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SORPTION OF PROTONS AND HEAVY METAL IONS FROM AQUEOUS SOLUTIONS BY THREE NEW RESINS HAVING A POLY (AMIDO-AMINE) STRUCTURE

Three new resins having a poly(amido-amine) structure have been synthesized in order to obtain efficient sorbents for several metal ions. Their active constituent is an amino-acid, i.e., glycine, β -alanine or 4-aminobutanoic acid. The protonation reactions have been investigated with a potentiometric technique and found to be predictable on the basis of the protonation behaviour of proper monomeric models. The sorption of many metal ions from aqueous solutions was studied at different acidities: qualitative predictions based on the structure of the chelating active constituents were experimentally verified, but the values of sorption coefficients depended on the nature and concentration of counterions in aqueous phase. Cu (II), Ni (II), Co (II), Zn (II), Cr (III), Fe (III) and uranyl ions can be quantitatively sorbed from neutral solutions, and eluted with 0.1 M hydrochloric acid.

1. INTRODUCTION

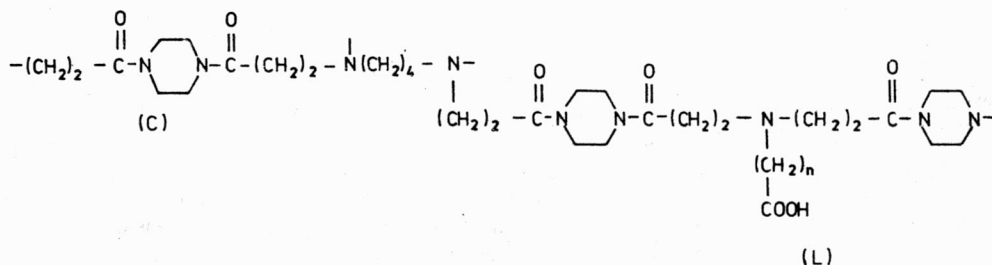
In some previous papers [1]–[5] a new class of chelating resins, named poly (amido-amines), has been described. Among many other interesting properties, they present a very peculiar behaviour when the sorption of protons and metal ions from aqueous solutions is considered. Their repeating units act independently of each other, as though they were small molecules in solution, and the protonation and complex formation constants in 0.1 M sodium chloride are very similar to those of the corresponding hydrosoluble polyelectrolytes and monomeric models which in some instances have been synthesized [1]–[3].

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These properties are useful in view of practical applications for sorbing heavy metal ions from aqueous solutions. Indeed, the best conditions for sorption, elution, preconcentration and separation can be calculated from the capacity of the resin, and protonation and complex formation constants in aqueous solution of the corresponding monomeric analogues, which can be either found in the literature, or easily and accurately determined with the well-established standard methods.

However, the poly(amido-aminic) resins so far synthesized are capable of sorbing only a few metal ions. Thus three new resins of the poly(amido-amine) family have been synthesized, in which the structural constituent which is expected to be complex metal ions (L) is an amino-acid (glycine, β -alanine and 4-aminobutanoic acid) instead of an amine. They have the following structure:

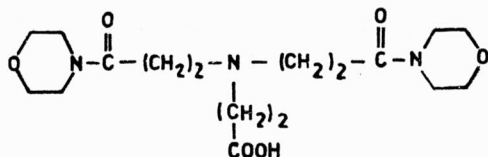


The symbols C and L indicate the cross-linking and the linear constituents, respectively.

The three resins are indicated with the following symbols: for $n = 1$, GLY; for $n = 2$, ALA; for $n = 3$, GABA.

The molar compositions (in mmoles of L and C per gram of dry resin) are: L = 1.596 and C = 1.198 for GLY; L = 1.562 and C = 1.172 for ALA; L = 1.517 and C = 1.138 for GABA.

The present research was undertaken with the aim of finding out new resins with better properties towards sorption of metal ions, for instance higher sorption coefficients or better selectivities. Besides, we wanted to confirm that the behaviour described above is typical of the poly(amido-amines), independently of the structure of the active part L. To check this point, a monomeric model of ALA, ALAm, was synthesized as well. It has the following structure:



2. EXPERIMENTAL METHODS AND CALCULATION

2.1. MATERIALS

Synthesis of the resins. They have been prepared by poly-addition of 0.0062 moles of the proper amino-acid, 0.0046 moles of 1,4-diamino-butane (as cross-linking agent) and 0.0155 moles of 1,4-bisacryloylpiperazine, prepared as previously described [6], mixed with 5 cm³ of water. The reaction mixtures were left at room temperature for 2 days, after which the gelly products were purified, dried at room temperature and controlled as previously described [1].

