Academician V. A. KARGIN, A. A. EFENDIEV, Z. Ya. BERESTNEVA

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Abstract

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Academician V. A. KARGIN, A. A. EFENDIEV, Z. Ya. BERESTNEVA

ELECTRON-MICROSCOPIC STUDY OF THE STRUCTURE OF A COPOLYMER OF THE DIETHYL ESTER OF VINYLPHOSPHINIC ACID AND ACRYLIC ACID POSSESSING COMPLEX-FORMING PROPERTIES

Previously ([1]), two of us obtained a complex-forming copolymer based on the diethyl ester of vinylphosphinic acid (VPA) and acrylic acid. From the copolymer a film was prepared, which was cross-linked with triallyl cyanurate. The polymer material obtained is capable of selectively extracting from solutions ions of copper, iron, cobalt, and nickel, forming complexes with them; at the same time, ions of alkali and alkaline-earth metals are practically not extracted.

In studying the kinetics of the processes of sorption and desorption of copper ions by this polymer material, a large difference in the rates of the indicated processes was revealed. Below are data on the kinetics of sorption and desorption of copper ions by a film with a content of cross-linking reagent of 4%. Sorption was carried out from a 0.1 N solution of $CuSO_4$ at pH 5.2. Desorption was carried out by contacting the copper-saturated film with a 1N solution

0.5	1	2	4	8	12	24	48	72	144	288
Duration of contact of the film with 0.1N $CuSO_4$ solution (hr) 0.5	1	2	4	8	12	24	48	72	144	288

0.5	1	2	4	8	12	24	48	72	144	288
Amount of copper extracted (mg-eq/g)	1.2	2.2	3.2	4.0	4.8	5.1	5.6	5.8	6.0	6.4	6.4

	5	10	15	30	60	120
Duration of contact of the copper-saturated film with HCl (min)	5	10	15	30	60	120
Amount of desorbed copper (mg-eq/g)	3.6	5.1	5.7	6.4	6.4	6.4

The sorption process occurs at pH values from 2.5 to 6, increasing strongly with increasing pH. Desorption of copper ions from the polymer film occurs at pH equal to 2 and below ([1]).

As is seen from the data presented, sorption of copper by the polymer film proceeds very slowly; complete equilibrium is reached only after several days, while the amount of copper corresponding to half the absorption capacity of the material is extracted by it in 2 hours.

Desorption proceeds considerably faster: the greater part of the copper ions is displaced by the acid already in the first 10 minutes; complete desorption of copper ions from the film occurs in 30 minutes.

Earlier ([2]), electron-microscopic studies by V. A. Kargin and N. F. Bakeeva on pure polyacrylic acid showed that, depending on the pH of the medium, its molecules have two structural forms. These are either globules, representing

coiled molecular chains, or fibrils, formed as a result of the parallel aggregation of several extended molecules.

The large difference observed by us in the rates of the processes of sorption and desorption of copper ions by the polymer material studied makes it possible to assume that, as in the case of pure polyacrylic acid, the molecules of the copolymer of the diethyl ester of VPA with acrylic acid in these two pro-

processes at different pH values of the medium have different structures. Therefore, an electron-microscopic study was undertaken of the structure of the copolymer of the diethyl ester of VPA with acrylic acid as a function of the pH of the medium.

The object under study is a copolymer of an alkyl ester of a strong acid with a weak acid. The literature [3,4] describes studies of the structures of strong and weak polyacids and their copolymers, as well as copolymers of a weak acid with an ester of a weak acid. Information concerning studies of the structures of copolymers of a weak acid with an ester of a strong acid, however, has not been described in the literature. Therefore this question is also of independent interest.

The copolymer studied was prepared by the method described by us previously [1]. A mixture of monomers of the diethyl ester of VPA and acrylic acid was taken in a ratio of 70 : 30 parts by weight, with the addition of 1% cumene hydroperoxide. The components of copolymerization entered into the copolymer in a ratio of 50 : 50 (calculated from the phosphorus content). For the study, two copolymers obtained in different ampoules were used.

