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The Possibility for Separation of Lanthanum by Solid-State Complexes with 2-Ethylhexyl Phosphoric Acids

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ABSTRACT

The elemental composition, molecule, and crystal structure of precipitates obtained from an acetone solution of $Ln(NO_3)_3$ (Ln = Pr + Er or La + Nd) with a mixture of bis- and mono-(2-ethylhexyl) phosphoric acids and their sodium salts were studied. In this study we found enrichment of the precipitate with the heavier lanthanide. The separation factor for the La–Nd couple is much greater than for the Er–Pr couple, and decreases with increasing rare-earth yield in the precipitate. We discuss the significant role of the stability of LnA_3 against HNO_3, especially the formation of La complexes with mono-(2-ethylhexyl) phosphoric acid during enrichment.

INTRODUCTION

The synthesis and some of the properties of the solid-state complexes of the LnA_3-type of rare-earth elements (RE, Ln) with bis-(2-ethylhexyl) phosphoric acid [HA, A = $(C_8H_{17}O)_2PO_2^-$] were described in the literature (1–7). Some of them have been applied as catalyzers (3) as well as in the purification of bis-(2-ethylhexyl) phosphoric acid from neutral organic impurities (3). Their ability to form liquid crystals was shown (8). Recently, the possibility of their use in Ln separation was pointed out (9, 10). Mixed-ligand complexes $LnA(NO_3)_2 \cdot nH_2O$ (11) and $LnA(NO_3HA)_2$ (9) have also been obtained. We recently prepared and studied solid state

RE complexes with mono-(2-ethylhexyl) phosphoric acid of the type $Ln(HA')_3 \cdot nH_2O$, $Ln(HA')_2NO_3 \cdot 1.5H_2O$ and $La_2A'_3 \cdot nH_2O$ ($A' = C_8H_{17}OPO_3^{2-}$) (12).

A few years ago it was found (13) that the precipitate formed by a reaction of commercially available bis-(2-ethylhexyl) phosphoric acid (solution in 0.01 M HCl) with $LaCl_3$ and $NdCl_3$ is enriched with neodymium. The distribution of RE between the solid and liquid phases obtained by the precipitation of LnA_3 from their solution in an octane-octanol-NH_3 mixture has been studied by Trifonov et al. (10). They found that the solution is enriched with the lighter RE. They proposed that the length of the LnA_3 polymer chains formed increases with the Ln atomic number and, accordingly, their solubility decreases. The same authors studied the separation of europium from other RE, precipitating LnA_3 from their HNO_3 solution (8). It has been established that the separation factor depends on the RE ionic radius.

In the above cited paper (12) we reported that praseodymium, neodymium, and erbium form a solid phase consisting of LnA_3 complexes when specific experimental conditions are applied [reaction of $Ln(NO_3)_3$ acetone solution with a partially neutralized commercial product bis-(2-ethylhexyl) phosphoric acid, the latter of which contains 62% HA and 37% H_2A']. In the same conditions, lanthanum forms a solid phase only with H_2A' of the type $La(HA')_3 \cdot nH_2O$ or $La(HA')_2NO_3 \cdot nH_2O$. The results show that the complexes studied can be used for separating lanthanum from other rare earths. Since the separation of lanthanum, which is the main component in cerium-free rare-earth mixtures, is an essential step in their processing, the search for easier lanthanum separation is of significant interest.

In the present paper, results are reported on the composition of the solid phase formed in the system $Ln(NO_3)_3$–$Ln'(NO_3)_3$–HA–H_2A'–NaA–NaHA'–$(CH_3)_2CO$–H_2O in coexistence of lanthanum and neodymium or praseodymium and erbium. The established separation of lanthanum from neodymium is quantitatively described.

EXPERIMENTAL

Materials

Puriss p.a. reagents were used to prepare the investigated compounds. The nitrates of RE were prepared from the corresponding oxides with an assay of more than 99.9%. Potentiometric titration shows the presence of 37% monoester in the bis-(2-ethylhexyl) phosphoric acid (Fluka) used.

Synthesis

The method used (12) is analogous to the one described in Ref. 3. Equal volumes of 0.5 M NaOH and a mixture of alkylphosphoric esters were mixed. The two phases were separated after prolonged agitation. Equal volumes of acetone solutions of the corresponding lanthanide nitrates (100 g anhydrous salts/dm^3) were added to the organic phase. When water and acetone were added, a solid phase was obtained. The latter was filtered after 12 hours, washed with water and acetone, and dried in a dessicator above concentrated H_2SO_4 for 48 hours.

Analysis

The composition of the investigated solid phases was determined by common organic analysis methods (C, H, and N) and by IPC atomic emission spectroscopy (phosphorus and RE).

