

Complex-Forming Polymeric Sorbents with Macromolecular Arrangement Favorable for Ion Sorption

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Synopsis

Crosslinked polymeric sorbents with macromolecular arrangement favorable for sorption of copper ions have been obtained on the base of copolymer of diethyl ester of vinylphosphonic acid with acrylic acid. The general principle involves interaction of linear polymer and sorbing ions in solution where the segments of the macromolecules are still mobile enough, subsequent fixation of optimal ion uptake conformations of macromolecules by crosslinking of metal polymer complexes, and removal of ions from crosslinked sorbent. Such treatment increases the exchange capacity of the sorbents more than twice and improves essentially its kinetic characteristics in comparison with the same copolymer crosslinked by conventional methods without special arrangement of macromolecules. The rate of the uptake on the sorbents with macromolecular arrangement favorable for ion sorption first increases with increase in the degree of crosslinking and then decreases. Apparently the rise of the crosslinking degree leads to more rigid fixation of the optimum ion uptake conformations of the macromolecules' segments. Further increase of the crosslinking degree alongside with fixation prevents ions from diffusion into the sorbent.

INTRODUCTION

Interest in ion-exchange resins with active groups able to enter into complex formation has largely grown in the last few years because of the specific analytical uses of such resins. However, they have no wide commercial application because the rate of the uptake and binding of cations by this type of resins is much slower than that by usual cation exchangers.

During the past 15 years there have been a number of studies on kinetics and mechanism of the ion uptake by complex-forming sorbents¹⁻⁹ and opinions conflict on a number of issues. In several cases the kinetic behavior appeared to be controlled by the rate of diffusion of ions into the resin particles,^{2-4,8} but some workers also found that the rate of chemical reaction to form the chelated species was a controlling factor.^{5,6,9}

In some cases authors do not come to any conclusions, pointing out that experimental data are not described by equations developed for both diffusion processes and chemical reaction.¹⁰ In the majority of cases the exchange of the complex-forming cations against Na^+ was studied.^{1,3-9} In such cases the rate of exchange increases greatly in comparison with the H form of such resins. However, it should always be followed by a decrease in selectivity because the exchange capacity of charged resin with respect to nonspecific sorption of ions must be higher than that of the undissociated hydrogen form.

In previous papers the kinetics was described of ion uptake by complex-

forming resin prepared by copolymerization of diethyl ester of vinylphosphonic acid with acrylic acid followed by crosslinking of the formed linear copolymer.^{11,12} It was assumed that the rate of arrangement of segments of macromolecules to the favorable position for ion uptake might be a rate-controlling step in the sorption process. With this point in mind we have made an attempt to prepare complex-forming polymeric sorbent with macromolecules being favorably prearranged for sorption of certain ions. Such arrangement being fixed by crosslinking might be "remembered" by macromolecules, and this might lead to essential improvement of sorption characteristics.

Some literature data give good reasons to make such assumption. For example, a number of papers have been published in which specific silica gels with high selectivity of adsorption toward previously chosen substances were described.¹³⁻¹⁶ Such adsorbents were prepared by formation of the gel in the presence of the adsorbing substance. However, the explanations of the mechanism of adsorption were quite different. The authors proposed hypotheses on "imprints," "matrices," "traces," and the role of a substance remaining in the gel. The last assumption, however, has been rejected¹⁷ because no correlation was found between the amount of a substance not being extracted and specifically adsorbed in silica gel. Specificity of such adsorbents is easily lost during washing and drying of the gels.

Regarding the macromolecular models of enzymes, a few years ago one of the authors of the present paper proposed a principle of preparation of polymers with tertiary structure optimized for sorption of corresponding low molecular weight substrates.¹⁸ Based on this principle we suggested a method of preparation of complex-forming polymeric sorbents with macromolecular arrangement favorable for ion sorption.^{19,20} Later on, Japanese authors described a method of preparation of crosslinked poly(vinylpyridine) resin with metal ion used as a template.^{21,22}

The general principle of our method involves as a first-step treatment of a linear polymer by ions to be sorbed in solution, i.e., under conditions when segments of macromolecules are still mobile enough. The second step is fixation of the optimum for the ion uptake conformations of macromolecules by crosslinking of metal-polymer complex, and the third step is removal of template ions from the crosslinked sorbent. As an object for such treatment we used the above-mentioned copolymer of diethyl ester of vinylphosphonic acid (DEVPA) and acrylic acid (AA), macromolecules of which were being arranged for the uptake of copper ions. *N,N'*-Methylenediacrylamide (MDAA) has been used as a crosslinking agent.

