

Influence of the Matrix Porosity on the Synthesis and Adsorption Behavior of Dithiocarbamate Styrenic Resins Toward Zinc(II) and Cadmium(II) Ions

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ABSTRACT: The dependence of the adsorption behavior toward Zn^{2+} and Cd^{2+} on the synthesis conditions of dithiocarbamate styrenic resins was investigated. We synthesized styrene-divinylbenzene copolymers with different kinds of porous structures by varying the divinylbenzene (DVB)-to-styrene ratio and the dilution degree of the monomers with *n*-heptane. The porous structure of these materials was characterized. The introduction of the dithiocarbamate moiety on the copolymers followed a synthetic pathway based on the nitration reaction, reduction of the nitro group to the amino one, and finally, the addition of the amino group to CS_2 . All of the synthesis steps were monitored by Fourier transform infrared spectroscopy. Only the addition reaction to CS_2 was greatly influenced by the copolymer porosity. The effect of the

dilution degree on the reaction extension was more pronounced than the effect of the DVB content. The more porous materials with higher dithiocarbamate contents adsorbed a higher amount of ions in a faster way, with Zn^{2+} being preferable over Cd^{2+} ions. The difference between the Zn^{2+} and Cd^{2+} adsorption rates was enhanced with the copolymer porosity, and also enhanced was the difference between the amounts of ions adsorbed by the copolymer; this suggested that the selectivity toward these ions could be controlled by the copolymer porous structure. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3070–3078, 2010

Key words: crosslinking; ion exchangers; macroporous polymers; metal-polymer complexes

INTRODUCTION

All kinds of human activities generate waste that should be treated in accordance with its characteristics. Recycling and reusing are often good alternatives, but these procedures can rarely be applied. Fortunately, in the case of industrial wastes containing toxic heavy metals, a remediation process can be applied before the wastes are thrown away. If waste treatment offers the possibility of recycling the metal species, economic importance can be attributed to the remediation process.^{1,2}

Many separation processes can be applied to remediate systems containing metal ions. Precipitation is the most classical followed by solvent extraction. Precipitation generates high amounts of solids and cannot be applied to dilute solutions where sol-

vent extraction is disadvantageous because of the high volumes of organic solvents used in the process.³ To solve some of these problems, solid-phase extraction has become a good alternative because it allies the high selectivity of solvent extraction and the high separation performance of the chromatographic process. This separation method has also been used extensively in metal-ion analysis, specifically for the elimination of matrix effects and for the preconcentration of trace amounts of analyte.⁴⁻⁶

In the beginning, solid-phase extraction was based on the use of solid supports loaded with the same organic extractors already used in solvent extraction.⁷ However, these liquid extractors were only physically adsorbed on a natural or polymeric support, and the continuous use of this stationary phase in a chromatographic column promotes liquid desorption and, as a consequence, a loss of efficiency. Therefore, a good solution for improving the lifetime of these materials is the chemical modification of the solid support by the introduction of a fixed reactive group.

On this basis, when producing a functionalized chromatographic packing material, one must consider two basic criteria: the chemical and physical

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nature of the precursor support and the chemical structure of the final attached reactive group. The literature about the chemical modification of polymers and natural supports is extensive,^{8–11} and readers can easily conclude that the main focus of the studies on reactive supports has been the enhancement of material selectivity toward a single species or a group of species. This trial of enhancing selectivity is usually based on the chemical characteristics of the fixed functional group, and the role of the support matrix is not related in detail. Considering polymer supports, there have also been a great number of works dealing with their synthesis, especially with porous structure control, because the porosity is directly related to the resin capacity and the rate of adsorption.^{12–17} However, there have been few works dealing with the dependence of the polymer modification reaction extension and of the chelating resin performance on the porous structure of the precursor support.¹⁸ With the aim of obtaining a chelating resin for Zn^{2+} and Cd^{2+} ion adsorption, in this article, we present, in detail, the dependence of the adsorption behavior of dithiocarbamate styrenic resins on their synthesis conditions from the production of the polymer support to the immobilization of the chelating group.

The choice of the dithiocarbamate group was based on the acid–base Pearson's concept.¹⁹ From this concept, Cd^{2+} is considered a soft acid because of its low charge density but Zn^{2+} can act as either a soft or a hard acid because its charge-to-radius ratio is not so low. From Pearson's concept, soft bases prefer to bind to soft acids, and as a result, Zn^{2+} and Cd^{2+} form relatively stable compounds with sulfur-based ligands, which are considered soft bases.^{19,20} Among this class of ligands, dithiocarbamates are considered attractive groups for immobilization on a solid support because of their insensibility to alkaline metal ions.²¹

The literature describes many reaction routes for the introduction of the dithiocarbamate moieties onto styrene–divinylbenzene (S–DVB) copolymers. Crosslinked polychloromethylstyrene can be readily reacted with sodium salts of dithiocarbamates,²² but most synthetic pathways are based on the introduction of an amino moiety onto the copolymer structure followed by an addition to carbon disulfide in an alkaline medium.^{23–25} The main difference between these routes is the structure of the final amino group incorporated into the polymer matrix. This high number of synthetic pathways presented in the literature represents the trial of enhancing selectivity by modifying the chemical environment around the chelating group. The simplest dithiocarbamate structure that can be incorporated onto S–DVB copolymers is attained by the nitration of the support followed by the reduction of the nitro

group.^{23,24} This methodology is often used to attach the amino group directly to the aromatic rings of styrenic copolymers. In this study, we chose this simplest synthetic route on the basis of the nitration of S–DVB copolymers by an HNO_3/H_2SO_4 mixture followed by a reduction step with $SnCl_2$.

