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Synthesis and physicochemical properties of chelating sorbents containing functional groups of *N*-aryl-3-aminopropionic acids

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Two types of chelating sorbents with different types of addition of iminodipropionate groups to a polymeric matrix were synthesized: carboxyethylated aminopolystyrene (sorbent **1**) based on linear polystyrene and carboxyethylaminomethylpolystyrene (sorbent **2**) based on the copolymer of styrene and divinylbenzene. The ionization constants and concentrations of functional groups of the sorbents (exchange capacity for hydrogen ions) were determined. The sorbents exhibit high selectivity for copper(II) ions with the maximum of sorption from ammonia—acetate buffer solutions lying in a range of pH 5.0—7.5. The time needed for a solution of copper(II)—sorbent system with continuous stirring to reach exchange equilibrium is 3.5 and 2 h for sorbents **1** and **2**, respectively. The exchange capacity for copper(II) ions is 2.54 and 0.10 mmol g^{-1}, respectively.

Key words: synthesis, carboxyethylaminopolystyrene, carboxyethylaminomethylpolystyrene, ionization constant, exchange capacity for hydrogen ions, exchange capacity for copper(II) ions, selectivity of ion exchange.

Chelating sorbents are widely used for separating, isolating, and concentrating metal ions as well as for removal of interfering ions from the examined solution at the preliminary stage of analysis.[1—3]

Sorbents containing iminodiacetate groups, for example, Chelex 100, Dowex A-1, ANKB-10, ANKB-35, are used for the group isolation of transition metal ions.[4—6] They sorb ions in a wide pH range rather rapidly and have high sorption capacity; they are hardly suitable for isolating individual transition metal ions, in particular, copper(II).[2,3,7] The known methods for preparation of chelating sorbents are mainly based on two procedures: polymer-analogous transformations of the ready polymers for the purpose of introduction of chelating functional groups and polymerization (polycondensation) of compounds containing the corresponding groups.[1,4,8] The introduction of chelating groups of a new type into the sorbent structure always requires the development of original procedures of synthesis.

The properties of chelating sorbents are mainly determined by the nature of functional groups.[1] Therefore, it is of considerable interest to introduce fragments of the earlier synthesized *N*,*N*-di(2-carboxyethyl)anilines,[9] which are highly selective for copper(II) ions, into the chelating sorbents.

The purpose of the present work is to synthesize two sorbents with different types of addition of iminodipropionate groups to the polymeric matrix and to study their physicochemical and analytical properties.

Results and Discussion

Synthesis of carboxyethylaminopolystyrene. Carboxyethylaminopolystyrene (sorbent **1**) was synthesized by the method of polymer-analogous transformations (Scheme 1).

Crosslinked polystyrene containing 2% divinylbenzene (DVB) is used, as a rule, for the preparation of styrene copolymer sorbents.[2,8] In the present work, we used linear polystyrene for the synthesis, and partial crosslinking of the polymer occurred during both nitration and carboxyethylation.[10]

Fuming nitric acid,[11] its mixture with sulfuric acid,[12] and a mixture of sulfuric acid and potassium nitrate can be used for polystyrene nitration. Performance testing showed that only nitration with fuming nitric acid gave a uniformly nitrated object, which is necessary to predict the sorption properties of the synthesized products.

Nitropolystyrene is reduced with tin—hydrochloric acid[13] and tin chloride—hydrochloric acid mixtures in

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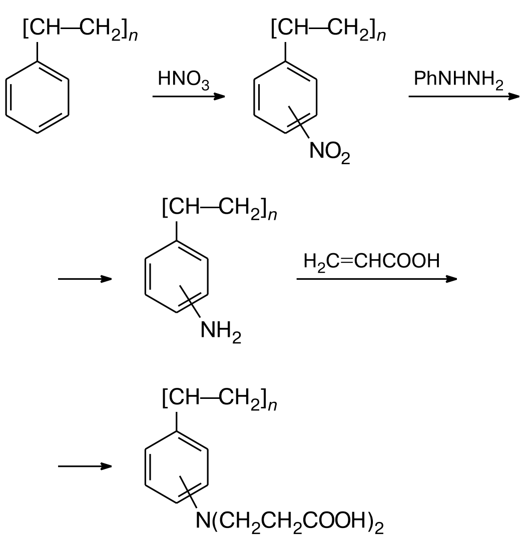
Scheme 1



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water[13] or alcohol[11,14] and sodium polysulfide,[11] sodium dithionite,[15] or phenylhydrazine.[16] Tin(II) chloride in a hydrochloric acid—alcohol mixture is used most frequently for reduction. It is known[13] how difficult is to wash off the reduced product from residues of tin-containing compounds. As our experiments showed, the amount of ash (residue from burning off the polymer samples) is 1—2%, which is inappropriate for subsequent analytical studies. In other cases, the nitro groups are not completely reduced. In the synthesis we used reduction with phenylhydrazine, because a minimum number of unreduced nitro groups is remained after this process.

