SELECTIVE POLYMER COMPLEXONS PREARRANGED FOR METAL IONS SORPTION

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Abstract - A new approach to a problem of producing polymer complexons to be used as sorbents selective to metal ions has been developed. The general principle is based on the use of "memory" of polymer composition and consists in the conformational prearrangement of macromolecules of non-crosslinked complex-forming polymer to a favorable for sorbing ions position and subsequent fixation of conformations optimum for the ion uptake by means of intermolecular cross-linking. Crosslinked macromolecules "keep in mind" the conformations advantageous for sorption and as a result the basic sorption characteristics - exchange capacity, kinetics and selectivity of the sorbents are essentially improved.

INTRODUCTION

Interest in selective ion-exchange resins has largely grown in the last few years because of specific use of such resins. Intensive development of technological processes of metal uptake from solutions is accompanied by processing of raw materials often containing just a small amount of the desirable element. As a result requirements for the selectivity of sorption processes become more rigid. Modern technology requires a higher selectivity when using ion-exchangers which in turn puts forward the problem of an essential increase in sorbents selectivity and makes it necessary to look for new routes of their synthesis.

So far there exist two main approaches to the problem of producing selective ion-exchange sorbents. The first consists in changing the degree of permeability of ion-exchanger, that is, preparation of so-called ion sieves separating ions of different sizes. However, the method of using the sieve

effect justifies itself only in the case of large organic ions. The method may be applied to inorganic ions to a very limited extent. First, the sizes of the hydrated ions of various metals do not differ considerably enough and the existing differences often do not correspond to the objectives. Secondly, the ions hydration degree is not constant and may change with concentration of solution, its total ionic strength, temperature, pH and other factors.

Another approach is preparation of crosslinked polymers with functional groups known as specific complexons. Thus, Skogseid (1) and later Stamberg (2) obtained sorbents selective to potassium and nickel by means of incorporation into the polymer functional groups similar to dipicrylamine and dimethylglyoxime. Attempts to prepare ion-exchange resins containing complex-forming groups selective to certain ions have also been made by some other researchers (3,4), but they achieved only a limited success.

Certainly it would be very attractive to have a set of polymer sorbents specific to each kind of ions. However, the demand for complex-forming resins is still far from the situation and those available exhibit rather modest selectivity. In analytical and coordination chemistry we but rarely come across the individual or at least limited selectivity similar to that of dipicrylamine to potassium or dimethylglyoxime to nickel. In most cases the functional groups exhibit selectivity to a more or less large group of ions. Thus, the problem of preparation of complex-forming polymer sorbents selective to each kind of ions is restrained by the absence of an adequate set of functional groups.

The situation appears more hopeful if we take into account the recent conceptions of the reactivity of polymers. At present there exist sufficient experimental data on specific polymer effects in the chemical reactions of functional groups linked with macromolecules (5). This may also be used for preparation of complex-forming polymer sorbents. Such an approach will allow to regulate the selectivity of the sorbents even when using a small set of functional groups.

Kinetics of the ion uptake plays an important role in sorption processes. In selective sorption processes on complex-forming polymers some difficulties arise because of the low rate of metal ions uptake. Mechanism and

kinetics of the sorption processes on complex-forming sorbents have not been sufficiently studied and a few published works are contradictory (6-9). In the available papers the mechanism of sorption processes is considered from the point of view of the nature of sorbing ions and that of functional groups of the sorbents. The features of the polymer nature of sorbents are usually not considered.

The objective of our work is the development of methods of preparation, regulation of properties and formation of a three-dimensional structure of polymer complexons with improved sorption characteristics - exchange capacity, rate of sorption and selectivity using opportunities provided by the polymer nature of the sorbents.

RESULTS AND DISCUSSION

Diethyl ester of vinylphosphonic acid (DEVPA) and acrylic acid (AA) have been chosen as initial monomers to prepare polymer sorbents. DEVPA contains electron-donating phosphorylic groups able to form coordination bonds with ions of some transition metals. AA has a weakly acidic carboxylic group also able to enter into complex formation. Polymer materials with phosphorylic and carboxylic groups do not react as standard ion-exchangers within a rather wide interval of pH, and ion uptake may take place only under formation of the coordination bonds. Consequently, such polymers may be used as selective sorbents.