EXPERIMENTAL

Chemicals

Styrene (S) and divinylbenzene (DVB), donated by Petroflex Indústria e Comércio S. A. and Nitriflex S. A. Indústria e Comércio, respectively, were previously washed with a 5%w/v NaOH aqueous solution and then by water. 2,2'-Azobisisobutyronitrile (donated by Metacril S. A.) was recrystallized from a methanol solution. Nitrogen (White Martins Praxair, Inc.) was 99% pure. Poly(vinyl alcohol) (Hoechst) had an 89% hydrolysis degree. All of the other reagents [pro analysis (PA) grade, Vetec Química Fina, Ltd.] were used with no further purification.

Instruments

The pore size distribution curves and specific surface area analysis of S–DVB copolymers were tested with a Micromeritics (Norcross, GA) ASAP 2010. The pore size distribution curves were also obtained by mercury intrusion in a Quantachrome Co. Autoscan 33 porosimeter. The chemical modifications of the S–DVB copolymers were evaluated by Fourier transform infrared (FTIR) spectroscopy in a PerkinElmer Spectrum One spectrometer. Twenty scans in the 400–4000- cm^{-1} range were performed to analyze the samples as KBr pellets. pH measurements were performed by an Analyser (São Paulo, Brazil) 300M pH meter fitted to a 2A13-HH glass electrode.

Synthesis of the S–DVB copolymers

S–DVB copolymers with different kinds of porous structures were synthesized by the aqueous suspension polymerization technique. Poly(vinyl alcohol) was used as a suspension stabilizer agent, and sodium chloride was used as salting-out agent (both 5% w/v in a water solution). 2,2'-Azobisisobutyronitrile (1% molar to monomers) was the initiator of the polymerization reaction, and *n*-heptane in different proportions was the pore-forming agent. The molar ratio between S and DVB was varied. The polymerization reactions were carried out for 24 h at 70°C. The obtained copolymer beads were purified by washing with hot water before sieving. The 45–80-mesh copolymer fraction was also purified with hot ethanol. Finally, the material was dried at 60°C for 48 h.

Chemical modification of the S-DVB copolymers by the immobilization of the dithiocarbamate group

The reaction scheme adopted in this study for the immobilization of the dithiocarbamate functionality followed the one described by Roy et al.²⁴ All of the reaction steps were evaluated by FTIR spectroscopy, as already described in the Instruments section.

Nitration of the S-DVB copolymers

The 45–80-mesh fraction of each S-DVB copolymer was first submitted to the nitration reaction by a mixture of concentrated nitric and sulfuric acids. In this step, 10 mL of concentrated H₂SO₄ and 4 mL of concentrated HNO₃ were added to a flask containing 0.5 g of the copolymer. The system was kept under stirring for 2.5 h at 60°C. The nitrated S-DVB copolymers were washed with distilled and deionized water (DDW) until they reached neutrality and were then dried as described previously.

Amination of the S-DVB copolymers

The nitro group was reduced to the amino one by a reaction with stannous chloride. A copolymer mass of 0.5 g was added to a three-necked, round-bottom flask containing 5 mL of ethanol and 4.5 mL of concentrated HCl. Nitrogen was bubbled in the solution, and 4 g of stannous chloride was added. The reaction proceeded under an inert atmosphere for 16 h at 65°C. In the end, the amino S-DVB copolymer was washed with DDW, a 2 mol/L NaOH aqueous solution, and DDW again. After the purification procedure, the copolymer was dried.

Dithiocarbamate group immobilization

The last step of the synthesis route was the reaction of the amino copolymer with CS₂. Into a flask, 50 mL of a 1 mol/L NaOH/1.5 or 6 mol/L CS₂ ethanolic solution were mixed with 0.5 g of the amino copolymer. The system was kept under stirring at room temperature for 6 days. The product was filtered and washed with ethanol and then by diethyl ether. Finally, it was dried as described before.

Characterization of the S-DVB copolymer porous structure

The porous characteristics of the S-DVB copolymers were evaluated by the determination of apparent density, pore volume, and swelling degree in toluene.²⁶ The specific surface area was determined by nitrogen adsorption from the Brunauer–Emmett–Teller method. Pore size distribution curves were constructed by nitrogen desorption data from the

Barrett–Joyner–Halenda method and also by mercury intrusion data.