The carboxyethylation of aromatic amines with acrylic acid can afford both monocarboxyethylated and dicarboxyethylated products.[17,18] We found no published data on aminopolystyrene carboxyethylation. The study of this reaction showed that the carboxyethylation of aminopolystyrene with solutions of acrylic acid in organic solvents (chloroform, benzene, carbon tetrachloride) gave monocarboxyethylation products. When the reaction is carried out in excess acrylic acid, aminopolystyrene with a high degree of carboxyethylation can be obtained.

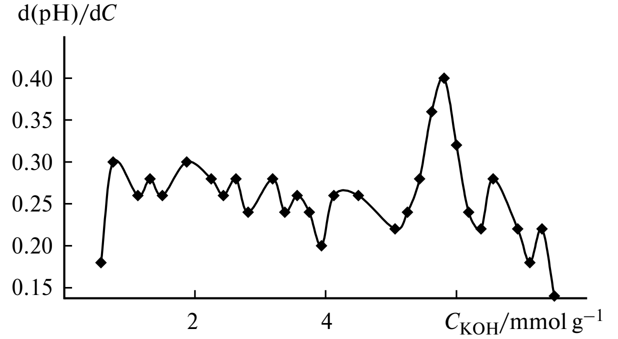


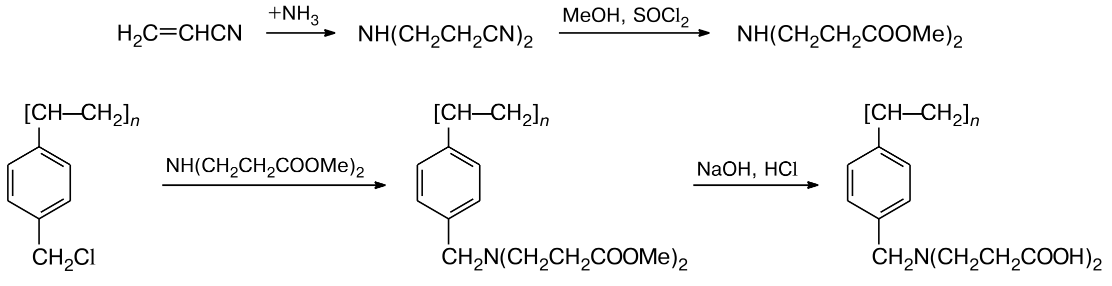
Fig. 1. Differential curve of potentiometric titration of sorbent **1**, $\mu = 0.1$ M KCl, $T = 20\pm2$ °C.

Synthesis of carboxyethylaminomethylpolystyrene. The sorbent containing residues of methyliminodipropionic acid (sorbent **2**) was synthesized by the method of polymer-analogous transformations (Scheme 2).

Two main methods of the synthesis are described. The first method is the interaction of chloromethylated polystyrene with an intermediate of the functional group, *viz.*, dinitrile[19] or dimethyl iminodipropionate.[20—22] The second method includes the transformation of chloromethylated polystyrene into aminomethylpolystyrene followed by the addition of an acrilic acid derivative.[23] It is shown[23] that the variation of the synthesis conditions allows one to prepare sorbents with different exchange capacities (characteristics). In the present work, we used the first method of synthesis.

Acid-base properties of the sorbents. The acid-base properties of the sorbents were studied by direct potentiometric titration in the case of sorbent **1** (Fig. 1) and by the method of individual weighed samples for sorbent **2** (Fig. 2). The titration curves of the both sorbents exhibit one jump, which can be attributed to the ionization of the betainic proton of the amino group.[24] No dissociation of the carboxyl groups was detected by potentiometric measurements.

