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ASSESSMENT OF INFLUENCE OF VARIOUS FACTORS ON STABILITY OF MOLYBDENUM HETEROPOLY ANIONS WITH KEGGIN STRUCTURE

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Abstract

The conditional stability constants for various modifications of molybdenum heteropoly anions (HPAs) having Keggin structure were calculated using the results obtained when constructing the molar ratio curves. A comparative study of the stability of the main analytical forms of HPAs, which were used to determine phosphorus(V) and gallium(III), was carried out including oxidized, metal-substituted, reduced and oxidized forms, as well as those obtained in non-ionic surfactant medium. Based on the results of the study, molybdenum HPAs of phosphorus(V) can be arranged in the next row according to the values of conditional stability constant: $\text{PMo}_{12}\text{O}_{40}^{3-}$ (in a non-ionic surfactant medium) ($\beta = (1.6 \pm 0.6) \cdot 10^{40}$) > $\text{H}_4\text{PBi}^{3+}_2\text{Mo}_4^{\text{V}}\text{Mo}_7^{\text{VI}}\text{O}_{40}^{6-}$ ($\beta = (5.6 \pm 1.6) \cdot 10^{39}$) > $\text{H}_4\text{PMo}_4^{\text{V}}\text{Mo}_8^{\text{VI}}\text{O}_{40}^{3-}$ ($\beta = 4.9 \pm 0.4 \cdot 10^{37}$) > $\text{PMo}_{12}\text{O}_{40}^{3-}$ ($\beta = 10^{36}$). The members of the series with $n = 2-4$ were the most stable in the series of gallium molybdotungsten HPAs. The stability of various forms of molybdenum HPAs of phosphorus(V) is not very different and is determined by the stability of the entire skeleton of Keggin heteropoly anion. When assessing overall stability of reduced forms of HPAs, it is important to consider their kinetic stability.

Key words: heteropoly anion; conditional stability constant; phosphorus(V); gallium(III)

ОЦІНКА ВПЛИВУ РІЗНИХ ФАКТОРІВ НА СТІЙКІСТЬ МОЛІБДЕНОВИХ ГЕТЕРОПОЛІАНІОНІВ СТРУКТУРИ КЕГГІНА

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Анотація

З використанням результатів побудови кривих насичення розраховані умовні константи стійкості для різних модифікацій молібденових гетерополіаніонів (ГПА) структури Кеггіна. Проведено порівняльне дослідження стійкості основних аналітичних форм ГПА, у вигляді яких визначають фосфор(V) і галій(III), включаючи окислені, металозаміщені, відновлені і окислені форми, а також отримані в середовищі неіонних ПАВ. Виходячи з результатів дослідження молібденові ГПА фосфору(V) по стійкості можна розташувати в наступний ряд: $\text{PMo}_{12}\text{O}_{40}^{3-}$ (в середовищі неіонних ПАВ) > $\text{H}_4\text{PBi}^{3+}_2\text{Mo}_4^{\text{V}}\text{Mo}_7^{\text{VI}}\text{O}_{40}^{6-}$ > $\text{H}_4\text{PMo}_4^{\text{V}}\text{Mo}_8^{\text{VI}}\text{O}_{40}^{3-}$ > $\text{PMo}_{12}\text{O}_{40}^{3-}$. В ряду молібдовольфрамів ГПА галію найбільш стійкими виявилися члени ряду з $n = 2-4$.

Ключові слова: гетерополіаніон, умовна константа стійкості, фосфор(V), галій(III)

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ОЦЕНКА ВЛИЯНИЯ РАЗЛИЧНЫХ ФАКТОРОВ НА УСТОЙЧИВОСТЬ МОЛИБДЕНОВЫХ ГЕТЕРОПОЛИАНИОНОВ СТРУКТУРЫ КЕГГИНА

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Аннотация

С использованием результатов построения кривых насыщения рассчитаны условные константы устойчивости для различных модификаций молибденовых гетерополианионов (ГПА) структуры Кеггина. Проведено сравнительное исследование устойчивости основных аналитических форм ГПА, в виде которых определяют фосфор(V) и галлий(III), включая окисленные, металламещенные, восстановленные и окисленные формы, а также полученные в среде неионных ПАВ. Исходя из результатов исследования молибденовые ГПА фосфора(V) по устойчивости можно расположить в следующий ряд: $\text{PMo}_{12}\text{O}_{40}^{3-}$ (в среде неионных ПАВ) > $\text{H}_4\text{Pb}^{3+2}\text{Mo}_4^{\text{V}}\text{Mo}_7^{\text{VI}}\text{O}_{40}^{6-}$ > $\text{H}_4\text{PMo}_4^{\text{V}}\text{Mo}_8^{\text{VI}}\text{O}_{40}^{3-}$ > $\text{PMo}_{12}\text{O}_{40}^{3-}$. В ряду молибдовольфраматовых ГПА галлия наиболее устойчивыми оказались члены ряда с $n = 2-4$.