FT-IR spectra (400–4000 cm^{-1}) were recorded by Bomem Michelson-100 in Nujol. The spectral curve decomposition was done using the SPECTRA CALC program. Strongly overlapping bands were subjected to deconvolution prior to decomposition.

The diffractograms were made by a URD-6 powder diffractometer (Siemens) at CoKα, 30 mA, and 40 kV with a step width of 0.025 (in 2Θ) and a counting time of 200 seconds per step.

RESULTS AND DISCUSSION

Elemental Composition

Table 1 contains data for the composition of precipitates obtained with different yields from initial solutions which differ in the ratio between the two REs.

The yield was regulated by the quantity of desalting agent that was added in the last stage of preparation of the complexes. The yield, along with the distribution coefficients and separation factors, are shown in Table 2. The Ln contents in equilibrium solutions were determined as differences between their experimentally found contents in the initial solution and those found in the precipitate.

Molecule Structure

The IR spectrum of the precipitate containing praseodymium and erbium does not show any essential differences from the spectra of the individual compounds PrA_3 and ErA_3. Because the spectra of these com-

TABLE 1

Elemental Composition of the Precipitates Prepared from Solutions Containing Two Rare Earths

No.	Approximate formula[a] of the complexes	Ln/Ln′[b] mole ratio in initial solution	H		C		Ln		Ln′	
			Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
1	$Pr_{0.28}Er_{0.72}A_3$	1: 0.84	8.74	8.88	50.20	50.20	2.9	3.4	9.4	9.5
2	0.0006 $La(HA')_3$ + 0.9994 NdA_3	1:99.00	9.09	9.27	52.46	52.00	0.009	0.008	14.2	13.0
3	0.034 $La(HA')_3$ + 0.966 NdA_3	1: 2.33	8.90	9.22	52.61	51.62	0.46	0.43	13.9	13.7
4	0.036 $La(HA')_3$ + 0.964 NdA_3	1: 1.00	9.19	9.21	52.70	51.60	0.49	0.46	13.8	13.6
5	0.014 $La(HA')_3$ + 0.986 NdA_3	1: 0.43	9.03	9.25	52.25	51.85	0.15	0.18	12.0	12.2

[a] Better expressed with the formula $a La(HA')_3 \cdot 1.5H_2O + b La_x Nd_{1-x} A_3$.

[b] Ln′ = RE element with a higher atomic number.

TABLE 2
Lanthanium–Neodymium separation

	Ln mass (n), mmol				Nd content (C),[b] mol%							
	Initial solution (IS)		Precipitate (P)		Solution			Yield (Y),[b] (%)		Distribution coefficient (D)		
No.[a]	Nd	La	Nd	La	Initial (IS)	Equilibrium (ES)	Precipitate (P)	Nd	La	Nd	La	Separation factor (F)[b]
2	6.8663	0.0694	2.3502	0.0015	99.0	98.5	99.94	34.2	2.2	1.02	0.04	25
3	4.8918	2.0965	1.7443	0.0598	70.0	60.7	96.7	35.6	2.8	1.59	0.08	19
4	3.5316	3.5371	0.6981	0.0259	50.0	44.6	96.4	19.8	0.7	2.16	0.06	36
5	2.1222	4.9518	1.9627	4.9496	30.0	28.4	98.6	7.5	0.04	3.47	0.019	182

[a] Numbers according to Table 1.

[b] $C = 100n_{\mathrm{Nd}}/(n_{\mathrm{Nd}} + n_{\mathrm{La}})$.
$Y = 100n_{\mathrm{P}}/n_{\mathrm{IS}}$.
$D = C_{\mathrm{P}}/C_{\mathrm{ES}}$.
$F = D_{\mathrm{Nd}}/D_{\mathrm{La}}$.

pounds are rather close (12), their similarity with the "mixture" precipitate is to be expected.

The spectra of the neodymium and lanthanum complexes obtained under the conditions described in the Experimental Section (but in the presence of one RE) are shown on Figs. 1 and 2. As mentioned in the conditions described for the synthesis of NdA_3, $La(HA')_2NO_3 \cdot 1.5H_2O$ are formed. The spectra of the "mixture" precipitates (prepared in the same conditions but from solutions containing lanthanum and neodymium in different mole ratios, Table 2, Exps. 2–5) are rather close to the spectrum of NdA_3. At the same time, two significant differences could be seen in the band intensities at 1027 and 1187 cm^{-1}. The intensive absorptions at 1030 and at 1150 cm^{-1} (Fig. 2) are characteristics for $La(HA')_2NO_3 \cdot 1.5H_2O$ (12) while the 1187 cm^{-1} band is the most intensive in the LaA_3 spectrum (Fig. 3). The relative increase of these bands in the spectra of the mixture precipitates in comparison with NdA_3 show that La^{3+} ions are included in NdA_3, most probably in the form of $La(HA')_2NO_3 \cdot 1.5H_2O$

