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Thin-layer chromatographic behavior of rare earths on silica gel with aqueous alkaline earth metal nitrate solutions as mobile phases

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Abstract The TLC behavior of all the rare earths except Pm has been surveyed on silica gel (pH 7.0) pretreated with 0.1 mol L⁻¹ tris(hydroxymethyl)aminomethane and 0.1 mol L⁻¹ HCl with aqueous nitrate solutions of alkaline earth metals as mobile phases. The R_F values of the lanthanides varied in a regular and characteristic way accompanied by the tetrad effect with increasing atomic number, and when the mobile phases were changed the R_F values of each metal decreased in the order Mg²⁺ > Ca²⁺ > Sr²⁺ > Ba²⁺, as the crystal ionic radii of the alkaline earth metals increased. This adsorption sequence was not observed with alkali metal nitrate and alkali metal chloride mobile phases. A brief discussion concerning the effect on R_F values of the solvent cations and the adsorption mechanism is included; also presented are typical chromatograms for the separation of multi-component mixtures containing adjacent lanthanides.

Introduction

A variety of thin-layer chromatographic (TLC) systems effective in separating rare earths from each other has already been proposed, and the literature [1–6] have been reviewed. Most of the work has been performed by reversed-phase partition chromatography, and has usually involved the use of a special support and/or a complicated mobile phase containing an organophosphorus compound. In particular, bis(2-ethylhexyl)hydrogen phosphate (HDEHP) [7–15] has been utilized effectively as an essential component of the stationary or mobile phase, because it provides the best resolution of adjacent pairs of the lanthanides. It is worth noting that the first successful separation of all the lanthanides except promethium has been

achieved in the TLC system consisting of silanized silica gel and a diethyl ether–HDEHP–nitric acid mixture as mobile phase [10].

In contrast, little attention has been paid to the development of normal-phase adsorption TLC. We have so far surveyed the TLC behavior of all the rare earths except promethium on silica gel with aqueous solutions of ammonium salts (nitrate [16], chloride [17], and sulfate [18]) and of alkali metal salts (nitrates [19] and chlorides [20]) as mobile phases, and suggest that these chromatographic systems have great potential as a characteristic and effective separation medium in the TLC of the rare earths.

This work was undertaken to compile the R_F data of the rare earths on silica gel with aqueous solutions of alkaline earth metal nitrates (magnesium, calcium, strontium, and barium) as mobile phases and to clarify the outstanding features of the systems. As stationary phase, silica gel (pH 7.0) pretreated with 0.1 mol L⁻¹ tris(hydroxymethyl)aminomethane and 0.1 mol L⁻¹ HCl [17], which gave reproducible R_F values, was used throughout the study, to facilitate comparison of these results for alkaline earth metals and those obtained previously for alkali metals [19, 20]. Comparison of both results reveals the effects of the solvent cations on the adsorption of the rare earths, leading to the clarification of the adsorption mechanism. Also included is a brief discussion on the variation of the separation factor of the lanthanides, relative to gadolinium, with increasing concentration of magnesium nitrate in the mobile phase. In addition, several chromatograms showing the separation of adjacent lanthanides are presented, to demonstrate the effectiveness of the silica gel–alkaline earth metal nitrate systems for the separation of the rare earths.

Experimental

Materials. Stock solutions of the trivalent rare earths were prepared in a way similar to that described earlier [18]. R_F values were measured for 0.001 mol L⁻¹ metal solutions in 0.1 mol L⁻¹ nitric acid. Exceptions were Sc(III), La(III), and Ce(III), for which the concentrations were 0.01, 0.002, and 0.002 mol L⁻¹, respec-

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tively. Solutions of the nitrates of alkaline earth metals (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}) were prepared by dissolving appropriate amounts of the salts in distilled and deionized water. All chemicals used were of analytical grade.

