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Short communication

SHORT COMMUNICATION

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

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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.[10]

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.[11–14]

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_3COONH_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_2O_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).[1]

The percentage of samarium in yttrium was determined by X-ray fluorescence analysis (XRF) on a CANBERRA PACKARD, USA, spectrometer.[1]

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

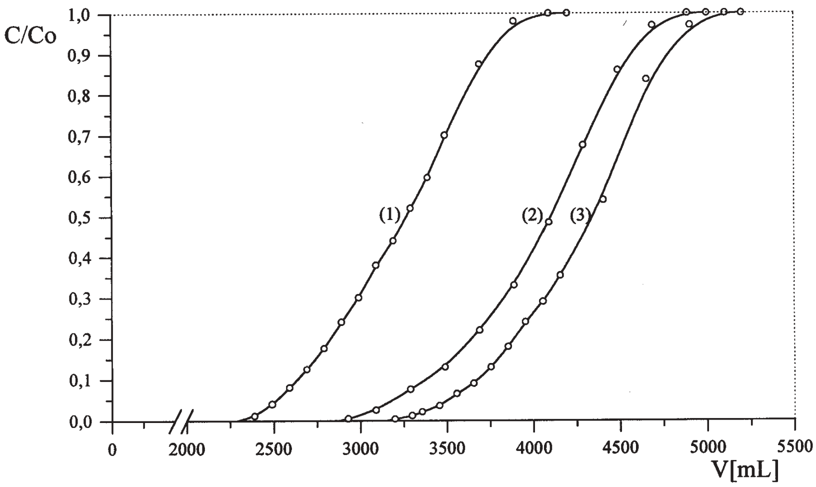

Fig. 1. Breakthrough curves of: (1)–Y(III), (2)–Sm(III) and (3)–Nd(III) complexes with DCTA (Ln(III):DCTA = 1:1, pH 4.8) on the anion-exchanger Amberlite IRA 458 in the acetate form.

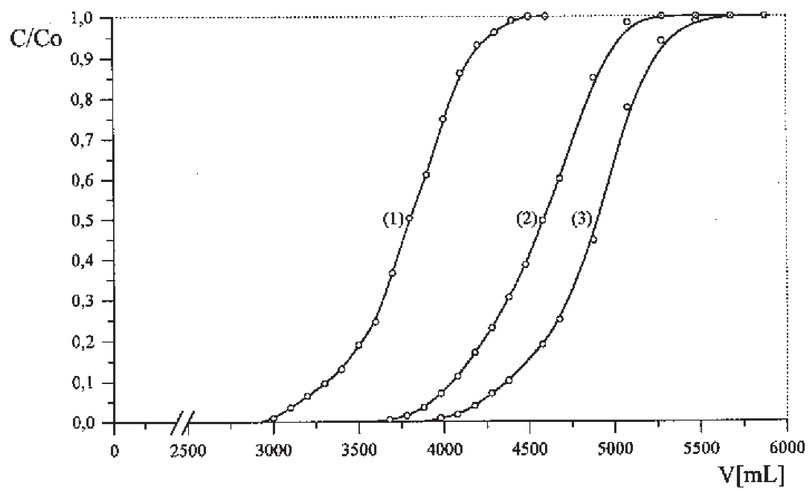

Fig. 2. Breakthrough curves of: (1)–Y(III), (2)–Sm(III) and (3)–Nd(III) complexes with DCTA (Ln(III):DCTA = 1:1, pH 4.8) on the anion-exchanger Amberlite IRA 68 in the acetate form.

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 $–N^+(CH_3)_2C_2H_4OH$.