EXPERIMENTAL

DEVPA was prepared in accordance with the method of Kolesnikov et al.²³; and after double distillation, the product with bp 62°C/2 torr, n_D^{20} 1.4300 (lit. bp 68-70°C/3 Torr, n_D^{20} 1.4300) was isolated. Conventional AA was twice distilled in vacuo (bp 39°C/10 Torr) before use.

Bulk copolymerization of the monomers was carried out by photochemical initiation of the mixture of 7-g DEVPA and 3-g AA with 0.1-g cumene hydroperoxide in a sealed test tube of quartz glass which was evacuated at 10^{-4} Torr. UV light was supplied from a high-pressure mercury lamp of 300 W. The co-

polymerization reaction was substantially complete in 2 hr. The resulting copolymer was dissolved in ethanol and then precipitated dropwise in excess diethyl ether. After two reprecipitations, the copolymer was dried in a vacuum desiccator at only slightly elevated temperature and analyzed for phosphorus. Phosphorus content was determined in accordance with the molybdenum blue method.²⁴

Viscosimetric measurements were carried out in a capillary viscosimeter at 25°C using 0.1M LiCl ethanol solution as a solvent. Number-average molecular weight was determined osmotically using a Packard Model 50 osmometer. The measurements were carried out at 30°C using membranes of Hydrocella Filters 90 μm thick and pore size 0.01 μm . 0.1M LiCl ethanol solution was used as solvent.

IR spectra in the range of 400–2000 cm^{-1} were recorded on a UR-20 double-beam spectrophotometer. The samples for IR spectra were finely ground in a vibrating ball mill before mixing with KBr.

H-NMR spectra were obtained by a Tesla BS-487C Model nuclear magnetic resonance spectrometer at 80 MHz and temperature of 30°C. NMR sample solutions were prepared to contain 10-g copolymer in 100 cm^3 pyridine. As external reference hexamethyldisiloxane was used.

A fairly dilute ethanol solution of copolymer (0.8 g/100 cm^3) was mixed with a double amount of 0.075M CuSO_4 solution adjusted to pH 1.1 with H_2SO_4 . The resulting mixture was then slowly titrated by copper ammonia solution (0.05M CuSO_4 , 5M NH_4OH) until a pH value of 3.95 was achieved. The rate of titration was so chosen that pH increase was not greater than 0.2 per hour. The precipitated metal-polymer complex was filtered, repeatedly washed with distilled water until the washings gave a negative test for copper, and dried in vacuo at 35–40°C.

Dry metal-polymer complex was mixed with MDAA, and the mixture was ground in a vibrating ball mill with ball diameter 0.8 cm for 1 min. The resulting mixture had a particle size within the range of 150–200 mesh. A small amount (up to 5%) of smaller particles was set aside.

Tablets with thickness of 0.025 cm and diameter 0.8 cm were prepared from the mixture by pressing. The tablets were evacuated at 10^{-4} Torr and heated in sealed test tubes at 150° for 5 hr. The copper held by the crosslinked copolymer was fully desorbed into 1M HCl. Crosslinked tablets of the initial copolymer without copper were prepared using the same procedure. They were heated at 100°C.

Swelling degree was determined by weighing the dry and swollen samples after removal of excess water by centrifuging at 1500 g for 5 min.

Kinetics of the uptake of copper ions was studied by using the limited bath method. The sorption processes proceeded in the weak acidic medium (pH 4), i.e., under conditions when acidic groups of the sorbents are essentially un-ionized and ion uptake takes place only by means of complex formation. The experiments were carried out at 40°C in a series of identical jacketed flasks mounted in a shaker which was agitated vigorously. Themostated water was circulated through the flask jackets so that the temperature was controlled to $\pm 0.1^\circ\text{C}$. 50-ml 0.05M CuSO_4 solution adjusted to pH 4 with H_2SO_4 was placed in each flask, and when the desired temperature had been reached, a sample of approximately 50 mg of the sorbent swollen in dilute acid at pH 4 was added. After

a measured time the sample was quickly separated and washed with distilled water until the washings gave a negative test for copper. Separate samples of the sorbent and solution were used to obtain the data for each time interval selected. The copper held by the sorbent was fully desorbed into 1M HCl and determined by titration with EDTA using Murexide as indicator.

RESULTS AND DISCUSSION

The starting linear copolymer of DEVPA with AA contained 9.2% by weight of phosphorus. Intrinsic viscosity in 0.1M LiCl ethanol solution was 1.01 at 25°C. Number-average molecular weight of the copolymer was 160,000.

