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Corresponding Member of the Academy of Sciences of the USSR
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Abstract

Full Text

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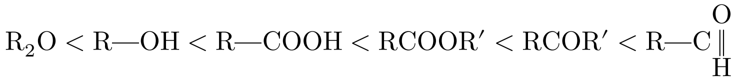
COMPLEXES OF POLYACROLEIN WITH SALTS OF HEAVY METALS

Simple and complex ethers, ketones, and diketones form fairly stable complexes with salts of certain heavy metals (^{1}). This ability may be compared with the tendency of oxygen-containing organic molecules to form oxonium compounds. In the series



$$R_2O < R{-}OH < R{-}COOH < RCOOR' < RCOR' < R{-}\underset{H}{\overset{O}{C\|}}$$

the ability to form oxonium salts increases from left to right (^{2}, ^{3}). Such compounds as diethyl ether, thenoyltrifluoroacetone, methyl isobutyl ketone, acetylacetone, dibenzoylmethane, and others are used in the practice of the extraction separation of uranium from solutions (^{1}). For complexes of uranyl nitrate it is very characteristic that one molecule of inorganic salt contains two molecules of addend. There are indications (^{4}, ^{5}) that the ability to form coordination complexes of uranyl nitrate and the associated solubility in organic oxygen-containing solvents decrease as the ratio in the organic molecule increases: number of C atoms/number of O atoms. The mechanism of extraction separation of salts of heavy metals by low-molecular organic substances is discussed by Kuznetsov (^{6}) and Vdovenko (^{1}).

Fig. 1. Dependence of the amount of uranium extracted (in 10^{-6} g/g) on the concentration of the initial solution; curve numbers correspond to sample numbers in Table 1.

There are no indications in the literature of the ability of high-molecular-weight synthetic oxygen-containing products to form coordination complexes with salts of heavy metals. We found that samples of powdered polyacrolein obtained under different conditions possess a substantially differing ability to form coordination complexes with salts of heavy metals. Of the many salts investigated, uranyl nitrate has the most pronounced ability for reactions of this kind. Within the pH range studied, salts of lead, cobalt, manganese, copper, nickel, and iron do not give stable complexes.

Information on the methods of preparation and on certain properties of the polyacrolein samples studied by us is given in Table 1. Figure 1 presents data on the extraction of uranyl nitrate from aqueous solutions under static conditions, and Figure 2 presents the dependence of extraction on the uranium concentration in the initial solution. The dependence of the apparent distribution coefficient of uranium between the organic and aqueous phases on the salt concentration is presented in Table 2.

Table 1

Methods of preparation and certain properties of polyacrolein samples

Sample No.	Methods of preparation	Content of aldehyde groups by the oximation method, mol. %	Amount of extracted uranium (in 10^{-6} g/g)
1	In aqueous solution, in the presence of $K_2S_2O_8 + AgNO_3$	74	2305
2	The same, in the presence of $K_2S_2O_8 + (NH_4)_2Fe(SO_4)_2$	65	1450
3	The same, in the presence of $K_2S_2O_8 + Na_2S_2O_3$	30	1000
4	Diacryl	60	1400
7	Spontaneous polymerization in an ampoule in the presence of hydroquinone	5–7	1000

Sample No.	Methods of preparation	Content of aldehyde groups by the oximation method, mol. %	Amount of extracted uranium (in 10^{-6} g/g)
8	Bulk polymerization in the presence of BF_3 at a temperature from 0° to −20°	No	250
9	The same, with BF_3, in the presence of traces of water at −20°	No	450
10	In a methylene chloride solution in the presence of BF_3 at −20°	No	500
11	In benzene solution, in the presence of metallic sodium	22	2000
12	Bulk polymerization in the presence of butyllithium at room temperature	9	560

Table 2

Dependence of the distribution coefficient $(K \cdot 10^{-5})$ *on the concentration of uranium in solution*

Fig. 2. Dependence of the percentage of uranium extraction on the concentration of the initial solution

Figure 2: Fig. 2. Dependence of the percentage of uranium extraction on the concentration of the initial solution

Uranium concentration, mg/ml	No. 1	No. 2	No. 3	No. 4	No. 7	No. 8	No. 9	No. 10	No. 11	No. 12
0.001	4803	4712	2564	1253	2564	0	0	0	2040	250
0.005	4803	4712	551	2459	–	502	503	–	2564	122
0.01	4393	4167	503	2145	2564	502	756	1010	2564	256
0.05	3950	1936	806	1010	1265	2506	908	1010	2060	1010
0.10	1942	1213	1010	1419	1010	1506	2506	2506	1522	–

Polyacrolein has the most favorable ratio of the number of carbon atoms to the number of oxygen atoms for the formation of coordination complexes.

The greatest capacity for extracting uranium from aqueous solutions is possessed by polyacrolein samples obtained by polymerizing acrolein in aqueous solutions under the action of the oxidation-reduction system of potassium persulfate and silver nitrate, as well as potassium persulfate and Mohr' s salt. The uranyl nitrate is extracted to a lesser extent by the disacryl sample, as well as by polyacrolein obtained under the action of potassium persulfate and hyposulfite.

The lowest extraction capacity is characteristic of polymer samples obtained in the presence of boron trifluoride at low temperature, and also in the presence of butyllithium. There is a definite dependence (see Table 2) between the content of aldehyde groups, determined by the oximation method, and the capacity for extracting uranium from aqueous solutions.

Fig. 2. Dependence of the percentage of uranium extraction on the concentration of the initial solution

The uranium extraction process takes place within a narrow pH range from 3 to 4. Outside these limits the extraction percentage decreases sharply. The distribution coefficients for the different polyacrolein samples vary within the range from 0.005025 to 0.04803, i.e., by a factor of ten.

Uranium absorbed by polyacrolein can again be quantitatively transferred into solution by treatment with a dilute solution of hydrochloric acid.

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Note: Figure translations are in progress. See original paper for figures.