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SORPTION AND ION EXCHANGE PROCESSES

Adsorbent of Noble Metals, Based on Copolymers of Divinyl Sulfide and 4-Vinylpyridine

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Abstract—Radical copolymerization of divinyl sulfide and 4-vinylpyridine was used to synthesize 3D copolymers having in their structure “pyridine” nitrogen atoms and sulfide sulfur. It was found that the copolymers have high sorption capacities reaching for Au(III), Ag(I), Pt(IV) and Pd(II) values of 1200, 340, 1040, and 520 mg g^{-1}, respectively. The results obtained indicate that divinyl sulfide is promising as a cross-linking monomer in syntheses of ion-exchange resins.

Keywords: divinyl sulfide, 4-vinylpyridine, copolymers, sorption capacity, ion-exchange resins

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Ion-exchange resins, or ion exchangers, find wide industrial use for recovery of noble and rare metals. Among 94 brands of resins admitted for application, Russia manufactures only KU-2-8 cation exchanger. The raw-material base for synthesis of resins is permanently shrinking, and, therefore, it is necessary to restore the Russia’s production of main kinds of ion-exchange resins on a renewed technological basis. Divinyl sulfide (DVS) is one of promising monomers for development of ion-exchange resins because the presence of atoms of sulfide sulfur from DVS (“mild” easily polarized basicity and complexation centers) in the skeleton of a polymer matrix will impart to an ion exchanger a highly selective complexation affinity toward rare and noble metals.

DVS is synthesized by the reaction of acetylene with hydrogen sulfide or sodium sulfide [1, 2]. The main advantage of this way to obtain a sulfur-containing monomer is the availability and low cost of the starting substances. DVS has been used to produce a set of ion exchangers with properties substantially surpassing those of the already existing or novel ion-exchange resins [3].

The radical copolymerization of DVS with 4-vinylpyridine (VP) was used to synthesize an ion exchanger containing a “pyridine” atom of nitrogen and sulfide sulfur in the polymer chain, which provides a high sorption activity of the copolymerization products for noble metal ions. In this way, anion exchangers have been produced from VP and technical-grade divinyl benzene with sorption capacity of 7.18 mequiv g^{-1} (0.1 MH Cl); performing a similar reaction with *para*-divinylbenzene can raise the capacity of the ion exchanger to 7.90 mequiv g^{-1} [4]. The method for obtaining divinylbenzene is multistage and occurs to give isomers of the divinyl monomer, whereas the technique used to synthesize DVS is simple and occurs in a single stage from acetylene and potassium sulfide in dimethylsulfoxide with yield of 82%. The main advantage of the DVS–VP sorbents over that of the divinylbenzene–VP type consists in the simplicity of obtaining DVS.

The tendency of noble metal ions toward formation of stable complexes with N- and S-donor ligands [5] is actively used in the development of sorption materials. For example, functional resins containing guanyl thiourea and 2-mercapto-1-methylimidazole exhibited a high selectivity with respect to gold(I) and silver(I) in ammonia solutions. At the same time, these resins did not sorb ammonia complexes of copper(II). The kinetics of gold(I) sorption on these resins was improved via immobilization of ligands of *N,N*-dimethylethanolamine, which are responsible for the increase in the hydrophilicity of the polymeric material. The degree of gold sorption was 99.5% [6].

A set of 18 copolymers of 4-vinylpyridine or 4-methyl-4’-vinylbipyridine with various cross-linking agents were examined as sorbents for Ag(I), Au(III), Pd(II), and Pt(II) ions. These chelate polymers possess a significant sorption selectivity for Au(III) against Ag(I) and for Pd(II) against Pt(II) [7].

A new chelate resin was synthesized from a macroresistant polystyrene–divinylbenzene copolymer including a functional group of β-hydroxydithiocinnamic acid. A study of the adsorption capacity demonstrated that the resin is highly selective for silver(I), mercury(II), gold(III) and platinum(IV) in a strongly acidic aqueous solution [8].

A set of high-efficiency sorbents of noble metals was produced by sol-gel synthesis on the basis of organosilicon N,S-functional monomers. A distinctive feature of polymers of this kind is, together with a remarkable complexing activity, the high chemical and thermal stability [9–11].

On the whole, the N,S-containing ion-exchange and complexing sorbents occupy a leading position in the vast group of polymeric materials suggested for recovery of noble metal ions.