Copolymerization of DEVPA with AA was carried out by means of photochemical initiation of the monomer mixture in the presence of 1% of cumene hydroperoxide in sealed test tubes of quartz glass which were evacuated at 10^{-2} Pa. UV-light was supplied from a high-pressure mercury lamp of 300 W. The copolymerization reaction was substantially complete in 2 h. The resulting copolymers were purified by means of double reprecipitation from ethanol solution by diethyl ether and dried in a vacuum desiccator at slightly elevated temperature. Complex-forming sorbents with three-dimensional structure were obtained by crosslinking of copolymers. N,N' - methylenediacrylamide (MDAA) was used as a crosslinking agent.

Sorption properties of the crosslinked sorbents have been studied. It appears that the sorbents do not practically take up ions of alkaline and alkaline earth metals from acidic and neutral solutions. The sorption of

alkaline metals is noticeable in alkaline media only. The sorbents are able to take up copper, cobalt and nickel ions from neutral and weakly acidic solutions which is indicative of the formation of coordination bonds.

The synthesis and sorption characteristics of crosslinked copolymers of DEVPA and AA were described in more detail in our previous papers and it was assumed that the rate of the rearrangement of macromolecules of complex-forming polymers in conformations favorable for ion uptake might be a rate-limiting step in the sorption processes (10,11). With this point in mind we proposed a principle of preparation of selective complex-forming sorbents which is based on the use of "memory" of polymer composition. The principle consists in the conformational prearrangement of macromolecules of non-crosslinked complex-forming polymer to a favorable for sorbing ions position and subsequent fixation of conformations optimum for the ion uptake by means of intermolecular crosslinking (12-15). Crosslinked macromolecules might "keep in mind" conformations advantageous for sorbing ions and this should lead to an improvement of basic sorption characteristics of the sorbents.

Such a possibility would not seem doubtful if we take into consideration some literature data. For example, a number of papers have been published in which specific silica gels with increased adsorption selectivity with respect to previously chosen substances were described (16-19). The adsorbents were prepared by forming gels in the presence of the adsorbing substance. However, the adsorption mechanism was explained differently in these papers, various hypotheses being advanced regarding "imprints", "templates", "traces" and the role of the persistent substance. The last assumption was apparently refuted by ref. (20) in which it was shown that there was no correspondence between the amount of unextracted and specifically adsorbed substances. The adsorption specificity of silica gels is easily lost during the subsequent treatment, washing, drying and even storage of the gels.

Several years ago, when studying the macromolecular models of enzymes, one of us proposed the principle of the "adjustment" of macromolecular chains to the tertiary structure optimum for the sorption of corresponding substrates (21). Subsequently, we proposed a method of preparation of complex-forming polymer sorbents with macromolecular arrangement favorable for sor-

bing ions (12-15). Later on Japanese authors described a method of prepa-
ration of crosslinked polyvinylpyridine resin with metal ion used as a tem-
plate (22,23).

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 conformations of macromolecules optimum for the ion up-
take by crosslinking the metal-polymer complex, and the third step is re-
moval of template ions from the crosslinked sorbent.

As an object for such treatment we used the above mentioned copolymer of
DEVPA and AA, macromolecules of which were arranged for the uptake of
copper ions. The copolymer contained 9.2% by weight of phosphorus. In-
trinsic viscosity of the copolymer in 0.1M LiCl ethanol solution was 1.01
at 25°C, its number-average molecular mass was 160 000.