Scheme 2



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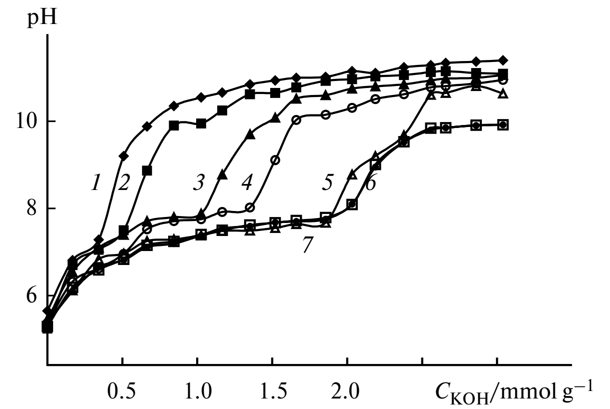

Fig. 2. Curves of potentiometric titration for sorbent **2** obtained using the method of individual weighed samples. Equilibration time is 5 h (*1*), 1 (*2*), 2 (*3*), 3 (*4*), 5 (*5*), 9 (*6*), and 14 days (*7*); $\mu = 0.1$ *M* KCl, $T = 20\pm2$ °C.

In the case of sorbent **2**, the presence of a methylene bridge between the nitrogen atom of the iminodipropionate group and benzene ring increases the basicity of the nitrogen atom, which becomes apparent from the shapes of curves in Figs 1 and 2. The pH jump for sorbent **1** is rather pronounced only when the differential form of the titration curve is used (see Fig. 1), whereas for sorbent **2** the jump is only ~2 pH units (see Fig. 2). Sorbent **2** is a crosslinked polymer and, hence, it is only after 9 days when the titration curve of this sorbent becomes time-independent (see Fig. 2, curve *6*).

The ionization constants were calculated by the Henderson—Hesselbach equation.[1] The values obtained for sorbent **1** are comparable with the ionization constants for the monomeric analog (Table 1). The differences are caused, most likely, by the presence of remaining nitro groups or amino groups not only in the *para*- but also in the *ortho*-position. We could not find the value of the ionization constant for benzyliminodipropionic acid but that for benzyliminodiacetic acid is published.[24]

The static exchange capacities (SEC) for hydrogen atoms for sorbents **1** and **2** determined from the data of potentiometric titration are given in Table 1.

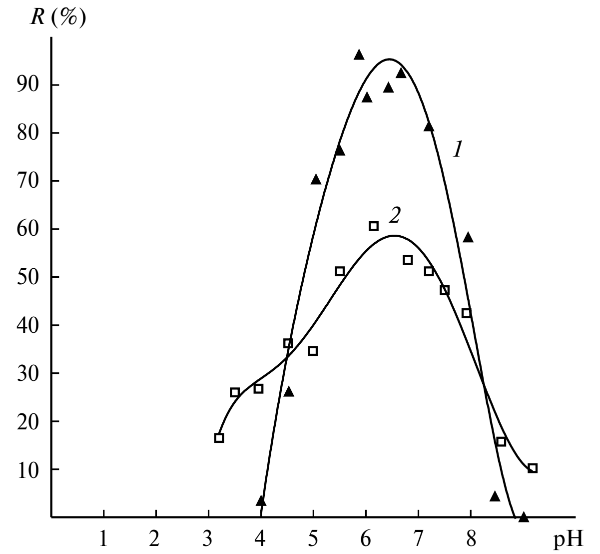

Fig. 3. Plots of the degree of extraction (*R*) of copper(II) ions on sorbents **1** (*1*) and **2** (*2*) *vs.* pH of buffer solutions at $C_{Cu^{II}} = 5\cdot10^{-4}$ (*1*) and $1\cdot10^{-4}$ mol L^{-1} (*2*).

Sorption of copper(II) ions as a function of pH of the solution. As can be seen from the data in Fig. 3 for sorbents **1** and **2**, the maximum sorption from a ammonia—acetate buffer solution is achieved in a range of pH 5.0—7.5. The optimum pH values at which the highest amounts of copper(II) ions are sorbed from solutions are 6.0—6.5 for both sorbents. These pH intervals agree with the optimum pH values of complexation of monomeric arylaminopropionic acids with copper(II) ions (pH 5.5—8.0).[26]