Determination of the pH influence on the adsorption of Zn²⁺ and Cd²⁺ on the dithiocarbamate resins

Standard stock solutions of Cd(NO₃)₂ and ZnSO₄ (0.01 mol/L) were prepared. Two acetic buffer solutions of pH 5.0 and 6.0 and two ammoniacal buffer solutions of pH 8.25 and 9.0 were also prepared to dilute the metal solutions in a 1 : 10 proportion. In a 0.1-mg precision balance, 0.1 g of the resin was weighed into a flask. Then, 25.00 mL of the buffered metal solution was added, and the system was stirred for 24 h. After filtration, the solution was titrated with a 0.01 mol/L ethylene diamine tetraacetic acid standard solution. This procedure was repeated for each dithiocarbamate resin. The adsorbed amounts of Zn²⁺ and Cd²⁺ were calculated by the differences between their initial and final concentrations in the solution, and they were expressed as millimoles per gram.

Construction of the kinetic curves for Zn²⁺ and Cd²⁺ adsorption on the dithiocarbamate resins

The kinetic curves were constructed in the best adsorption pH already determined for Zn²⁺ and Cd²⁺, as described previously. A 0.1-g portion of the resin was weighed, and 50 mL of the buffered standard metal solution was added. The Zn²⁺ solution was 1 × 10⁻³ mol/L, and the Cd²⁺ solution was 5 × 10⁻³ mol/L. Aliquots of 1.00 mL were taken after some determined time intervals, and the metal concentration was determined by ethylene diamine tetraacetic acid titration. A plot of C/C₀ (where C and C₀ are the metal concentrations after and before contact with the resin, respectively) versus time was constructed for each resin in the presence of each cation.

RESULTS AND DISCUSSION

To create a dithiocarbamate moiety in the S-DVB copolymers, we followed the procedure described by Roy et al.²⁴ The synthetic route was based on the nitration of the copolymer, followed by a reduction reaction with SnCl₂ and the addition of the aminated copolymer to CS₂. These reactions were evaluated in the modification of S-DVB copolymers with different kinds of porous structures to establish a relationship between the porous structure and the performance of the chelating resins.

With this aim, six S-DVB copolymers were synthesized by aqueous suspension polymerization. The synthesis conditions are presented in Table I. The

TABLE I
Synthesis Conditions and Porous Characteristics of the S–DVB Copolymers

Copolymer	Dilution (%; <i>n</i> -heptane)	DVB/S	d_a (g/cm ³)	V_p (cm ³ /g)	V_{pf} (cm ³ /g)	A (m ² /g)	I_{tol} (%)
01	50	25/75	0.59	0.15	0.03	6	61
06	100	15/85	0.35	0.87	0.73	74	59
02		25/75	0.33	0.94	0.80	92	41
03	200	15/85	0.30	1.22	1.03	51	114
04		25/75	0.21	2.11	1.85	69	47
05		40/60	0.19	2.26	2.18	143	28

d_a = apparent density; V_p = fixed pore volume as determined by mercury porosimetry; V_{pf} = fixed pore volume as determined by water uptake; A = surface area; I_{tol} = swelling degree in toluene.

copolymers were synthesized in the presence of *n*-heptane as a pore-forming agent. This solvent had a poor affinity for the S–DVB copolymer and acted as a precipitant agent for the growing polymer chains during the polymerization reaction. Therefore, the amount of *n*-heptane added to the monomer mixture (S and DVB) was one of the main parameters that governed the formation of the copolymer porous structure. The amount of crosslinking agent (DVB) present in the monomer mixture was another important factor because it also influenced the precipitation mechanism of the copolymer chains.

To evaluate the influence of these two parameters (monomer dilution with *n*-heptane and copolymer crosslinking degree) on the extent of the S–DVB copolymer modification with dithiocarbamate groups, we synthesized five copolymers. Copolymers 01, 02, and 04 were all synthesized with a constant DVB-to-S ratio of 25/75, but the dilution degree with *n*-heptane was enhanced from 50 to 200%. The formation of more porous structures provoked by the enhancement of the dilution degree was characterized by the lower values of the apparent densities and the higher values of the fixed pore volume for copolymers 02 and 04. The specific surface area was also enhanced when the dilution degree was varied from 50 to 100% (copolymers 01 and 02), which was justified by the formation of a higher amount of true pores. However, when the dilution degree was enhanced to 200% (copolymer 04), the specific surface area was not enhanced in the same extension as before. This is shown in Figures 1 and 2, which show the copolymer pore size distribution curves obtained by nitrogen desorption and mercury intrusion, respectively. These are two complementary techniques that, together, can offer a good overview of a wide range of pore sizes. The analysis of these figures showed that the high dilution degree promoted the formation of larger pores, which did not contribute to the enhancement of the specific surface area as the formation of narrower pores did. These three copolymers formed a group of materials with comparable crosslinking degrees and elasticities, as was confirmed by the similar values of swelling in

toluene. However, these copolymers were different in pore size distribution because the pore diameter was enhanced proportionally by the dilution degree.

The evaluation of the influence of the copolymer matrix rigidity on the modification of the S–DVB copolymer with the dithiocarbamate group was also our goal. Thus, we synthesized copolymers 03 and 05, which formed, with copolymer 04, a group of supports with different crosslinking degrees. The enhancement of the matrix rigidity could be characterized by the swelling degree in toluene, which became lower as the DVB-to-S ratio became higher.

