Separation of Y(dcta)– complexes from Nd(dcta)– and Sm(dcta)– complexes on polyacrylate anion-exchangers

HALINA HUBICKA* and DOROTA KOŁODYŃSKA

Department of Inorganic Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland

(Received 20 September, revised 4 December 2002)

Abstract: The formation of anion rare earth element complexes with aminopolycarboxylic acids gives new possibilities for the separation of these elements on anion-exchangers. The higher affinity of the Nd(dcta)– and Sm(dcta)– complexes for the anion-exchangers compared to Y(dcta)– complexes indicates the possibility of yttrium purification as a macrocomponent from the former by frontal analysis. The weakly basic polyacrylate gel anion-exchanger Amberlite IRA 68 was more effective in the purification of Y(III) from Nd(III) and Sm(III) complexes with DCTA than the strongly basic anion-exchangers of this type.

Keywords: rare earth elements, polyacrylate anion-exchangers, DCTA.

INTRODUCTION

Ion-exchange chromatography is one of the methods which enables the preparation of rare earth elements in a high state of purity.

The formation of anion rare earth element complexes with aminopolycarboxylic acids gives new possibilities for the separation of these elements on anion-exchangers.

Recent investigations pointing to the affinity series of anion lanthanide complexes with aminopolycarboxylic acids for strongly basic polystyrene anion-exchangers are non-typical and non-monotonic.1–5 An unusual order of elution: Lu(III), Yb(III), Tm(III), Er(III), Y(III), Ho(III), Dy(III), Tb(III), Sc(III), La(III), Gd(III), Eu(III), Ce(III), Pr(III), Sm(III), Nd(III), Pm(III), was obtained on an anion-exchanger in DCTA solution.6–8

The affinity of rare earth element complexes with DCTA for anion-exchangers proved very useful for their separation in the macro-micro system by the frontal analysis technique for the separation of Y(III) from Nd(III), Sm(III) and Eu(III) on the polystyrene anion-exchangers Dowex 1×4 and Dowex 1×2.9

The studies also showed that this affinity depends not only on the structure of the complex but also on the physicochemical properties of the anion-exchanger. Acrylate anion-exchangers have unique physicochemical properties, high ion-exchange capacity,
quick kinetic exchange. Moreover, they provide a long, flexible, pendant spacer arm for the functional group unlike the conventional polystyrene anion-exchangers. Acrylate anion-exchangers are applied in industrial methods to remove Fe cyanide from mill wastewater and to recover polyvalent metal (Ni, Fe, Cu, Co) cyanide complexes in a fluidized-bed as well as to separate rare earth element complexes with IMDA. The aim of the paper was to study the applicability of strongly and weakly basic anion-exchangers with a polyacrylic skeleton for the separation of selected pairs of rare earth complexes with DCTA (Ln(dcta)\(^{-}\)).

EXPERIMENTAL

Amberlite IRA 458, Amberlite IRA 68 and Amberlite IRA 958, produced by Rohm and Haas Co., and Dowex 2×8, produced by the Dow Chemical Company, were used in the investigations.

Amberlite IRA 458 – polyacrylic, type 1, strongly basic, gel, bead size 600–900 μm, capacity 1.25 meq/mL.

Amberlite IRA-68 – polyacrylic, type 1, weakly basic, gel, bead size 550–750 μm, capacity 1.6 meq/mL.

Amberlite IRA 958 – polyacrylic, type 1, strongly basic, macroporous, bead size 675–875 μm, capacity 0.80 meq/mL.

Dowex 2×8 – polystyrene, type 2, strongly basic, gel, bead size 150–300 μm, capacity 1.4 meq/mL.

The complexed solutions of rare earth elements were prepared by dissolving the oxides with 1% excess of the stoichiometric quantity of DCTA solution (Ln(III):DCTA = 1:1) under heating. The breakthrough curves were determined using 40 mL of the anion-exchanger in the Cl– form or OH– form (commercial form). For the separation of the pairs of lanthanides, 80 mL of the anion exchanger were used. These anion-exchangers were used in the acetate form obtained by contacting with an excess of 1 M CH\(_3\)COONH\(_4\) at pH 7.0 and the anion-exchanger Amberlite IRA 458 was also used in the DCTA form obtained by contacting with an excess of 0.1 M DCTA at pH 4.8.

