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IMMOBILIZATION OF MOLYBDO-PHOSPHORIC, MOLYBDO-ANTIMONO-PHOSPHORIC AND MOLYBDO-SILICIC HETEROPOLY ACIDS ONTO SILICA VIA ADSORPTION

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The adsorption of reduced forms of molybdo-phosphoric, molybdo-antimono-phosphoric and molybdo-silicic heteropoly acids with few anion-exchanger on the base of tetradecylammonium nitrate adsorbed onto amorphous silica was investigated. The interaction of heteropoly acids with immobilized quaternary ammonium salts was investigated *via* UV/VIS and solid-phase spectrophotometric methods. The significant influence of the surface groups on the chromophorous system of adsorbed heteropoly anions was shown. Unexpected strong fixing of HPA on the surface was found to be a result of formation of ion associates between heteropoly acids and immobilized tetradecylammonium nitrate and HPA interaction with active groups of the nonmodified silica surface. *Keywords:* Adsorption; Silica gel, Quaternary ammonium salt, Heteropoly acid, Phosphate, Silicate

1. Introduction

Heteropoly acids (HPA) are the unique class of inorganic complexes. They are widely used for development of heat resistant varnishes, ion exchangers, coprecipitation agents, semiconductor and magnetic materials [1]. HPA and their salts are applied as heterogeneous catalysts for a number of reactions [1, 2]. In addition, heteropoly compounds are the major analytical forms for P, Si, As and Ge determination using spectroscopy, sorption-spectroscopy and chromatography [1, 3, 4].

The materials used for development of catalysts on the base HPA or preconcentration of elements in the form of heteropoly compounds should have high affinity to HPA or their salts. That is why the development of materials able to provide strong fixing of heteropoly compounds onto the surface is the actual task of materials science. Such matrixes as active carbon, sephadex gel, cellulose (including nitrated and acetylated cellulose), polyacrylic, naphthalene or polyurethane foam were proposed earlier for HPA adsorption [3, 5, 6]. However the reported supports are characterized by the low surface area and as a result low HPA adsorption capacity. Moreover HPA physically adsorbed onto these sorbents can be easily leached in water or organic solvents due to their high solubility. Special demands are made of matrixes for development of catalysts on the base of HPA because of great influence of the nature of supports and interaction of HPA on catalytic activity [7, 8]. Among so many supports silica is remarkable for low cost of production, high physical and chemical stability, ease of modification of physiochemical properties. It is well established that physiochemical properties of silica has an important role in the final properties of grafted compounds [8]. Moreover because of absence of swelling and absorbance in the visible part of the spectra, satisfactory kinetic characteristics [9] silica matrix are successfully used for preconcentration and solid-phase spectrophotometric determination of elements in the form of HPA [10].

The aim of the present paper was the studying of the interface interaction of aqueous solution of reduced forms of molybdo-phosphoric (HPA1), molybdo-antimono-phosphoric (HPA2) and molybdo-silicic (HPA3) heteropoly acids with silica modified with aliphatic quaternary ammonium salt (QAS). For these purposes UV/VIS and solid-phase spectroscopic techniques were used.

2. Experimental

2.1. Materials

Water was purified according to [11]. Chloroform and hexane for liquid chromatography (Merck) were used. Tetradecylammonium nitrate ($[N(C_{10}H_{21})_4]NO_3$, QAS) 99% purity obtained from [12] was used to prepare $1 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ solution in chloroform - hexane (1:15). Silica gels SG 60 (Merck) (SG) was used without pretreatment. SG loaded with QAS (QAS-SG) was prepared by adsorption of QAS

