# Acrylic Three-Dimensional Networks. II. Behavior of Different Acrylic Ion Exchangers in the Retention and Elution Processes of Some Metal Cations

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**ABSTRACT:** The retention process of the Cu(II) and Ni(II) cations from CuSO<sub>4</sub> and NiSO<sub>4</sub> aqueous solutions by eight acrylic ion exchangers was studied. Also, the elution process of these cations with 0.5 mol  $\cdot$  L<sup>-1</sup> HCl solution was analyzed. The quantitative retention and elution as well as the development aspects of the two processes were observed by the column method. Seven ion exchangers contained weak base, weak acid, and amphoteric functional groups, these being known as chelating agents. Also, an ion exchanger with carboxylic groups, as a model, was taken in this study. The experiments show that the ion exchangers can be divided in three types as follows: (a) bad chelating agents; (b) chelating ion exchangers with the limited efficiency; (c) ion exchangers with good chelating properties and a high application efficiency; especially, the ion exchanger with hydroxamic functional groups is considered in this class. Also, the experimental data prove that, both for Cu(II) and Ni(II) cations, the volume of the purified effluent is higher than the HCl volume needs for their complete elution. This fact means concentration of the metal cations in the liquid phase. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1387–1394, 1999

Key words: acrylic ion exchangers; retention and elution of metal cations; three-dimensional chelating agents; Cu(II) and Ni(II) cations uptaken by acrylic ion exchangers

## INTRODUCTION

The retention of metal cations by some functional crosslinked copolymers can take place by ion exchange or chelating processes, depending on chemical structure of their functional groups.

The ion exchange process is involved, especially, in the case of the cation exchangers as well as in the case of strong-base anion exchangers, if the metal cations there are in the condition to form complex anions.

The chelating functional groups are those that contain one or more electron-donor elements such as N, S, O, and P, their chemical structures being very different and generally complicated.<sup>1</sup>

From the literature data the chelating properties of the primary, secondary, and tertiary amine groups grafted on linear and crosslinked polymers are well known.<sup>2-8</sup>

The presence of both O and N ligands in the carboxyamine structures obtained by the carboxymethylation of the primary or secondary amine functional groups of the crosslinked copoly-

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mers improves the affinity of these structures for heavy metal cations.  $^{9-11}$ 

The insertion of the specific ligand in the linear or crosslinked polymers is considered to be the most promising technique for the achievement of specific chelating supports.<sup>12–16</sup>

In our previous article<sup>17,18</sup> we reported the retention of Fe(III) ions on crosslinked ionic polymers prepared by the chemical modifications of 4-vinylpyridine-divinylbenzene copolymer.

The present article deals with a comparative study of the retention of Cu(II) and Ni(II) cations by crosslinked acrylic copolymers with different functional groups prepared in our laboratory.<sup>19–23</sup> Also, the elution process of these cations is analyzed.

# **EXPERIMENTAL**

## **Materials**

For the retention study of Cu(II) and Ni(II) cations we used crosslinked functional acrylic copolymers obtained by: (a) aminolysis with ethylenediamine, diethylenetriamine, triethylenetetramine, and hydroxylamine, the latter in the presence of sodium ethoxylate, of the divinylbenzene-ethylacrylate-acrylonitrile copolymers (AS-98, AS-135, AS-32, and CCH-01 sample codes, respectively) or by aminolysis with N,N-dimethylaminopropylamine of the divinylbenzeneethylacrylate-vinylacetate copolymer (AS-154 sample code); (b) the carboxymethylation of AS-98 ion exchanger (AS-98 CM1 and AS-98 CM2 sample codes); and (c) alkaline hydrolysis of divinylbenzene-ethylacrylate-acrylonitrile copolymer (CC-31 sample code).

CuSO<sub>4</sub>, NiSO<sub>4</sub>, and HCl aqueous solutions of 0.01600, 0.01731, and 0.5 mol  $\cdot$  L<sup>-1</sup>, respectively.

