Acrylic Weak-Base Anion Exchangers and Their Behaviors in the Retention Process of Some Heavy-Metal Cations

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ABSTRACT: Two macroporous acrylonitrile/10% vinyl acetate/10% divinylbenzene copolymers as beads were obtained by the aqueous suspension copolymerization of the three comonomers in the presence of toluene as a diluent, which was used in two different amounts. These copolymers were chemically modified by their reactions with ethylenediamine, diethylenetriamine, and triethylenetetramine in the presence of water when the aminolysis–hydrolysis reaction of the nitrile groups and the hydrolysis reaction of the acetate groups occurred. From these reactions, weak-base anion exchangers with high ion-exchange capacities, between 1.6 and 2.2 mequiv/mL and 6.5 and 10.5 mequiv/g, were obtained. For these anion exchangers, the behaviors in the retention processes of the Ni(II), Cd(II), and Pb(II) cations were evaluated with the bath method. All the resins exhibited retention properties, but the retained amounts of the metal cations differed as a function of the resin and cation nature. Thus, the resin from the reaction with triethylenetetramine of the copolymer obtained in the presence of a larger amount of toluene could be considered the most suitable sorbent for the three metal cations, especially for Ni(II). Its maximum retention capacity for this cation was 2.67 mequiv/g of dried resin. From the noncompetitive and competitive retentions was observed the following selectivity order: Ni(II) > Cd(II) > Pb(II). The retention took place by the chelating processes between the functional groups with the ligand role, especially free amine groups, and metal cations. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 930–938, 2005

Key words: ion exchangers; metal-polymer complexes; resins

INTRODUCTION

The removal and separation of metal ions with their retention process by solid supports are technological challenges for industrial and environmental applications.

Natural substances such as humic acids, polysaccharides, and clay have the ability to complex metal cations, but the synthetic chelating resins represent the most important category of substances for the removal of metal cations because they have structures with higher hydrolytic and oxidative stabilities as well as better defined physical features. These resins consist of a polymerization or polycondensation three-dimensional network, a so-called matrix, carrying functional groups with a ligand role.

The polycondensation polymers can easily undergo hydrolytic breaking reactions, whereas the polymerization ones have higher chemical stability; therefore, the polymerization matrices are preferred over polycondensation ones.

The ligand groups are those containing atoms able to form donor–acceptor bonds, which represent the base of the functional-group/metal complexes, namely, synthetic chelating resins. At present, a large number of resins incorporating ligand groups, such as aminocarboxylic acids, hydroxamic acids, oximes, pyridine carboxylic acids, hydrazides, arsonic acids, phosphonic acids, dithiocarbamates, thiols, Schiff bases, crown ethers, cryptands, and amine groups, have been synthesized. The structures of the ligand groups are very different and generally complicated. The primary, secondary, and tertiary amine groups are probably the simplest.

The chelating resins have been extensively studied, and there are many reviews on their synthesis and applications.[1–5]

Among the various methods used to prepare chelating resins, by far the most used technique is chemical modification by polymer-analogue reactions of polymerization matrices, which are, in fact, crosslinked copolymers of a monovinylic monomer with a divinylic one, the styrene/divinylbenzene copolymers being the most used matrices. Some types of polystyrene chelating resins show slow kinetics for the retention process of the metal cations because of the hydrophobic character of the polystyrene backbone.

| Sample | Divinyl benzene (wt %) | | Vinyl acetate (wt %) | Acrylonitrile (wt %) | Toluene $(D)^a$ | N (%) | | Apparent density (g/cm³) |
	Divinylic compound	Monovinylic compound				Calcd	Found	
DAcN-11	10	5.39	10	74.61	0.3	19.71	18.27	0.7552
DAcN-14	10	5.39	10	74.61	0.4	19.71	18.59	0.6343

^{a} $D = V_{toluene}/V_{monomers} + V_{toluene}$, where: $V_{toluene}$ and $V_{monomers}$ are the volumes of toluene and monomers, respectively.

Therefore, resins with higher hydrophilic character, such as acrylic resins, are made.

Acrylic resins with primary, secondary, and tertiary amine groups, in particular, can be achieved with two methods: (1) the aminolysis of the ester groups from crosslinked copolymers of different (meth)acrylic esters with polyamines containing one or more primary and/or secondary amine groups and (2) the aminolysis–hydrolysis reaction of nitrile groups from crosslinked acrylonitrile copolymers with the same aforementioned amine types.[6]

In our previous studies, we reported the synthesis of acrylic weak-base anion exchangers through the reaction of ethyl acrylate/acrylonitrile/divinylbenzene copolymers as beads with ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), and N,N-dimethylaminopropylenamine; both the aminolysis of ester groups and the aminolysis and hydrolysis of nitrile groups occurred.