To determine whether fractionation or degradation of copolymer takes place during titration or heat treatment, the starting copolymer and its complex after desorbing of copper both before and after heat treatment carried out at the same conditions but without crosslinking agent were investigated. Phosphorus content for all samples was $9.2 \pm 0.3\%$ by weight. Intrinsic viscosity of the samples was within a range of $0.98 \div 0.01$. IR and H-NMR spectra of the samples are given in Figures 1 and 2. It can be seen that both the IR and the NMR spectra of all three samples are identical.

Investigation of the samples before and after grinding in the vibrator and after preparation of the tablets showed that intrinsic viscosity did not change due to these operations.

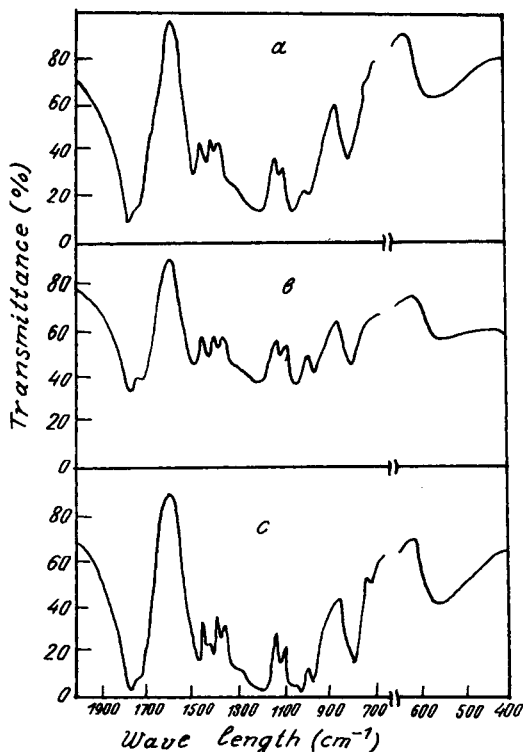


Fig. 1. IR-spectra of the starting copolymer (a) and its complex washed off copper ions before (b) and after heat treatment (c).

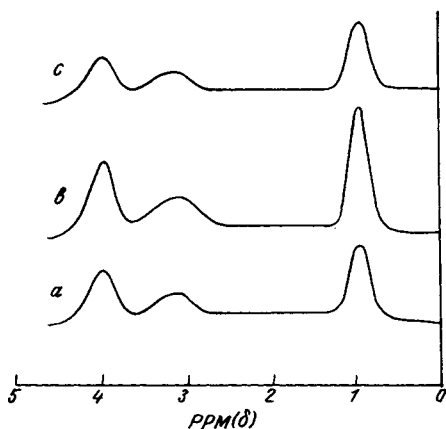


Fig. 2. H-NMR spectra of the starting copolymer (a) and its complex washed off copper ions before (b) and after heat treatment (c).

In the process of titration when the pH value of the solution reaches 2.75, the metal-polymer complex precipitates. Further increase in pH up to 3.95 is followed by essential increase of the amount of complexed copper. The dependence of the amount of copper ions sorbed by the linear copolymer during titration on pH of the medium is shown in Figure 3.

The following scheme illustrates the possible coordination of copper with the functional groups of the sorbent:

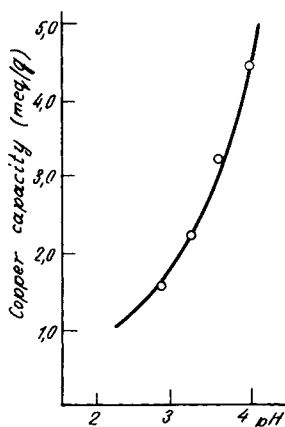
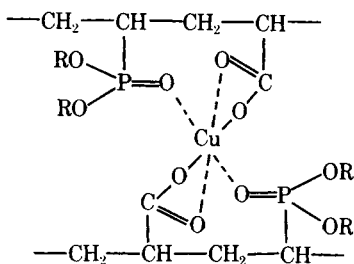


Fig. 3. Plot of the amount of copper ions sorbed by the linear copolymer vs pH of the medium.

The scheme is based on the data of copper uptake, IR spectroscopy, and viscosimetric measurements. The uptake of copper ions by the sorbent from CuSO_4 solution is not accompanied by a change in SO_4^{2-} anion concentration. At the same time the concentration of H^+ increases equivalent to that of sorbed Cu^{2+} . This points out that the sorption occurs by means of the replacement of hydrogen atoms of carboxylic groups by copper ions. Meanwhile, the ions of alkali and alkali earth metals are not sorbed by the sorbent within this pH range. This shows that sorption involving non-ionized carboxylic groups might take place only due to formation of additional coordination bonds between the sorbing ions and corresponding functional groups of the sorbent.