#### **Methods**

Crosslinked functional acrylic copolymers were characterized by the following features: (a) the volume weight  $(W_v)$  expressed as  $g \cdot mL^{-1}$ , which is determined by the measurement of the weight loss of a known volume of fully hydrated resin in the desired ionic form, up to constant weight; (b) the volume and weight exchange capacities ( $C_v$ and  $C_{Wt}$ , respectively) expressed as mEq  $\cdot mL^{-1}$ and mEq  $\cdot g^{-1}$ , namely: weak-base exchange capacities for AS-98, AS-135, AS-32, and AS-154 as well as weak acid exchange capacities for CCH-01 and CC-31 samples, performed according to known methods.<sup>24</sup> For the amphoteric resins, the exchange capacity values obtained by ionic exchange process represent the total number of their ionic groups. The contents of carboxylic groups was evaluated by standardized complexometric method for the determination of the weak acid exchange capacity;<sup>25</sup> (c) metal cation retention capacity, expressed as mg Me(II)  $\cdot$  g<sup>-1</sup> or mg Me(II)  $\cdot$  mL<sup>-1</sup>.

The retention capacity values were determined by the percolation of the metal cation solution through 10 mL of the ion exchanger bed with a debit of the 0.8 mL influent · min<sup>-1</sup> at room temperature. The retention process was controlled by the monitoring of the metal cation concentration in the effluent according to the complexometric method.<sup>26</sup> The retention capacity  $(C_R)$  is the difference between the influent metal cation concentration and effluent one and was expressed as mg  $Me(II) \cdot g^{-1}$  dry sample or mg  $Me(II) \cdot mL^{-1}$  wet sample. For the discussion of the experimental data, the  $(C_R)$  retention capacity was considered to be composed of two components: (a) the complete retention capacity  $(C_{\rm RC})$  representing the metal cation quantity retained in the condition in which the effluent is free of its presence, and (b) the retention capacity at the saturation  $(C_{\rm RS})$  calculated from the moment when the metal cation breaks through the sample bed until the metal cation concentration is equal for both influent and effluent solutions.

The amphoteric ion exchangers were tested in two ionic forms: (1) free-base amine and sodium carboxylate (AS-98  $CM_1$  sample); (2) free-base amine and free acid (AS-98  $CM_2$  sample).

The metal cation elution was accomplished by percolation of the 10-mL sample bed with 0.5 mol·L<sup>-1</sup> HCl solution at room temperature and a flow rate of 0.5 mL HCl per minute. The concentration coefficient  $(C_e/C_O)$  represents the ratio of the average eluted metal cation concentration and the initial one.

# **RESULTS AND DISCUSSION**

Table I presents the physicochemical characteristics of the crosslinked functional acrylic copolymers tested in this study.

It shows that all the resins, except for the CC-31 sample, contain functional groups known to have chelating properties towards metal cations. The CC-31 ion exchanger retains the metal