The changes in the IR spectra of the complexed ion-exchange resins as compared to the IR spectra of the initial ion-exchange resins can serve as a direct proof for the formation of a coordination bond between the metal ion and ionogenic groups of the polymer.[8] The IR spectra of sorbent **1** before and after sorption (Table 2) exhibit almost no shift of the absorption band of the carbonyl group and no noticeable signals indicating the formation of the O—Cu bond. The IR spectrum of sorbent **2** manifests a noticeable shift of the absorption band of the carbonyl group from 1721 to 1706 cm^{-1}, which points out a stronger complexation. The same evidence comes from the appearance of the absorption band of the O—Cu bond

Table 1. Selected physicochemical properties of sorbents and monomeric analogs

Compound	pK_1	pK_2	SEC$_{H^+}$/mmol g^{-1}		SEC$_{Cu^{II}}$ /mmol g^{-1}
			Calculation	Experiment	
Sorbent **1**	—	6.49±0.31	5.1—6.58	5.4—7.5	2.54
Sorbent **2**	—	7.54±0.12	1.5	1.7	0.12
Anilinedipropionic acid[25]	3.89	6.41	—	—	—
Benzyliminodiacetic acid[24]	2.24	8.90	—	—	—

Table 2. Wave numbers (ν) of absorption bands in the IR spectra of sorbents **1** and **2** before (I) and after sorption (II)

Sorbent	ν/cm^{-1}			
	C=O		O—Cu	
	I	II	I	II
1	1713	1714	—	—
2	1721	1706	—	452

(see Ref. 8) at 452 cm^{-1}. These facts suggest that the complexes based on arylaliphatic amino acid are stronger than those on the basis of aromatic amino acid. The methylene bridge decreases the interaction of the aromatic ring with a lone electron pair of the nitrogen atom of the functional group and increases its basicity and, hence, the strength of a forming compound with metal ions.[24]

Time dependence of the sorption of copper(II) ions. Equilibrium in a sorbent **1**—copper(II) solution system with continuous stirring of a $5 \cdot 10^{-4}$ *M* solution of copper sulfate is achieved within 3 h (Fig. 4, *a*), while periodic stirring requires from 24 h to 3 days for equilibration. At least 2 h of continuous stirring are necessary to equilibrate a sorbent **2**—copper(II) solution system (Fig. 4, *b*). The amount of sorbed copper(II) ions decreases upon contact of the phases for more than 3 h. The shape of the curve (see Fig. 4, *b*) indicates that copper(II) sorption on sorbent **2** is a multistage process. It is known[27] that on some crosslinked polymeric sorbents transition metal ions first add *via* the so-called "dangling model," when a metal ion is attached to one functional group of the sorbent. Later the "bridge model" can be operative when a metal ion is bound to two functional groups from one chain or from different macromolecular chains. In the last case, the total amount of the metal ion retained by the sorbent decreases. The multistage character of sorption of transition metal ions on complexing ion-exchange resins was mentioned in a monograph.[8] According to published data,[2] the time needed to attain sorption equilibrium on similar chelating sorbents (iminodiacetic acid derivatives) with periodical stirring ranges from 3 to 30 days.

Sorption capacity for copper(II) ions. The sorption isotherms were plotted to determine the sorption capacity. The sorption isotherms of copper on sorbents **1** and **2** are presented in Fig. 5. The shape of the isotherms indicates that the surface of sorbent **1** contains energetically uniform sorption sites and the plots show a classical shape of the Langmuir isotherm. For sorbent **2** we obtained a stepped isotherm, whose shape implies at least two types of sorption sites, and its nature needs additional studies. The static exchange capacity for copper(II) ions determined from the sorption isotherms is 2.54 and 0.10 mmol g^{-1} for sorbents **1** and **2**, respectively. A possible reason for the fact that the exchange capacity for copper ions is lower than that for hydrogen ions is a larger radius of the hydrated copper(II) ion as compared to the radius of the hydrated proton, which results in a worse accessibility of sorption sites in the sorbent grain depth for copper(II) ions.