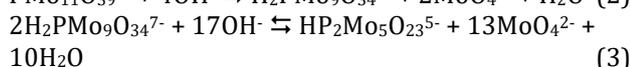
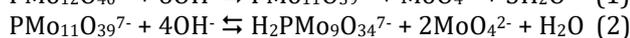
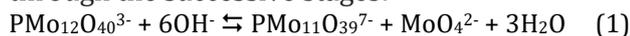
Ключевые слова: гетерополианион, условная константа устойчивости, фосфор(V), галлий(III)

Introduction

The study of changes in the stability of molybdenum heteropoly anions (HPAs) with a Keggin structure depending on the nature and number of substituent atoms, the degree of reduction, and the medium is still very important in analytical chemistry [1]. Such changes include the formation of metal-substituted [2; 3] and mixed-ligand HPAs [4], the transition from oxidized to reduced forms [5], and the influence of an organized medium of non-ionic surface-active substances (NSAS). Just the stage of formation of HPA determines the optimal conditions of the analytical methods using such complex anions or their ionic associates with organic dyes [6; 7]. Therefore, it seems useful to undertake a comparative assessment of the stability constants for the corresponding formation reactions. Despite the fact that the calculations carried out in this work do not give the values of thermodynamic stability constants, the obtained estimates of conditional constants make it possible to arrange the complexes in order of increasing stability and evaluate the contribution of certain changes in the structure or the medium to its change. The study was conducted under conditions of constant ionic strength and the solution acidity in order to exclude the influence of these important variables on the values of the constants.

The stability constants were calculated only for HPAs of phosphorus(V) due to the fact that there is a large amount of experimental data for these complexes in the literature. The evaluation of the stability constants for molybdenum heteropoly complexes (HPCs) with other heteroatoms was carried out only occasionally. The most thoroughly studied, among others, is the PO_4^{3-} –

MoO_4^{2-} – H^+ system [8; 9]. 12-molybdophosphate is formed in aqueous solutions at pH <1.5. With increasing pH, it undergoes alkaline hydrolysis, which in dilute solutions (<10⁻³ mol/L) passes through the successive stages:



The stability constants for heteropoly complexes, indicated in equations (1) – (4), and their protonated forms have been determined by Pettersson et al. [10; 11]. In addition, equilibria for molybdenum HPAs of As(V) were also studied in detail [10]. In solutions, many polyoxometallates are characterized by the coexistence of several substances. The equilibrium state depends on the pH and addendum atom (Mo(VI), W(VI), V(V)) concentration. Establishing equilibrium in HPC solutions takes from a few fractions of a second (labile molybdate systems) to several months (inert tungstate systems). Unfortunately, for most of the HPAs, including the reduced ones, slow establishment of formation or destruction equilibria is typical. Nevertheless, the formation of, for example, tungstophosphoric HPA was studied in several papers [8].

12-molybdophosphoric HPA $\text{PMo}_{12}\text{O}_{40}^{3-}$ (12-MPA) is the basis of the structural series of molybdenum HPCs of phosphorus(V) and belongs to the complexes with medium stability. Its formation becomes noticeable only in a relatively narrow pH range close by 1.4 provided that the sufficiently high concentration of molybdate-ions is created in the solution [10; 11]. To ensure the

completeness of the formation, a large excess of molybdate ions is commonly introduced. This often prevents to achieve a sufficiently high sensitivity, reproducibility, etc. Under the conditions typical for HPA formation, molybdate ions can form isopoly anions, which absorb the radiation in the same spectral region, can be reduced with the formation of isopoly blues, or form ion association complexes with dye cations [5]. Stability constant of 12-MPA was calculated in several papers [10; 11]. At the same time, for the derivatives of 12-MPA, such data are practically absent. Therefore, the stability of HPAs is often evaluated and compared indirectly – with respect to the decomposition by acid or hydroxy acids [12], which is not a reliable basis for evaluation. There is an opinion that the stability of molybdenum HPAs increases by introduction of metal ion into HPA. The very fact that a metal ion replaces molybdenum in 12-HPA also indicates this.