The respective copolymers had a low acrylonitrile percentage of 10%.[7,8]

Another previous study showed the achievement of acrylic anion exchangers through the aminolysis–hydrolysis reaction with N,N-dimethylaminopropylenamine and water of some acrylonitrile/divinylbenzene copolymers with and without the third comonomer (ethyl acrylate or styrene).[9]

Other literature data describe the chemical modifications of some acrylonitrile/alkyl(meth)acrylate/divinylbenzene copolymer beads through reactions with NaOH aqueous solutions to obtain carboxylic groups attached at the matrix or hydroxylamine to form amidoxime and hydroxamic acid groups. For these resins, the ability to retain U(VI), Cu(II), and Ag(I) cations was investigated.[10–13]

In this study, we synthesized macroporous weakbase anion exchangers through the aminolysis–hydrolysis reaction with EDA, DETA, and TETA in the
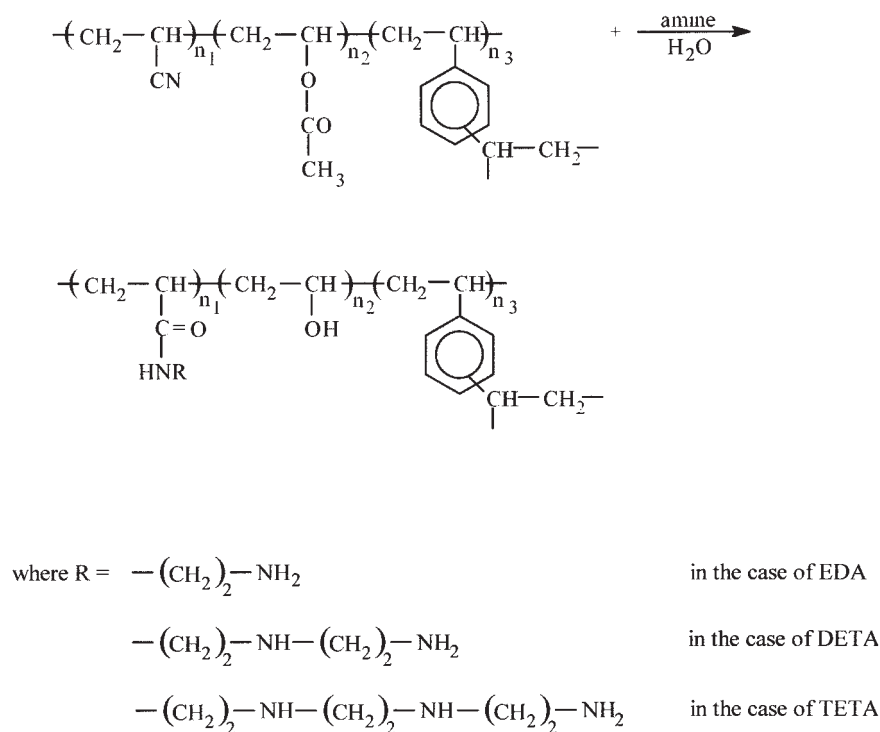

Figure 1 Reactions of the chemical modification of the acrylic copolymers.
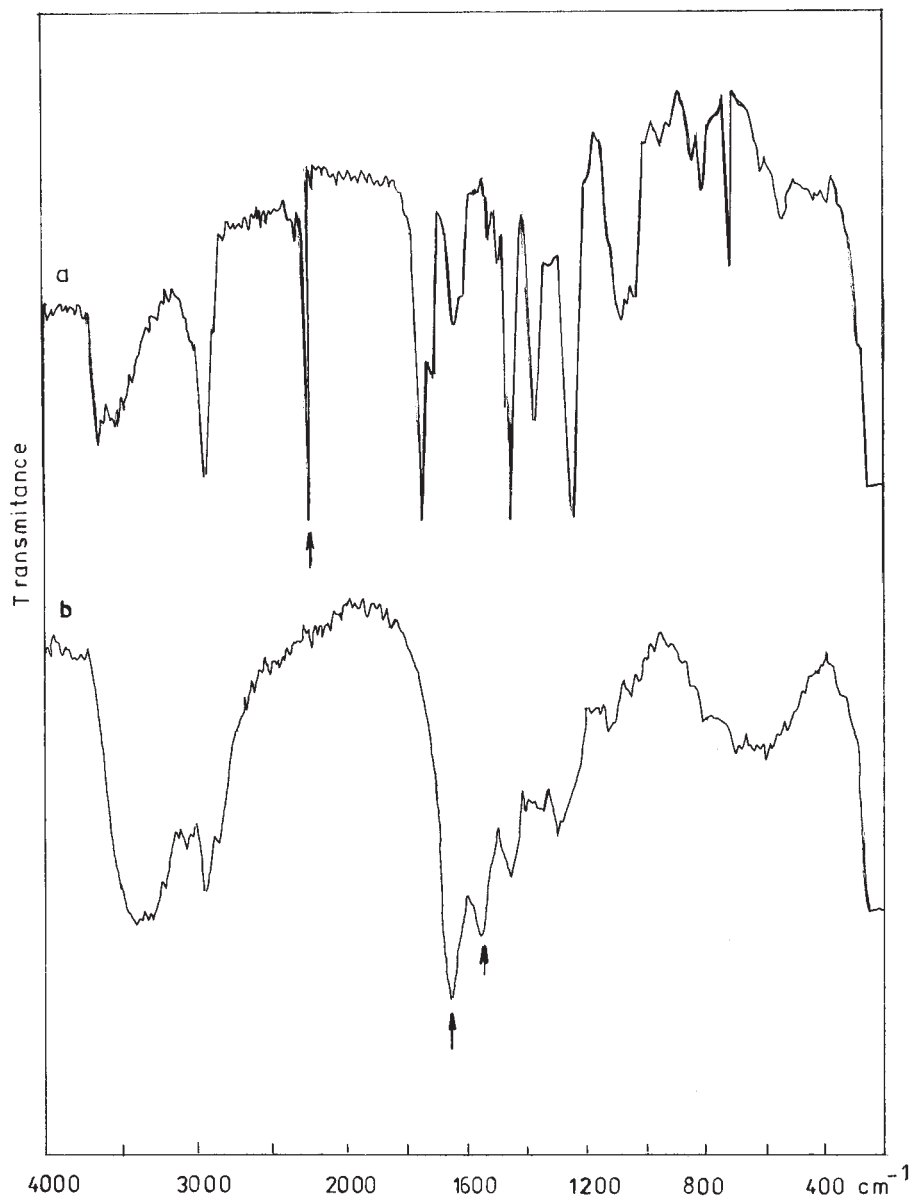
Figure 2 IR spectra of (a) the DAcN-14 copolymer and (b) the DAcN-14 copolymer modified with TETA.