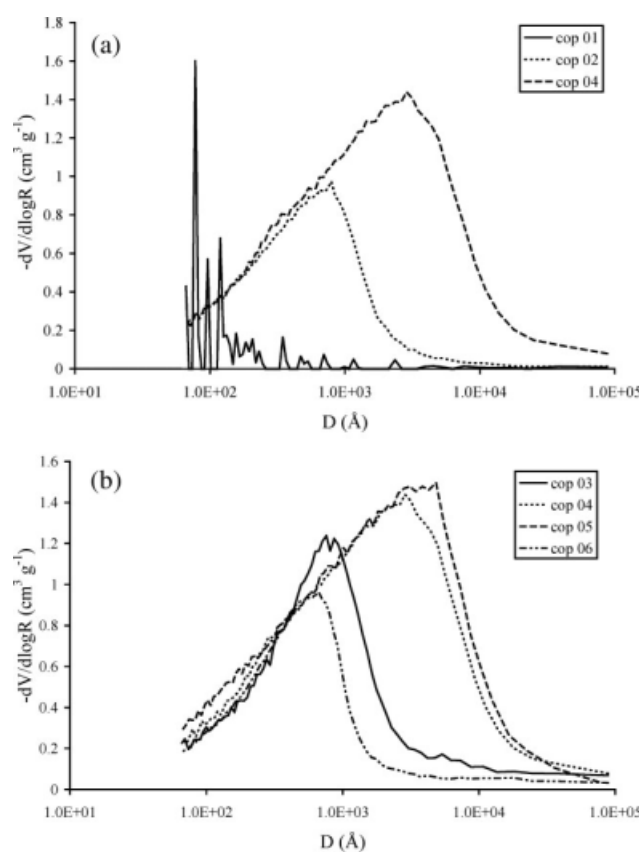


Figure 1 Pore size distribution curves obtained by nitrogen desorption (Barrett–Joyner–Halendar method) of the S–DVB copolymers: (a) 01, 02, and 04 and (b) 03, 04, 05, and 06. V , pore volume; R , pore radius; D , pore diameter; COP, copolymer.

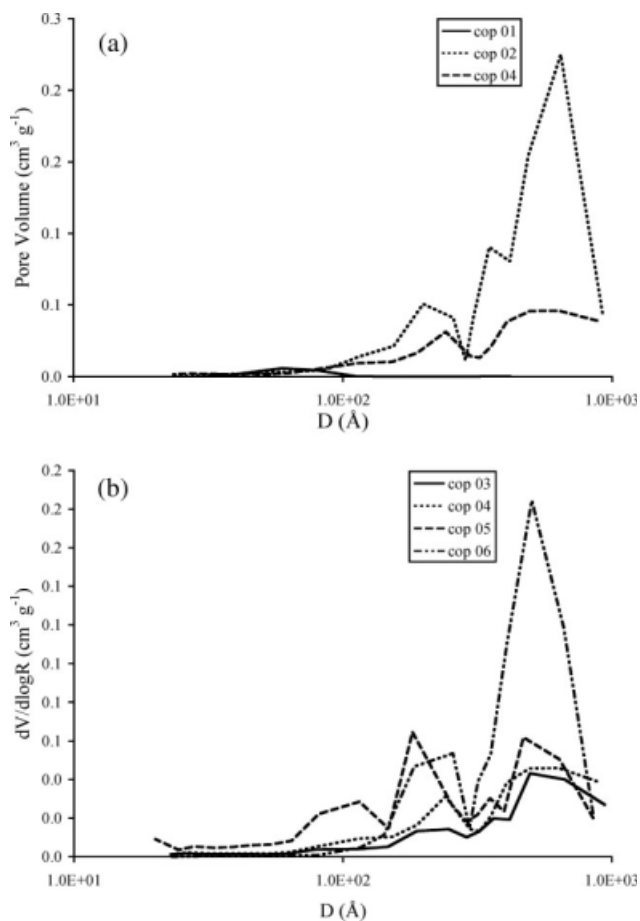


Figure 2 Pore size distribution curves obtained by mercury intrusion porosimetry of the S-DVB copolymers: (a) 01, 02, and 04 and (b) 03, 04, 05, and 06. V, pore volume; R, pore radius; D, pore diameter; COP, copolymer.

The copolymer porosity was also influenced by the changes in the DVB content. The lower apparent density and higher pore volume of the copolymers synthesized with higher amounts of DVB proved the higher porosity of the materials synthesized under these conditions. The enhancement of the specific surface area observed from copolymers 03–05 was evidence of the formation of a higher volume of pores with lower diameters when higher DVB amounts were used in the synthesis (Figs. 1 and 2).