Ethanol solution of the copolymer with a concentration about 0.8 g/100 cm^3
was mixed with a double amount of 0.075M $CuSO_4$ in 0.05M solution of H_2SO_4.
The mixture was titrated by copper ammonia solution (0.05M $CuSO_4$, 0.5M
NH_4OH). The rate of titration was selected such that the pH values should
not increase greater than 0.2 units per hour. In the process of titration
copper-copolymer complex precipitates when the pH value of solution reaches
2.75. Further rise of pH results in an increase of the amount of complexed
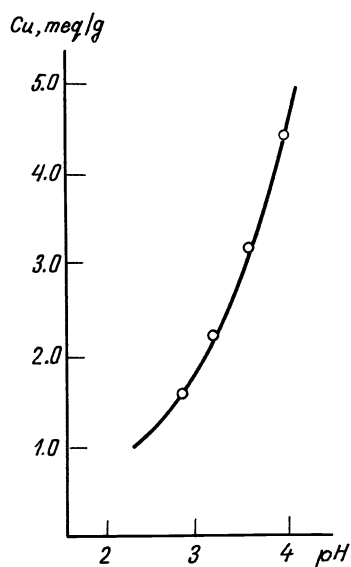copper (Fig. 1).

Fig. 1 Plot of the amount of
copper ions sorbed by the linear
copolymer vs pH of the medium.

The resulting copper-polymer precipitate was filtered (copper excess was re-
moved) and dried in vacuo at slightly elevated temperature. Dry metal-po-
lymer complex was mixed with MDAA and the mixture was ground in a vibrating
ball mill. 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^{-2}
Pa and heated in sealed test tubes at $150^{\circ}C$ for 5 h. The copper held by
the crosslinked samples was desorbed into 1M HCl solution. Crosslinked
samples of initial copolymer were also prepared using the same procedure.
They were heated at $100^{\circ}C$.

In order to determine whether fractionation or degradation of the copolymer
takes place during titration or heat treatment, the initial copolymer and
its complexes after desorption of copper both before and after heat treat-
ment carried out under the same conditions but without crosslinking agent
were analysed. Phosphorus content for all samples was 9.2 ± 0.3%. Intrin-
sic viscosity of the samples was within a range of 0.98 + 0.01. IR- and
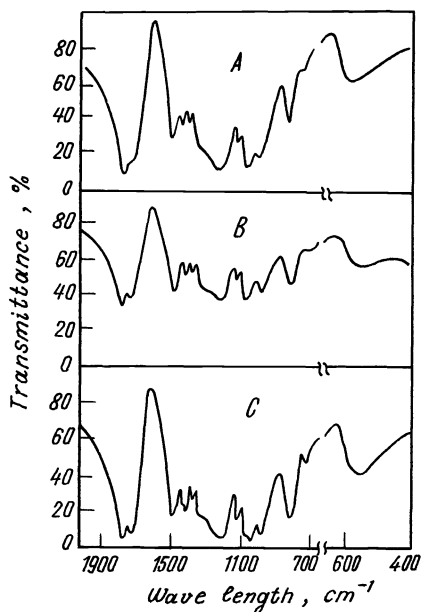H-NMR spectra of the samples are also identical (Figs. 2 & 3).

Fig. 2 IR-spectra of the ini-
tial copolymer (A) and its com-
plex after removal of copper
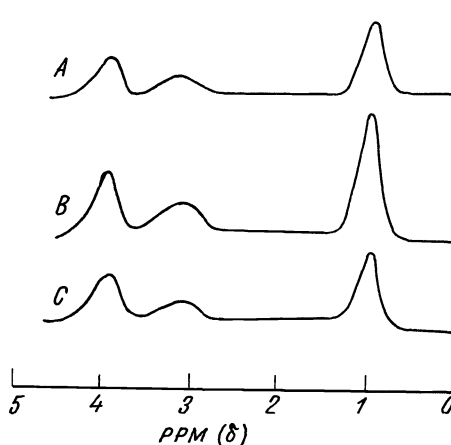ions before (B) and after heat
treatment (C).

Fig. 3 H-NMR spectra of the ini-
tial copolymer (A) and its com-
plex after removal of copper ions
before (B) and after heat treat-
ment (C).