Synthesis of ALAm. β -alanine and N-acryloylmorpholine (1 M methanolic solution) [7] are mixed at 1 to 2 molar ratio and maintained at room temperature for 1 week with occasional stirring. Isolation, purification and characterization were carried out as previously reported [1] for the same kind of monomers.

All other reagents, obtained from C. Erba, were of analytical grade, RPE or RSE. Deionized water was further purified by redistillation in a quartz apparatus.

2.2. APPARATUS

Potentiometric titrations were carried out at 25°, with an Orion Research model 701A digital Ionalyzer, equipped with an Orion Research 810100 Ross type pH electrode, and a Wilhelm type reference electrode with a fritted glass junction, to prevent the resin from forming the salt bridge. This cell was standardized before each titration by determining E_0 and E_j using the method described in a previous paper [8]. Other experimental details have been previously reported [1].

Determinations of metal concentrations in the aqueous phase were made by atomic absorption spectrometry, either in air-acetylene flame or by furnace atomization using Spectrophotometer IL 551 and standard techniques.

2.3. PROTONATION OF THE RESIN

The protonation reactions of the resins have been investigated by titrating with standard acid or base a weighed amount of the considered resin suspended in a known volume of aqueous solution at the proper ionic composition. The experimental details and the calculation methods have been previously described [1].

2.4. SORPTION OF METAL IONS

The sorption of metal ions at concentrations lower than $5 \cdot 10^{-4}M$, which cannot be detected by acid-base titration, was studied by determining directly the concent-

ration of the metal ion in solution at different acidities. The pH values, adjusted by adding to the suspension small amounts of concentrated acid or base, were determined potentiometrically. When the equilibrium was reached, the resin was separated by centrifuging and a measured volume of clear solution was analyzed for its metal concentration ($[M]$) by atomic absorption spectrometry. The fraction of sorbed metal ion (z) is given by the following relationship

$$z = \frac{\text{(mmoles of sorbed M)}}{\text{(mmoles of total M)}} = \frac{1}{1 + \frac{[H] V}{K_s [HL]_r w}} \quad (1)$$

where V is the volume of the aqueous phase, and w indicates the grams of dry resin. The concentrations are indicated by the symbols of the species in square brackets. Those in the resin phase, indicated by the subscript r , are in mmoles per gram of dry resin [1], while those in aqueous solution are in moles per liter (M). K_s is the equilibrium constant of the sorption reaction



3. RESULTS AND DISCUSSION

3.1. PROTONATION

Protonation and deprotonation of the three resins here considered are very slow processes, as each titration point requires at least one hour to reach the equilibrium. This is probably due to the fact that the resins are tightly cross-linked. Thus a titration curve of about 30 points requires more than a day, which causes the precision of the calculated protonation constants to be rather poor. As an example, a titration curve of resin ALA is reported in fig. 1. It is evident that one proton for each linear constituent L of the resin is titrated in the acidic part of the curve, while one proton for each linear and two protons for each cross-linking component C are titrated in the more basic portion. The same holds for GABA, while GLY undergoes only a partial second protonation at the pH values higher than about 2, here considered.

In fig. 2 the protonation curves of ALA and GABA are shown. They report the average number of protons (n) versus the pH of the solution and are relative to

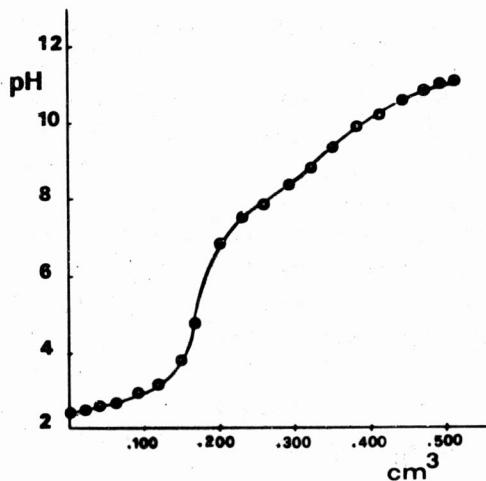


Fig. 1. Titration curve of ALA in 0.1 M sodium chloride

Titrant, 1.02 M NaOH; volume of aqueous solution, $V = 30.3 \text{ cm}^3$; amount of dry resin, $w = 0.06070 \text{ g}$; analytical excess of acidity present before any titrant addition, 0.3233 meq