Preparation of TLC plates. Silica gel without binder (Wako gel B-0; Wako, Japan) was used as TLC adsorbent. Silica gel (42 g) was mixed with aqueous tris(hydroxymethyl)aminomethane solution (0.1 mol L^{-1} , 100 mL), and the pH of the suspension was adjusted to 7.0 with 0.1 mol L^{-1} hydrochloric acid. The silica gel was isolated by filtration, under vacuum, through a filter paper (12 cm diameter, No.5C, Toyo, Japan), washed with ethyl alcohol ($5 \times 60 \text{ mL}$), and sucked dry. Washing with distilled water should be avoided. If not, the adsorptivity of the silica gel will decrease, because of adsorption of the hydronium ion. Subsequently, the treated silica gel was activated at 110°C for 1 h in a constant-temperature oven, based on forced convection. After cooling, it was stored in a sealed box containing dry silica gel as a desiccant.

The TLC plates were prepared similarly to the method described previously [17]. The treated silica gel (17 g) was homogenized with poly(vinyl alcohol) (1%, 40 mL) solution of an ethyl alcohol–water mixture (3:2, v/v), and the slurry was spread to a thickness of $375 \mu\text{m}$ on glass plates ($20 \times 15 \text{ cm}$) with an applicator. The plates were left to stand at 90°C for 1 h in a constant-temperature oven. After cooling, they were stored in a sealed box containing a saturated LiCl solution until ready for use.

Procedure. R_F measurements of the rare earths and separations of mixtures of lanthanides were performed by a procedure similar to that described previously [17]. Test solution ($0.5 \mu\text{L}$) was applied to the TLC plate at a point 2.5 cm from one edge. The plate was left to stand in air for 10 min and then was developed to 10 cm

from the starting point with 30 mL mobile phase. For separation of mixtures the development distance was 15 cm. After development the plate was dried at ca. 80°C and the metals were visualized by spraying with a 0.02% aqueous chlorophosphonazo III solution and then 0.5 mol L^{-1} HCl, followed by gentle heating. The rare earths (except Pm) were all detected as green spots on a violet background.

The R_F value of each rare earth was measured as an average of the R_F values of the front and rear of the spot and expressed as an average, with the error limits from three replicate runs. The R_M value and the separation factor ($\alpha_{Z/64}$, $Z = \text{atomic number}$) of each metal relative to Gd ($Z=64$) were calculated by use of the equations:

$$R_M = \log (R_F^{-1} - 1)$$

$$\alpha_{Z/64} = [R_{F(Z)}^{-1} - 1] / [R_{F(64)}^{-1} - 1]$$

Results and discussion

Adsorption behavior

Tables 1 and 2 list the R_F values of all the trivalent lanthanides (except Pm), Sc(III), and Y(III) on silica gel layers developed with 0.4 mol L^{-1} aqueous solutions of the nitrates of the alkaline earth metals magnesium, calcium, strontium, and barium, and with 1.0 mol L^{-1} aqueous solutions of the nitrates of the same alkaline earth metals except barium – because of the low solubility of the barium

Table 1 R_F values ($\times 100$) of the rare earths on silica gel developed with 0.4 mol L^{-1} aqueous alkaline earth metal nitrate solutions

Solvent	$R_F \times 100^a$							
	Sc	Y	La	Ce	Pr	Nd	Sm	Eu
$\text{Mg}(\text{NO}_3)_2$	1 ± 3	26 ± 7	83 ± 6	71 ± 6	63 ± 6	64 ± 6	44 ± 6	40 ± 6
$\text{Ca}(\text{NO}_3)_2$	2 ± 3	22 ± 7	86 ± 6	69 ± 6	60 ± 7	61 ± 7	39 ± 7	35 ± 7
$\text{Sr}(\text{NO}_3)_2$	2 ± 3	21 ± 6	82 ± 7	66 ± 7	56 ± 7	56 ± 7	36 ± 7	32 ± 7
$\text{Ba}(\text{NO}_3)_2$	2 ± 3	19 ± 6	80 ± 7	62 ± 7	52 ± 6	52 ± 7	31 ± 6	27 ± 7
Solvent	$R_F \times 100$							
	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
$\text{Mg}(\text{NO}_3)_2$	42 ± 6	29 ± 6	23 ± 6	23 ± 6	18 ± 6	10 ± 5	7 ± 4	6 ± 4
$\text{Ca}(\text{NO}_3)_2$	37 ± 6	25 ± 6	20 ± 6	20 ± 6	14 ± 6	8 ± 5	6 ± 4	5 ± 4
$\text{Sr}(\text{NO}_3)_2$	34 ± 6	24 ± 6	19 ± 6	19 ± 6	13 ± 6	8 ± 5	5 ± 4	5 ± 4
$\text{Ba}(\text{NO}_3)_2$	29 ± 7	20 ± 6	16 ± 6	16 ± 6	11 ± 6	7 ± 4	5 ± 4	5 ± 4