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onto SG surface from chloroform - hexane (1:15) mixture. The sorbent was dried at room temperature for 24 hours to evaporate the solvent from SG surface. The solution of ammonium molybdate was prepared by mixing of 7.500 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ with 10 mL of 18.5 mol L^{-1} sulphuric acid and then was made up to the total volume of 100 mL with deionised water. The solution of "mixed reagent" containing 2.6 mmol L^{-1} of ammonium molybdate, 1.25 mol L^{-1} of sulphuric acid and 0.03 mol L^{-1} of ascorbic acid was prepared before using. Aqueous solutions of HPA of Keggin structure were prepared as given below. The solution of HPA1 was prepared in such way: the portion of P(V) solution was mixed with 5.00 mL of "mixed reagent" solution and made up to the total volume of 25 mL with deionised water. Then the mixture was heated for 5 min in boiled water and then cooled to the room temperature. The solution of HPA2 was prepared in such way: the portion of P(V) solution was mixed with 5.00 mL of "mixed reagent" and 0.12 mL of 1.0 mg L^{-1} potassium-antimony tartrate, made up to the total volume of 25 with deionised water. The solution of HPA3 was prepared in such way: the portion of Si(IV) solution was mixed with 1.0 mL of ammonium molybdate and made up to the volume of 10 mL with deionised water. In 20 min 2.00 mL of 4.0 mol L^{-1} sulphuric acid and 1.00 mL of 0.06 mole L^{-1} ascorbic acid were added to the mixture and solution was made up to the total volume of 25 with deionised water. Sorbents with HPA impregnated were prepared in such way: isobutyl extracts of HPA1 ($0.5 \text{ } \mu\text{mole L}^{-1}$), HPA2 ($2 \text{ } \mu\text{mole L}^{-1}$) and HPA3 ($2 \text{ } \mu\text{mole L}^{-1}$) were mixed with 0.150 g of SG end then dried at room temperature to evaporate the solvent.

2.2. Apparatus

The absorbance spectra of solutions and sorbents were registered with UV/VIS spectrophotometers Specord M-40 (Carl Zeiss Jena, Germany) and KFK-3 (Russia). A potentiometer model EV-74 with glass electrode (Gomel, Belarus) was used for pH measurements. Sorption was developed by magnetic stirrers.

2.3. Procedures

The batch technique was used for the investigation of HPA adsorption onto QAS-SG. The weighed amount ($0.010\text{--}0.200 \text{ g}$) of modified sorbent was stirred with $5\text{--}50 \text{ mL}$ of $1\cdot 10^{-6}\text{--}1\cdot 10^{-3} \text{ mol L}^{-1}$ HPA solutions for $1\text{--}30 \text{ min}$. The value of adsorption (a , mol g^{-1}), recovery (R , %) and the coefficient of distribution of HPA (D , L g^{-1}) were calculated according to the equations: $a=(C_0-C)Vm^{-1}$; $R=(C_0-C)100C_0^{-1}$; $D=RV[(100-R)m]^{-1}$, where C_0 and C was the initial and equilibrium concentration of HPA in aqueous solution (mol L^{-1}); V was the volume of solution (L); m was the mass of sorbent (g). The equilibrium concentration of HPA1, HPA2 and HPA3 in aqueous solution was controlled spectrophotometrically by the own absorbance at 830 nm, 880 nm and 810 nm respectively using calibration graphs.

3. Results and Discussion

The reduced forms of HPA are preferable for determination of a number of elements because of their ability for absorption of electromagnetic radiation of the visible part of spectra and low influence of the blank [3, 13]. That is why the reduced forms of phosphoric and silicic HPA were chosen for the research in this work.

Non-modified silica show no tendency for the adsorption of HPA anions from aqueous solution in a wide range of pH that agrees well with the data reported [14]. In aqueous solution at $\text{pH}>3$ (where silica surface recharges negative [15]) the sorption of HPA is not observed because of electrostatic repulsion. Absence of HPA recovery at $\text{pH}<3$ (where silica surface recharges positive in consequence of its protonization [15]) is caused by low affinity of HPA anion to the silica surface because of its cation-exchange properties. That is why anion-exchangers on the base of silica modified with QAS (QAS-SG) were used for immobilization of HPA.