In micellar media of non-ionic SAS (nonionic surfactants), like the aqueous-organic mixtures [13; 14], the apparent stability constant of HPA increases. Stability of HPA grows in organic or water-organic media. It has been shown by electrical conductivity method that such heteropoly acids as $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_4SiMo_{12}O_{40}$ and $H_4PVMo_{11}O_{40}$ are resistant to hydrolysis in ethanol, acetone and acetic acid at 10^{-5} – 10^{-6} mol/L concentrations [15]. Heteropoly acids having Keggin structure are strong, completely dissociated polybasic Bronsted acids in water. One or two protons of these acids remain strong when dissolved in organic solvents. Another consequence of the weakening of acidic properties of heteropoly acid in the micellar medium is the decrease in the number of cations of basic organic dyes attached to the HPA because weak protons lose their ability to be replaced by dye cations.

The aim of this work is a comparative study of the stability of oxidized form of 12-MPC in aqueous and micellar media, as well as reduced derivatives of 12-MPC, including metal-substituted ones, under the conditions used in chemical analysis. The effect of partial substitution of molybdenum atoms in HPA by tungsten atoms was studied using molybdotungstic HPAs of gallium(III).

Experimental part

Reagents and equipment. The solutions of the reagents used in the work were prepared in distilled and bidistilled water and stored in a polyethylene container in order to avoid

contamination with silicon(IV) impurities. A stock solution of 0.01 mol/L potassium dihydrophosphate was prepared by dissolving pre-recrystallized “chemically pure” KH_2PO_4 , which had been dried for 3 hours at 120 °C. 0.01 mol/L solution of Si(IV) was prepared by dissolving an exact weighed $Na_2SiO_3 \cdot 9H_2O$ p.a. and standardized gravimetrically. 0.1 mol/L solution of $Ga(NO_3)_3$ was prepared from metallic gallium (99.999 %) by dissolving an exact weight in concentrated nitric acid, standardized by back complexometric titration with $ZnSO_4$. 0.1 mol/L solutions of Na_2MoO_4 and Na_2WO_4 were prepared from $Na_2MoO_4 \cdot 2H_2O$ and $Na_2WO_4 \cdot 2H_2O$ with “chemically pure” grade recrystallized from a water-ethanol medium. 5 mol/L and 0.5 mol/L H_2SO_4 were prepared from concentrated H_2SO_4 (“chemically pure” grade). A hydrochloric acid with “especially pure” grade was also used. $SbCl_3$ solution was prepared by dissolving $SbCl_3$ sample in 10 mol/L HCl. Its standardization was performed by bromatometric method. 0.1 mol/L solution of $Bi(NO_3)_3$ was prepared by dissolving $Bi(NO_3)_3 \cdot 5H_2O$ sample in 1 mol/L H_2SO_4 and standardized by complexometric titration with Trilon B. 1% solution of neonol (analog of Triton X-100) was prepared by dissolution of 1 mL of reagent in distilled water by gentle warming.

Absorbance and absorption spectra were measured on an SF-26 spectrophotometer (LOMO, St. Petersburg, Russia). The pH was monitored on a pH-150 MI pH meter with an ES-10601 glass indicator electrode and an ESD-10101 silver chloride reference electrode.

Results and its discussion

Evaluation of the stability of 12-molybdophosphate and 11-molybdophosphate heteropoly blues as well as 12-molybdophosphate in a micellar medium of nonionic surfactant. When assessing stability of phosphorus(V) heteropoly blues (HPBs), two representatives of these complexes – products of reduction of 12-MPC and its metal-substituted derivative – 11-molybdo-2-bismuthophosphate HPC (11,2-MBPC) were studied. According to [8; 16; 17] in both cases, the product of reduction are four-electron heteropoly blues. These substances are analytical forms formed in the corresponding methods for orthophosphate determination. The data for the calculation were obtained from the molar ratio curves as the concentration of molybdate was varied. In the course of preliminary studies, the range of molybdate concentration was found, in which the degree of complex formation was significantly different from 100 %. This was a

prerequisite for calculating the stability constant. The results of the experiment are shown in Fig. 1.

