}$), a nepotpuna pri višim koncentracijama ($5 \cdot 10^{-2} \text{ mol dm}^{-3}$).
- Rastvori WPA koncentracije $5 \cdot 10^{-2} \text{ mol dm}^{-3}$ pri pH vrednostima između 6,5 i 8,0 su veoma stabilni u toku vremena u kojem su praćeni (1 godina).
- U biohemijskim primenama POM odabir pufera mora biti veoma pažljiv, jer može imati uticaj na biohemijski efekat i na njegovo tumačenje. U slučaju primene TRIS pufera, uz dominantan lakunarni KA, formiraju se i drugi polivolframofosfati.
- Dobijeni rezultati mogu biti iskorišćeni za utvrđivanje oblika HPK prisutnih u različitim sistemima.

- U slučaju polianilin 12-volframofosfatnih mikro/nanostrukture utvrđeno je da je KA dominantno prisutna vrsta, ali su male količine DA i monolakunarnog KA takođe registrovane uz pomoć IC spektara.
- WPA i WSiA u inkubacionom medijumu uz prisustvo ATP i komercijalnog enzima Na⁺/K⁺-ATPaze su u obliku monolakunarnog KA. Prema tome, aktivni oblici koji dovode do inhibicije enzima su [PW₁₁O₃₉]⁷⁻ i [SiW₁₁O₃₉]⁸⁻.

Dobijeni rezultati imaju veliki značaj u biohemiji i biomedicini, kao i u fizičkoj hemiji materijala, jer mogućnosti za proširenje njihove primene rastu sa boljim upoznavanjem njihovih osobina.

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7. PRILOZI

PRILOG A

Skraćenice korišćene u tekstu

M	<i>adendni atom</i>
X	<i>heteroatom</i>
WPA	<i>12-volframfosforna kiselina</i>
WSiA	<i>12-volframsilicijumova kiselina</i>
MoPA	<i>12-molibdenfosforna kiselina</i>
HPK	<i>heteropoli kiselina</i>
POM	<i>poliokso metalati</i>
HPOM	<i>heteropoliokso metalati</i>
HPA	<i>heteropoli anjon</i>
HPJ	<i>heteropoli jedinjenja</i>
KA	<i>Keggin-ov anjon</i>
DA	<i>Dawson-ov anjon</i>
TRIS	<i>tris(hidroksimetil)aminometan</i>
PANI	<i>polianilin</i>

PRILOG B

Naučni radovi i saopštenja u kojima su publikovani rezultati iz doktorske disertacije

Rad u vrhunskom međunarodnom časopisu M₂₁

1. G. Ćirić-Marjanović, I. Holclajtner-Antunović, S. Mentus, D. Bajuk-Bogdanović, D. Ješić, D. Manojlović, S. Trifunović, J. Stejskal, “*Self-assembled polyaniline 12-tungstophosphate micro/nanostructures*”, *Synthetic Metals*, 160 (2010) 1463

Rad u istaknutom međunarodnom časopisu M₂₂

1. I. Holclajtner-Antunović, D. Bajuk-Bogdanović, A. Popa, S. Uskoković-Marković, “*Spectroscopic identification of molecular species of 12-tungstophosphoric acid in methanol/water solutions*“, *Inorg. Chim. Acta*, 383 (2012) 26

2. M. Čolović, D. Bajuk-Bogdanović, N. Avramović, I. Holclajtner-Antunović, N. Bošnjaković-Pavlović, V. Vasić, D. Krstić, “*Inhibition of rat synaptic membrane Na⁺/K⁺-ATPase and ecto-nucleoside triphosphate diphosphohydrolases by 12-tungstosilicic and 12-tungstophosphoric acid*“, *Bioorg. Med. Chem.*, 19 (2011) 7063

3. I. Holclajtner-Antunović, D. Bajuk-Bogdanović, M. Todorović, U. Mioč, J. Zakrzewska, S. Uskoković-Marković, “*Spectroscopic study of stability and molecular species of 12-tungstophosphoric acid in aqueous solution*“, *Can. J. Chem.*, 86 (10) (2008) 996

Rad u međunarodnom časopisu M₂₃

1. D. Bajuk-Bogdanović, I. Holclajtner-Antunović, M. Todorović, U. Mioč, J. Zakrzewska, “*A study of 12-tungstosilicic and 12-molybdophosphoric acids in solution*“, *J. Serb. Chem. Soc.*, 73 (2) (2008) 197

Rad u časopisu nacionalnog značaja M₅₂

1. D. Bajuk-Bogdanović, I. Holclajtner-Antunović, U. B. Mioč, M. Todorović “*Ispitivanje stabilnosti 12-volframfosforne, 12-volframsilicijumove i 12-molibdenfosforne kiseline u vodenim rastvorima*“, *Tehnika- Novi materijali*, 14 (6) (2005) 3



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JSCS–3702

A study of 12-tungstosilicic and 12-molybdophosphoric acids in solution

DANICA BAJUK-BOGDANOVIĆ¹, IVANKA HOLCLAJTNER-ANTUNOVIĆ^{1*#},
MARIJA TODOROVIĆ², UBAVKA B. MIOČ^{1#} and JOANNA ZAKRZEWSKA³

¹Faculty of Physical Chemistry, P.O. Box 47, 11158 Belgrade 118, ²Faculty of Chemistry,
P.O. Box 157, 11001 Belgrade and ³Institute of General and
Physical Chemistry, P.O. Box 551, 11001 Belgrade, Serbia

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Abstract: The behaviour of two heteropolyacids (HPAs) with quite different stability in aqueous solutions was systematically investigated by UV, IR and NMR spectroscopy and potentiometric titration. It was shown that the Keggin structure of 12-tungstosilicic acid ($H_4SiW_{12}O_{40}$, WSiA) anion was sustained over a wide range of pH from 1.0 to 7.0, while the same anion type of 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$, MoPA) was present only at pH 1.0. This means that under physiological conditions WSiA is dominantly present in the form of a Keggin-anion, whereas the structure of MoPA is completely decomposed to molybdate and phosphate. The obtained results are of special importance for bio-medical and catalytic applications of these compounds and for a better understanding of the mechanism of their action.

Keywords: heteropolyacids of Keggin structure; 12-tungstosilicic acid; 12-molybdophosphoric acid; hydro-stability; UV; IR and NMR spectroscopy.

INTRODUCTION

Polyoxometalates (POMs) of various classes are very interesting compounds with unusual behaviour: they are good catalysts, superionic proton conductors, compounds with photoconductive and magnetic characteristics and biochemical active species.^{1–6}

The properties of POMs in the solid state are extensively studied and rather well established but their behaviour in the liquid state is not well understood and explained in spite of numerous publications. However, the behaviour of these interesting compounds in solution is important from the aspect of their bio-medical and catalytic applications and from the aspect of their formation and degradation.

For more than 20 years, the antiviral, antitumour and anticoagulant activities of POMs have been studied.^{1–3,6} A fundamental limitations in the interpretation

* Corresponding author. E-mail: ivanka@ffh.bg.ac.yu

Serbian Chemical Society member.

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and application of the results on the behaviour of these compounds in physiological media, as well as their application as biochemical active compounds derives from their nature and equilibrium between different molecular forms in aqueous solutions. Namely, the problem of all biological/medicinal investigations of POMs is whether these compounds reside in their original form during biomedical treatment, and for how long and under which conditions. Generally, it is considered that the parent form of the POMs anion is active.^{1-3,6} In order to consider and elucidate the proper mechanism of the bio-medical activity of POMs, it is indispensable to identify the real active species under physiological conditions, both *in vitro* and *in vivo*.

Due to their properties, POMs are also used as catalysts in oxidation reactions, in acid catalyzed reactions and as bifunctional catalysts both in homogeneous and heterogeneous catalysis.^{1-3,7,8} With the purpose of improving the catalytic characteristics of these compounds and explaining the mechanism of their action, it is also (as in the case of bio-medical applications) important to specify the nature of the active species present. Many studies considered the hydro stability of heteropolyacids (HPA), mostly of Keggin type, and their reaction pathways in solution.^{1,3,9-15}

It was shown that many POMs degrade into a mixture of inorganic products in aqueous solution.¹ Kepert and Kyle^{16,17} studied the decomposition of Keggin anions containing silicon, phosphorus or boron as the central, heteroatom and tungsten as the addenda metal atom. These authors found that the equilibrium reaction in solution proceeds in three distinct stages, with $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ and $[\text{SiW}_9\text{O}_{34}]^{10-}$ as intermediates. A few years later, stopped-flow kinetics studies of 12-molybdophosphate formation and decomposition were performed by Kircher and Crouch.¹⁸ Molybdophosphate complexes in aqueous solutions were identified by ^{31}P -NMR and Raman spectroscopy, as well as by differential pulse polarography.¹⁹ Additionally, ^{31}P -NMR spectroscopy was applied in a stability study of HPAs through the rate of exchange of structural units between WPA and MoPA.¹⁵ Moreover, McGarvey and Moffat followed the major species present in tungstophosphate and molybdophosphate solutions as a function of pH by NMR and IR spectroscopy.¹³ They found that both acids decompose to a lacunary form of the Keggin anion, which further decomposes to phosphate species in alkaline solutions. The same system was investigated over a wide pH range (1-12) using preparative high performance liquid chromatography combined with IR, UV-Vis and ICP spectroscopy.^{20,21} Smith and Patrick applied ^{31}P - and ^{183}W -NMR spectroscopy in a detailed study of tungstophosphoric and tungstosilicic acids in aqueous solutions.²²⁻²⁴ The species present in these systems were identified and quantified as a function of pH.

The conclusions reached in all these studies were not consistent, although the conditions of the investigations were similar. Generally, it can be concluded

that the hydrolytic stability of HPAs depends on the anion structure, the nature of the heteroatom and the peripheral metal atom which comprise the anion, as well as on the conditions of the solution.

The aim of this study was to investigate thoroughly the behaviour of two HPAs of the Keggin type with quite different hydro-stability, *i.e.*, 12-phosphorsilicic (WSiA) and 12-molybdophosphoric (MoPA) acids, in order to contribute to a better explanation of their base hydrolysis. For this purpose, UV, IR and ^{31}P -NMR spectroscopic methods and potentiometric titration were applied and the results were summarized and compared in order to determine the dominant species present in aqueous solutions at various pH values, with special attention to physiological conditions.

EXPERIMENTAL

Materials

MoPA was prepared by literature method²⁵ and confirmed by infrared spectroscopy, while WSiA was commercially available (Fluka). Both acids were recrystallized prior to use.

Methods

The pH values of the solutions were adjusted by the addition of NaOH or HCl solutions and measured using a pH meter with a glass electrode. The pH values of the solutions were monitored until no apparent changes were observed. The samples were prepared one day prior to the measurements.

The UV spectra of aqueous 2.0×10^{-5} mol dm⁻³ solutions of the HPAs were obtained using a Cintra 10e (GBS) spectrophotometer.

Solid samples for IR measurements were obtained by evaporation of the water from 5.0×10^{-2} mol dm⁻³ solutions of the HPAs of different pH values. The IR spectra were recorded on a Perkin-Elmer 983G spectrophotometer using the KBr pellets technique, in the wave number range 1500–300 cm⁻¹, where the bands characteristic for Keggin anions are to be found.

Sample solutions for NMR measurement were prepared by adding the estimated quantities of NaOH just after dissolving. The NMR experiments were performed with a Bruker MSL 400 spectrometer at 161.978 MHz. The concentration of the HPAs was 5.0×10^{-2} mol dm⁻³, with 2048 scans, 9.0 μs pulse and 500 ms repetition time at 25 °C. The sample volume was about 2.5 ml in a 10 mm tube. Methylendiphosphonate (MDP) at 17.05 ppm was used as the external reference relative to 85 % H₃PO₄.

The UV, IR and ^{31}P -NMR spectra were recorded at pH values of 1.0, 2.0, 3.5, 5.0, 7.0, 8.5, 10 and 11.5.

Potentiometric titrations were performed by adding 0.192 mol l⁻¹ NaOH standard aqueous solution into each of the solutions of the HPAs (20 ml, 0.064 mol l⁻¹ MoPA and 0.087 mol l⁻¹ WSiA) at a rate of 2 drops per second at room temperature.

RESULTS AND DISCUSSION

UV Spectra

In the UV range, the electronic spectra of HPAs having a Keggin structure exhibit two intense absorption bands at about 200 and 260 nm, attributed to the transitions O_d-M and O_b/O_c-M, respectively.²⁶

The UV spectra of the WSiA solutions at various pH values, presented in Fig. 1, show that this HPA was stable in the pH range from 1.0 to 8.5, with an absorption maximum at 262.6 nm. This band disappeared in solutions of higher pH values.

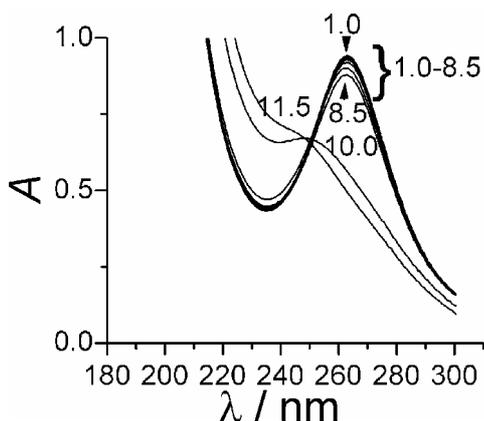


Fig. 1. UV spectra of WSiA solutions of various pH values.

In contrast, the UV spectra of the MoPA solutions changed drastically in the pH range from 1.0 to 7.0 (Fig. 2a) but remained unchanged with further increase in the pH value of the solution (Fig. 2b). This finding could be explained by the fact that the Keggin anions were completely decomposed into PO_4^{3-} and MoO_4^{2-} at pH 7.0. At pH 1.0 and 2.0, the absorption maximum was at about 220 nm, while at pH 3.5 and 5.0, there was a maximum at 210 nm with shoulder at about 230 nm (Fig. 2a).

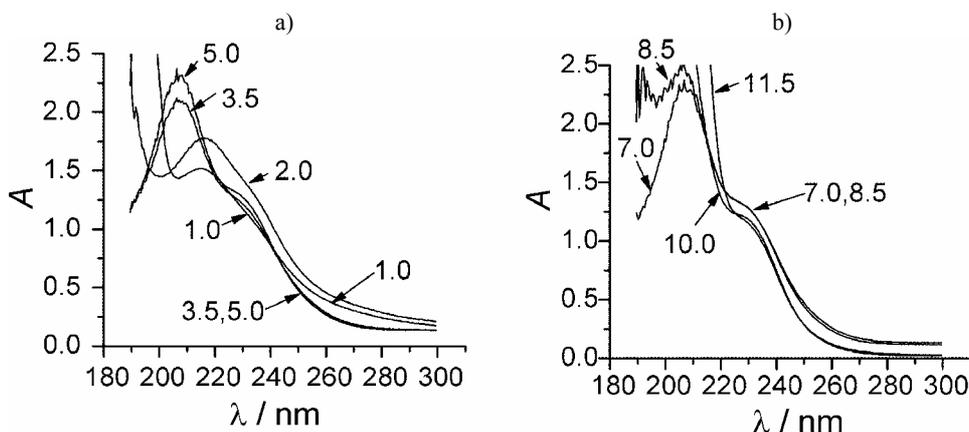


Fig. 2. UV Spectra of MoPA solutions of various pH values:
a) from pH 1.0 to 5.0 and b) from pH 7.0 to 11.5.

All the changes in the UV spectra of HPA solutions of different pH can be attributed to changes in the structure of the individual forms of the HPAs. However, it is difficult to conclude about the nature of the observed changes and to identify with certainty the formed products.

IR Spectra

IR Spectra of evaporated and dried sample solutions were recorded over the same pH range 1.0 to 11.5 as in the case of the UV spectra and are presented in Figs. 3 and 4. It is necessary to point out that although the pH values of solutions changed during evaporation of the water, there was no reversible change of the given forms of HPAs to the parent Keggin anion.

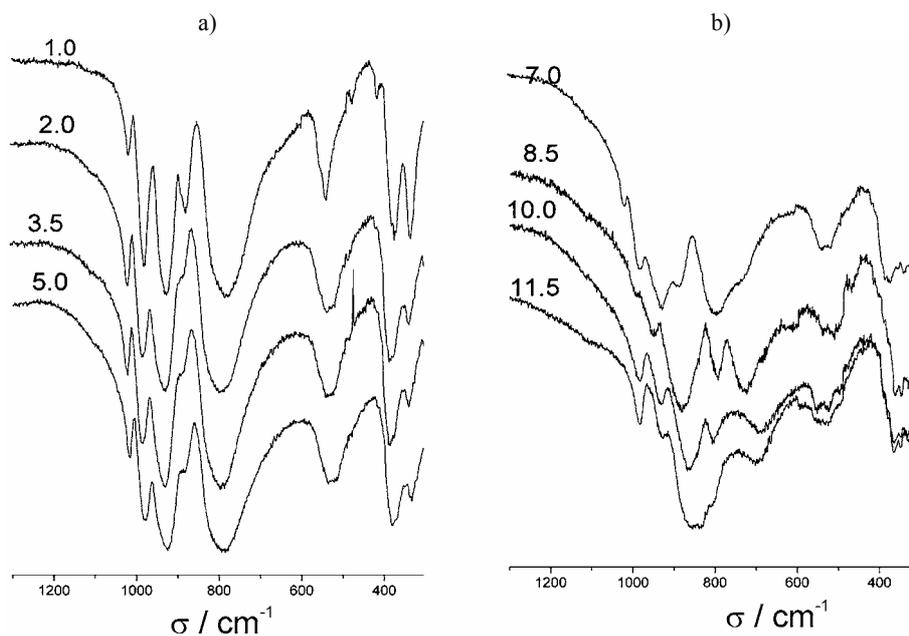


Fig. 3. IR Spectra of evaporated aqueous WSiA solutions of various pH values: a) from pH 1.0 to 5.0 and b) from pH 7.0 to 11.5.

As in the case of the UV spectra, the changes in the IR spectra of the dry residues of aqueous solutions of WSiA (Fig. 3) appeared at higher pH values than in the case of MoPA. The spectrum at pH 1 corresponds to the spectrum of solid acid. It is characterized by four bands characteristic for the Keggin anion $[\text{SiW}_{12}\text{O}_{40}]^{4-}$: 981, 928, 880 and 785 cm^{-1} ,²⁷ corresponding to vibrations $\nu_{\text{as}}(\text{W}-\text{O}_{\text{d}})$, $\nu_{\text{as}}(\text{Si}-\text{O}_{\text{a}})$, $\nu_{\text{as}}(\text{W}-\text{O}_{\text{b}}-\text{W})$ and $\nu_{\text{as}}(\text{W}-\text{O}_{\text{c}}-\text{W})$, respectively.

It can be noticed from the data given in Fig. 3 and Table I, that there was almost no change in the positions of the characteristic bands for samples up to pH 7.0, confirming that the Keggin anion was preserved in the solutions up to this pH value. However, the first changes in spectrum were registered at pH 7.0, which indicate the appearance of some new species in solution. This species present at pH 8.5 can be identified as the lacunary anion, $[\text{SiW}_{11}\text{O}_{39}]^{8-}$, characterized by bands at 952, 885, 870, 797 and 725 cm^{-1} .²⁸ Some of these bands disappeared at pH 10 and pH 11.5. It is evident that at pH 11.5, the WSiA had

completely decomposed to SiO_4^{4-} (bands at about 1000 cm^{-1}) and WO_4^{2-} ions (bands at about $860, 700$ and 525 cm^{-1}).

TABLE I. Vibration bands for the solid residues of aqueous WSiA solutions of various pH values

pH							
1.0	2.0	3.5	5.0	7.0	8.5	10.0	11.5
1017 _w	1017 _m	1016 _m	1016 _m	1018 _w			
					1000 _{sh}		
980 _s	979 _s	979 _s	978 _s	980 _w		982 _w	983 _w
					952 _w		
925 _{vs}	924 _{vs}	926 _{vs}	925 _{vs}	923 _m			927 _{sh}
879 _{sh}	880 _{sh}	880 _{sh}	880 _{sh}	880 _w	885 _{s,b}		
					865 _{sh}	868 _{s,b}	860 _{s,b}
800 _{vs,b}	800 _{vs,b}	800 _{vs,b}	800 _{vs,b}	800 _{vs,b}	795 _m	807 _w	
					726 _{s,b}		
						690 _{w,b}	700 _{w,b}
538 _m	535 _{m,b}	535 _{m,b}	535 _{m,b}	535 _{m,b}	530 _{m,b}	530 _{m,b}	525 _{w,b}
373 _m	383 _m	380 _m	380 _m	375 _m			
					360 _w	360 _w	365 _w
334 _m	335 _w	335 _w	335 _w	335 _w			
					325 _w	324 _w	321 _w

The present results are in accordance with the generally accepted knowledge that tungstosilicates are more stable than other tungsten heteropolyanions. A general scheme for the decomposition of WSiA in aqueous solution with increasing pH was proposed in the literature.^{16,17} In the first stage, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ is hydrolyzed to the lacunary $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ anion, a further increase in the pH results in the formation of the $[\text{SiW}_9\text{O}_{34}]^{10-}$ anion, which finally decomposes to SiO_4^{2-} and WO_4^{2-} . A quantitative determination of speciation of WSiA over the pH range 3–13.5, performed by Smith and Patrick by NMR spectroscopy,²² showed that the Keggin $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ anion is stable up to pH 3.7; the main component in the pH range from 3.8–9.2 is the lacunary $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ monovacant anion, which is decomposed with further increase in the pH value. The present results confirm that the decomposition pathways of WSiA in solution proceed through the formation of the lacunary monovacant anion, which is completely decomposed at $\text{pH} > 8.5$. However, contrary to the findings of Smith and Patrick,²² the presented UV and IR spectra show that the Keggin anion is stable up to pH 7.0. Based on IR spectra, it can also be concluded that the degradation to tungstate and silicate occurs in alkaline solution of $\text{pH} > 10.0$.

The IR spectra recorded for the samples of MoPA are shown in Fig. 4, while the major vibration bands are listed in Table II. It can be seen that only spectrum at pH 1.0 of dry residue of aqueous solution of acid have the four characteristic bands of the Keggin anion $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ at $1067, 975, 870$ and 810 cm^{-1} .²⁷ The

changes in the spectrum started even at pH 2.0. The splitting of the band corresponding to the vibration P–O into two bands at about 1063 and 1035 cm^{-1} can be ascribed to the presence of the lacunary $[\text{PMo}_{11}\text{O}_{39}]^{6-}$ anion.¹³ The spectra for pH 2.0 and 3.5 are complex, indicating the presence of different structures, which cannot be exactly identified from the IR spectra. At pH 5.0, the decomposition of the MoPA anion to molybdate and phosphate commenced. In alkaline solutions (pH > 7.0), complete decomposition is evident. In contrast to these results, Song and Barteau²⁹ found no change in the IR spectra of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ evaporated from aqueous solutions of pH 2.6–3.1. The authors explained their results as being the consequence of the short time interval between acid dissolution and IR measurements (20 min). However, in the present study it was found that equilibrium with respect to the decomposition process was attained within the time required to prepare the solutions for WSiA and MoPA, which is in accordance with the conclusions of Jurgensen and Moffat.³⁰

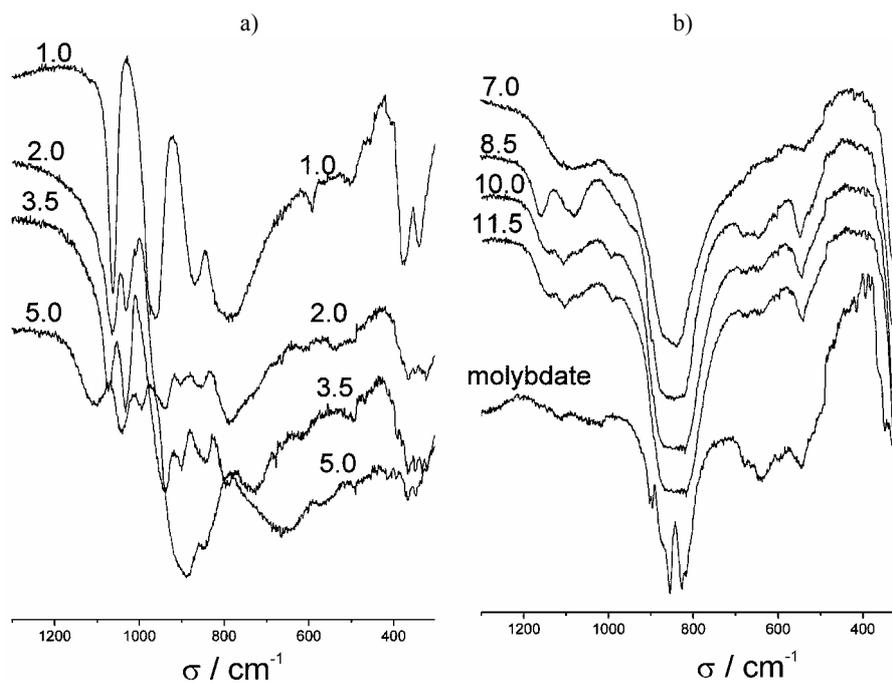


Fig. 4. IR Spectra of evaporated aqueous MoPA solutions of various pH values:
a) from pH 1.0 to 5.0 and b) from pH 7.0 to 11.5.

The solutions of MoPA, in contrast to other solutions of HPAs, are coloured and with increasing pH values, the change in their colour can be followed visually, *i.e.*, from the intense yellow of the pure acid, through green to light blue at pH > 5.0, which indicates the reduction of molybdenum.

It is obvious that pH influences the stability of both the investigated HPAs but in different ways. The present results indicate that the Keggin anion of WSiA is sustained in aqueous solutions up to pH 7.0, while this structure of MoPA is present only at pH 1.0, with other Keggin anion structures appearing with further increase in the pH value.

TABLE II. Vibration bands for the solid residues of aqueous MoPA solutions of various pH values

pH								Molybdate
1.0	2.0	3.5	5.0	7.0	8.5	10.0	11.5	
					1155 <i>m</i>	1157 <i>sh</i>	1155 <i>sh</i>	
			1099 <i>m</i>			1107 <i>w</i>	1107 <i>w</i>	
		1074 <i>s</i>		1077 <i>w,b</i>	1079 <i>m</i>			
1063 <i>s</i>	1065 <i>s</i>							
	1032 <i>m</i>	1033 <i>s</i>	1040 <i>s</i>					
			995 <i>m</i>	983 <i>sh</i>		995 <i>vw</i>	995 <i>vw</i>	
964 <i>vs</i>								
	940 <i>w,b</i>	938 <i>m</i>			937 <i>sh</i>			
	903 <i>vw</i>	901 <i>w</i>						902 <i>w</i>
			889 <i>vs,b</i>					880 <i>sh</i>
869 <i>s</i>	855 <i>vw,b</i>	846 <i>w</i>	848 <i>sh</i>	836 <i>w</i>	844 <i>vs,b</i>	845 <i>vs,b</i>	843 <i>vs,b</i>	855 <i>vs</i>
								827 <i>vs</i>
790 <i>vs,b</i>	789 <i>m,b</i>	797 <i>w</i>						
		726 <i>w</i>						
			660 <i>m,b</i>					
					675 <i>w</i>	674 <i>w</i>	674 <i>w</i>	680 <i>w</i>
					645 <i>w</i>	643 <i>w</i>	650 <i>w</i>	640 <i>w</i>
592 <i>w</i>								
				536 <i>w</i>	546 <i>m</i>	545 <i>m</i>	544 <i>m</i>	547 <i>w</i>
504 <i>w</i>								
459 <i>sh</i>								
374 <i>m</i>	365 <i>w</i>	365 <i>w</i>	365 <i>w</i>					
341 <i>m</i>								
	324 <i>w</i>	325 <i>w</i>	325 <i>w</i>	320 <i>s</i>	320 <i>s</i>	318 <i>s</i>	318 <i>s</i>	320 <i>s</i>

All the changes in the UV spectra of the HPAs solutions of different pH can be attributed to changes in the structure of the individual HPA, but identification of the formed products is limited. The IR spectra present a further improvement in the identification of the dominant chemical species present in the HPAs solutions of differing pH, in relation to the UV spectra, but it is difficult to identify all the structures present. The IR spectra at higher pH values indicate the total degradation of the parent anion to tungstate and silicate or molybdate and phosphate anions.

NMR Spectra

In order to overcome the drawbacks of UV and IR spectroscopy in the identification of molybdophosphate species in solutions of differing pH values, the complementary method of ^{31}P -NMR spectroscopy was applied.

The ^{31}P -NMR spectra and chemical shifts of the peaks for solutions of MoPA of different pH values are shown in Fig. 5 and Table III, respectively. At pH 1.0, the most intensive peak corresponding to $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ is at -2.87 ppm, while the peaks at -2.16 ppm and -0.65 can be assigned to $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ and $[\text{Mo}_9\text{PO}_3\text{OH}(\text{OH}_2)_2]^{4-}$, respectively.^{19,31} The presence of these structures manifests the very complex reaction pathway of MoPA in acidic solution. The most intensive peaks in solutions of pH 2.0 (-0.95 ppm) and 3.5 (-0.77 ppm) correspond to the lacunary $[\text{PMo}_{11}\text{O}_{39}]^{6-}$ ion, which is the dominant component under these conditions. In solution with pH 5.0, the strong peak with a chemical shift of 2.15 ppm is ascribed to $[\text{P}_2\text{Mo}_5\text{O}_{23}]^{6-}$, a structure with two P atoms, the peak at 0.65 ppm is assigned to $[\text{PMo}_6\text{O}_{25}]^{9-}$ and the peak at -0.49 ppm is assigned to $[\text{PMo}_{11}\text{O}_{39}]^{6-}$.³¹ The difference between chemical shifts of the $[\text{PMo}_{11}\text{O}_{39}]^{6-}$ ion observed at low and at high pH (at -0.95 to -0.49 ppm, respectively) can be explained by extensive protonation.¹⁹ In solutions of pH 7.0 and higher, peaks corresponding to phosphate ions, H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} appear, which means that the complex structure of MoPA is completely destroyed under physiological conditions.