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,

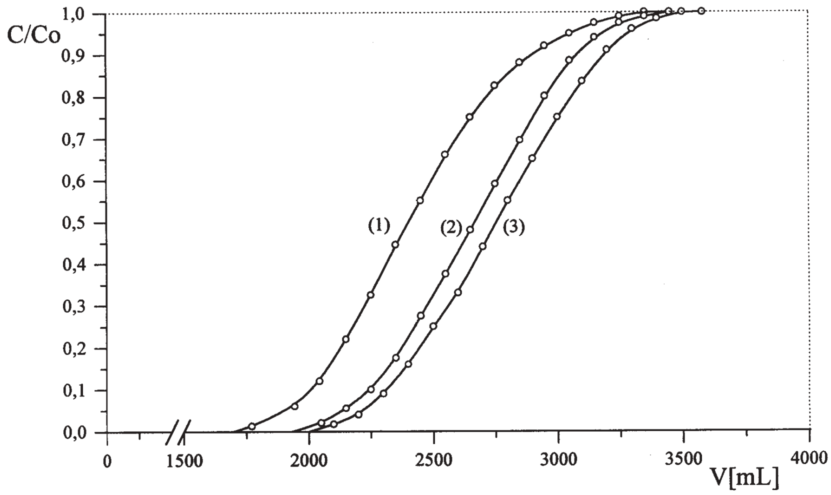

Fig. 3. Breakthrough curves of: (1)–Y(III), (2)–Sm(III) and (3)–Nd(III) complexes with DCTA (Ln(III):DCTA = 1:1, pH 4.8) on the anion-exchanger Amberlite IRA 958 in the acetate form.

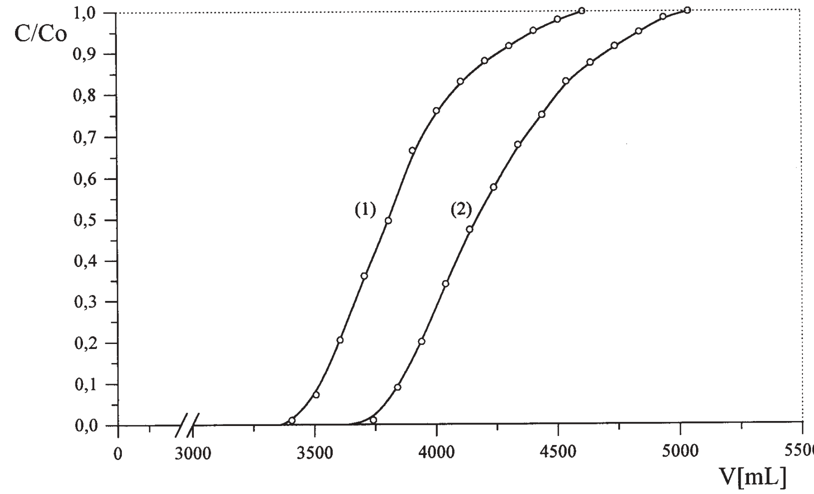

Fig. 4. Breakthrough curves of: (1)–Y(III) and (2)–Nd(III) complexes with DCTA (Ln(III):DCTA = 1:1, pH 4.8) on the anion-exchanger Dowex 2×8 in the acetate form.

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 Y(III) and 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 Nd(III) and Sm(III) complexes with DCTA exhibit a higher affinity for both the strongly basic and the weakly basic polyacrylate anion-exchangers for the corresponding Y(III) complexes and their affinity follows the same order as for strongly basic polystyrene anion-exchangers.

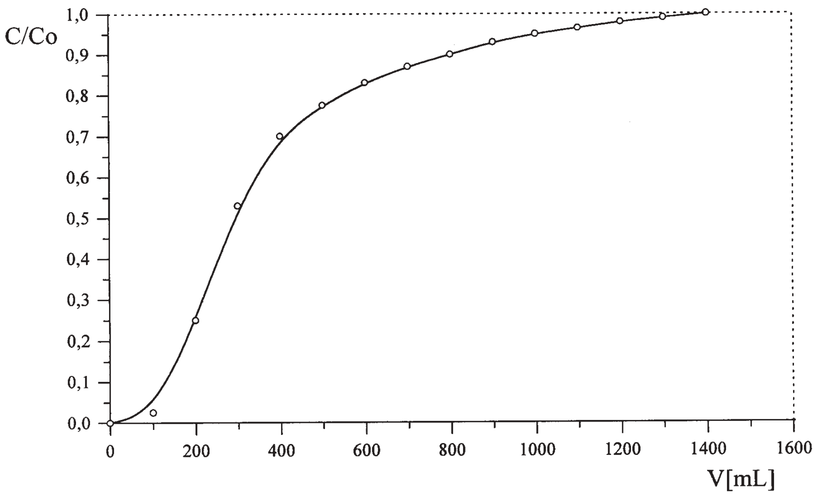

Fig. 5. Breakthrough curves of Nd(III) complexes with DCTA (Ln(III):DCTA = 1:1, pH 4.8) on the anion-exchanger Amberlite IRA 458 in the DCTA form.