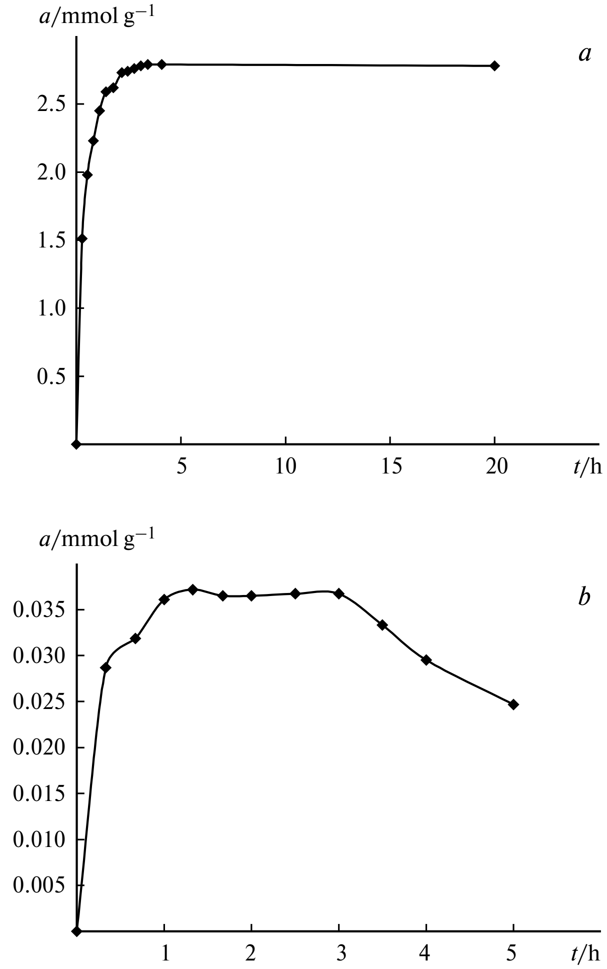

Fig. 4. Plots of the number of copper(II) ions in the phases of sorbent **1** (*a*) and **2** (*b*) *vs.* time at $T = 20 \pm 2$ °C.

Selectivity of the sorbents. The results of studying the sorption of cobalt(II) and nickel(II) ions on sorbent **1** at different pH values of ammonia—acetate buffer solutions are presented in Fig. 6.

The maximum sorption of cobalt(II) ions falls on the pH interval 6.4—7.0, and that for nickel(II) ions lies at pH 7.0—8.5 (see Fig. 3). Equilibration in a sorbent **1**—cobalt(II) or nickel(II) solution requires ~1.5 h; the degree of extraction of nickel(II) is 70—75%, and that of cobalt(II) is 60—65%. Under the same conditions, as already mentioned, the maximum of sorption of copper(II) ions lies in an interval of pH 5.0—6.5 and the degree of extraction is 90—97%. The partition coefficients of copper(II), cobalt(II), and nickel(II) ions for the maximum degree of extraction of these ions on sorbent **1** are

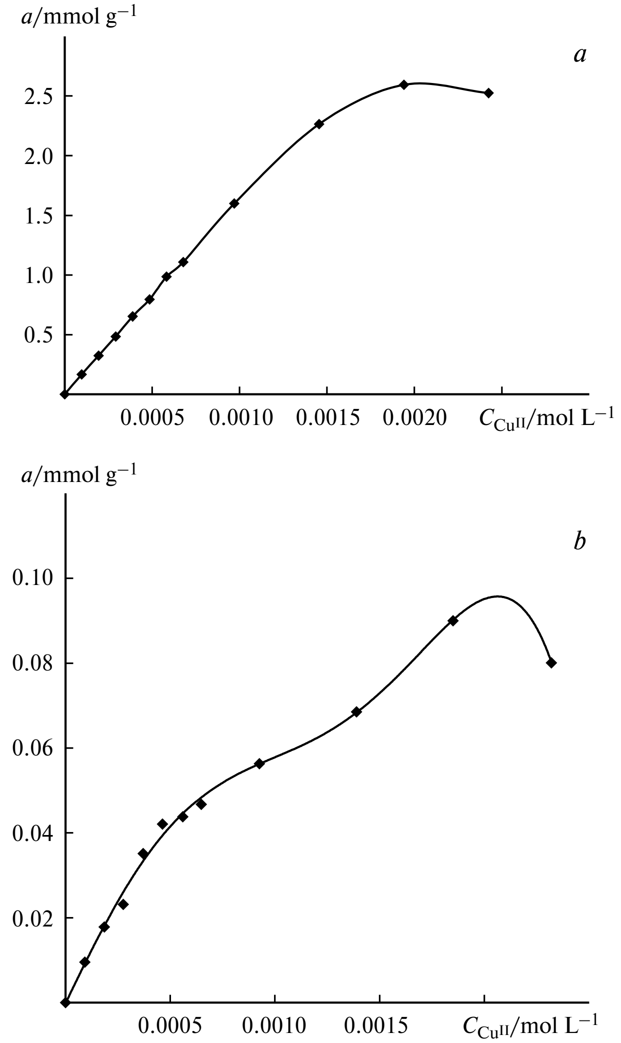

Fig. 5. Sorption isotherms of copper(II) ions on sorbents **1** (*a*) and **2** (*b*) at $T = 20\pm2$ °C.