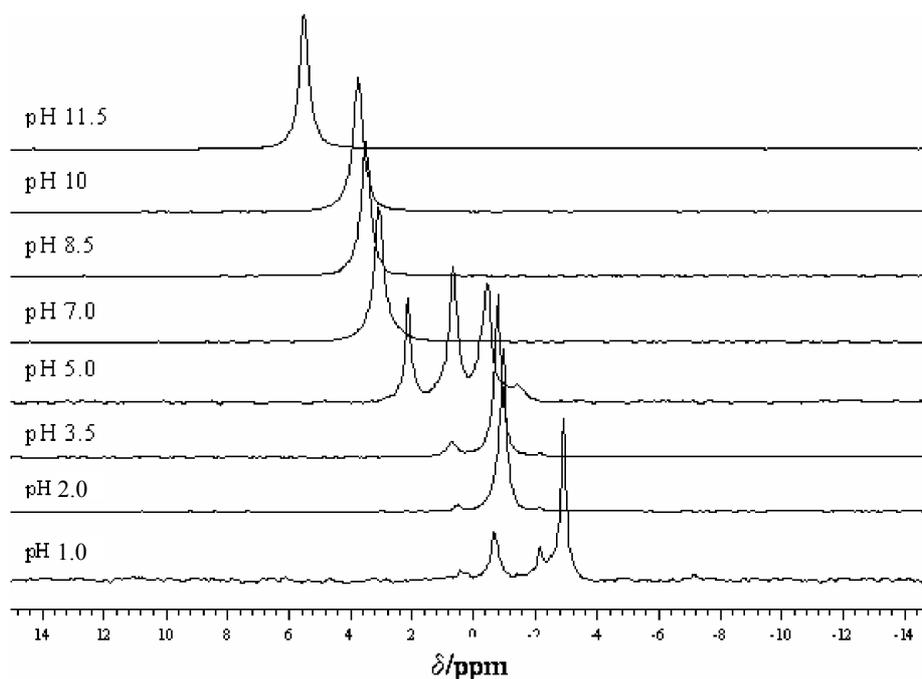


Fig. 5. ^{31}P -NMR Spectra of MoPA solutions of different pH values.

Table III. Chemical shifts of the signals in the ^{31}P -NMR spectra of MoPA solutions of various pH values

pH	1.0	2.0	3.5	5.0	7.0	8.5	10.0	11.5
Chemical shift, ppm	0.44	0.53	0.71	2.15	3.10	3.51	3.78	5.50
	-0.65	-0.95	-0.77	0.65	–	–	–	–
	-2.16	-2.16	-2.16	-0.49	–	–	–	–
	-2.87	–	–	-1.39	–	–	–	–

Potentiometric titration

The potentiometric titrations showed how the pH of the solutions of the HPAs changed on addition of 0.192 mol l^{-1} NaOH. Initially, the pH increased slowly from pH 1.7 to 3.0 as the NaOH was added. Continued addition of NaOH to the solution of WSiA led to a rapid increase in the pH, with the endpoint at a hydroxide to acid ratio of 4.0 (Fig. 6a). This is in accordance with conclusions obtained from the spectroscopic results. In this pH region, WSiA is stable and behaves as a tetrabasic acid in water. On the contrary, the potentiometric titration of MoPA, $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ showed a broad endpoint at about 4 mole equivalences of base at pH ≈ 3.8 (Fig. 6b). The spectroscopic results showed that at this pH value, the Keggin anion is decomposed and that aqueous solutions of MoPA contain mixture of various species, resulting in a higher basicity than expected based on its parent structure.

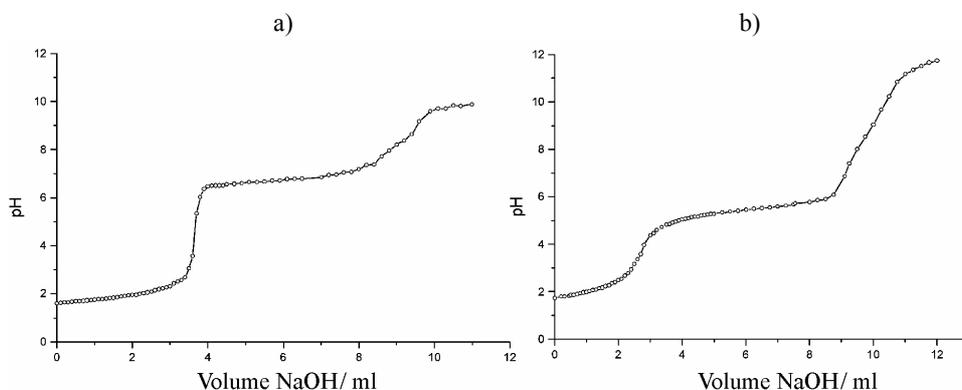


Fig. 6. Potentiometric curves for the base decomposition of:
a) $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ and b) $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$.

Further addition of base to the acid solution caused no change in the pH, indicating the ability of the POMs to maintain the pH of the solution, *i.e.*, both acids have a high buffering capacity.

The second broad endpoint in the potentiometric curve signifies the total decomposition of the HPAs.

It is evident that the electrochemical results are in agreement with the spectroscopic ones.

CONCLUSIONS

In this study, special attention was placed on the importance of the molecular species of the POMs present in solution and their role in catalytic and biochemical and biomedical processes on a molecular level. When POMs are employed as catalysts for homogeneous or heterogeneous catalysis, their activity depends on the general characteristics of the solution, *i.e.*, the nature of the solvent—organic or aqueous, their concentration, the pH of the solution and the reduction potential of the hetero- and addenda atoms, as well as on the strength of the acid centres. Such studies are important if one wishes to follow the mechanism of catalytic processes, the formation of activation complexes, as well as in formation of complex catalysts on different supports by the sol–gel process or impregnation. All the bonds formed in the activation complexes and between the substrate and the parent catalysts depend on the molecular forms of the POMs.

It would seem that hitherto in spite of the large number of references, insufficient attention has been paid to this problem. In order to contribute to the solution of the molecular forms of the PMOs existing in solution, spectroscopic methods, *i.e.*, UV, IR and ^{31}P -NMR spectroscopy, and a potentiometric method were employed to gain more information.

It can be concluded that all the spectroscopic methods employed in this work indicate the existence of different forms of HPAs in aqueous solutions with a considerable dependence on pH with regard to the parent acid. Considering this, literature data are not always consistent due to the complexity of the system; many factors influence the equilibrium, primarily the pH and concentration of the HPA, while the performances of different analytical techniques used for identification should also be taken into account.

Based on the results presented in this paper, the following can be concluded: UV spectroscopy only indicates that some changes occur in the system but they cannot be specified with certainty. IR Spectroscopy gives more information, which enables the identification of the dominant species as a function of the pH of the solution. However, in some cases, because of the similar spectra, it is not possible to perform an exact identification of the major components. NMR Spectroscopy provides unique data which can be employed for more accurate interpretations of the changes in the solutions in dependence on pH.

The presented results indicate that the reaction pathway of MoPA in acidic solution is very complex. Only at pH 1.0 is the parent Keggin anion the dominant molecular form, with additionally two other minor components, $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ and $[\text{Mo}_9\text{PO}_3\text{OH}(\text{OH}_2)_2]^{4-}$. The main component in solutions of pH 2.0 and 3.5 was the lacunary $[\text{PMo}_{11}\text{O}_{39}]^{6-}$ anion. In the solution of pH 5.0, in addition to the lacunary anion, $[\text{P}_2\text{Mo}_5\text{O}_{23}]^{6-}$ and $[\text{PMo}_6\text{O}_{25}]^{9-}$ ions were present. In the solution of pH 7.0, and in more alkaline solutions, complete decomposition to phosphate and molybdate occurred.

The results concerning aqueous solutions of WSiA confirmed that the tungstosilicate is more stable than the molybdophosphate and that the decomposition pathways of WSiA in solution proceed *via* the formation of the lacunary monovacant anion, which decomposes into SiO_4^{2-} and WO_4^{2-} at $\text{pH} > 8.5$. However, in contrast to literature data, it was shown that the Keggin anion structure is preserved over a wide range of pH values, from pH 1.0 to 7.0.

Considering the activity of POMs, it is not sufficient to define only the concentration of the POM, but also the molecular forms of the species present in solution under the experimental conditions. It is important to point out that under physiological conditions WSiA is dominantly present as the Keggin anion, while the parent structure of MoPA is completely destroyed.

These conclusions are of special importance for both biomedical and catalytic applications of heteropolyacids and other compounds of this type and for a better understanding of the mechanism of their activities.

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ИЗВОД

ИСПИТИВАЊЕ 12-СИЛИЦИЈУМВОЛФРАМОВЕ И 12-ФОСФОРМОЛИБДЕНОВЕ КИСЕЛИНЕ У РАСТВОРУ

ДАНИЦА БАЈУК-БОГДАНОВИЋ¹, ИВАНКА ХОЛЦЛАЈТНЕР-АНТУНОВИЋ¹, МАРИЈА ТОДОРОВИЋ²,
УБАВКА Б. МИОЧ¹ И JOANNA ZAKRZEWSKA³

¹Факултет за физичку хемију, б. бр. 47, 11158 Београд 118, ²Хемијски факултет, б. бр. 157, 11001 Београд и
³Институт за општу и физичку хемију, б. бр. 551, 11001 Београд

У раду је систематски испитано понашање две хетерополи-киселине (НРА) различите стабилности у воденом раствору, применом метода UV, IR и NMR спектроскопије и потенциометријске титрације. Показано је да је структура родитељског анјона 12-силицијумволфрамове киселине (WSiA) сачувана у широкој области pH вредности, од 1,0 до 7,0, док је иста структура анјона 12-фосформолибденове киселине (MoPA) присутна само при pH 1,0. Ово значи да је при физиолошким условима WSiA присутна у облику Кегиновог анјона, док је структура анјона МоРА потпуно разграђена до фосфата и молибдата. Добијени резултати су од посебног значаја за биомедицинске и каталитичке примене ових једињења као и за боље разумевање механизма њиховог деловања.

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Spectroscopic study of stability and molecular species of 12-tungstophosphoric acid in aqueous solution

Ivanka Holclajtner-Antunović, Danica Bajuk-Bogdanović, Marija Todorović, Ubavka B. Mioč, Joanna Zakrzewska, and Snežana Uskoković-Marković

Abstract: The various molecular species of 12-tungstophosphoric acid (WPA) in aqueous solutions of different pH values (from 1 to 11.5) were investigated by UV, IR, and NMR spectroscopy. The dependence of the attained equilibrium composition in solution on time, concentration of WPA, and type of buffer used was studied. Obtained results indicate that the buffer type and pH value greatly determine the equilibrium composition in the solution. The Keggin structure of the WPA is sustained only up to pH 1.5. With further increase in pH, the decomposition of Keggin anion does not lead directly to the mono vacant lacunary anion. Between 1.5 and 2.0, the structures with 2 phosphorus atoms from the Dawson series are dominant as intermediate species. In the pH range 3.5-7.5, WPA is present in the form of the monovacant lacunary Keggin anion. These results are of special importance for the biomedical and catalytic applications of heteropoly compounds (HPCs) and for an improved understanding of the mechanism of their functioning.

Key words: heteropolyacids of the Keggin structure, hydrostability, UV, IR and NMR spectroscopy.

Résumé : Faisant appel aux méthodes de spectroscopie UV, IR et RMN, on a étudié diverses espèces moléculaires de l'acide 12-tungstophosphorique (ATP), dans des solutions aqueuses dont les pH s'étalent de 1 à 11,5. On a étudié la relation entre la composition de l'équilibre obtenu et le temps, la concentration en ATP et le type de tampon utilisé. Les résultats obtenus indiquent que le type de tampon et la valeur du pH jouent un rôle considérable sur la composition de l'équilibre en solution. La structure de Keggin pour l'ATP n'est maintenue que jusqu'à un pH de 1,5. Avec des augmentations supplémentaires de la valeur du pH, la décomposition de l'anion de Keggin ne conduit pas directement à l'anion lacunaire monovacant. Entre 1,5 et 2,0, les structures comportant deux atomes de phosphore des séries de Dawson sont les espèces intermédiaires dominantes. Dans la zone de pH allant de 3,5 à 7,5, l'ATP est présent sous la forme de l'anion lacunaire mono vacant de Keggin. Ces résultats sont particulièrement important pour les applications biomédicales et catalytiques des composés hétéropolyacides (CHP) et pour une meilleure compréhension du mécanisme de leur fonctionnement.

Mots-clés : hétéropolyacides de la structure de Keggin, hydrostabilité, spectroscopies UV, IR et RMN.

[Traduit par la Rédaction]

Introduction

Polyoxometalates (POMs), made up of a great number of structures and compositions, constitute a large category of compounds that are interesting for theoretical investigations and practical applications. Their applications are based on

their unique properties including size, mass, structure, electron and proton transfer/storage abilities, thermal stability, labile nature of lattice oxygen, and high Brönsted acidity of the corresponding acids. Therefore, POMs are used as good catalysts, superionic proton conductors, compounds with photoconductive and magnetic characteristics, reagents in analytical chemistry, and biochemically active species (1-6).

The properties of POMs in the solid state are rather well-established, but their behavior in solutions is not well explained in spite of numerous publications. The behavior of these compounds in solution is important from the aspect of their formation and degradation but particularly from the aspect of their analytical, biomedical, and catalytic applications.

In medicinal chemistry, POMs that are generally nontoxic to normal cells, exhibit highly selective inhibition of enzymes and antitumoral, antiviral, antibacterial, and anticoagulant activities (1-4, 6-7). However, a fundamental limitation in their application in physiological media in vitro and in vivo derives from their inorganic nature and in their con-

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I. Holclajtner-Antunović, D. Bajuk-Bogdanović, and U.B. Mioč. Faculty of Physical Chemistry, University of Belgrade, P.O.Box 47, 11158 Belgrade, Serbia.
M. Todorović. Faculty of Chemistry, University of Belgrade, P.O.Box 157, 11001 Belgrade, Serbia.
J. Zakrzewska. Institute of General and Physical Chemistry, P.O.Box 551, 11001 Belgrade, Serbia.
S. Uskoković-Marković.¹ Faculty of Pharmacy, University of Belgrade, P.O.Box 146, 11001 Belgrade, Serbia.

¹Corresponding author (e-mail: snezaum@pharmacy.bg.ac.yu).

sequent instability in aqueous solutions. Namely, the problem of all biological and medical investigations of POMs relates to whether these compounds remain in their original molecular form during biomedical treatment. Generally, research articles consider the parent form of POMs anion as active, which is generally not the case. To consider and elucidate the proper mechanism of biomedical activity of POMs, it is indispensable to identify the real active molecular species present under physiological conditions, which is the main subject of this study.

Because of their properties, POMs have also been used as homogeneous and heterogeneous catalysts in oxidation reactions, in acid-catalyzed reactions, and as bifunctional catalysts (1–4, 8, 9). To improve the catalytic characteristics of these compounds and to follow the mechanism of catalytic processes, the formation of activation complexes, as well as the formation of complex catalysts on different supports by sol-gel processes or impregnation, it is essential to specify the nature of the active species present.

In spite of extensive study of stability and reaction pathways of heteropoly acids (HPAs) mostly of the Keggin type in solution, the obtained results and conclusions often are confusing and not in agreement, although obtained under similar experimental conditions (1, 4, 10–15).

Keper and Kyle (16, 17) have studied the decomposition of the Keggin anions containing silicon, phosphorus, or boron as the central heteroatom and tungsten as an addenda metal atom. They have found that the equilibrium reaction in the solution proceeds in three distinct stages with $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ and $[\text{SiW}_9\text{O}_{34}]^{10-}$ as intermediates. A few years later, stopped-flow kinetics studies of 12-molybdophosphate formation and decomposition were performed by Kircher and Crouch (18). Molybdophosphate complexes in aqueous solutions have been identified by ^{31}P NMR and Raman spectroscopy and differential pulse polarography (19), while ^{31}P NMR spectroscopy was applied to the stability study of HPAs by the rate of exchange of structural units between 12-tungstophosphoric acid (WPA) and 12-molybdophosphoric acid (MoPA) (15). Detusheva et al. (20) identified decomposition products of tungstophosphoric acid during its titration with NaOH up to pH 7.8 by NMR, IR, and Raman spectroscopy. McGarvey and Moffat (13) followed the major species present in tungstophosphate and molybdophosphate solutions as a function of pH by NMR and IR spectroscopy. They found that both acids decompose to the lacunary form of the Keggin anion that further decomposes to a phosphate species in alkaline solutions. The tungstophosphate system has been investigated over a wide range of pH (1–12) using preparation high performance liquid chromatography combined with IR, UV–vis, and ^{31}P NMR and ICP spectroscopy (21, 22). Smith and Patrick applied ^{31}P and ^{183}W NMR spectroscopy to the detailed study of tungstophosphoric and tungstosilicic acids in aqueous solutions (23–25). Identification and quantitative determination of the species present in these systems as a function of pH have been performed after a few months, which was considered an appropriate time for attaining equilibrium. Investigations of equilibria of α - and β -isomers of WPA as a function of pH have shown that β -type lacunary complexes are precursors for the formation of β -PW₁₂, and

that β -type lacunary complexes always coexist with the corresponding α -type lacunary complexes (26).

On the basis of all these results, it can be concluded that the hydrolytic stability of HPAs depends on the anion structure, nature of the heteroatom, and peripheral metal atom that comprise the anion, as well as on the solution conditions. It is generally accepted that most POMs based on W or Mo are stable in acid solution, degrade in a complex way into a mixture of inorganic products with increasing pH and are totally decomposed in alkaline medium. However, the influence of buffer type on equilibrium composition has not been studied thus far. Also, the time data needed for establishing the equilibrium state and possible reversibility of the considered system when pH was increased and (or) decreased, were also not available.

The aim of this paper is to pay attention to the importance of molecular species of 12-tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) in aqueous solutions of various pH, adjusted by addition of NaOH and HCl or by applying TRIS and acetate buffers. It is necessary to emphasize that TRIS and acetate buffers are frequently applied for pH adjustment when HPAs are used for biochemical and biomedical applications. For this purpose, three different spectroscopic methods were applied and their results were summarized and compared, to determine the dominant species present in solutions of various pH, with special attention to physiological conditions. The equilibrium composition of the solution was investigated for various buffers and for different time intervals. It was established that phosphate buffer is not appropriate for biochemical studies. The reversibility of the reaction pathway in the considered system, in which pH was increased to the values when the Keggin anion is decomposed and then decreased back to the pH values when it is formed, was also studied.

Experimental

Materials

WPA was prepared according to the literature method (27), recrystallized prior to use, and confirmed by IR spectroscopy. All chemicals were of analytical grade and were provided by Merck.

Methods

The pH of the solutions was adjusted with addition of NaOH, HCl and acetate, TRIS, and phosphate buffers and measured using a pH meter with a glass electrode. Solution pH was monitored until no apparent changes were observed.

UV spectra of aqueous solutions of 2×10^{-5} mol/dm³ of WPA were obtained by the Cintra 10e (GBS) spectrophotometer.

Solid samples for IR measurements were obtained after evaporation of water from solutions of 5×10^{-2} mol/dm³ WPA of different pH. The IR spectra were recorded on a PerkinElmer 983G spectrophotometer using the KBr pellet technique in the wavenumber range 1500–300 cm⁻¹.

The sample solutions for NMR measurements were prepared by adding the estimated quantities of NaOH or buffer solutions just after dissolving. The NMR experiments were carried out with a Bruker MSL 400 spectrometer at 161.978 MHz. The concentration of WPA was 5×10^{-2} mol/dm³, with 2048 scans, 9.0 μs pulse, and 500 ms repetition time at 25 °C. Sample volume was about 2.5 mL

in a 10 mm tube. A metilenediphosphonate (MDP) solution of 17.05 ppm was used as the external reference relative to 85% H_3PO_4 .

Results and discussion

UV spectra

The electronic spectra of HPAs of the Keggin structure exhibit two intense absorption bands in the UV range, with maxima at about 200 and 260 nm attributed to the transitions $\text{O}_d \rightarrow \text{M}$ and $\text{O}_b/\text{O}_c \rightarrow \text{M}$, respectively, (28).

The UV spectra of aqueous solutions of WPA of various pH are presented in Fig. 1. At pH 1, the absorption band maximum is at 263 nm, which corresponds to electron transition $\text{O}_b/\text{O}_c \rightarrow \text{M}$ of the parent Keggin's anion and is shifted to 252.5 nm at pH 3.5. If pH is increased to 7 by adding NaOH, the band maximum remains at the same position.

The further increase in pH to 11.5 causes the disappearance of this band, confirming the destruction of the parent Keggin structure. These results indicate the existence of various structural forms in pH regions: up to 2, from 3.5 to 7, and above 8.5, but it is hard to identify the individual formed products.

Our results are only partly in accordance with the findings of Z. Zhu et al. (21) who applied UV spectra for the identification of components eluted from an HPLC instrument. Namely, they identified the maximum absorption at 244 nm of the main component at pH 3.5 and 5.4 as $[\text{PW}_{11}\text{O}_{39}]^{7-}$. Our results show that the component with maximum absorption at 252.5 nm is stable in the pH region from 3.5 to 7.0. The differences can be explained by different experimental conditions, because the mentioned authors applied HPLC for the separation of decomposition products of WPA, where besides pH changes there is a continual change in eluent composition.

It is evident that pH influences the stability of WPA. All changes in the UV spectra of WPA solutions of different pH can be attributed to changes in the structure of an individual HPA at various pH values, but it is difficult to derive conclusions about the nature of the observed changes and identify the new formed products.

IR spectra

IR spectra of evaporated and dried sample solutions were recorded over the pH range 1 to 11.5, as in the case of UV spectra. IR spectra of dry residua of WPA solutions of different pH are presented in Fig. 2, while Table 1 summarizes the positions and intensities of some IR absorption bands. The bands of Na_2WO_4 are given for comparison.

The spectrum of WPA at pH 1 (5×10^{-2} mol/dm³ of WPA, with no addition of HCl) is equivalent to the spectrum of solid WPA. This spectrum possesses vibration bands characteristic of the Keggin anion: 1080, 990, 890, and 810 cm^{-1} , corresponding to vibrations $\nu_{\text{as}}(\text{P}-\text{O}_a)$, $\nu_{\text{as}}(\text{W}-\text{O}_d)$, $\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W})$, and $\nu_{\text{as}}(\text{W}-\text{O}_c-\text{W})$, respectively (29). It can be noticed that already at pH 2, bands associated with the Keggin anion are modified; some bands have disappeared, while new bands have appeared and remained to pH 7. Based on the obtained spectra, it can be observed that the stretching P-O vibration at 1080 cm^{-1} is split into two bands at 1100 and 1050 cm^{-1} . This indicates the existence of an anion structure with lower

Fig. 1. UV spectra of WPA solutions at varying pH.

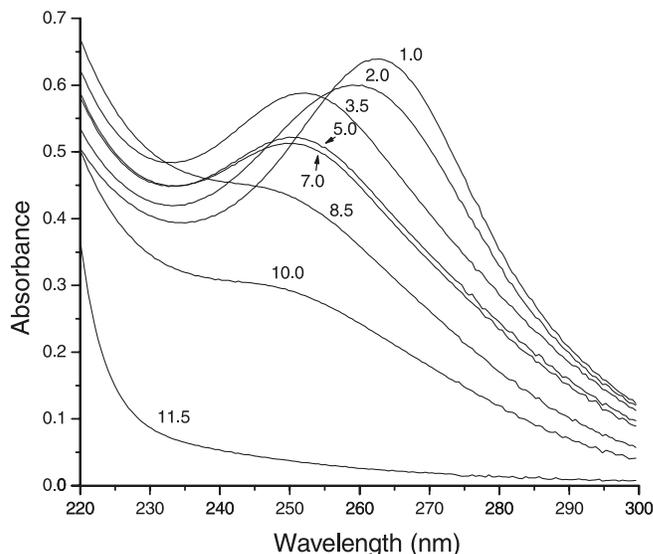
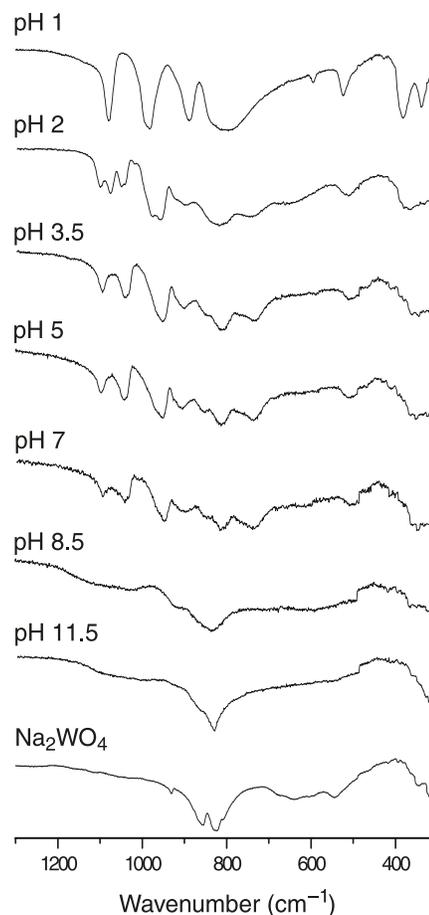


Fig. 2. IR spectra of evaporated WPA solutions at varying pH and Na_2WO_4 .



symmetry than T_d symmetry of the Keggin anion. Such a structure can be the lacunary $[\text{PW}_{11}\text{O}_{39}]^{7-}$ that belongs to the C_s symmetry group, or a structure with two P atoms such as $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ with C_{3v} symmetry. Typical bands that characterize the former monolacunary structure (arising by remov-

Table 1. Vibration bands of dry residua of WPA solutions of various pH and of sodium tungstate.

Vibration bands (cm ⁻¹)								
pH 1	pH 2	pH 3.5	pH 5	pH 7	pH 8.5	pH 10	pH 11.5	Na ₂ WO ₄
	1102m	1097m	1096m	1097m				
1079s	1078s							
	1052m	1042m	1042m	1044m				
982vs	980s							
	960s	956s	951s	950s				
	920sh							
888s	902w	903w	905w	900w	910sh			
		850sh	852vw	850sh				855s
	821s,b	816s,b	812m	819m	935s,b	835s,b	835s,b	822s
795vs,b								
	747w,b	742m,b	730m,b	742m,b				
	664w,b							
593w								
523m	514w	515w,b	504w,b	513w,b				
381s	380sh							
	368m							
		350m,b	350w,b	350w,b				
338m	330sh							

Note: Very strong (vs), strong (s), medium (m), weak (w), shoulder (sh), broad (b).

ing one WO unit from the Keggin anion) are 1085, 1040, 950, 900, 860, 810, and 725 cm⁻¹ (30). The latter is the Dawson structure characterized by bands at 1108, 1050, 957, 920, 885, 818, and 735 cm⁻¹ (13). There are also some slight changes in the spectrum related to the spectra of the Keggin anion's structure: bands at about 1050 and 990 cm⁻¹ are split, while the band at about 900 cm⁻¹ has a shoulder at 920 cm⁻¹.

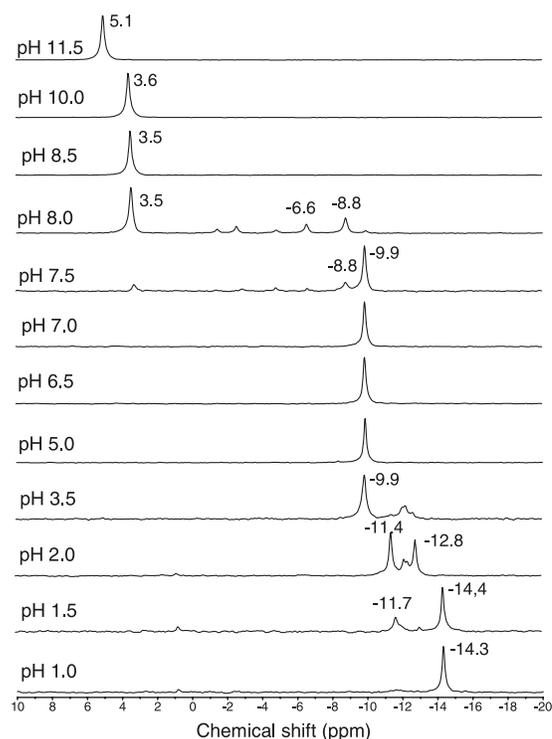
IR spectra present further improvements in identification of dominant chemical species present in HPA solutions of various pHs, compared with UV spectra. However, bearing in mind that characteristic bands of the components of the Dawson series are close to the characteristic bands of the lacunary Keggin structure, it is difficult to recognize and identify properly all the structures present. The IR spectra at higher pH values indicate the total degradation of the parent anion to tungstate and phosphate anions.

NMR spectra

To overcome the drawbacks of UV and IR spectroscopy in the identification of tungstophosphate species in solutions of various pH values, a complementary sensitive method of ³¹P NMR was applied.

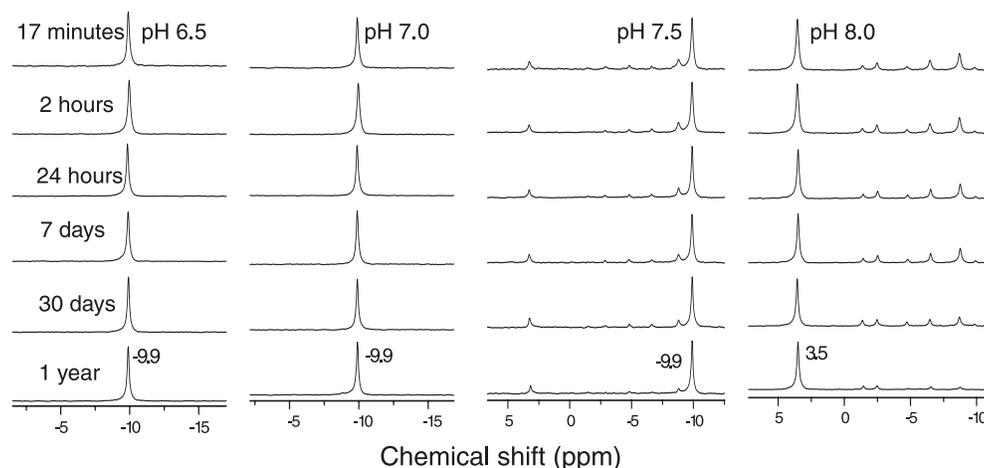
The ³¹P NMR spectra of WPA samples over the pH range 1 to 11.5 are presented in Fig. 3. Literature values of chemical shifts were used for the identification of ions formed in solutions. As can be seen, the parent Keggin anion [PW₁₂O₄₀]³⁻ can be easily recognized through its intense single signal at -14.3 ppm (13, 20–22, 25, 31–33). This signal was observed as dominant under our experimental conditions at pH 1 and 1.5, while at pH 2 this peak disappeared.

