Cation Exchange Sorption of Some Metal Ions from Aqueous Ammonium Acetate Medium: Separation of Ce(IV) from Ce(III), La(III) & Other Metal Ions

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The cation exchange (Dowex 50W-X8; NH_4^+-form) characteristics of 19 metal ions in various concentrations (0·02-1·60M) of NH_4OAc are reported. At low [NH_4OAc] the sorption of cerium(IV) is low whereas other metal ions show appreciable sorption. Through the determination of distribution coefficients and separation factors as a function of [NH_4OAc], separation of Ce(IV) from its binary mixtures with Ce(III), La(III), Co(II), Ni(II), Cu(II), Zn(II) or Pb(II) has been achieved. The possibility of separation by column chromatography in a number of ternary mixtures such as Ce(IV)-UO_2(VI)-Ba(II)/Hg(II)/Al(III); Ce(IV)/UO_2(VI)-Ce(III)/La(III)/Co(II)/Ni(II)/Cu(II)/Zn(II)/Pb(II)-Ba(II)/Hg(II)/Al(III), has been indicated. Separation factors, elution curves and the results of resolution of synthetic binary mixtures are presented.

MINAMI and Ishimori[1] separated Ba(II) and Pb(II) on R-NH_4 type resin using aq. NH_4OAc ($pH = 6·1$), while Honda[2] described the separation of Mg(II), Ca(II), Sr(II) and Ba(II). Khopkar and De[3] studied the cation exchange behaviour of Ba(II) on Dowex 50W-X8 and obtained a high value for the separation factor with respect to Pb(II). De and Majumdar[4] reported the separation Ag(I), Pb(II) and Hg(II) using NH_4OAc medium. The separation factors of Ce(III), Pm(III), Eu(III), Tb(III), Tm(III) and Y(III) determined by column elution method in this medium by Ward and Choppin[5] showed that separations were comparatively poorer than in other complexing media. A systematic study of the cation exchange behaviour of metals in nitric acid-NH_4OAc medium has been reported earlier from this laboratory[6], and this work has now been extended using aqueous NH_4OAc medium to achieve a number of useful and quantitative cation exchange separations.

Materials and Methods

Dowex 50W-X8 (H^+ form), 100-200 mesh, was treated in a column alternately with 1N HCl and 1N NaOH before use. The resin was then converted to NH_4^+-form by treating with 20% ammonia solution, and washing with water under suction till the effluent was free from alkali (negative test with phenolphthalein). It was treated with ethanol, dried under suction and finally in an oven at 60° for about 4-5 hr, and stored. The water content of this resin was found to be 9·2% ($\pm$ 0·3%) by heating the samples to a constant weight at 110°. The capacity was 4·12 meq/g resin.

All the chemicals used were of reagent grade. Standard solutions of metal ions were prepared from their nitrates (BDH, analar), except those of

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Ce(IV) and Ce(III) which were prepared from ceric ammonium nitrate (E. Merck) and cerous chloride (Johnson Matthey), respectively. Solutions of Ce (IV) and Hg(II) were prepared in aq. NH_4OAc, while those of other reagents were prepared in doubly distilled water.

The solutions were mechanically shaken with a wrist-motion microid flask shaker (Griffin & George) in glass stoppered pyrex flasks (100 ml) in batch experiments. A graduated column (65 cm long, int. diam. 0·85 cm) was used for chromatographic separations.

Distribution coefficients — Distribution coefficients (D) were determined by the batch equilibration method. One gram portions of the resin were shaken for 1 hr (it was previously ascertained that this time was adequate to attain equilibrium) with suitable amounts of metal ion solutions containing different NH_4OAc concentrations. The solutions were filtered and analysed for total metal contents, irrespective of species, either titrimetrically against EDTA or by colorimetry. The concentrations of NH_4OAc used were in the range of 0·02 to 1·60M. All determinations were made at least in duplicate. The D values were obtained by Eq. (1).

$$D = \frac{\text{meq metal ion per g resin}}{\text{meq metal ion per ml solution}} \quad \text{...(1)}$$

The metal concentrations employed were around 12% of the total exchange capacity of the resin, to ensure complete equilibration. The total volume of aq. phase was 25 ml. The experiments were performed at 30° $\pm$ 2°. The relative experimental errors in the determination of the D values were $\pm$ 10 and $\pm$20% for low and high D values, respectively.