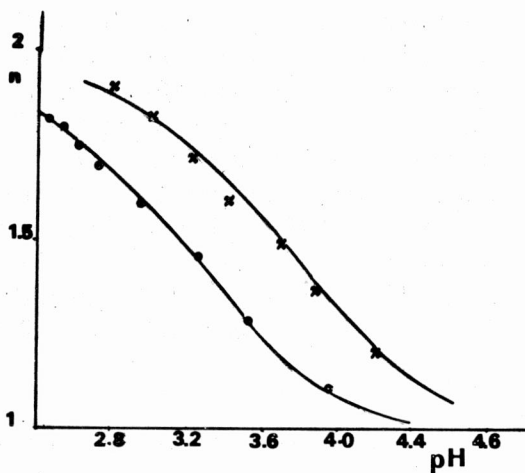


Fig. 2. Protonation curves of ALA and GABA (second protonation of L) in 0.1 M NaCl

o — ALA: protonation curve obtained from the titration reported in fig. 1. Continuous curve calculated with $\log K_{2,L} = 3.16$
 x — GABA: $w = 0.04351 \text{ g}$, $V = 27.9 \text{ cm}^3$. Continuous curve calculated with $\log K_{2,L} = 3.70$

the second protonation of each repeating constituent L, which takes place in the acidic part of the titration. The curves acceptably fit to those calculated with $\log K_{2,L} = 3.16$ and $\log K_{2,L} = 3.70$ for ALA and GABA, respectively. The coefficients are those of the reaction



$$K_{2,L} = \frac{[\text{H}_2\text{L}]_r}{[\text{HL}]_r [\text{H}]}$$

The good fitting demonstrates that the protonation of each monomeric L unit is independent of that of the other monomeric units constituting the polymeric chain. Thus the resins considered here present also the very peculiar behaviour of the other poly(amido-amines) so far studied.

This straightforward treatment cannot be applied to the basic part of the titration curve, because the first three protonation reactions are partially or totally overlapped. Instead, the three protonation coefficients have been estimated, and then refined with the program Miniquad [9]. This was possible because the coefficients are independent of the protonation degree. The values obtained are expected to be much less accurate than $K_{2,L}$, particularly because it is impossible to obtain a sufficiently large number of titration points at the required accuracy, due to the slowness of the protonation reaction.

The results are reported in table 1, together with the protonation constants of the amino acids having a structure similar to L. The protonation constants of the carboxylic groups are similar to those of the resins, while those of the aminic nitrogen ($K_{1,L}$) are higher. This can be ascribed to the fact that in the resins the aminic nitrogen is triply substituted and in a position near to two amidic groups which reduce its electron density. Indeed, the protonation constants of a more realistic model of ALA, ALAm, which are also reported in table 1, are in better agreement with those calculated for the resin ALA. This confirms that the observed difference was mainly due to structural reasons, and that even in the case of poly(amido-amino acidic) resins a tight similarity exists between the protonation of the resin and the corresponding hydrosoluble monomers.

Table 1
Observed protonation constants of the resins in 0.1 M NaCl
at 25°C

Resin	Reaction	$\log K_{j,L}$ or $\log K_{j,c}^*$	$\log K$ of the corresponding amino acid
GLY	$L_r + H \leftrightarrow HL_r$	6.7	9.60 ^a
	$HL_r + H \leftrightarrow H_2L_r$	1.82(4)	2.34
	$C_r + H \leftrightarrow HC_r$	9.0	
	$HC_r + H \leftrightarrow H_2C_r$	8.3	
ALA	$L_r + H \leftrightarrow HL_r$	7.5	10.21 ^b
	$HL_r + H \leftrightarrow H_2L_r$	3.16(3)	3.52
	$C_r + H \leftrightarrow HC_r$	9.8	
	$HC_r + H \leftrightarrow H_2C_r$	8.4	
GABA	$L_r + H \leftrightarrow HL_r$	7.0	10.26 ^c
	$HL_r + H \leftrightarrow H_2L_r$	3.7(3)	4.04
	$C_r + H \leftrightarrow HC_r$	9.2	
	$HC_r + H \leftrightarrow H_2C_r$	8.4	
ALAm	$L + H \leftrightarrow HL$	8.13(2)	
	$HL + H \leftrightarrow H_2L$	3.47(2)	

* The uncertainty is of 1 in the last figure, if not differently specified by a figure in round brackets.