28.4, 2.0, and 2.4, respectively. Sorbent **2** does not virtually sorb cobalt(II) and nickel(II) ions.

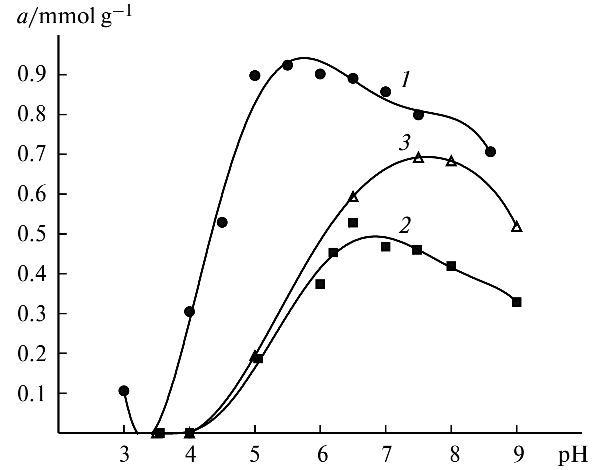

Fig. 6. Plots of the number of copper(II), cobalt(II), and nickel(II) ions in the phase of sorbent **1** *vs.* pH of solutions: ammonia—acetate buffer solutions of copper(II) (*1*), cobalt(II) (*2*), and nickel(II) (*3*) ions; t is 2 h, $T = 20\pm2$ °C. The fraction size is 0.1—0.125 mm.

Thus, sorbent **1** manifests high selectivity for copper(II) ions. The order of selectivity for sorbent **1** is $Cu^{II} > Ni^{II} > Co^{II}$, which is consistent with the Irwing—Williams series for O,N-ligands and with the data on selectivity of the polymeric chelating sorbents containing residues of iminodiacetic acid[1] (Table 3).

In view of substantial differences in the partition coefficients for sorbent **1** it is possible to propose the scheme for separation of Cu^{II} from Co^{II} and Ni^{II} controlling the pH of the solution. At pH = 5.0 only about 20% of Co^{II} and Ni^{II} ions introduced are extracted, whereas extraction of Cu^{II} ions is as high as 90%. Therefore, at pH = 7.0—8.0 the sum of Cu^{II}, Co^{II}, and Ni^{II} ions can be extracted, while pH = 5.0 is suitable for the selective extraction of copper(II) ions.

Although the exchange capacity is low (see Table 1), the absence of sorption of Co^{II} and Ni^{II} ions on sorbent **2** allows us to propose this sorbent for selective extraction

Table 3. Selectivity patterns for chelating sorbents[1]

Sorbent	Matrix*	Functional analytical group	Order of selectivity
Chelex-100	PS-DVB	$—CH_2N(CH_2COOH)_2$	Hg > U^{VI} > Cu > V^V > Pb > Ni > > Cd > Zn > Co > Fe^{II} > Mn^{II} > > Be > Ca > Mg > Ba
GMA—EDMA—IDAA	Copolymer of glycidyl methacrylate with ethylenedimethacrylate	$—N(CH_2COOH)_2$	$Cu^{II} > Fe^{III} > Co^{III} > Al^{III} > Ni^{II} > Mn^{II} > Ag^I > Zn^{II} > Pb^{II} > U^{VI}$
ANKB-2	PS-DVB	$—CH_2N(CH_2COOH)_2$	$Cu^{II} > Ni^{II} > Co^{II} > Zn^{II} > Mn^{II}$
Dowex A-1	PS-DVB	$—CH_2N(CH_2COOH)_2$	$Cr^{III} > Fe^{III} > Pd^{II} > Cu^{II} > Hg^{II} > Ni^{II} > Pb^{II} > Zn^{II} > Co^{II}$

* PS-DVB is the copolymer of styrene and divinylbenzene.

of copper(II) ions. Sorbents with a low exchange capacity (0.01—0.1 mmol g^{-1}) and a small grain size (grain diameter less than 20 μm) find wide use for the preparation of columns in ion chromatography.[28] These characteristics of the sorbent make it possible to extract copper(II) ions from fairly dilute solutions, and a small volume of the eluate can be used for elution.

