

## Homopolymer of N,N'-bis(vinyloxyethyl)thiuramdisulphide as a Selective Sorbent of the Ions of Mercury and Precious Metals

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### Abstract

A homopolymer of N,N'-bis(vinyloxyethyl)thiuramdisulphide was synthesized *via* cationic polymerization and investigated as a sorbent of the ions of mercury and precious metals. The effect of the nature and concentration of acid, phase contact time on the extraction of metals was revealed; sorption capacities of the polymer and metal partition coefficients were estimated. It was shown that the sorbent exhibits high sorption activity to metal ions in the cationic form: with respect to mercury ( $\text{Hg}^{2+}$ ) from 1 M  $\text{HNO}_3$  solution – 1100 mg/g, 1M  $\text{H}_2\text{SO}_4$  – 990 mg/g, 1 M  $\text{HCl}$  – 280 mg/g; with respect to silver ( $\text{Ag}^+$ ) from 1 M  $\text{HNO}_3$  – 850 mg/g, from 1 M  $\text{H}_2\text{SO}_4$  – 900 mg/g. A mechanism of the interaction of active groups of the sorbent with metal ions was proposed on the basis of IR spectroscopic data. The homopolymer of N,N'-bis(vinyloxyethyl)thiuramdisulphide sorbs mercury and silver ions selectively from a mixture of copper, nickel, iron and zinc salts. The possibility to use the sorbent for concentrating precious metals and for analytical purposes was demonstrated. A method of sorbent regeneration was developed.

### INTRODUCTION

Environmental protection makes provision for the development and mastering of the methods of analytical control of the content of toxic elements, in particular mercury. High mercury content in the objects of the environment is due to the industrial activities. An increased interest to the problem of mercury determination is caused by its highest toxicity in comparison with other heavy metals, its ability to migration and bioconcentrating [1, 2]. A broad range of the concentrations of heavy metals and mercury in the objects of the environment requires determination of small amounts of these elements in food, water, air and biological objects, their extraction and concentrating as the necessary stage. One of widely spread up-to-date methods is sorption concentrating, which

is distinguished by simplicity, rapidity, the possibility of combination with various methods of metal determination in the concentrate (X-ray fluorescence, atomic absorption, spectrophotometry, *etc.*) thus increasing the sensitivity of these methods by several orders of magnitude [3, 4]. The application of polymer sorbents for concentrating allows one to eliminate or to decrease substantially the effect of the matrix and to extract the elements from aggressive media of rather complicated composition. The data obtained by us [5, 6] indicate that the new polymer nitrogen- and sulphur-containing sorbents possess high sorption capacity toward silver and mercury cations. For example, a ternary copolymer of 2-vinyloxyethylisothiocyanate, maleic anhydride and styrene with the molar fraction of 2-vinyloxyethylisothiocyanate 15.2 % is characterized by the following sorption

capacities and metal ion partition coefficients: with respect to mercury, from 1 M HNO<sub>3</sub> solution - 790 mg/g ( $D = 5 \cdot 10^4$ ), 1 M H<sub>2</sub>SO<sub>4</sub> - 740 mg/g ( $D = 1 \cdot 10^5$ ), 1 M HCl - 290 mg/g ( $D = 4.7 \cdot 10^3$ ); with respect to silver, from 1 M HNO<sub>3</sub> solution - 290 mg/g ( $D = 5.7 \cdot 10^3$ ), 1 M H<sub>2</sub>SO<sub>4</sub> - 390 mg/g ( $D = 2.9 \cdot 10^4$ ).

In order to improve sorption characteristics and selectivity, we propose a new sorbent of multiple use: homopolymer with dithiocarbamate groups. It is known [7] that dithiocarbamate groups exhibit activity in the formation of complexes with metals.

A polymer was obtained on the basis of N,N'-bis(vinyloxyethyl)thiurame disulphide and investigated as a sorbent of gold, silver, mercury, platinum and palladium.

## EXPERIMENTAL

The reaction of homopolymer formation was carried out under the conditions of cation polymerization. The solution containing 0.004 g of a mixture of SnCl<sub>4</sub> and FeCl<sub>3</sub> at a ratio of 3 : 1 in 1 ml of CCl<sub>4</sub> was added under mixing to 4 g of N,N'-bis(vinyloxyethyl)thiurame disulphide in 20 ml of CCl<sub>4</sub>. Reaction time was 30 min. The resulting powder polymer was washed with dimethyl ether and chloroform, and dried in vacuum. The yield was 98 %. According to the data of elemental analysis, the homopolymer contained (mass %): 36.52 C, 4.90 H, 8.56 N and 38.92 S. Molecular mass determined by isopyestic method was 5000-6700 (with azobenzene as a reference). The polymer is a yellow powder which is stable during lengthy storage, insoluble in 1-7 M solutions of acids, alkalis, and in organic solvents.