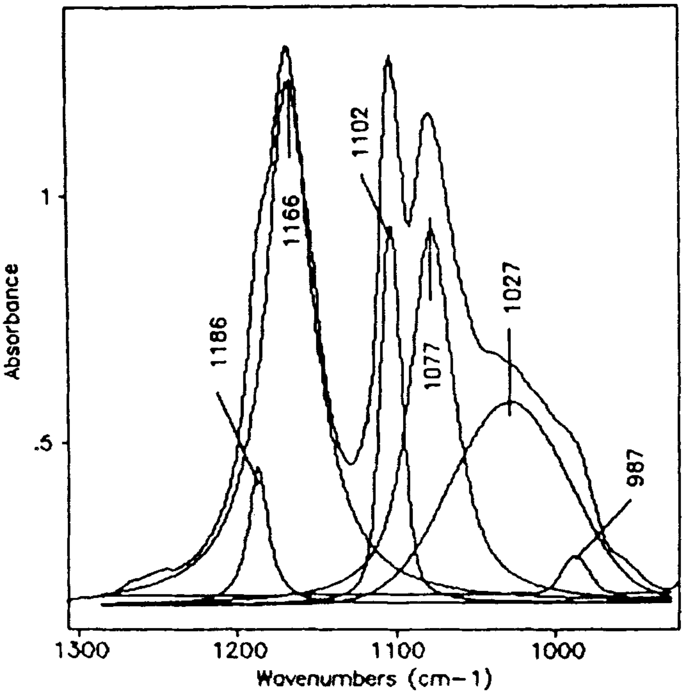

FIG. 1 IR spectra of NdA_3.

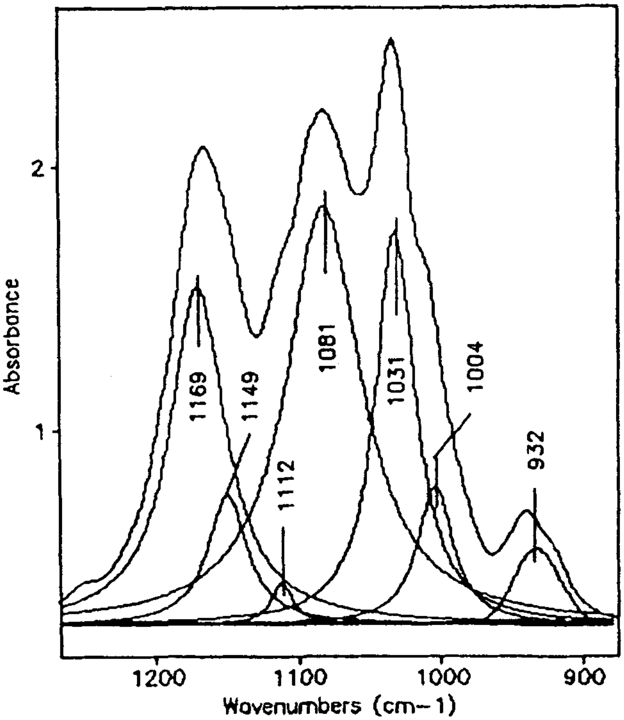

FIG. 2 IR spectra of La(HA')$_2$NO$_3$·1.5H$_2$O.

and LaA$_3$. This is confirmed by Fig. 4 which presents the spectrum of a "mixture" precipitate obtained at high yield with RE. It may be expected that LaA$_3$ will form a solid solution with NdA$_3$. The presence of La(HA')$_2$-NO$_3$·1.5H$_2$O is also confirmed by the band at 3500–2720 cm^{-1}. These results are in full agreement with the crystal structure data.

Crystal Structure

The crystal structures of PrA$_3$ and ErA$_3$ are practically identitical (both compounds crystallize in orthorombic symmetry) (14). This explains the observed identity between the diffractograms of the mixed Pr–Er–precipitate and those of the individual compounds (Fig. 5). Along with the IR data and elemental composition, the x-ray diffraction study shows that the mixed precipitate represents a solid solution of PrA$_3$ and ErA$_3$ or copolymer of the type Pr$_x$Er$_{1-x}$A$_3$. The reflexes between 2 and 28° were successfully indexed in orthorombic symmetry using the program POW-