^a average and error limit of three repeated runs

Table 2 R_F values ($\times 100$) of the rare earths on silica gel developed with 1.0 mol L^{-1} aqueous alkaline earth metal nitrate solutions

Solvent	$R_F \times 100^a$							
	Sc	Y	La	Ce	Pr	Nd	Sm	Eu
$\text{Mg}(\text{NO}_3)_2$	2 ± 3	42 ± 6	91 ± 5	84 ± 5	79 ± 6	80 ± 6	65 ± 6	61 ± 6
$\text{Ca}(\text{NO}_3)_2$	2 ± 3	31 ± 6	90 ± 5	79 ± 6	72 ± 6	73 ± 6	56 ± 6	49 ± 6
$\text{Sr}(\text{NO}_3)_2$	2 ± 3	28 ± 5	87 ± 5	74 ± 6	66 ± 6	67 ± 6	49 ± 6	43 ± 6
Solvent	$R_F \times 100$							
	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
$\text{Mg}(\text{NO}_3)_2$	63 ± 6	46 ± 6	38 ± 6	38 ± 6	29 ± 6	17 ± 6	10 ± 5	8 ± 5
$\text{Ca}(\text{NO}_3)_2$	52 ± 6	35 ± 6	27 ± 6	27 ± 6	19 ± 5	12 ± 5	7 ± 4	7 ± 4
$\text{Sr}(\text{NO}_3)_2$	45 ± 6	32 ± 5	25 ± 6	24 ± 6	18 ± 5	11 ± 5	7 ± 3	6 ± 3

^a average and error limit of three repeated runs

salt. To clarify the outstanding features of the adsorption behavior in these systems, variations in the R_F values of the lanthanides with their atomic number (Z) are shown in Fig. 1, where the R_F data obtained by development with 1.0 mol L^{-1} nitrate solutions are quoted, because larger variations in R_F values were observed when these solutions, rather than in 0.4 mol L^{-1} solutions, were used. In general, the R_F values of the lanthanides decreased in a regular and characteristic way, accompanied by the tetrad effect, with increasing atomic number in all the salt solutions examined. Yttrium was located between Tb and Dy, and Sc remained near the point of application for all the mobile phases tested. Similar tendencies in adsorption behavior have already previously been found for all TLC systems [16–20] comprising silica gel developed with solutions of ammonium salts (nitrate, chloride, and sulfate) and alkali metal salts (nitrates and chlorides), although the R_F values of each lanthanide vary considerably, depending on the nature and the concentration of the salt used. From these similarities, it can be expected that the adsorption of the rare earths in these systems, as described previously [19, 20], seems to proceed by the competitive cation-exchange between hydrated lanthanide cations and hydrated solvent cations, followed by partial dehydration of the lanthanide cations and subsequently by the formation of inner-sphere complexes between the dehydrated lanthanide cations and oxygen atoms of the surface silanol groups of silica gel. In these systems, however, the R_F values of each lanthanide decreased in the order, $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$, i.e. with increasing crystal ionic radii of the solvent cations, as is apparent from Tables 1 and 2 and Fig. 1. This sequence was the opposite of that obtained by use of alkali metal nitrate and chloride mobile phases, when the R_F values of each lanthanide decreased in the order, $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$, i.e. with decreasing the crystal ionic radii. This unexpected discrepancy will be discussed in the next paragraph.