A few peaks near -12 ppm appear at pH 1.5 and 2. These peaks can be assigned to the structures with 2 phosphorus atoms from the Dawson series, such as [P₂W₂₁O₇₁]⁶⁻, [P₂W₁₈O₆₂]⁶⁻, and [P₂W₂₀O₇₀]¹⁰⁻ (25, 33, 34). With further

Fig. 3. ³¹P NMR spectra of WPA solutions at varying pH.

increases in pH, the peaks at ca. -12 ppm remain at pH 3.5, but their intensities decrease, while a dominant peak appears at ca. -9.9 ppm, which corresponds to the lacunary Keggin anion [PW₁₁O₃₉]⁷⁻ (25, 34, 35). This peak remains the only one in the spectra of solutions of pH up to 7. Analysis of NMR spectra indicates the complex decomposition scheme of the Keggin anion in acidic region that does not lead directly to the lacunary monovacant anion, which was stated

Fig. 4. ^{31}P NMR spectra of WPA solutions of pH 6.5, pH 7.0, pH 7.5, and pH 8.0, recorded 17 min, 2 h, 24 h, 7 days, 30 days, and one year after preparation of solutions.



previously (13). Our results confirm the findings of Smith and Patrick (25) that under these conditions, structures with 2 phosphorus atoms of the Dawson series are formed before their degradation to lacunary monovacant anions in the pH range from 3.5 to 5.

Because of the importance of the pH region found in physiological systems for biomedical investigations and in order to determine exactly the region of existence of the $[\text{PW}_{11}\text{O}_{39}]^{7-}$ anion, the NMR spectra are recorded for the pH values between 6.5 and 8.5, at each 0.5 pH. It is evident from these spectra that up to pH 7, the lacunary anion is the only structure present in the solution. At pH 7.5, which almost corresponds to physiological conditions, some other products also appeared in addition to the dominant lacunary anion. The change in pH from 7.5 to 8.0 causes complete destruction of the $[\text{PW}_{11}\text{O}_{39}]^{7-}$ anion and an increase in the intensity of the other peaks. The most intensive peak corresponds to the phosphate anion. One of the peaks, -8.8 ppm, corresponds to $[\text{P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]^{14-}$ and another at -6.6 ppm corresponds to $[\text{PW}_9\text{O}_{34}]^{9-}$. It can be supposed that the former consists of two $\text{PW}_9\text{O}_{34}^{9-}$ units bridged by one WO_2 group (25, 35). That is, in the pH range 7.5–8, in the course of decomposition of the major anion $[\text{PW}_{11}\text{O}_{39}]^{7-}$ to $[\text{PW}_9\text{O}_{34}]^{9-}$ and other unidentified species (corresponding to peaks with higher chemical shifts), some of the $[\text{PW}_9\text{O}_{34}]^{9-}$ anions dimerize, producing $[\text{P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]^{14-}$. It is obvious that in this narrow pH region (7.5–8) the dramatic decomposition of tungstophosphates occurs. In spectra of alkaline solutions of pH > 7.5 , a total degradation to phosphate and tungstate is observed. A peak appeared at different chemical shifts, corresponding to the protonated phosphate anions, $[\text{H}_2\text{PO}_4]^{-1}$, $[\text{HPO}_4]^{2-}$, and $[\text{PO}_4]^{3-}$.

As mentioned in the introduction, literature data are not always in accordance. Thus, Nomiya et al. (36) have studied the insulin mimetic effect of POMs with Dawson structure and their stability, varying their concentration in the range 1.0–30.0 mmol/L. They found only one peak at -12.7 ppm in the ^{31}P NMR spectra due to the $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ anion in pH range 5.37–5.77, while a minor peak at -9.7 ppm assigned as the Preyssler $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ structure appeared in addition to the main peak at ca. -12.6 ppm in the pH range 4.7–5.09. Our results and those of Smith and Patrick (25) show

that the mentioned species are not stable at pH > 4.7 . The findings in (36) related to the acidic region, for pH below 2.0, are in complete accordance with ours. It should be underlined again that the right explanation of any biochemical effects is impossible without proper and detailed knowledge of the considered system.

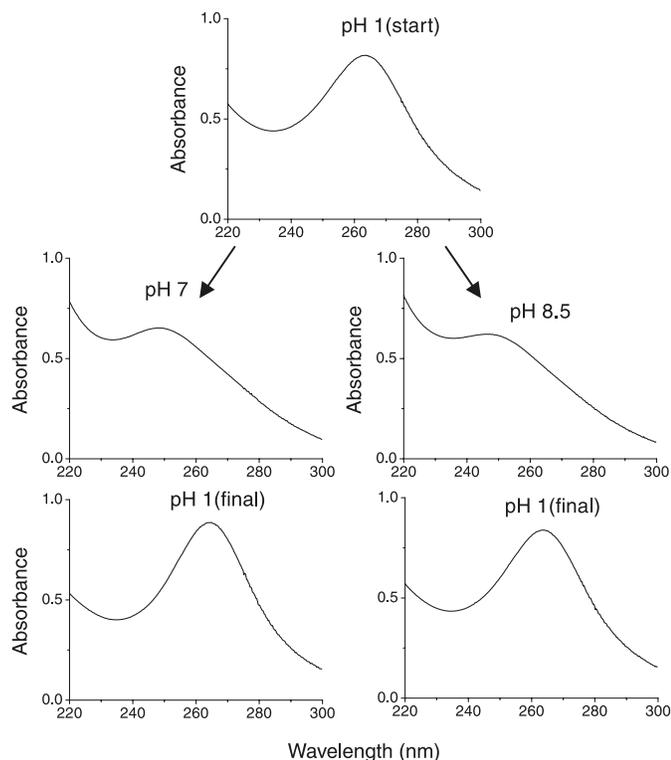
Time stability

In numerous studies of POMs, various time intervals for synthesis of the compounds were used. Thus, it could be very useful to consider the influence of time interval on WPA solutions stability in the range of pH between 6.5 and 8.0, which is very important for biomedical investigations. In Fig. 4 are shown ^{31}P NMR spectra of WPA solutions of several pH values (6.5, 7.0, 7.5, and 8.0), recorded immediately after preparation, after 2 h, 24 h, 7 days, 30 days, and one year, while kept at room temperature. All spectra confirmed pH stability of WPA solutions in the time ranges, except for minor changes in the spectra for pH 8.0 after one year, when total degradation of WPA was almost complete. It can be seen that the peaks at -8.8 and -6.6 ppm, corresponding to $[\text{P}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]^{14-}$ and $[\text{PW}_9\text{O}_{34}]^{9-}$, respectively, slowly disappear with time.

Reversibility

Identification of species existing in solution by UV, IR, and ^{31}P NMR spectra was used to investigate the reversibility of the reaction pathway of WPA degradation and formation during pH changes. By adding NaOH to the WPA solution, pH is raised from pH 1 to 7 and to 8.5; then by HCl addition, pH was decreased back to pH 1. Figure 5 shows UV spectra obtained for solutions of 2×10^{-5} mol/dm³ of WPA, where pH is changed from 1 to 7 (left side of figure) and from 1 to 8.5 (right side), and then changed back to 1. These data show that the absorption band maximum at 263 nm, characteristic for the Keggin anion at pH 1, disappears at pH 7 but appears again when pH 1 was attained. IR spectra of dried solutions of 2×10^{-2} mol/dm³ concentration, where pH values were changed as in the case of UV spectra, confirmed that the Keggin anion is formed almost completely when pH was changed from 7 to 1, while in the case of pH 8.5 the reversibility is not complete (Fig. 6). ^{31}P NMR

Fig. 5. UV spectra of WPA solutions at several pH values after HCl addition (left) in solution with pH 7 and (right) in solution with pH 8.5.

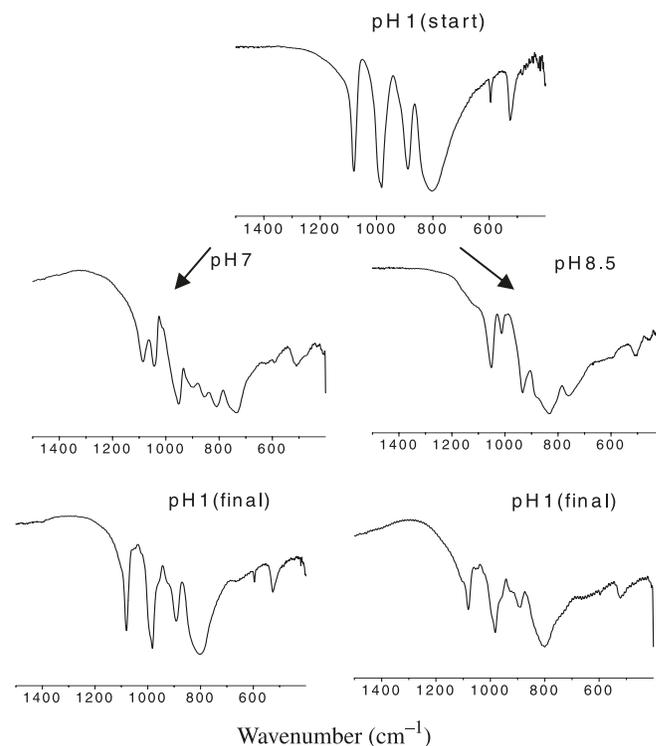


spectra of the solution, with concentration and pH values as in IR measurements (Fig. 7), also show that reversibility is not complete. A peak at -14.3 ppm, characteristic for the Keggin anion, is dominant but there are also peaks at ca. -13 ppm, indicating the presence of species of the Dawson series. Therefore, it could be concluded that there is not complete but partial reversibility during the changes in pH, in the case of higher concentrations of WPA. Also, it is evident that concentration is also a parameter that determines the equilibrium of different forms in solutions of HPCs.

Buffered solutions

In *in vitro* experiments where heteropoly compounds are used as biochemical agents, pH values are usually adjusted by different buffers. For this kind of investigation, TRIS and phosphate buffers are most commonly used. However in the case of WPA, the use of phosphate buffer is not possible because of its interaction with WPA, i.e., destruction and precipitate formation. For pH values lower than physiological levels, acetate buffer could be used. Therefore, ^{31}P NMR and UV spectra are recorded for aqueous solutions of WPA buffered with acetate and TRIS buffers, and results are presented in Figs. 8 and 9. It is evident that the application of acetate buffer causes no change in UV and ^{31}P NMR spectra (spectra are identical to those obtained for solutions whose pH was adjusted with addition of NaOH). But it is evident that TRIS buffer at pH 7 causes the formation of lacunary WPA anion as dominant along with some other phosphorus-containing polytungstophosphates. Therefore, the application of this buffer is not recommended in such experiments. The

Fig. 6. IR spectra of evaporated WPA solutions at several pH values after HCl addition (left) in solution with pH 7 and (right) in solution with pH 8.5.



results indicate that in biochemical applications of POMs, the buffer type must be chosen with care because of its significant importance for the obtained biochemical effects and their elucidation.

Conclusions

It can be concluded that all spectroscopic methods used in this work indicate the instability of WPA in aqueous solutions and considerable dependence on pH with regard to the dominant species present in the solution. Considering this, literature data are not always consistent because of the complexity of the system; many factors influence the equilibrium, primarily pH and HPA concentration, while the performance of different analytical techniques used for speciation should be taken in account as well. The concentration of the HPA in unbuffered solution can affect the pH (23). We have observed that plant juices can affect the pH and the observed structures, as seen by UV and NMR measurements (37).

Based on the results presented in this study, the following can be concluded. UV spectroscopy only indicates that some changes occur in the system but they cannot be specified. IR spectroscopy gives more information that is the basis for the identification of the dominant species as a function of the pH of the solution. However in some cases of similar spectral data, it is not possible to perform exact identification of major components. NMR spectroscopy provides unique data, which can be used for more accurate interpretation of changes in the solutions of various pH values, but is applica-

Fig. 7. ^{31}P NMR spectra of WPA solutions at pH 7.0 and 8.5 after HCl addition (left) in solution with pH 7 and (right) in solution with pH 8.5.

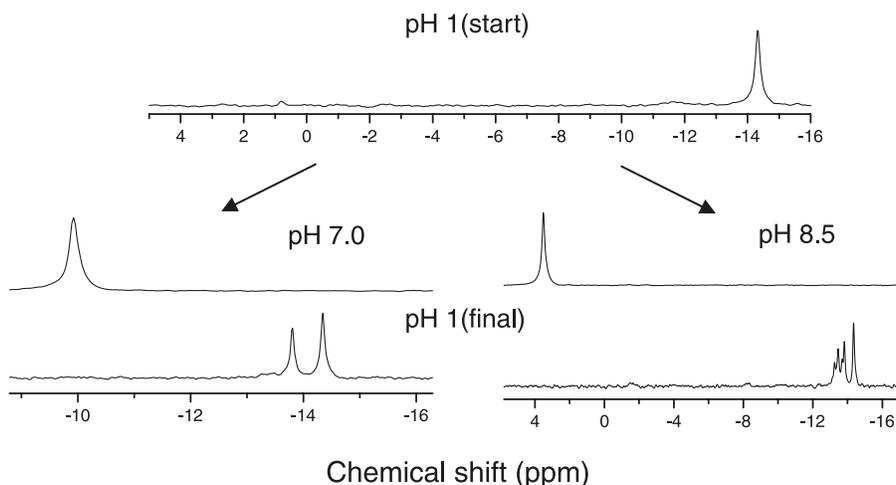
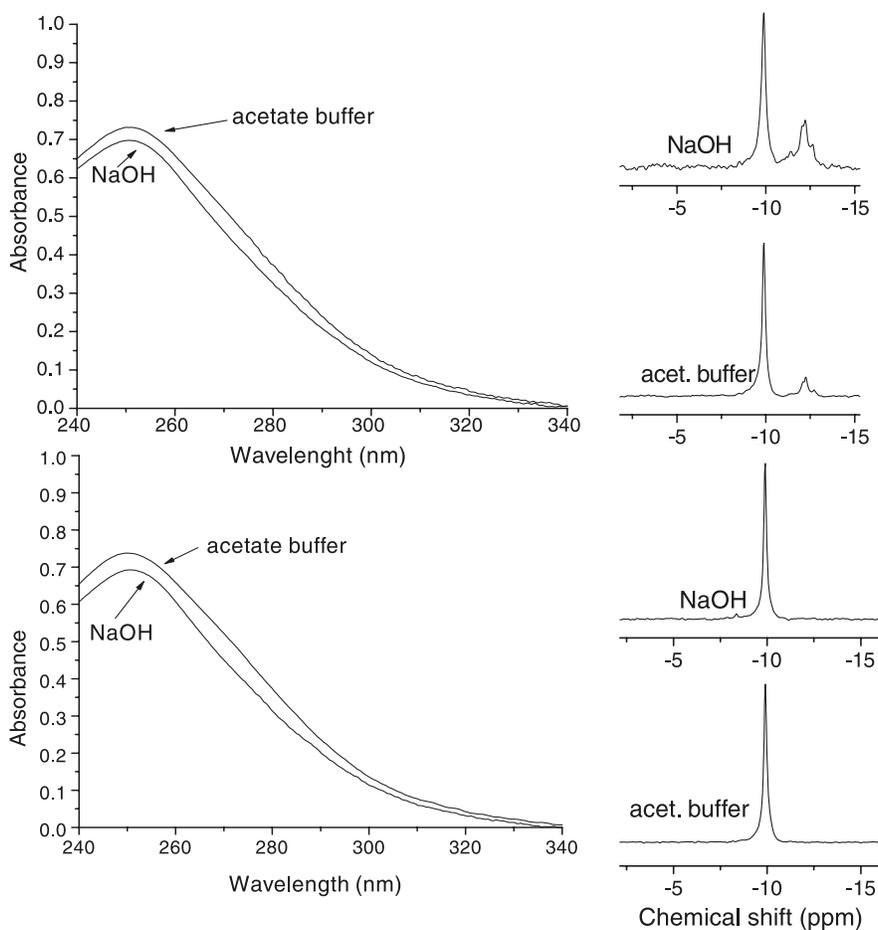


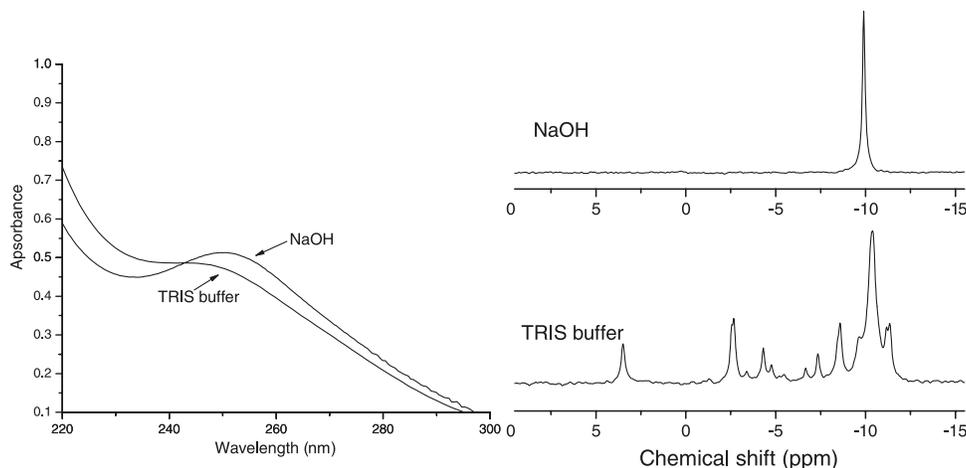
Fig. 8. (left) UV spectra and (right) ^{31}P NMR spectra of WPA solutions at (top) pH 3.5 and (bottom) pH 5 adjusted by acetate buffer and NaOH.



ble to higher concentrations as used in this work. Given that the behavior and nature of heteropoly and isopoly compounds is very complex, one must bear in mind whether the conclusions obtained for very low concentrations (e.g., $0.01\text{--}0.0001\text{ mol L}^{-1}$) when using UV spectrometry, can be

applied to higher concentrations (ca. 0.1 mol L^{-1}) of HPAs when IR and NMR spectrometry were employed to follow various species present in the equilibrium system.

The results presented indicate that in the case of aqueous solutions of WPA, the parent anion is present only in a very

Fig. 9. (left) UV spectra and (right) ^{31}P NMR spectra of WPA solution at pH 7 adjusted by NaOH and TRIS buffer.

acidic solution of ca. pH 1. It should be pointed out that in aqueous solution, WPA decomposes first to components of the Dawson series, $[\text{P}_2\text{W}_{21}\text{O}_{71}]^{6-}$, $[\text{P}_2\text{W}_{20}\text{O}_{70}]^{10-}$, and $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ in the pH range 1–3.5. With further increases in pH greater than 3.5, these species convert to the lacunary monovacant anion, $[\text{PW}_{11}\text{O}_{39}]^{7-}$, which is a major constituent in pH range up to 7.5. In the narrow pH range 7.5–8.0, remarkable changes occur; $[\text{PW}_{11}\text{O}_{39}]^{7-}$ decomposes to $[\text{PW}_9\text{O}_{34}]^{9-}$, but other tungstophosphate ions are also observed. The total decomposition of the Keggin anion to phosphate and tungstate occurs at $\text{pH} > 7.5$.

Some differences in interpretation of the molecular species present under various experimental conditions can be ascribed to some extent to the diversity of chemical shifts data of NMR found in the literature.

In the pH region 6.5–7.5, the equilibrium composition is established quickly after solution preparation, and the monovacant lacunary form of WPA is stable for a period of one year.

UV spectrometry has shown that when changing pH from 1 to higher values and back to pH 1 in a 2×10^{-5} mol/dm³ aqueous solution of WPA, the reversibility of changes in molecular structures is completely attained. But for solutions of higher concentration, 0.05 mol/dm³, the changes are not reversible. That is, when the pH of the solution is adjusted again to pH 1, the Keggin anion is formed only partially, and other molecular forms of the Dawson series are present as well.

The molecular forms present in the equilibrium system under specific conditions depend significantly on the buffer type. Therefore, the choice of buffer used for maintaining the physiological conditions must be made with care to attain the appropriate biochemical effect of POMs.

Under physiological conditions attained with the addition of NaOH, WPA is dominantly present in the form of the lacunary monovacant anion. This is of special importance for biomedical application of heteropoly acids and other compounds of this type.

The results presented have shown that before any use of HPCs as biochemical or biomedically active compounds and as catalysts, it is necessary to control their behavior under defined conditions. Without that, it is not possible to discuss

the equilibrium between different forms of heteropoly anions and any mechanism of reactions.

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Spectroscopic identification of molecular species of 12-tungstophosphoric acid in methanol/water solutions

I. Holclajtner-Antunović^a, D. Bajuk-Bogdanović^a, A. Popa^b, S. Uskoković-Marković^{c,*}

^a Faculty of Physical Chemistry, University of Belgrade, P.O. Box 47, 11158 Belgrade, Serbia

^b Institute of Chemistry Timișoara, Bl. Mihai Viteazul 24, 300223 Timișoara, Romania

^c Faculty of Pharmacy, University of Belgrade, P.O. Box 146, 11001 Belgrade, Serbia

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ABSTRACT

The various molecular species formed by decomposition of 12-tungstophosphoric acid (WPA) in methanol/water solutions of different composition, and over a pH range 1–12, were identified by UV, FTIR, micro Raman and ³¹P NMR spectroscopy. The dependence of stability on organic solvent amount, pH and concentration of WPA in solution is investigated in detail.

It is shown that addition of methanol in aqueous solution of WPA with varied pH causes extension of the pH region where parent Keggin anion is stable. While Keggin anion is preserved in aqueous solution with pH < 2, in solution with 25% of methanol it is stable up to pH 2.5, in solution with 50% of methanol up to pH 3.5, and in solution with 75% of methanol Keggin anion is observed up to pH 4.5.

Various molecular species, such as monovacant and trivacant lacunary Keggin structures and dimeric Wells–Dawson derivatives, are observed as a result of Keggin anion destruction with increasing of pH, but speciation in both aqueous and methanol/water solutions is similar. It is also shown that lacunary anions are less soluble in solutions with higher methanol content and with higher pH. In aqueous solution at pH > 8, the solution contains only tungstates and phosphates with no precipitation. In solution with 25% of methanol, precipitate is formed at pH 8.0 and contains trivacant lacunary Keggin anion. In solution with 50% of methanol the precipitation is at pH 6.5, and in solution with 75% of methanol it is observed at pH 4.5, but in both solutions the precipitate contains monovacant lacunary anion as the main component.

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1. Introduction

The 12-tungstophosphoric acid, H₃PW₁₂O₄₀·nH₂O (WPA), a heteropoly acid (HPA) of tungsten (VI) and phosphorus (V), belongs to a large class of nano-sized early transition metal oxygen ion complexes called polyoxometalates (POMs). The basic structural unit of WPA is the Keggin anion (PW₁₂O₄₀)³⁻ consisting of the central PO₄³⁻ tetrahedron surrounded by twelve WO₆ octahedral [1,2]. The Keggin anions are interconnected by hydrogen-bonded water molecules forming, in solid state, a unique ionic structure consisting of heteropolyanions and counteranions, which underlines the distinctive and unusual physicochemical properties of POMs and make them exceptionally suitable for various applications (superionic proton conductors, catalysts, analytical reagents, sensors, etc.) [3–5]. For the last three decades, HPAs and their derivatives have been used successfully in redox and acid catalyzed reactions, both in homogeneous and heterogeneous phases in the laboratory and in industrial scales [3–9]. In recent years the interest for POMs application in medicinal chemistry has increased. These compounds

are generally nontoxic to normal cells, exhibit highly selective inhibition of enzymes, and exhibit antitumoral, antiviral, antibacterial and anticoagulant activities [10–12]. Due to both the high industrial relevance of this class of compounds as effective catalysts for a variety of reactions, and their importance in medicinal applications, information of their structural stability under various experimental conditions is essential. The knowledge of structural transformations of HPAs during catalyst activation or biochemical interactions is important suppositions for fundamental understanding of the mechanism of the considered processes and thus improvement of their efficiency.

HPAs are not stable in aqueous solutions and several molecular species exist in equilibrium depending on the pH of the solution [13–22]. The Keggin anion is present only in a very acidic solution of ca. pH 1, while with increase in pH it is decomposed to various components.

In order to increase stability of HPAs in solutions, organic solvents are added to the aqueous solutions of HPAs. Thus, the loading of HPAs on various supports by sol–gel or wet incipient methods is performed from aqueous–organic solutions. It is also shown that catalysts prepared using methanol solvent gave a higher catalytic activity for the alkylation of iso-butane with 2-butene than those

* Corresponding author.

E-mail address: snezaum@pharmacy.bg.ac.rs (S. Uskoković-Marković).

prepared from aqueous solvent [23]. Furthermore, the electrochemical and redox properties of HPAs could be tuned by replacing aqueous by organic solvents [24]. It is revealed that the redox potential and the number of transferred electrons can be controlled by proper choice of POMs, organic solvents and cations constituting supporting electrolytes, thus improving electrocatalytic activity of POMs [25,26]. The synthesis of various molybdophosphates as well as the α - and β -Keggin type $[\text{PW}_{12}\text{O}_{40}]^{3-}$ and α - $[\text{H}_3\text{W}_{12}\text{O}_{40}]$ are highly dependent on solvent composition [27–30]. The substitution reaction of the molybdenum or tungsten unit in the Keggin-anions with vanadium(V) ion depends on the total anion charge and the permittivity of organic solvents $[\text{XM}_{12}\text{O}_{40}]^{n-}$ [31,32].

All the mentioned indicate that nonaqueous chemistry of POMs is obviously important for various applications, is very complex, and is dependent on many factors.

There is no detailed study and explanation of the behavior of WPA in organic solvents and/or their mixture with water. Actually, most of available data considered the molybdophosphate or molybdosilicate anions' behaviors. Therefore, this paper screens the stability and molecular speciation of WPA in aqueous-methanol solutions, as a model system, under different pH's, through FTIR, Raman, ^{31}P NMR and UV spectroscopy.

2. Experimental

2.1. Materials

WPA was prepared according to the literature [33], recrystallized prior to use and confirmed by infrared spectroscopy. All chemicals were of analytical grade, provided by Merck. Samples were prepared as solutions either in distilled water or in methanol/distilled water mixtures of different concentrations.

2.2. Methods

The pH of the solutions was adjusted with addition of NaOH or HCl and measured using a pH meter with a glass electrode.

UV spectra of solutions of 2×10^{-5} mol/dm³ of WPA were obtained by the Cintra 10e (GBS) spectrophotometer.

Solid samples for IR measurements were obtained after evaporation of water/methanol from solutions of 5×10^{-2} mol/dm³ WPA of different pH. The IR spectra were recorded on Thermo Nicolet 6700 using the KBr pellets technique, in the wave number range from 1500 cm⁻¹ to 400 cm⁻¹ with 64 scans per spectrum and 2 cm⁻¹ resolution.

The Raman spectra of sample solutions of 5×10^{-2} mol/dm³ were recorded on Thermo DXR Raman microscope, using the fiber optic probe with the 780 nm laser excitation line, with a constant power of 150 mW, exposure time of 5.00 s, with repetition of 20, grating of 400 lines/mm, spectrograph aperture of 25 μm slit and resolution of 8 cm⁻¹. The spectra were recorded *in situ*, after the adjustment and stabilization of pH in solution. The aliquot of 1 mL of solutions with different pH were dried and Raman spectra of solid residua were recorded under microscope, using the 532 nm laser excitation line, with a constant power of 10 mW, exposure time of 10.00 s, number of exposures of 10, grating with 1800 lines/mm, spectrograph aperture of 25 μm pinhole and resolution 2 cm⁻¹.

The NMR experiments were carried out on a Bruker MSL 400 spectrometer at 161.978 MHz, with 2048 scans, 9.0 μs pulse and 500 ms repetition time at 25 °C. A metilenediphosphonate (MDP) solution of 17.05 ppm was used as the external reference relative to 85% H₃PO₄. The concentration of WPA was 5×10^{-2} mol/dm³ and sample volume of about 2.5 mL was put in a 10 mm tube.

The contents of tungsten and phosphorus were determined by ICP–OES, using a Thermo Scientific iCAP 6500 Duo ICP spectrometer,

sodium by a PerkinElmer AAAnalyst 300, and H by an Elemental Analyzer VARIO EL III (Elementar).

3. Results and discussion

3.1. pH measurements

The direct comparison of aqueous and water–methanol pH values is limited. The operational definition of pH is dependent on the autoprotolysis constant of the solvent and liquid junction potential effects will differ. Several studies have been made on pH measurements in water–methanol mixtures [34–37]. In particular, the apparent pH differences between aqueous and water–methanol mixtures increasingly differ with increasing methanol quantity [34]. Hence, the pH values reported here should be considered as “apparent pH values”. The apparent pH values of water–methanol mixtures increase relative to aqueous pH values as the pH increases [34]. At lower methanol content, the differences may be small, on the order of 0.2, while at 50% methanol, around 1.1. In spite of these differences, the pH trends reported here at a given methanol content provide relative changes vs. what is known in aqueous solutions. The trends at lower methanol concentrations can be more directly related to aqueous solution.