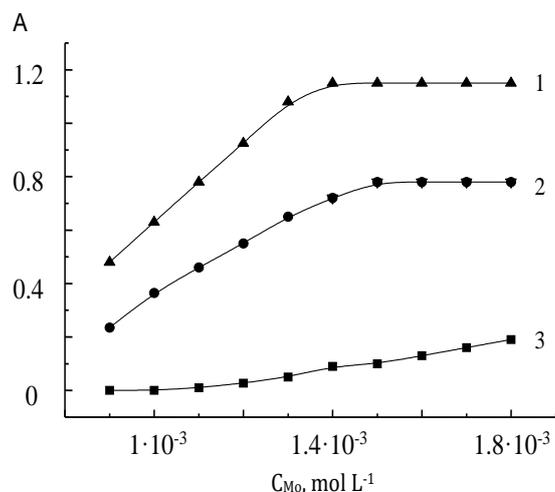


Fig. 1. Influence of molybdate concentration on absorbance of reduced 12-MPC (1), 11,2-MBPC (2) and isopoly molybdates (3). $C_P = 4 \cdot 10^{-5}$ M, $C_H = 0.2$ M, $C_{Asc} = 0.04\%$, $l = 1$ cm. 1, 3 - $\lambda = 820$ nm; 2 - $C_{Bi(III)} = 1.6 \cdot 10^{-4}$ M, $\lambda = 716$ nm. Time of reduction: 1, 3 - 40 min of boiling; 2 - 15 min of standing

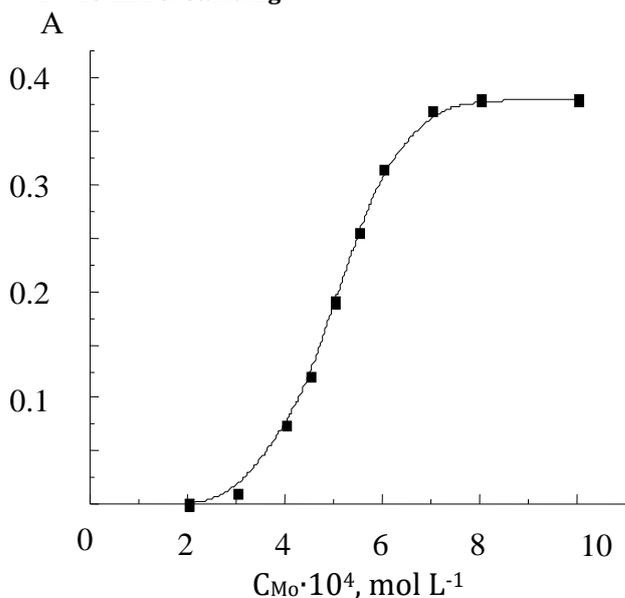


Fig. 2. Dependence of absorbance of 12-MPC on molybdate concentration in medium of non-ionic surfactant. $C_P = 8 \cdot 10^{-6}$ M, $C_H = 0.2$ M, $C(\text{neonol}) = 0.04\%$, $\lambda = 350$ nm, $l = 5$ cm

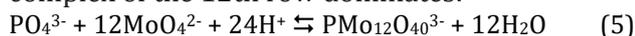
In the absence of bismuth(III) ions, even 15 minutes after the components mixing, the degree of 12-molybdophosphate formation was insignificant, so the solutions were heated until equilibrium was reached (Fig. 1, curve 1). 11,2-MBPC formation is almost complete already after 15 minutes of standing and the heating slightly affects the character of obtained curves (Fig. 1, curve 2). As can be seen from Fig. 1, for the complete formation of both complexes, it is

sufficient to create a molybdate concentration of about $1.5 \cdot 10^{-3}$ mol/L.

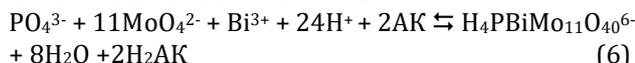
We have shown in a number of works [18; 19] that a much lower concentration of molybdate ions is required in a non-ionic surfactant medium for the quantitative formation of saturated molybdenum HPCs of phosphorus and arsenic in comparison with the formation of oxidized or reduced phosphorus HPA in an aqueous medium. Stability of 12-MPA in micellar media has not been previously evaluated. A series of experiments was carried out with the same acidity of the solution. It can be seen that the quantitative formation of 12-MPA is observed at molybdate concentrations $> 7 \cdot 10^{-4}$ mol/L (Fig. 2).