The copolymers were purified by double reprecipitation from an ethanol solution with sulfur ether. The copolymers studied, with molecular weights of 95,000-100,000 (determined by the osmometric method), had intrinsic viscosities of 0.98 and 1.0, respectively. (Both of these constants were determined under conditions in which the dissociation of the ionogenic groups of the copolymer was suppressed.)

Samples for study were prepared from solutions of the copolymers in ethanol (a good solvent) and in water (a poor solvent). The concentration of the solutions varied from 10^{-3} to 10^{-7} g/100 ml of solution. The solutions had pH: 1.1; 3; 6-8; 10.5.

The pH was changed by adding specified amounts of hydrochloric acid or an aqueous ammonia solution to the copolymer solutions, and the pH value was recorded on an LPP-58 potentiometer. A drop of the solution was placed on a collodion substrate. In the case of solutions having pH 6-8, the collodion substrates were applied to a copper grid; in all other cases platinum grids were used.

In most cases, to increase the contrast of the images, the samples were shadowed with palladium. The studies were carried out in electron microscopes of the UEMB-1 and JEM-5u types.

According to electron-diffraction data, the copolymer is amorphous in acidic, neutral, and alkaline media.

In Fig. 1A (see inset facing p. 1312) are shown microphotographs of copolymer samples obtained from alcoholic (a) and aqueous (b) solutions having pH 1.1. In the photographs, fibrillar formations with a completely random arrangement stand out clearly. In Fig. 1A, a, two types of fibrils are visible, with cross-sectional dimensions of 0.01-0.02 μ and 0.08-0.1 μ; in an aqueous medium at the same pH (Fig. 1A, b), larger particles are visible. Water is a poor solvent for this copolymer, and under these conditions larger aggregates arise, reaching 0.5-0.7 μ in length.

When the pH of the copolymer solutions is raised to 3, its molecules assume the form of globules, 0.02-0.03 μ in diameter in the alcoholic medium (Fig. 1B, a, see inset facing p. 1312) and 0.1-0.2 μ in the aqueous medium (Fig. 1B, b).

A similar picture, with approximately the same globule sizes, is also observed in samples obtained from solutions whose pH lies in the region close to neutral (pH 6-8).

On passing to the well-dissociating ammonium salt of the copolymer (pH 10.5), its molecules again straighten out, forming fibrils with transverse dimensions up to 0.02 μ in the alcoholic medium and up to 0.1 μ in the aqueous medium.

This dependence of the structure of the copolymer of the diethyl ester of VPA and acrylic acid on the pH of the medium is explained by us as follows: the copolymer contains two types of functional groups joined cova-

by a hydrogen bond with the molecular chain. These are carboxyl groups and groups

$$-\mathrm{P}(=\mathrm{O})\,(\mathrm{OR})_2.$$

At pH 1.1, the COOH groups are practically nonionized, and the difference between the charges arising at their ends is insignificant. The group

$$-\mathrm{P}(=\mathrm{O})\,(\mathrm{OR})_2,$$

however, is sufficiently polarized even in this medium. This is due to the fact that the electrons from the phosphorus atom are strongly drawn toward the electronegative oxygen atom bound to it by a double bond. The repulsion of the charges $^{+}\mathrm{P}=\mathrm{O}^{-}$ that arise in this case straightens the copolymer molecule into a rigid rod, in contrast to pure polyacrylic acid, whose molecules in the nonionized state have a globular form ([2]).

With an increase in the pH of the copolymer solutions to 3, partial ionization of the carboxyl groups begins.

Under these conditions, the hydrogen bonds that apparently contributed to the formation of regular structures are destroyed, and the molecule coils into a globule.

In the pH region close to neutral, the same picture is observed, explained by the same factors.

When the pH is increased to 10.5, a well-dissociating salt of the copolymer is formed and, in this case, as was shown in the previously mentioned work of V. A. Kargin and N. F. Bakeev ([2]), fibrillar structures again arise owing to electrostatic repulsion of the charges of the chain.

This dependence of the structural forms of the copolymer on the pH of the medium is in good agreement with the data given above on the kinetics of sorption and desorption of copper ions by this polymeric material.

The kinetics of the process are slowed if the copolymer molecule is in globular form, and sharply accelerated when the molecules pass into fibrillar form.

Physical-Chemical Institute
named after L. Ya. Karpov

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