3.2. FT-IR and Raman spectra of solid samples

In order to identify the formed molecular species and to determine the influence of methanol addition on them, complementary spectroscopic methods (FT-IR, Raman, NMR) were performed in almost saturated WPA solutions of concentration 5×10^{-2} mol/dm³.

The evolution of molecular species at increasing pH is commonly followed by recording the FT-IR spectra. It has been shown that 12-tungstophosphate exists in aqueous solution at pH ≤ 1.7 , while in pH region 2–3 it is present in traces besides dimeric Wells–Dawson derivatives and traces of monovacant lacunary Keggin [3,20,22]. With increasing pH from 3 to 7 only monovacant lacunary Keggin exists, while at pH 7.4 the spectrum is changed and new species appear with characteristic bands in the region of P–O, W–O and W–O–W vibrations. At pH > 8 the main species are WO₄ and PO₄.

IR spectra of evaporated and dried WPA solutions with different methanol/water ratios and increasing pH by addition of NaOH were recorded and presented in Fig. 1. Only spectra recorded at pH values where some changes appear are presented.

The spectra of WPA in all methanol/water solutions at pH 1.0 are equivalent to the spectrum of solid WPA. This spectrum possesses vibration bands characteristic of the Keggin anion: 1080, 982, 890 and 812 cm⁻¹, corresponding to vibrations $\nu_{\text{as}}(\text{P}-\text{O}_a)$, $\nu_{\text{as}}(\text{W}-\text{O}_d)$, $\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W})$ and $\nu_{\text{as}}(\text{W}-\text{O}_c-\text{W})$, respectively [30]. While in aqueous solutions bands associated with the Keggin anion are modified already at pH > 1.5, in water/methanol solutions these changes appear at: pH > 2.5 in solution with 25% methanol; pH > 3.5 in solution with 50% methanol and pH > 4.5 in solution with 75% methanol. It can be noticed that the main change in the spectra at pH 2.6, 4.5 and 5.0 for increasing amount of methanol is splitting of the stretching P–O vibration into two bands at 1103 and 1046 cm⁻¹, which indicates the existence of an anion structure of lower symmetry than T_d symmetry of the Keggin anion. Such a structure is monovacant lacunary $[\text{PW}_{11}\text{O}_{39}]^{7-}$ anion that belongs to the C_s symmetry group.

In solution with 25% (v/v) of methanol in narrow pH region from 2.5 to 3.0 bands at about 1089, 1022, 960 and 920 cm⁻¹ indicate presence of a structure with two P atoms such as $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ with C_{3v} symmetry [14,38–43]. With increasing pH up to 7.0, lacunary anion $[\text{PW}_{11}\text{O}_{39}]^{7-}$ with bands at 1103, 1046, 956, 900, 856, 811,

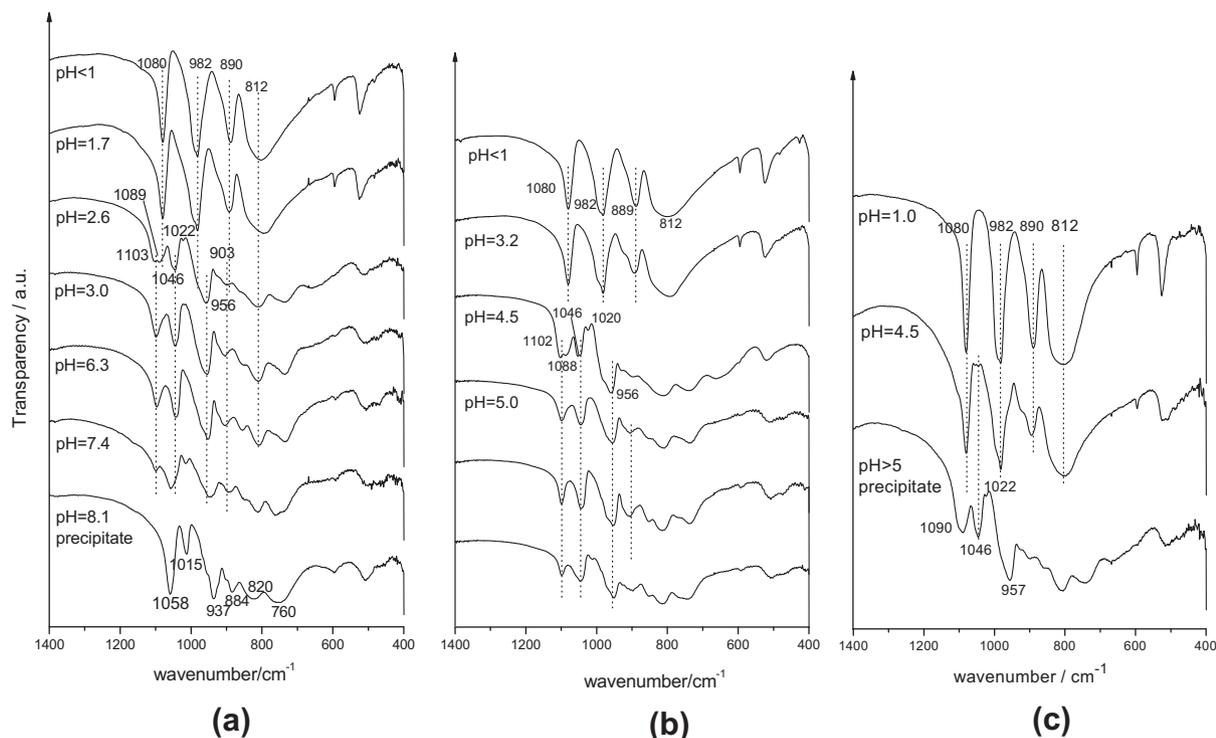


Fig. 1. FT-IR spectra of evaporated WPA from methanol/water solutions: (a) 25% (v/v), (b) 50% (v/v) and (c) 75% (v/v).

734 and 590 cm^{-1} is the only component in solution [35,44,45]. This anion is decomposed at higher pH values to trivalent lacunary anion $[\text{PW}_9\text{O}_{34}]^{9-}$ with slight formation of a precipitate which is dissolved rapidly. At pH 8.1 a precipitate is formed and it corresponds to $[\text{PW}_9\text{O}_{34}]^{9-}$ with bands at 1058, 1015, 937, 884, 820 and 760 cm^{-1} [40]. A decrease of stretching frequencies is consequence of a weakening of the lacunary anion cohesion. The results of elemental analysis confirmed the presence of $\text{Na}_9\text{PW}_9\text{O}_{34}\cdot 14\text{H}_2\text{O}$: *Anal. Calc.* W, 61.54; P, 1.15; Na, 7.70; H, 1.05. *Found:* W, 62.33; P, 1.30; Na, 7.55; H, 1.12%.

The precipitation of $\text{Na}_9[\text{PW}_9\text{O}_{34}]$ from solution with 25% (v/v) of methanol and at about pH 8.1 could be an easy way for preparation of this lacunary form.

In solution with 50% (v/v) of methanol, the stability region of the Keggin anion is extended up to pH 4.5, followed by similar changes in spectra as in the solution with 25% of methanol. The spectrum at pH 4.5 in this solution is identical to the spectrum of solution with 25% of methanol at pH 2.6. A monovacant lacunary $[\text{PW}_{11}\text{O}_{39}]^{7-}$ anion is stable up to pH 6.3 when the precipitate is formed. The precipitate contains $[\text{PW}_{11}\text{O}_{39}]^{7-}$ anion with traces of $[\text{PW}_9\text{O}_{34}]^{9-}$; further addition of NaOH causes decomposition of the precipitate to soluble phosphate and tungstate.

In solution with the highest amount of methanol, 75% (v/v), FTIR spectra show the presence of Keggin anion with traces of lacunary monovacant anion up to pH 4.5, when a precipitate of Keggin anion starts to form but it is dissolved instantaneously. Further increase of pH causes precipitation of $[\text{PW}_{11}\text{O}_{39}]^{7-}$ anion with traces of $[\text{PW}_9\text{O}_{34}]^{9-}$ and Keggin $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anion.

Solid samples obtained after evaporation of solvent were placed under microscope and their Raman spectra, shown in Fig. 2, were analysed. The Raman spectra of WPA obtained after evaporation of aqueous solution exhibit bands between 950 and 1010 cm^{-1} ($\nu_s(\text{W}=\text{O})$) and 825–930 cm^{-1} ($\nu_{as}(\text{W}=\text{O})$) as well as bands at lower frequencies arising from bridging W–O–W vibrations which correspond to the spectrum of solid WPA [38,42,43]. The Raman bands in the region of stretching, bending and lattice vibrations

confirm stability of the Keggin anion up to pH 1.7 in solution with 25% methanol. Bands at 986, 967, 904, 870, 510, 377 and 217 cm^{-1} indicate that monovacant lacunary anion is dominant from pH 2.0 to 6.5 [41–45]. This shift of the symmetric stretch of the W–O_d bond, recorded at 1010 cm^{-1} for the regular structure, to 986 cm^{-1} is a result of lower symmetry of the formed structure, as a consequence of one terminal atom removal. In more alkaline solutions with pH > 6.5 further removal of WO_3 groups causes formation of trivalent lacunary structure $[\text{PW}_9\text{O}_{34}]^{9-}$ with lower symmetry which causes additional shift in position of symmetric stretching vibration to 955 cm^{-1} . This component becomes dominant with further raise in pH, and at about pH 8.0 it precipitates. This is in complete accordance with FTIR spectral data.

Solid sample obtained from solution with 50% of methanol shows in the Raman spectrum at pH 4.5 a broad intensive band between 990 and 960 cm^{-1} in the region of stretching W–O vibrations, which indicates presence of new components confirmed by FT-IR spectra. At pH 5.0, the spectrum contains bands characteristic for monovacant lacunary anion, but in more alkaline solutions, a band about 960 cm^{-1} increases, showing presence of trivalent lacunary anion which is present in the precipitate besides monovacant lacunary anion.

In solution with 75% of methanol, Keggin anion is stable up to pH 4.5, when this anion starts to precipitate, but it dissolves quickly. Further addition of NaOH causes loss of WO unit and precipitate of $[\text{PW}_{11}\text{O}_{39}]^{7-}$ is formed.

3.3. ^{31}P NMR and Raman spectra of solutions

With the intention of checking if the tungstophosphoric species recovered intact after evaporation, further investigations through Raman and ^{31}P NMR analysis of solutions were performed and compared with those obtained from solids.

Raman spectroscopy was performed *in situ* by fibre optic probe after the adjustment of pH of the solution by addition of NaOH and the pH stabilization. These data are presented in Fig. 3.

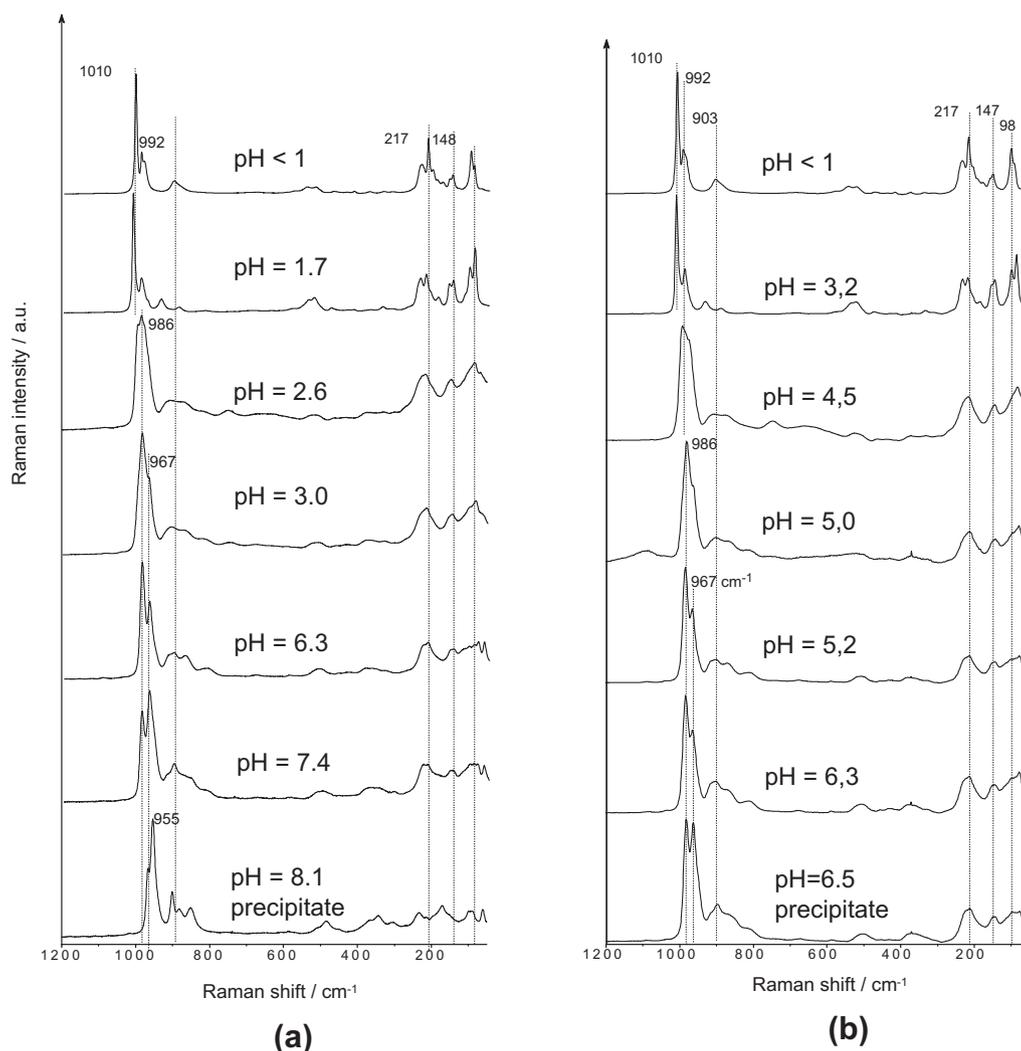


Fig. 2. Micro Raman spectra of evaporated WPA from methanol/water solutions: (a) 25% methanol (v/v) and (b) 50% methanol (v/v).

In solutions the strongest signals were followed. The stronger one at 1010 cm^{-1} which corresponds to stretching $\nu_s(M-O_d)$ vibration, and a weaker one at 993 cm^{-1} which corresponds to convolution of stretching $\nu_{as}(M-O_d)$ at 992 cm^{-1} and $\nu_s(P-O_a)$ at 983.5 cm^{-1} (not resolved due to low resolution of the recordings), are characteristic of Keggin anion. In aqueous solution these peaks are dominant up to pH 1.5 when a band at about 995 cm^{-1} starts to grow in intensity until it reaches a maximum at pH 1.65, when it is more intense than the band at 1010 cm^{-1} ; up to pH 2.5 this band is the most intense and then gradually decreases up to pH 3.6. Generally, in more alkaline solutions, positions of the main bands are shifted towards lower frequencies. The band at 995 cm^{-1} corresponds to a component with two P atoms, while the band at 978 cm^{-1} which appears from pH 2.0 corresponds to monovacant anion. This component is the only one up to pH 5.0 when a shoulder at about 960 cm^{-1} appears and in more alkaline solutions it transforms to a peak corresponding to trivacant lacunary anion. From pH 6.9, monovacant and then trivacant anions start to decompose to tungstate and phosphate. Obviously, such measurements *in situ*, enable more detailed monitoring of decomposition pathway of WPA alkaline decomposition.

In solutions with 25% of methanol, changes in the Raman spectra indicate changes in solution composition. The peak at 1010 cm^{-1} , corresponding to the Keggin anion, is present up to pH 2.7, the strong peak at about 995 cm^{-1} and the weak one at

about 1020 cm^{-1} , assigned to a structure with two P atoms, is present in spectra in a narrow pH region from pH 2.2 to 3.0, while the peak at 978 cm^{-1} , assigned to monovacant lacunary anion, appears as a shoulder at pH 2.2, and it grows in intensity in more alkaline solutions. Shoulder at 963 cm^{-1} appears from pH 3.0 when signals of two lacunary species dominate. A peak at 930 cm^{-1} , indicating gradual generation of tungstate anion, was not observed in spectra of solid samples.

In solution with 50% of methanol, Keggin anion is present up to pH 4.5. Spectra at this pH contain peaks corresponding to structure with 2 P atoms, monovacant and trivacant lacunary anions. From pH 5.0 only peaks at 978 and 963 cm^{-1} are observed in spectra. At about pH 6.5 the precipitate is forming.

The Raman spectra are the simplest in solution with 75% of methanol. Peaks corresponding Keggin anion are present up to pH 4.5 when precipitate is formed. Comparison of Raman spectra of solutions and evaporated residue shows quiet good accordance, but more details can be obtained from the former, especially for aqueous solution. Slight shift of symmetric stretching W–O vibration towards lower wavenumbers in Raman spectra of very acid solutions with increasing amount of methanol are indication of weak interaction between Keggin anions and solvent.

^{31}P NMR spectra of aqueous solutions are compared with spectra of solutions with 50% (v/v) of methanol in Fig. 4. The identification of ions present in solution at different pH was performed

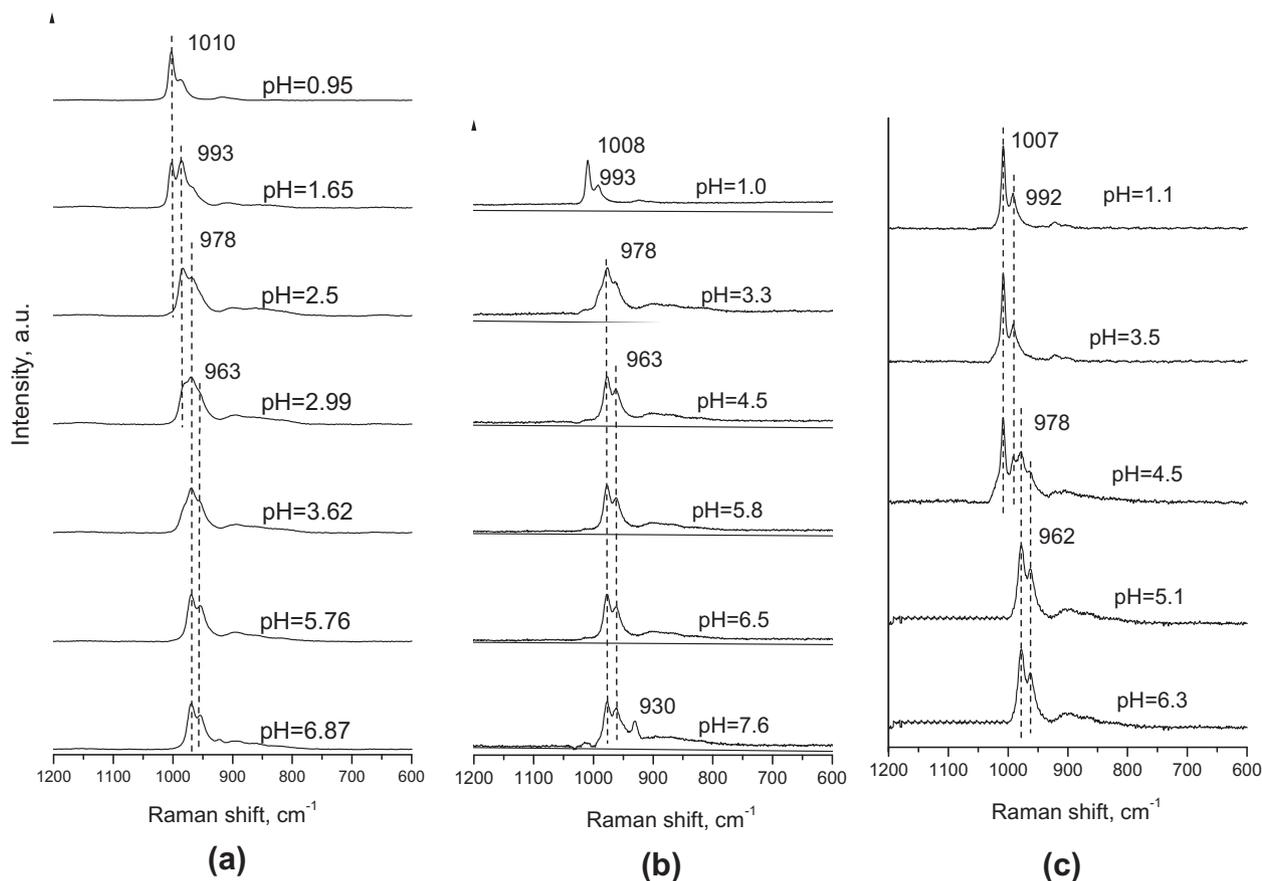


Fig. 3. Raman spectra of: (a) aqueous, (b) 25% (v/v) methanol/water solution; (c) 50% (v/v) methanol/water solution (solvent extracted).

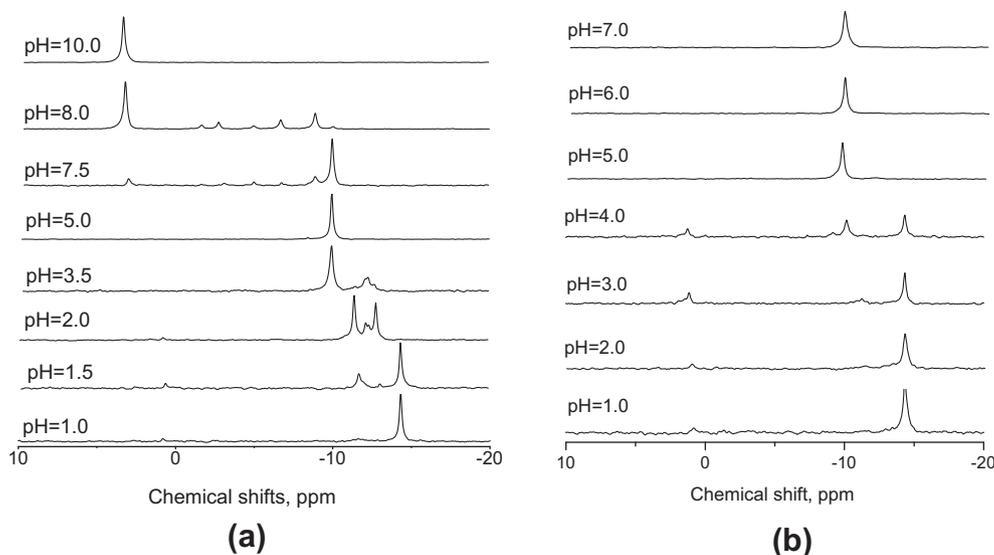


Fig. 4. ^{31}P NMR spectra of: (a) aqueous solution and (b) 50% (v/v) methanol/water solutions of WPA.

based on the literature values of chemical shifts [14,19–22, 29,31,40]. While in aqueous solution the intense single signal at -14.3 ppm, characteristic of parent Keggin anion is present up to pH 1.5, in methanol/water solution it is present up to pH 4.0. The region from pH 1.5 to 3.5 in aqueous solution is characterized by few signals between -11 and -13 ppm. These peaks are indication of components of the Dawson series: $\text{P}_2\text{W}_{21}\text{O}_{71}^{6-}$, $\text{P}_2\text{W}_{20}\text{O}_{70}^{10-}$ and

$\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ [14,19,20,22,29,31]. This is in accordance with the findings of Smith and Patrick [20] that in low pH region decomposition of the Keggin anion is going through structures with 2 P atoms. However the pathway of decomposition of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ to $[\text{PW}_{11}\text{O}_{39}]^{7-}$ in methanol/water mixture with increasing of pH is simpler than in aqueous solution. In the region between pH 2 and 3, only weak signal corresponding to $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ besides

Keggin anion is observed. Lacunary monovacant $[\text{PW}_{11}\text{O}_{39}]^{7-}$ anion is present from pH 4.0 to 6.5 when precipitate is formed. Solution over the precipitate at pH 7.0 contains only $[\text{PW}_{11}\text{O}_{39}]^{7-}$ according ^{31}P NMR spectra.

3.4. UV spectra

The influence of added methanol quantity on the stability of WPA in solution of very low concentration $ca. 2 \times 10^{-5} \text{ mol/dm}^3$ and at pH 3.5 was investigated by UV absorption spectrophotometry. The UV spectra of aqueous solution of WPA with different methanol contents presented in Fig. 5a show that characteristic band maximum appears at 265 nm for solutions with methanol quantity ranging from 50% to 100%. This band corresponds to the oxygen-to-metal charge transfer transition of Keggin structure of WPA [19,21,22], it depends on pH and varies only slightly with the sort of solvent [46]. However it depends on methanol concentration. For solutions with quantities of methanol lower than 50 v/v% the spectra maximum is shifted towards the lower wavelengths, indicating existence of other structures.

Based on these results, further investigations were related to the influence of pH on the stability of WPA in solution with the same concentration of $2 \times 10^{-5} \text{ mol/dm}^3$ and methanol/water mixture of 50/50% (v/v).

While in aqueous solution the absorption band maximum remains at 265 nm up to pH 3 (Fig. 5b), in water/methanol solution it remains at the same position up to pH 7 (Fig. 5c). In solutions with higher pH, the absorption maximum is shifted towards the lower wavelengths (252–248 nm), corresponding to the mixture of different molecular species formed from WPA Keggin anion. These results show that the stability range of WPA in very dilute solution with 50% (v/v) of methanol is considerably extended up

to pH 7, related to physiological-like conditions. Further addition of NaOH in such solution does not cause any precipitation.

Based on all presented spectral data, Table 1 summarizes the characteristics of WPA solutions of various concentrations and with different ratios of water to methanol.

If spectra of solutions with the same pH and increasing quantity of methanol are compared, it can be concluded that up to pH 2, Keggin anion is preserved independently of methanol quantity, while in aqueous solution at pH 2 it is absent. At pH 3, in solution with 25% of methanol, lacunary anion is present. At pH 4.5 in solution with 50% of methanol, the mixture of traces of Keggin anion is present besides the lacunary anion which is dominant. At pH 6.4, the solution and precipitate contain monovacant lacunary anion with traces of trivacant lacunary anion. In solution with 75% of methanol, Keggin anion is present up to pH 5, but from pH 4.5 precipitation of monovacant lacunary anion is starting and at pH 5.4 precipitate is composed of $[\text{PW}_{11}\text{O}_{39}]^{7-}$ anion. FTIR spectra indicate a small quantity of $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ which was observed as intermediate in formation of $[\text{PW}_{11}\text{O}_{39}]^{7-}$ from $[\text{PW}_{12}\text{O}_{40}]^{3-}$. It is obvious that lacunary anions are less soluble in solutions with higher methanol content and with higher pH.

From all presented results, it is evident that methanol, an organic solvent commonly used in daily laboratory work, extends the pH region of Keggin anion structure stability. The methanol molecules interact with Keggin anion framework through hydrogen bonds thus protecting it from hydrolysis. These solvated structures are not observed in solid state due to high volatility of methanol and relatively weak hydrogen bonds. However in solid polyoxometalate chemistry an important advance is achieved by the modification of polyoxometalates with various organic ligands and transition metal complexes to obtain organic–inorganic hybrid materials [47–49] or to investigate the isomerism of Keggin and/or lacunary

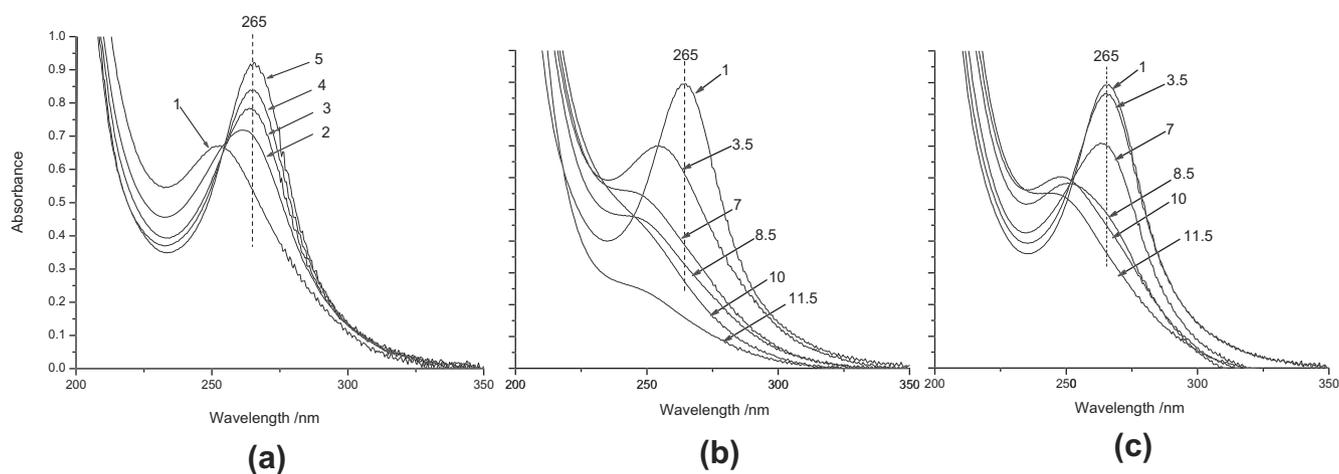


Fig. 5. UV spectra of WPA solutions ($c = 2 \times 10^{-5} \text{ mol/dm}^3$): (a) with different methanol content, 1–0, 2–25%, 3–50%, 4–75% and 5–100% (v/v) and pH 3.5; (b) aqueous solutions with varying pH; (c) methanol/water mixtures 50% (v/v), with varying pH.

Table 1

Characteristics of WPA solutions with different methanol content.

WPA conc. (mol/dm^3)	5×10^{-2}			2×10^{-5}	
Methanol (v/v)%	0	25	50	75	50
Keggin anion at pH	<2	2.5	3.5	4.5	7.0
Precipitate at pH	No precipitate	8.0	6.5	4.5	No precipitate
Precipitate composition		$\text{Na}_9\text{PW}_9\text{O}_{34}$	$\text{Na}_7\text{PW}_{11}\text{O}_{39}$ $\text{Na}_9\text{PW}_9\text{O}_{34}^*$	$\text{Na}_7\text{PW}_{11}\text{O}_{39}$ $\text{Na}_3\text{PW}_{12}\text{O}_{40}^*$ Na_2WO_4^*	

* Components present in traces.

anions [46]. With increasing basicity of the solution, the protective role of methanol is decreased due to destruction of the solvation layer of the Keggin anion, as in an excess of Na^+ in solution, and formation of alkoxy species is possible.