Preparation and pretreatment of resin bed — The resin slurry ($\sim$5 g) was prepared in water and transferred to the column. The resin bed had a

length of $\sim$7·5 cm and was treated with 0·10M NH$_4$OAc solution.

The feed, 25 ml of 0·10M/0·06M NH$_4$OAc, was prepared by mixing an aliquot of standard solution of Ce(IV) and one of the other metal ions to be separated. It was passed through the resin bed and the flow rate maintained at 1·0 ± 0·3 ml/minute. During this operation all the metal ions were sorbed on the resin except Ce(IV). The effluent was collected in 5 ml fractions.

The column was washed with 0·06M or 0·10M NH$_4$OAc, and then eluted with 0·50M or 0·80M NH$_4$OAc.

Chromatographic separation — After sorption, the column was washed with 30 ml of 0·10M NH$_4$OAc and the effluent again collected in 5 ml portions. The total (55 ml) eluent volume (25 ml feed + 30 ml washing solution) was sufficient to recover Ce (IV) quantitatively. Sorbed Co(II), Ni(II), Cu(II), Zn(II), Pb(II) and UO$_2$(VI) were eluted by passing about 200 ml of 0·50M NH$_4$OAc solution, while La(III) and Ce(III) by 80 ml of 0·80M NH$_4$OAc. Ba(II), Hg(II) and Al(III) were retained strongly on the column, and the breakthrough of these ions was still not observed after the passage of 200 ml of 0·50M NH$_4$OAc or of 80 ml of 0·80M NH$_4$OAc.

Results and Discussion

The D values for 19 cations are reported in Table 1. Ions known to hydrolyse under these conditions have been omitted. In all the cases sorption of the metal ion decreased with increasing [NH$_4$OAc] as indicated from the D values. The probable reaction occurring in solution may be given by Eq. (2).

$$M^{n+} + mOAc^- \rightleftharpoons M(OAc)_m^{(n-m)+} \qquad ...(2)$$
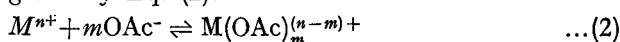
where the complex will be cationic when $n > m$; neutral when $n = m$; and anionic when $n < m$. The sorption will be less, if the complex formed has a small positive, zero, or a negative charge. A negative charge is not always necessary for an

effective decrease in sorption, and in fact the concentration of negatively charged metal acetate complexes in most cases [except UO$_2$(VI)] in aq. solution is negligible[7].

As [NH$_4$OAc] is increased, acetate ion replaces the coordinated water molecules resulting in the formation of complex species of a small positive charge, and consequently D is lowered. A further increase in [NH$_4$OAc] leads to the formation of neutral species and this also results in a decrease of D. When [NH$_4$OAc] is higher, and a neutral metal acetate is present in solution, the predominant species[5,10] in the resin phase will be M^{II}(OAc)$^+$ or M^{III}(OAc)$^{2+}$ as the case may be.

A more definite proof that M(OAc)$^{2+}$ and M(OAc)$_3$ are the species involved in La(III) and Ce(III) systems at higher [NH$_4$OAc], is obtained from a consideration of the dependency of the separation factors on the stability constants[5]. It follows that in 0·80M NH$_4$OAc solution, the species M(OAc)$^{2+}$ and M(OAc)$_3$ are present in resin and solution respectively. This implies that $D = \overline{M(OAc)^{2+}}/M(OAc)_3$ (bar represents the resin phase) or $D \propto (K_2K_3)^{-1}$, where K_2 and K_3 are the second and third step stability constants[11], respectively. The same dependency on $(K_2K_3)^{-1}$ should exist for the separation factors since these are the ratios of D values. It has been observed that the agreement between experimental and theoretical values of separation factors (Table 2) is good only for $\overline{M(OAc)_3}$ —M(OAc)$_3$ system. The order of D values for La(III), Al(III), Ce(III), and Cr(III) follows the order of solubility of the complexes of these metal ions with acetate.