^a KROLL H., J. Amer. Chem. Soc., 74, 2034 (1932). $I = 0.1$ M KCl, $T = 25^\circ\text{C}$:

^b LEUSSING D. L., HANNA E. M., J. Amer. Chem. Soc., 88, 693 (1966). $I = 0.5$ M KCl, $T = 25^\circ\text{C}$.

^c RAMANUJAM V. V., RENGARAJ K., Indian J. Chem., 19A, 382 (1980). $I = 0.1$ M NaClO₄, $T = 30^\circ\text{C}$.

3.2. SORPTION OF METAL IONS

By considering that GLY, ALA and GABA are able to form five-, six- and seven-membered chelation rings, respectively, it is expected that GLY is the best sorbing agent among those here considered. This view is supported by the fact that

the corresponding amino acids, glycine, β -alanine and 4-aminobutanoic acid, have complexing abilities which decrease by passing from glycine to 4-aminobutanoic acid.

In practice it has been verified that the same holds for the resins: GLY is able to sorb metal ions from more acidic solutions than ALA, while GABA does not sorb metal ions from the aqueous solutions here considered, at pH values lower than about seven. More basic solutions were not considered in order to avoid problems arising from the hydrolysis of metal ions.

The sorption coefficients (calculated by equation (1)) of GLY and ALA with copper (II) in 0.1 M sodium chloride are reported in table 2, together with the corresponding complex formation constant of ALAm. This is considerably higher than K_s of ALA. The same trend on passing from the model monomer to the resin was noticed also for other poly(amino-aminic) resins, for example RN_2 [4], and was attributed to the rigidity of the resin.

Table 2

Exchange coefficients of copper (II) (eq. (1)) at 25°C

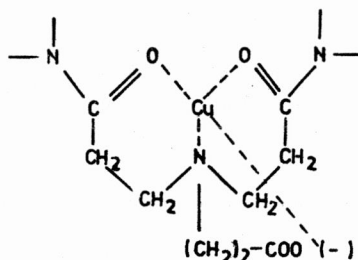
Resin	$\log K_s$ 0.1 M NaCl	$\log K_s$ 0.1 M acetate	$\log K$ of the monomeric analogue*	$\log K$ of the corresponding amino acid*
GLY	-.78(6)	0.4		-1.33 ^a
ALA	-3.65(5)	-2.4	-2.07(2)	-3.16 ^b

* K is the equilibrium constant of the reaction $M+HL \leftrightarrow ML+H$.

^a SIEGEL H., GRIESSER G., Helv. Chim. Acta, 50, 1842 (1967). $I = 0.1$ M $NaClO_4$, $T = 25^\circ C$.

^b SCHARMA V. S., MATHUR H. B., KILKARNI P. S., Indian J. Chem., 3, 146, $I = 0.2$ M KCl, $T = 25^\circ C$.

The fact that ALAm forms with copper (II) complexes more stable than β -alanine (its complex formation constants are also reported in table 2), can be ascribed to the presence of the two amidic carbonylic groups, which occupy further positions in the coordination sphere of copper (II):



The sorption of other metal ions by GLY is shown in figures 3 and 4. It has been studied in acetate or chloroacetate solutions, which are widely used as efficient buffers. The relative positions of the curves are in agreement with the order of the stability constants of the complexes formed in aqueous solution by glycine with the considered metal ions [10].

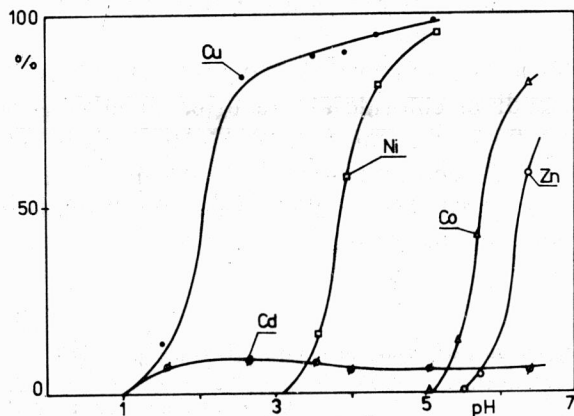


Fig. 3. Sorption curves of some metal ions by GLY
 Aqueous solutions: 0.1 M chloroacetate (up to pH = 3.8) or acetate (pH higher than 3.8)
 Cu_3 (●), Ni (□), Co (△), Zn (○), Cd (∅)
 $V = 50 \text{ cm}^3$, $w = 0.22183 \text{ g}$, total concentration of metal $2 \times 10^{-4} \text{ M}$
 Continuous curves interpolated from the experimental points