The analysis of molecular species present in solutions with different methanol concentration and different pH is important because it is known that when HPAs are supported with different dispersion (from solutions of different concentrations of WPA causing different acidity of solution), the modified catalytic behaviour is observed [50].

4. Conclusions

Previous studies demonstrated that the Keggin type anion $[\text{PW}_{12}\text{O}_{40}]^{3-}$ decomposes in aqueous media and this process is pH dependent. This problem may be overcome by dissolution of WPA in organic media. The present study demonstrates that the heteropoly structure stability is extended in organic media due to interaction of WPA and methanol through weak hydrogen bonds which protect Keggin anion from hydrolysis. The dependence of stability effect on organic solvent amount, pH and concentration of WPA in solution is investigated in detail.

From FT-IR and Raman spectra, it is concluded that addition of methanol in aqueous solution of WPA with varied pH causes extension of the pH region where parent Keggin anion is stable. Various molecular species are observed as a result of Keggin anion destruction, but speciation in both aqueous and methanol/water solutions is similar. Raman and ^{31}P NMR spectroscopy showed that the pathway of decomposition of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ to $[\text{PW}_{11}\text{O}_{39}]^{7-}$ in methanol/water mixture with increasing of pH is similar as in aqueous solution, but the pH region where a structure with two P atoms, such as $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$, appears is very narrow in methanol–water solutions.

In contrast to aqueous solution, in methanol/water mixtures precipitation is observed in more alkaline solutions because the lacunary anions become insoluble. In solution with 25% methanol, trivalent lacunary anion starts to precipitate at pH 8, in solution with 50% of methanol, monovalent lacunary anion with traces of trivalent lacunary anion are precipitated at pH about 6.5, while in the solution with 75% of methanol, monovalent lacunary anion with traces of parent anion are deposited at about pH 4.5.

The detailed knowledge of molecular species present under different pH conditions and concentrations of POMs and organic solvents are essential for explanation of mechanisms of effects of POMs in their numerous applications.

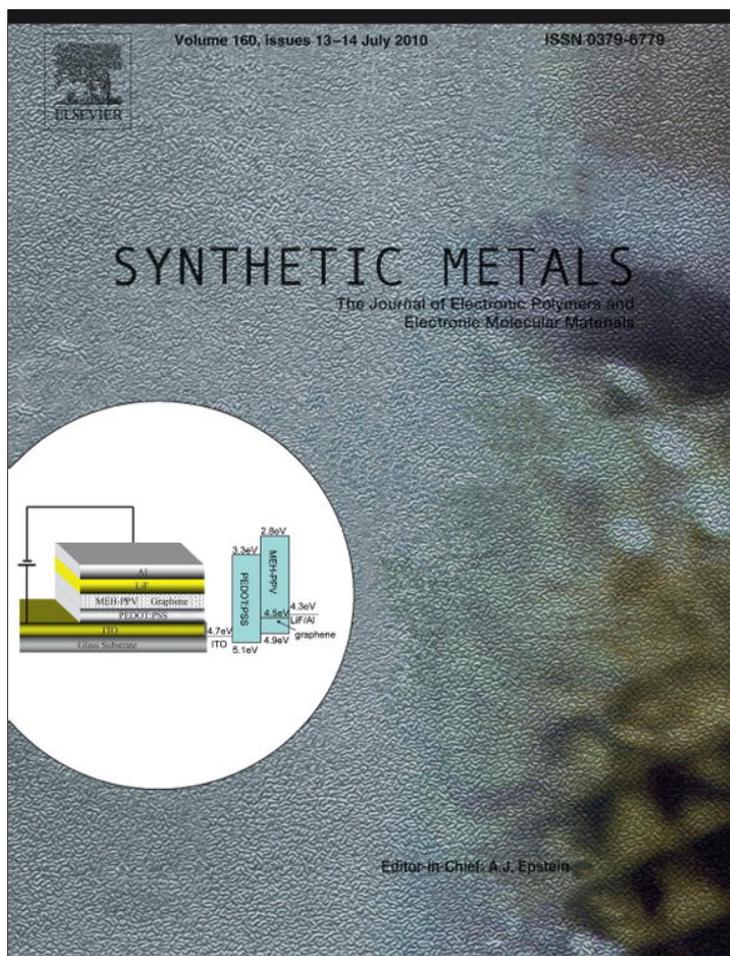
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Self-assembled polyaniline 12-tungstophosphate micro/nanostructures

Gordana Ćirić-Marjanović^{a,*}, Ivanka Holclajtner-Antunović^a, Slavko Mentus^a,
Danica Bajuk-Bogdanović^a, Dragana Ješić^a, Dragan Manojlović^b, Snežana Trifunović^b, Jaroslav Stejskal^c^a Faculty of Physical Chemistry, University of Belgrade, Studentski Trg 12-16, 11158 Belgrade, Serbia^b Faculty of Chemistry, University of Belgrade, Studentski Trg 12-16, 11158 Belgrade, Serbia^c Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

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ABSTRACT

Polyaniline (PANI) micro/nanostructures were synthesized by the external-template-free oxidative polymerization of aniline in aqueous solution of 12-tungstophosphoric acid (WPA), using ammonium peroxydisulfate (APS) as an oxidant and starting the oxidation of aniline from slightly acidic media (pH 5.4–5.9). The effect of the initial weight ratio of WPA to aniline on molecular structure, morphology, and physicochemical properties of polyaniline 12-tungstophosphate (PANI-WPA) was investigated by FTIR, Raman and inductively coupled plasma optical emission (ICP-OES) spectroscopies, elemental analysis, X-ray powder diffraction (XRPD), scanning and transmission electron microscopies (SEM and TEM), thermogravimetric analysis (TGA), differential thermal analysis (DTA), and conductivity measurements. The morphological change of polymerization products during a single polymerization process, from non-conducting submicro-/microspherical oligoaniline intermediates to semiconducting PANI-WPA consisted of self-assembled nanotubes and/or nanorods co-existing with submicro-/microspheres, has been revealed by SEM and TEM. The average diameter of nanorods in PANI-WPA samples decreased with increasing the initial WPA/aniline weight ratio. The incorporation of 12-tungstophosphate counter-ions into PANI matrix has been proved by FTIR, Raman and ICP-OES spectroscopies, TGA and DTA analysis. Electrical conductivity of PANI-WPA increased in the range $(2.5\text{--}5.3) \times 10^{-3} \text{ S cm}^{-1}$ with the increase of the initial WPA/aniline weight ratio. The presence of branched structures and phenazine units besides the ordinary paramagnetic and diamagnetic emeraldine salt structural features in PANI-WPA was proved by FTIR and Raman spectroscopies.

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1. Introduction

It has been shown that the dispersibility and processibility of nanostructured PANI, as well as its performance in numerous conventional applications, are significantly improved in comparison with PANI having granular morphology [1–4]. The synthesis of self-assembled PANI nanotubes and nanorods has been the subject of numerous investigations during the last decade [5–20]. Conducting PANI nanotubes have been synthesized by the chemical oxidative self-assembly process in the presence of inorganic acids [5,6], sulfonic acids [7–9], carboxylic acids [10–14], and polymeric acids [15]. PANI nanotubes and nanorods were formed even when aniline has been oxidized in aqueous solution without added acid [10,16–19]. Slightly alkaline, neutral or slightly acidic conditions at the beginning of aniline oxidation, the increase in acidity during the oxidation to pH < 2 at the end of polymerization, and the use of

APS as the oxidant, are found to be common reaction conditions for almost all chemical oxidative polymerizations of aniline which lead to self-assembled conducting PANI nanotubes, frequently accompanied with nanorods. PANI nanotubes have also been obtained by the oxidation of aniline with APS at constant acidity (pH = 2 and 3), in the presence of *p*-toluenesulfonic acid [20].

The understanding of the genesis of molecular structure and nanotubular morphology of PANI without added templates is crucial for efficient and controllable synthesis of self-assembled PANI nanotubes. Cylindrical micelles of aniline salts with dopant acids were proposed by Wan's group to govern the formation of PANI nanotubes and other nanostructures [4,7]. A model based on the "surfactant" role of aniline dimer (4-aminodiphenylamine) cation-radicals, which could aggregate to form different sizes and types of micelles has also been proposed to explain the formation of PANI nanotubes [17]. However, the mechanistic details of this model are not supported by quantum chemical studies of the early stages of the oxidative polymerization of aniline with APS [21–23]. Also, the surfactant role of 4-aminodiphenylamine cation-radicals is not consistent with their pronounced charge/spin delocalization [21].

* Corresponding author. Tel.: +381 11 3336623; fax: +381 11 2187133.

E-mail address: gordana@ffh.bg.ac.rs (G. Ćirić-Marjanović).

It was recognized that the morphology of PANI, granular or tubular, depended on the acidity profile of the reaction rather than on the chemical nature of the acid. It was proposed that, during the course of aniline oxidation, pH-dependent self-assembly of aniline oligomers rather than that of aniline monomers, predetermined the final PANI morphology [10,12–14,16,21–26].

Heteropolyacids (HPAs) have attracted increased interest in catalysis, owing to their ability to catalyze both acid-catalyzed and redox processes [27]. HPAs can be prepared with a wide variety of structural and chemical compositions, but those of the Keggin structure have been more extensively studied because of their easier availability, higher stability, and better catalytic performance [27]. The Keggin-type HPAs are formed by heteropolyanions having the general formula $[(XO_4)(M_{12}O_{36})]^{n-}$ where X is the central atom or heteroatom, typically Si or P, M is the peripheral atom, such as W or Mo, and n depends upon the oxidation numbers of X and M . The most stable and strongest acid in the Keggin series is 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, WPA), and for this reason it has been extensively studied as a catalyst for many acid-catalyzed organic reactions, both in homogeneous and heterogeneous systems [27,28]. The protons in Keggin HPAs can be readily exchanged, totally or partially, by different cations without affecting the primary Keggin structure of the heteropoly anion. When large cations (NH_4^+ , Cs^+ , K^+ , Rb^+ , etc.) are introduced, the obtained solid salts are characterized by an increased surface area, higher thermal stability, and lower solubility in water than the parent acid [29]. Furthermore, the high surface area of these salts possessed a well-defined microporous structure. Some of the WPA salts showed higher catalytic activity than the pure WPA for a number of redox and acid-catalyzed reactions. PANI-WPA emeraldine salt was also found to exhibit good catalytic activity [30–32]. Other applications of PANI-WPA include sensors [33], and especially fuel cells [34,35], because both PANI and WPA exhibit proton conductivity. PANI-WPA has been prepared by the chemical [31,36–38] and electrochemical [33,39] oxidative polymerization of aniline in the presence of WPA, or by the protonation of PANI base with this acid [30–32,37]. PANI doped with tungstophosphoric acid of Dawson type ($H_6P_2W_{18}O_{62}$) has also been synthesized electrochemically [40,41] and used as a material for gas sensor [41], exhibiting higher sensitivity to ammonia than the PANI hydrochloride.

Heteropolyacids have a special role in the synthesis of PANI. It has been demonstrated that the formation of PANI is substantially delayed in the presence of such acids [38], in the contrast to any other acid. In other words, they prolong the induction period several times even when added in minute quantities. The formation of any polymers by a chain growth is associated with three distinct phases: (1) the initiation, (2) the propagation, and (3) the termination. It is obvious that heteropolyacids, in some way, affect the initiation step. In the chemistry of PANI, this step has never been analyzed in convincing detail. It has been proposed that the initiation centres containing the phenazine heterocycle, the nucleates, are able to self-organize by π - π stacking or hydrophobic interactions [13]. PANI chains growing from such organized structures produce the morphologies, such as nanotubes or nanofibers. For

that reason, the possibility to alter the nature of nucleation centres, and possibly the morphology of PANI, is of fundamental importance, and stimulated this study.

In this paper, semiconducting PANI-WPA micro/nanostructures, i.e. nanotubes and nanorods accompanied with submicro-/microspheres, produced by a self-assembly process are reported for the first time. The oxidative polymerization of aniline was performed in aqueous solution of WPA using APS as an oxidant, starting from slightly acidic media (pH 5.4–5.9). The influence of the synthetic conditions on the molecular, supramolecular and crystalline structure, thermal stability, structure transformations upon heating, and electrical properties of PANI-WPA was investigated by various techniques. The evolution of molecular structure and morphology of PANI-WPA is discussed.

2. Experimental

2.1. Materials

Aniline (p.a., >99.5%, Centrohem, Serbia), was distilled under reduced pressure and stored at room temperature, under argon, prior to use. APS (analytical grade, Centrohem, Serbia) was used as received. 12-Tungstophosphoric acid hexahydrate, $H_3PW_{12}O_{40} \cdot 6H_2O$ (WPA-6H₂O), was synthesized according to the literature method [42], recrystallized prior to use, and identified by FTIR spectroscopy.

2.2. Synthesis of PANI-WPA micro/nanostructures

In a typical procedure for preparing PANI-WPA micro/nanostructures, the aqueous solutions (30 cm³) of WPA (1.86 g WPA-6H₂O) and aniline (1.86 g, 0.02 mol) were mixed at 20 °C and distilled water was added up to 100 ml total volume of resulting aniline/anilinium 12-tungstophosphate solution. Then the aqueous solution (100 cm³) of APS (5.705 g, 0.025 mol) was poured into the monomer solution with constant stirring. The progress of reaction was monitored by recording the temperature and the acidity of the reaction mixture with a digital thermometer and pH meter, respectively. The resulting mixture was allowed to react 24 h at 20 °C. The precipitated PANI-WPA was then collected on a filter, rinsed with aqueous and ethanolic solution of sulfuric acid (5×10^{-3} M), and diethyl ether several times, and dried in vacuum at 60 °C for 3 h. For each experiment, concentrations of aniline (0.1 M) and APS (0.125 M) were kept constant. Various initial weight ratios of WPA-6H₂O to aniline were used: 0.2, 0.25, 0.5 and 1. Synthetic conditions for various PANI-WPA samples are given in Table 1. As a reference sample, PANI was prepared by the same procedure, without WPA.

2.3. Characterization

A scanning electron microscope JEOL JSM 6460 LV and a transmission electron microscope Tecnai G2 Spirit (FEI, Brno, Czech Republic) have been used to characterize the morphology of the

Table 1
Synthetic conditions for PANI-WPA samples and pure PANI.^a

Initial WPA-6H ₂ O to aniline weight ratio	Concentration of WPA [mol dm ⁻³] ^b	Polymerization time t_{pol} [h]	pH of the monomer solution ^c	Initial pH ^d	Final pH
0	0	2	8.4	6.2	1.1
0.2	6.2×10^{-4}	2	6.1	5.9	1.4
0.25	7.8×10^{-4}	3	6.0	5.9	1.1
0.5	1.6×10^{-3}	24	5.8	5.7	1.2
1	3.1×10^{-3}	24	5.5	5.4	1.1

^a Starting concentrations of aniline (0.1 M) and APS (0.125 M) were the same in all experiments.

^b In the initial reaction mixture.

^c The solution of aniline/anilinium 12-tungstophosphate before adding the solution of APS.

^d pH measured immediately after mixing the solutions of aniline/anilinium 12-tungstophosphate and APS.

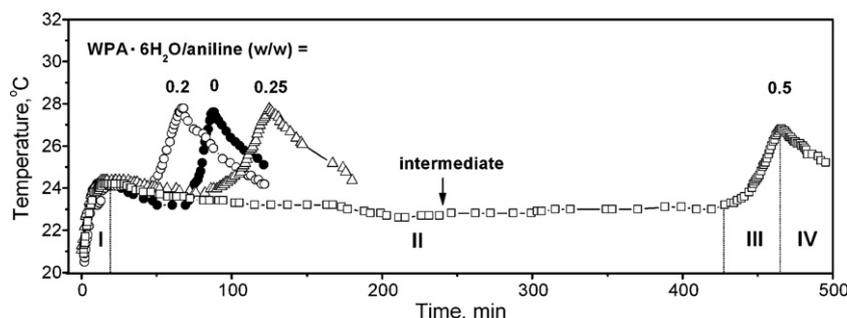


Fig. 1. Temperature changes during the oxidation of aniline (0.1 M) with APS (0.125 M) in water at various initial WPA-6H₂O/aniline weight ratios: (○) 0.2, (△) 0.25 and (□) 0.5, and without added WPA (●). Phases I–IV correspond to the course of aniline polymerization in the presence of WPA, for the initial WPA-6H₂O/aniline weight ratio = 0.5.

samples. Powdered materials were deposited on adhesive tape fixed to specimen tabs and then coated by ion sputtered gold using a BAL-TEC SCD 005 Sputter Coater prior to SEM measurements. The thermal analysis (TGA, DTA) was carried out using a TA Instruments Model SDT 2960 thermoanalytical device with air purging gas, at a flow rate of 50 cm³ min⁻¹ and at a heating rate of 10 °C min⁻¹. Elemental Analysis (C, H, N, and S) was performed using an Elemental Analyzer VARIO EL III (Elementar). The content of tungsten in PANI-WPA samples was determined by ICP-OES, using a Thermo Scientific iCAP 6500 Duo ICP spectrometer. Prior to analysis by ICP-OES, the microwave-assisted acid digestion of samples was performed by means of ETHOS 1 Advanced Microwave Digestion System (Milestone, Italy) using HPR-1000/10S high pressure segmented rotor. The acid mixture consisting of 65% HNO₃ (2 cm³), 96% H₂SO₄ (5 cm³) and 40% HF (2 cm³) was used for the acid digestion per ~50 mg of the sample. ICP-OES analysis was performed using an emission line W II 207.911 nm. The electrical conductivity of PANI-WPA and PANI powders compressed between stainless steel pistons, within an isolating hard-plastic die, was measured at room temperature by means of an ac bridge (Wayne Kerr Universal Bridge B 224), working at fixed frequency of 1.0 kHz. During the measurement, the pressure was kept constant at 124 MPa. FTIR spectra of the powdered samples, dispersed in potassium bromide and compressed into pellets, were recorded in the range of 4000–400 cm⁻¹ at 64 scans per spectrum at 2 cm⁻¹ resolution using a Nicolet 6700 FTIR Spectrometer (Thermo Scientific). Raman spectra excited with a diode-pumped solid state high-brightness laser (532 nm) were collected on a Thermo Scientific DXR Raman microscope, equipped with an Olympus optical microscope and a CCD detector. The powdered sample was placed on an X–Y motorized sample stage. The laser beam was focused on the sample using an objective magnification ×50. The scattered light was analyzed by the spectrograph with a grating 900 lines mm⁻¹. Laser power was kept at 0.1 mW on the samples PANI-WPA and PANI in order to avoid their degradation. The X-ray powder diffraction (XRPD) patterns were obtained on a Philips PW-1710 automated diffractometer using Cu tube ($\lambda = 1.5418 \text{ \AA}$) operated at 40 kV and 30 mA. Diffraction data were collected in the range of $2\theta = 3 - 70^\circ$, by a step size of 0.05° and a counting time of 10.45 s per step.

3. Results and discussion

3.1. The course of aniline polymerization in the presence of WPA

The oxidation of aniline in aqueous solutions of WPA, at various initial weight ratios of WPA-6H₂O to aniline, proceeds in two exothermic phases (phases I and III, Fig. 1) which are well separated with an athermal period (phase II, Fig. 1). This temperature profile as well as underlying chemistry is quite similar to that observed for the oxidative polymerization of aniline in water without added acid [16], where phases I and III were proved to be oligomeriza-

tion and polymerization processes, respectively. However, it can be seen that the presence of WPA has marked effect on the kinetics of aniline oxidation [38]. The increase of initial WPA-6H₂O/aniline weight ratio leads to the significant prolongation of athermal period (Fig. 1), i.e. to the delay of subsequent autoacceleration phase of aniline polymerization (phase III). The onset of second exothermic phase appears at 43, 83 and 427 min for WPA-6H₂O/aniline ratio 0.2, 0.25, and 0.5, respectively. It was revealed that small quantities of WPA (weight ratio WPA-6H₂O/aniline = 0.2) act as a catalyst for the redox reactions of oligoaniline intermediates during an athermal period, while larger quantities of WPA (weight ratio WPA-6H₂O/aniline = 0.25 to 1) act as an inhibitor, possibly because WPA at higher concentrations sterically blocks oligoaniline intermediates, and their conversion to initiation centers that start the growth of PANI chains. The course of the subsequent polymerization, however, was not affected by the addition of WPA: during the phase III the slope of temperature profile (proportional to the rate of polymerization), and the increment of temperature (proportional to the yield of polymerization) virtually did not change with changing the initial concentration of WPA. The pH of reaction mixture continuously decreases because of the formation of the protons as by-product [10,16]. The acidity profile of the polymerization (Fig. 2), indicates that some structural changes of the

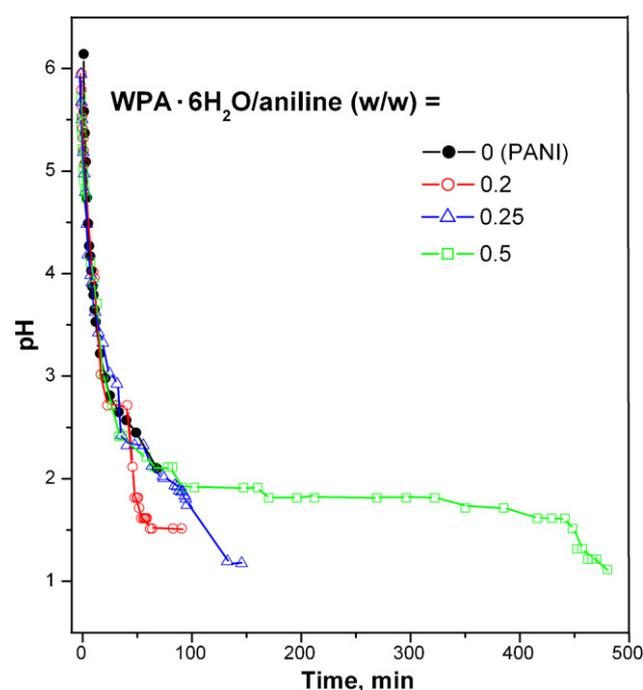


Fig. 2. Acidity profiles of aniline (0.1 M) oxidation with APS (0.125 M) in water at various initial WPA-6H₂O/aniline weight ratios.

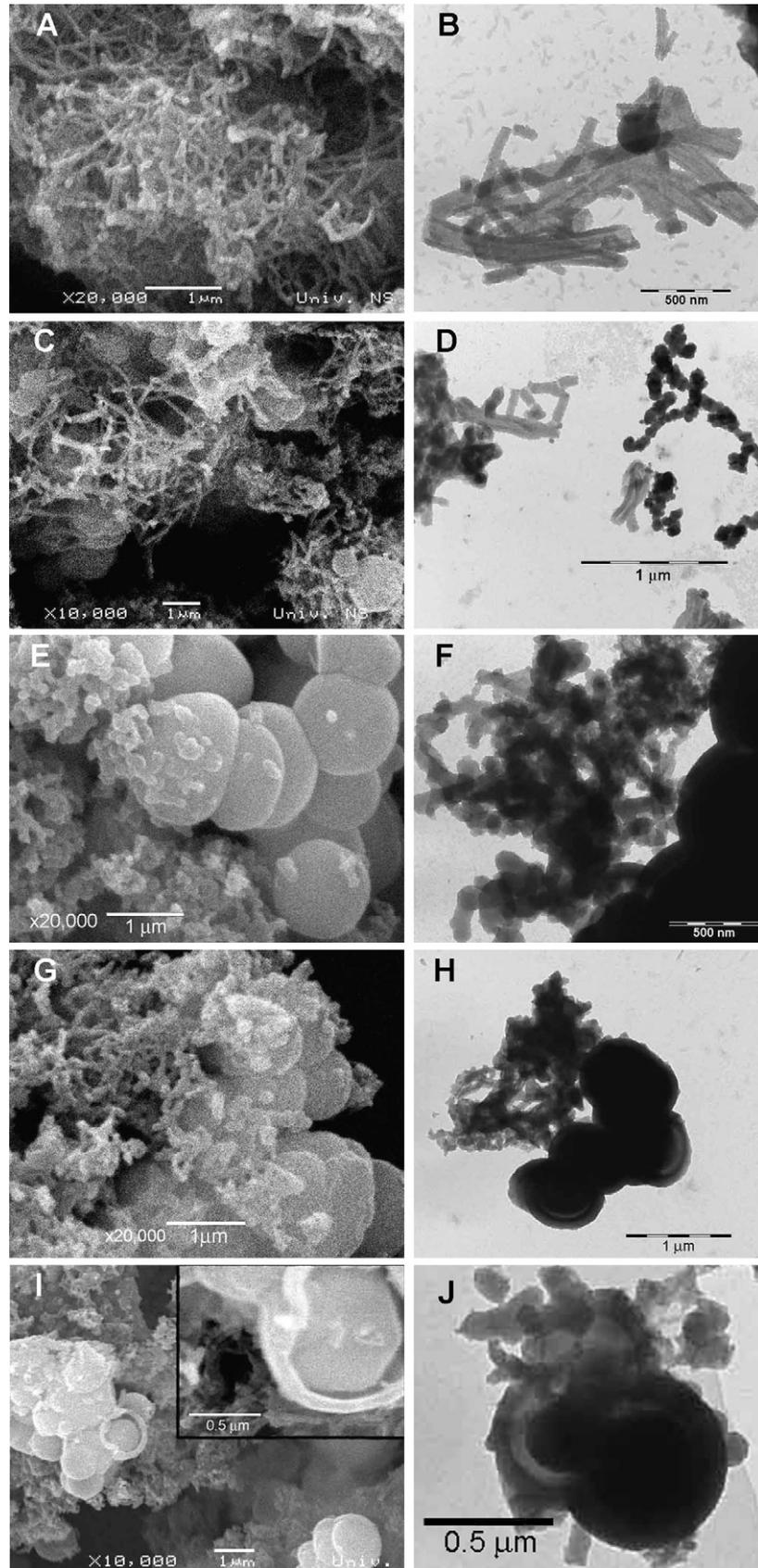


Fig. 3. (A, C, E, G, I) SEM and (B, D, F, H, J) TEM images of nanostructured PANI sulfate/hydrogen sulfate (A and B) and PANI-WPA samples synthesized at the initial weight ratios WPA·6H₂O/aniline = (C and D) 0.2, (E and F) 0.25, (G and H) 0.5 and (I and J) 1. The inset in (I) shows a broken microsphere having a core with rhombic dodecahedral shape.

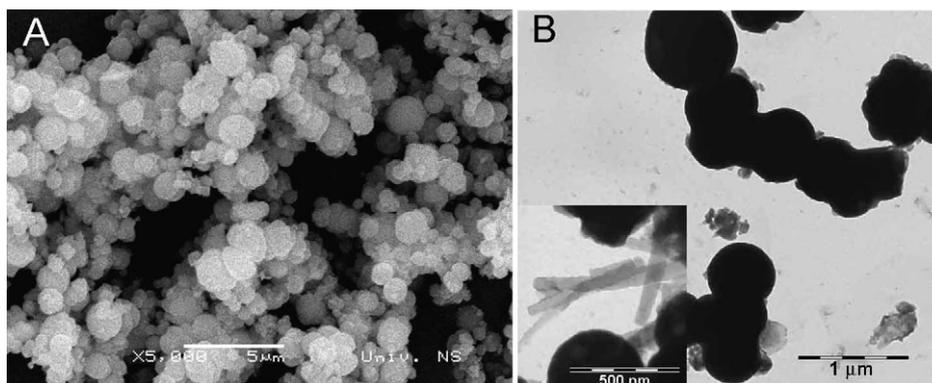


Fig. 4. (A) SEM and (B) TEM images of the intermediate isolated during the athermal phase of aniline oxidation ($t_{\text{pol}} = 4$ h) at the initial weight ratio WPA-6H₂O/aniline = 0.5.

Keggin-type WPA caused by the acidity changes [43] are possible during the course of polymerization, leading thus to the existence of the Dawson [P₂W₁₈O₆₂]⁶⁻ and the lacunary [PW₁₁O₃₉]⁷⁻ structures, besides the Keggin-type WPA, in the final PANI-WPA at pH = 1.1–1.4. The incorporation of sulfate and hydrogen sulfate anions, formed by reduction of peroxydisulfate anions, in PANI matrix is also possible.

3.2. Morphology

SEM and TEM images show the influence of the initial WPA-6H₂O/aniline weight ratio and polymerization time (t_{pol}) on the morphology of PANI-WPA (Figs. 3 and 4). The sample of pure nanostructured PANI in the salt form (sulfate/hydrogen sulfate) contains predominately nanotubes which are accompanied with nanorods (Fig. 3A and B, Table 2). This is in agreement with similar earlier experiments [16]. The introduction of 12-tungstophosphate anions in the polymerization system leads to the appearance of submicro- and microspheres (Fig. 3C–J), which are accompanied with nanotubes, nanorods and solid microspheres in the sample prepared at WPA-6H₂O/aniline = 0.2 (Fig. 3C and D, Table 2), and with nanorods in the samples prepared at WPA-6H₂O/aniline = 0.25, 0.5 and 1 (Fig. 3E–J, Table 2). Microspheres have usually been observed in alkaline media [13], because of limited miscibility of aniline with aqueous medium. Aniline forms microdroplets, and oligomers are produced at aniline–water interface. We can speculate that the addition of WPA reduces the solubility of aniline due to salting-out effect, thus creating the template for the formation of oligoaniline microspheres. When the acidity increases during the polymerization, the aniline may form an insoluble salt with WPA inside the microspheres.

