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Synthesis of Polymers Based on Polyvinyl Alcohol Glycidyl Ether of Ethylene Glycol and Amines as Possible Sorbents for Mercury and Uranium Salts

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Abstract

Cross-linked copolymers were obtained by modifying polyvinylglycidylic ether of ethylene glycol with ammonia and ethylenediamine. The sorption capacity of these copolymers and the coefficients of metal distribution for of $Hg(NO_3)_2$ and UO_2Cl_2 aqueous solutions were determined.

Key words: polyvinyl alcohol glycidyl ether of ethylene glycol, modification, ammonia, ethylene diamine, sorbents, mercury nitrate (II), uranyl chloride

INTRODUCTION

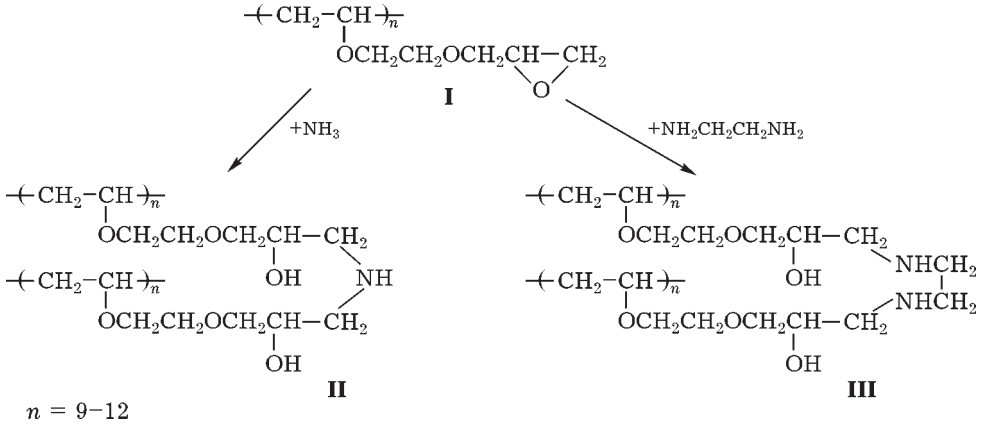
Among such waste water pollutants as heavy metals, mercury and uranium salts are considered most hazardous. This is connected with the known mercury ability of migration and bioconcentration [1, 2] as well as with uranium radio activity [3].

Currently, a sorption technique is used as a rule for waste water treatment. At the same time, various nitrogen-containing polymers are widely used as sorbents [4–8].

With the purpose of developing novel sorbent types, we obtained cross-linked, water-swelling polymers **II**, **III** based on the polyvinyl alcohol glycidyl ether of ethylene glycol, ammonia and ethylene diamine (Scheme 1).

The presence of the hydroxyl in the molecule in β-position with respect to the amino group provides the formation of chelate complexes with metal cations.

Taking into account this fact, we studied the sorption properties of polymers **II**, **III** with respect to $Hg(NO_3)_2$ and UO_2Cl_2.



Scheme 1.

EXPERIMENTAL

Polymer I. The initial polyvinyl alcohol glycidyl ether of ethylene glycol **I** was obtained according to the procedure described in [9], *via* the polymerization of ethylene glycol vinyl glycidyl ether in the presence azobisisobutyric acid dinitrile.

Polymer II. To 120 mL of a 15 % aqueous ammonia solution (0.1 mol) was added 14.4 g (0.1 mol) of ethylene glycol polyvinyl alcohol glycidyl ether **I**, under stirring. The reaction time was equal to 30 min. A solid polymer formed was washed with water to obtain rinsing water pH 7.3 and dried then under vacuum (5 mmHg) at 80 °C, up to constant mass. The yield of polymer **II** was equal to 14.6 g (96 %). According to elemental analysis, the polymer exhibited the following composition (mass %): C 55.26, H 9.21, N 4.66. For $C_{14}H_{24}N_2O_6$, it was calculated (mass %): C 55.07, H 8.91, N 4.59. IR (ν, cm^{-1}): 3405, 3292, 2925, 2910, 2885, 2830, 1445, 1430, 1325, 1300, 1270, 1215, 1105, 1055, 960, 855, 840.