The calculation of HPA stability constant requires the simultaneous consideration of several possible equilibria. These are, firstly, the equilibria of the formation of isopoly molybdate anions [10] and in a strongly acidic solution of cationic forms of molybdenum(VI) [20] (more than 10 such compounds are known). Secondly, these are the equilibria of the formation of molybdenum HPAs of phosphorus(V) (equations 1-4) [10; 11]. The calculation of all these equilibria is complex and often impossible. Therefore, other simplified methods for calculating the HPC stability constants have been adopted in the literature.

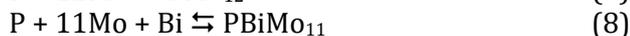
Pettersson et al. showed [11] that in a relatively wide range of pH with an excess of molybdate ions, the equilibrium of the formation of a saturated complex of the 12th row dominates:



or for metal-substituted HPC



In a brief record, these equations can be written in the form:



Hydrogen ions and ascorbic acid are omitted in order to simplify calculations on the basis that their concentrations were constant and high in all solutions.

In this system, the only compound absorbing light in visible region of the spectrum is heteropoly blue. Since its molar absorption coefficient can be easily obtained from the absorbance data at the saturation region, this makes it possible to calculate the equilibrium concentration of the complex at all points. Concentrations of other substances can be found from the material balance conditions:

$$\begin{aligned}
 [P] &= C_P - [\text{complex}]; \\
 [\text{Mo}] &= C_{\text{Mo}} - 12(11) \cdot [\text{complex}]; \\
 [\text{Bi}] &= C_{\text{Bi}} - [\text{complex}]
 \end{aligned}
 \tag{9}$$

The stability constants of 12-molybdophosphate and 12-MPC in the neonol medium were calculated using equation (10), and for 11-MBPC using equation (11):

$$\beta_{12\text{-MPC}}^y = \frac{[PMo_{12}]}{[P][Mo]^{12}} \tag{10}$$

$$\beta_{11\text{-MBPC}}^y = \frac{[PBiMo_{11}]}{[P][Bi][Mo]^{11}} \tag{11}$$

The absence of the drift in the stability constants values (Table) indicates the correctness of the model chosen for the calculation. The metal-substituted complex is more stable than purely molybdenum. This explains shift of the equilibrium towards HPC formation according to reaction (8). 12-MPC is even more stable in the medium of nonionic surfactant.

$$\begin{aligned}
 \beta^{12\text{-MPC}} &= (4.9 \pm 0.4) \cdot 10^{37}; & \beta^{11\text{-MBPC}} &= \\
 (5.6 \pm 1.6) \cdot 10^{39}; & \beta^{12\text{-MPC}}(\text{neonol}) &= (1.6 \pm 0.6) \cdot 10^{40}.
 \end{aligned}$$

In the reference [21] the stability constant of oxidized form of 12-MPC was calculated from the results of a paper chromatography study using the same formalism of writing the equations for complex formation. It was equal to $2.5 \cdot 10^{31}$, which is noticeably lower than the values obtained for metal-substituted HPA, as well as for 12-MPC in a micellar medium. In another reference [20], the conditional stability constant of 12-MPC was estimated according to spectrophotometry data with the same acidity (0.2 mol/L) as in this work and equaled to $1.2 \cdot 10^{29}$.

Higher stability of reduced forms compared to oxidized ones was noticed long ago. These substances are more stable not only to decomposition by acid, but, in particular, are kinetically stable to alkaline hydrolysis. Some of the heteropoly blues are stable even in 1 mol/L alkali [22]. This, however, is largely determined by kinetic factors.

