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Yu.I. Maznaya, O.V. Zuy

CHEMILUMINESCENT REACTIONS OF HETEROPOLY ACIDS AND THEIR COMPLEXES WITH CATIONIC SURFACTANTS IN AQUEOUS SOLUTIONS AND ON THE CELLULOSE SURFACE

Dumansky Institute of Colloid and Water Chemistry of National Academy of Sciences of Ukraine
42 Vernadsky Boulevard, Kyiv, 03142, Ukraine, E-mail: olegzuy@gmail.com

The properties of heteropoly acids and of their complexes with cationic surfactants at the trace level have been studied by ESR spectroscopy, UV-VIS spectrophotometry, NMR and FTIR spectroscopy, by the method of chemiluminescence analysis applied in aqueous solutions and on the cellulose surface. For elucidation of the mechanism of chemiluminescence reactions of heteropoly acids with luminol kinetic methods, diffuse reflectance spectroscopy and liquid chromatography have been applied. For the first time one-electron reduction of heteropoly acids by luminol was confirmed by registration of diffuse reflectance spectra of reduced heteropoly acids on cellulose surface. It has been suggested that the mechanism of heteropoly acids immobilization on cellulose includes combination of Coulomb and hydrophobic interactions. A scheme of heteropoly acids immobilization on the surface was proposed based on ion exchange processes on cellulose or diethylaminoethyl cellulose surface. It has been shown that ionic associates heteropoly acid – cationic surfactant react with an alkaline solution of luminol with light emission similarly to heteropoly acids themselves. For the first time, heterogeneous chemiluminescence, namely, the chemiluminescence of heteropoly acids immobilized on cellulose, with luminol, has been used for examining the composition of ionic associates heteropoly acid - cationic surfactant. By using Bjerrum's method it has been found that in strongly acidic media (at pH 1.0) vanadomolybdophosphoric acid forms with cationic surfactant, namely, with dodecylpyridinium bromide, not tetra-substituted but triply substituted ionic associate. This result can be explained by the fact that the fourth proton in $H_4PVMo_{11}O_{40}$ is weakly dissociated; it is more strongly bound to heteropoly anion and is localized on the oxygen atom of the Mo–O–Mo angular bond. Ionic associates of heteropoly acids were used as analytical forms for highly sensitive chemiluminescence determination of P, As, Si, Ge in waters of different types. Detection limits for P, As, Si, Ge are 0.02–0.07 µg/L. Due to the high sensitivity of the method, phosphorus was successfully determined in surface water and ultrapure water, arsenic – in river and mineral water, silicon – in ultrapure water and vapor condensate of electric power stations, germanium – in water of electronic industry.

***Keywords**: heteropoly acids, heterogeneous reactions, ionic associates, chemiluminescence analysis at the surface*

INTRODUCTION

Heteropoly acids (HPAs) constitute a wide class of coordination compounds, their molecules consist of a central atom and assemblies of metal-oxygen polyhedra which include molybdenum, tungsten or fragments of oxide crystal grating [1]. Structures of some heteropoly acids of Keggin type studied here are presented in Fig. 1.

HPAs have wide application in catalysis, analytical chemistry and in other fields. While developing heterogeneous catalysts as well as analytical forms for determining phosphorus, arsenic, silicon, germanium immobilization of HPAs on different carriers is necessary – on silica gel, titanium oxide, aluminum, zirconium, activated carbon *et al.* For heterogeneous-chemiluminescent determination of HPA cellulose carriers were used [2].

To tailor the compatibility of HPA with organic materials and biological tissues, cationic surfactants have been applied to improve the surface properties of their clusters [3]. Dioctadecyldimethylammonium ($DODA^+$) was used to encapsulate metal-centered HPAs, resulting in surfactant-encapsulated HPA complexes [4]. Hybrid assemblies based on surfactant-encapsulated polyoxometalates (POMs) are described [5]. The hybrid structure arises from the rearrangement of surfactants on the polyoxometalate, which is driven by hydrophobic forces. An overview of fundamental

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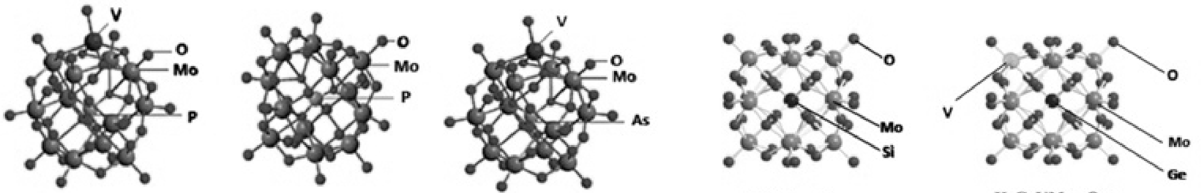
POM-cation interactions in solution, including interactions with cationic surfactants, and behaviour and properties that emerge from these POM-cation interactions has been done [6]. However, there is little evidence on the composition of HPA – cationic surfactant complexes with P, As, Si and Ge as central atoms. Surfactant-encapsulated polyoxometalate building blocks were described as well as their catalytic properties using mainly $(DODA)_3PW_{12}O_{40}$ and $(DODA)_4SiW_{12}O_{40}$ as initial HPA – surfactant complexes formed in aqueous solution [7].