The adsorption of reduced HPA onto QAS-SG was studied under optimal conditions of their formation in solution: $0.25 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ (HPA1 and HPA2) and $0.40 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ (HPA3). The sorption of HPA was found to be quantitative. The equilibrium in the heterogeneous systems was reached in 15 min for HPA1 and HPA3 and 4 min for HPA2 (Fig. 1). Unexpectedly rapid equilibrium reaching in case of HPA2 may be explained by its higher hydrophobicity in comparison with HPA1 and HPA3 [1].

The isotherms of HPA adsorption can be referred to H2-type [16] and linearized in Langmuir coordinates with k , L mol^{-1} : $3.8\cdot 10^5$ (HPA1), $9.3\cdot 10^5$ (HPA2), $3.7\cdot 10^5$ (HPA3) ($R^2 \div 0.986\text{--}0.997$, $n=10$).

Such type of isotherms points out high affinity of HPA anions to QAS-SG surface and may be explained by formation of ion associates (IA) on the surface. The formation of IA between HPA and amine ligands covalently grafted onto silica was mentioned to be observed and confirmed by FT-IR spectroscopy in [8]. Taking into account the predominance of three charged anion form of HPA in the solution under indicated conditions [1, 3] we supposed that the IA with the ratio QAS:HPA=3:1 is formed on the surface. The maximum adsorption capacity of QAS-SG was $8.7 \mu\text{mol g}^{-1}$ for HPA1, $7.6 \mu\text{mol g}^{-1}$ for HPA2 and $8.3 \mu\text{mol g}^{-1}$ for HPA3 at $a_{\text{QAS}}=25 \mu\text{mol g}^{-1}$. The ratio of the values of maximum adsorption capacity of HPA and adsorption capacity of QAS on the surface (3.0–3.2) confirms the supposition about the composition of IA. The data obtained point out that sorption of HPA with QAS-SG is mainly a result of electrostatic interaction. However the significant increasing of ionic strength has no influence on the sorption of HPA with QAS-SG. So strong binding of HPA with the surface of QAS-SG can probably be explained by a sum of different types of interface interaction.

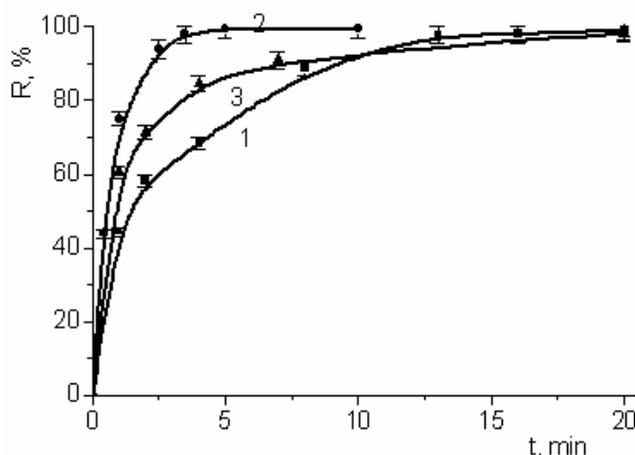


Fig. 1. The adsorption of HPA1 (1), HPA2 (2) and HPA3 (3) from aqueous solution with QAS-SG as a function of adsorption time. $T=290 \pm 1 \text{ K}$, $V/m, \text{ mL g}^{-1}$: 200 (1, 2), 130 (3); $C(\text{H}_2\text{SO}_4), \text{ mol L}^{-1}$ 0.25 (1, 2), 0.40 (3); $C(\text{P}) = 5 \mu\text{mol L}^{-1}$ (1, 2); $C(\text{Si}) = 7 \mu\text{mol L}^{-1}$ (3); $a_{\text{QAS}} = 25 \mu\text{mol g}^{-1}$