The average diameter of nanorods in PANI-WPA samples, grown in the aqueous phase outside the microspheres, decreased with the increase of the initial WPA-6H₂O/aniline weight ratio (Table 2). This result can be correlated with the decrease of starting pH value of the reaction mixture from 5.9 to 5.4 going from WPA-6H₂O/aniline = 0.2 to 1, respectively (Table 1). The decrease of initial pH as well as the separation of neutral aniline into micro-

droplets causes the decrease of the initial amount of dissolved non-protonated aniline molecules that, being more oxidizable than the anilinium cations, are responsible for the formation of non-protonated low-molecular-weight oligomers which contain branched and phenazine-like units [21]. These oligomers, self-organized into rod-like internal templates, dictate the growth of 1D nanostructures in subsequent polymerization phase [9,16]. We can speculate that the decreased amount of non-protonated aniline at the start of oxidation leads to the reduced diameter of rod-like nano-crystalline/nano-liquid-crystalline oligomeric templates, and thus to the decreased diameter of subsequently formed PANI nanorods with non-conducting core and conducting walls [9].

TEM images (Fig. 3F, H and J) revealed that submicro- and microspheres in PANI-WPA have a core-shell structure. The spherical core in a broken microsphere is clearly seen on SEM image (Fig. 3I). However, with higher SEM magnification (inset in Fig. 3I) it was observed that this core actually has a rhombic dodecahedral shape. Very similar crystal form was found in WPA-6H₂O [44].

It was found that the morphology of polymerization products changed during a single polymerization process. The oligomeric intermediate isolated during the athermal phase II of aniline oxidation ($t_{\text{pol}} = 4$ h, Fig. 1) at the initial weight ratio WPA-6H₂O/aniline = 0.5 consists predominately of submicro- and microspheres with diameter of 0.4–1.7 μm, as revealed by SEM and TEM (Fig. 4), accompanied with small amount of nanorods, as observed by TEM (inset in Fig. 4B). The formation of large amount of nanotubes and/or nanorods is related with longer polymerization time, i.e., with the occurrence of second exothermic phase, as revealed for the sample PANI-WPA synthesized at the same initial weight ratio WPA-6H₂O/aniline = 0.5, but collected after $t_{\text{pol}} = 24$ h (Fig. 3G and H).

3.3. Elemental analysis

The elemental composition of PANI-WPA samples shows the decrease of content of sulfur and the increase of content of tungsten with the increase of the initial WPA concentration in the reaction mixture (Table 3). This means that the extent of incor-

Table 2
Diameter (d) and length (l) of PANI and PANI-WPA objects observed by SEM and TEM.

Initial WPA-6H ₂ O to aniline weight ratio	Nanotubes			Nanorods		Submicro-/microspheres d (μm)
	d_{outer} (nm)	d_{inner} (nm)	l (μm)	d (nm)	l (μm)	
0 (PANI)	60–170	7–95	0.3–1.5	40–80	0.5–1.0	–
0.2	70–130	10–40	0.4–0.7	50–110	0.2–0.6	0.7–1.4
0.25	–	–	–	40–115	0.2–0.3	0.5–2.0
0.5	–	–	–	40–95	Network	0.7–1.5
1	–	–	–	10–75	Network	0.3–1.4

Table 3

Elemental composition of PANI and PANI-WPA samples determined by the elemental analysis (C, H, N, and S), and ICP-OES measurements (W).

Initial WPA·6H ₂ O to aniline weight ratio	Content (wt.%)				
	C	H	N	S	W
0 (PANI)	57.33	4.69	11.12	5.86	–
0.2	50.43	4.05	9.69	5.04	10.87
0.25	47.72	3.76	9.14	4.91	13.09
0.5 (intermediate)	30.77	2.44	5.89	1.56	38.62
0.5	40.89	3.25	7.74	3.81	21.09
1	31.75	2.57	6.05	2.97	32.78

Table 4

Empirical formulae of prepared PANI-WPA samples (based on the elemental analysis of C, H, N, S and W).

Initial WPA·6H ₂ O to aniline weight ratio	Empirical formula
0 (PANI)	C ₆ H ₅ N(HSO ₄ ⁻) _{0.204} (SO ₄ ²⁻) _{0.026} (H ₂ O) _{0.328}
0.2	C ₆ H ₅ N(HSO ₄ ⁻) _{0.181} (SO ₄ ²⁻) _{0.046} (WPA ³⁻) _{0.007} (H ₂ O) _{0.314}
0.25	C ₆ H ₅ N(HSO ₄ ⁻) _{0.208} (SO ₄ ²⁻) _{0.026} (WPA ³⁻) _{0.009} (H ₂ O) _{0.251}
0.5	C ₆ H ₅ N(HSO ₄ ⁻) _{0.186} (SO ₄ ²⁻) _{0.029} (WPA ³⁻) _{0.017} (H ₂ O) _{0.322}
1.0	C ₆ H ₅ N(HSO ₄ ⁻) _{0.191} (SO ₄ ²⁻) _{0.024} (WPA ³⁻) _{0.034} (H ₂ O) _{0.355}

poration of sulfate/hydrogen sulfate anions as counter-ions in positively charged PANI matrix decreases, while the amount of 12-tungstophosphate anions as dopant anions increases with the increase of the initial WPA·6H₂O/aniline weight ratio. The sample of intermediate, isolated in the middle of an athermal period, has the highest content of tungsten (38.62%) and the lowest content of S (1.56%), Table 3. These findings indicate that aniline salt with WPA is present inside oligomeric microspheres, and that the ratio of sulfate (hydrogen sulfate) anions/12-tungstophosphate anions incorporated in polymer matrix increases with the polymerization time.

Based on the elemental analysis data, empirical formulae C₆H₅N(HSO₄⁻)_w(SO₄²⁻)_x(WPA³⁻)_y(H₂O)_z of PANI-WPA samples are determined (Table 4), where C₆H₅N denotes unit of positively charged PANI chain and WPA³⁻ denotes 12-tungstophosphate anion (PW₁₂O₄₀³⁻). The determined C/N mole ratio (6.07–6.16) corresponds well to the theoretically expected value (6.0). Assuming that all S content originated from sulfate/hydrogen sulfate anions, the mole ratio of sulfate and hydrogen sulfate anions incorporated in PANI-WPA samples is determined by using the formula $\log([\text{SO}_4^{2-}]/[\text{HSO}_4^-]) = \text{pH} - \text{pK}_a(\text{HSO}_4^-)$, where final pH values of reaction mixtures are used. The water content is calculated taking into account the difference of total hydrogen content and the content of hydrogen originated from both the hydrogen sulfate anions and C₆H₅N units. It can be seen (Table 4) that the content of WPA³⁻ anions significantly increases (0.007 → 0.034 mole per mole of C₆H₅N unit) with the increase of the initial WPA·6H₂O/aniline weight ratio (0.2 → 1). The average charge of C₆H₅N unit in PANI-WPA (0.29–0.34) indicate oxidation state somewhat higher than that of protoemeraldine polycation $[(-\text{C}_6\text{H}_4\text{NH}-)_{3n}(-\text{C}_6\text{H}_4\text{NH}^{+\bullet}-)_n]$ and lower compared with emeraldine polycation $[(-\text{C}_6\text{H}_4\text{NH}-\text{C}_6\text{H}_4\text{NH}^{+\bullet}-)_n]$. Positively charged N-phenylphenazinium units are also probably present.

3.4. Conductivity of PANI-WPA

The conductivity and mass yield of PANI-WPA samples (dried in vacuum at 60 °C for 3 h prior to measurement) increased linearly with the increase of the initial WPA·6H₂O/aniline weight ratio (Fig. 5). These findings, in accordance with elemental analysis, suggest a more efficient protonation of PANI with added WPA than with released sulfuric acid, and simultaneous incorporation of 12-tungstophosphate counter-ions into

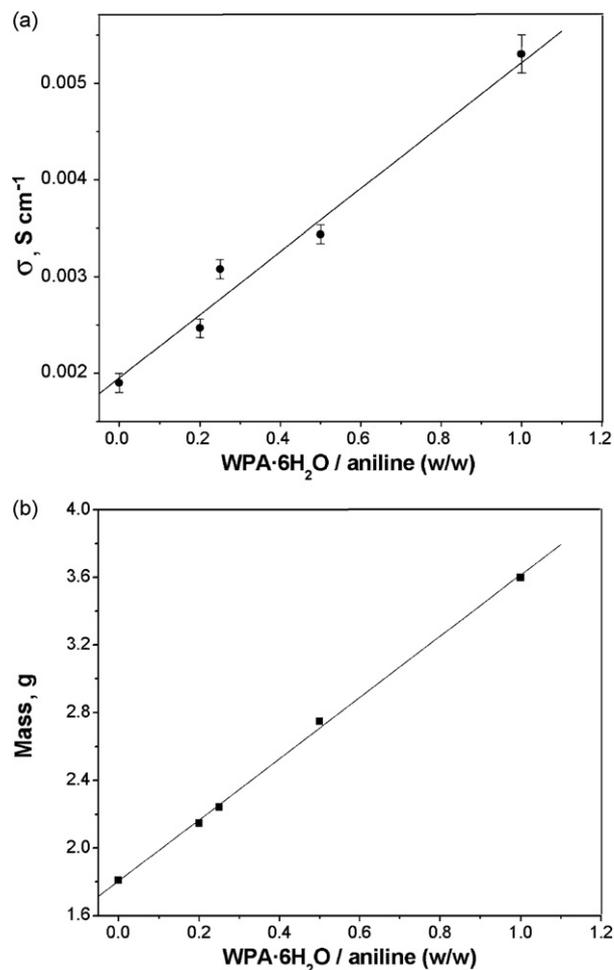


Fig. 5. The conductivity (a) and mass (b) of PANI-WPA and nanostructured PANI sulfate/hydrogen sulfate samples.

the PANI matrix, leading thus to the formation of conducting PANI-WPA emeraldine salt segments. On the other hand, the oligomeric intermediate (submicro- and microspheres) was non-conducting ($3.8 \times 10^{-9} \text{ S cm}^{-1}$). The lower conductivity of micro/nanostructured PANI-WPA $[(2.5\text{--}5.3) \times 10^{-3} \text{ S cm}^{-1}]$ in comparison with ordinary dry granular PANI emeraldine salt $[(1\text{--}10) \text{ S cm}^{-1}]$ can be explained by the fact that final product of aniline oxidation in the presence of WPA is composed of non-conducting oligomers and conducting PANI. Their mutual proportion determines the final conductivity. The existence of non-conducting segments (phenazine-like, etc.) in PANI chains, in addition to ordinary emeraldine segments, as well as large contact resistance between micro- and nanoparticles can additionally reduce the conductivity of final PANI-WPA. The non-conducting nature of oligomeric intermediate, containing substantial amount of WPA, can be explained by its oxidation state higher than that of emeraldine (pernigraniline- and phenazine-like). The charge of 12-tungstophosphate anions in intermediate is most probably partially compensated with anilinium and NH_4^+ cations. It is known that various insoluble salts of WPA exhibit submicro- and microsphere morphology [45], that is well correlated with observed morphology of intermediate sample.

3.5. Thermal analysis

The first weight loss from 25 to ~ 200 °C (3–5 wt.%) observed in TGA curves of all PANI-WPA samples (Fig. 6), and an endothermic

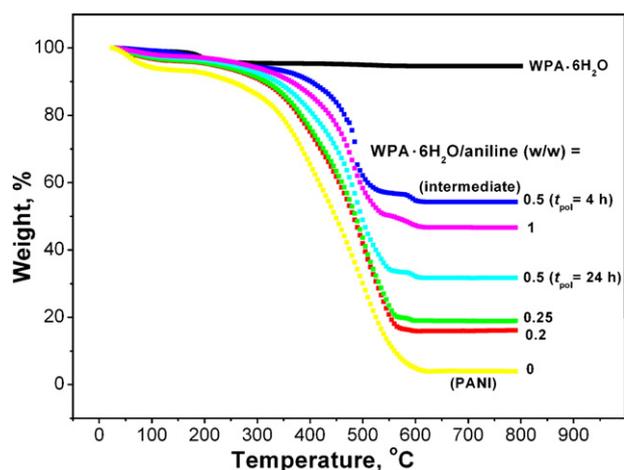


Fig. 6. TGA curves for PANI-WPA samples, intermediate, nanostructured PANI sulfate/hydrogen sulfate, and WPA·6H₂O, recorded in an air stream.

peak around 50 °C present in their DTA curves (Fig. 7a), correspond to the release of residual water from the polymer matrix [37,46]. Pure WPA·6H₂O loses crystalline water, and this is evidenced as an endothermic DTA peak at 195 °C (Fig. 7a).

The main weight loss of the PANI-WPA samples in an air stream that occurred in the temperature range from ~300 to 630 °C is due to the degradation and decomposition of the PANI backbone (Fig. 6). The corresponding combustion of nanostructured PANI sulfate/hydrogen sulfate in air was completed at ~630 °C (Fig. 6). The residue obtained after heating of PANI-WPA samples up to 800 °C represents an inorganic compound, a PW₈O₂₆ bronze [44]. Based on TGA results, the contents of PANI, the PW₈O₂₆ bronze residue, and water in PANI-WPA samples have been determined (Table 5). The mass of PW₈O₂₆ bronze residue increases with the increase of the initial WPA·6H₂O/aniline weight ratio (Table 5). The content of W determined by ICP-OES (Table 3) agrees well with that determined from TGA measurements (Table 5).

The DTA thermograms of all PANI-WPA samples and nanostructured PANI sulfate/hydrogen sulfate (Fig. 7a) show an exothermic hump at around 200 °C, which is most likely related to a crosslinking reaction (inter- and/or intramolecular) of PANI chains and

Table 5

Content of PANI, the PW₈O₂₆ bronze residue obtained at 790 °C, water and W in PANI-WPA samples, determined by TGA.

Initial WPA·6H ₂ O to aniline weight ratio	Content (wt.%)			
	PANI	PW ₈ O ₂₆ bronze residue	H ₂ O	W
0.2	79.39	16.06	4.55	12.32
0.25	76.76	18.87	4.37	14.47
0.5 (intermediate)	42.52	54.19	3.29	41.56
0.5	64.80	31.65	3.55	24.27
1	50.38	46.63	2.99	35.76

subsequent formation of phenazine or phenoxazine segments [47–49]. With further growth in temperature, four exothermic peaks with maxima at about 400 °C, ~475–495 °C, ~540–545 °C, and at 590–600 °C appear at DTA curves of PANI-WPA samples. The first broad peak around 400 °C can be attributed to the thermal oxidative degradation and combustion of oligoaniline fraction in PANI-WPA. The remained products, having higher molecular weights, show a combustion process splitted into two phases, with peak temperature at ~475–495 °C for the first, and at ~540–545 °C for the second phase. For both phases, the peak temperature moves to lower values with increasing WPA content in PANI-WPA, possibly due to the catalytic effect of WPA on the oxidation of PANI, similarly to its catalytic influence on the oxidation of other aromatic amines [50]. It seems that this catalytic effect is different for the products with lower and higher extent of carbonization. To the best of our knowledge, the mentioned DTA peak at ~540–545 °C was not previously reported for polyanilines, and is not observed in the DTA curve of pure nanostructured PANI sulfate/hydrogen sulfate (Fig. 7a). Its peak area decrease with increasing WPA content in PANI-WPA sample and it completely disappears in DTA curve of oligomeric intermediate sample (Fig. 7b). The process of PW₈O₂₆ bronze formation corresponds to the last exothermic DTA peak observed at 610 °C for pure WPA·6H₂O and at 590–600 °C for PANI-WPA samples (Fig. 7a) [44].

3.6. FTIR and Raman spectra of PANI-WPA

The characteristic bands of PANI emeraldine salt are observed in the FTIR spectra of all PANI-WPA samples (Fig. 8, Table 6) at around 1571, 1495, 1304, 1246, and 1148 cm⁻¹ [9,16].

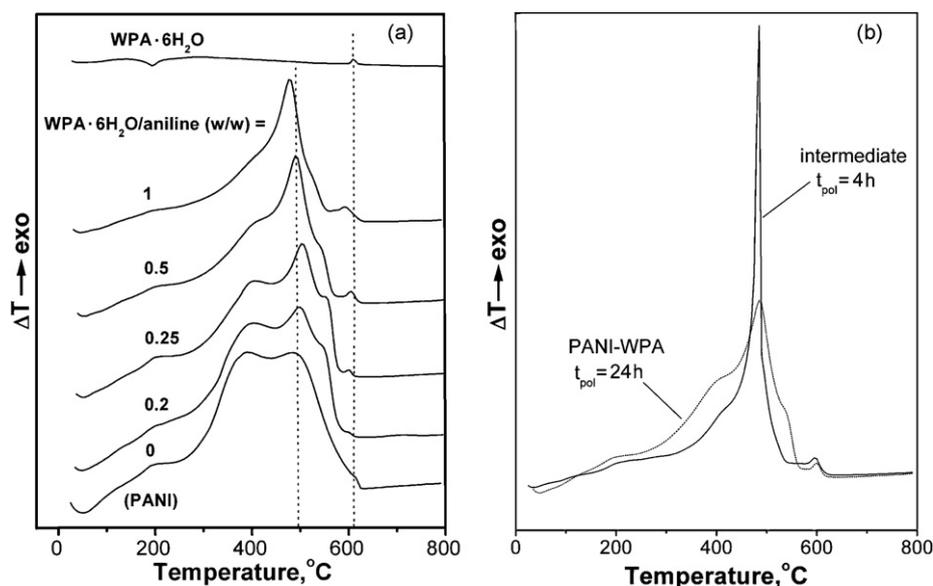


Fig. 7. DTA curves for (a) PANI-WPA samples, nanostructured PANI sulfate/hydrogen sulfate, WPA·6H₂O, and (b) PANI-WPA and its intermediate, both samples synthesized at the initial weight ratio WPA·6H₂O/aniline = 0.5 and isolated at $t_{\text{pol}} = 24$ h and 4 h, respectively.

Table 6
Assignments of main FTIR and Raman bands for PANI-WPA and its intermediate.

Wavenumbers (cm ⁻¹)		Assignments		
PANI-WPA ^a		Intermediate ^a		
FTIR	Raman	FTIR	Raman	
3218		3586		$\nu_{as}(\text{N-H})$ of primary amino group
		3210		$\nu(\text{N-H})$ or $-\text{NH}^+=$ stretching, H-bonded
		3142		$-\text{NH}^+=$ stretching, H-bonded
3054		3064		H-bonded $\nu(\text{N-H})$, aromatic $\nu(\text{C-H})$
	1632	1634 sh	1630 sh	$\nu(\text{C}=\text{C})$ in Phz, Saf, $\nu(\text{C}=\text{N})$ in Phz, Saf
	1592	1601		$\nu(\text{C}\sim\text{C})_{\text{B}}$, $\nu(\text{C}\sim\text{C})$ in Phz, Saf
1571		1571		$\delta(\text{N-H})$ of primary aromatic amine
	1562		1573	$\nu(\text{C}=\text{C})_{\text{Q}}$, $\nu(\text{C}\sim\text{C})_{\text{SQ}}$
	1511		1536	$\nu(\text{C}=\text{C})_{\text{Q}}$
1496		1505		Phz, $\nu(\text{C}\sim\text{C})_{\text{Q}}$
	1477		1475	Phz, Saf
1452		1449		$\delta(\text{N-H})$
	1405	1402	1405	$\nu(\text{C}\sim\text{C})_{\text{B}}$
		1353		Ring stretching in Phz, Saf
	1337		1355	$\nu(\text{C}\sim\text{N}^+)$, Phz, Saf
1306		1302		$\nu(\text{C}\sim\text{N}^+)$
	1250	1268 sh	1254	$\nu(\text{C}\sim\text{N})$ of secondary aromatic amine
1246			1229	$\nu(\text{C}\sim\text{N})$ of primary aromatic amine
	1235		1229	$\nu(\text{C}\sim\text{N})_{\text{B}}$
	1175		1148	$\nu(\text{C}\sim\text{N}^+)$
1150			1148	$\nu(\text{C}\sim\text{N})_{\text{B}}$
			1148	$\delta(\text{C-H})_{\text{SQ}}$
		1102		$\text{B-NH}^+=\text{Q/B-NH}^+\sim\text{B}$ stretching
1080		1079		$\delta(\text{C-H})_{\text{Q}}$
1041		1043		monovacant lacunary Keggin anion $[\text{PW}_{11}\text{O}_{39}]^{7-}$
	1005		999	$\nu_{as}(\text{P-O}_a)$ in the central PO_4 tetrahedron of Keggin anion
973		974		HSO_4^- or SO_3^- on sulfonated aromatic ring
954		954		Keggin anion
878		895		$\nu_{as}(\text{W-O}_d)$ (terminal oxygen in Keggin anion)
			827	$[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ (Dawson)/ $[\text{PW}_{11}\text{O}_{39}]^{7-}$ (lacunary)
813		816		$\nu_{as}(\text{W-O}_b\text{-W})$ (W-O-W bridges between corner-sharing WO_6 octahedra in Keggin anion)/ $\gamma(\text{C-H})$ of 1,2,4-trisubstituted benzene ring/ HSO_4^-
	811		827	$\nu_{as}(\text{W-O}_c\text{-W})$ (W-O-W bridges between edge-sharing octahedra in Keggin anion)/ $\gamma(\text{C-H})$ of 1,4-disubst. benzene
620		620		$\gamma(\text{C-H})$
	233		235	HSO_4^- , SO_4^{2-}
			235	Keggin anion

Abbreviations: B, benzenoid ring; Q, quinonoid ring; SQ, semi-quinonoid ring; \sim , bond intermediate between the single and double bonds; ν , stretching; δ , in-plane deformation; γ , out-of-plane deformation; sh, shoulder; Phz, phenazine-like segment; Saf, safranin (N-phenylphenazine)-like segment.

^a Both PANI-WPA (nanorods and submicro/microspheres) and its intermediate (submicro- and microspheres) were prepared at the initial weight ratio WPA-6H₂O/aniline = 0.5 and isolated at t_{pol} = 24 h and 4 h, respectively.

FTIR spectroscopy proved that 12-tungstophosphate anions serve as counter-ions in the positively charged PANI matrix (Fig. 9). The bands characteristic of the Keggin anion $\text{PW}_{12}\text{O}_{40}^{3-}$ are observed in the FTIR spectra of PANI-WPA samples (Fig. 8, Table 6) at ca. 1080, 977–968, and 892–877 cm⁻¹ [29,43,44,51]. The overlapping of $\nu_{as}(\text{W-O}_b\text{-W})$ band (Table 6) with the band due to $\gamma(\text{C-H})$ vibration of 1,2,4-trisubstituted benzene ring in branched PANI unit [52], and with the band due to hydrogen sulfate ions is possible. The strong band at 821–810 cm⁻¹ in the spectra of all PANI-WPA samples is attributed to the mixed contributions of the $\gamma(\text{C-H})$ vibration of 1,4-disubstituted benzene ring in the linear PANI backbone [9,16,19,52] and the $\nu_{as}(\text{W-O}_c\text{-W})$ vibration of Keggin anion [43,51] (Table 6).

The band at ~ 970 cm⁻¹ due to Keggin anion is accompanied with a peak or shoulder at ~ 955 cm⁻¹. This feature indicates the presence of an anion structure with lower symmetry than T_d symmetry of the Keggin anion, such as the Dawson $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ or the lacunary $[\text{PW}_{11}\text{O}_{39}]^{7-}$ structures, which were found to exist in the aqueous solutions of WPA at pH > 1 [43]. UV and IR spectroscopic investigations have shown that the changes in molecular structures of WPA are reversible with pH changes when low concentrations of aqueous solutions of WPA (2×10^{-5} – 2×10^{-2} mol dm⁻³) were

used [43]. When the pH of the WPA aqueous solution was raised from 1 to 7 and then decreased back from 7 to 1, the spectral features characteristic of Keggin anion at pH 1 disappeared at pH 7, but appeared again when pH 1 was attained. When pH was changed from 7 to 1, other molecular species were found to be converted almost completely to the Keggin anion [43]. In the present study, concentration of WPA in the initial reaction mixture was in the range (6×10^{-4} – 3×10^{-3}) mol dm⁻³ (Table 1), and the reversible changes of WPA molecular species are expected with pH change. That is why we can speculate that during the oxidation of aniline in aqueous solutions of WPA, starting at pH ~ 6 and finishing at pH ~ 1.1 – 1.4 , the Keggin anion is finally incorporated in PANI-WPA materials, but certain amount of other tungstophosphate molecular species of lower symmetry is present, especially in samples prepared at the initial weight ratios WPA-6H₂O/aniline = 0.2, 0.25 and 0.5. The presence of competitive hydrogen sulfate and sulfate counter-ions is indicated by the bands at ~ 1040 and 620 cm⁻¹ in the FTIR spectra of all PANI-WPA samples (Table 6).

Since the conductivity, elemental composition and morphology of intermediate and PANI-WPA collected at different phases of aniline oxidation (t_{pol} = 4 h and 24 h, respectively) differ considerably, a question about differences in their molecular structure arises.

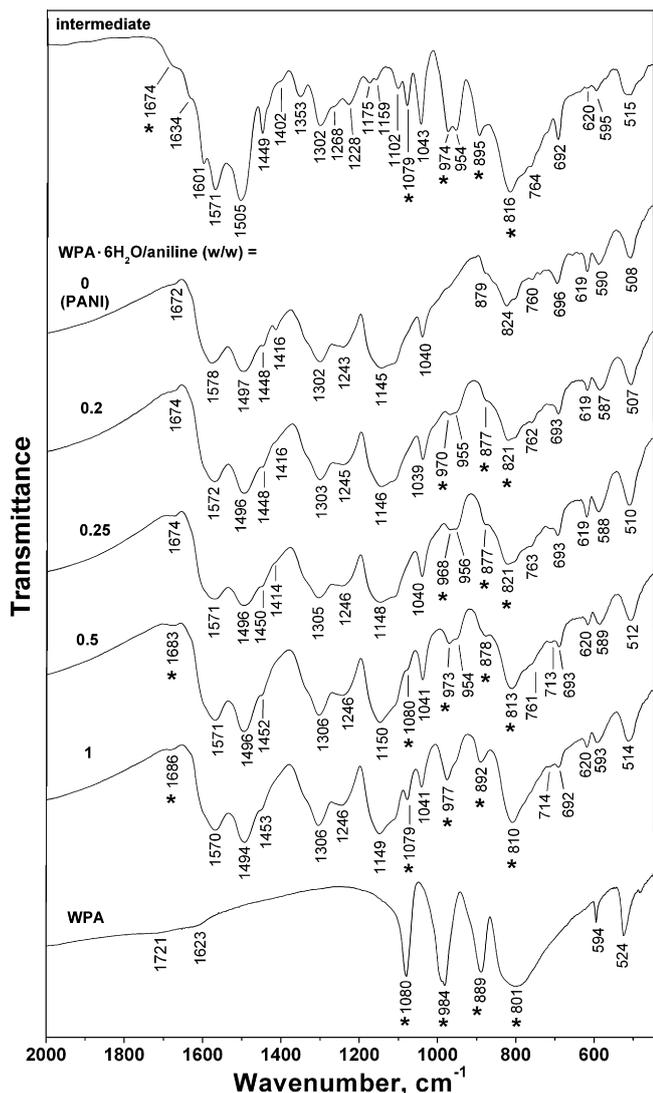


Fig. 8. FTIR spectra of PANI-WPA samples synthesized at various initial WPA:6H₂O/aniline weight ratios, nanostructured PANI sulfate/hydrogen sulfate, WPA:6H₂O, and intermediate synthesized at the initial weight ratio WPA:6H₂O/aniline = 0.5 and isolated at $t_{\text{pol}} = 4$ h. The bands corresponding to Keggin anion are marked by asterisk.

The FTIR bands due to 12-tungstophosphate anions, observed in the FTIR spectrum of intermediate at 1080, 974, 895 and 816 cm^{-1} , are relatively stronger in comparison with corresponding bands in the spectrum of PANI-WPA (Fig. 8). This feature is in accordance with significantly higher content of tungsten found in intermediate

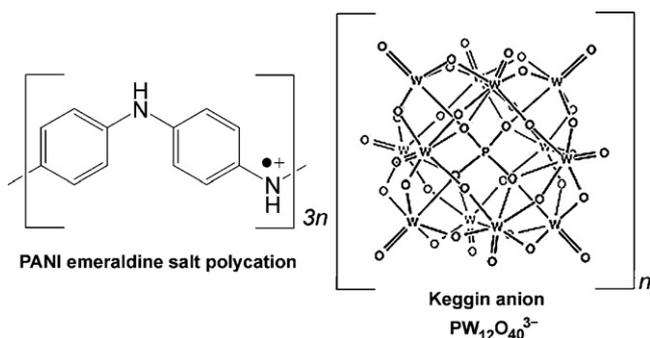


Fig. 9. The emeraldine salt form of PANI-WPA.

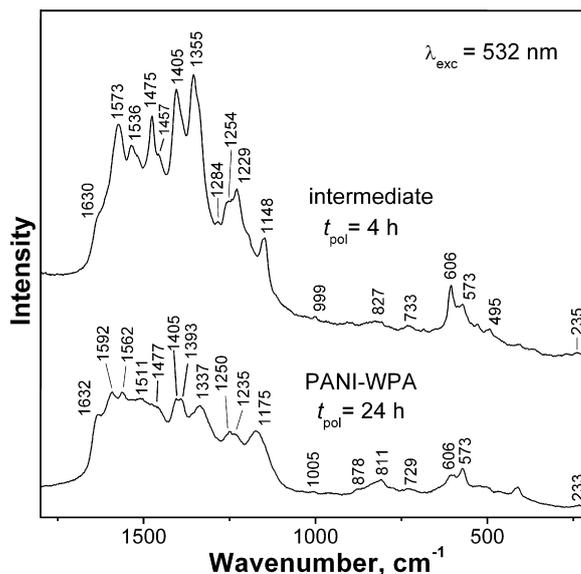


Fig. 10. Raman spectra of intermediate and PANI-WPA samples, both synthesized at the initial weight ratio WPA:6H₂O/aniline = 0.5, and isolated at $t_{\text{pol}} = 4$ h and 24 h, respectively (excitation wavelength 532 nm).

related to PANI-WPA. In addition to the characteristic bands of Keggin structure, the presence of other tungstophosphate molecular species with lower symmetry (Dawson structure) in the intermediate is indicated by the band at 954 cm^{-1} [43]. It is expectable that Dawson structure is present in considerable amount at the end of intermediate synthesis (pH 1.9). The splitting of the band at $\sim 1080 \text{ cm}^{-1}$ due to the P–O stretching vibration into two bands at 1102 and 1043 cm^{-1} , observed in the spectrum of intermediate, is characteristic of the monovacant lacunary Keggin anion $[\text{PW}_{11}\text{O}_{39}]^{7-}$.