Comparison of the IR spectra recorded for both initial copolymer and its complexes, containing 1.48 and 4.2 meq/g copper (Figs. 1 and 4) shows that characteristic frequencies at 1740 cm^{-1} and a broadened band with two maxima at 1180 and 1240 cm^{-1} , associated respectively with $\text{C}=\text{O}$ and $\text{P}=\text{O}$ groups, undergo changes due to complex formation. In the spectrum of the complex with copper content 1.48 meq/g, the peak at 1740 cm^{-1} diminishes and an extra peak at 1630 cm^{-1} appears. The latter one resolves into two peaks at 1630 and 1580 cm^{-1} when copper content increases to 4.2 meq/g. The ratio of the maximum at 1180 cm^{-1} to that at 1240 cm^{-1} also changes because of the complexing with copper ions. This shows that both $\text{C}=\text{O}$ and $\text{P}=\text{O}$ groups participate in the coordination with copper.

Copper ions in the amount of 10^{-3} mol/l , which corresponds to the relative degree of stoichiometric equivalence from 11.6 to 3.1% (for concentration of copolymer solution respectively from 0.3 to 1.1 g/100 ml), were added to the copolymer solution. In this case the reduced viscosity decreases comparatively much more with addition of noncomplex-forming ions, e.g., magnesium ions taken in the same amount (Fig. 5). It was shown in our previous papers that the

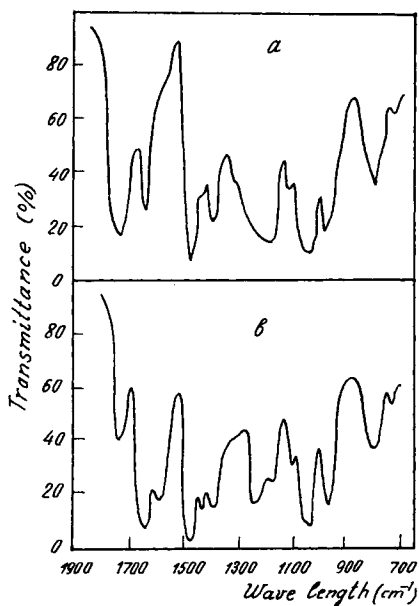


Fig. 4. IR-spectra of the copper-copolymer complexes containing (a) 1.48 and (b) 4.2 meq/g of copper.

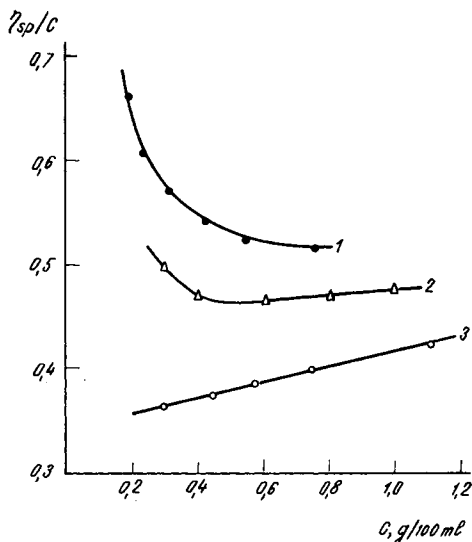


Fig. 5. Plots of reduced viscosity of the starting copolymer solutions versus concentration at 25°C. Solvent: 1:1 water-ethanol solution (1); 0.001M MgSO₄ water-ethanol solution (2); 0.001M CuSO₄ water-ethanol solution (3).

complex formation makes the macromolecules coil more tight.^{12,25} Marked contraction of polymeric ligand due to intrapolymer chelation was also shown somewhere else.²² The scheme shows all possible ways of formation of coordination bonds. Any particular ion might form just some of them.

The starting copolymer and two samples of its complexes with copper content of 1.48 and 4.2 meq/g were chosen for subsequent crosslinking by MDAA and investigation of sorption properties.

Plots of the swelling capacity of the sorbents versus amount of introduced crosslinking agent are shown in Figure 6. The samples were swollen in distilled

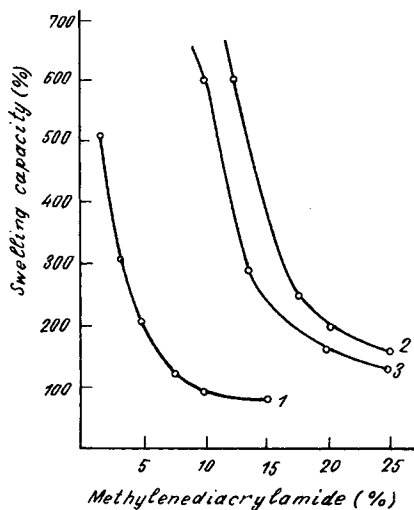


Fig. 6. Plots of swelling capacity of crosslinked starting copolymer (1) and its complexes containing 4.2 (2) and 1.48 meq/g (3) of copper, vs the amount of crosslinked reagent.