Table

The results of the calculation of the stability constants of the reduced 12-MPC, 11,2-MBPC and 12-MPC in non-ionic surfactant medium
 $C_P = 4 \cdot 10^{-5} \text{ M}$, $C_H = 0.2 \text{ M}$, $C_{\text{Asc}} = 0.04\%$, $C_{\text{Bi}} = 1.6 \cdot 10^{-4} \text{ M}$. Formation time 15 min, $\lambda = 716 \text{ nm}$, $l = 1 \text{ cm}$, $\epsilon_{\text{Blue}} = 1.5 \cdot 10^4 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$

$C_{\text{Mo}} \cdot 10^4, \text{ M}$	A	$C_P \cdot 10^5, \text{ M}$	$[P] = [\text{Bi}] \cdot 10^5, \text{ M}$	$[\text{Mo}] \cdot 10^4, \text{ M}$	$K_{\text{stability}} \cdot 10^{-39}$
10	0.51	2.61	1.38	7.12	5.69
11	0.57	2.92	1.07	7.78	3.96
12	0.65	3.33	0.67	8.33	5.57
13	0.70	3.59	0.41	9.05	6.39
14	0.73	3.74	0.25	9.88	6.49

12-molybdophosphate heteropoly blue. $C_P = 4 \cdot 10^{-5} \text{ M}$, $C_H = 0.2 \text{ M}$, $C_{\text{Asc}} = 0.04\%$, 40 min of boiling, $\lambda = 820 \text{ nm}$, $l = 1 \text{ cm}$, $\epsilon_{\text{Blue}} = 2.47 \cdot 10^4 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$

$C_{\text{Mo}} \cdot 10^4, \text{ M}$	A	$C_P \cdot 10^5, \text{ M}$	$[P] \cdot 10^5, \text{ M}$	$[\text{Mo}] \cdot 10^4, \text{ M}$	$K_{\text{stability}} \cdot 10^{-37}$
9	0.48	1.67	2.33	7.60	5.21
10	0.63	2.19	1.81	7.37	4.71
11	0.78	2.71	1.28	7.74	4.53
12	0.925	3.22	7.83	8.13	4.86
13	1.04	3.62	3.83	8.65	5.32

12-MPC. $C_P = 8 \cdot 10^{-6} \text{ M}$, $C(\text{neonol}) = 0.04\%$, $C_H = 0.2 \text{ M}$, $\lambda = 350 \text{ nm}$, $l = 5 \text{ cm}$, $\epsilon = 9.50 \cdot 10^3 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$

$C_{\text{Mo}} \cdot 10^4, \text{ M}$	A	$C_P \cdot 10^6, \text{ M}$	$[P] \cdot 10^6, \text{ M}$	$[\text{Mo}] \cdot 10^4, \text{ M}$	$K_{\text{stability}} \cdot 10^{-40}$
4	0.075	1.58	6.42	3.81	2.62
4.5	0.12	2.52	5.47	4.20	1.55
5	0.19	4.00	4.00	4.52	1.38
5.5	0.255	5.37	2.63	4.86	1.19
6	0.315	6.63	1.37	5.20	1.23

Analysis of the stability of gallium molybdotungstic heteropoly complexes with Keggin structure. When determining the stability constants of molybdotungstic HPAs, in particular of oxidized yellow forms, problems arise associated with the effect of absorbance caused by an excess of reagent. When using molybdenum

HPA, the conditions under which the absorbance of oxidized and reduced forms of HPA is selective can be found quite simply. At the same time, the stability of molybdotungsten isopoly anions is much higher than that of molybdenum isopoly anions; therefore, it is difficult to convert them

into slightly colored cationic forms by acidification.

Gallium HPA is obtained by heating in a boiling water bath for a certain time until reaching equilibrium. After cooling the solution, we get a state of "frozen equilibrium", which reflects the state of equilibrium at higher temperature. At

room temperature, equilibrium does not shift more due to the inertness of the obtained HPA. Therefore, if we separate the HPA by extraction, then such an amount will pass into the organic phase, which corresponds to the equilibrium concentration of HPA at $\sim 90^\circ\text{C}$.