The band at $\sim 1150 \text{ cm}^{-1}$, which has been associated with the vibrations of the charged units $\text{Q}=\text{NH}^+-\text{B}$ or $\text{B}-\text{NH}^+-\text{B}$ and high degree of electron delocalization in PANI, is absent in the spectrum of intermediate, but it is very strong in the spectrum of PANI-WPA. This feature, as well as the absence of so-called “free-carrier absorption” at wavenumbers higher than $\sim 1700 \text{ cm}^{-1}$ in the FTIR spectrum of intermediate, correlates well with the results that intermediate is non-conducting, while PANI-WPA is semiconducting. The bands at 3586 and 1601 cm^{-1} , and the shoulder at 1268 cm^{-1} , present in the spectrum of intermediate but absent in the FTIR spectra of PANI-WPA samples, can be ascribed to primary aromatic amine (Table 6), and indicate the oligomeric nature of intermediate sample [52,53]. The presence of substituted phenazine and *N*-phenylphenazine (safranin) segments in macromolecular chains of intermediate is indicated by the FTIR bands at 1634, 1402, and 1353 cm^{-1} [16,53] (Fig. 8). The strong and broad band with maxima at 3210, 3142 and 3064 cm^{-1} observed in the spectrum of intermediate can be assigned to different types of intra- and intermolecular hydrogen-bonded N–H and $-\text{NH}^+=$ stretching vibrations, such as $\text{N}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{O}_d$ (O_d is terminal oxygen in the 12-tungstophosphate anion) [16,53]. The hydrogen bonding between 12-tungstophosphate anions and aniline/oligoanilines possibly plays an important role in directing the spherical growth of submicro- and microparticles.

The Raman spectra of intermediate ($t_{\text{pol}} = 4$ h) and PANI-WPA ($t_{\text{pol}} = 24$ h), showed also remarkable differences (Fig. 10, Table 6). The Raman bands attributed to conducting emeraldine salt segments, observed in the spectrum of PANI-WPA at 1592, 1511, 1337, and 1175 cm^{-1} , are absent in the spectrum of intermediate [25] (Table 6). The band attributed to the substituted phenazine or safranin segments is observed in the Raman spectra of intermediate

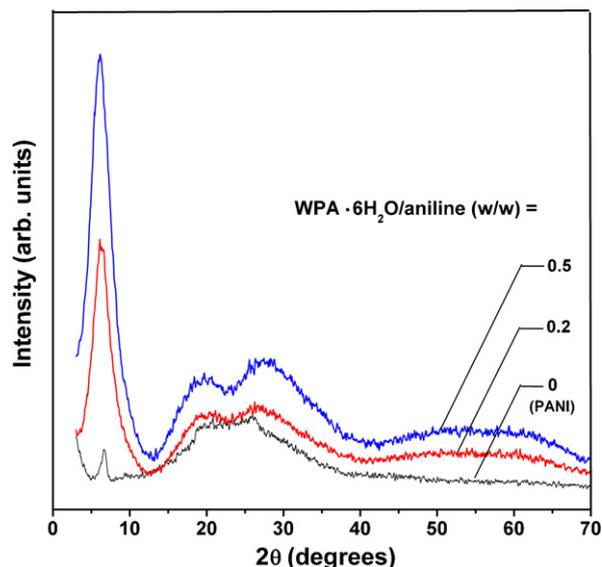


Fig. 11. XRPD patterns of nanostructured PANI sulfate/hydrogen sulfate and PANI-WPA samples synthesized at various initial WPA·6H₂O/aniline weight ratios.

and PANI-WPA at 1405 cm⁻¹, being significantly stronger in the former spectrum (Table 6) [25]. The very strong band at 1355 cm⁻¹ appears only in the spectrum of intermediate, and can be ascribed to the C~N⁺ ring-stretching vibration of substituted phenazines and N-phenylphenazines [25,54]. Phenazine-like units are formed by the process of oxidative intramolecular cyclization of branched aniline oligomers [21–23,25]. The bands attributable to WPA are observed at 999 and 235 cm⁻¹ in the Raman spectrum of intermediate, and at 1005 and 233 cm⁻¹ in the spectrum of PANI-WPA [44].

The FTIR and Raman spectra of the yellow residue obtained after heating of PANI-WPA up to 800 °C in air (Supporting Information, S1) correspond well to the literature spectra attributed to PW₈O₂₆ bronze prepared by heating of WPA at 700 °C [44]. The most intense FTIR band at 825 cm⁻¹ corresponds to the O–W–O stretching, and main Raman bands at 796, 688 and 248 cm⁻¹ are attributable to O–W–O and W–O–W stretching modes, respectively [44]. Characteristic FTIR and Raman bands of PANI completely disappear in the spectra of product obtained upon heating of PANI-WPA.

3.7. X-ray powder diffraction

The XRPD patterns of nanostructured PANI sulfate/hydrogen sulfate and micro/nanostructured PANI-WPA samples (Fig. 11) are typical for partially crystalline polymers, consisting of diffraction peaks which are superimposed on the amorphous halo. The sharp and distinct peak for PANI sulfate/hydrogen sulfate at 2θ = 6.7° (corresponding to the *d* spacing of 13.2 Å), is related with the presence of sulfate/hydrogen sulfate counter-ions, since the diffraction pattern of PANI base did not give any peak in this range of 2θ [55,56]. A peak at similar position has been previously observed for PANI doped with heteropolyanions (2θ ~ 7°) [55,56], nanostructured PANI doped with dicarboxylic acids (2θ = 6.5°) [11], and nanostructured PANI sulfate (2θ = 6.4°) [24]. This peak has been associated with the ordering of counter-ions in the PANI matrix and the position of this peak depended on the doping level of PANI [55,56]. In the XRPD patterns of PANI-WPA samples (Fig. 11), this peak is observed at 2θ = 6.1° and 6.2° (corresponding to *d* spacing of 14.5 Å and 14.3 Å) for the initial WPA·6H₂O/aniline ratios of 0.2 and 0.5, respectively. It is much stronger than corresponding peak of nanostructured PANI sulfate/hydrogen sulfate. The shifting of this peak to lower 2θ values is most probably due to the presence of

large 12-tungstophosphate counter-ions beside sulfate and hydrogen sulfate counter-ions in PANI-WPA samples. Relative intensity of this peak increases with the increase of 12-tungstophosphate anion content in PANI-WPA, because the areas of their ordering also increase [55,56]. The broad peaks in the XRPD patterns of nanostructured PANI sulfate/hydrogen sulfate centered at 2θ = 20.8° and 26.0° correspond to the (100) and (110) reflections, respectively, indexed previously in a pseudoorthorhombic cell of PANI emeraldine salt [57]. PANI-WPA samples also show these broad peaks at 2θ = 20.4° and 26.3° for WPA·6H₂O/aniline = 0.2, and at 2θ = 19.7° and 27.3° for WPA·6H₂O/aniline = 0.5. Set of distinct sharp Bragg reflections characteristic for WPA [44] are not detected for PANI-WPA samples, indicating that 12-tungstophosphate anions are dispersed at the molecular level in the PANI matrix and that phase segregation in PANI-WPA does not take place [56].

4. Conclusions

Aniline has been oxidized in the presence of 12-tungstophosphoric acid, using ammonium peroxydisulfate as an oxidant. Oxidation started from slightly acidic aqueous solutions with pH value in the range 5.4–5.9, depending on the used initial WPA·6H₂O/aniline weight ratio (1, 0.5, 0.25 and 0.2). The reaction proceeded in two exothermic phases which are well separated with an athermal period. The kinetics of oxidation was substantially affected by the presence of WPA. The increase of initial WPA·6H₂O/aniline weight ratio leads to the prolongation of athermal period, i.e. to the delay of subsequent autoacceleration phase of aniline polymerization.

The morphology of polymerization products changed with polymerization time, during a single polymerization process, from non-conducting submicro-/microspheres containing oligoaniline intermediates and ammonium/anilinium 12-tungstophosphate, to semiconducting PANI-WPA consisted of nanotubes and/or nanorods co-existing with submicro-/microspheres. Submicro- and microspheres in PANI-WPA are accompanied with nanotubes and nanorods in the sample prepared at the initial weight ratio WPA·6H₂O/aniline = 0.2, and with nanorods in the samples prepared at WPA·6H₂O/aniline = 0.25, 0.5 and 1. The average diameter of nanorods decreased with increase of the initial WPA/aniline weight ratio. TEM investigations revealed that submicro- and microspheres possess a core-shell structure. A rhombic dodecahedral shape of core was observed by SEM.

The incorporation of 12-tungstophosphate counter-ions into PANI matrix has been proved by FTIR, Raman and ICP-OES spectroscopies, as well as by TGA and DTA. The Keggin anions predominate in PANI-WPA, but smaller amount of tungstophosphate species of lower symmetry, such as Dawson structure and monovacant lacunary Keggin anion, were also detected by FTIR spectroscopy. The submicro- and microspheres, formed before nanotubes and nanorods, contain significant amount of incorporated 12-tungstophosphate ions. The extent of 12-tungstophosphate counter-ions incorporation decreased, while the extent of sulfate/hydrogen sulfate competitive incorporation increased with the polymerization time in a single polymerization process, as revealed by ICP-OES and FTIR spectroscopies, TGA and elemental analysis. The diffraction patterns of PANI-WPA exhibited sharp and very strong peak at 2θ ~ 6.2° which reflects the ordering of 12-tungstophosphate counter-ions in the PANI matrix.

The conductivity of PANI-WPA is higher than that of nanostructured PANI sulfate/hydrogen sulfate prepared without WPA and increased from 2.5 × 10⁻³ S cm⁻¹ to 5.3 × 10⁻³ S cm⁻¹ as the initial WPA·6H₂O/aniline weight ratio increased from 0.2 to 1, respectively.

The new micro/nanostructured PANI-WPA materials, which combine unique properties of self-assembled PANI micro/nanostructures and WPA salts, could be applied as catalysts and sensors.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.synthmet.2010.04.025.

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Inhibition of rat synaptic membrane Na⁺/K⁺-ATPase and ecto-nucleoside triphosphate diphosphohydrolases by 12-tungstosilicic and 12-tungstophosphoric acid

Mirjana B. Čolović^{a,†}, Danica V. Bajuk-Bogdanović^b, Nataša S. Avramović^c, Ivanka D. Holclajtner-Antunović^b, Nada S. Bošnjaković-Pavlović^b, Vesna M. Vasić^a, Danijela Z. Krstić^{c,*}

^a Department of Physical Chemistry, Vinča Institute of Nuclear Sciences, University of Belgrade, M. Petrović 12-14, PO Box 522, 11001 Belgrade, Serbia

^b Faculty of Physical Chemistry, University of Belgrade, Belgrade, Serbia

^c University School of Medicine, Institute of Medicinal Chemistry, University of Belgrade, Višegradska 26, 11000 Belgrade, Serbia

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ABSTRACT

The in vitro influence of Keggin structure polyoxotungstates, 12-tungstosilicic acid, H₄SiW₁₂O₄₀ (WSiA) and 12-tungstophosphoric acid, H₃PW₁₂O₄₀ (WPA), and monomer Na₂WO₄ × 2H₂O on rat synaptic plasma membrane (SPM) Na⁺/K⁺-ATPase and E-NTPDase activity was studied, whereas the commercial porcine cerebral cortex Na⁺/K⁺-ATPase served as a reference. Dose-dependent Na⁺/K⁺-ATPase inhibition was obtained for all investigated compounds. Calculated IC₅₀ (10 min) values, in mol/l, for SPM/commercial Na⁺/K⁺-ATPase, were: 3.4 × 10⁻⁶/4.3 × 10⁻⁶, 2.9 × 10⁻⁶/3.1 × 10⁻⁶ and 1.3 × 10⁻³/1.5 × 10⁻³ for WSiA, WPA and Na₂WO₄ × 2H₂O, respectively. In the case of E-NTPDase, increasing concentrations of WSiA and WPA induced its activity reduction, while Na₂WO₄ × 2H₂O did not noticeably affect the enzyme activity at all investigated concentrations (up to 1 × 10⁻³ mol/l). IC₅₀ (10 min) values, obtained from the inhibition curves, were (in mol/l): 4.1 × 10⁻⁶ for WSiA and 1.6 × 10⁻⁶ for WPA. Monolacunary Keggin anion was found as the main active molecular species present under physiological conditions (in the enzyme assays, pH 7.4), for the both polyoxotungstates solutions (1 mmol/l), using Fourier transform infrared (FT-IR) and micro-Raman spectroscopy. Additionally, commercial porcine cerebral cortex Na⁺/K⁺-ATPase was exposed to the mixture of Na₂WO₄ × 2H₂O and WSiA at different concentrations. Additive inhibition effect was achieved for lower concentrations of Na₂WO₄ × 2H₂O/WSiA (≤ 1 × 10⁻³/4 × 10⁻⁶ mol/l), while antagonistic effect was obtained for all higher concentrations of the inhibitors.

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1. Introduction

Polyoxometalates (POMs) are polyanionic oligomeric aggregates of transition metal ions, such as tungsten, molybdenum, vanadium, etc. held together by oxygen bridges, with a high density of negative charge. They are relatively stable, some even highly stable in aqueous solutions at biological pH values.^{1,2} In addition to applications in catalysis, separations, analysis, and as electron-dense imaging agents, some of these complexes have been shown to exhibit biological activity in vitro as well as in vivo ranging from anti-cancer, antibiotic, and antiviral to antidiabetic effects.^{2–6} Due

to their negative charges they bear resemblance to nucleotides and therefore affect activity of nucleotide-dependent enzymes.^{7–12}

Na⁺/K⁺-ATPase (sodium pump) belongs to the P-type ATPase family, the members of which are able to utilize the energy of ATP to transport ions against their electrochemical gradient. Na⁺/K⁺-ATPase is a cell membrane located enzyme that establishes and maintains the high internal K⁺ and low internal Na⁺ concentrations, characteristic and essential for normal cellular activities of most animal cells.^{13,14} The activity of this enzyme is very sensitive to the presence of some metal ions and organic compounds of various structures, especially some drugs and pesticides.^{15–18} Moreover, recent studies show that in addition to pumping ions, Na⁺/K⁺-ATPase interacts with neighboring membrane proteins and organized cytosolic cascades of signaling proteins to send messages to the intracellular organelles.^{19,20} Thus, this function of sodium pump as a receptor and signaling mediator suggests that Na⁺/K⁺-ATPase has pivotal role in cancer cell migration and supports the view that Na⁺/K⁺-ATPase could be an important target for development of anti-cancer drugs.^{21–24}

Abbreviations: ADP, adenosine diphosphate; ATP, adenosine triphosphate; E-NTPDases, ecto-nucleoside triphosphate diphosphohydrolases; FT-IR, Fourier transform infrared; POMs, polyoxometalates; SPM, synaptic plasma membrane; WPA, 12-tungstophosphoric acid; WSiA, 12-tungstosilicic acid.

* Corresponding author. Tel.: +381 11 3607 137; fax: +381 11 3607 134.

E-mail addresses: colovicm@vinca.rs (M.B. Čolović), danijela.krstic@med.bg.ac.rs (D.Z. Krstić).

† Tel.: +381 11 3408 636/64 357 27 10; fax: +381 11 8066 434.

The ecto-nucleoside triphosphate diphosphohydrolases, E-NTPDases, (ecto-ATPase) which do not belong to the P-type ATPase family, represent plasma membrane bound enzymes that, in the presence of divalent cations (Ca^{2+} or Mg^{2+}), hydrolyses extracellular nucleotides (ATP and ADP) because of the outward orientation of its active site.^{25,26} Since extracellular adenosine and adenine nucleotides induce various cellular responses (through activation of P1 and P2 receptors), E-NTPDases represent the major part of purinergic signaling.^{8,26} Moreover, inhibition of E-NTPDases may explain or contribute to some observed *in vitro* and *in vivo* polyoxometalate effects, including anti-cancer activity, protection against viral, bacterial and protozoa infections, antidiabetic activity.^{7,27,28}

The aim of this work was the investigation of the *in vitro* effect of two representative polyoxotungstates possessing Keggin structure: 12-tungstosilicic acid, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (WSiA) and 12-tungstophosphoric acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (WPA) (Fig. 1), that are not cytotoxic,²⁹ on Na^+/K^+ -ATPase, and E-NTPDases activity using rat synaptic plasma membrane (SPM) as a model system, while the commercial porcine cerebral cortex Na^+/K^+ -ATPase served as a reference. Na^+/K^+ -ATPase and E-NTPDases were chosen because of their key role in normal functioning most cells of higher eukaryotic organisms^{26,30} as well as in development and progression of different cancers²³ and, on the other hand, of the known influence of POMs on nucleotide-dependent enzymes^{9–11,31,32} as well as their anti-cancer activity. In order to determine the truly active species in water at physiological pH, the stability and molecular speciation of WPA and WSiA under enzyme assay conditions, using FT-IR and micro-Raman spectroscopy, was screened. In addition, the influence of $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$, the starting monomer in the POMs synthesis, on Na^+/K^+ -ATPase and E-NTPDases activity was studied, as well as its simultaneous effect, in combination with WSiA, on the commercial Na^+/K^+ -ATPase.

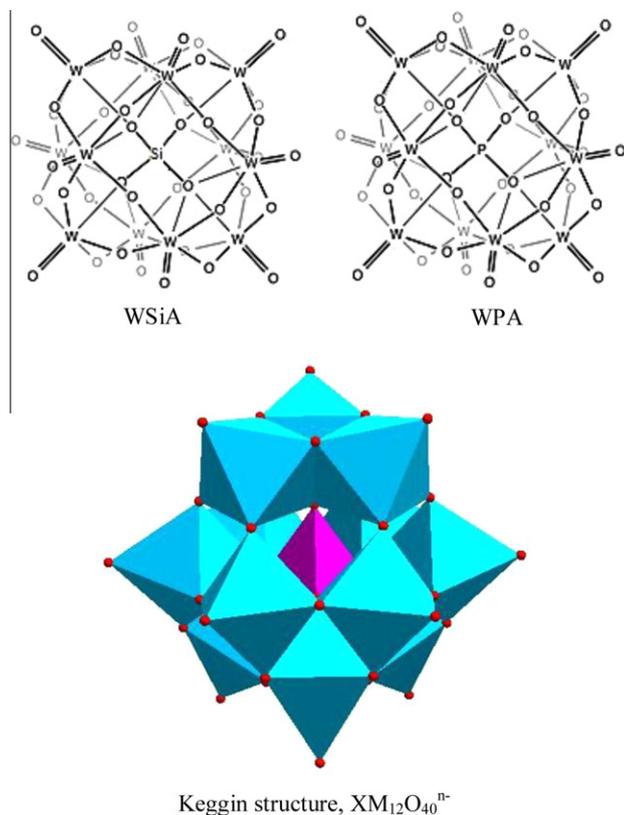


Figure 1. The chemical structures of WSiA and WPA.

2. Material and methods

2.1. Chemicals

All chemicals were of analytical grade. Na^+/K^+ -ATPase from porcine cerebral cortex and ATP were purchased from Sigma Chemicals Co. (Germany), as well as some chemicals for medium assay (magnesium chloride and Tris-HCl). The specific Na^+/K^+ -ATPase activity was $25.8 \mu\text{mol Pi/h/mg protein}$ (Pi—inorganic orthophosphate). Other medium assay chemicals (sodium chloride, potassium chloride), chemicals for determination of Pi (stannous chloride and ammonium molybdate) were from Merck (Germany). $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$ and WSiA were commercially available (Fluka, Germany), while WPA was prepared according to the literature method³³ and confirmed by infrared spectroscopy. Both acids were recrystallized prior to use and heated about 10 min at 80°C in order to get stable acid hexahydrate ($\text{WPA} \cdot 6\text{H}_2\text{O}$, $\text{WSiA} \cdot 6\text{H}_2\text{O}$).

2.2. Preparation of 12-tungstosilicic acid and 12-tungstophosphoric acid solutions

Stock solutions of POMs (10^{-2} mol/l , $\text{pH} \approx 1$) were prepared daily, by solving the solid compounds in water shortly before use, while prepared $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$ (10^{-2} mol/l , $\text{pH} \approx 7$) stock solution was kept frozen. Working solutions were prepared daily by diluting the stock solutions to desired concentrations. Preliminary studies showed that the presence of POMs (at $5 \times 10^{-4} \text{ mol/l}$ and lower concentrations) did not change pH of the medium assay ($\text{pH} 7.4$). As shown in our earlier studies, the investigated solutions of 12-tungstosilicid and 12-tungstophosphoric acid are stable at $\text{pH} 7.4$ and at 37°C even in concentration of $5 \times 10^{-2} \text{ mol/l}$.^{34,35}

2.3. Fourier transform infrared and Raman spectroscopy

Solid samples for IR measurements were obtained after evaporation of solvent from the aliquot of 1 mL of analyzed solutions. The FT-IR spectra of the solid residua were recorded on Thermo Nicolet 6700 spectrophotometer using the KBr pellets technique, in the wavenumber range from 4000 to 400 cm^{-1} , at room temperature.

The same solid residua were analyzed by micro-Raman spectroscopy using Thermo DXR Raman microscope. 532 nm laser excitation line was used with a constant power of 10 mW and exposure time of 10.00 s .

The Raman spectra of freshly prepared solutions were recorded *in situ*, using the fiber optic probe with the 780 nm laser excitation line, with a constant power of 150 mW , exposure time of 60.00 s and 5 scans. The pH of solution was controlled before and after recording spectra and it was not changed.

2.4. Synaptic plasma membrane preparation

SPMs were isolated from the whole brain of 3-month-old male Wistar albino rats from the local colony. Animals were kept under controlled illumination (lights on: $5:00 \text{ am}$ – $5:00 \text{ pm}$) and temperature ($23 \pm 2^\circ\text{C}$), and had free access to food and water. The Guiding Principles for the Care and Use of Animals based upon Helsinki Declaration (1964) and Protocol of the 'Vinča' Institute on Care and Treatment of Laboratory Animals were strictly followed. After decapitation with a guillotine (Harvard Apparatus), brains were rapidly excised and pooled (6/pool) for immediate preparation of SPM isolated according to the method of Cohen et al.,³⁶ as modified by Towle and Sze.³⁷ The mitochondrial contamination and protein content were determined according to the standard procedure.³⁸ SPMs were stored at -70°C until used.

2.5. ATPase assays

The standard assay medium for investigation of Na⁺/K⁺-ATPase activity contained (in mmol/l): 50 Tris-HCl (pH 7.4), 100 NaCl, 20 KCl, 5 MgCl₂, 2 ATP and 125 mg/l SPM proteins (i.e. 290 mg/l commercial porcine cerebral cortex proteins) in a final volume of 200 μl. Assay for SPM ecto-ATPase activity contained (in mmol/l): 50 Tris-HCl (pH 7.4), 5 MgCl₂, 2 ATP and 125 mg/l SPM proteins. After preincubation for 10 min at 37 °C in the absence (control) or in the presence of investigated compounds (separate and simultaneous), the reaction was initiated by addition of ATP and stopped after 10 min by adding 22 μl ice cold of 3 mol/l HClO₄ and immediate cooling on ice. The released Pi liberated from the hydrolysis of ATP was determined by a modified spectrophotometric method.³⁹ The spectrophotometric measurements were performed on a Perkin Elmer Lambda 35 UV-vis spectrophotometer. The activity obtained in the presence of Mg²⁺ alone was attributed to E-NTPDases activity. SPM Na⁺/K⁺-ATPase activity was calculated by subtracting the E-NTPDases activity from the total ATPase activity in the presence of Na⁺, K⁺ and Mg²⁺ ions. The results are expressed as mean percentage enzyme activity compared to the corresponding control value ± S.E.M. of at least three independent experiments done in triplicate.

2.6. Statistical analysis

Analysis of variance (One way ANOVA) was used to compare the mathematical sum of inhibitions caused by single exposure to investigated inhibitors with inhibitions induced by exposure to both compound in combination (simultaneously). When a significant continuous probability distribution (*F* value) (*P* < 0.05) was obtained, post hoc test Bonferoni was used to determine differences.

3. Results

3.1. Molecular species of 12-tungstosilicic acid and 12-tungstophosphoric acid under physiological conditions

The speciation of WSiA and WPA under the enzyme assay conditions (physiological pH 7.4) was investigated by two common, complementary spectroscopic methods: FT-IR and micro-Raman spectroscopy.

The FT-IR spectra of solid residue of following solutions:

- 1 mmol/l WSiA/WPA water solution, pH 1 (WSiA/WPA, pH 1)
- 1 mmol/l WSiA/WPA water solution, pH 7.4 (WSiA/WPA, pH 7.4)
- Na⁺/K⁺-ATPase assay containing (in mmol/l): 50 Tris-HCl (pH 7.4), 100 NaCl, 20 KCl, 5 MgCl₂, 2 ATP and 290 mg/l commercial porcine cerebral cortex proteins (solution 1)
- 1 mmol/l WSiA/WPA in the presence of the Na⁺/K⁺-ATPase assay components, pH 7.4 (solution 2/solution 3)

were recorded and presented in Figure 2.

As may be seen in Figure 2a, FT-IR spectrum of solution 1 possesses vibration bands corresponding Tris-HCl with the main bands at 1133, 1035, 903, 629 and 599 cm⁻¹ and this spectrum is identical with spectrum of incubation mixture. The bands originating from ATP and Na⁺/K⁺-ATPase are not observed because of their low concentrations. However in FTIR spectra of solution 3 with WPA, new bands appear. Band at 954 cm⁻¹ corresponds to W-O_a, band at 900 cm⁻¹ corresponds to W-O_b-W and bands at 814 and 735 cm⁻¹ correspond to W-O_c-W vibrations. P-O vibrations at 1100 and 1042 cm⁻¹ are overlapped with bands of solution 1. The spectra of solution 3 does not corresponding to the Keggin WPA anion, which is stable at very acid solution of about pH ~1

(WPA, pH 1 spectrum) but is identical with spectrum of monolacunar Keggin anion (WPA, pH 7.4 spectrum), obtained by removal one WO unit from the parent acid.^{37,38} Also, bands characteristic for monolacunar Keggin anion (WSiA, pH 7.4) are present in FTIR spectra of solution 2 which contains WSiA (Fig. 2b).

The Raman spectra of the same samples are presented in Figure 3 for solid residua of WPA, Figure 3a and WSiA, Figure 3b.

Bands of monolacunar Keggin anion of WPA and WSiA are present in spectra at physiological pH 7.4, confirming results obtained from FT-IR spectra.^{40,41} However, in spectra of solid residue of solutions WSiA, pH 7.4 and 2, Keggin structure of parent WSiA acid (WSiA, pH 1 spectrum) can be observed in traces, indicating higher stability of WSiA at physiological conditions compared to WPA acid.

In order to prove that solid residua recovered intact after evaporation, the Raman spectra were recorded in situ from solutions by fiber optic probe. The obtained spectra are given in Figure 4a for WPA and in Figure 4b for WSiA.

In spectra of solution WPA, pH 7.4 and solution 3 the main band at 983 (ν_{as} W-O_d), characteristic for monolacunar anion, confirms unchanged form of WPA present in solutions at physiological conditions. The same is observed for solution with addition of WSiA, but here the traces of the parent WSiA Keggin anion (WSiA, pH 1) are also noticed, in accordance with higher stability of WSiA.³⁴

3.2. The in vitro influence of Na₂WO₄ × 2H₂O and polyoxo-metalates on Na⁺/K⁺-ATPase activity

The separate influence of Na₂WO₄ × 2H₂O, WSiA and WPA on SPM and commercial porcine cerebral cortex Na⁺/K⁺-ATPase activity was investigated in the concentration range from 1 × 10⁻⁸ to 1 × 10⁻³ mol/l, by in vitro exposure to the enzymes. The results show that increasing concentrations of investigated compounds induce inhibition of enzymatic activity in a concentration-dependent manner in all cases (Figs. 5a and b). The dependence of enzyme activity, expressed as a percentage of the control value (obtained without inhibitor), on inhibitor concentration fits a sigmoidal function (Eq. (1)) for both enzymes.

$$y = \frac{A_1 - A_2}{1 + (x/x_0)^p} + A_2 \quad (1)$$

where *x* is inhibitor concentration in mol/l, *x*₀ is equal to IC₅₀ value and *y* is enzyme activity (percentage of control).

The inhibition parameters, the concentrations of investigated compounds with capability to inhibit 50% of the enzyme after given exposure time (IC₅₀ values) and Hill coefficient, *n*_H, determined using the Hill method (Eq. 2) (Fig. 5a(inset) and 5b(inset)) are summarized in Table 1,

$$\log \left(\frac{\% \text{ activity}}{100 - \% \text{ activity}} \right) = -n \log [I] + n \log \text{IC}_{50} \quad (2)$$

where *n* is Hill coefficient and [*I*] is inhibitor concentration.

It is clearly apparent that in both cases (Figs. 5a and b) inhibitor efficiency of polyoxometalates and Na₂WO₄ is quite different. At the concentration of 1 × 10⁻⁵ mol/l polyoxometalates inhibit both SPM and commercial Na⁺/K⁺-ATPase up to 75%, while the effect of the same concentration of Na₂WO₄ on the enzyme activity is negligible. IC₅₀ (10 min) of the enzyme activity is achieved at (3.6 ± 0.5) × 10⁻⁶ mol/l of WSiA for SPM Na⁺/K⁺-ATPase, (3.8 ± 0.3) × 10⁻⁶ mol/l of WSiA for commercial Na⁺/K⁺-ATPase and (3.0 ± 0.4) × 10⁻⁶ mol/l of WPA for SPM Na⁺/K⁺-ATPase, (3.1 ± 0.4) × 10⁻⁶ mol/l of WPA for commercial Na⁺/K⁺-ATPase, while the same effect is observed at several orders of magnitude higher concentration of Na₂WO₄: >1 × 10⁻³ mol/l, for both enzymes (Figs. 5a and b) (Table 1).