The goal of our study was to obtain copolymers of DVS with 4-VP and examine the adsorption of noble metals by ion exchangers based on the copolymers.

EXPERIMENTAL

Divinyl sulfide was synthesized by the method described in [1]. Immediately before a run, it was purified by distillation.

4-Vinylpyridine is a commercial product from Sigma-Aldrich. It was purified by vacuum distillation at 58°C/5 mmHg, $n_D^{20} = 1.5499$. The purity of the monomers was monitored by chromatography.

Azobisisobutyric dinitrile (AD) is a commercial product from Sigma-Aldrich. The product was preliminary purified by recrystallization from ethanol.

Radical copolymerization of divinyl sulfide and 4-vinylpyridine. The radical copolymerization of DVS and VP was performed by the ampule method in the presence of AD at 60°C. A glass ampule was charged with calculated amounts of DVS, VP, and AD. The reaction mixture was kept in the mass of comonomers in the atmosphere of argon at a temperature of 60°C for 4 h. After the synthesis, the copolymer obtained was successively washed with solvents (benzene, acetone, and water) in Soxhlet apparatus and dried in a vacuum to constant weight. The compositions of the resulting copolymers were calculated from elemental analysis data. The degree of swelling of the DVS–VP copolymer was determined by weighing method.

The specific surface area of the copolymers was determined by the method of low-temperature nitrogen adsorption–desorption [12] on a SORBTOMETR-M instrument. The total pore volume W was calculated by the equation $W = X_{\max}/\rho$, where $X_{\max}$ is the maximum volume of sorbed gas (g g^{-1}), and ρ is the density of the gas (g cm^{-3}).

IR spectra were recorded in KBr and Vaseline oil on an IFS-25 spectrometer. UV spectra were recorded with a Specord UV-VIS instrument.

Standard solutions of noble metal ions with concentration of 10 mg L^{-1} were prepared by dissolution of the following preparations: $H_2PtCl_6 \cdot 6H_2O$ (pure, AURAT OAO), $PdCl_2 \cdot 2H_2O$ (pure, AURAT OAO), $HAuCl_4 \cdot 4H_2O$ (chemically pure, AURAT OAO) in 3 M hydrochloric acid, and $Ag(NO_3) \cdot 4H_2O$ (pure, REAKhIM OOO) dissolved in 3 M nitric acid. The sorption of noble metals from hydrochloric acid solutions of various concentrations was performed under static conditions at a temperature of 25°C. The solutions were agitated in a 6410 M shaking apparatus (300 swings per 1 min). The concentration of noble metal ions in solutions was varied from 10^{-4} to 10^{-2} M. Freshly prepared solutions were used in all cases. The DVS–VP sorbent was used in the static variant without preliminary swelling. The mass of the air-dry sorbent was 0.02 g, and the solution volume, 50 mL. After the sorption was complete, the copolymer was separated from solution by filtering. The content of gold in solutions after the sorption was determined by the atomic-absorption method on an S-115M1 instrument (Ukrrospribor Research and Production Enterprise), and that of palladium and platinum, by the photometric method bsed on the reaction in which their chlorine-tin complexes are formed [13]. The optical density was measured with a KFK-3-1 photoelectric colorimeter.

The efficiency of the extraction of metal ions from solution was evaluated by the degree of recovery *W* (%)

Table 1. Copolymerization of divinyl sulfide with 4-vinylpyridine (AD = 0.5 wt %, 60°C, 6 h)

Run no.	Composition of starting mixture, wt %		Content of nitrogen and sulfur, wt %		Composition of copolymer, mol %		Yield, %
	VP	DVS	N	S	VP	DVS	
1	20.0	80.0	5.01	23.42	32.11	67.89	65
2	40.1	59.9	7.90	16.83	54.36	45.64	75
3	50.0	50.0	8.78	12.67	61.23	38.77	92
4	80.0	20.0	12.11	3.45	88.75	11.25	80

calculated as the ratio of the difference between the initial c_{in} (mg L^{-1}) and final c_{fin} (mg L^{-1}) metal ion concentrations in solution to the initial concentration of metal ions:

$$W = \frac{c_{\text{in}} - c_{\text{fin}}}{c_{\text{in}}} \times 100\%.$$

The static sorption capacity A (mg g^{-1}) was calculated by the formula

$$A = \frac{c_0 - c}{m} V,$$

where c_0 and c are the initial and equilibrium concentrations of metal ions in solution (mg L^{-1}); V, solution volume (L); and m, sorbent mass (g).