presence of water of some macroporous acrylonitrile/vinyl acetate/divinylbenzene copolymer beads. Toluene was used as a diluent for the achievement of the copolymers. For the synthesized weak-base anion exchangers, the behavior in the retention processes of Ni(II), Cd(II), and Pb(II) cations under both noncompetitive and competitive conditions was evaluated.

The acrylic weak-base anion exchangers of this study were synthesized with the aforementioned synthesis strategy to create resins with more suitable characteristics than the weak-base acrylic resins from our previous studies had.[7–9] The expected characteristics were higher weight and volume ion-exchange capacities and relatively low crosslinking degrees in conjunction with an effective porous structure of the matrix. All this should lead to ion exchangers with very

good physical stability, with more chelating sites and fast sorption rates of cations, and this could allow their use in sorption processes through columns with superior results.

EXPERIMENTAL

Materials

Commercial divinylbenzene (divinylic component concentration = 55.66 wt % and monovinylic component concentration = 30.00 wt % according to gas chromatography) was used as received.

Commercial acrylonitrile with a concentration of 99.50% (Fluka) and commercial vinyl acetate with a concentration of 99.00% (Fluka, Germany) were freshly distilled.

TABLE II
Physicochemical Characteristics of the Tested Acrylic Weak-Base Anions

| Resin | Compounds used in chemical modification | | Functional group | Characteristics of the resin | | |
| | Copolymer | Amine | | Exchange capacity | | Water retention (g/g) |
				mequiv/g	mequiv/mL	
AS-52	DAcN-11	TETA	$\overset{O}{\overset{\|}{-C}}$—NH—[(CH$_2$)$_2$—NH]$_2$—(CH$_2$)$_2$—NH$_2$	10.55	2.09	0.6277
AS-53	DAcN-14	TETA	$\overset{O}{\overset{\|}{-C}}$—NH—[(CH$_2$)$_2$—NH]$_2$—(CH$_2$)$_2$—NH$_2$	8.65	2.18	0.8456
AS-55	DAcN-11	DETA	$\overset{O}{\overset{\|}{-C}}$—NH—[(CH$_2$)$_2$—NH]$_1$—(CH$_2$)$_2$—NH$_2$	10.35	1.83	0.7515
AS-56	DAcN-14	DETA	$\overset{O}{\overset{\|}{-C}}$—NH—[(CH$_2$)$_2$—NH]$_1$—(CH$_2$)$_2$—NH$_2$	8.27	1.88	1.4087
AS-57	DAcN-14	EDA	$\overset{O}{\overset{\|}{-C}}$—NH—(CH$_2$)$_2$—NH$_2$	6.52	1.60	1.1885

Benzoyl peroxide purum moistened with water ($\cong$25.0% water) and toluene puriss pro analysis (p.a.) were used as received.

Ammonium salt of the styrene/maleic anhydride copolymer, the component of the aqueous phase used in the suspension copolymerization, was synthesized in our laboratory.

EDA, DETA, and TETA from Fluka were used as received.

Aqueous Ni(II), Cd(II), and Pb(II) solutions of different concentrations were obtained from Ni(NO$_3$)$_2$ · 6H$_2$O, Cd(NO$_3$)$_2$ · 4H$_2$O, and Pb(NO$_3$)$_2$, respectively, which were analytical-grade. Also, analytical-grade NiSO$_4$ · 7H$_2$O was used.