Assuming that 1:1 complexes are formed, the ion-exchange can be written as:

$$RCH_3COO + Ln(dcta)^- \rightleftarrows RLn(dcta) + CH_3COO^-$$

The determined curves make is possible to calculate the values of the weight (D_g) 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:[15]

$$D_g = \overline{U} - U_o - V / m_j$$

$$D_v = D_g \times d_z$$

where: $\overline{U}$ – the effluent volume (mL) at $c = c_o/2$; 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_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 458 in the acetate form

Anion-exchanger	Ln(III)	D_g	D_v
	Y(III)	320.27	72.57
Amberlite IRA 458	Sm(III)	400.49	90.75
	Nd(III)	422.45	95.73

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 coefficient 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

Anion-exchanger	Ln(III)	D_g	D_v
	Y(III)	431.65	80.76
Amberlite IRA 68	Sm(III)	508.37	95.11
	Nd(III)	545.22	102.01

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

Anion-exchanger	Ln(III)	D_g	D_v
	Y(III)	312.18	52.88
Amberlite IRA 958	Sm(III)	346.68	58.73
	Nd(III)	360.33	61.04

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

Anion-exchanger	Ln(III)	D_g	D_v
Dowex 2×8	Y(III)	313.19	80.46
	Nd(III)	343.58	88.27

The results of the separation of Y(III) from Nd(III) (Nd_2O_3 0.35 %) complexes with DCTA at pH 4.8 and a concentration of about 1.5 g Ln_2O_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_2O_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_2O_3/L; pH 4.8).

Anion-exchanger	Type of anion-exchanger	Form of anion-exchanger	Mass of Y_2O_3 ($Nd_2O_3 \leq 0.005$ %)/g	Ln_2O_3 absorbed on the exchanger/g
Amberlite IRA 458	gel	acetate	6.5288	7.2131
Amberlite IRA 68	gel	acetate	7.3712	7.2388
Amberlite IRA 958	macroporous	acetate	2.5833	4.5811
Dowex 2×8	gel	acetate	6.6531	6.9732

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 g Ln_2O_3/L; pH 4.8)

Anion-exchanger	Type of anion-exchanger	Form of anion-exchanger	Mass of Y_2O_3 ($Sm_2O_3 \leq 0.005$ %)/g	Ln_2O_3 absorbed on the exchanger/g
Amberlite IRA 458	gel	acetate	5.4698	7.1200
Amberlite IRA 68	gel	acetate	6.4297	7.4001
Amberlite IRA 958	macroporous	acetate	1.7865	4.6238

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_2O_3 in which the Nd_2O_3 content was reduced from 0.35 % to below 0.005 % and about 81 g Y_2O_3 in which the Sm_2O_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 ЈОНОИЗМЕЊИВАЧИМА

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Стварање анјонских комплекса елемената ретких земаља са аминополикарбоксилним киселинама даје нове могућности за међусобно раздвајање ових елемената на анјонским јоноизмењивачима. Већи афинитет Nd(dcta)$^-$ и Sm(dcta)$^-$ комплекса од афинитета Y(dcta)$^-$ комплекса према јоноизмењивачима указује на могућности пречишћавања итријума као макрокомпоненте од ових других, коришћењем методе фронталне анализе. Слабо базни

полиакрилатни гел анјон јоноизмењивач Amberlite IRA 68 показао се знатно ефикаснијим за пречишћавање Y(III) од Nd(III) и Sm(III) комплекса са DCTA него јако базни анјонски јоноизмењивачи истог типа.

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