$H_4PVMo_{11}O_{40}$ $H_3PMo_{12}O_{40}$ $H_4AsVMo_{11}O_{40}$ $H_4SiMo_{12}O_{40}$ $H_5GeVMo_{11}O_{40}$

Fig. 1. Keggin type heteropoly acids

The purpose of present work was to examine the mechanism of chemiluminescent reactions of HPAs of phosphorus, arsenic, silicon and germanium with luminol in aqueous solutions and that of immobilized HPAs on carriers surface, also to use heterogeneous chemiluminescence for studying the composition and properties of ionic associates of HPAs with cationic surfactants (quaternary ammonium salts) on cellulose surface.

EXPERIMENTAL PART

Detection of analytical forms on the surface of solid carrier was accomplished mainly by chemiluminescence (CL) method and in some cases – by diffuse reflectance spectroscopy. For these purposes a luminometer Triathler (Finland) with injection unit for luminol solution and a spectrophotometer Shimadzu 2450 (Japan) were used. A set of complementary physicochemical and physical methods was also used: spectrophotometry (Specord UV-VIS, Germany), FTIR spectroscopy (Nicolet FTIR 4700/6700, Thermo), methods of chemical kinetics, NMR (AVANCE 400, Bruker), ESR spectroscopy (JEOL JES-RE3X, Japan), high performance liquid chromatography (HPLC system Varian 940-LC).

As matrices for HPA immobilization cellulose filters Filtrak No.388 and diethylaminoethyl cellulose (DEAE-cellulose) filters Whatman DE81 were used. On denser filters blank signal increases which is caused by non-specific adsorption of isopolymolybdate. Filters used here also give the possibility to collect maximum of CL emission while detecting sorbate on the surface by adding luminol solution to the filter. Sorption of HPA on cellulose was examined using molybdovanadophosphoric acid $H_4PVMo_{11}O_{40}$ which was obtained in aqueous solution in excess of molybdate and vanadate. Reagents KH_2PO_4, H_2SO_4, KOH, NH_4VO_3, $(NH_4)_6Mo_7O_{24}\times 4H_2O$ were of chemically pure grade, luminol (97 %), 3-aminophthalic acid technical grade (90 %), Bromopyrogallol Red, cationic surfactants cetyltrimethylammonium bromide (CTB), cetylpyridinium bromide (CPB), dodecylpyridinium bromide (DDPB) from Aldrich, tetradecylpyridinium bromide (TDPB) from Shebekino, nonionic surfactant OP-10 (Barva, Ukraine) were used without further purification. Luminol solution was prepared in 1 M KOH. Reagent solutions were prepared using freshly obtained doubly distilled water. Water and all solutions were stored in high-pressure polyethylene or in polytetrafluoroethylene vessels.

For registration of diffuse reflectance spectra of luminol-HPA (1:1) and ascorbic acid-HPA (1:1) mixtures reduced (“blue”) HPAs were obtained in aqueous solution at pH 12.0. Concentrations of luminol, 12-molybdophosphoric acid and ascorbic acid were 1.0 mM. For HPA immobilization on cellulose surface the following technique was applied: immediately after the formation of “blue” HPA the luminol-HPA and ascorbic acid-HPA mixtures were filtered through the paper filters Filtrak No.388 and diffuse reflectance spectra of immobilized HPAs were recorded on a spectrophotometer.

For the registration of ESR spectrum of $H_3Mo_{12}O_{40}$, a solution of HPA was placed on a narrow strip of filter paper situated inside a fused silica tube (3–4 mm inner diameter) so that the solution was completely absorbed by the strip in the tube, and then frozen in liquid nitrogen. After a "blank" ESR spectrum was recorded, the fused silica tube was taken out of the instrument cavity and left at room temperature for equilibration. One drop of alkaline luminol solution was put into the tube, allowed to reach the strip of filter paper and to be absorbed on it. After freezing in liquid nitrogen (123 K), the ESR spectrum of luminol–HPAmixture on the strip was recorded. Experimental conditions: X-field sweep; center field, 3300.0 G; sweep width, 500 G; frequency, 9.08900 GHz; power, 1.000 mW; modulation width, 3.2 G; time constant, 0.3 s; sweep time, 5.0 min. The concentration of HPA was 0.05 M, and 0.05 M luminol solution was prepared with 1 M NaOH.

For studies of the kinetics of P–Mo HPA decomposition at pH 12.0 CL method was used. For this purpose, 5×10^{-6} M and 5×10^{-7} M HPA solutions were prepared at pH 3.0, 0.5-mL portions were placed into the luminometer cell and 0.5 mL of NaOH solution was added from a syringe to obtain pH 12.0, allowed to stand for a certain period of time (0, 5, 10, 15, 20 and 30 s), and then neutral 2×10^{-4} M luminol solution was added with light emission registration.

For highly sensitive chemiluminescence measurements of HPA concentrations in aqueous solutions sorption preconcentration of HPA on cellulose filters in dynamic conditions was done. A teflon Buchner funnel with diameter of filtering surface 12 mm was used as filter holder. 150 mL of HPA containing solution was filtered. After filtration, the filter was washed with 10 mL of doubly distilled water and transferred into the glassy cell of luminometer. Then 0.5 mL of alkaline luminol solution was added with registration of chemiluminescence. Maximum CL intensity and integral light amount were registered and saved in computer memory with the help of CommFiler program.