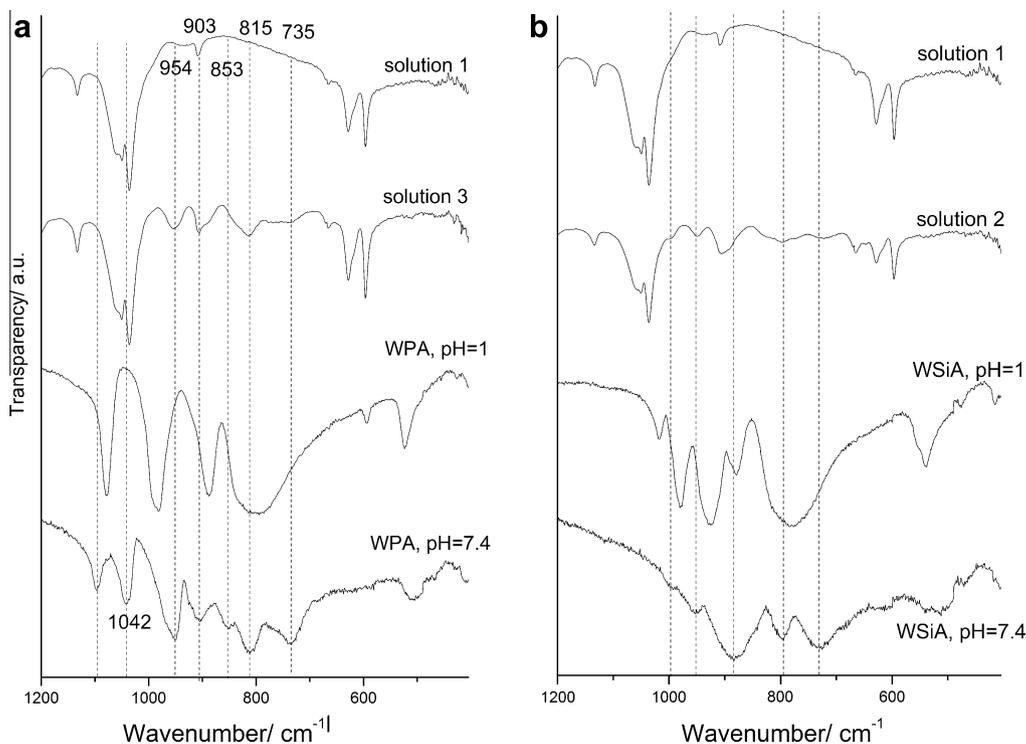


Figure 2. FTIR spectra of solid residues from: (a) solutions 1 and 3, WPA evaporated from 1 mmol/l water solution of pH 1, WPA evaporated from 1 mmol/l water solution of pH 7.4; (b) solutions 1 and 2, WSiA evaporated from 1 mmol/l water solution of pH 1, WSiA evaporated from 1 mmol/l water solution of pH 7.4.

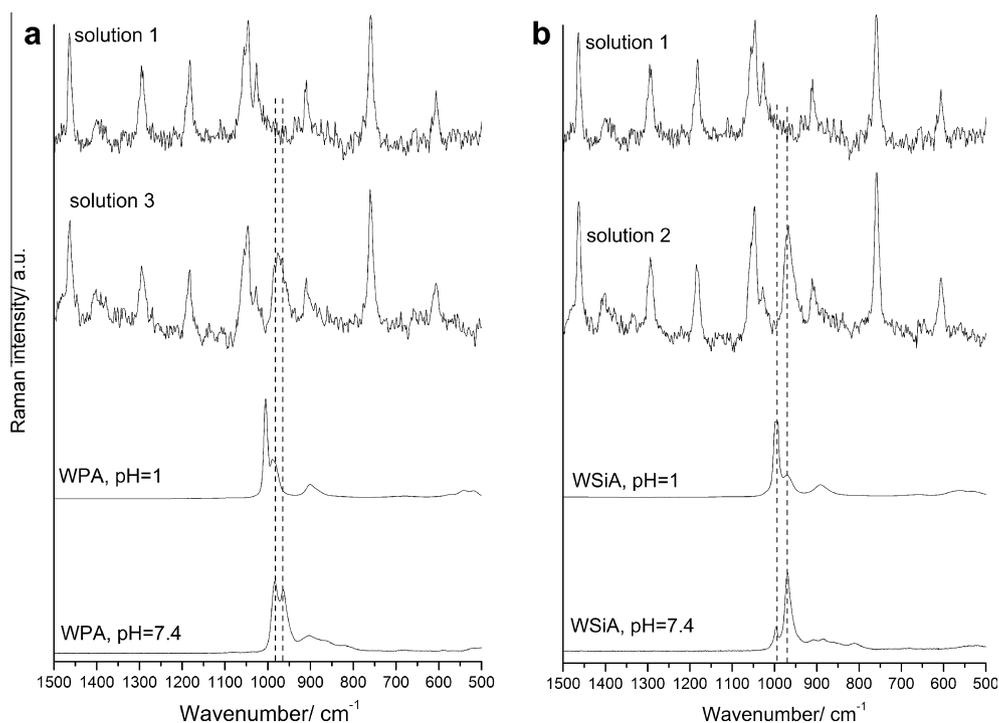


Figure 3. Raman spectra of solid residues from: (a) solutions 1 and 3, WPA evaporated from 1 mmol/l water solution of pH 1, WPA evaporated from 1 mmol/l water solution of pH 7.4; (b) solutions 1 and 2, WSiA evaporated from 1 mmol/l water solution of pH 1, WSiA evaporated from 1 mmol/l water solution of pH 7.4.

3.3. The *in vitro* influence of $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$ and polyoxometalates on synaptic plasma membrane ecto-ATPase activity

The influence of $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$, WSiA and WPA on SPM ecto-ATPase activity was investigated by *in vitro* exposure to the enzyme in the same concentration range as Na^+/K^+ -ATPase (from

1×10^{-8} to 1×10^{-3} mol/l). The results (Fig. 6) show that increasing concentrations of both investigated polyoxometalates (WSiA and WPA) induce inhibition of enzymatic activity in a concentration-dependent manner.

It is obvious that WSiA and WPA show similar inhibitor potencies. IC_{50} (10 min) value of the ecto-ATPase activity, according to

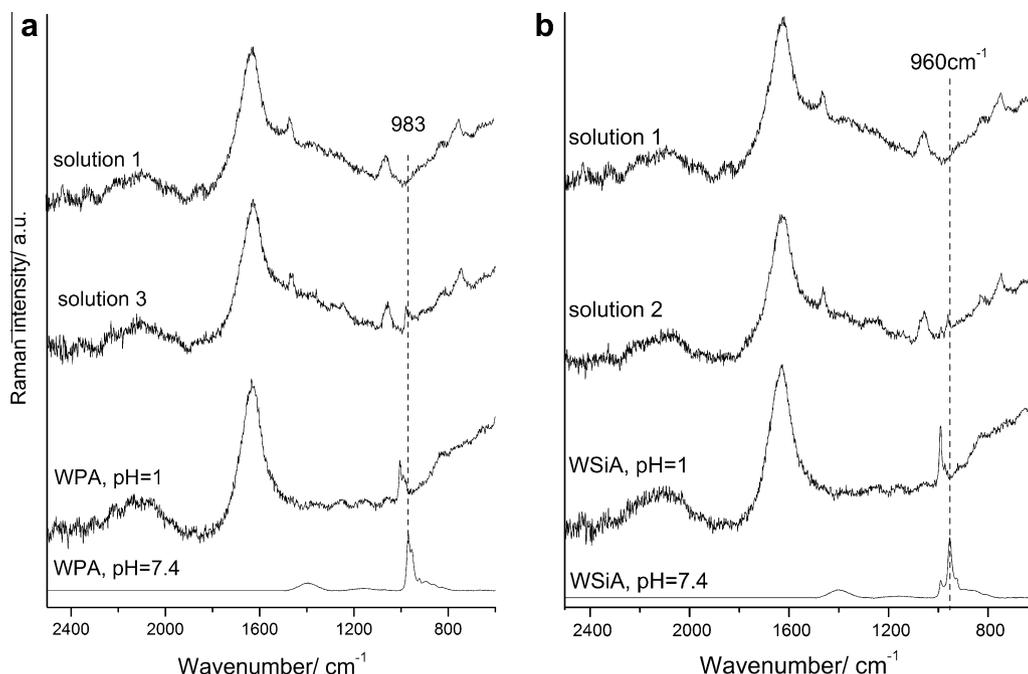


Figure 4. Raman spectra of: (a) solutions 1 and 3, 1 mmol/l water solution of WPA pH 1, 1 mmol/l water solution of WPA pH 7.4; (b) solutions 1 and 2, 1 mmol/l water solution of WSiA pH 1, 1 mmol/l water solution of WSiA pH 7.4.

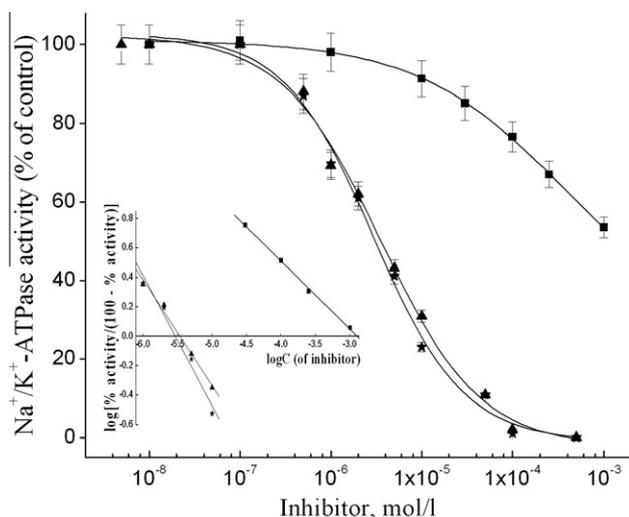


Figure 5a. The concentration-dependent inhibition of SPM Na^+/K^+ -ATPase by $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$ (square), WSiA (triangle) and WPA (asterisk). The values are expressed as mean \pm S.E.M. Inset: Hill analysis of inhibition of SPM Na^+/K^+ -ATPase activity induced by $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$ (square), WSiA (triangle) and WPA (asterisk).

sigmoidal function, is achieved at $(3.4 \pm 0.1) \times 10^{-6}$ mol/l of WSiA and $(1.7 \pm 0.2) \times 10^{-6}$ mol/l of WPA (Table 1). On the contrary, $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$ up to concentration of 1 mmol/l did not cause a marked reduction of SPM ecto-ATPase activity (Fig. 6). The inhibition parameters, the IC_{50} (10 min) value and Hill coefficient n_H , determined using the Hill method (Eq. 2) (Fig. 6(inset)), are in good agreement with the values obtained by sigmoidal fitting (Table 1).

3.4. Effects of simultaneous exposure to 12-tungstosilicic acid and Na_2WO_4 on Na^+/K^+ -ATPase activity

The effect of simultaneous exposure to combinations of WSiA and $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$ on the commercially purified Na^+/K^+ -ATPase activity was studied by using the mixtures of the investigated

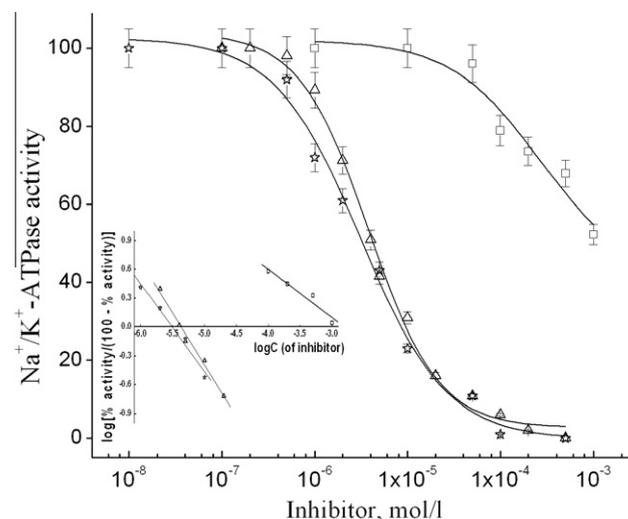


Figure 5b. The concentration-dependent inhibition of commercially available Na^+/K^+ -ATPase by $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$ (open square), WSiA (open triangle) and WPA (open asterisk). The values are expressed as mean \pm S.E.M. Inset: Hill analysis of inhibition of commercially available Na^+/K^+ -ATPase activity induced by $\text{Na}_2\text{WO}_4 \times 2\text{H}_2\text{O}$ (open square), WSiA (open triangle) and WPA (open asterisk).

compounds. The chosen concentrations of WSiA (1×10^{-6} – 5×10^{-6} mol/l) and Na_2WO_4 (1×10^{-4} – 1×10^{-3} mol/l) produced by individual exposure around 50% of inhibition or less. The inhibition obtained by exposure to several combinations was compared to the inhibition in the presence of each single inhibitor (Table 2). An antagonistic effect is defined as a statistically significant ($P < 0.05$) difference between the inhibitions caused by simultaneous exposure and mathematical sum of the values of WSiA and Na_2WO_4 inhibitions assayed separately, where the former is lower than latter. If simultaneously induced inhibition is equally to the calculated sum of the values of single enzyme activity reductions, the inhibition effect is additive.

Table 1
The inhibition parameters (IC₅₀ values (10 min) and Hill coefficients n_H) of Na₂WO₄ × 2H₂O, WSiA and WPA for SPM Na⁺/K⁺-ATPase, ecto-ATPase and commercially purified Na⁺/K⁺-ATPase, obtained by Hill analysis and fitting the experimental data by sigmoidal function

Compound	Enzyme	Sigmoidal fitting	Hill analysis	
		IC ₅₀ (10 min), mol/l	IC ₅₀ (10 min), mol/l	n_H
Na ₂ WO ₄ × 2H ₂ O	Na ⁺ /K ⁺ -ATPase	>1.0 × 10 ⁻³	1.3 × 10 ⁻³	0.5 ± 0.1
	ecto-ATPase	—	—	—
	Commercial Na ⁺ /K ⁺ -ATPase	>1.0 × 10 ⁻³	1.5 × 10 ⁻³	0.5 ± 0.1
WSiA	Na ⁺ /K ⁺ -ATPase	(3.6 ± 0.5) × 10 ⁻⁶	3.4 × 10 ⁻⁶	0.7 ± 0.1
	ecto-ATPase	(3.4 ± 0.1) × 10 ⁻⁶	4.1 × 10 ⁻⁶	1.4 ± 0.1
	Commercial Na ⁺ /K ⁺ -ATPase	(3.8 ± 0.3) × 10 ⁻⁶	4.3 × 10 ⁻⁶	1.1 ± 0.1
WPA	Na ⁺ /K ⁺ -ATPase	(3.0 ± 0.4) × 10 ⁻⁶	2.9 × 10 ⁻⁶	0.9 ± 0.1
	ecto-ATPase	(1.7 ± 0.2) × 10 ⁻⁶	1.6 × 10 ⁻⁶	1.0 ± 0.1
	Commercial Na ⁺ /K ⁺ -ATPase	(3.1 ± 0.4) × 10 ⁻⁶	3.1 × 10 ⁻⁶	0.9 ± 0.1

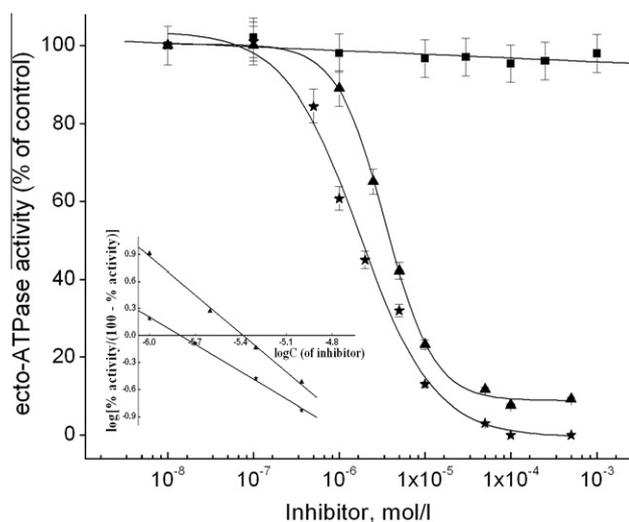


Figure 6. The concentration-dependent inhibition of SPM ecto-ATPase by Na₂WO₄ × 2H₂O (square), WSiA (triangle) and WPA (asterisk). The values are expressed as mean ± S.E.M. Inset: Hill analysis of inhibition of SPM E-NTPDases-ATPase activity induced by WSiA (triangle) and WPA (asterisk).

Table 2
Inhibition of commercial Na⁺/K⁺-ATPase activity induced by simultaneous exposure of Na₂WO₄ × 2H₂O and WSiA

Na ₂ WO ₄ × 2H ₂ O (mol/l)	Inhibition (%)			
	WSiA (mol/l)			
	1 × 10 ⁻⁶ (10.7)	2 × 10 ⁻⁶ (28.7)	4 × 10 ⁻⁶ (49.0)	5 × 10 ⁻⁶ (58.0)
1 × 10 ⁻⁴ (21.0)	29.0	45.4	68.8	55.0
2 × 10 ⁻⁴ (26.4)	34.4	54.6	42.3	51.0
5 × 10 ⁻⁴ (32.1)	42.7	36.3	40.2	53.0
1 × 10 ⁻³ (47.7)	57.0	45.3	65.0	68.0

Values in paranthesis represent the enzyme inhibition obtained during separate exposure to Na₂WO₄ × 2H₂O or WSiA.

Note: Measurement error is ±5%.

As can be seen from Table 2, during the simultaneous exposure of enzyme to WSiA and Na₂WO₄ in various concentration ratios, additive inhibition effects are observed at lower concentrations of the inhibitors (in the presence of WSiA (mol/l)/Na₂WO₄(mol/l) at concentrations: 1 × 10⁻⁶/1 × 10⁻⁴, 1 × 10⁻⁶/2 × 10⁻⁴, 1 × 10⁻⁶/5 × 10⁻⁴, 1 × 10⁻⁶/1 × 10⁻³, 2 × 10⁻⁶/1 × 10⁻⁴, 2 × 10⁻⁶/2 × 10⁻⁴ and 4 × 10⁻⁶/1 × 10⁻⁴), while a statistically significant antagonistic inhibition is obtained for all higher concentrations of the inhibitors.

4. Discussion

In the present study we investigated the in vitro effect of two representative polyoxometalates (12-tungstosilicic and 12-tungstophosphoric acids) on the activity of rat synaptic plasma membrane Na⁺/K⁺-ATPase and E-NTPDase. The obtained FT-IR and Raman spectra (Figs. 2–4) show that investigated POMs in the incubation medium (in the presence of commercial enzyme and its substrate-ATP) form monolacunary Keggin anion, the main molecular species present in the physiological conditions. The species arises by removal of one WO unit from Keggin anion thus forming very unstable form which reacts with various ligands.

The obtained results (Table 1 and Fig. 5) show that WPA and WSiA exhibit concentration-dependent inhibitory effect on the activity of Na⁺/K⁺-ATPase. It is obvious that sodium pumps from both model systems show similar sensitivity toward the investigated compounds. These results are in agreement with previously reported findings that POMs inhibit several nucleotide-dependent enzymes,^{9,12,42,43} while the data about the influence of polyoxotungstates on Na⁺/K⁺-ATPase activity are scant. The obtained results for Na⁺/K⁺-ATPase are consistent with previously published inhibition of Ca²⁺-ATPase (belongs to, as well as Na⁺/K⁺-ATPase, E1E2 ATPase) by vanadium coordination complexes, and the influence of decavanadate on Ca²⁺-ATPase and Na⁺/K⁺-ATPase activity. The obtained IC₅₀ values indicate that polyoxotungstates are more potent inhibitors than the vanadium coordination complexes (approximately 10–100 times), while decavanadate IC₅₀ values are lower from one to two orders of magnitude.^{12,44}

The obtained results (Table 1 and Fig. 6) show that activity of SPM E-NTPDase was inhibited in dose-dependent manner by WPA and WSiA in the investigated concentration range. The obtained sensitivity of ecto-ATPase toward WPA and WSiA (Table 1) confirms previously reported findings that polyoxometalates are generally more potent than standard E-NTPDase inhibitors.⁷ Although three different isoforms of rat E-NTPDase have been known (NTPDase 1, 2 and 3),⁷ the obtained monophasic inhibition curves (Fig. 6) do not indicate the heterogeneity of the polyoxotungstate binding sites, which is in agreement with previously published findings that H₃PW₁₂O₄₀ is a non-selective inhibitor of all three rat recombinant NTPDases.⁷ In comparison with previously investigated inhibitors (different metal ions, decavanadate),^{12,17,39} the investigated polyoxotungstates are a few orders of magnitude more potent inhibitors of SPM E-NTPDase. Unlike the polyoxotungstates, Na₂WO₄ × 2H₂O did not affect ecto-ATPase activity up to concentration 1 mmol/l (Fig. 6). On the other side, Na₂WO₄ × 2H₂O inhibited SPM and commercial Na⁺/K⁺-ATPase at concentration higher than 1 × 10⁻⁵ mol/l, although with lower inhibitor efficiency than the polyoxotungstates (IC₅₀ >1 × 10⁻³ mol/l) (Fig. 5), suggesting that orthotungstate, WO₄²⁻, (similarly to orthovanadate) probably affects phosphorylation step in the enzyme cycle of P-type ATPase.^{42,45,46}

The additive inhibition of commercial Na⁺/K⁺-ATPase activity obtained by simultaneous exposure to low concentrations of Na₂WO₄ and WSIA (Table 2) suggests that both inhibitors compete for the same set of inhibitory binding sites and there is an excess of these sites over the concentration ranges examined.⁴⁷ The observed antagonistic inhibition, in the presence of mixtures of the inhibitors at higher concentrations (Table 2), indicates effectively competing for a limited number of inhibitory binding sites on Na⁺/K⁺-ATPase.⁴⁷ These effects might be assigned to binding the polyoxotungstates, due to analogy in charge to ATP,⁷ and Na₂WO₄, probably affecting phosphorylation step because of similarity to orthophosphate and orthovanadate,^{42,45,46,48} to the same, that is active site of this P-type ATPase.

It could be summarized that the investigated polyoxotungstates are potent inhibitors of the chosen ATPases and belong to the most potent E-NTPDase inhibitors described to date. Considering the role of Na⁺/K⁺-ATPase and E-NTPDase in normal cell functioning as well as in the development of pathological states, the inhibition of the selected enzymes by POMs may contribute to (in vitro and in vivo) observed anti-cancer, anti-viral and anti-bacterial activity of polyoxometalates.

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Supplementary data

Supplementary data (Infrared and Raman wave numbers for the solid residua of the investigated solutions) associated with this article can be found, in the online version, at doi:10.1016/j.bmc.2011.10.008.

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8. BIOGRAFIJA

Danica Bajuk-Bogdanović je rođena 3.1.1977. godine u Rumi. Godine 1995. upisala se na Fakultet za fizičku hemiju, Univerziteta u Beogradu. Diplomirala je 2003. godine sa prosečnom ocenom 8,61 i ocenom 10 na diplomskom radu pod nazivom "Ispitivanje ponašanja nekih heteropoli jedinjenja u vodenim rastvorima", čiji je mentor bila prof. dr. Ubavka Mioč.

Pod rukovodstvom prof. dr Ubavke Mioč, prof. dr Ivanke Holclajtner-Antunović sa Fakulteta za fizičku hemiju i prof. dr Marije Todorović sa Hemijskog fakulteta, Univerziteta u Beogradu, posle diplomiranja nastavlja sinteze i ispitivanja različitih heteropoli jedinjenja.

Godine 2003. upisala je poslediplomske studije na Fakultetu za fizičku hemiju, a 2006. prešla na doktorske studije, kada je Fakultet za fizičku hemiju, Univerziteta u Beogradu prešao na program studiranja po Bolonjskoj konvenciji.

Učestvovala je na projektima:

2003-2005. godine - "Sinteza i karakterizacija polioksometalata i sličnih jedinjenja i njihova primena u novim tehnologijama, biomedicini i zaštiti čovekove okoline", projekat br.1730, čiji je rukovodilac bila prof. dr Ubavka Mioč;

2006-2010. godine - "Struktura, termodinamičke i elektrohemijske osobine materijala za konverziju energije i nove tehnologije", projekat br. 142047, čiji je rukovodilac bio prof. dr Slavko Mentus.

Trenutno je angažovana na projektima: "Elektroprovodni i redoks-aktivni polimeri i oligomeri: sinteza, struktura, svojstva i primena" projekat br. 172043, rukovodioca prof. dr Gordane Ćirić-Marjanović (2010-2014. godine) i "Procesi urbanizacije i razvoja srednjovekovnog društva, projekat br. 177021, pod rukovodstvom prof. dr Vujadina Ivaniševića (2010-2014. godine).

Zaposlena je na Fakultetu za fizičku hemiju kao samostalni saradnik.

9. IZJAVE

Прилог 1.

Изјава о ауторству

Потписана Даница Бајук- Богдановић

број индекса 323/06

Изјављујем

да је докторска дисертација под насловом

ИСПИТИВАЊЕ СТАБИЛНОСТИ 12-ВОЛФРАМФОСФОРНЕ, 12 -
ВОЛФРАМСИЛИЦИЈУМОВЕ И 12-МОЛИБДЕНФОСФОРНЕ КИСЕЛИНЕ У
РАСТВОРИМА

- резултат сопственог истраживачког рада,
- да предложена дисертација у целини ни у деловима није била предложена за добијање било које дипломе према студијским програмима других високошколских установа,
- да су резултати коректно наведени и
- да нисам кршио/ла ауторска права и користио интелектуалну својину других лица.

Потпис докторанда

У Београду, 13.5.2013. год.

Даница Бајук-Богдановић

Прилог 2.

Изјава о истоветности штампане и електронске верзије докторског рада

Име и презиме аутора Даница Бајук- Богдановић

Број индекса 323/06

Студијски програм _____

Наслов рада ИСПИТИВАЊЕ СТАБИЛНОСТИ 12-ВОЛФРАМФОСФОРНЕ, 12-ВОЛФРАМСИЛИЦИЈУМОВЕ И 12-МОЛИБДЕНФОСФОРНЕ КИСЕЛИНЕ У РАСТВОРИМА

Ментор Редовни професор, др Иванка Холцлајтнер-Антуновић

Универзитет у Београду, Факултет за физичку хемију

Потписани/а Даница Бајук- Богдановић

Изјављујем да је штампана верзија мог докторског рада истоветна електронској верзији коју сам предао/ла за објављивање на порталу **Дигиталног репозиторијума Универзитета у Београду**.

Дозвољавам да се објаве моји лични подаци везани за добијање академског звања доктора наука, као што су име и презиме, година и место рођења и датум одбране рада.

Ови лични подаци могу се објавити на мрежним страницама дигиталне библиотеке, у електронском каталогу и у публикацијама Универзитета у Београду.

Потпис докторанда

У Београду, 13. 5. 2013. год.

Даница Бајук-Богдановић

Прилог 3.

Изјава о коришћењу

Овлашћујем Универзитетску библиотеку „Светозар Марковић“ да у Дигитални репозиторијум Универзитета у Београду унесе моју докторску дисертацију под насловом:

ИСПИТИВАЊЕ СТАБИЛНОСТИ 12-ВОЛФРАМФОСФОРНЕ, 12-ВОЛФРАМСИЛИЦИЈУМОВЕ И 12-МОЛИБДЕНФОСФОРНЕ КИСЕЛИНЕ У РАСТВОРИМА

која је моје ауторско дело.

Дисертацију са свим прилозима предао/ла сам у електронском формату погодном за трајно архивирање.

Моју докторску дисертацију похрањену у Дигитални репозиторијум Универзитета у Београду могу да користе сви који поштују одредбе садржане у одабраном типу лиценце Креативне заједнице (Creative Commons) за коју сам се одлучио/ла.

1. Ауторство
2. Ауторство - некомерцијално
3. Ауторство – некомерцијално – без прераде
4. Ауторство – некомерцијално – делити под истим условима
5. Ауторство – без прераде
6. Ауторство – делити под истим условима

(Молимо да заокружите само једну од шест понуђених лиценци, кратак опис лиценци дат је на полеђини листа).

Потпис докторанда

У Београду, 13.5.2013. год.

Заница Ђарж-Ђојановић

1. Ауторство - Дозвољавање умножавање, дистрибуцију и јавно саопштавање дела, и прераде, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце, чак и у комерцијалне сврхе. Ово је најслободнија од свих лиценци.

2. Ауторство – некомерцијално. Дозвољавање умножавање, дистрибуцију и јавно саопштавање дела, и прераде, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце. Ова лиценца не дозвољава комерцијалну употребу дела.

3. Ауторство - некомерцијално – без прераде. Дозвољавање умножавање, дистрибуцију и јавно саопштавање дела, без промена, преобликовања или употребе дела у свом делу, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце. Ова лиценца не дозвољава комерцијалну употребу дела. У односу на све остале лиценце, овом лиценцом се ограничава највећи обим права коришћења дела.

4. Ауторство - некомерцијално – делити под истим условима. Дозвољавање умножавање, дистрибуцију и јавно саопштавање дела, и прераде, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце и ако се прерада дистрибуира под истом или сличном лиценцом. Ова лиценца не дозвољава комерцијалну употребу дела и прерада.

5. Ауторство – без прераде. Дозвољавање умножавање, дистрибуцију и јавно саопштавање дела, без промена, преобликовања или употребе дела у свом делу, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце. Ова лиценца дозвољава комерцијалну употребу дела.

6. Ауторство - делити под истим условима. Дозвољавање умножавање, дистрибуцију и јавно саопштавање дела, и прераде, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце и ако се прерада дистрибуира под истом или сличном лиценцом. Ова лиценца дозвољава комерцијалну употребу дела и прерада. Слична је софтверским лиценцама, односно лиценцама отвореног кода.