Copolymer 06 was synthesized with 15% DVB and a 100% dilution degree to evaluate the synthetic route chosen for the immobilization of the dithiocarbamate group. Because of these synthesis conditions, it was a porous copolymer with a high pore volume and a good swelling ability in toluene. These were important properties that improved the access of the reagent solution to the polymer matrix and did not limit the reaction yield. Figure 3 shows the FTIR spectra of S-DVB copolymer 06 before and after each synthesis step. The success of the nitration reaction by the $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture is shown in Figure 3(b) by the presence of two strong bands at 1537 and 1347 cm^{-1} ,

which were assigned to the asymmetric and symmetric stretching vibrations of the aromatic nitro group.²⁷ The characteristic S-DVB copolymer bands were also seen but in lower relative intensities when compared to those in Figure 3(a). The second step was the reduction of the nitro group to the amino one by SnCl_2 in acid medium, and it was also possible to observe the high extension of this reaction in the FTIR spectrum, as shown in Figure 3(c). The strong and broad band in the 3350- cm^{-1} region was attributed to the asymmetric and symmetric stretching vibrations of the NH_2 group, and the 1621- cm^{-1} band was attributed to the bending vibration of this group. The sharp band at 1513 cm^{-1} was attributed to the substituted aromatic ring, and the weak band at 1275 cm^{-1} was attributed to the stretching of the phenyl carbon–nitrogen bond. The third and last step of the dithiocarbamate group immobilization on the S-DVB copolymer was the addition of the amino moiety to CS_2 in an alkaline medium. This substitution reaction was confirmed by the characteristic absorption bands of the dithiocarbamate group shown in Figure 3(d): the 2118- cm^{-1} band attributed to the C=S bond,^{24,28} the 1131- cm^{-1} band attributed to the NCS₂ bond,²⁵ and the 673- cm^{-1} band attributed to the stretching vibration of the C–S bond. The absorption band at 1001 cm^{-1} was attributed to interactions of the C=S and C–N stretching vibrations. This FTIR spectrum also shows a lower intense NH_2 bending vibration band at 1621 cm^{-1} ; this indicates the substitution of a hydrogen atom on this group. After the reaction with CS_2 , the beads were broken by what can be explained as the stress of the polymer matrix promoted by the introduction of that bulky group. Because of this problem, the final reaction was satisfactorily carried out under low-speed stirring, but a higher CS_2 concentration (6 mol/L) was necessary to favor the reaction. This condition was applied to the modification of copolymers 01–05, which were different in their porous structures.

The nitration reaction was efficient for all kinds of porous structures. However, there was a slight difference in the intensity ratios between the 1537- and 1605- cm^{-1} bands (assigned to the stretching vibrations of the NO_2 group and the aromatic carbon–carbon bond, respectively) for the more porous copolymers; this indicated a discrete higher nitration degree for these structures.

The reduction of the nitro group to the amino one occurred in a high extension, and it was not limited by the kind of porous structure of the S-DVB copolymers. On the other hand, the extent of the addition reaction of the amino group to CS_2 was greatly influenced by the copolymer porosity. The spectrum of copolymer 01, a low porous material, showed only a weak band at 2118 cm^{-1} . This band was stronger for copolymer 06, which was a more