Ce(IV) inspite of its high charge, has a poor affinity towards the resin. Similar behaviour has also been observed for UO$_2$(VI), where a moderate sorption in 0·02M NH$_4$OAc medium is noted, which starts falling as [NH$_4$OAc] increases, and at a high [NH$_4$OAc] the sorption is very poor or even less than that of Ce(IV). The low D values of Ce(IV) and UO$_2$(VI) are due to the pronounced formation

TABLE 1 — VALUES OF DISTRIBUTION COEFFICIENTS (D) IN NEUTRAL NH$_4$OAC

Metal ion	Ammonium acetate concentrations (M)							
	0·02	0·06	0·10	0·20	0·30	0·50	0·80	1·60
Ag(I)	112·7	75·0	41·66	34·80	27·08	15·98	9·96	6·25
Mg(II)	767·5	408·3	239·7	80·28	45·84	18·27	5·75	—
Ca(II)	1098	678·2	327·2	151·1	86·01	34·25	14·76	2·45
Sr(II)	847·6	692·4	323·5	185·3	118·5	55·27	24·39	8·52
Ba(II)	814·5	758·5	426·5	320·6	192·6	116·6	57·75	20·54
Mn(II)	839·7	508·1	284·5	98·11	47·47	16·94	5·13	0·05
Co(II)	2370	674·2	316·1	96·40	46·98	18·28	6·62	0·81
Ni(II)	3891	839·9	461·1	114·0	54·96	20·25	7·54	1·72
Cu(II)	1767	328·6	89·36	34·20	17·30	5·81	2·58	0·66
Zn(II)	621·8	406·5	225·5	71·68	26·78	7·27	0·55	—
Cd(II)	945·0	403·4	169·1	49·85	19·53	5·45	0·72	—
Hg(II)	ppt	ppt	ppt	161·4	155·9	116·3	51·25	14·05
Pb(II)	1212	416·9	154·3	39·12	14·54	3·13	0·10	—
Al(III)	—	5447	5447	2711	785·7	31·74	6·57	0·96
Cr(III)	410·8	288·5	83·14	16·22	12·31	8·63	7·65	6·98
La(III)	—	41591	16296	722·9	203·5	30·57	7·00	3·76
Ce(III)	4788	652·8	609·4	518·0	177·4	36·17	6·55	0·22
Ce(IV)	ppt	3·35	3·67	4·45	2·77	2·10	1·57	1·57
UO$_2$(VI)	676·1	53·95	13·78	2·39	1·44	0·003	0·003	0·003

TABLE 2 — SEPARATION FACTORS $(\alpha_{M_{II}}^{M_I})$ EVALUATED AT SUITABLE [NH$_4$OAc]

System	[NH$_4$OAc] M	$\alpha_{M_{II}}^{M_I}$	System	[NH$_4$OAc] M	$\alpha_{M_{II}}^{M_I}$
La(III)-Ag(I)	0·10	391·2	Co(II)-Ce(IV)	0·06	201·3
La(III)-Mg(II)	0·06	101·7	Ni(II)-Ce(IV)	0·06	250·7
La(III)-Cu(II)	0·06	126·3	Cu(II)-Ce(IV)	0·06	98·1
La(III)-Zn(II)	0·06	102·1	Zn(II)-Ce(IV)	0·06	121·3
La(III)-Cd(II)	0·06	109·9	Cd(II)-Ce(IV)	0·06	120·4
La(III)-Pb(II)	0·06	99·6	Pb(II)-Ce(IV)	0·06	124·5
La(III)-Cr(III)	0·10	196·0	Al(III)-Ag(I)	0·10	130·8
La(III)-Ce(IV)	0·06	12394	Al(III)-Cr(III)	0·20	167·1
La(III)-UO$_2$(VI)	0·10	1183	Al(III)-Ce(IV)	0·06	1626
Mg(II)-Ce(IV)	0·06	121·9	Al(III)-UO$_2$(VI)	0·20	1134
Ca(II)-Ce(IV)	0·06	202·5	Cr(III)-Ce(IV)	0·06	86·1
Sr(II)-Ce(IV)	0·06	206·7	Ce(III)-Ce(IV)	0·06	194·9
Sr(II)-UO$_2$(VI)	0·30	82·3	Ce(III)-UO$_2$(VI)	0·20	258·6
Ba(II)-Zn(II)	0·80	105·0	Hg(II)-Zn(II)	0·80	93·2
Ba(II)-Pb(II)	0·80	577·5	Hg(II)-Cd(II)	0·80	71·2
Ba(II)-Ce(IV)	0·06	226·4	Hg(II)-Pb(II)	0·80	512·5
Ba(II)-UO$_2$(VI)	0·50	46632	Hg(II)-UO$_2$(VI)	0·50	46516
Mn(II)-Ce(IV)	0·06	151·7			