Methods

The acrylonitrile/vinyl acetate/divinylbenzene cross-linked copolymers were obtained through the aqueous suspension copolymerization of the three comonomers in the presence of toluene as the diluent. The aqueous phase contained 0.5% (g/v) ammonium salt of the styrene/maleic anhydride copolymer. The organic phase consisted of the three monomers, benzoyl peroxide (1.5 g/100 g of comonomers), and toluene (Dilution, $D = 0.3$ or 0.4). The copolymerization was allowed to proceed for 10 h at 80°C and for 2 h at 90°C. At the copolymerization end, the beads were filtered, washed with warm water, dried at 60°C, then extracted with dimethylformamide in a Soxhlet apparatus, and finally vacuum-dried at 50°C for 48 h. The copolymers were characterized by their nitrogen content, which was determined by elemental analysis, apparent density, and specific density.

The chemical modifications of the copolymer were performed through their reaction with EDA, DETA, or TETA in the presence of water with a nitrile group/amine/water molar ratio of 1/6/2 at 110°C for EDA and at 160°C for the other two amines for 16 h. The resin beads were recovered by filtration and washed with distilled water for the removal of excess amine up to the neutral pH of the washing water.

The resins were sieved at a particle size of 0.4–0.8 mm and were characterized by weight and volume weak-base exchange capacities (mequiv g^{-1} and mequiv mL^{-1}, respectively) and water retention.

The apparent densities of the starting copolymers were determined with a mercury pycnometer at 13 mPa, and the water retention of the anion exchangers was determined by the centrifugation of these resins at 2000 rpm for 30 min after their immersion for 48 h in water.

The measurements of the retentions of metal cations were performed by the batch method as follows. Each resin sample (0.2 g) with known humidity was put in contact at 25°C with a 20-mL aqueous solution of metal cations of different concentrations, as discussed in the next section. Different contact times with permanent shaking were used. The retained amount of metal cations was determined from the difference between the cation concentrations in the solution before and after the retention process with atomic absorption spectroscopy and was expressed as milliequivalents of metal cations per gram of dried resin [i.e., the retention capacity (Q)].

For the competitive retention properties, the Q values of the metal cations from the Ni(II)–Pb(II) and
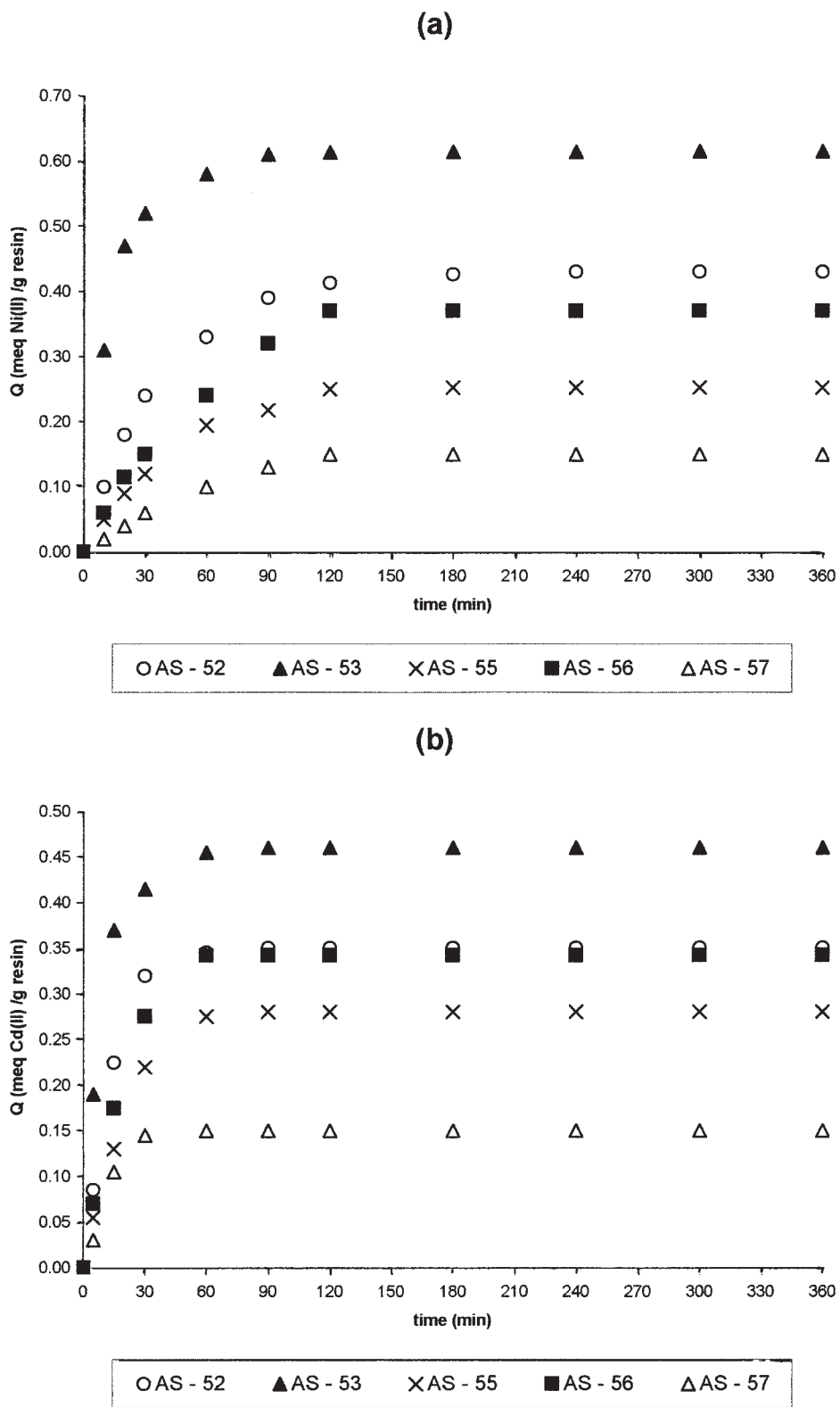
(a)