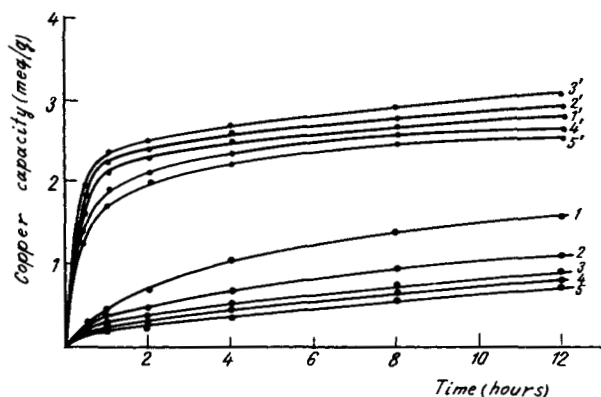


Fig. 7. Kinetic curves of the uptake of copper ions by the crosslinked starting copolymer (1-5) and its complex containing 1.48 meq/g of copper (1'-5'). Amount of crosslinking reagent, % by weight: (1-1), 5; (2-3), 0; (3-5), 0; (4-7), 5; (5-15), 0; (1'-5), 0; (2'-10), 0; (3'-15), 0; (4'-20), 0; (5'-25), 0.

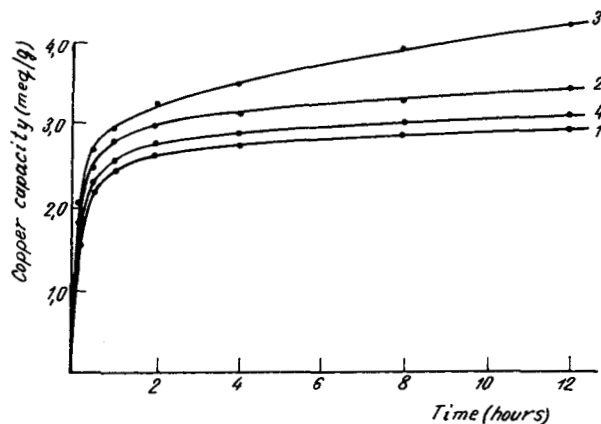


Fig. 8. Kinetic curves of the uptake of copper ions by the crosslinked copper-copolymer complex containing 4.2 meq/g of copper. Amount of crosslinking reagent, % by weight: (1-6), 0; (2-10), 0; (3-17), 5; (4-25), 0.

water at pH 6.2 and a temperature of 20-22°C for 24 hr. It can be seen that the character of the curves does not change very much. However, for crosslinking of complexes of copolymer with copper a greater amount of the crosslinking reagent is needed to achieve the same value of swelling capacity. The more copper is contained in the complex, the greater amount of crosslinking reagent is needed. Preliminary investigations show that the more copper is contained in the complex, the less MDAA takes part in the crosslinking reaction.

Investigation of copper ion uptake by the crosslinked sorbents from 0.05M CuSO_4 solution shows that the arrangement of macromolecules favorable for ion uptake more than twice increases the exchange capacity of the sorbents and improves essentially their kinetic characteristics in comparison with the copolymer crosslinked without such prearrangement.

The effect of improvement of exchange capacity and kinetics of the copper ion uptake is already achieved when the copper content in the polymeric complex reaches a value of 1.48 meq/g. Increase in copper content to 4.2 meq/g leads to further increase of sorption capacity and rate of the uptake.

The copper taken up by the crosslinked sorbents was fully desorbed after treatment of the samples by 1M HCl for 2 hr. Desorption of copper ions does not take place when the samples are treated by water or HCl solution at a pH value higher than 2.

Kinetic curves of the uptake of copper ions by the crosslinked sorbents are given in Figures 7 and 8. The rate of the uptake of copper ions by the sorbents prepared by crosslinking of the starting copolymer decreases with increase in the degree of crosslinking. On the contrary, in case of the sorbents with macromolecule arrangement favorable for uptake of copper ions, the sorption rate first increases with rise in the crosslinking degree and then decreases.

We believe that in the case of the sorbents with special arrangement of macromolecules, the rise in the crosslinking degree leads to more rigid fixation of the optimum for the ion uptake conformations of macromolecular segments. Further increase in the crosslinking degree along with fixation prevents ions from diffusion into the sorbent.

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