TABLE 3 — ELUTION CHARACTERISTICS OF METAL IONS

Metal ions	BTV (ml)	VEP (ml)	TEV (ml)	Eluting agent [NH$_4$OAc] M
Ce(IV)	3·5	15	45	0·06/0·10
Ce(III)	5	15	75	0·80
La(III)	5	15	80	0·80
UO$_2$(VI)	5	10	50	0·50
Co(II)	25	70	190	0·50
Ni(II)	25	80	190	0·50
Cu(II)	5	30	130	0·50
Zn(II)	15	45	105	0·50
Pb(II)	5	30	100	0·50
Ba(II)	>200	—	—	0·50
Ba(II)	>80	—	—	0·80
Hg(II)	>200	—	—	0·50
Hg(II)	>80	—	—	0·80
Al(III)	>200	—	—	0·50
Al(III)	>80	—	—	0·80

BTV = breakthrough volume.
VEP = volume elution peak.
TEV = terminal elution volume.

of complexes of these ions with acetate. At [NH$_4$OAc] $\geqslant 0.20M$, the sorption of UO$_2$(VI) abruptly falls, probably due to the formation of an anionic complex[7]. At lower [NH$_4$OAc] (0·02-0·10M), Ag(I) has the lowest D values [except Ce(IV) and up to some extent UO$_2$(VI) when compared with other metal ions. Ag(I) exhibited a similar behaviour[6] in HNO$_3$-NH$_4$OAc system, which was attributed to the presence of NH$_4^+$ ions in the medium. The behaviour became more pronounced in the present case since the resin used was also in the ammonium-form.

The remaining metal ions behave normally as the D values are either guided by the complexation reaction with acetate[7] or by the competition of NH$_4^+$ counter ions. Precipitation of Hg(II) and Ce(IV) was observed in certain concentrations of NH$_4$OAc.

The values of the separation factors $(\alpha_{M_{II}}^{M_I})$ (Table 2) were calculated for a number of pairs of metal

ions on the basis of large differences in D values. The batch experiment data on the effect of NH$_4$OAc on the sorption of Ce(IV), and of Ce(III) and La(III) showed that a medium of 0·06-0·30M NH$_4$OAc is most suitable for the separation of Ce(IV) from Ce(III) and La(III). At higher concentrations (0·80-1·60M) of NH$_4$OAc, these ions have low D values, showing almost identical sorption behaviour leading to no possibility of separation. Similar behaviour has also been observed in the cases of Co(II), Ni(II), Cu(II), Zn(II) and Pb(II). When [NH$_4$OAc] is 0·06M, UO$_2$(VI) has a high value of D and is retained quantitatively on the resin, and, therefore, its separation from Ce(IV) is possible. But at 0·10M NH$_4$OAc (as in other cases) a clearcut separation is not possible. At 0·80M NH$_4$OAc, both Ba(II) and Hg(II) have a higher affinity [except Ca(II) and Sr(II)] towards the resin than the other investigated ions, and hence a large number of separations can be achieved with metal ions having very low D values at this [NH$_4$OAc]. On the basis of these results some actual separations were carried out using suitable eluents for effecting clearcut separations of Ce(IV) from Ce(III), La(III), and other metal ions.