Preparation of sorbents with macromolecules favorably prearranged for the
sorption of copper ions consists of a number of consequent stages:
1) mixing of the linear copolymer with copper ions in acidic solution un-

der condition when the sorption does not take place;

2) slow titration of the mixture by copper ammonia solution and isolation of copper-copolymer complex precipitate;

3) fixation of conformations optimal for the uptake of copper ions by cross-linking of the copper-copolymer complex;

4) desorption of copper ions from the crosslinked sorbent.

When the dilute acidic solution of the copolymer is slowly titrated by the copper-ammonia solution the pH value is increased and the functional groups begin to form coordination bonds with metal ions. Due to complex formation macromolecules take conformations favorable for sorption. Such optimal conformations are fixed after crosslinking of the copper-copolymer complex and "remembered" by macromolecules. This leads to an essential improvement of the basic sorption characteristics of the sorbent - sorption capacity, kinetics and selectivity.

The following scheme (Fig. 4) illustrates the possible coordination of copper with the functional groups of the sorbent.
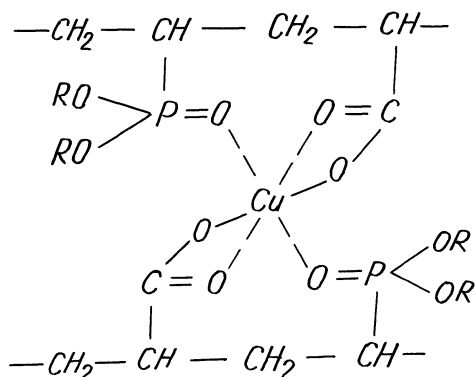

Fig. 4 Scheme of copper-copolymer complex.

The scheme is based on the data of copper uptake, IR spectroscopy and viscometric measurements. The uptake of copper ions by the sorbent from $CuSO_4$ solution is not accompanied by a change in the SO_4^{2-} anion concentration. At the same time the concentration of H^+ increases correspondingly to that of sorbed Cu^{2+}. This points out that the sorption occurs by means of replacement of the hydrogen atoms of carboxylic groups by copper ions. Meanwhile, 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. IR spectra of the initial copolymer and its comple-
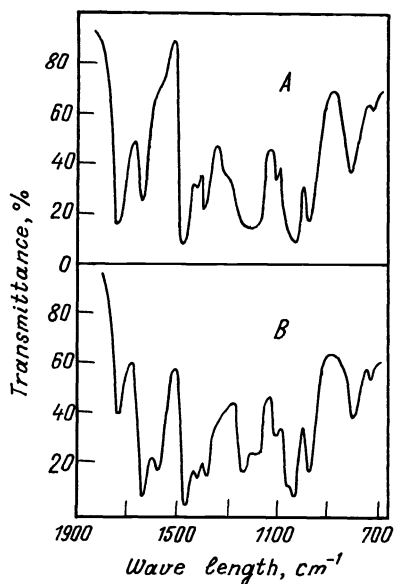xes containing 1.48 and 4.2 meq/g of copper are given in Figs. 2 and 5.

Fig. 5 IR spectra of the copper-
copolymer complexes containing
(A) 1.48 and (B) 4.2 meq/g of Cu.

Comparison of the spectra shows that characteristic frequencies at 1740
cm^{-1} and a broadened band with two maxima at 1180 and 1240 cm^{-1}, associated
respectively with C=O and P=O groups, undergo changes due to complex forma-
tion. 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 con-
tent increases to 4.2 meq/g. The ratio of the maximums at 1180 and 1240
cm^{-1} also changes because of the complexing with copper ions. This shows
that both C=O and P=O groups participate in the coordination with copper.