(b)

Figure 3 Effect of the chemical and morphological structure of the resins on their behaviors in the retention processes under noncompetitive conditions of the metal cations: (a) Ni(II), (b) Cd(II), and (c) Pb(II). The initial concentration of each cation from the nitrate was 100 mg/L.
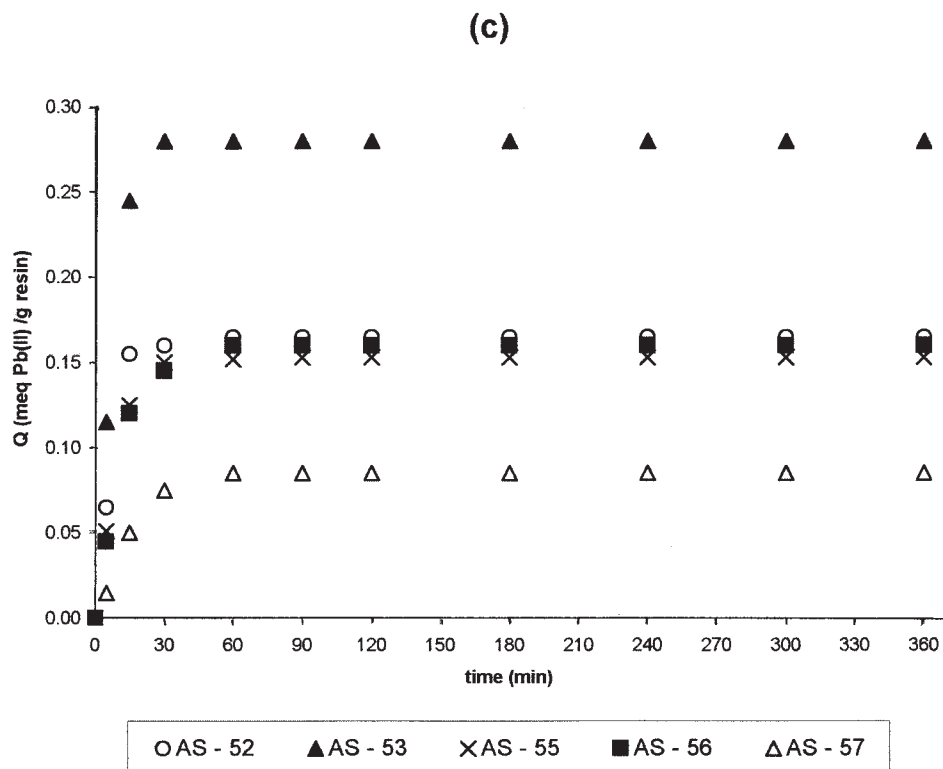
(c)

Figure 3 (*Continued from the previous page*)

Ni(II)–Cd(II) binary mixtures were evaluated. The following method was used. A resin (0.2 g) with known humidity was put in contact at 25°C for 24 h with a 20-mL mixture: (1) 10 mL of a $Ni(NO_3)_2$ aqueous solution with a Ni(II) concentration of 50 mg/L and 10 mL of a $Cd(NO_3)_2$ aqueous solution with a Cd(II) concentration of 50 mg/L and (2) 10 mL of a $Ni(NO_3)_2$ aqueous solution with a Ni(II) concentration of 50 mg/L and 10 mL of a $Pb(NO_3)_2$ aqueous solution with a Pb(II) concentration of 50 mg/L.

At the end of the retention process, the amount of each metal cation was determined, and Q was calculated as described previously.

RESULTS AND DISCUSSION

Table I shows the physicochemical characteristics of the acrylic copolymers used in this study. The data show that the two acrylic copolymers have macroporous morphologies. This affirmation is based on the following observations: the opaque aspect of the copolymer beads and apparent densities much lower than the specific density. This is a normal situation because toluene, a solvent with a low affinity for polyacrylonitrile, is a bad solvent for acrylonitrile-rich copolymers. Also, Table I shows that the nitrogen content calculated from the mixture of comonomers is practically equal with that found from copolymer analysis.