The breakthrough curves of yttrium(III), neodymium(III) and samarium(III) were determined using solutions of the complexed rare earth elements at a concentration 4.0 mM. Solutions containing about 1.5 g Ln\(_2\)O\(_3\)/L at pH 4.8 were used for the separation of Y(III) from Nd(III) and Y(III) from Sm(III). The frontal analysis process was carried out in glass columns of diameter 2.0 cm filled with the anion-exchanger keeping the flow rate at 0.2 cm\(^3\)/cm\(^2\) min. The effluent was collected as fractions of 25–100 mL for the breakthrough and 50–250 mL for the separation, from which the oxalates were precipitated and converted to oxides.

The percentage of neodymium in yttrium was determined by spectrophotometric analysis using a SPECORD, M 40 spectrophotometer (Zeiss, Germany). The percentage of samarium in yttrium was determined by X-ray fluorescence analysis (XRF) on a CANBERRA PACKARD, USA, spectrometer.

RESULTS AND DISCUSSION

The rare earth element complexes with DCTA of the Ln(dcta)\(^{-}\) type show an unusual sequence of affinity for strongly basic polystyrene anion-exchangers. The affinity of the Y(dcta)\(^{-}\) complex is lower than that of Nd(dcta)\(^{-}\) and Sm(dcta)\(^{-}\) and the position of the Y(III) complex in the affinity series indicates the possibility of purification of Y(III) from Nd(III), as well as Y(III) from Sm(III) using frontal analysis, which is very useful for the separation of microquantities from the major components which are sorbed by the ion-exchanger to a much lesser extent. The unique properties of polyacrylate anion-exchangers, such as having a long, flexible, pendant spacer arm for the functional group and
the hydrophilic character, mean that these resins providing two or three appropriately spaced exchange sites can show preference for polyvalent ions.

The chromatographic separation of Y(III) from Nd(III) and Y(III) from Sm(III) complexes with DCTA using a polyacrylate gel and a macroporous strongly basic, as well as a weakly basic gel anion-exchanger were investigated in this paper. For the analogous complexes of Y(III) and Nd(III), comparative studies were carried out on the polystyrene anion-exchanger Dowex 2×8 (type 2) with the functional group −N+(CH₃)₂C₂H₄OH.

The breakthrough curves of the Y(III), Sm(III) and Nd(III) complexes with DCTA at pH 4.8 on the polyacrylate anion-exchangers: strongly basic, gel Amberlite IRA 458,
weakly basic, gel Amberlite IRA 68 and strongly basic, macroporous Amberlite IRA 958 in the acetate form are presented in Figs. 1–3.

The breakthrough curves of $\text{Y(III)}$ and $\text{Nd(III)}$ complexes on the strongly basic polyacrylate anion-exchangers for the corresponding $\text{Y(III)}$ complexes and their affinity follows the same order as for strongly basic polystyrene anion-exchangers.

weakly basic, gel Amberlite IRA 68 and strongly basic, macroporous Amberlite IRA 958 in the acetate form are presented in Figs. 1–3.

The breakthrough curves of $\text{Y(III)}$ and $\text{Nd(III)}$ complexes on the strongly basic polystyrene, gel resin Dowex 2×8 are presented in Fig. 4.

As follows from the breakthrough curves, the $\text{Nd(III)}$ and $\text{Sm(III)}$ complexes with DCTA exhibit a higher affinity for both the strongly basic and the weakly basic polyacrylate anion-exchangers for the corresponding $\text{Y(III)}$ complexes and their affinity follows the same order as for strongly basic polystyrene anion-exchangers.
Assuming that 1:1 complexes are formed, the ion-exchange can be written as:

$$\text{RCH}_3\text{COO} + \text{Ln(dcta)}^- \rightarrow \text{RLn(dcta)} + \text{CH}_3\text{COO}^-$$

The determined curves make it possible to calculate the values of the weight ($D_w$) and bed ($D_v$) distribution coefficients of Y(III), Sm(III) and Nd(III) complexes with DCTA on the polyacrylic anion-exchangers (Tables I–III) as well as on the polystyrene anion-exchanger Dowex 2×8 (Table IV) from the following equations:

$$D_w = \frac{U - U_o - V}{m_j}$$

$$D_v = D_w \times d_z$$

where: $U$ – the effluent volume (mL) at $c = c_0/2$; $U_o$ – the dead volume (mL) in the column; $V$ – the void (inter-particle) resin bed volume (mL) which amounts to ca. 0.4 of the resin bed volume; $m_j$ – the dry resin weight (g) and $d_z$ – resin density.