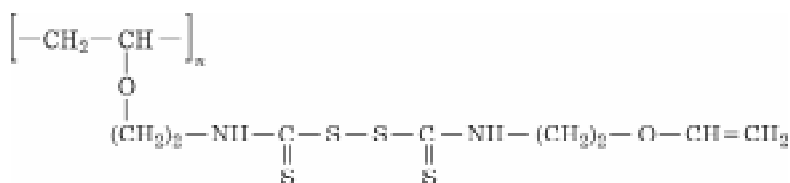
The spectra were recorded with IFS-25 instrument in KBr tablets.

Investigation of sorption properties of the homopolymer was carried out under static con-

ditions at room temperature. The solid phase was separated by filtering; the residual concentrations of gold, silver and palladium in the solution were determined by means of atomic absorption, mercury by extraction photometry with Dithizone, platinum by photometry with tin (II) chloride [8, 9]. The sorption characteristics of the homopolymer with respect to silver were investigated using nitric and sulphuric solutions, gold, platinum and palladium from hydrochloric and sulphuric solutions, and mercury from the solutions of hydrochloric, sulphuric and nitric acids.

## RESULTS AND DISCUSSION

In order to confirm the structure of the obtained homopolymer, we carried out a comparative analysis of the spectral characteristics of the monomer and the homopolymer. In comparison with the IR spectrum of the monomer, the polymer exhibits a sharp decrease in the relative intensities of the bands at 1632, 1340, 1389 cm<sup>-1</sup> relating to the vinyloxy group. This is the evidence of a substantial decrease in the relative content of vinyloxy groups. The appearance of an intensive band at 1058 cm<sup>-1</sup> assigned to the stretching vibrations of the C-O-C fragment with saturated carbon atoms confirms the formation of polymer chains. These changes in spectral characteristics occur as a consequence of polymerization with the participation of vinyloxy groups. At the same time, the bands at 1518, 935, 645 and 555 cm<sup>-1</sup> attributed to the vibrations of (N)C=S, C-S- and S-S bonds and deformations of the H-N-C angle, though somewhat change their position, but remain rather intensive, which is the evidence of the conservation of (-HN-C(S)-S-) grouping and of some change in the formed hydrogen bonds. This is confirmed by the inverse relation between the intensities of the bands at 3292,



Scheme 1.

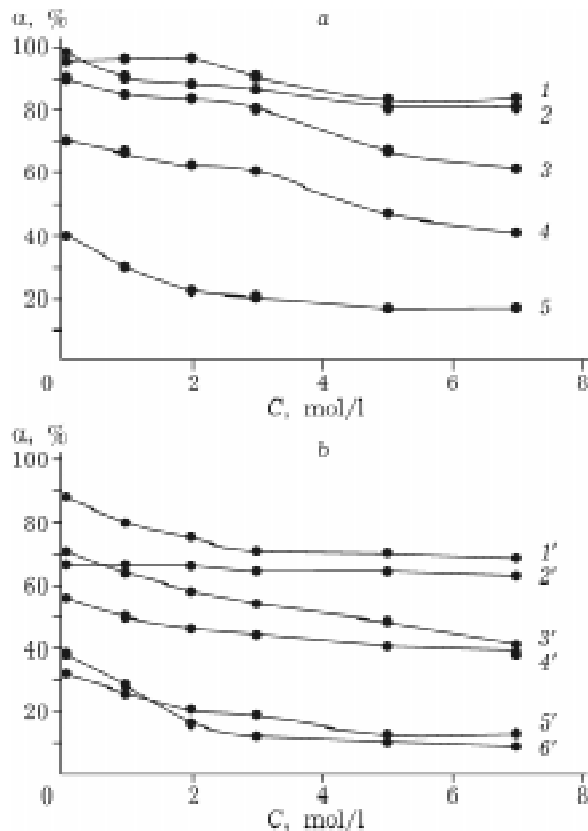


Fig. 1. Influence of the nature and concentration of an acid on the extraction degree  $\alpha$  of the ions of silver (1, 2), mercury (3-5), palladium (1', 2'), gold (3', 4'), platinum (5', 6') from the solutions of  $\text{H}_2\text{SO}_4$  (1, 3, 1', 3', 5'),  $\text{HNO}_3$  (2, 4),  $\text{HCl}$  (5, 2', 4', 6').  $m_{\text{sorb}} = 10$  mg, sorption time: 2 h;  $V_{\text{sol}} = 20$  ml;  $m_{\text{Au}} = 1.28$  mg,  $m_{\text{Ag}} = 7.0$  mg,  $m_{\text{Hg}} = 8.8$  mg,  $m_{\text{Pt}} = 0.94$  mg,  $m_{\text{Pd}} = 1.12$  mg.