HPLC experiments were accomplished on a Varian 940-LC liquid chromatograph with Nova-Pak C18 analytical column (3.9×150 mm). Before injection of sample into chromatograph HPA and alkaline luminol solutions were mixed (pH of mixture 12.0) and set aside for 5 min. Then before analysis pH was made 2.5 using H_2SO_4 solution. Volume of reaction mixture was 1.16 cm^3, consisting of 0.5 cm^3 $H_4PVMo_{11}O_{40}$ (1.0 mM) and 0.66 cm^3 luminol (1.0 mM in 1.0 M KOH). Eluent – $CH_3CN:H_2O = 18:82$ in presence of 0.1 % trifluoroacetic acid, flow rate 1 cm^3/min. UV detection – at 350 nm.

Conditions for recording the MAS ^{31}P NMR spectra: pulse duration – 15 μs, interval between pulses – 60 s, frequency – 161.87899 MHz; room temperature. The ^{31}P chemical shift was measured relatively to external standard – 85 % H_3PO_4. Speed of rotation of samples at a magic angle – 7.0 kHz, number of scans – 1024.

Fourier transform IR spectra were recorded on a Nicolet Nexus 470 device manufactured by Thermo Scientific with a functional Smart Orbit attachment (optical element – diamond, incident beam angle $\theta = 45$ °) for obtaining spectra in the mode of disturbed total internal reflection. The range used was 4000–400 cm^{-1}, the number of scans was 128, and the resolution was 4 cm^{-1}. The background was recorded relative to an optical element without a sample.

For evaluation of the composition of ionic associates (IA) of HPAs with cationic surfactants, HPA solutions were prepared keeping the mixture of components for 15 min, then their mixtures with cationic surfactant were prepared with necessary concentrations ratio and kept aside during 30 min to achieve the equilibrium of IA formation. After that solutions were transferred into Buchner funnel and filtered through paper filters at the rate of 20 mL/min. Volume of solution for filtration using equilibrium shift method is 150 mL, using molar ratio method – 10 mL. Filters with concentrates were transferred into the cuvette situated in the cuvette compartment of the luminometer and 0.5 mL of 2×10^{-3} M luminol solution in 1 M KOH were injected with registration of chemiluminescence.

For examination of ionic associates composition by Bjerrum's method, equilibrium concentration of cationic surfactant DDPB had to be determined. Light absorbance was measured of the solution of complex Bromopyrogallol Red – Mo – DDPB in presence of nonionic surfactant OP-10 at $\lambda = 630$ nm in filtrates obtained after filtration of aqueous solutions of $H_4PVMo_{11}O_{40}$ (1.0 μM) with different concentrations of DDPB.

Solutions were kept aside for 30 min to achieve equilibrium at pH 1.0. Bromopyrogallol Red (1.8 mM) was prepared using water – ethanol mixture (1:1), OP-10 – 2.0 mM in water. The procedure was as follows. Distilled water (140 cm^3) was put into conical flask, 0.15 cm^3 KH_2PO_4 (1.0 mM), 0.6 cm^3 $(NH_4)_6Mo_7O_{24}\times4H_2O$ (0.25 M), 6 cm^3 NH_4VO_3 (1.0 mM), 1.2 cm^3 H_2SO_4 (9 M) added, stirred and kept for 10 min to form 1.0 µM $H_4PVMo_{11}O_{40}$ in solution. Portions of 10 cm^3 each of the resulting solution were taken, 0.02–0.09 cm^3 of a DDPB solution (1.0 mM) added, stirred, held for 30 min to form IA, then filtered through a nitrocellulose membrane filter with a pore diameter of 0.3–0.5 µm. The filtrate was collected in a test tube, 0.2 cm^3 2.0 mM OP-10, 0.5 cm^3 1.8 mM Bromopyrogallol Red added, mixed and the optical density was measured on a spectrophotometer at 630 nm in a cuvette with $l = 1$ cm. A calibration graph was built to determine DDPB in presence of 1.0 mM molybdate, 0.04 mM vanadate, and 0.05 M H_2SO_4. Using the calibration graph, the equilibrium concentration of the surfactant in the filtrate was determined, the $\tilde{n}$ value was calculated, and a dependence of $\tilde{n}$ on -lg [DDP] was elucidated.

RESULTS AND DISCUSSION

Non-reduced HPAs are designated as “yellow”, reduced forms – as “blue” HPAs. It is known that in acidic aqueous solutions reduction of HPA proceeds through several two-electron stages: for example, polarogram of $H_4SiMo_{12}O_{40}$ is characterized by the group of three two-electron waves. It was impossible to examine the behavior of molybdophosphoric acid by electrochemical methods in alkaline media because of instability of this HPA in alkaline solutions. However, for more stable $H_4SiMo_{12}O_{40}$ the data were obtained that with increasing solution pH polarographic waves of $H_4SiMo_{12}O_{40}$ reduction split into one-electron waves. This is observed at pH 2.4 for the first wave, at pH 9.5 – for the second one and in 0.1 M LiOH – for the third wave. Therefore, the formation of one-electron-reduced “blues” in the reactions of HPA with luminol in alkaline solutions seems to be quite probable.