TABLE I. The values of the weight ($D_w$) and the bed ($D_v$) distribution coefficients of Y(III), Sm(III) and Nd(III) complexes with DCTA (Ln(III):DCTA = 1:1, pH 4.8) on the anion-exchanger Amberlite IRA 458 in the acetate form

<table>
<thead>
<tr>
<th>Anion-exchanger</th>
<th>Ln(III)</th>
<th>$D_w$</th>
<th>$D_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlite IRA 458</td>
<td>Y(III)</td>
<td>320.27</td>
<td>72.57</td>
</tr>
<tr>
<td></td>
<td>Sm(III)</td>
<td>400.49</td>
<td>90.75</td>
</tr>
<tr>
<td></td>
<td>Nd(III)</td>
<td>422.45</td>
<td>95.73</td>
</tr>
</tbody>
</table>

The estimated values of the distribution coefficients are presented in Tables I–IV. The breakthrough curve of the Nd(III) complex with DCTA was also determined on Amberlite IRA 458 in the DCTA form (Fig. 5). The value of the volume distribution coeffi-
cient determined from this curve ($D_v = 6.35$) indicates a higher affinity of this kind of complex for the Amberlite IRA 458 in the acetate form than in the DCTA form.

### TABLE II. The values of the weight ($D_g$) and the bed ($D_v$) distribution coefficients of Y(III), Sm(III) and Nd(III) complexes with DCTA (Ln(III):DCTA = 1:1, pH 4.8) on the anion-exchanger Amberlite IRA 68 in the acetate form

<table>
<thead>
<tr>
<th>Anion-exchanger</th>
<th>Ln(III)</th>
<th>$D_g$</th>
<th>$D_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlite IRA 68</td>
<td>Y(III)</td>
<td>431.65</td>
<td>80.76</td>
</tr>
<tr>
<td></td>
<td>Sm(III)</td>
<td>508.37</td>
<td>95.11</td>
</tr>
<tr>
<td></td>
<td>Nd(III)</td>
<td>545.22</td>
<td>102.01</td>
</tr>
</tbody>
</table>

### TABLE III. The values of the weight ($D_g$) and the bed ($D_v$) distribution coefficients of Y(III), Sm(III) and Nd(III) complexes with DCTA (Ln(III):DCTA = 1:1, pH 4.8) on the anion-exchanger Amberlite IRA 958 in the acetate form

<table>
<thead>
<tr>
<th>Anion-exchanger</th>
<th>Ln(III)</th>
<th>$D_g$</th>
<th>$D_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlite IRA 958</td>
<td>Y(III)</td>
<td>312.18</td>
<td>52.88</td>
</tr>
<tr>
<td></td>
<td>Sm(III)</td>
<td>346.68</td>
<td>58.73</td>
</tr>
<tr>
<td></td>
<td>Nd(III)</td>
<td>360.33</td>
<td>61.04</td>
</tr>
</tbody>
</table>

### TABLE IV. The values of the weight ($D_g$) and the bed ($D_v$) distribution coefficients of Y(III) and Nd(III) complexes with DCTA (Ln(III):DCTA = 1:1, pH 4.8) on the anion-exchanger Dowex 2×8 in the acetate form

<table>
<thead>
<tr>
<th>Anion-exchanger</th>
<th>Ln(III)</th>
<th>$D_g$</th>
<th>$D_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dowex 2×8</td>
<td>Y(III)</td>
<td>313.19</td>
<td>80.46</td>
</tr>
<tr>
<td></td>
<td>Nd(III)</td>
<td>343.58</td>
<td>88.27</td>
</tr>
</tbody>
</table>

The results of the separation of Y(III) from Nd(III) (Nd$_2$O$_3$ 0.35 %) complexes with DCTA at pH 4.8 and a concentration of about 1.5 g Ln$_2$O$_3$/L on the polyacrylate and polystyrene anion-exchangers in the acetate form by frontal analysis are presented in Table V and the results of the separation of Y(III) from Sm(III) (Sm$_2$O$_3$ 0.36 %) are presented in Table VI.

### TABLE V. The results of separation of Y(III) from Nd(III) (0.35 %) on polyacrylate and polystyrene anion-exchangers in the acetate form (89 mL anion-exchanger in the Cl$^-$ form or free base form; Ln(III):DCTA = 1:1; $c = 1.5$ g Ln$_2$O$_3$/L; pH 4.8).