Copper ions in an 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/100ml), were added to
the copolymer solution. In this case the reduced viscosity decreases compa-
ratively much more with addition of noncomplex-forming ions, e.g., magnesi-
um ions taken in the same amount (Fig. 6). It was shown in our previous
papers (10,24) that the complex formation makes the macromolecules coil
tighter. Marked contraction of polymeric ligand due to intrapolymer che-
lation was also shown elsewhere (22,23). The scheme shows all pos-
sible ways of formation of coordination bonds. Any particular ion might
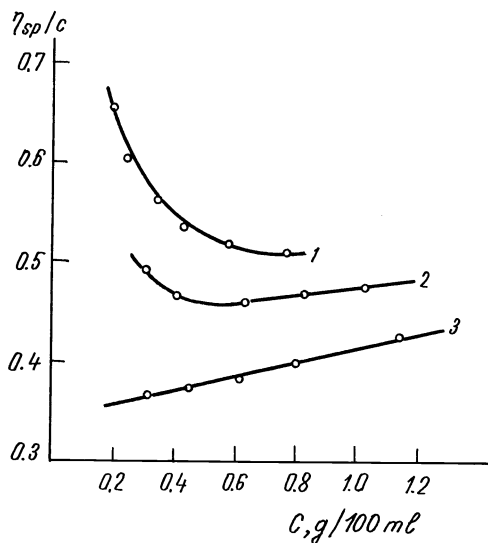form just some of them.

Fig. 6 Plots of reduced viscosity of the initial copolymer solutions vs concentration at 25°C. Solvent: 1:1 water-ethanol solution (1); 0.001M MgSO$_4$ water-ethanol solution (2); 0.001M CuSO$_4$ water-ethanol solution (3).

The initial copolymer and two samples of its complexes with copper content of 1.48 and 4.20 meq/g were chosen for crosslinking and study of sorption properties.

The swelling capacity of the samples crosslinked by a different amount of MDAA was determined by weighing dry and swollen samples after removal of excess water by centrifugation at 1500 g for 5 min. Figure 7 shows the dependence of the swelling capacity of sorbents on the amount of MDAA introduced.
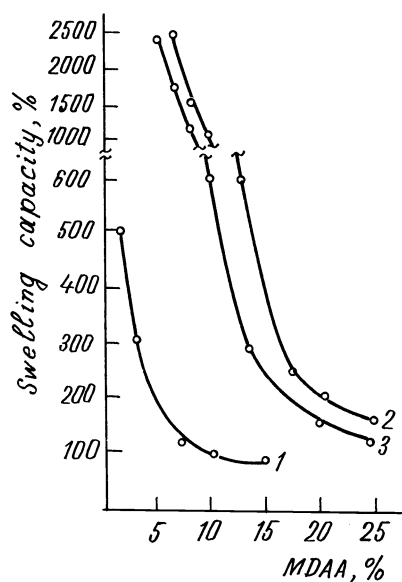

Fig. 7 Plots of swelling capacity of crosslinked initial copolymer (1) and its complexes containing 4.2 (2) and 1.48 meq/g (3) of copper vs the amount of MDAA.

It can be seen that the character of the curves does not change significantly. However, for crosslinking of the copper-copolymer complexes a higher amount of MDAA is required in order to achieve the same swelling capacity. The more copper is contained in the complex the higher amount

of crosslinking agent is required.

In order to determine the amount of MDAA interacting with the copolymer a special IR technique has been developed. IR spectra of the initial copolymer, poly-MDAA and their mixtures were recorded. Peaks at 1555 and 1740 cm^{-1} assosiated with NH- and C=O groups respectively were chosen as analytical ones for poly-MDAA and the copolymer. Plot of the amount of poly-MDAA vs the ratio of optical densities of peaks at 1555 and 1740 cm^{-1} is shown in Fig. 8.
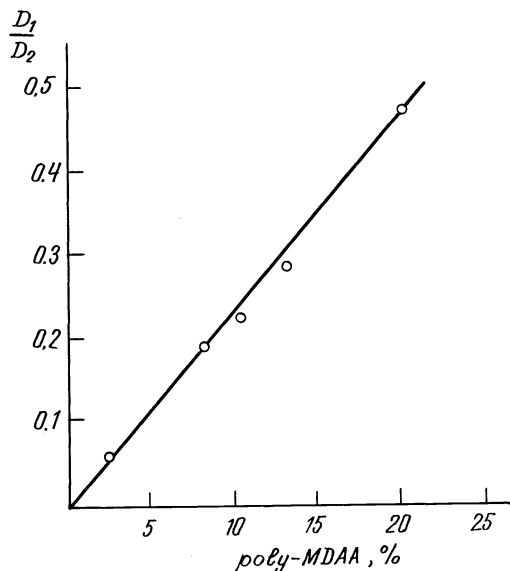

Fig. 8 Plot of the amount of poly-MDAA vs the ratio of optical densities of analytical peaks.