Effect of solvent cation on R_M values

To clarify the effect of the solvent cations on the adsorption behavior, the R_M values of several lanthanides were plotted as a function of the crystal ionic radii [21] of the mobile phase cations (Fig. 2). For comparison, the R_M values of Gd on the same amine-pretreated silica gel as that used in this study, with 0.5 mol L^{-1} alkali metal nitrate solutions as mobile phases are also quoted in Fig. 2. It should be noted that there was a remarkable discrepancy between the adsorptive behavior of the alkaline earth metal solutions used in this work and the previous alkali metal solutions [19, 20]. Comparing the R_F data obtained with the nitrate solutions of the alkaline-earth metals mutually on the basis of the same concentrations, the R_M values of each lanthanide increased in the order, $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$ as the six-coordinated crystal ionic radii of the solvent cations became larger, whereas with the alkali metal nitrate and chloride solutions, as represented by the R_M values of Gd with nitrate mobile phases in Fig. 2, they

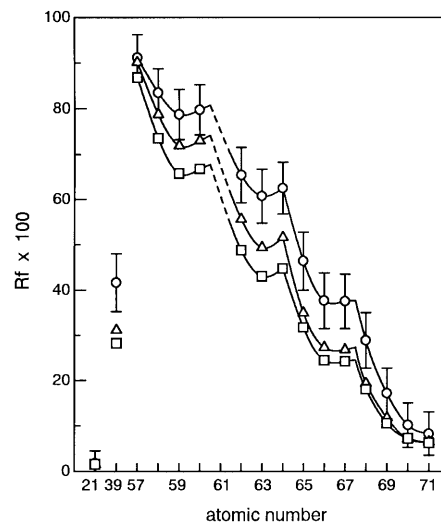
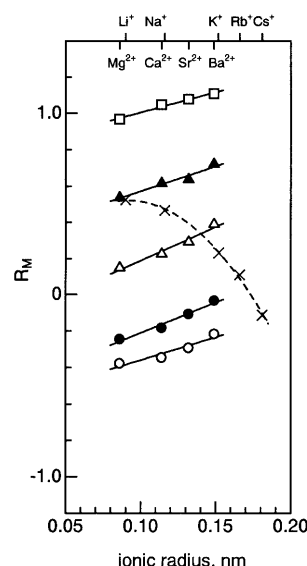


Fig. 1 Variation with atomic number of the R_F values ($\times 100$) of the rare earths on silica gel developed with 1.0 mol L^{-1} aqueous alkaline earth metal nitrate solutions. Alkaline earth metal: magnesium (\circ); calcium (\triangle); strontium (\square). The vertical lines (\updownarrow) are the error limits obtained from three repeated runs for magnesium

Fig. 2 Effect of the ionic radii of the mobile phase cations on the R_M values of several lanthanides. Mobile phase: 0.4 mol L^{-1} aqueous alkaline earth metal nitrate solutions: cerium (\circ); neodymium (\bullet); gadolinium (\triangle); holmium (\blacktriangle); thulium (\square). Mobile phase: 0.5 mol L^{-1} aqueous alkali metal nitrate solutions: gadolinium (\times)



decreased in the order, $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ as the ionic radii of the alkali metals increased and, furthermore, as the selectivity coefficients [22] of alkali metal cations relative to sodium ion on silica gel increased.