In a similar way we studied the sorption of silver ions from nitric acid solutions. The residual concentration of silver in the solutions was determined by the atomic-absorption method on an S-115M1 instrument.

When the sorption of Pt(IV), Pd(II), and Au(III) from sulfuric acid solutions was performed, the starting chloride solutions of noble metals were mixed with aqueous solutions of sulfuric acid having a required concentration. The sorption was performed and the solutions were analyzed as this was done for the hydrochloric acid solutions.

RESULTS AND DISCUSSION

The radical polymerization of DVS with VP was used to obtain insoluble copolymers, which are yellow powders and possess a high mechanical strength and osmotic stability, and are resistant to salts and dilute acids and alkalis (boiling of samples for 6 h in 10% solutions of hydrochloric, sulfuric, and nitric acids and sodium hydroxide does not destruct the skeleton). The copolymers well swell in organic solvents: by 500% in acetone and 300% in hexane. The swelling capacity of the copolymers in an aqueous solution of an acid and alkali is substantially lower, up to 100 and 60%, respectively. By varying the amount of DVS in a copolymer, it is possible to purposefully raise the degree of cross-linking, which leads to a decrease in the degree of swelling, and it becomes possible to use the copolymers in column processes of recovery of noble metal ions. The specific surface area for nitrogen is 2.3 m^2 g^{-1} and the total pore volume of 0.22 cm^3 g^{-1} of the copolymers are comparable with similar parameters for known copolymers with about the same structure [14, 15].

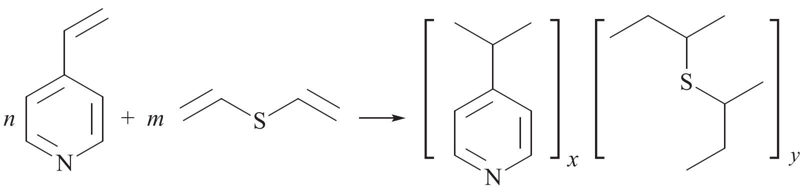
The copolymerization process occurs with high yield at any ratios of the monomer mixture (Table 1). The compositions of the copolymers, calculated from the content of nitrogen and sulfur, are in satisfactory agreement with each other. The number of DVS links in a copolymer decreases as its concentration in the starting mixture is lowered. As the content of DVS in the starting mixture is raised, a decrease in the yield of the target product is observed.

The IR spectra of the copolymers have no absorption bands characteristic of the vinyl group at 960, 1580, and 1640 cm^{-1}, but the absorption bands of the pyridine ring remain unchanged (1600, 1555, 1490, 1068 cm^{-1}). The absorption band at 660 cm^{-1} can be attributed to stretching vibrations of the C–S bond.

The formation of the insoluble product and the IR spectroscopic data indicate that the copolymerization of DVS with VP occurs with opening of two double bonds in DVS, which yields a copolymer with network structure (see the scheme).

Preliminary experiments demonstrated that the DVS-VP copolymer containing 8.78% nitrogen and 12.67%

Scheme.



sulfur (Table 1, run no. 3) possesses a high sorption activity. Therefore the sorption properties were studied in detail for this copolymer sample.

The adsorption of silver ions by this DVS-VP copolymer was examined in nitric acid solutions in which the metal is present as the Ag^+ cation. The recovery of Pt, Pd, and Au ions was examined in hydrochloric and sulfuric acid solutions in which these metals exist in the form of acid complexes of various compositions [5, 16–18].

For Pt, Pd, and Au acid complexes, the degree of extraction of metal ions somewhat decreases with increasing acid concentration, with the exception of a tetrachloride complex of gold in a sulfuric acid medium (Fig. 1). The decrease in the degree of extraction of metal ions is manifested to a greater extent for chloro complexes of platinum and gold in a hydrochloric acid solution (Fig. 1). This run of the dependence serves as evidence in favor of the anion exchange at the pyridine nitrogen atom and manifestation of the competing effect of acid anions with consideration for their size and mobility. It is also possible that there occurs a coordination interaction of metal ions with nitrogen and sulfur atoms, which is characteristic to a greater extent of the cationic form of silver.