The chemical modifications of the synthesized copolymers take place according to Figure 1. The qualitative evaluation of the chemical modifications has been performed with IR spectra. These show in the starting copolymers the characteristic absorption band of the nitrile groups at 2250 cm^{-1}, whereas in the IR spectra of the chemically modified copolymers, the disappearance of this band can be observed with the appearance of the absorption bands for the secondary amides at 1550 and 1650 cm^{-1}. As an example, Figure 2 illustrates the IR spectra of copolymer DAcN-14 and its product chemically modified with TETA.

In Table II are shown some characteristics of weak-base anion exchangers. The data establish that by the reactions according to Figure 1, the weak-base anion exchangers are synthesized with high values of the exchange capacities.

The water retention of a resin is a measure of its three features: the hydrophilic character due to the number of hydrophilic groups, the permanent porosity of its three-dimensional network, and the swelling potential in water of this network.

Theoretically, the resins synthesized with TETA should exhibit higher water retention than those synthesized with DETA and EDA when the same starting copolymer is used. However, an inverse situation is observed. Clearly, the copolymer synthesized in the presence of a larger amount of toluene leads to anion

exchangers with higher water retention, regardless of the amine used, DETA or TETA.

For the five resins shown in Table II, the behaviors of the retention processes of the Ni(II), Cd(II), and Pb(II) cations were investigated. At first, the variation of the Q values as a function of time was determined and plotted (Fig. 3). The profiles of the retention process kinetics are common ones for the adsorption processes of some soluble compounds by solid supports: the Q values increase quickly in the initial phase, then the process proceeds slowly, and finally equilibrium is reached. For this study, the time required to achieve the equilibrium is reached, and it is up to 2 h; however, a fast retention rate can be observed during the first 15 min.

The data from Figure 3, compared with those from Table II, show that the major role in the retention processes does not belong to the number of ligand amine groups, expressed as the weight exchange capacity (mequiv g^{-1}). This affirmation is because resins AS-52 and AS-55, with the highest values of the weight exchange capacity, have much lower Q values than resin AS-53, which possesses a low exchange capacity, but exhibit the highest Q values. Also, resins AS-56 and AS-53, with weight exchange capacities of very close values, have different behaviors in the retention processes. A more major role is probably played by the volume ion-exchange capacity.

The agreement between the values of the weight weak-base exchange capacity (mequiv g^{-1}) and the metal-cation retention capacity (mequiv of metal cation/g of resin) is observed only for resin AS-57, for which the two types of capacities are lowest.

We assume that the metal-cation retention capacities and the retention process kinetics depend at least on three factors: the conformational requirements for complex formation between the ligand groups and metal cation, the accessibility of the metal cation in the matrix to attain the fixed ligand groups, and the stability constant of the complex.

The results and discussion up to now can lead to the affirmation that among the five resins of this study, resin AS-53 has the possibility of satisfying the aforementioned conditions in the highest measure, especially with respect to the Ni(II) cation.

All the resins synthesized in this study have the following retention order: Ni(II) > Cd(II) > Pb(II).

Although the retention order from the solutions containing a single cation gives an indication of the potential selectivity of the resins for the three cations, the resin selectivity can be more realistically determined under competitive conditions. Figure 4 shows the results from competitive retention by resin AS-53 with two binary systems, Ni(II)–Cd(II) and Ni(II)–Pb(II), under the conditions mentioned in the Experimental section. Figure 4, like Figure 3, shows that resin AS-53 has the best selectivity for the Ni(II) cation.
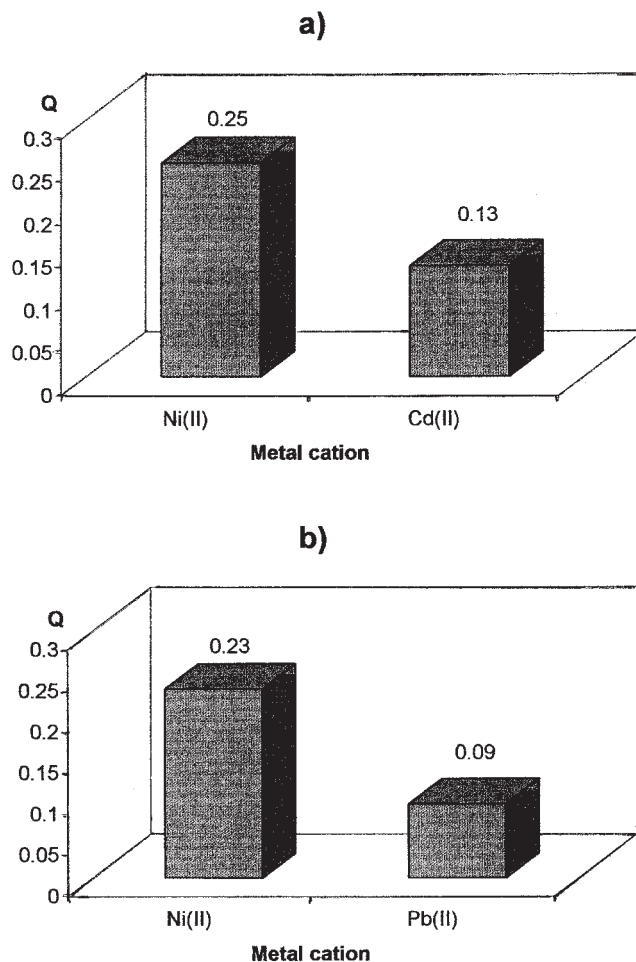

Figure 4 Retention under competitive conditions by the resin AS-53.