The ratio of optical densities of analytical peaks was also determined in spectra of the sorbents crosslinked both in the usual way and after prearrangement. Then the amount of MDAA involved in the crosslinking reaction was calculated using the calibrating plot. Figure 9 shows the dependence of the taken amount of MDAA on its amount involved in the crosslinking reaction both for the copolymer crosslinked in the usual way and after prearrangement. It is seen (curve 1) that in the case of the initial copolymer MDAA content in the crosslinked sorbent is higher than in the mixture taken for crosslinking. On the contrary, in the case of the copper-copolymer complex not all the amount of MDAA is involved in the crosslinking reaction (curve 2). As is seen from the plots of swelling capacity vs the amount of MDAA involved in the crosslinking reaction (Fig. 10), the curves for both types of the sorbents are practically identical.

An investigation of the copper ion uptake by the crosslinked sorbents from 0.05M $CuSO_4$ solution shows that the prearrangement of macromolecules for

ion uptake makes it possible to increase the sorption capacity more than twice and significantly improves their kinetic characteristics in comparison with the same copolymer crosslinked by the usual method without such prearrangement. The effect of improvement of the 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. An increase in copper content to 4.2 meq/g leads to a 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 solution for 2 h.
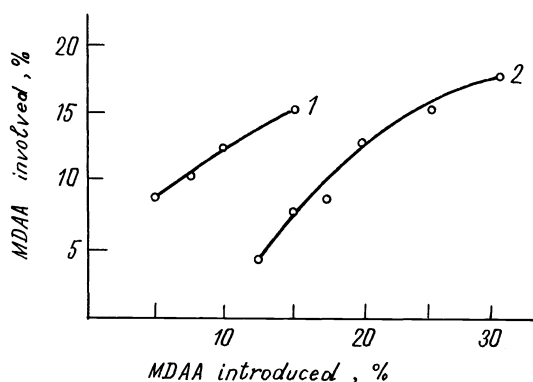

Fig. 9 Plots of the taken amount of MDAA vs its amount involved in the crosslinking reaction: 1 - copolymer crosslinked by the usual method; 2 - copolymer crosslinked in the presence of copper ions.
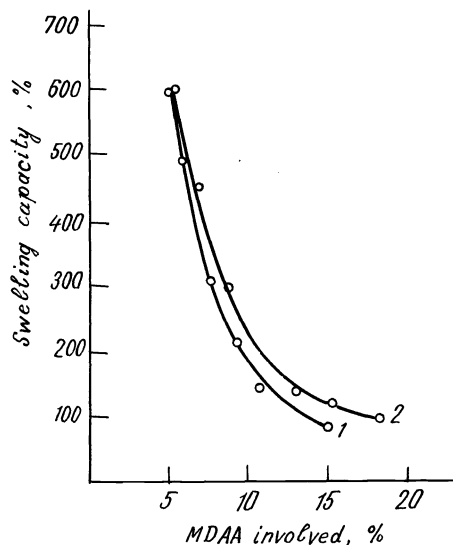

Fig. 10 Plots of swelling capacity of the sorbents vs the amount of MDAA involved in the crosslinking reaction: 1 - copolymer crosslinked by the usual method; 2 - copolymer crosslinked in the presence of copper ions.