3268, 3226  $\text{cm}^{-1}$  and the appearance of an intensive band at 3442  $\text{cm}^{-1}$  which relates to the vibrations of the free N-H bonds.

A substantial decrease in the relative content of vinyloxy group revealed by the IR spectrum of the polymer gives us grounds to assume that the polymer has a cross-linked structure and polymerization proceeds simultaneously with two vinyloxy groups, which is confirmed by the insolubility of the polymer. At the same time, inclusion of the links with

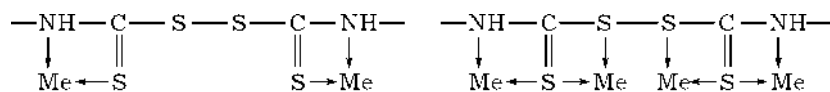
suspended vinyloxy groups into the cross-linked polymer is possible (Scheme 1).

It was shown in the investigation of the dependence of metal extraction degree on concentrations and nature of acids that its decrease is observed for all the metals with an increase in the acidity of solution from 1 to 7 mol/l (Fig. 1, a, b). The character of the dependence is explained by the form in which the metals are present in solution (anion, cation) and by sorption mechanism.

In order to reveal the mechanism by which the sorbent interacts with metal ions, we studied the IR spectra of the sorbent samples treated with acids and the samples after metal sorption (concentrate). The comparison reveals changes. For instance, the band of stretching vibrations of the N-H bond shifts from 3289 to 3268  $\text{cm}^{-1}$ , while the band at 1600  $\text{cm}^{-1}$  corresponding to the bending vibrations of this bond disappears. In addition, the relations between the intensities of bands at 1206 and 1175  $\text{cm}^{-1}$ , 949 and 921  $\text{cm}^{-1}$ , 608 and 538  $\text{cm}^{-1}$  change; the band at 1186  $\text{cm}^{-1}$  shifts to 1175  $\text{cm}^{-1}$ ; the band at 1067 disappears. These data provide evidence of the participation of dithiocarbamate group (NHC(S)S) in the formation of complex with a metal, and provide that metal is coordinated both to the nitrogen atom and to the sulphur atom, because these bands relate to the vibrations of NH, (N)C=S, CS and SS bonds.

Taking into account high sorption capacity of the polymer with respect to silver and mercury, we may assume 2 types of coordination centres (Scheme 2).

For nitrogen- and sulphur-containing sorbents, the ion exchange mechanism over nitrogen atoms is possible, while the coordination mechanism is possible over the nitrogen and sulphur atoms [7]. For mercury and silver, which are sorbed from nitric and sulphuric so-



where Me is metal.

TABLE 1

Sorption capacity (SC) of the polymer and metal partitioning coefficients  $D$  in the solutions of acids with a concentration of 1 mol/l

| Metal form                         | SC, mg/g ( $D$ )           |                                |                             |
|------------------------------------|----------------------------|--------------------------------|-----------------------------|
|                                    | HCl                        | H <sub>2</sub> SO <sub>4</sub> | HNO <sub>3</sub>            |
| Hg <sup>2+</sup>                   | 280 (6.8 10 <sup>2</sup> ) | 990 (1.3 10 <sup>4</sup> )     | 1100 (2.4 10 <sup>4</sup> ) |
| Ag <sup>+</sup>                    | –                          | 900 (4.0 10 <sup>5</sup> )     | 850 (3.0 10 <sup>5</sup> )  |
| [AuCl <sub>4</sub> ] <sup>–</sup>  | 208 (1.9 10 <sup>3</sup> ) | 252 (3.2 10 <sup>3</sup> )     | –                           |
| [PtCl <sub>6</sub> ] <sup>2–</sup> | 58 (4.2 10 <sup>3</sup> )  | 534 (1.9 10 <sup>3</sup> )     | –                           |
| [PdCl <sub>4</sub> ] <sup>2–</sup> | 89 (7.6 10 <sup>4</sup> )  | 110 (1.5 10 <sup>5</sup> )     | –                           |

lutions mainly in the cationic form, the coordination interaction over nitrogen and sulphur atoms should be considered as predominant. A decrease in sorption extent with an increase in the acidity of solutions can be connected with changes in the strength (stability) of the formed complexes. A substantial decrease in the sorption capacity of the homopolymer in hydrochloric solutions (see Fig. 1, *a*, *b*) with respect to mercury is due to the formation of chloride complexes. For the anion chloride complexes of gold, platinum and palladium, the analysis of the character of curves allows considering the donor-acceptor interaction over the active atoms as predominant. For acid complexes of gold and platinum metals, the coordination according to the second type is not very probable due to the steric factor (the ion size).