ESR measurements gave following results. When one drop of 0.05 M luminol in 1 M NaOH reached the filter paper impregnated with 0.05 M phosphomolybdic acid in the fused silica tube, an intense blue color developed instantly. The ESR spectrum of this blue species at 123 K showed an isotropic signal. This signal is attributed to a one-electron reduction compound in which one molybdenum atom is in a (5+) valence state. So, phosphomolybdic HPA appears to be one-electron oxidant to luminol. Consequently, the formation of short-lived radical species would be expected to be the intermediate products.

In order to examine the dependence of CL intensity in the luminol – PMo HPA system at pH 12.0 on HPA concentration, CL intensity was plotted against HPA concentration in logarithmic coordinates. The dependence was a straight line in the concentration range of 1×10^{-7} M to 1×10^{-6} M, the slope of the straight line in the HPA concentration range between 1×10^{-7} M and 1×10^{-6} M was approximately 1, which means that CL intensity is directly proportional to HPA concentration, indicating that a first-order reaction takes place.

The results of investigation of kinetics of P–Mo HPA decomposition at pH 12.0 and its comparison with kinetics of chemiluminescence HPA–luminol are following. The kinetic curves of HPA decomposition suggest that the decomposition reaction proceeds according to the first order, namely, the rate of decomposition does not depend on the concentration of HPA. The rate constant and half-life time of the HPA decomposition reaction were determined to be 0.069 ± 0.004 s^{-1} and 14.4 s at pH 12.0 at 293 K, respectively. Kinetics of chemiluminescence of 5×10^{-6} M HPA with luminol (2×10^{-4} M) at pH 12.0 indicate that light emission due to the chemiluminescence comes to an end in 7–8 s, namely, the rate of CL reaction is much higher than the rate of HPA decomposition. In this connection, when HPA solution is mixed with alkaline luminol solution, only a slight portion of HPA decomposed with the formation of the initial ions (phosphate and molybdate), and most HPA took part in the reaction with luminol.

To clarify the nature of the “blue” formed in a mixture of luminol – 12-molybdophosphoric acid its electronic spectrum was recorded and compared with the spectrum of “blue” HPA obtained with typical two-electron reductant – ascorbic acid. As luminol reacts with HPA only in alkaline solutions, the “blue” HPAs were obtained in aqueous solution at pH 12.0. It is known that reduced HPAs in alkaline solutions decompose gradually but they are more stable after immobilization on the surface. Therefore, diffuse reflectance spectra of HPAs immobilized on cellulose filters were recorded. The spectra obtained are shown in Fig. 2.

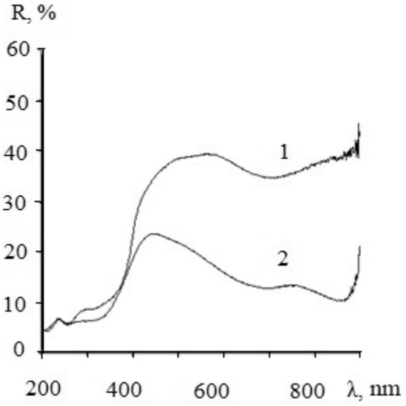


Fig. 2. Diffuse reflectance spectra of the mixtures luminol-HPA (*1*), ascorbic acid-HPA (*2*) at pH 12.0 on paper filters Filtrak No.388. Concentrations of luminol, 12-molybdophosphoric acid, ascorbic acid – 1.0 mM

One minimum at $\lambda = 715$ nm is observed in the reflectance spectrum of luminol-HPA (see Fig. 2, curve 1), but two minima were registered in the reflectance spectrum of ascorbic acid-HPA (Fig. 2, curve 2) – at $\lambda = 704$ and 861 nm. In [8] absorbance spectra of one- and two-electron "blues" are described, these "blues" were obtained by electrochemical reduction. One-electron "blue" was characterized by a wide band with one maximum at $\lambda = 800$ nm, two-electron "blue" – by two bands with maxima at $\lambda = 730$ and 1000 nm.

So, minima in diffuse reflectance spectra of "blue" HPAs immobilized on the filter surface are characterized by a hypsochromic shift compared to maxima in absorbance spectra of aqueous solutions of one- and two-electron "blues" known from the literature. This phenomenon is always observed at immobilization of corresponding HPAs on carriers surface. However, from the form of diffuse reflectance spectra observed by us, a conclusion may be drawn that in luminol-HPA mixture at pH 12.0 one-electron "blue" exists, and in ascorbic acid-HPA mixture – two-electron "blue". This finding confirms one-electron reduction of 12-molybdophosphoric acid by luminol and, consequently, the possibility of radical compounds formation in this process.

Results of HPLC experiments clearly indicate the appearance of a new peak of 3-aminophthalic acid in luminol – $H_4PVMo_{11}O_{40}$ mixture, this peak was absent on chromatograms of standard solutions of HPA and luminol. Clear separation of the peaks is observed, retention time of $H_4PVMo_{11}O_{40}$ was 0.95 min, that of 3-aminophthalate – 2.9 min and of luminol – 6.5 min.

Mechanism of luminol chemiluminescence under interaction with HPAs proposed in [9] is shown in Fig. 3.