Concerning the extent of adsorption of the alkaline earth metal cations on silica, Malati et al. [23] have reported that adsorption on quartz at a constant pH of 10.5 increases in the order $\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$. Tadros et al. [24] have also found that the surface charge or the affinity for silica at $\text{pH} > 7.5$ in the presence of a high concentration of electrolyte increases in the order $\text{Mg}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Ba}^{2+}$ (this sequence differs slightly from that obtained by Malati et al. [23]), though the alkaline earth metal cations, and the alkali metal cations, are physically adsorbed below pH ca. 7.5. On the other hand, Persello [25] has re-

cently reported that on high-purity colloidal silica at pH 9.0, in the absence of added monovalent electrolyte, a series of alkaline earth metal ions forms surface complexes with silanol, and the selectivity sequence on the colloidal silica is $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. This sequence is in accordance with the reversed order of the M–O bond length of the alkaline earth metals (M), reported by Marcus [26]. Thus, the M–O bond strength might decrease in the order $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. Furthermore, the stability constants ($\log K$, at the ionic strength of 1.0, and 25 °C) of silicate complexes (ML^{2-}) formed by the reaction with alkaline earth metals (M^{2+}) and hydrogen silicate (silicic acid, H_4L_4) are 4.17 for Mg^{2+} and 3.09 for Ca^{2+} [27]. From these facts, if the alkaline earth metal ions, retained by chemisorption on the silica gel in the same way as the rare earth ions, were unhydrated and adsorbed as inner-sphere complexes on the silanol groups of the silica gel, the adsorption of these ions would be expected to decrease in the order $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$, in contrast with the order found with the alkali metal mobile phases, because of competitive chemisorption between the rare earth ions and alkaline earth metal ions. If it is assumed that the chemisorption occurs as a result of the formation of inner-sphere complexes through the oxygen atoms of the surface silanol groups, it can be expected that the R_M values of the lanthanides (M^{3+}) in any salt solution system will increase with increasing stability constant (K) of their hydroxo complexes (ML^{2+} , $L = OH^-$; for example, $\log K$ values are: 4.67 for La^{3+} ; 5.38 for Gd^{3+} ; 5.69 for Ho^{3+} ; and 5.83 for Lu^{3+} at the ionic strength of 0.5, and 25 °C [27]) in accordance with the increasing order of their atomic numbers. It can also be expected that the R_M values of any lanthanide will increase with decreasing stability constant of the hydroxo complexes (ML^+) of the alkaline earth metals ($\log K$ values are: 1.85 for Mg^{2+} ; 0.64 for Ca^{2+} ; 0.23 for Sr^{2+} ; and 0.00 for Ba^{2+} at the ionic strength of 1.0 and at 25 °C [27]) in good agreement with the adsorption sequence evidenced in Fig. 2. From these arguments, it seems

reasonable to suppose that the extent of adsorption of the rare earths in these systems results from competitive cation-exchange between the hydrated rare earth cations and the hydrated solvent cations, followed by partial dehydration of the rare earth and solvent cations, and subsequently by competitive formation of inner-sphere complexes through the oxygen atoms on the silanol groups between the rare earths and the alkaline earth metals.

Effect of salt concentration on R_F values

The R_F values of all the lanthanides (except Pm), Sc(III), and Y(III) on silica gel developed with aqueous magnesium nitrate solutions of different concentration are summarized in Table 3, and the variations in the R_M values of several lanthanides are shown as a function of the concentration of the salt in Fig. 3, in which the R_M values of Gd on the same amine-pretreated silica gel as that used in this study developed with sodium nitrate solutions are also plotted against the salt concentration for comparison. On the whole, the R_M values of each metal at first decreased sharply and then gradually, with increasing salt concentration, by means of competitive cation-exchange, and finally reached nearly constant values with a further increase in the salt-concentration (2.0 mol L⁻¹ or more). This depends chiefly on the involvement of a salting-out effect, as found with the previous mobile phases such as ammonium nitrate [16], alkali metal nitrates [19], and alkali metal chlorides [20]. For example, the variation in R_M values of each lanthanide with magnesium nitrate mobile phases was very similar to that in the sodium nitrate system, although the R_M values of each metal in the former were much smaller than those in the latter because of the much stronger adsorption of the divalent ions. These facts also suggest that the hydration of the solvent ions, except for the competitive cation-exchange adsorption already described, is more important in the aqueous solution systems of alkaline earth metal salts than in the alkali metal