Among the systems where actual separations were carried out, the conditions predicted from batch experiment data were found to be true for column chromatographic separations of Ce(IV) from Ce(III), La(III), and other metal ions. The elution characteristics of a number of metal ions investigated in these media are shown in Table 3. A general procedure involves feeding a mixture (25 ml) containing metal ions and NH$_4$OAc (overall concentration 0·10M) through the resin bed at the rate of 1·0 ± 0·3 ml/minute. Ce(IV) is quantitatively recovered by washing the column with 30 ml of 0·10M NH$_4$OAc, while other ions are retained. 0·50M NH$_4$OAc was next used for the desorption of Co(II), Ni(II), Cu(II), Zn(II) or Pb(II) (Fig. 1), and 0·80M NH$_4$OAc for Ce(III) and La(III) (Fig. 2). When UO$_2$(VI) was taken as one of the components of the feed (25 ml) the overall [NH$_4$OAc] was kept 0·06M; because in 0·10M NH$_4$OAc UO$_2$(VI) is not
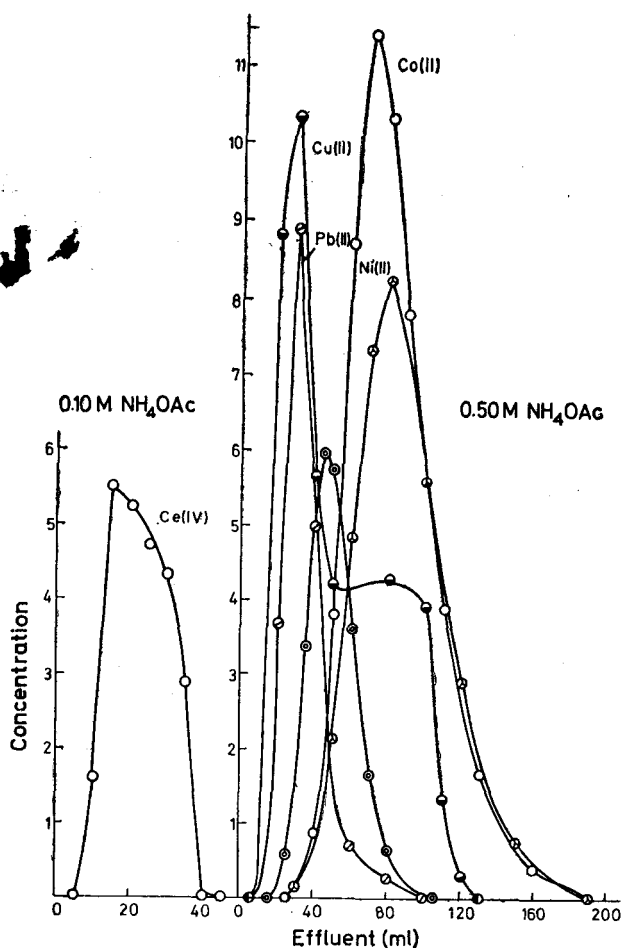
Fig. 1 — Elution curves of Ce(IV)-Co(II)/Ni(II)/Cu(II)/Zn(II)/Pb(II) (7·5±0·3 ml) on Dowex 50W-X8 resin (NH$_4^+$-form) column
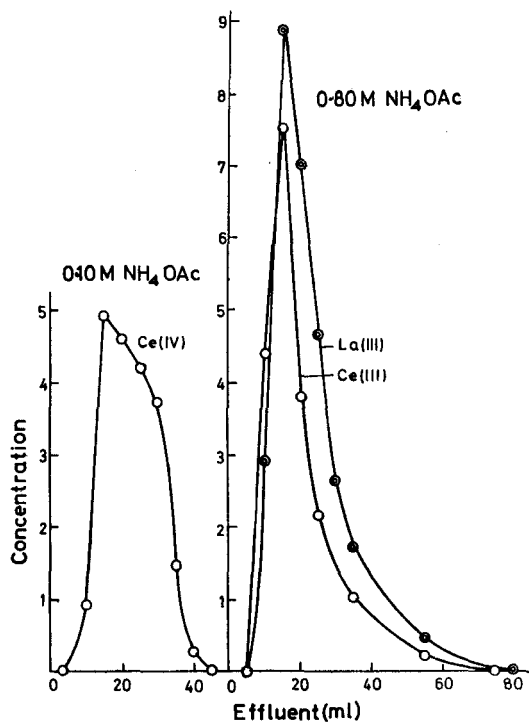

Fig. 2 — Elution curves of Ce(IV)-Ce(III)/La(III) (7·5±0·3 ml) on Dowex 50W-X8 resin (NH$_4^+$-form) column