The higher Q values for this cation were obtained with higher Ni(II) initial concentrations, as can be seen in Figure 5. The plot shows that the Q values increase first with an increasing initial Ni(II) concentration, and then a plateau value is reached at an initial Ni(II) concentration of approximately 500 mg/L. The Q value at the plateau, which is the maximum retention capacity (Q_{max}), is 2.67 mequiv/g [78.36 mg of Ni(II)/g of resin].

The previous literature data describe different resins and their Q_{max} values for the Ni(II) cation. Some of them are poly(ethylene imine)-attached poly(p-chloromethylstyrene) beads with Q_{max} = 78.2 mg of Ni(II)/g of resin, crosslinked polyamides with divinylbenzene or N,N'-methylene bisacrylamide containing glycine functions with Q_{max} = 2.5 mequiv of Ni(II)/g of resin, and poly(N-vinylimidazole) hydrogels with Q_{max} = 2.75 mequiv of Ni(II)/g of resin.[14–16]

Comparing those data with the data of this study, we assume that Q_{max} achieved for the Ni(II) cation with resin AS-53 is satisfactory.

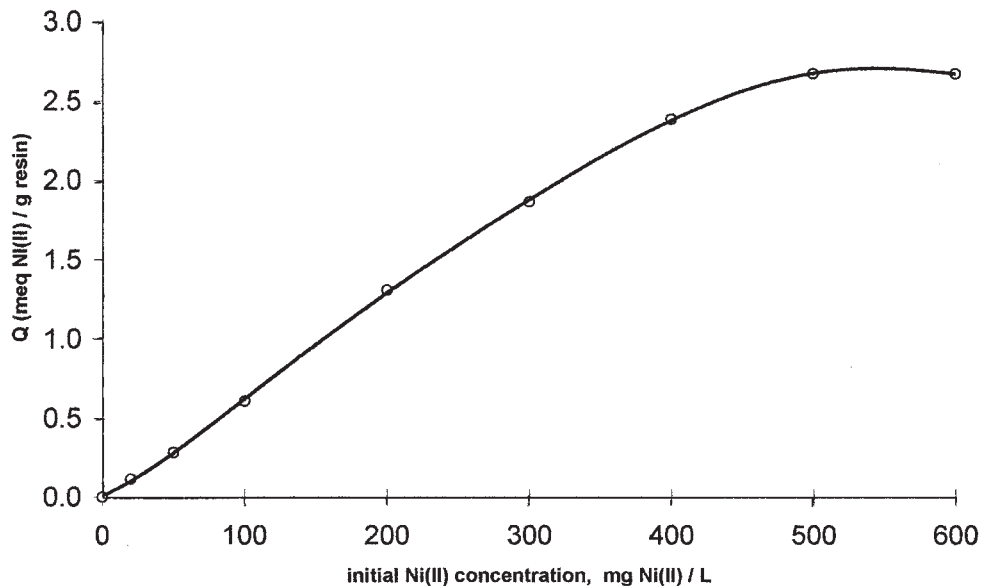The influence of the anion of the cation on its retention is shown in Figure 6. The data show that in the

Figure 5 Effect of the initial Ni(II) concentration from the $Ni(NO_3)_2$ aqueous solutions on the retention of this cation by the resin AS-53. The contact time was 24 h.

initial phase the retention of the Ni(II) cations from $NiSO_4$ has a lower rate than that from $Ni(NO_3)_2$. This may be attributed to a slower diffusion into the resin