The sorption equilibrium is attained in extraction of metals from 1 M solutions of acids in 60 min for the silver cation at a half-sorption time $\tau_{1/2}$ = 15 min; for anionic

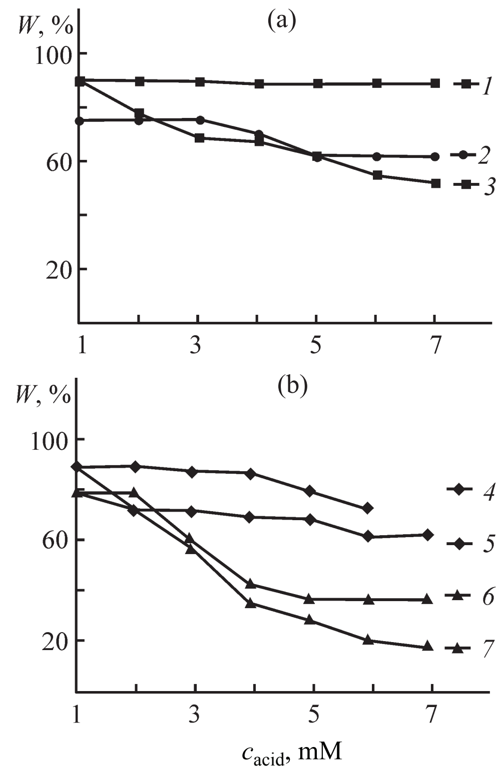


Fig. 1. Effect of the nature and concentration of acids on the degree of extraction of Au(III) in (*1*) H_2SO_4 and (*3*) HCl, (*2*) Ag(I) in HNO_3, Pd(II) in (*4*) H_2SO_4 and (*5*) HCl, and Pt(IV) in (*6*) H_2SO_4 and (*7*) HCl.

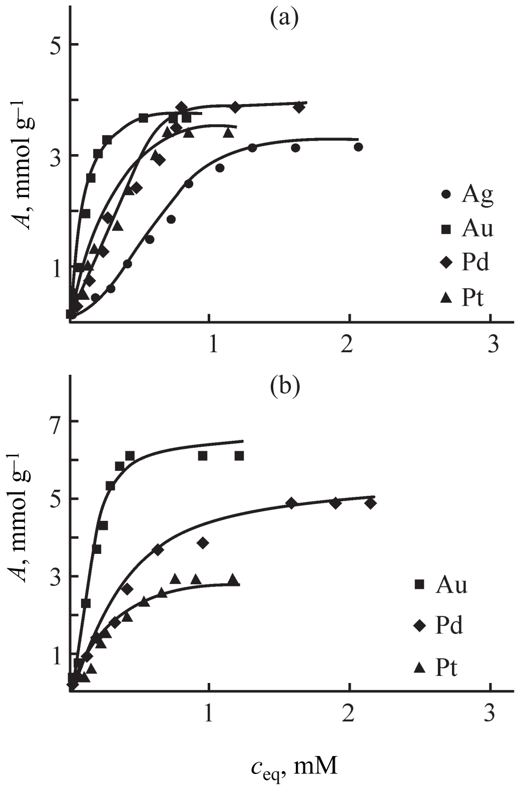


Fig. 2. Adsorption isotherms of (a) Ag ions in 1 M HNO_3 and Au, Pt, Pd in (a) 1 M HCl and (b) 1 M H_2SO_4 (m_{sorb} = 10 mg, V = 20 mL, t = 2 h).

Table 2. Static sorption capacity A in 1 M acid solutions

Metal	A, mg g^{-1}/mmol g^{-1}	
	HCl	H_2SO_4
Pt	670/3.44	570/2.92
Pd	410/3.88	520/4.91
Au	730/3.71	1200/6.09
Ag	330/3.06 (HNO_3)	

complexes of Pt and Pd, $\tau_{1/2}$ = 30 min, and for chloro complexes of Au, $\tau_{1/2}$ = 5–10 min.

The adsorption isotherms in 1 M acid solutions (Fig. 2) characterize the distribution of metal ions in the liquid and solid phases in the equilibrium state and make it possible to calculate the sorption capacity (Table 2).