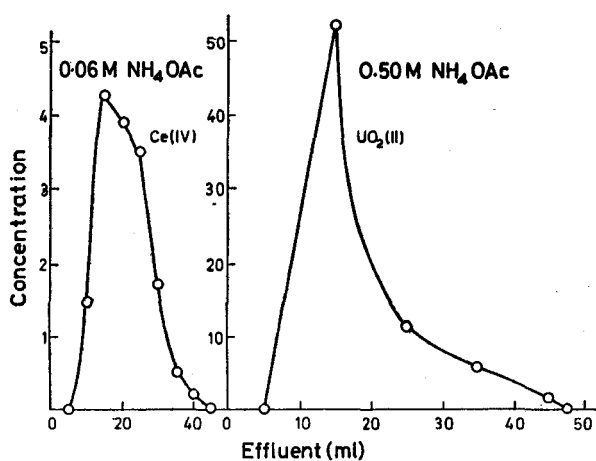Fig. 3 — Elution curve of Ce(IV)-UO$_2$(VI) (7·5±0·3 ml) on Dowex 50W-X8 resin (NH$_4^+$-form) column

TABLE 4 — QUANTITATIVE SEPARATION OF SYNTHETIC MIXTURES

Taken (mg)		Found(a) (mg)	
Ce(IV)	Other element	Ce(IV)	Other element
35·03	La(III) 45·15	35·05±0·14	45·15±0·60
28·02	La(III) 45·15	28·22±0·08	45·15±0·28
35·03	Ce(III) 32·07	35·13±0·17	32·07±0·55
28·02	Ce(III) 32·07	28·22±0·20	32·07±0·42
21·01	UO$_2$(VI) 120·12	21·11±0·10	120·12±0·98
35·03	Co(II) 34·77	34·93±0·29	34·7±0·10
35·03	Ni(II) 27·77	35·08±0·16	27·77±0·18
35·03	Cu(II) 31·77	35·09±0·18	31·87±0·26
35·03	Zn(II) 30·46	35·23±0·23	30·46±0·50
35·03	Pb(II) 42·44	35·00±0·30	42·24±0·40
28·02	Pb(II) 42·44	28·00±0·12	42·42±0·32

(a) Mean of duplicate runs with calculated standard deviation.

retained quantitatively on the resin and some UO$_2$(VI) passes along with Ce(IV) in the effluent as also evidenced from the batch experiments. The washing was followed with the same NH$_4$OAc solution (30 ml). UO$_2$(VI) was eluted with 50 ml of 0·50*M* NH$_4$OAc (Fig. 3). In Figs 1-3, the volume of effluent includes the volume which passes out of the resin from the original feed. The results, presented in Table 4, indicate that complete separation of Ce(IV) from other metal ions can successfully be achieved. The strongly sorbed Ba(II), Hg(II), and Al(III) ions can also be separated from La(III), Ce(III), UO$_2$(VI), Co(II), Ni(II), Cu(II), Zn(II), or Pb(II). The metal ion La(III) or Ce(III) retained on the resin was eluted with 80 ml of 0·80*M* NH$_4$OAc, while UO$_2$(VI), Co(II), Ni(II), Cu(II) or Pb(II) with 0·50*M* NH$_4$OAc. Ba(II), Hg(II) or Al(III) was then eluted with conc. HCl or HNO$_3$.

The ternary separation involves a more detailed column chromatographic investigation, since changes in the degree of loading, ionic strength and factors concerning the column operation have a marked effect. In the present studies the column chromatographic experiments have also revealed the possibility of a number of ternary separations, since breakthrough of Ba(II), Hg(II) or Al(III) was not reached

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after the passage of about 200 ml of $0.50M$ or 80 ml of $0.80M$ NH_4OAc, though this volume of NH_4OAc is sufficient to complete the elution of other metal ions in the respective experiments. Therefore, Ba(II), Hg(II) or Al(III) can be separated from ternary mixtures. After the complete elution of other ions as described above, these ions can be stripped off with conc. mineral acids. The other possible ternary mixtures which can be separated are: Ce(IV)-UO_2(VI)-Ba(II)/Hg(II)/Al(III); Ce(IV)/UO_2(VI)-Ce(III)/ La(III) /Co(II)/Ni(II)/Cu(II)/Zn(II)/Pb(II)-Ba(II) / Hg(II) / Al(III).

An abnormal behaviour has been observed in the elution of Al(III). At or above $0.50M$ NH_4OAc the batch distribution coefficient of Al(III) is of the same order as that of La(III) or Ce(III), but the behaviour on column was different. It appears that amphoteric nature and the formation of basic salts of polynuclear hydrolytic species[8,9], and polymerization of the hydroxopolynuclear species are among factors responsible for this abnormal behaviour of Al(III).

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