|     | ~ 1              |   | ~     | Volume                     | Exchange Cap          | acity Values         |
|-----|------------------|---|-------|----------------------------|-----------------------|----------------------|
| No. | Sample<br>Code   | Functional Groups   | (g %) | Weight $(g \cdot mL^{-1})$ | $(mEq \cdot mL^{-1})$ | $(mEq \cdot g^{-1})$ |
| 1.  | AS-98            | $\overset{\textbf{O}}{\overset{\parallel}{}_{-\text{C}}-\textbf{NH}-\textbf{CH}_2-\textbf{CH}_2-\textbf{NH}_2}$   | 3.00  | 0.0415                     | 0.31                  | 7.47                 |
| 2.  | AS-98 $CM_1$     | O<br>   | 3.00  | 0.0407                     | 0.33                  | 8.05                 |
|     |                  | -C-NH-(CH <sub>2</sub> ) <sub>2</sub> -NH-CH <sub>2</sub> -COONa  |       |                            | $0.16^{\mathrm{a}}$   | $3.95^{\mathrm{a}}$  |
| 3.  | AS-98 $\rm CM_2$ | O<br>II   | 3.00  | 0.2204                     | 1.66                  | 7.53                 |
|     |                  | -C-NH-(CH <sub>2</sub> ) <sub>2</sub> -NH-CH <sub>2</sub> -COOH   |       |                            | 0.83*                 | $3.76^{\mathrm{a}}$  |
| 4.  | AS-135           | $\stackrel{\textbf{O}}{\parallel}$<br>C(NHCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub>  | 15.00 | 0.2215                     | 1.34                  | 6.05                 |
| 5.  | AS-32            | $\overset{O}{\overset{\ }{=}}_{-\!$   | 15.00 | 0.3384                     | 2.20                  | 6.50                 |
| 6.  | AS-154           | $\begin{array}{c} \mathbf{O} & \mathbf{CH}_{3} \\ \parallel & \downarrow \\ -\mathbf{C} - \mathbf{NH} - (\mathbf{CH}_{2})_{3} - \mathbf{N} \\ \end{array}; - \mathbf{OH}$ | 1.00  | 0.0910                     | 0.52                  | 5.74                 |
| 7.  | CCH-01           | о СН <sub>3</sub><br>  <br>СNHОН  | 8.00  | 0.3280                     | 1.80                  | 5.48                 |
| 8.  | CC-31            | —COONa  | 3.00  | 0.0928                     | 0.85                  | 9.20                 |

Table I The Physicochemical Characteristics of the Tested Acrylic Ion Exchangers

<sup>a</sup> Obtained by the complexometric method.

cations only by the ion exchange process and was tested for purposes of comparative discussion. The selected samples, in terms of the functional group nature, are monofunctional resins (1, 4, 5, 7, and 8 sample numbers) or bifunctional resins (2, 3, and 6 sample numbers).

Also, from Table I data one can see that the amphoteric resins (2 and 3 sample numbers) have numerical ratios between weak base exchange capacity and a weak acid one of 1.04, meaning that for each amine functional group there is a corresponding carboxylic one.

Figure 1 presents the relation between the  $CuSO_4$  effluent concentration and effluent bed volumes for all the tested samples.

The above-mentioned relation is a quantitative measure of the retention process efficiency, and resin may be considered to have good properties in this field if it completely retains certain metal cations from sufficiently large effluent bed volumes and then its exhaustion suddenly takes place. From this point of the view the tested weakbase acrylic anion exchangers having different crosslinking values and various acrylamido-alkyleneamine functional groups are, generally, the weak complexation agents because they retain the Cu(II) cation from the low numbers of effluent bed volumes (curves 2-5, namely 1, 4, 5, and 6 sample numbers from Table I). Among these anion exchangers a certain convenient position displays the AS-135 sample (curve 5), which retains Cu(II) ions from somewhat higher effluent bed volumes, namely 3.5 for the AS-135 sample compared to 0.5 for the other weak-base acrylic anion exchangers. This result suggests the correlation between the Cu(II) complexation ability of the weak-base anion exchanger and the chemical nature of their functional groups. It seems that the anion exchanger having the acrylamidodiethylenediamine functional groups (AS-135 sample) offers convenient conditions for the Cu(II) coordination sphere. It must mentioned that this anion



**Figure 1** The variation versus the effluent bed volume of the percolated  $\text{CuSO}_4$  molar solution concentration on the different acrylic ion exchangers. Test conditions: influent concentration 0.01600 mol Cu(II)  $\cdot$  L<sup>-1</sup>; percolation debit equal with 0.8 mL  $\cdot$  min<sup>-1</sup>; ion exchanger bed volume = 10.0 mL.

exchanger has the same crosslinking with AS-32 sample (curve 3) but a much higher crosslinking degree than AS-98 and AS-154 samples (curve 2 and curve 4, respectively).

A separate observation is that the presence in the acrylic three-dimensional network of the hydroxyl functional groups (provided by the hydrolyzation of the vinyl acetate structural units) together with N,N-dimethylaminopropyl does not improve the chelating properties of the weak-base anion exchanger (Fig. 1, curve 4, namely AS-154 sample from Table I).