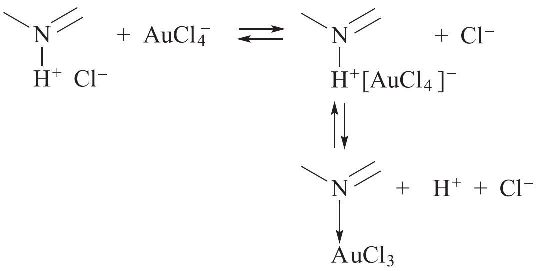
On the whole, the DVS-VP copolymers have high static sorption capacities reaching for Au(III), Ag(I), Pt(IV), and Pd(II) values of 1200, 340, 1040, and 520 mg g^{-1}, respectively.

The high sorption activity of the copolymers under consideration (Table 2) is determined by the rather high content of nitrogen and sulfur atoms in the copolymer composition (Table 1, run no. 3). The specific contents of nitrogen and sulfur in the copolymer were used to calculate the theoretical values of the total sorption capacity for noble metals on the assumption that noble metal ions interact with nitrogen and sulfur atoms in a 1 : 1 ratio (Table 3). Comparison of the experimental (Table 2) and theoretically accessible values (Table 3) of the sorption capacity of the DVS–VP copolymer for noble metal ions shows a large degree of filling of chemically active centers on the adsorbent surface.

The results obtained indicate that the DVS and 4-VP copolymers under study compare well in the efficiency of sorption recovery of noble metals with the known complexing and ion-exchange sorbents containing similar chemically active groups, including heterocyclic amines [19–21].

To elucidate the sorption-interaction mechanism, we examined IR spectra of the starting copolymers and those treated with mineral acids and concentrates of these after the sorption. A broad absorption band at 2600–3000 cm^{-1}, characteristic of the ammonium cation, appears in the IR spectrum of the copolymer treated with 1 M hydrochloric acid. The shift of the absorption band from 1600 to 1630 cm^{-1} also shows that a protonated nitrogen atom is formed in the pyridine fragment of the copolymer. The same changes are also preserved in the IR spectra of the copolymer saturated with noble metal ions. The data obtained suggest that, for acid complexes of Pt, Pd, and Au, the sorption occurs via an ion exchange followed by displacement of ligands from the inner sphere of a metal chloro complex.

By analogy with published data on recovery of ions of transition metals, including noble metals, by sorbents with similar functional groups [22–25], we can assume that, first, an anion exchange occurs in sorption of metals from solution, followed by coordination. Thus, the interaction at the nitrogen atom can be represented by the following scheme: for the protonated form of the compound, the sorption initially occurs by the ionic mechanism, and then the chloride ion is displaced from the first coordination sphere of the metal:



The sorption on the unprotonated form occurs only via substitution of chloride ions by the ligand groups of the complex:

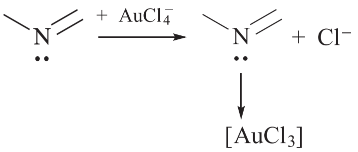


Table 3. Theoretical values of the total sorption capacity of DVS–VP copolymer

Specific content, mmol g^{-1}		Total sorption capacity, mg g^{-1}							
		calculated from the specific content of nitrogen in the sorbent				calculated from the specific content of sulfur in the sorbent			
N	S	Ag(I)	Au(III)	Pt(IV)	Pd(II)	Ag(I)	Au(III)	Pt(IV)	Pd(II)
6.27	3.96	677	1236	1223	665	428	780	772	420

The shift of the absorption band of the DVS fragment in the polymeric matrix from 600 to 700 cm^{-1} indicates that sulfur atoms of the copolymer are involved in metal sorption processes.

It was found that, under the conditions in which noble metals are sorbed from 1 M acid solutions, iron, cobalt, nickel, and zinc are not sorbed. At its initial concentration of 1 mg mL^{-1}, 18% of copper is extracted.

CONCLUSIONS

(1) The radical copolymerization of divinyl sulfide with 4-vinylpyridine in the presence of azobisbutyric dinitrile was used to obtain in up to 92% yield network polymers having a specific surface area for nitrogen of 2.3 m^2 g^{-1} and total pore volume of 0.22 cm^3 g^{-1}.

(2) The divinyl sulfide–4-vinylpyridine copolymers have high static sorption capacities, which reach for Au(III), Ag(I), Pt(IV), and Pd(II) values of 1200, 340,1040, and 520 mg g^{-1}, respectively.

(3) The interaction of noble metal ions with the adsorbent surface is due to the formation of ion-coordinated complexes by chemically active groups of the copolymer with nitrogen and sulfur atoms.

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