The investigation of the dependence of ion metal extraction degree on the time of contact between phases (Fig. 2) showed that the establishment of the sorption equilibrium occurs at a high rate: within 10–15 min for the cationic

form of metals and within 30–60 min for the anionic ones.

We investigated the dependence of extraction degree of metal ions on their concentration in solution under the conditions of sorption equilibrium. The sorption capacity under static conditions and metal partitioning coefficients were calculated using the obtained data (Table 1).

The values of sorption capacity of the polymer and the partitioning coefficients for mercury and silver ions provide evidence of the efficiency of the sorbent; this allows using it to extract metal ions in case of their low concentrations.

The ability of hydrochloric acid to form chloride complexes was used to elutriate mercury from the sorbent phase. The solutions of 7, 9 and 12 M HNO<sub>3</sub> were tested as elutriators. The experiment was carried out according to the following procedure. A weighed portion of the sorbent with a mass of 50 mg was brought into the solution in which mercury was present in the concentration of 0.25 mg/ml of 1 M H<sub>2</sub>SO<sub>4</sub> or HNO<sub>3</sub> solution. The concentrate was treated with 10 ml of hydrochloric acid of the indicated concentrations for 30 min, the solid phase was separated and analyzed for the mercury content of the solution by means of the extraction photometry. Mercury is elutriated by 95–98 %, but we observe a decrease in the sorption activity for the sorbent regenerated with the concentrated hydrochloric acid. It was established that, under the conditions of extracting the listed metals, copper, cobalt, nickel, iron and zinc are not extracted.

We studied the possibility to extract mercury in the presence of nonferrous metals. A weighed portion of the sorbent was placed in

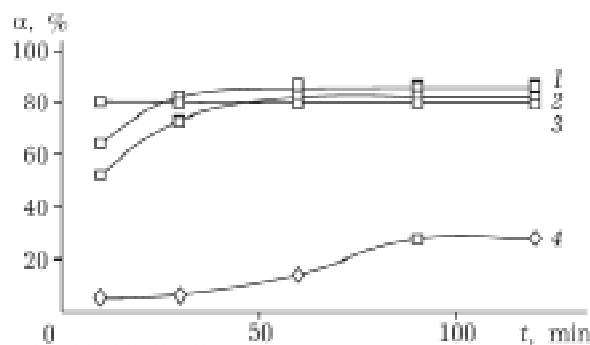


Fig. 2. Dependence of sorption on the time of contact between phases in the solution of 1 M H<sub>2</sub>SO<sub>4</sub> for the ions of silver (1), palladium (2), mercury (3), platinum (4).

100 ml of the solution of 1 M HNO<sub>3</sub> containing 25 mg of mercury and a 10<sup>3</sup>–10<sup>4</sup>-fold excess of the metals. Sorption was carried out for 30 min; after that, the experiment was performed according to the above-described procedure. This procedure allows determining 90–95 % of the amount of mercury taken into the experiment.

For silver determination with preliminary sorption, the concentrate was incinerated at 450–500 °C, the residue was transferred into the nitric solution, which was analyzed by means of atomic absorption. The determined amount of silver accounts for 90–95 % of the initially taken amount.

## CONCLUSION

A homopolymer of N,N'-bis(vinyloxyethyl)-thiurame disulphide containing active complex-forming dithiocarbamate groups in the unit link was obtained by the cation polymerization.

The formation of the cross-linked polymer was confirmed by means of the IR spectroscopy. It was proved that complex formation is participated by the dithiocarbamate group [NHC(S)S], and metal coordination occurs through the nitrogen and sulphur atoms.

The sorption capacity and metal partitioning coefficients were determined in the solutions of acids with a concentration of 1 mol/l. The sorbent exhibits high sorption activity to the metal ions in the cation form: for mercury,

from 1 M HNO<sub>3</sub> solution – 1100 mg/g ( $D = 2.4 \cdot 10^4$ ), 1 M H<sub>2</sub>SO<sub>4</sub> – 990 mg/g ( $D = 1.3 \cdot 10^4$ ); for silver, from 1 M HNO<sub>3</sub> – 850 mg/g ( $D = 3.0 \cdot 10^5$ ), 1 M H<sub>2</sub>SO<sub>4</sub> – 900 mg/g ( $D = 4.0 \cdot 10^5$ ).

The polymer sorbs the ions of mercury and precious metals selectively from the acidic solutions with the acid concentration of 1 mol/l at the background of substantial (10<sup>3</sup>-fold) excess of copper, nickel, iron and zinc. A method of the regeneration of the sorbent was developed. It involves the treatment of the sorbent with thiocarbamide solution. This is accompanied by the desorption of silver from the sorbent phase by 90–95 %.

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