A significant improvement of the chelating ability takes place by the carboxymethylation of the weak-base anion exchanger having acrylamidoethylenamine functional groups (compare curve 2 with curves 6 and 7). The amphoteric ion exchangers completely retain the Cu(II) ions from 14 bed volumes of the effluent solution then they go to exhaustion in different ways, depending on their ionic form (see AS-98 CM<sub>1</sub> and CM<sub>2</sub> samples from Table I).

The presence of the hydroxamic functional groups in the three-dimensional acrylic network provides high efficiency for the metal cation retention process. Also, one can observe from Figure 1 data that the CCH-01 sample retains the Cu(II) cations from about 10 bed volumes of effluent solution, then it suddenly goes to exhaustion. The Cu(II) retention pattern by the above-mentioned sample is similar to that of the CC-31 cation exchanger sample presented as the model (Fig. 1, curve 1).

Figure 2 shows the same aspect as Figure 1, but for the Ni(II) cations from the  $NiSO_4$  aqueous solution.

Curve 1 data represents the Ni(II) cation retention process performed on the CC-31 sample taken as a model. From Figure 2 data one can observe the fact that AS-98 and AS-154 samples (curves 2 and 3, namely 1 and 6 sample numbers, respectively, from Table I) completely retain the metal cations from the effluent bed volumes of 1 and 2 values, respectively, then they quickly go to exhaustion. Also, samples AS-135 and CCH-01 (curves 5 and 6, respectively) purify significant quantities of the effluent solution (5 and 8 bed volumes, respectively) then they suddenly go to saturation. The shape of the Ni(II) retention curves for these supports is similar to the one for ionic mechanism (curve 1) providing their good chelation properties. A very interesting result is obtained on a sample having acrylamidotriethylenetriamine functional groups (see curve 4). This support completely retains the Ni(II) cations from nine effluent bed volumes, then it slowly goes to saturation.



**Figure 2** The variation versus the effluent bed volume of the percolated NiSO<sub>4</sub> molar solution concentration on the different acrylic ion exchangers. Test conditions:  $C_0 = 0.01731 \text{ Ni}(\text{II}) \cdot \text{L}^{-1}$ , the percolation debit equal with 0.8 mL  $\cdot \text{min}^{-1}$ ; ion exchanger bed volume = 10.0 mL.

Having in the mind the retention pattern of the Cu(II) and Ni(II) cations by the ionic process performed on the CC-31 sample, the data from Figures 1 and 2 suggest that the acrylic ion exchangers can be divided in three distinct types as follows: (1) the bad chelating agents: AS-98, AS-32, AS-154, and AS-135 samples towards Cu(II) cations; AS-98 and AS-154 for Ni(II) cations. (2) The limited efficient chelating ion exchangers namely  $AS-98CM_1$ ,  $AS-98CM_2$  samples towards the Cu(II) cation, and AS-32 sample for the Ni(II) cation, which completely retain the metal cations from a sufficiently large effluent bed volumes, but exhaustion slowly occurs while Cu(II) and Ni(II) cations break through the sample bed. (3) Ion exchangers with good chelating properties and high application efficiency, namely a CCH-01 sample for both the Cu(II) and Ni(II) cations and an AS-135 sample only for the Ni(II) cations. They completely retain the metal cations from sufficiently large effluent bed volumes, then they suddenly go to saturation.

To analyze the quantitative contribution of the  $(C_{\rm RC})$  and  $(C_{\rm RS})$  components to the total retention capacity  $(C_R)$ , their values were evaluated for the retention process of Cu(II) and Ni(II) cations on acrylic ion exchangers, as shown in Table II.