In order to study the nature of interaction of HPA with modified surface the solid-phase and UV/VIS spectroscopy were applied. The significant short-wave shift of maximum in the spectra of adsorbed HPA (Fig. 2) ($\Delta\lambda$, nm: 165 (HPA1), 180 (HPA2), 140 (HPA3)) in comparison with the spectra of HPA in aqueous solution and redistribution of adsorption bands testify the indignation of electron system of heteropoly anion as a result of its interaction with the surface. The maximums in absorbance spectra of HPA2 aqueous solution and the one of chloroform IA extract (Fig. 2, curves 5, 9) are similar. This fact testifies weak influence of QAS on the chromophor system of HPA in IA and correlates well with data reported [17]. That is why we supposed the significant influence of OH-surface groups on the electronic system of heteropoly anion obviously prevails over the influence of adsorbed QAS. This supposition is confirmed by the significant short-wave shift of maximum in the spectra of HPA adsorbed onto QAS-SG aside the maximum in the spectra of HPA impregnated onto unloaded SG (Fig. 2, curves 3, 4, 7, 8, 12, 13). The short-wave shift of maximums is also observed in spectra of protonated forms HPA in isobutyl alcohol extract (Fig. 2, curves 1, 2, 5, 6, 10, 11). This phenomenon testifies the similar mechanism of surface and oxygen-containing solvents influence on the electron system of HPA. This fact, unexpected strong fixing of HPA on the surface and unusually high stoichiometry of the components in IA (QAS:HPA=3:1) permit to suppose arrangement of HPA anion directly on the nonmodified silica surface surrounded by the grafted QAS molecules.

The adsorption of HPA as a function of V/m was studied. HPA was shown to be quantitatively adsorbed from the solution up to $V/m = 700 \text{ mL g}^{-1}$. The maximum distribution coefficients for HPA were found to be $D=66 \text{ L g}^{-1}$. The data obtained confirm high affinity of HPA to QAS-SG surface and high effectivity of QAS-SG for recovery of phosphate and silicate in the form of HPA.

It was shown that the intensity of absorbance bands at 670 – 700 nm in the spectra of QAS-SG that were treated with HPA grows with the increasing of phosphate and silicate concentration in the solu-

tion. This phenomenon permits to use the absorbance of QAS-SG with adsorbed HPA as analytical signal for determination of phosphorus and silicon concentration in solution. Moreover the increase of HPA concentration in the solution was accompanied with changing of sorbent colour from white to dark blue that can be used for development of colour scales for visual-test phosphorus and silicon determination at ppb levels [10].