Table 3 R_F values ($\times 100$) of the rare earths on silica gel developed with aqueous magnesium nitrate solutions

Mg(NO ₃) ₂ (mol L ⁻¹)	$R_F \times 100^a$							
	Sc	Y	La	Ce	Pr	Nd	Sm	Eu
0.2	2 ± 3	17 ± 6	77 ± 6	57 ± 6	47 ± 6	47 ± 6	28 ± 6	24 ± 7
0.4	1 ± 3	26 ± 7	83 ± 6	71 ± 6	63 ± 6	64 ± 6	44 ± 6	40 ± 6
1.0	2 ± 3	42 ± 6	91 ± 5	84 ± 5	79 ± 6	80 ± 6	65 ± 6	61 ± 6
2.0	2 ± 3	45 ± 6	95 ± 5	89 ± 6	85 ± 6	86 ± 6	74 ± 6	70 ± 6
3.0	1 ± 2	45 ± 6	96 ± 4	91 ± 6	87 ± 6	88 ± 6	77 ± 6	71 ± 7
Mg(NO ₃) ₂ (mol L ⁻¹)	$R_F \times 100$							
	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
0.2	26 ± 6	19 ± 6	14 ± 6	15 ± 6	12 ± 5	7 ± 5	5 ± 4	5 ± 4
0.4	42 ± 6	29 ± 6	23 ± 6	23 ± 6	18 ± 6	10 ± 5	7 ± 4	6 ± 4
1.0	63 ± 6	46 ± 6	38 ± 6	38 ± 6	29 ± 6	17 ± 6	10 ± 5	8 ± 5
2.0	72 ± 6	55 ± 6	44 ± 6	43 ± 6	33 ± 7	20 ± 6	12 ± 5	10 ± 5
3.0	73 ± 6	56 ± 7	44 ± 6	43 ± 6	32 ± 7	19 ± 6	12 ± 5	10 ± 5

^a average and error limit of three repeated runs

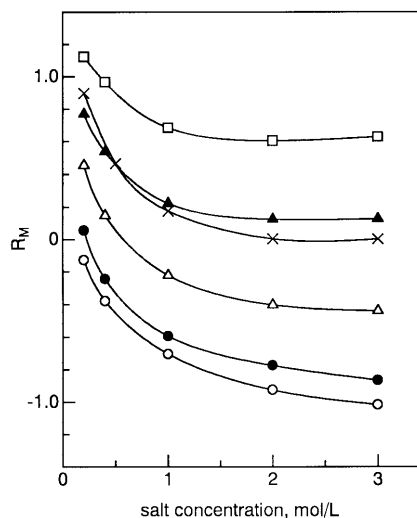


Fig. 3 Variation of the R_M values of several lanthanides with salt concentration in the aqueous magnesium nitrate mobile phases: cerium (○); neodymium (●); gadolinium (△); holmium (▲); thulium (□). Mobile phase: aqueous sodium nitrate solutions: gadolinium (×)

salt solution systems in determining the R_M values of the rare earths.

Separation

Current knowledge about the adsorption behavior of the rare earths suggests that, among the alkaline earth metal systems examined, the magnesium nitrate mobile phase is the most advantageous for the separation of lanthanides

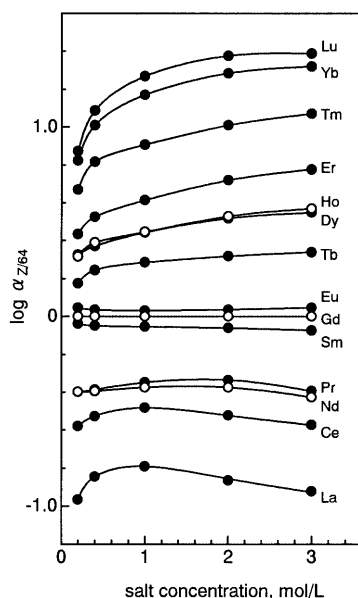


Fig. 4 Variation in the separation factors of lanthanides relative to Gd with salt concentration in aqueous magnesium nitrate mobile phases