From Table II one can observe that the Cu(II) total retention capacity values range between 30.20 and  $555.94 \text{ mg} \cdot \text{g}^{-1}$  or 9.21 and  $28.98 \text{ mg} \cdot \text{ml}^{-1}$ , while Ni(II) total retention capacity values range between 20.18 and 125.30 mg  $\cdot \text{g}^{-1}$  or 3.98 and  $12.54 \text{ mg} \cdot \text{mL}^{-1}$ , representing good results. Despite the fact that some of the tested acrylic ion exchangers have relative high total retention capacity values towards Cu(II) (Table II, samples 1, 5, and 6) and Ni(II) (Table II, sample 1), they are not efficient in the chelation process because at the same time the metal cation retention process and the breakthrough of the sample bed take place (see again the data of Figs. 1 and 2).

In the case of the acrylic ion exchangers with limited efficiency in the Cu(II) and Ni(II) chelation process (Table II, numbers 2, 3, and 5, respectively) the  $C_{\rm RS}$  component has an important contribution to total retention capacity values. Although the  $(C_{RS})$  component has an important contribution to the total retention capacity values, only the complete retention step of the retention process justifies their efficient application in this domain.

For the acrylic ion exchangers with good Cu(II) and Ni(II) retention properties (Table II, CCH-01 and AS-135 samples, respectively) an insignifi-

| al       | le II The      | Cu(II) ar                         | nd Ni(II) R                        | <b>Retention</b> C                | apacity Val                        | ues of the                        | e Acrylic Io                       | n Exchan                          | gers                               |                                   |                                      |                                   |                            |
|----------|----------------|-----------------------------------|------------------------------------|-----------------------------------|------------------------------------|-----------------------------------|------------------------------------|-----------------------------------|------------------------------------|-----------------------------------|--------------------------------------|-----------------------------------|----------------------------|
|          |                |                                   |                                    | G                                 | u(II)                              |                                   |                                    |                                   |                                    | Ni                                | (II)                                 |                                   |                            |
|          |                | C                                 | RC                                 | $C_1$                             | RS                                 | C                                 | 'R                                 | C                                 | RC                                 | C                                 | RS                                   | $C_I$                             | ~                          |
| <u>.</u> | Sample<br>Code | $\mathrm{mg}\cdot\mathrm{g}^{-1}$ | $\mathrm{mg}\cdot\mathrm{mL}^{-1}$ | $\mathrm{mg}\cdot\mathrm{g}^{-1}$ | $\mathrm{mg}\cdot\mathrm{mL}^{-1}$ | $\mathrm{mg}\cdot\mathrm{g}^{-1}$ | $\mathrm{mg}\cdot\mathrm{mL}^{-1}$ | $\mathrm{mg}\cdot\mathrm{g}^{-1}$ | $\mathrm{mg}\cdot\mathrm{mL}^{-1}$ | $\mathrm{mg}\cdot\mathrm{g}^{-1}$ | $\mathrm{mg} \cdot \mathrm{mL}^{-1}$ | $\mathrm{mg}\cdot\mathrm{g}^{-1}$ | ${ m mg}\cdot{ m mL}^{-1}$ |
|          | AS-98          |                                   |                                    | 250.84                            | 10.41                              | 250.84                            | 10.41                              |                                   | I                                  | 125.30                            | 5.20                                 | 125.30                            | 5.20                       |
| ~i       | $AS-98CM_1$    | 349.38                            | 14.22                              | 206.56                            | 8.40                               | 555.94                            | 22.62                              |                                   |                                    |                                   |                                      |                                   |                            |
| ÷.       | $AS-98CM_2$    | 64.52                             | 14.22                              | 66.97                             | 14.76                              | 131.49                            | 28.98                              |                                   |                                    |                                   |                                      |                                   |                            |
| ÷        | AS-135         | 15.80                             | 3.50                               | 25.78                             | 5.71                               | 41.58                             | 9.21                               | 14.25                             | 3.22                               | 3.43                              | 0.76                                 | 17.68                             | 3.98                       |
| ю.       | AS-32          |                                   |                                    | 30.20                             | 10.22                              | 30.20                             | 10.22                              | 17.14                             | 5.80                               | 19.91                             | 6.74                                 | 37.05                             | 12.54                      |
| ю.       | AS-154         |                                   |                                    | 159.01                            | 14.47                              | 159.01                            | 14.47                              | 22.30                             | 2.03                               | 22.98                             | 2.00                                 | 45.28                             | 4.03                       |
| 2.       | CCH-01         | 29.02                             | 9.52                               | 1.95                              | 0.64                               | 30.97                             | 10.16                              | 15.73                             | 5.16                               | 4.45                              | 1.46                                 | 20.18                             | 6.62                       |
| с.       | CC-31          | 87.60                             | 8.13                               | 51.50                             | 4.47                               | 139.10                            | 12.60                              | 34.60                             | 3.22                               | 12.82                             | 1.19                                 | 47.42                             | 4.41                       |
|          |                |                                   |                                    |                                   |                                    |                                   |                                    |                                   |                                    |                                   |                                      |                                   |                            |