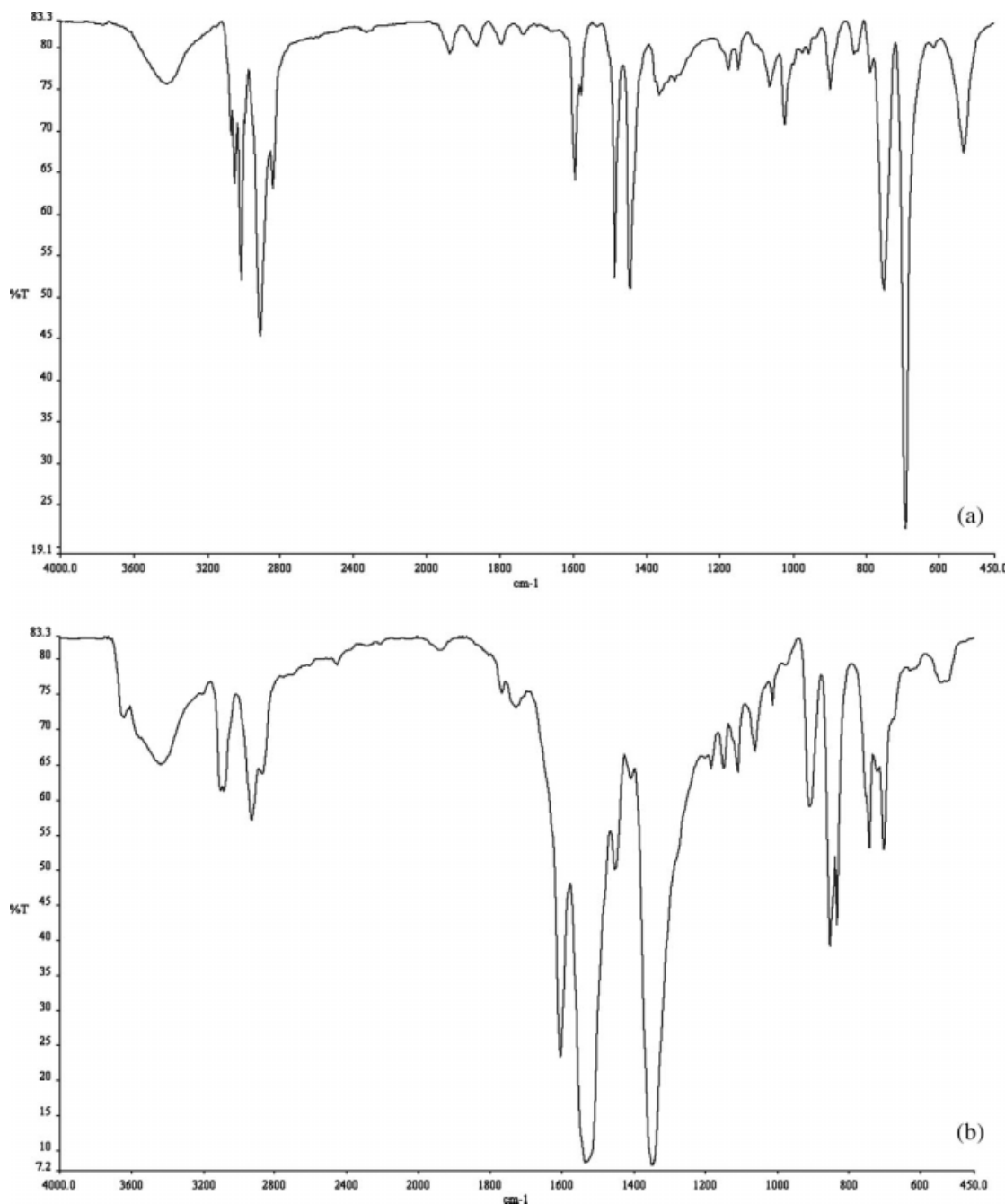


Figure 3 FTIR spectra of S-DVB copolymer 06: (a) basic copolymer, (b) nitrated copolymer, (c) aminated copolymer, and (d) dithiocarbamate copolymer.

porous material than copolymer 01. Copolymer 02, synthesized with a higher DVB content, was more porous (with a higher specific surface area and pore volume) than copolymer 06, and again, the 2118-cm^{-1} band of that copolymer was more intense. Copolymers synthesized with a 200% dilution degree presented a higher relative intensity for the C=S band. Therefore, the extension of the reaction with CS_2 was clearly governed by the access of the reagent solution to the polymer matrix. In other words, copolymers with a higher pore volume were

more reactive in the final reaction step. The copolymers synthesized with a higher dilution degree contained larger pores, which permitted better diffusion of the reagent solution through the inner regions of the solid material. The crosslinking degree was also another determining factor of the porosity. The increase in the DVB amount contributed to the formation of high amounts of pores with low diameter. However, narrow pores did not impart the improvement of reagent diffusion through the polymer matrix, and as a consequence, the extension of the