Experimental

All reagents used were reagent grade. A solution of copper(II) sulfate (0.1 mol L^{-1}) was prepared by the dissolution of a weighed sample of $CuSO_4 \cdot 5H_2O$ in 500 mL of distilled water. An exact concentration of the prepared solution was determined by complexonometric titration with ethylenediaminetetraacetic acid disodium salt (EDTA) in the presence of the murexide indicator.[29] Solutions of cobalt and nickel (1 g L^{-1}) were prepared from pure metals (99.99%) using known procedures,[29] and their solutions of lower concentrations were prepared by the dissolution of the initial solutions directly before experiment.

The influence of the pH of the solution and duration of contact of the phases on the sorption of transition metal ions (Cu^{II}, Co^{II}, and Ni^{II}) was studied and the sorption capacity was determined under static conditions by the method of restricted volume with continuous stirring.[2,3] Acid-base properties of sorbents were studied by direct potentiometric titration and using the method of individual weighed samples.[2]

Ionization constants of functional groups and exchange capacities for hydrogen ions for sorbent **1** were determined by direct potentiometric titration with a 0.01 *M* solution of KOH. After addition of each portion of the titrant, the time required to establish a constant pH value was 30—40 min. For sorbent **2**, the ionization constants of functional groups and exchange capacity values for hydrogen ions were determined by the method of individual weighed samples. Weighed samples of the sorbent (0.03 g) were placed in solutions with a specified pH value (necessary pH values were set using a KOH solution) and stored to equilibration. To control equilibration, portions of the solution above the sorbent were taken periodically and the pH was measured.

The dependence of the sorption of transition metal ions (Cu^{II}, Co^{II}, and Ni^{II}) on pH of the solution was studied under static conditions by the method of restricted volume with continuous stirring. Solutions with the concentration $n \cdot 10^{-4}$ mol L^{-1} were used for sorption in the interval of pH 3.0—9.0. Specifically acetate (pH 3.2), ammonia—acetate (pH 3.5—8.0), and ammonia (pH 8.5—9.0) buffer solutions were applied.

Sorption isotherms were obtained under static conditions with continuous stirring for 3.5 h (sorbent **1**) and 2 h (sorbent **2**) at pH 6.0—7.0 from solutions with the content of copper(II) ions from $1.0 \cdot 10^{-4}$ to $2.5 \cdot 10^{-3}$ mol L^{-1}. The amount of the sorbed metal ion was determined from the difference of concentrations of copper(II) ions in the solution above the sorbent before and after sorption.

The concentration of metal ions in the solution above the sorbent before and after sorption was determined by spectrophotometry using 4-(2-pyridylazo)resorcinol.[30] The absorbance of solutions was measured on an SF-26 spectrophotometer at λ_{max} = 495 nm and l = 1.0 cm, using a blank entry as a reference solution. The pH value was monitored on an EV-74 ionometer equipped with glass (ESL-43-07) and saturated Ag/AgCl (EVL-1M3.1) electrodes at 20±1 °C and the ionic strength of the solution μ = 0.1 mol L^{-1} (KCl). Standard buffer solutions were used for calibration of the ionomer, and a carbonate-free solution of potassium hydroxide was used as the titrant.

Sorbents were synthesized by the method of polymer-analogous transformations and identified by elemental analysis and IR spectroscopy at the Laboratory of Oligomers of the Institute of Organic Synthesis (Ural Branch of the Russian Academy of Sciences). Diffuse reflectance IR spectra were obtained on a Perkin—Elmer Spectrum-One spectrometer. Elemental analysis was carried out on a Perkin—Elmer automated analyzer.

Synthesis of sorbent 1. ***Nitration of polystyrene.*** Finely crushed polystyrene (5 g) was slowly added to fuming nitric acid (22 mL, d = 1.5 g cm^{-3}) with stirring and cooling in a water bath. A yellow viscous solution that formed was heated for 1 h at 60 °C and poured into 1 L of water. The resulting solid mixture was crushed in a mortar, transferred onto a filter, washed with water to the neutral reaction, and dried *in vacuo* to constant weight. The yield was 7.5 g. Found (%): C, 60.60; H, 4.03; N, 9.57. Calculated (%): C, 60.68; H, 4.81; N, 9.55. The average degree of nitration per styrene cycle was 1.02.