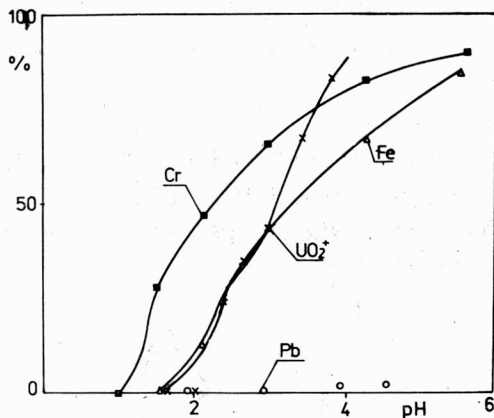


Fig. 4. Sorption curves of some metal ions by GLY
 Aqueous solutions: chloroacetate (up to pH = 3.8) or acetate (pH higher than 3.8)
 Cr (■), Fe (△), Pb (○)
 $V = 50 \text{ cm}^3$, $w = 0.10110 \text{ g}$, total metal ion concentration $2 \times 10^{-4} \text{ M}$
 UO_2^{2+} (χ): $V = 10 \text{ cm}^3$, $w = 0.05050 \text{ g}$, total metal concentration $2 \times 10^{-4} \text{ M}$
 Continuous curves interpolated from the experimental points

An important difference is that neither lead nor cadmium are sorbed, despite the fact that their stability constants with glycine in aqueous solutions are similar to those of cobalt and zinc. This can be ascribed either to the fact that the complexes of these ions are not stabilized by the carbonylic groups near the amino acid, or to their large dimensions, towards which the resin acts like a sieve.

Only copper (II) and nickel (II) are at least partially sorbed from chloroacetate and acetate solutions by ALA. This confirms the qualitative predictions made on the basis of the behaviour in aqueous solution.

The observed exchange coefficients of copper (II) from acetate solutions (equation (1)) are $\log K_s = +0.08(5)$ and $\log K_s = -3.44(5)$ for GLY and ALA, respectively. However, in this case the complexation of metal ions by acetate or chloroacetate, which are present at the relatively high concentration of 0.1 M, must be taken into account. Thus

$$z = \frac{[\text{ML}]_r w}{[\text{ML}]_r w + ([\text{M}] + [\text{MAc}]) V}$$

$$= \frac{1}{1 + \frac{[\text{H}] V}{K_s [\text{HL}]_r w} \left(1 + \frac{K c_{\text{Ac}}}{1 + K_{\text{Ac}} [\text{H}]} \right)}$$
(4)

where MAc is the complex metal ion-acetate (or chloroacetate) in aqueous solution, whose formation constant is

$$K = \frac{[\text{MAc}]}{[\text{M}] [\text{Ac}]}$$

c_{Ac} is the total concentration of acetate (or chloroacetate) and K_{Ac} is the protonation constant of acetate (or chloroacetate). These constants can be found in the literature [10]. Thus the coefficient obtained by direct applying of eq. (1) is

$$K_{\text{so}} = \frac{K_s}{1 + \frac{K c_{\text{Ac}}}{1 + K_{\text{Ac}} [\text{H}]}}$$

The true values of K_s are therefore +0.42 and -2.44, respectively, i.e., considerably higher than those obtained in chloride solution. This effect of the ionic medium composition is unexpected on the basis of structural considerations and requires further investigations.

4. CONCLUSIONS

Among many resins of the poly (amido-amines) family which have been so far synthesized and studied [1]–[5], [11], GLY is the one which can sorb copper

and other metal ions from the most acidic solutions. Even the previously studied resin RA [11], which has an exchange coefficient as high as $\log K_s = -0.2$ for copper (II), is less efficient than GLY. Indeed, its second protonation constant ($\log K = 4.25$) is so high that protons compete with copper (II) in acidic solutions. Thus GLY can be used to sorb many metal ions (copper, nickel, uranyl, cobalt, zinc, chromium and iron) from aqueous solutions of nearly neutral pH and to elute them by increasing the acidity.

Data reported in figures 3 and 4 demonstrate that it is possible to separate the ions here considered, either by selective sorption or elution, merely by proper selection of the acidity of the aqueous solution.