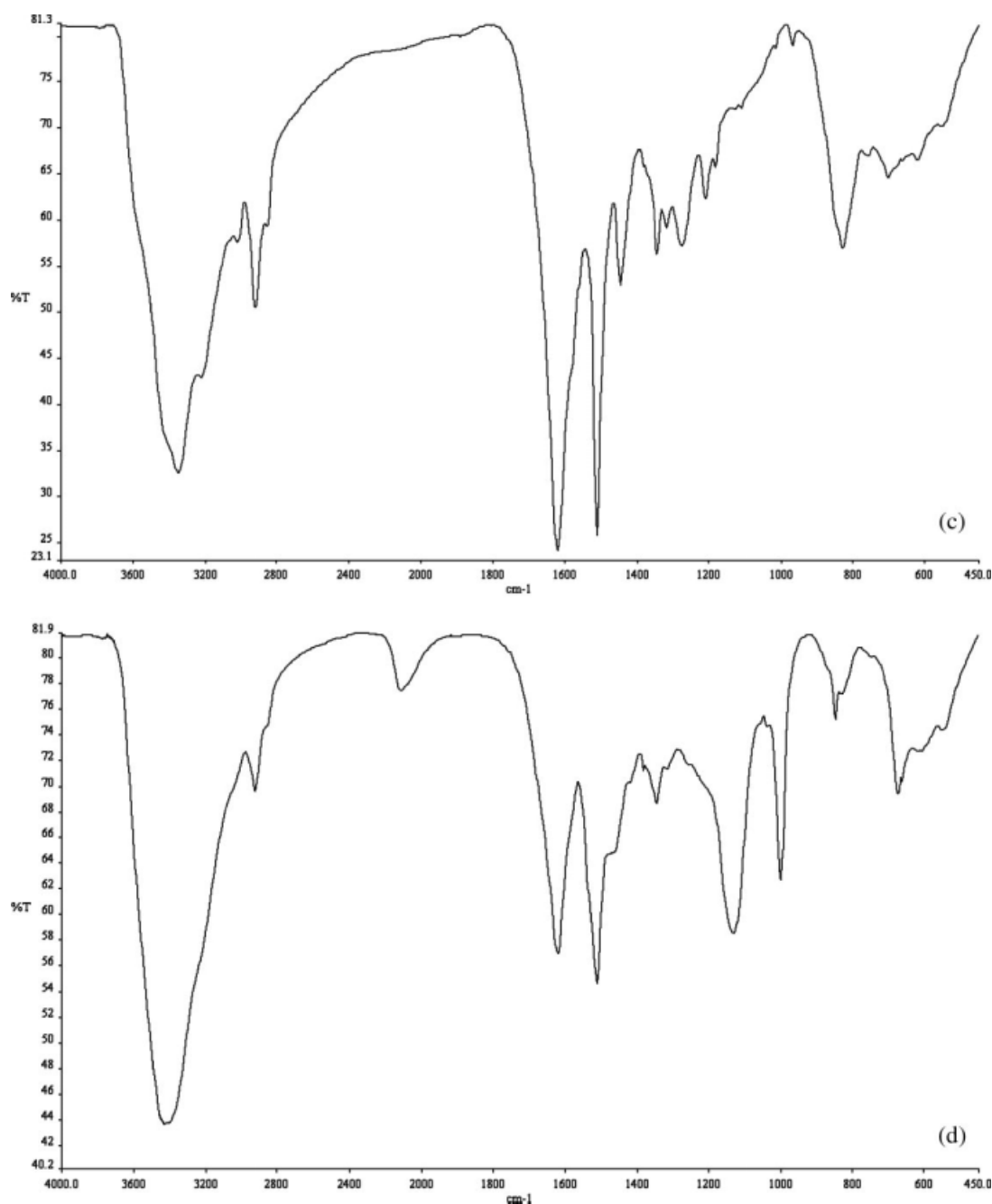


Figure 3 (Continued from previous page)

reaction was limited. Thus, the dilution degree with a nonsolvent was the main responsible factor for producing copolymers with larger pores and, then, the determining one of the extent of the last modification reaction. As discussed before, the extent of the nitration and reduction reactions was not so influenced by the kind of copolymer porous structure as the reaction with CS_2 was. This could be explained by the fact that the two first reactions were powerful ones, whereas the substitution of the amino hydrogen atom by the bulky CS_2 group was not as favored as those two processes were.

All of the dithiocarbamate resins were evaluated for the adsorption of Zn^{2+} and Cd^{2+} ions from aqueous solutions. The best pH value for the ions adsorption was determined by the testing of copolymer 04. This material was chosen because it had a high pore volume and a higher mechanical resistance than copolymer 05, the more porous material. Figure 4 shows that Cd^{2+} was adsorbed in a high yield at pH 6.0. Above this value, no enhancement of this ion adsorption was observed. At pH 9.0, there was a decrease in the amount of Cd^{2+} adsorbed by the copolymer, which can be explained

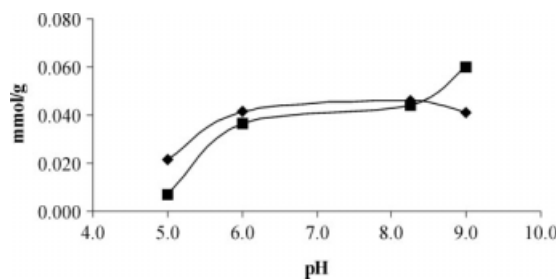


Figure 4 Influence of pH on the (◆) Zn²⁺ and (■) Cd²⁺ adsorption by dithiocarbamate copolymer 04.

by the increase in the NH₃ concentration and a subsequent competition between the two ligands, ammonia and dithiocarbamate. The amount of Zn²⁺ ions adsorbed on the copolymer increased with pH until the studied value. Values of pH above 9.0 were not studied because of the too-possible competition with the high NH₃ concentration.

According to these results, adsorption kinetic curves of Zn²⁺ at pH 9.0 and Cd²⁺ at pH 6.0 were constructed for all copolymers. Figure 5 summarizes the behavior of the copolymers with different porosities in the adsorption of Zn²⁺ and Cd²⁺ ions. Copolymer 01, which exhibited a low pore volume and also a low concentration of dithiocarbamate groups, did not adsorb a significant amount of ions, even after a 1 h of contact with the aqueous solutions. The hydrophobic character of the S-DVB copolymer and the narrow pore size of this polymer matrix hindered efficient ion adsorption. The kinetic curves constructed for copolymer 02 showed the higher adsorption capacity of this material and the faster rate of ion adsorption when compared to copolymer 01. The higher true porosity of copolymer 02 (with a higher pore volume and size), which was synthesized in a higher dilution degree with *n*-heptane than copolymer 01, was the factor responsible for the better adsorption performance of this material. These curves also showed that Zn²⁺ was adsorbed to a higher extent than Cd²⁺; this was in accordance with the results obtained in the pH adsorption study. The same behavior was observed when the dilution degree was increased to 200%. Copolymer 04 reached equilibrium faster than copolymers 01 and 02.

When the curves derived from copolymers 03, 04, and 05 (synthesized with the same dilution degree but with different DVB/S ratios) were compared; the differences in the adsorption rate and in the fraction of ions adsorbed were not as great as those observed for copolymers 01, 02, and 04. Therefore, the increase in the volume of narrow pores (promoted by the higher DVB amount in the monomer mixture) was not as effective as the increase in the pore diameter (promoted by the higher dilution degree with a nonsolvent). These observations sug-

gest that the diffusion rate of the solution through the polymer matrix must be the limiting factor for the ion adsorption rate, and it was maximized by the increase in pore diameter.