**Figure 3** The various versus 0.5 mol  $\cdot$  L<sup>-1</sup> HCl bed volume of the CuSO<sub>4</sub> molar concentration eluted from different acrylic ion exchangers. Test conditions: eluent debit equal with 0.5 mL  $\cdot$  min<sup>-1</sup>; room temperature.

cant contribution of the  $(C_{RS})$  component to the total retention capacity value was observed. The value of the  $(C_{RS})$  component is a quantitative measure of an efficient retention process by a certain support. From this point of view the Cu(II) and Ni(II) retention process by the chelation mechanism, on the supports of CCH-01 and AS-135, is qualitatively and quantitatively better than by the ionic mechanism effected by the CC-31 sample [see for comparison the shape of the retention curves from Figs. 1 and 2, and the values of the  $(C_{RS})$  component from Table II].

The elution pattern of the metal cations provides important information about the performance of the different supports in the retention process.

Figure 3 presents the results on the elution process of the Cu(II) ions by the tested acrylic ion exchangers.

The comparation between elution processes of the retained Cu(II) cations both by ion exchange and the chelation mechanism gives a real measure of efficiency of the tested samples in the retention process. The ionic-retained Cu(II) cations are completely eluted in 2.0 bed volumes of the 0.5 mol  $\cdot$  L<sup>-1</sup> HCl solution, while the acrylic ion exchangers, with bad chelation properties or with limited efficiency in this process (curves 2 and 3, namely sample AS-135 and AS-98 CM<sub>1</sub>, respectively) at the 3.0 eluent bed volumes, release approximately 83.0% of the total uptake of the Cu(II) cations. For these samples the second part of the elution process is a slow one, suggesting their efficient application, only in the complete retention domain (see Fig. 1, curves 5 and 6; Table II, numbers 2 and 4).

Also from Figure 3 data one can observe that the CCH-01 sample is not only a good chelation support but also an efficient compound in the retention process of Cu(II) cations (see Fig. 1, curve 8). It releases about 98.3% of the uptaken metal cations (Fig. 3, curve 4) at the 3.0 eluent bed volumes.

Figure 4 shows the elution levels for the Ni(II) cations uptaken by the tested ion exchangers.

Curve 2 shows the elution of the Ni(II) cations retained by the CC-31 sample by the ion exchange mechanism. As can be observed from the shape of this curve, for the complete elution of Ni(II) cations one uses only 2.5 eluent bed volumes.

In comparison with this result, the tested acrylic anion exchangers, namely AS-32 and AS-135 samples, initially show an efficient part of the elution process when a degree of 78.83 and 89.07% of uptaked Ni(II) cations are eluted at only 3.0 eluent bed volumes. The second part of the process is quite slow, and it needs, for complete elution of the chelated Ni(II) cations, up to approximately 8.0 and 17.0 eluent bed volumes for AS-135 and AS-32 samples, respectively. This



**Figure 4** The various versus 0.5 mol  $\cdot$  L<sup>-1</sup> HCl bed volume of the NiSO<sub>4</sub> molar concentration eluted from different acrylic ion exchangers. Test conditions: eluent debit of 0.5 mL  $\cdot$  min<sup>-1</sup>; room temperature.