<table>
<thead>
<tr>
<th>Anion-exchanger</th>
<th>Type of anion-exchanger</th>
<th>Form of anion-exchanger</th>
<th>Mass of Y$_2$O$_3$ (Nd$_2$O$_3$ ≤ 0.005 %)/g</th>
<th>Ln$_2$O$_3$ absorbed on the exchanger/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlite IRA 458</td>
<td>gel</td>
<td>acetate</td>
<td>6.5288</td>
<td>7.2131</td>
</tr>
<tr>
<td>Amberlite IRA 68</td>
<td>gel</td>
<td>acetate</td>
<td>7.3712</td>
<td>7.2388</td>
</tr>
<tr>
<td>Amberlite IRA 958</td>
<td>macroporous</td>
<td>acetate</td>
<td>2.5833</td>
<td>4.5811</td>
</tr>
<tr>
<td>Dowex 2×8</td>
<td>gel</td>
<td>acetate</td>
<td>6.6531</td>
<td>6.9732</td>
</tr>
</tbody>
</table>
TABLE VI. The results of separation of Y(III) from Sm(III) (0.36 %) on polyacrylate anion-exchangers in the acetate form (80 mL anion-exchanger in the Cl⁻ form or free base form; Ln(III):DCTA = 1:1; \( c = 1.5 \text{ g Ln}_2\text{O}_3/\text{L} \); pH 4.8)

<table>
<thead>
<tr>
<th>Anion-exchanger</th>
<th>Type of an-ion-exchanger</th>
<th>Form of an-ion-exchanger</th>
<th>Mass of ( Y_2\text{O}_3 ) (Sm₂O₃ ≤ 0.005 %)/g</th>
<th>Ln₂O₃ absorbed on the exchanger/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlite IRA 458</td>
<td>gel</td>
<td>acetate</td>
<td>5.4698</td>
<td>7.1200</td>
</tr>
<tr>
<td>Amberlite IRA 68</td>
<td>gel</td>
<td>acetate</td>
<td>6.4297</td>
<td>7.4001</td>
</tr>
<tr>
<td>Amberlite IRA 958</td>
<td>macroporous</td>
<td>acetate</td>
<td>1.7865</td>
<td>4.6238</td>
</tr>
</tbody>
</table>

The obtained data indicate that the strongly basic, polyacrylate, gel anion-exchanger Amberlite IRA 458 is more effective for the purification of Y(III) from Nd(III) compared to the strongly basic, macroporous anion-exchanger Amberlite IRA 958. It was shown that the weakly basic polyacrylate gel anion-exchanger Amberlite IRA 68 is more effective that the strongly basic, gel anion-exchangers of polyacrylate and polystyrene types (Table V). This weakly basic anion-exchanger is also more effective in the purification of Y(III) from Sm(III) complexes than the strongly basic anion-exchangers of the polyacrylate type. On 1 L of this anion-exchanger it is possible to obtain about 90 g \( Y_2\text{O}_3 \) in which the \( \text{Nd}_2\text{O}_3 \) content was reduced from 0.35 % to below 0.005 % and about 81 g \( Y_2\text{O}_3 \) in which the \( \text{Sm}_2\text{O}_3 \) content was reduced from 0.36 % to below 0.015 %. The values of the distribution coefficients (Tables I–IV) are also the largest for this anion-exchanger.

The polyacrylate anion-exchangers with respect to their applicability in the purification of Y(III) from Nd(III) and Sm(III) complexes with DCTA can be arranged as follows:

weakly basic, gel > strongly basic, gel > strongly basic, macroporous

CONCLUSION

The weakly basic polyacrylate gel anion-exchanger Amberlite IRA 68 is more effective in the purification of Y(III) from Nd(III) and Sm(III) complexes with DCTA than the strongly basic anion-exchangers of this type.

ИЗВОД

ОДВАЈАЊЕ Y(dcta) КОМПЛЕКСА ОД Nd(dcta) И Sm(dcta) КОМПЛЕКСА НА ПОЛИАКРИЛАТНИМ ЈОНИОИЗМЕЊИВАЧИМА

HALINA HUBICKA* и DOROTA KOŁODYŃSKA

Department of Inorganic Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland

Створање анионских комплекса елемената ретких земаља са аминополикарбоксилним киселинама дaje нове могућности за међусобно раздвајање ових елемената на анионским јонизмењивачима. Бих афтинитет Nd(dcta) i Sm(dcta) комплекса од афтинитета Y(dcta) комплекса према јонизмењивачима указује на могућности пречишћавања итријума као макрокомпоненте од ових других, коришћењем методе фронталне анализе. Слабо баци
полякритални гел а jon јоноимењивац Amberlite IRA 68 показао се знатно ефикаснијим за пречишћавање Y(III) од Nd(III) и Sm(III) комплекса са DCTA него јако базни а jonски јоноимењивац истог типа.

(Примљено 20. септембра, ревијирano 4. децембра 2002)

REFERENCES