HPA in the presence of luminol and alkali undergoes chemical transformations of two types: first type – process of decomposition of a part of HPA in alkaline solution with the release of primary anions (phosphate, molybdate and vanadate); second type – participation of most HPA in the reaction with luminol. Chemiluminescent reaction involving HPA, luminol and ambient oxygen is a radical process that proceeds with the formation of intermediate species, particularly, superoxide radicals. This is substantiated by the fact that light emission is inhibited by OsO_4 or *p*-aminophenol. The light emitter is aminophthalate, which is the same product formed under luminol oxidation, for example, by halogens – chlorine, bromine, and iodine. This has been proved by CL spectra in luminol–HPA reactions and by HPLC identification of the reaction products. Both HPA and oxygen are essential for the CL reaction. This is confirmed by the experimental fact that deoxygenation of solutions with argon of high purity leads to substantial reduction of the CL signal. It is known that reduced forms of HPA ("blues") at the moment of formation can be oxidized by air oxygen with the formation of initial oxidized ("yellow") forms of HPA and superoxide ion-radicals at room temperature. It is possible to propose that under conditions of CL reaction, luminol reacts with "yellow" HPA to form semiquinone radical (product of one-electron oxidation of luminol) and "blue" HPA; the latter reacts with air oxygen present in solution with formation of superoxide radical and initial "yellow" HPA. So, HPA acts as a catalyst, accelerating CL reaction of luminol with oxygen through the formation of semiquinone radical and superoxide radical. Such a catalytic reaction proceeds by chemiluminescence pathway, with formation of aminophthalate ion in excited state and with light emission at aminophthalate transition to the ground state.

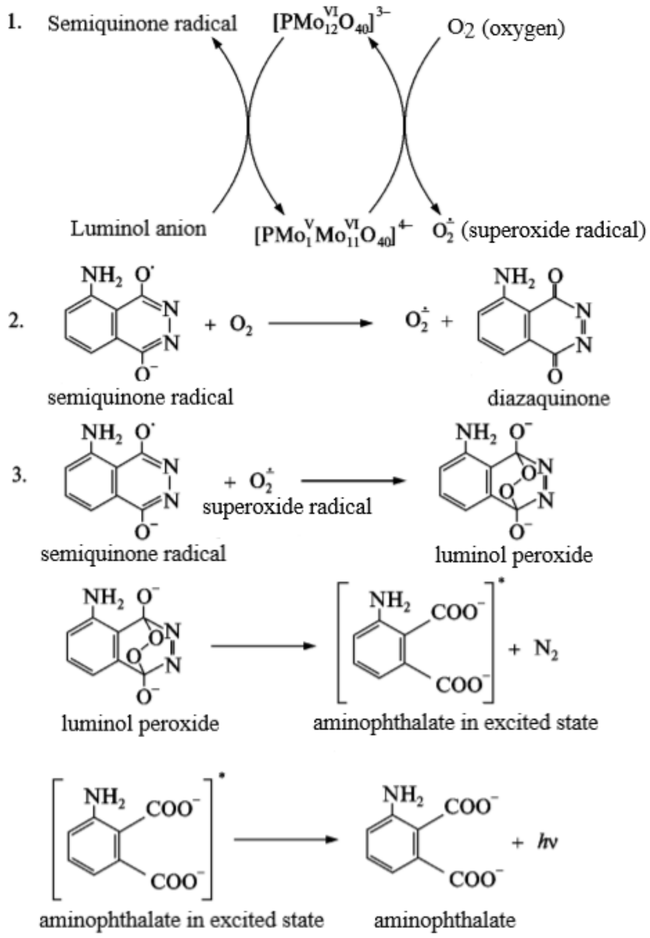


Fig. 3. Scheme of the reactions pathway of luminol with HPAs at pH 12.0

In the scheme proposed (Fig. 3) stage (1) is a catalytic process of oxidation of a luminol anion to a semiquinone radical by air oxygen through an oxidation/reduction cycle of HPA. Reaction (2) is an oxidation reaction of semiquinone radical by oxygen causing the formation of diazaquinone and superoxide radical. In reaction (3), the superoxide can further oxidize semiquinone to luminol peroxide. Under given conditions, the concentration of superoxide radicals in luminol–HPA mixture is much higher than that of semiquinone radicals. It is known [10] that even during incubation of alkaline luminol solution in the ambient atmosphere under daylight illumination, superoxide radicals are formed in amounts higher than semiquinone radicals concentration. Thus, the reaction of semiquinone radical with superoxide radical (reaction (3)) is a first-order reaction, which was proved experimentally by obtaining a logarithmic dependence of CL intensity on HPA concentration. Semiquinone – superoxide reaction is just the reaction which leads to chemiluminescence. Thus, reaction of luminol with oxygen and HPA is a complex multicomponent, multistage process, consisting of a series of sequential and parallel reactions.

The data on diffuse reflectance spectra of HPA-reductant mixtures on cellulose presented above along with ESR, kinetic and chemiluminescence inhibition data given in [9] confirm involvement of radical species in these reactions.