Polymer III. In a similar manner as it was done for the above mentioned synthesis, from 24 g of a 25 % aqueous solution of ethylene diamine (0.1 mol) and 14.4 g (0.1 mol) ethylene glycol polyvinyl alcohol glycidyl ether **I** we obtained 16.8 g (97 %) of polymer **III**. According to the elemental analysis data, the polymer **III** exhibited the following composition (mass %): C 53.96, H 9.03, N 8.81. For $C_{16}H_{32}N_2O_6$ it was calculated (mass %): C 55.15, H 9.26, N 8.04. IR spectrum (ν, cm^{-1}): 3430, 3285, 2921, 2869, 1462, 1357, 1324, 1295, 1235, 1203, 1130, 1095, 977, 876, 842.

The polymers represented yellow powders, insoluble in water, ethyl alcohol, acetone, benzene, dimethylformamide and dimethylsulphoxide.

The spectra were registered on a Bruker Vertex-70 spectrometer using tablets with KBr.

In the course of studying the sorption properties of polymers **II**, **III**, the determination of mercury was performed using atomic absorption method by means of Leco AMA-254 spectrometer, uranium was determined using fluorometric technique by means of a Fluorat 02-2M fluorometer (Lumex Co., St. Petersburg).

The initial concentration of mercury nitrate solution was equal to 4.9 mg/L that of uranyl chloride was equal to 4.0 mg/L. The mass of the sorbent in the case of the absorption of mercury was equal to 0.2 g, that in the case of uranyl chloride was equal to 0.1 g, the volume of the salt solution amounted to 100 mL, the contact time (under stirring) was equal to 2 days.

RESULTS AND DISCUSSION

In the course of synthesizing the polymers, in the reaction mixture we introduced 1 mol of amine per one elementary unit of ethylene glycol polyvinyl alcohol glycidyl ether **I**. However, according to the elemental analysis, the resulting polymers **II** and **III** contain about 0.5 mol of amine per an elementary unit of polyether **I**.

The IR spectrum of the polymer as compared with the original spectrum of the ethylene glycol polyvinyl alcohol glycidyl ether **I** dem-

TABLE 1

Sorption capacity values for polymers **II**, **III** and metal distribution coefficients (D)

Sorbents	Sorbed salt	Salt concentration in the equilibrium solution (c_1), mg/L	Equilibrium salt content in the sorbent (c_2), mg/g	$D = c_2/c_1$, mL/g
Polymer **II**	$Hg(NO_3)_2$	0.64	2.130	3328
Polymer **III**	$Hg(NO_3)_2$	1.58	1.66	1051
Polymer **II**	UO_2Cl_2	3.5	0.500	143
Polymer **III**	UO_2Cl_2	2.5	1.500	600
Activated charcoal AVZ-HT-3.0	$Hg(NO_3)_2$	0.09	0.007	77.8
The same	UO_2Cl_2	0.07	0.002	28.6

onstrates the absence of absorption bands at 3065, 1255, 910 cm^{-1} related to the epoxy group, whereas there are bands at 3430, 3405, 3292, 3285 cm^{-1} appeared, which indicates a complete disclosure of the epoxide cycle to form the hydroxyl and amino groups.

Polymers **II**, **III** were tested as the sorbents in the model solutions of mercury nitrate and uranyl chloride. For comparison, under the same conditions we investigated activated charcoal (AVZ-HT 3.0) widely used in practice. The results of the tests (Table 1) demonstrate that the polymers **II**, **III** obtained provide a good extraction level (the distribution coefficients for mercury and uranium are equal to 3328 and 600 mL/g, respectively) and are better than the results in the case of activated charcoal.

CONCLUSION

Using the reaction between ethylene glycol polyvinyl alcohol glycidyl ether with ammonia and ethylenediamine we obtained crosslinked polymers containing hydroxyl and amino groups those are active with respect to complexation.

It was established that the polymers obtained contain 1 mol of amine falling at two elementary units of the ethylene glycol polyvinyl alcohol glycidyl ether.

The sorption capacity and distribution coefficients for mercury nitrate and uranyl chloride were determined.

It was demonstrated with respect to these parameters the polymers obtained are significantly better than activated carbon AVZ-NT 3.0.

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