|     |                | Cu(II)                               |           | Ni(II)                               |           |
|-----|----------------|--------------------------------------|-----------|--------------------------------------|-----------|
| No. | Sample<br>Code | $C_e \ ({ m mol} \cdot { m L}^{-1})$ | $C_e/C_0$ | $C_e \ ({ m mol} \cdot { m L}^{-1})$ | $C_e/C_0$ |
| 1.  | AS-32          | 0.08500                              | 5.31      | 0.25900                              | 23.56     |
| 2.  | CC-31          | 0.09836                              | 6.14      | 0.08250                              | 7.50      |
| 3.  | CCH-01         | 0.06768                              | 4.22      | 0.05098                              | 4.63      |
| 4.  | AS-98CM        | 0.10072                              | 6.29      |                                      |           |
| 5.  | $AS-98CM_2^1$  | 0.24790                              | 15.49     |                                      |           |
| 6.  | AS-135         | 0.02754                              | 2.50      | 0.04600                              | 4.18      |

 Table III
 Data on the Concentration Possibility of Cu(II) and Ni(II) Cations Retained on Different

 Acrylic Ion Exchangers
 Particular State

Test conditions:  $C_0(\text{CuSO}_4) = 0.01600 \text{ mol} \cdot \text{L}^{-1}$ ;  $C_0(\text{NiSO}_4) = 0.01731 \text{ mol} \cdot \text{L}^{-1}$ .

result suggests that such anion exchangers have a limited efficiency in the Ni(II) chelation process. The similar elution pattern with the CC-31 sample follows the support having hydroxamic functional groups (compare the data of curve 4 with those of the curve 1). In this case, the total quantity of the chelated Ni(II) cations is eluted in 3.0 eluent bed volumes. This aspect confirms the high efficiency of the support with such functional groups.

The experimental data prove that, both for Cu(II) and Ni(II) cations, the volume of the purified effluent is higher than that of the HCl needs for their complete elution. This fact means increasing of the concentration of the metal cations in the liquid phase.

Table III gives the concentration coefficient values  $C_e/C_O$  for the Cu(II) and Ni(II) cations.

From Table III data one can observe that the concentration coefficient values for both Cu(II) and Ni(II) cations range between 2.50–15.49 and 4.18–23.56, respectively.

# **CONCLUSIONS**

- 1. The retention of the Cu(II) and Ni(II) cations on weak-base, weak-acid, and amphoteric acrylic ion exchangers was studied.
- 2. The total weight retention capacity values of the different acrylic exchangers range between 30.20 and 555.94 mg Cu(II)  $\cdot$  g<sup>-1</sup> or between 20.18 and 125.30 mg Ni(II)  $\cdot$ g<sup>-1</sup>, while the total volume retention capacity values range between 9.21 and 28.48 mg Cu(II)  $\cdot$  mL<sup>-1</sup> or between 3.98 and 12.54 mg Ni(II)  $\cdot$  mL<sup>-1</sup>.

- 3. The pattern of both retention and elution processes of the Cu(II) and Ni(II) cations suggests that the tested acrylic ion exchangers can be divided in the following three types: (a) bad chelating agents which, although, having relative high total retention capacity values have their sample beds broken through by the metal cations at the beginning of the chelation process; (b) the limited chelating ion exchangers, which completely retain the Cu(II) and Ni(II) cations at large enough numbers of the effluent bed volumes, but their saturation slowly occurs while the metal cations pierce the sample bed; (c) the good chelating ion exchangers, which completely retain Cu(II) and Ni(II) cations for a certain numbers of the effluent bed volumes, then they suddenly go to saturation, suggesting a high efficiency in hydrometallurgical applications.
- 4. The concentration coefficient values  $(C_e/C_O)$  of both Cu(II) and Ni(II) cations range between 2.50–15.49 and 4.18–23.56, respectively.

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