Kinetic curves of the uptake of copper ions by the crosslinked sorbents are
given in Figs. 11 & 12. The rate of the uptake of copper ions by sorbents
prepared by crosslinking of the initial copolymer decreases with rise in
the degree of crosslinking. On the contrary, in the case of prearranged
sorbents the sorption rate first increases with rise in the crosslinking
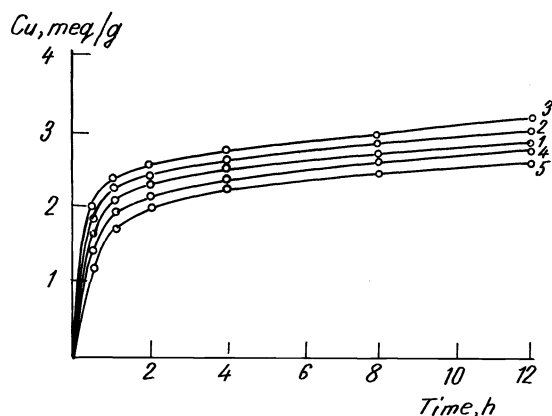degree and then decreases.

Fig. 11 Kinetic curves of the
uptake of copper ions by the
crosslinked copper-copolymer
complex containing 1.48 meq/g
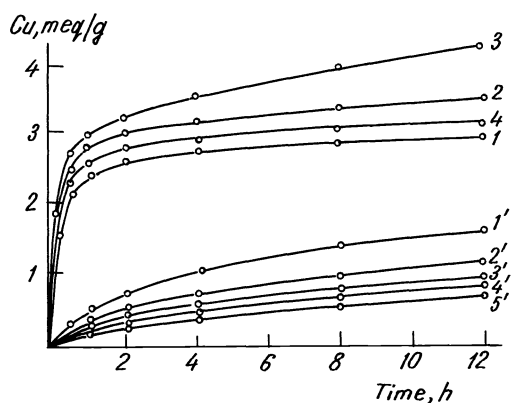of copper. Amount of MDAA, %:
1-5.0; 2-10.0; 3-15.0; 4-20.0;
5-25.0.

Fig. 12 Kinetic curves of the
uptake of copper ions by the
crosslinked initial copolymer
(1'-5') and its complex con-
taining 4.2 meq/g of copper
(1-4). Amount of MDAA, %;
1'-1.5; 2'-3.0; 3'-5.0;
4'-7.5; 5'-15.0; 1-6.0; 2-10.0;
3-17.5; 4-25.0.

It may be assumed that in the case of the sorbents favorably prearranged
for sorbing ions, the rise in the crosslinking degree results in a more ri-
gid fixation of the conformations of macromolecules optimum for the ion up-
take. Further increase in the crosslinking degree along with fixation cre-
ates hindrance to the diffusion of ions into the sorbent.

The next step was an investigation of the specificity of conformational
prearrangement, i.e. investigation of sorption properties of the sorbents
prearranged for the uptake of different ions. With this point in mind,
crosslinked sorbents prearranged for the uptake of cobalt and nickel ions

were also prepared on the base of the same copolymer. Ethanol solutions of
the copolymer with a concentration of 1 g/100 cm^3 were mixed with a double
amount of 0.075M CoCl$_2$ or NiCl$_2$ solution adjusted to pH 1.1 with H$_2$SO$_4$.
The obtained mixture was titrated by 0.5M ammonia solution until pH values
of 5.2 or 5.35 (for cobalt and nickel respectively) were achieved. The re-
sulting complexes of the copolymer with cobalt and nickel were treated and
crosslinked using the same procedure as in the case of copper complexes.

Plots of swelling capacity of the crosslinked sorbents prearranged for the
uptake of cobalt and nickel ions versus the amount of MDAA are shown in
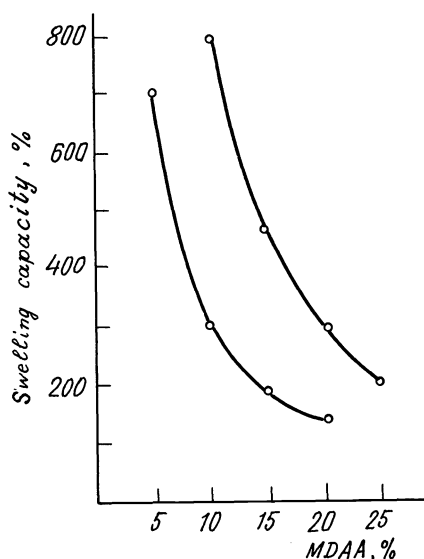Fig. 13.

