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Abstract

Full Text

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PREPARATION AND STUDY OF A HOMOGENEOUS POLYMER MEMBRANE POSSESSING COMPLEX-FORMING PROPERTIES

In connection with the fact that the ion-exchange materials currently used do not possess high selectivity toward a narrow group of ions, in recent years polymeric materials possessing complex-forming properties have attracted considerable attention from researchers ([1]). Certain ionites possessing selectivity toward divalent ions have been synthesized and studied ([2,3]).

It is known that phosphorylated organic compounds can form complexes with Fe^{3+}, Th, U, and certain other elements. Kennedy ([4]) synthesized a resin based on diallyl allylphosphonate capable of forming complexes with uranium, thorium, and trivalent iron, extracting them from nonaqueous solutions; the capacity varied from 1 to 3 mg-eq/g. However, when extracting the same elements from aqueous solutions, the capacity of this resin was insignificant (from 0.1 to 0.2 mg-eq/g).

We obtained a homogeneous polymer membrane based on a copolymer of the diisobutyl ester of vinylphosphonic acid and acrylic acid. The diisobutyl ester of vinylphosphonic acid was obtained by us by the method described by G. S. Kolesnikov, E. F. Rodionova, and L. S. Fedorova ([5]). The synthesis was carried out in two stages: in the first stage, the diisobutyl ester of β-chloroethylphosphonic acid was obtained; in the second stage, hydrogen chloride was eliminated to give the diisobutyl ester of vinylphosphonic acid. To obtain the diisobutyl ester of β-chloroethylphosphonic acid, a mixture consisting of aluminum chloride, phosphorus trichloride, and dichloroethane (1 : 1 : 0.5) was taken, heated for 4 hr at 75–80°, then cooled to −20°, and at this temperature isobutyl alcohol was introduced. The second stage of the process consisted in the elimination of hydrogen chloride with the aid of triethylamine. The resulting diisobutyl ester of vinylphosphonic acid had the constants: b.p. 86–88°/4 mm; n_D^{20} 1.4370; according to the literature: b.p. 78–78.5°/3 mm, n_D^{20} 1.4356. P content, %: 13.56; 13.64 (calculated 14.07). On the basis of the obtained diisobutyl ester of vinylphosphonic acid and acrylic acid, a copolymer was obtained. For this purpose, the copolymer mixture in a ratio of 50 : 50, with the addition of up to 1% cumene hydroperoxide, was placed in a quartz ampoule, repeatedly frozen with liquid nitrogen, thawed by immersing the ampoule in a

beaker with methanol at room temperature, and evacuated on a fore-vacuum pump to $8 \cdot 10^{-3}$ mm. After this the ampoule was sealed and exposed to ultraviolet light from a mercury-quartz PRK-2 lamp. Copolymerization was carried out at room temperature for 7–8 min. The resulting copolymer slowly dissolved in ethyl alcohol, was precipitated with sulfuric ether, and was dried under vacuum at 40° to constant weight. From the resulting copolymer an 8–10% alcoholic solution was prepared, into which a cross-linking agent—triallyl cyanurate—was introduced in an amount of 2–4%. The prepared solution was poured onto a substrate—

···of a glass ring set on a leveling table for evaporation of the solvent at room temperature. After evaporation of the solvent, the membrane was irradiated with ultraviolet light for 2–3 hours to obtain a cross-linked membrane insoluble in water and organic solvents. The resulting membrane is strong and resistant to acids and alkalis. The swelling of the membrane in water is from 10 to 40%, depending on the ratio of monomers in the copolymer. The capacity for Fe^{3+}, determined by the static method at a temperature of 20°, varied from 9 to 12 mg-eq/g. However, it was observed that a weakly swelling membrane, which extracts iron only slightly from aqueous electrolyte solutions, extracts it well from nonaqueous solutions. We studied the kinetics of sorption of Fe^{3+} from an aqueous electrolyte solution. For this purpose, a weighed portion of membrane was placed into a measured volume of freshly prepared 0.1 N $FeCl_3$ solution contained in a vessel with a water jacket for thermostating. The solution with the membrane placed in it was shaken on a mechanical shaker for a period depending on the duration of the experiment. All investigations were carried out at a temperature of $20 \pm 0.1°$. After completion of the experiment, the membrane was removed, and the concentration of Fe^{3+} in the solution was determined on an FEKN-54 electrophotocolorimeter. The following data were obtained:

Duration of contact of the membrane with the solution, h	2	4	24	48
Fe^{3+} absorbed, mg-eq/g	6.4	7.2	12.2	12.3

Equilibrium is practically established within one day. The Fe^{3+} absorbed by the membrane was completely desorbed in 4 hours by 0.5 N HCl.

In conclusion, the authors express their gratitude to Prof. G. S. Kolesnikov and E. F. Rodionova for providing the diisobutyl ester of vinylphosphinic acid and for a number of valuable instructions concerning its synthesis.

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