Sorption of heteropoly acids on the surface of cellulose and diethylaminoethylcellulose with molybdovanadophosphoric acid as an example has been studied by UV-VIS, infrared, and MAS-NMR spectroscopy [11]. It has been shown that sorption of HPA on diethylaminoethylcellulose is substantially higher than that on ordinary cellulose. The mechanism of sorption includes combination of

Coulomb and hydrophobic interactions. A scheme of HPA immobilization has been proposed based on ion exchange on cellulose and DEAE-cellulose surface:

$$(\equiv C{-}OH_2^+)_n{\cdot}SO_4^{2-} + HPA^{n-} \rightarrow$$
$$\rightarrow (\equiv C{-}OH_2^+)_n{\cdot}(HPA^{n-}) + SO_4^{2-},$$

$$[(\equiv C{-}O{-}(CH_2)_2{-}NH^+(C_2H_5)_2]_n{\cdot}SO_4^{2-} + HPA^{n-} \rightarrow$$
$$\rightarrow [(\equiv C{-}O{-}(CH_2)_2{-}NH^+(C_2H_5)_2]_n{\cdot}(HPA^{n-}) + SO_4^{2-}.$$

The signal ^{31}P in NMR spectrum of sorbed HPA is more wide compared to the signal ^{31}P in NMR spectrum of crystalline HPA which is due to removal of crystalline and structural water. Based on the evolution of the NMR spectra, it can be assumed that there is a partially dehydrated HPA on the surface of the sorbent, bonded electrostatically and due to hydrophobic interactions with the cellulose surface.

The FTIR spectrum of crystalline $H_4[PVMo_{11}O_{40}]$ in the range 400–1100 cm^{-1} exhibits four characteristic bands: 723 cm^{-1} and a shoulder at 785 cm^{-1}, which is due to the existence of an angular bridge bond Mo–O–Mo; 873 cm^{-1} – linear bridge bond Mo–O–Mo; 949 cm^{-1} – Mo=O bonds and 1050 cm^{-1} – P–O bonds. The P–O vibration band of crystalline HPA overlaps with the OH vibration band of the sorbent groups (1050 cm^{-1}); therefore, it is difficult to identify it in the sorbent phase; however, other bands characteristic of crystalline HPA are also manifested in the IR spectra of cellulose samples treated with HPA solutions. At the same time, an angular bridge band Mo–O–Mo is observed at 795 cm^{-1}. Its shift to the high-frequency region in comparison with the crystalline HPA indicates an increase in the energy of bending vibrations of this group and confirms the assumption about the electrostatic interaction between the bridging oxygen of the HPA and the functional groups of the cellulose surface.

Composition of IA of HPAs with cationic surfactants is an interesting issue, especially in microconcentrations range. The composition of poorly soluble IA of the listed HPAs with long-chain cationic surfactants (dodecylpyridinium bromide DDPB, tetradecylpyridinium bromide TDPB, cetyltrimethylammonium bromide CTB) was investigated by equilibrium shift method and by molar ratio method after filtration through cellulose filters using CL reactions of isolated IA with luminol. Integral light amount and maximum light intensity were used as characteristics of the system [12]. Molar ratio of components in IA determined by equilibrium shift method coincides with ratio found by molar ratio method.

Bjerrum's method was also used by us to investigate the composition of IA of vanadomolybdophosphoric acid with cationic surfactant dodecylpyridinium bromide. Curve of formation of IA of PVMo HPA with DDPB was constructed (Fig. 4).

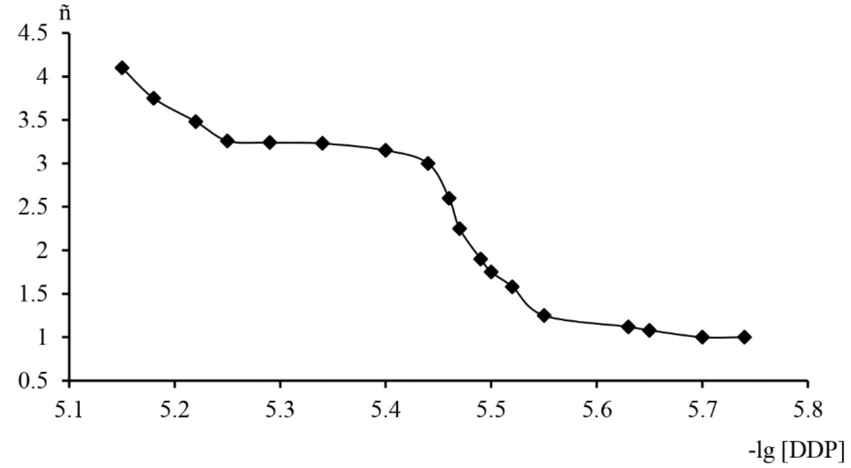


Fig. 4. Formation curve of ionic associate in the system $H_4PVMo_{11}O_{40}$ – DDPB obtained by Bjerrum's method. C_{HPA} = 1.0 μM

As can be seen in Fig. 4, one HPA anion is coordinated with three DDP cations in the wide range of DDPB concentrations. So, IA composition can be represented as $(DDP)_3HPVMo_{11}O_{40}$ which is consistent with literature data about substitution of only three protons in 1-vanado-11-molybdophosphate molecule in acidic media [13, 14].

The composition of IA HPA-surfactant was determined also by molar ratio method: $(CT)_4SiMo_{12}O_{40}$; $(CT)_5GeVMo_{11}O_{40}$; $(TDP)_4AsVMo_{11}O_{40}$; in the case of molybdovanadophosphoric acid, the composition of IA is different at different pH (see Fig. 5): at pH 1.0, the composition of IA is $(DDP)_3H[PVMo_{11}O_{40}]$; at pH 1.7 – $(DDP)_4[PVMo_{11}O_{40}]$. This result is consistent with the data that the fourth proton in $H_4PVMo_{11}O_{40}$ is weakly dissociated; it is more strongly bound to HPA and is localized on the oxygen atom of the Mo–O–Mo angular bond. Thus, as a result of protonation of HPA upon going from pH 1.7 to pH 1.0, the acid $H_4PVMo_{11}O_{40}$ forms not tetra-substituted, but triply substituted IA.