It has been proved that metal ions at concentrations as low as 1×10^{-6} M can be quantitatively sorbed from aqueous solutions by the batch technique. After separation from the resin, they are eluted quantitatively at pH = 1. At this step, they can be concentrated by a factor of 20. As an example, some results are reported in table 3.

Table 3

Sorption and elution of copper (II) and nickel (II) by GLY

Original concentration of ions (in molarity) ^a	Concentration of ions (in molarity) after sorption ^b		Concentration of ions (in molarity) in the eluting solution 0.1 M HCl ^c	
	Cu	Ni	Cu	Ni
1×10^{-5}	$< 2 \times 10^{-8}$	$< 2 \times 10^{-8}$	9.6×10^{-5}	1.01×10^{-4}
5×10^{-6}	$< 2 \times 10^{-8}$	$< 2 \times 10^{-8}$	5.0×10^{-5}	4.9×10^{-5}
1×10^{-6}	$< 2 \times 10^{-8}$	$< 2 \times 10^{-8}$	1.1×10^{-5}	1.3×10^{-5}

^a The original solution consists of 100 cm³ of triply distilled water containing a known concentration of metal ion.

^b The original solution was stirred with 0.3 g of resin for 1 h. The resin was separated and washed by centrifuging, and the concentration of the metal ions still present in the solution determined by ETE-AAS.

^c 10 cm³ of 0.1 M HCl (prepared from the RSE reagent C. Erba, containing less than 0.005 ppm of copper) are added to the resin, and stirred for 1 h. Metal ions concentrations are then determined in the solution phase by AAS. The reported values are the average of three independent determinations.

ACKNOWLEDGMENT

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SORPCJA PROTONÓW I JONÓW METALI CIĘŻKICH Z WODNYCH ROZTWORÓW NA TRZECH NOWYCH ŻYWICACH O STRUKTURZE POLY(AMIDO-AMINOWEJ)

Przeprowadzono syntezę trzech nowych żywic o strukturze poly(amido-aminowej). Otrzymane żywice są efektywnymi sorbentami jonów kilku metali. Składnikiem aktywnym tych żywic jest kwas aminowy, tzn. glicyna, β -alanina lub kwas 4-aminomasłowy. Reakcje przemiany protolitycznej zbadano za pomocą techniki potencjometrycznej i stwierdzono, że można je przewidzieć na podstawie przebiegu reakcji dla odpowiednich monomerycznych modeli. Zbadano proces sorpcji jonów wielu metali z roztworów wodnych w obecności różnych kwasów. Przewidywania dotyczące analizy jakościowej, oparte na strukturze aktywnych składników chelatujących, zostały doświadczalnie zweryfikowane, ale jednocześnie stwierdzono, że wartości współczynników sorpcji zależą od charakteru i stężenia przeciwjonów w fazie wodnej. Następujące jony: Cu(II), Ni(II), Co(II), Zn(II), Cr(III), Fe(III) i jon uranylu mogą być ilościowo sorbowane z obojętnych roztworów i wymywane za pomocą 0.1 M kwasu chlorowodorowego.

СОРБЦИЯ ПРОТОНОВ И ИОНОВ ТЯЖЕЛЫХ МЕТАЛЛОВ ИЗ ВОДНЫХ РАСТВОРОВ НА ТРЕХ НОВЫХ СМОЛАХ ПОЛИ(АМИДО-АМИННОЙ) СТРУКТУРЫ

Представлен синтез трех новых смол поли(амидо-аминной) структуры. Полученные смолы являются эффективными сорбентами по отношению к ионам нескольких металлов. Активным компонентом этих смол является аминная кислота, т.е. глицин, β -аланин или 4-аминомасляная кислота. Реакции протолитического превращения были исследованы при помощи потенциометрической техники и было установлено, что их можно прогнозировать на основе хода реакции для соответствующих мономерных моделей. Исследован процесс сорбции ионов многих металлов из

водных растворов в присутствии разных кислот. Прогнозы, касающиеся качественного анализа, базирующие на структуре активных хелатирующих компонентов, были экспериментально проверены, но одновременно было установлено, что значения коэффициентов сорбции зависят от характера и концентрации анионов в водной фазе. Следующие ионы: Cu(II), Ni(II), Co(II), Zn(II), Cr(III), Fe(III) и ион уранила могут количественно сорбироваться из нейтральных растворов и вымываться при помощи 0,1 M соляной кислоты.