matrix of the $NiSO_4$ salt containing the bulkier anion until more favorable access occurs because of the water resin swelling increase as a function of time. Fi-
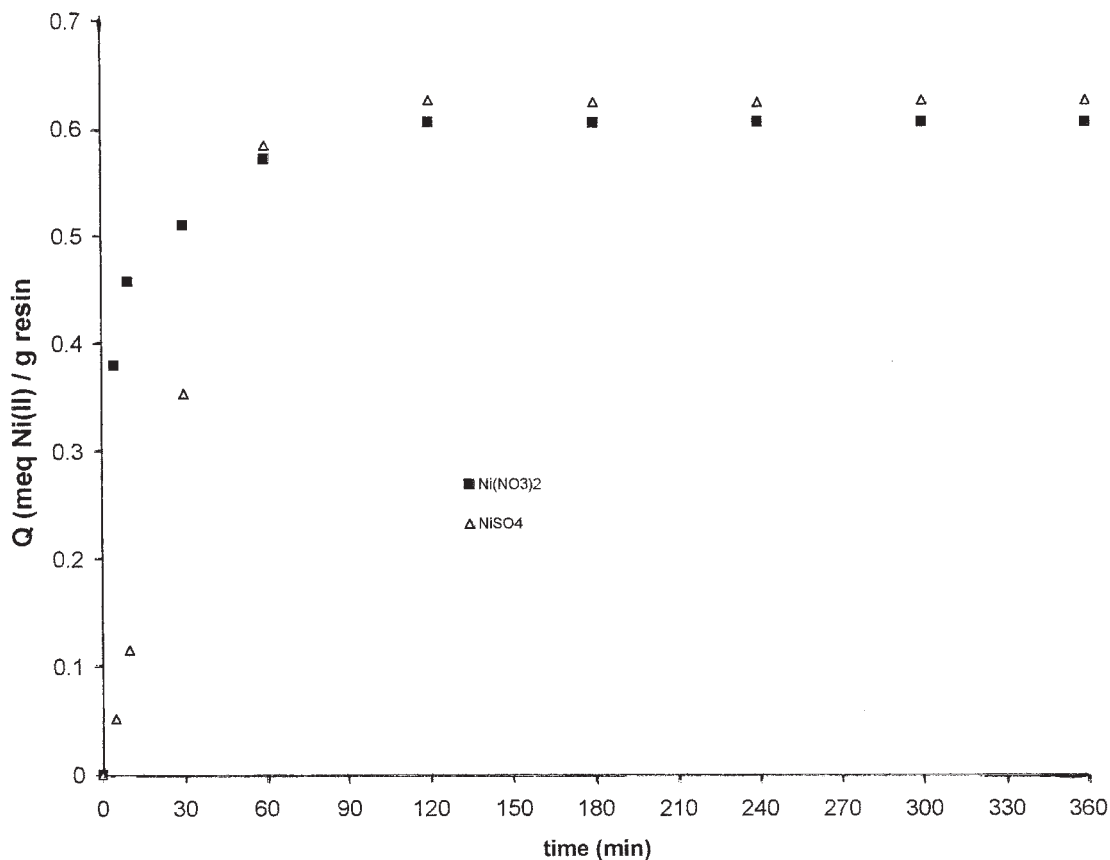

Figure 6 Effect of the anion nature on the Ni(II) cation retention processes by the resin AS-53. The initial Ni(II) concentration was 100 mg/L.

nally, Q of the Ni(II) cation from $NiSO_4$ is slightly higher than Q of the cation from $Ni(NO_3)_2$. This could be due to the affinity of a hydrophilic matrix for a more hydrophilic compound, as $NiSO_4$ is because the sulfate anion is more hydrophilic than the nitrate anion.

CONCLUSIONS

Macroporous acrylonitrile/10% vinyl acetate/10% divinylbenzene copolymers were obtained through the aqueous suspension copolymerization of the three comonomers in the presence of toluene as a diluent.

The reactions of these copolymers with EDA, DETA, and TETA led to weak-base anion exchangers with high exchange capacities between 6.5 and 10.5 mequiv g^{-1} and 1.6 and 2.2 mequiv mL^{-1}.

For the synthesized resins, the retention properties of some heavy-metal cations, [Ni(II), Cd(II), and Pb(II) ions] were evaluated.

All the resins had the ability to retain the aforementioned cations, as expected, but their behaviors in the retention processes depended on the chemical and morphological structure of the resin and the cation nature.

The resin synthesized from the reaction with TETA of the copolymer obtained in the presence of a higher amount of toluene exhibited the best Q values, the highest value being that for the Ni(II) cation. For this cation, Q_{max} was 2.67 mequiv of Ni(II)/g of resin.

The following selectivity order was observed: Ni(II) > Cd(II) > Pb(II). This order was available for all the resins.

Finally, we can affirm from the obtained results that the goal of this study was attained. Thus, copolymers were synthesized with effective porous structures, namely, porosities of 31.95 and 42.86% for a crosslinking degree of 10%, the porosity [P (%)] being calculated from the relation $P = (1 - \rho_{ap}/\rho_{sp}) \times 100$, where ρ_{ap} and ρ_{sp} are the apparent density and specific density, respectively.

These copolymers by their chemical modifications with the three chosen amines led to acrylic weak-base anion exchangers with higher weight and volume ion-exchange capacities than those in our previous studies. The ion exchanger synthesized through chemical modification with TETA of the copolymer with higher porosity, resin AS-53, had the highest Q values for the studied cations, the greatest value being that for the Ni(II) cation. The retention was a fast process because the time required to reach the equilibrium was about 90 min. Exchanger AS-53, like all the exchangers of this study, had very good physical stability.

The suitable physical features and stability, high Ni(II) retention capacity, and fast rate of the retention process could allow the use of this anion exchanger in sorption processes through columns.

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