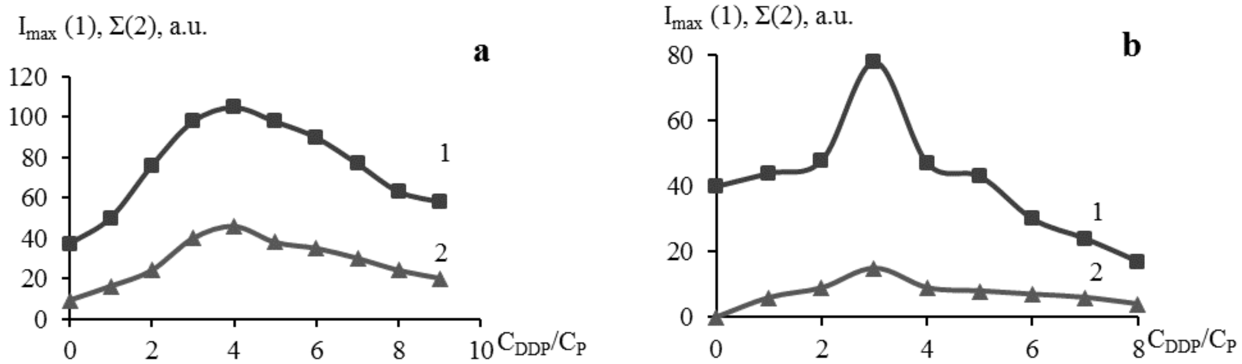


Fig. 5. Composition of IA dodecylpyridinium bromide (DDPB) : $H_4PVMo_{11}O_{40}$ obtained by molar ratio method using maximum CL intensity (*1*) and integral light amount (*2*): *a* – pH = 1.7; *b* – pH = 1.0

Interaction of HPA with cationic surfactants in aqueous solution and immobilization of IA formed on the surface during filtration through cellulose filters on the example of molybdosilicic acid and dodecyltrimethylammonium bromide may be represented as follows (see Fig. 6).

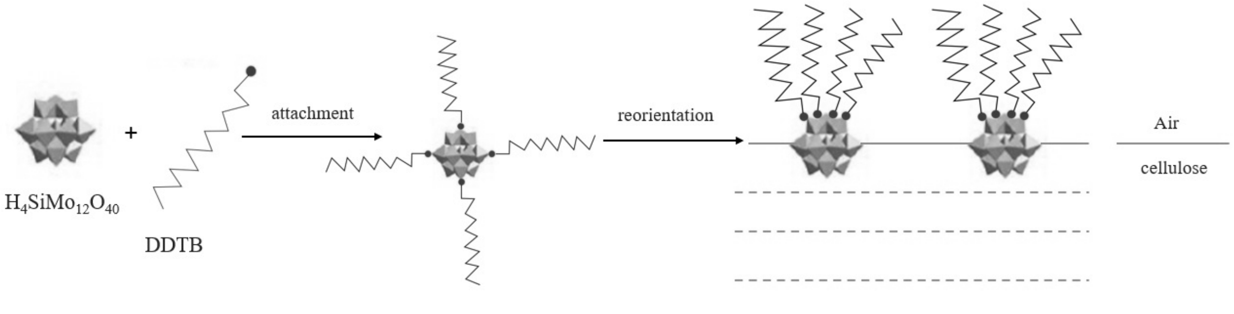


Fig. 6. Scheme of IA formation in aqueous solution and of its immobilization on cellulose

It has been shown that IAs HPA-cationic surfactant react with an alkaline solution of luminol with light emission similarly to HPAs themselves. Their isolation on cellulose filters and detection by CL method directly on the sorbent surface made it possible to improve substantially the sensitivity of the determination of phosphorus, arsenic, silicon, and germanium [15]. Characteristics of central atoms determination with CL detection of concentrates on filters are shown in the Table.

Table. Analytical parameters of P, As, Si, Ge determination by preconcentration of IA of HPAs on paper filters with CL detection

Element	**Analytical form**	**Working range, μg/L**	**Detection limit, μg/L**	**Relative standard deviation, %**	**Analysis duration, min**
P	$(DDP)_3HPVMo_{11}O_{40}$	0.06–10.0	0.02	14,3	25
As	$(TDP)_4AsVMo_{11}O_{40}$	0.06–3.5	0.02	14,5	25 (with distillation – 40)
Ge	$(CTA)_5GeVMo_{11}O_{40}$	0.1–110	0.05	13	25 (with distillation – 40)
Si	$(CTA)_4SiMo_{12}O_{40}$	0.07–10.0	0.07	15	22

Due to the high sensitivity of the method proposed, phosphorus was successfully determined in surface water (Dnipro river – 20.0 μg P/L) and in ultrapure water (Milli-Q water, 0.25 μg P/L), arsenic after distillation in the form of volatile AsH_3 – in river water (Dnipro river – < 0.2 μg As/L) and mineral water (mineral water “Shayans’ka” – 4.8 μg As/L), silicon – in ultrapure water (water of high purity for electronic industry – 2.4 μg Si/L) and in vapor condensate of electric power station (3.6 μg Si/L), germanium – in water of electronic industry (2.6 μg Ge/L).