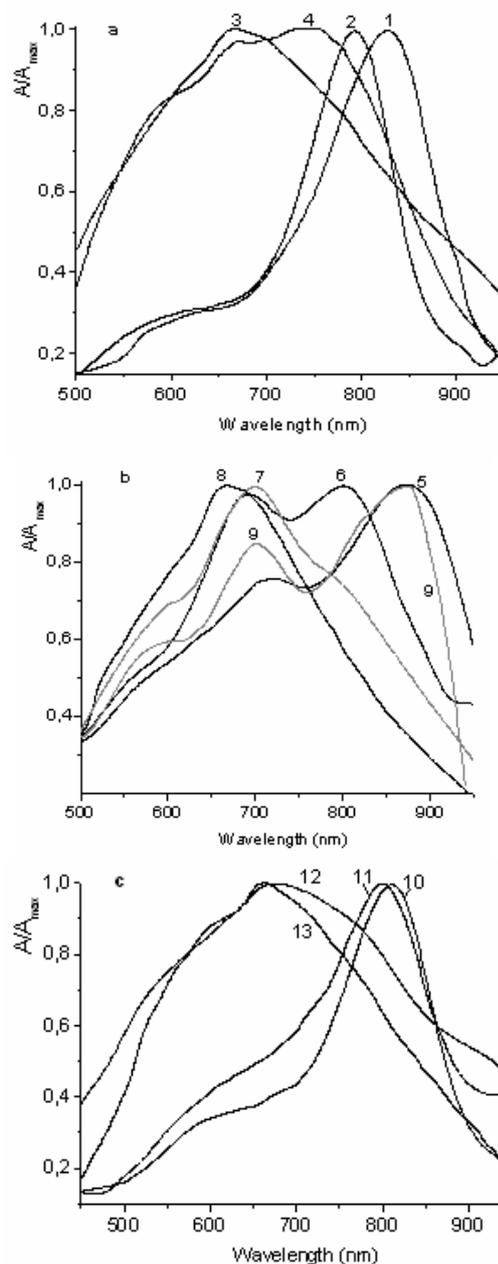


Fig. 2. Standardized absorbance spectra of HPA1 (1-4), HPA2 (5-9), HPA3 (10-13), in aqueous solution (1, 5, 10), isobutyl alcohol extract (2, 6, 11), adsorbed onto QAS-SG (3, 7, 12), impregnated onto SG (4, 8, 13) and chloroform extract of IA "QAS-HPA2" (9). $C(P) = 5.0 \mu\text{mol L}^{-1}$ (1-9), $C(\text{Sb}) = 25 \mu\text{mol L}^{-1}$ (5-9), $C(\text{Si}) = 7.0 \mu\text{mol L}^{-1}$ (10-13), $C(\text{H}_2\text{SO}_4)$, mol L^{-1} : 0.25 (1, 3, 5, 7), 0.40 (10, 12); V/m , mL g^{-1} : 200 (3, 7), 130 (12); $a(\text{QAS}) = 25 \mu\text{mol g}^{-1}$ (3, 7, 12).

It was shown that fixed in the form of IA HPA do not fail the ability for redox interaction. This allows to use immobilized HPA for development of solid-phase reagents for reducing and oxidizing agents determination [18, 19].

Stronger fixing of reduced HPA on the surface of QAS-SG in comparison with the matrixes reported earlier [3, 5, 6], numerous advantages of silica matrix and invariance of redox properties of immobilized HPA allow to propose sorbents developed not only for effective quantitative silicon and

phosphorus determination at ppb levels, but also for reducing and oxidizing agents determination. The increase of intensity of QAS-SG absorbance in direct proportion to phosphate and silicate concentration in the solution and changing of the sorbent colour from white to dark blue permit to use QAS-SG for simple, fast, ecologically safe and cost-effective solid-phase spectrophotometric and visual test determination of phosphate and silicate.

The proposed sorbent is characterized by the strong interaction of HPA with support like the silica prepared *via* covalent grafting of amine groups [8]. However duration, difficulty and complexity of chemical modification procedure should be regarded as its drawbacks. So simplicity, low cost of production along with heavy-duty grafting of HPA makes the worked out sorbent suitable for development of heterogeneous catalysts.

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Kharkov University Bulletin. 2008. № 820. Chemical Series. Issue 16(39). O. A. Запорожец, И. А. Качан, Л. С. Зинько, Ю. П. Бас. Адсорбционная иммобилизация молибдофосфорной, молибдосурьмянофосфорной и молибдкремниевой гетерополикислот на кремнеземе.

Изучена сорбция восстановленных форм молибдофосфорной, молибдотибиевофосфорной и молибдосилициевой гетерополикислот ионообменниками, полученными адсорбционным закреплением на поверхности аморфного кремнезема тетрадециламмония нитрата. Взаимодействие гетерополикислот с иммобилизованной на поверхности четвертичной аммониевой солью изучено методами УФ/Вид и твердофазной спектрофотометрии. Установлено существенное влияние поверхностных групп на хромофорную систему адсорбированных гетерополианионов. Показано, что высокое сродство ГПК к поверхности сорбента является результатом образования ионного ассоциата гетерополианиона с иммобилизованным тетрадециламмонием, а также взаимодействия ГПА с активными группами немодифицированной поверхности кремнезема. *Ключевые слова:* Адсорбция, Силикагель, Четвертичная аммониевая соль, Гетерополикислота, Фосфат, Силикат.