When all of the kinetic curves were compared, we observed an increase in the difference between the amounts of Zn²⁺ and Cd²⁺ adsorbed as the copolymer porosity became higher. The adsorption rate and the adsorption capacity for Zn²⁺ increased faster than they increased for Cd²⁺. This behavior was a very interesting finding because it led to the possibility of controlling the copolymer selectivity toward the studied species by controlling the kind of the matrix porous structure. Although resin selectivity is generally controlled by the chemical characteristics of the fixed chelating group, several authors have described this influence of the polymer matrix on the selectivity behavior of ion-exchange resins. Green and Hancock²⁹ referred that this influence was suggested by Bayer in 1964, and in 1980, those authors observed the importance of the matrix structure on the adsorption of platinum and zinc chloro complexes by anionic resins containing isothiuronium or pyridinium groups. The differences observed were attributed to the type of interaction between the loaded group and the chloro complex. They stated that a strong electrostatic interaction was not so influenced by the polymer porous structure as a weak one was, suggesting that the selectivity could be controlled by the synergism of the fixed group and the matrix properties. Mathew and Pillai²³ compared dithiocarbamate copolymers with different

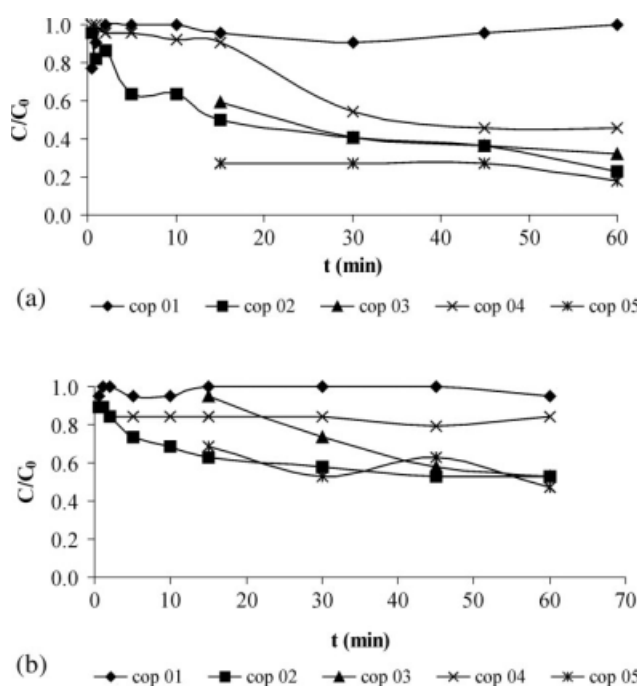


Figure 5 Kinetic curves of (a) Zn²⁺ and (b) Cd²⁺ adsorption by the synthesized dithiocarbamate copolymers. *t*, time.

crosslinking degrees on the adsorption of Cu^{2+} , Zn^{2+} , and Ni^{2+} . It is evident in this work, although not commented on in the text, that the selectivity was affected by the crosslinking degree because the adsorbed amount of Cu^{2+} increased faster with decreasing crosslinking than the amounts of Ni^{2+} and Zn^{2+} did. The dependence of the selectivity on the porous structure has also been explained on the basis of the restriction imposed by the pore size to the permeation of hydrated species larger than the pore diameters.^{30,31} The difference in the hydration ability of the water molecules localized in the inner and outer regions of the resin bead was also assumed to be one of the responsible effects for the selectivity of some anion exchangers. The entangled polymer matrix disturbs the water molecules that surround it, and thus, these aqueous regions have a higher affinity for structure breaker species, such as the perchlorate ion.³² The enhancement of the selectivity with the porosity was also stated by Alexandratos et al.³³ They showed that the interaction between some substituted benzoic acids and aminated crosslinked copolymers was stronger for the more flexible support, but the variation in the strength of the polymer–substrate interaction was more pronounced for the more crosslinked copolymer.

All of these results are in accordance with those obtained in our study, but here, we can say that the selectivity was probably influenced by the difference between the reaction rates of Cd^{2+} and Zn^{2+} with the polymer dithiocarbamate group. This difference became more pronounced with the better diffusion of the aqueous solution through the copolymers with higher pore diameters. This behavior could be attributed to different types of adsorption mechanisms for each ion on the polymer structure. This study is being conducted by our research group and will be published in a forthcoming article.

CONCLUSIONS

The influence of the matrix porosity on the reaction steps following the introduction of the dithiocarbamate group on the S–DVB copolymer was more pronounced for the mild addition reaction to CS_2 . The stronger reactions, such as nitration and reduction with SnCl_2 , were not limited by the copolymer porosity. Considering the adsorption capacity of the synthesized chelating resins toward Zn^{2+} and Cd^{2+} , we observed that the increase in the volume of the narrow pores (promoted by the higher DVB amount in the monomer mixture) was not as effective as the increase in the pore diameter (promoted by the higher dilution degree with a nonsolvent). These observations suggest that the diffusion rate of the solution through the polymer matrix was the limiting factor for the ion adsorption rate, and it was maxi-

mized by the increase in pore diameter. However, the most significant finding of this study was the possibility of controlling the resin selectivity toward the ions studied by controlling the diffusion rate of the solution through the polymer support.

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