Reduction of nitropolystyrene. Phenylhydrazine (50 mL) was placed in a flask equipped with a stirrer, a thermometer, a condenser, and a tube for argon supply. The flask was heated to 200 °C. Then nitropolystyrene (2 g) was added by small portions at the same temperature with stirring; during this process benzene and water were distilled off and nitropolystyrene was dissolved. The reaction mixture was heated at 200 °C for 1 h, and excess phenylhydrazine was distilled off *in vacuo* at the temperature of the bath not higher than 200 °C (90% phenylhydrazine were regenerated). Diethyl ether (100 mL) was poured to the viscous mixture that formed in the same flask, and the resulting mixture was periodically stirred until a solid mixture was formed, which was transferred onto a paper filter and extracted with hot diethyl ether for 30 h. The product was dried *in vacuo* and crushed in a mortar. The yield was 1.27 g. Found (%): C, 75.80; H, 7.55; N, 12.34. Calculated (%): C, 75.80; H, 7.41; N, 12.34. The ratio $NO_2 : NH_2$ was 3 : 7.

Carboxyethylation of aminopolystyrene. A mixture of aminopolystyrene (5 g) and acrylic acid (14 mL) was heated with stirring in a water bath for 5 h, cooled, filtered, and washed with water on the filter to the neutral reaction. The solid residue was transferred back to the flask, and potassium hydroxide (6 g) and distilled water (25 mL) were added. The mixture was boiled for 15 min. Then the contents of the flask was placed on a filter and washed with water to the neutral reaction. The product was dried *in vacuo*. The yield was 5.05 g. Found (%): C, 43.21; H, 5.98; N, 4.34. Calculated (%): C, 43.20; H, 5.98; N, 4.35. Two carboxyl groups fall per amino group (degree of carboxyethylation).

IR spectrum of sorbent **1**, ν/cm^{-1}: 2700—2900 (N—H); 1715 (C=O); 1600 (COO^-); 1370 (COO^-); 1330 (N—H).[31]

Prior to work the sorbent was transformed into the H^+ form with a 0.1 *M* solution of HCl followed by washing with water to remove chloride ions (test with $AgNO_3$).

Synthesis of sorbent 2. ***Preparation of iminodipropionitrile.*** A 75% aqueous solution of ammonia (18.8 mL) was added to acrilonitrile (33.25 mL). The reaction mixture was stirred and left to stand for 1 day. Then the two-phase liquid was distilled *in vacuo*, and the fraction with b.p. 165 °C (160 Torr) was collected. The yield was 13.3 g.

Synthesis of dimethyl iminodipropionate hydrochloride. Methanol (89.65 mL) and iminodipropionitrile (12.3 g) were placed in a flask equipped with a mechanical stirrer and a dropping funnel. The mixture was cooled down to 15 °C, and thionyl chloride (28.8 mL) was added with such a rate that the temperature of the reaction mixture would not exceed 15—20 °C. After the whole portion of thionyl chloride was added, the reaction mixture was stored at the same temperature for 18 h and then heated to boiling and kept boiling for 1.5 h. After 1 day, the reaction mixture was heated again, and a precipitate of ammonium chloride that formed was filtered off from the hot solution. The filtrate was cooled down, and methanol was distilled off *in vacuo*. The residue was dried *in vacuo* to constant weight. The yield was 16.27 g.

Introduction of fragments of methyliminodipropionic acid. A mixture of the chloromethylated styrene copolymer with 2% *p*-divinylbenzene (chlorine content 1.0—1.1 mg-equiv g^{-1}) (9.5 g), dimethyl iminodipropionate hydrochloride (8.135 g), and a solution of metallic sodium (0.85 g) in methanol (15 mL) was stored for 15 h on boiling (temperature 70 °C) in a water bath. The product was cooled down, filtered, and washed with methanol (200 mL). Methanol (12 mL), water (12 mL), and NaOH (2.9 g) were added to the grafted product, and the mixture was heated for 5 h at 55 °C. The obtained polymer was washed with water, 5% HCl (to pH < 7), and water again to remove chloride ions (test with $AgNO_3$). The sorbent was dried at 60 °C. The yield was 9.8 g. Found (%): C, 83.61; H, 7.88; N, 1.01. Calculated (%): C, 83.31; H, 7.81; N, 1.09.

IR spectrum of sorbent **2**, ν/cm^{-1}: 1722 (C=O).[31]

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