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Abstract

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CHEMISTRY

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REACTIONS OF AN AQUEOUS SOLUTION OF POLYACROLEIN WITH INORGANIC SALTS

The reactions of aqueous solutions of high-molecular-weight compounds with inorganic salts have been studied very little. For polyvinyl alcohol it is known (^{1}) that, under the action of boric acid salts, potassium bichromate, and an ammoniacal solution of copper sulfate, insoluble precipitates are formed under certain conditions. There are no data on the process of interaction of aqueous solutions of polyacrolein with inorganic salts.

Earlier we (^{2}) showed that water-insoluble polymers of acrolein are capable of giving coordination complexes with uranyl salts and salts of certain other elements, in accordance with the number of aldehyde groups detected by the oxime method. It was of interest to study the behavior of aqueous solutions of polyacrolein, obtained by the Kern–Schulz method (^{3}), toward inorganic salts. The condition for the stable existence of polyacrolein molecules in aqueous solution is the presence of hydrated aldehyde groups, which prevent the formation of intramolecular hemiacetal groupings, as well as an external hydration shell of the entire polymer molecule as a whole.

In this connection, molecules of polyacrolein dissolved in water should possess properties comparable with those of polyhydroxyl high-molecular-weight compounds, for example, polyvinyl alcohol, and, on the other hand, under certain conditions they should gradually dehydrate with the formation of free aldehyde groups, which subsequently pass into hemiacetals. The dehydration process should be accompanied by a change in the phase state of the system as a result of the formation of insoluble products.

Fig. 1. Dependence of the amount of thorium precipitated on the pH of the medium

In comparison with polyvinyl alcohol, which contains stable hydroxyls in its composition, polyacrolein has a number of special features. In the cold or on

Fig. 1. Dependence of the amount of thorium precipitated on the pH of the medium

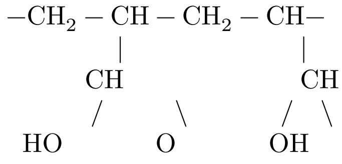
Figure 1: Fig. 1. Dependence of the amount of thorium precipitated on the pH of the medium

heating with sulfuric acid, sodium chloride, ferric nitrate, copper sulfate, uranyl nitrate, thorium sulfate, zirconium oxychloride, and ammonium vanadate, precipitates of insoluble polyacrolein are formed, containing variable amounts of the indicated elements. Figure 1 shows the dependence of the amount of thorium precipitated on the pH of the medium. The percentage of thorium extraction into the precipitate increases rapidly with increasing pH of the solution and reaches 100% at pH 3.75. The elemental composition of the precipitates as a function of the ratio of polymer to thorium nitrate and of the pH of the medium is given in Table 1. Attention is drawn to the···

Table 1

No.	Weight ratio polymer : thorium nitrate	pH	Ash content, %	C, %	H, %	O (by difference), %	C : H	Formula of the complex
1	1 : 3	2.36	6.90	49.90	6.46	36.74	7.76	$(C_6H_{10}O_3)_{28}Th$
2	1 : 1.66	2.40	7.85	46.16	6.48	39.51	7.12	$(C_6H_{10}O_3)_{24}Th$
3	1 : 6	2.35	7.00	50.57	6.67	35.76	7.58	$(C_6H_{10}O_3)_{30}Th$
4	1 : 3	4.73	18.60	41.37	5.63	34.40	7.35	$(C_6H_{10}O_3)_8Th$
5	1 : 3	8.32	19.05	41.41	5.64	33.90	7.34	$(C_6H_{10}O_3)_9Th$

The constancy of the value of the C : H ratio in the composition of the complex is noted, despite a substantial change in the conditions under which the complex is formed. The value found for the C : H ratio corresponds to the elementary unit:



$$-CH_2-CH-CH_2-CH- \quad (CH(HO)(O)\text{ under the first }CH,\ CH(OH)\text{ under the second }CH)$$

Data on the precipitation of polyacrolein by uranyl nitrate are given in Table 2. The reaction was carried out while boiling the mixture of the components for 0.5–1.0 h at a solution pH equal to 2.

When solutions of polyvinyl alcohol interact with the indicated salts, the phase state of the system does not change. With potassium dichromate, an ammoniacal solution of copper sulfate, titanium sulfate, and tannin, aqueous solutions of polyacrolein react analogously to aqueous solutions of polyvinyl alcohol.

With boric acid and its salts, and with a solution of iodine in potassium iodide, polyacrolein, unlike polyvinyl alcohol, does not react; at the same time, it gives reactions not characteristic of polyvinyl alcohol: for example, it reduces aqueous solutions of uranyl nitrate, ammonium vanadate, and an ammoniacal solution of silver nitrate. Such characteristic features in the behavior of aqueous solutions of polyacrolein, as compared with aqueous solutions of polyvinyl alcohol, can be explained if it is assumed that in aqueous solutions the molecules of polyacrolein have two hydration shells—an unstable outer shell around the entire molecule as a whole and an inner one around the aldehyde groups. Molecules of polyvinyl alcohol in aqueous solutions have only an outer hydration shell.

Table 2

No.	Initial amount, mg: uranium	Initial amount, mg: polyacrolein	Weight of precipitate, mg	Uranium content in precipitate, mg	Absorptive capacity, $n \cdot 10^{-6}$ g/g
1	20	500	100	2.2	20000
2	20	250	100	2.2	20000
3	20	100	30	0.4	10000
4	20	60	No precipitate formed	No precipitate formed	No precipitate formed
5	60	500	180	4.5	20000
6	40	500	200	2.3	12000
7	30	500	200	2.1	10000
8	10	500	180	0.4	2000

Depending on the nature of the salt used, if only the outer shell is destroyed, this leads to identical reactions for both polyacrolein and polyvinyl alcohol. In other cases, the inner shell of polyacrolein is also destroyed, as, for example, in reactions with salts of uranium, thorium, and zirconium; this leads to coagulation of polyacrolein and does not affect the strong hydroxyl groups of polyvinyl alcohol. In a third group of reactions, the aldehyde groups of polyacrolein enter into interaction, which accounts for its reducing ability with respect to elements of variable valence. Additional confirmations of this feature of the structure of the molecu-

polyacrolein in aqueous solutions can be seen in the results of reactions with boric acid and its salts and with a solution of iodine in potassium iodide. The strong hydroxyl groups of polyvinyl alcohol under these conditions give ether-like compounds, which leads to the formation of a gel. At the same time, the less strong hydroxyls of the inner shell of polyacrolein do not form ether bonds, and the system remains without visible changes. Titanium salts occupy an intermediate position in this respect, giving gels with polyvinyl alcohol and with polyacrolein.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.