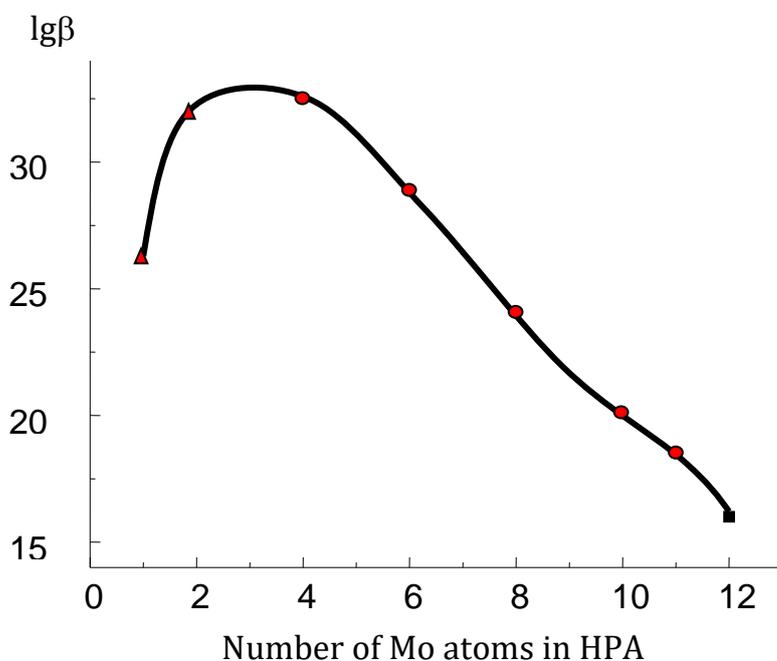
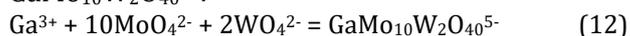


Fig. 3. Dependence between logarithm of conditional stability constant of HPA and number of molybdenum atoms in a row of molybdotungsten complexes of gallium of general formula $\text{GaMo}_n\text{W}_{12-n}\text{O}_{40}^{5-}$.

It is easy to calculate the remaining equilibrium concentrations provided that the yield of HPA is known. For example, the following equations are valid for the formation equilibria of HPA $\text{GaMo}_{10}\text{W}_2\text{O}_{40}^{5-}$:



$$[\text{HPA}] = C_{\text{Ga(III)}} \cdot \text{yield}; [\text{Ga}] = C_{\text{Ga(III)}} - [\text{HPA}] \quad (13)$$

$$[\text{Mo}] = C_{\text{Mo}} - 10 \cdot [\text{HPA}]; [\text{W}] = C_{\text{W}} - 2 \cdot [\text{HPA}] \quad (14)$$

$$\beta(\text{GaMo}_{10}\text{W}_2) = [\text{HPA}] / ([\text{Ga}] \cdot [\text{Mo}]^{10} \cdot [\text{W}]^2) \quad (15)$$

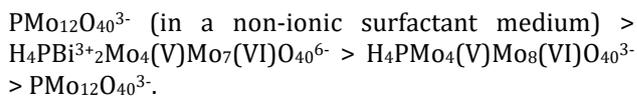
For a number of combinations of Ga(III), Mo(VI), and W(VI) concentrations, the degree of HPA formation was determined using extraction, and then conditional stability constants were calculated taking into account the above assumptions [23]. The stability constants help to predict the substances concentrations under conditions of analytical determination, as well as roughly compare the relative stability of a series of Ga(III) molybdotungsten HPAs and other HPAs. It can be seen from Fig. 3 that the members of the series, in which the number of molybdenum atoms is 2, 3 or 4, have the maximum stability. It would seem that these HPA should be mainly used in the analysis. But together with the increase in the number of tungsten atoms in the HPA, stability of molybdotungsten isopoly anions goes up, which

significantly enhances the complexity of their separation. Therefore, more simpler, reliable and highly sensitive methods would be developed when using HPA with 10 molybdenum atoms, which, on the one hand, is rather stable, and, on the other hand, allows completely separate excess of molybdotungsten isopoly anions for one extraction.

Conclusions

Various modifications of the molybdenum HPA with Keggin structure lead to an overall increase in the stability of these complex compounds, which manifests itself, for example, in reducing molybdate concentration necessary for the HPA complete formation, or in an increase of the stability to acid decomposition or hydroxy acids action. The conditional stability constants were calculated for various modifications of Keggin molybdenum HPA from the results obtained by construction of molar ratio curves. A comparative study of the stability of the main analytical forms of HPA used for determination of phosphorus(V) and gallium(III), including oxidized, metal-substituted, reduced and oxidized forms, and those obtained in a medium of non-ionic

surfactant was carried out. Based on the results of the study, molybdenum phosphorus(V) HPAs can be arranged in the following row according to the decrease of stability constant:



The members of the series with $n = 2-4$ were the most stable in the series of gallium molybdotungsten HPAs, although even the replacement of two molybdenum atoms with tungsten increases the stability of gallium (III) HPA to such an extent that they can be formed quantitatively with a sufficiently large excess of molybdate. It is worth mentioning that when assessing the overall stability of the reduced forms of HPAs, it is necessary to take into account their kinetic stability.

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