CONCLUSIONS

The properties of heteropoly acids and of their complexes with cationic surfactants were studied by ESR spectroscopy, UV-VIS spectrophotometry, NMR and FTIR spectroscopy, by the method of chemiluminescence analysis applied in aqueous solutions and on the cellulose surface. One-electron luminol oxidation was substantiated by ESR spectra and diffuse reflectance spectra of HPAs on cellulose surface; superoxide generation confirmed by selective inhibitory effect of OsO_4 and *p*-aminophenol; the proposed mechanism of CL reaction was proved by coincidence of CL spectra with spectra of aminophthalate fluorescence, HPLC identification of reaction products, elucidation of reaction kinetics, reaction order, and checking the effect of O_2.

It has been shown that heteropoly acids immobilized on paper filters as well as their complexes with cationic surfactants (C12–C16) cause light emission with luminol like HPAs in aqueous solutions. Heterogeneous chemiluminescence was used to study the composition and properties of HPAs and their ionic associates on cellulose surface. Evidence was obtained on formation of triply substituted molybdovanadophosphoric acid at pH 1.0. Composition of the PVMo HPA – dodecylpyridinium bromide complex obtained by shift of equilibrium, molar ratio and Bjerrum’s methods at pH 1.7 is $(DDP)_4PVMo_{11}O_{40}$, and at pH 1.0 – $(DDP)_3HPVMo_{11}O_{40}$. Fourth proton in $H_4PVMo_{11}O_{40}$ is weakly dissociated, it is more strongly bonded with HPA than three other protons and is localized on the bridging oxygen atom of Mo–O–Mo bond. Scheme of IA formation in aqueous solution and of their immobilization on cellulose surface was proposed. Silicomolybdic acid is stable in dilute aqueous solutions and on cellulose surface even at pH 0 (0.5 M H_2SO_4) unlike molybdovanadophosphoric, molybdovanadoarsenic and molybdovanadogermanic acids which are stable at pH 1.0–1.7 but decompose at pH 0. These features made it possible to detect selectively P, As, Si, Ge in waters of different types at the sub-ppb level.

Хемілюмінесцентні реакції гетерополікислот та їхніх комплексів з катіонними поверхнево-активними речовинами у водних розчинах та на поверхні целюлози

Ю.І. Мазна, О.В. Зуй

Інститут колоїдної хімії та хімії води ім. А.В. Думанського Національної академії наук України
Бул. Академіка Вернадського, 42, Київ, 03142, Україна, olegzuy@gmail.com

Властивості гетерополікислот та їхніх комплексів з катіонними поверхнево-активними речовинами на рівні мікроконцентрацій вивчені за допомогою спектроскопії ЕПР, UV-VIS спектрофотометрії, спектроскопії ЯМР та ІЧ-спектроскопії з Фур'є-перетворенням, методом хемілюмінесцентного аналізу у водних розчинах та на поверхні целюлози. Для встановлення механізму реакцій хемілюмінесценції гетерополікислот з люмінолом застосовані кінетичні методи, спектроскопія дифузного відбиття та рідинна хроматографія. Вперше одноелектронне відновлення гетерополікислот люмінолом було підтверджено реєстрацією спектрів дифузного відбиття відновлених гетерополікислот на поверхні целюлози. Було висловлено припущення, що механізм іммобілізації гетерополікислот на целюлозі включає поєднання кулонівських та гідрофобних взаємодій. Запропоновано схему іммобілізації гетерополікислот на поверхні, що базується на процесах іонного обміну на поверхні целюлози або діетиламіноетилцелюлози. Показано, що іонні асоціати гетерополікислот з катіонними поверхнево-активними речовинами реагують з лужним розчином люмінолу з випромінюванням світла подібно до самих гетерополікислот. Вперше гетерогенна хемілюмінесценція, а саме хемілюмінесценція гетерополікислот, іммобілізованих на целюлозі, з люмінолом використана для дослідження складу іонних асоціатів гетерополікислота – катіонна поверхнево-активна речовина. Використанням методу Б'єррума встановлено, що у сильнокислих середовищах (pH 1.0) ванадомолібдофосфорна кислота утворює з катіонною поверхнево-активною речовиною, а саме з додецилпіридиній бромідом, не тетразаміщений, а тризаміщений іонний асоціат. Цей результат пояснюється тим, що четвертий протон в $H_4PVMo_{11}O_{40}$ слабко дисоційований; він міцніше зв'язаний з гетерополіаніоном і локалізується на атомі кисню місткового зв'язку Mo–O–Mo. Іонні асоціати гетерополікислот використані як аналітичні форми для високочутливого хемілюмінесцентного визначення фосфору, арсену, силіцію, германію у водах різних типів. Межі виявлення для P, As, Si, Ge становлять 0.02–0.07 мкг/л. Завдяки високій чутливості методу фосфор був успішно визначений у поверхневих водах та воді особливої чистоти, арсен - у річковій та мінеральній воді, силіцій - у воді особливої чистоти та конденсаті пари електростанцій, германій - у воді електронної промисловості.

***Ключові слова**: гетерополікислоти, гетерогенні реакції, іонні асоціати, хемілюмінесцентний аналіз на поверхні*

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