Fig. 13 Plots of swelling capacity
of crosslinked sorbents prearranged
for the uptake of cobalt (1) and
nickel (2) ions vs the amount of MDAA

Comparison of Figs. 7 & 13 shows that when complexes of the copolymer with
metal ions were crosslinked, a larger amount of MDAA was required in order
to achieve the same value of swelling capacity than in the case of the ini-
tial copolymer. The largest amount of MDAA was required for nickel com-
plexes, less for copper complexes and least of all for cobalt complexes.

For an investigation of sorption properties samples prearranged for the
uptake of copper, cobalt and nickel ions were chosen. They were cross-
linked by MDAA taken in such amounts that the swelling capacities of all
three samples were kept within a range of 280-300%. The MDAA amount taken
for the crosslinking was 20, 17.5 and 10% for nickel, copper, cobalt com-
plexes respectively. Kinetic curves of the uptake of copper, cobalt and
nickel ions are shown in Figs. 14-16. It is seen that sorption capacity
and rate of the uptake on the prearranged sorbents are significantly

higher than those on the sorbents crosslinked by the usual method. In all cases the sorbents exhibit higher selectivity with respect to metals for the ions of which they have been prearranged.
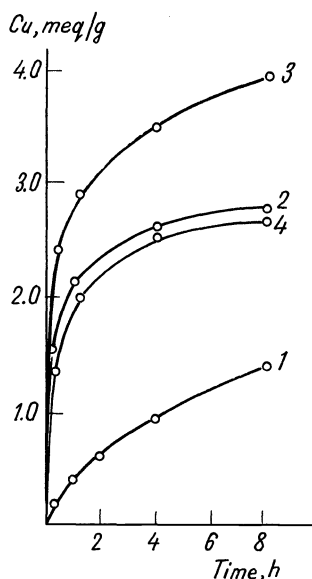
Fig. 14 Kinetic curves of the sorption of copper ions on the sorbents crosslinked by the usual method (1) and prearranged for the uptake of cobalt (2), copper (3) and nickel (4) ions.
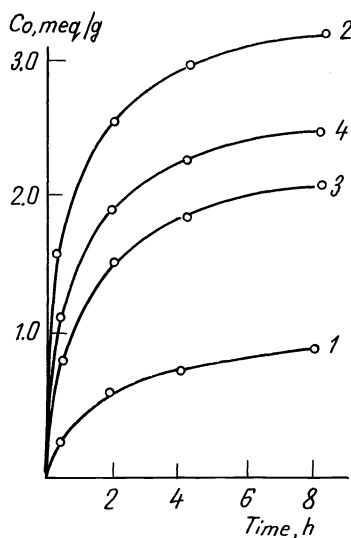
Fig. 15 Kinetic curves of the sorption of cobalt ions on the sorbents crosslinked by the usual method (1) and prearranged for the uptake of cobalt (2), copper (3) and nickel (4) ions.
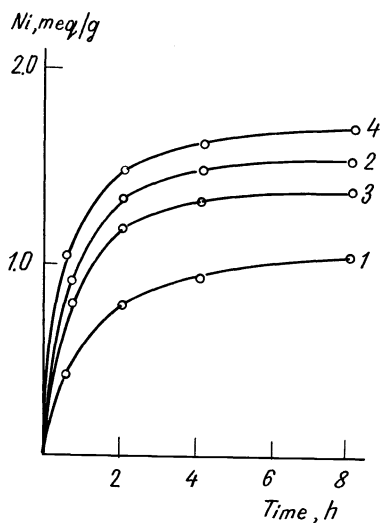
Fig. 16 Kinetic curves of the sorption of nickel ions on the sorbents crosslinked by the usual method (1) and prearranged for the uptake of cobalt (2), copper (3) and nickel (4) ions.

The obtained results show that the sorbents may exhibit different sorption properties depending on the prearrangement of their macromolecules. This is indicative of selectivity of the conformational prearrangement of macromolecules and shows the important role played by fixation of a certain location of functional groups in chemical reactions of polymers.

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