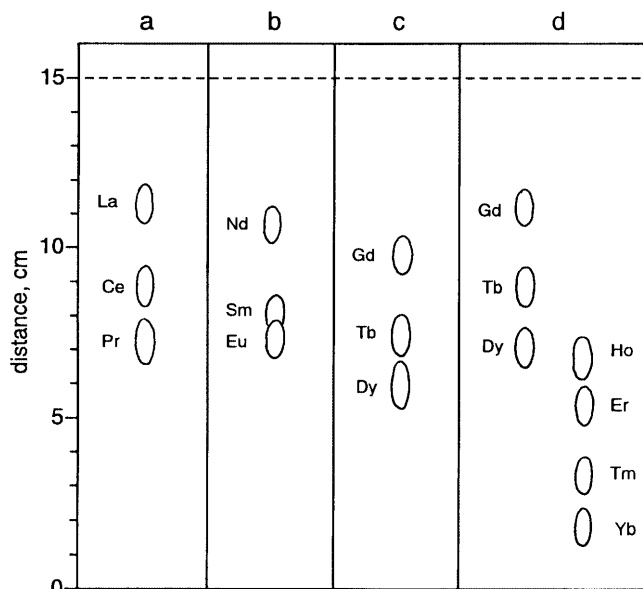


Fig. 5 Separation of multi-component mixtures containing adjacent lanthanides. Mobile phase: **a**, 0.2 mol L⁻¹ Mg(NO₃)₂; **b**, 0.5 mol L⁻¹ Mg(NO₃)₂; **c**, 1.0 mol L⁻¹ Mg(NO₃)₂; **d**, 3.0 mol L⁻¹ Mg(NO₃)₂; Solvent front: ----

with adjacent atomic numbers, because the R_F values vary most strongly with increasing salt concentration. For example, magnesium-containing mobile phases of lower concentration are favorable for the separation of lighter lanthanides, and mobile phases of higher concentration are applicable to that of heavier metals.

Fig. 4 shows the variation in separation factors of the lanthanides, relative to Gd, with magnesium nitrate mobile phases of increasing concentration. It is worth noting that the separation factors of the heavier lanthanides clearly increase as the salt concentration increases, although those for lighter metals are nearly constant over the entire range of salt concentration tested. On the other hand, the salting-out effect, which brings about the lowering in R_F values, is slightly weaker for lighter lanthanides than for heavier ones, because the stability constants [27] of the nitrate complexes are somewhat larger for the lighter lanthanides than for heavier ones. Thus, differences between the possibility of complexation for two lanthanides result in slight increases in the separation factors for heavier lanthanides (Gd to Er) at higher salt concentrations. Several examples of separations achieved by use of magnesium nitrate mobile phases of different concentration are given for illustration in Fig. 5.

Conclusion

In these systems the R_F values of the lanthanides varied in a regular and characteristic way, accompanied by the tetrad effect, with increasing atomic number, as with the alkali metal systems, and those of each metal decreased in the order, Mg²⁺ > Ca²⁺ > Sr²⁺ > Ba²⁺, i.e. with increasing

crystal ionic radii of the mobile phase components. This adsorption sequence is contrary to that in the alkali metal systems, where the R_F values decreased in the order, $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$, i.e. with decreasing crystal ionic radii. From these facts it can be presumed that these systems involve competitive formation reaction of inner-sphere complexes through the oxygen atoms on the silanol groups between the partially dehydrated rare earth and the alkaline earth metal cations, as well as the competitive cation-exchange adsorption between the hydrated rare earth and alkaline earth metal cations. Thus, these systems enable several characteristic procedures effective for the separation of the rare earths by arbitrarily selecting appropriate salt solutions of different concentration, because the separation factors for neighboring lanthanides vary according to the nature and concentration of the salts used, owing to the participation of several factors controlling R_F values.

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