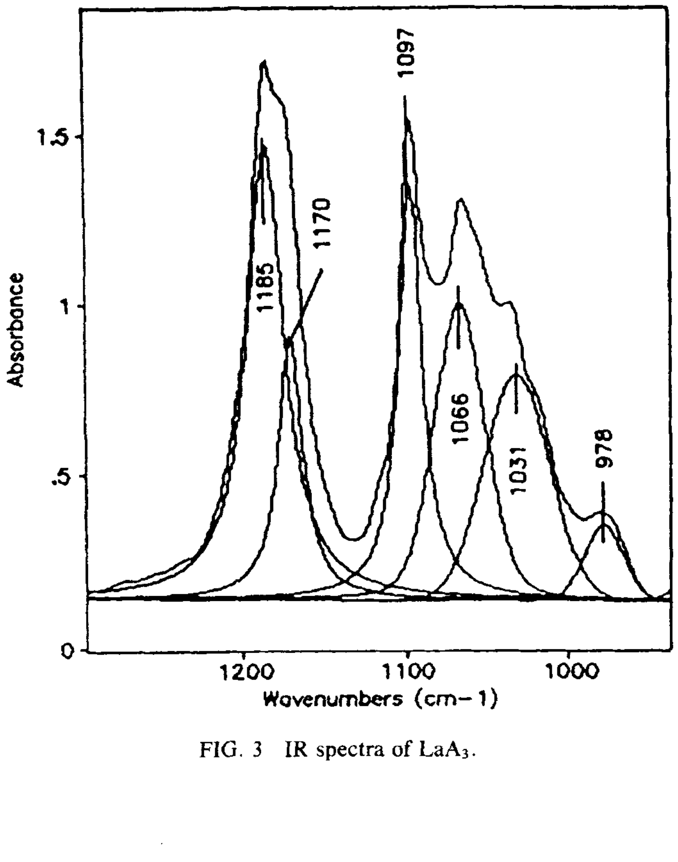

FIG. 3 IR spectra of LaA_3.

DER (Table 3). The cell parameters ($n10^{-10}$ m), a = 19.24 ± 0.10, b = 11.75 ± 0.06, and c = 16.78 ± 0.06, are the same (within the error limit) as those of the individual compounds. Some small portion of the amorphous (nanocrystalline) phase could also be seen on the diffractogram. Its origin will be discussed below.

The diffractogram (Fig. 5.3, Table 3) of the precipitate containing >99.9 mol% Nd (relative to the sum La + Nd) (Exp. 2, Table 2, Fig. 4) is practically the same as that of NdA_3 (14). Amorphous or nanocrystallized regions are overlapped in the NdA_3 reflexes when the La content in the precipitate is increased (Exp. 4, Table 2, Fig. 5.4). They are contributed by the $La(HA')_2NO_3 \cdot 1.5H_2O$ (Fig. 5.5) present in the precipitate in these conditions. At the same time, the interlayer distances are shifted to greater values (Table 3), and the cell parameters and mol volume are slightly increased. These data suggest that the La–Nd precipitate probably consists of a mixture of $La(HA')_2NO_3 \cdot nH_2O$ and $La_yNd_{1-y}A_3$.

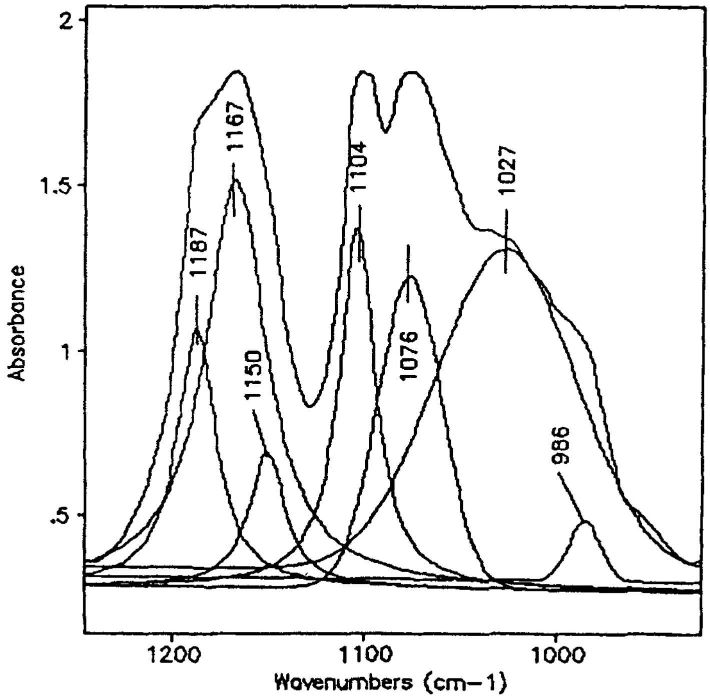

FIG. 4 IR spectra of La–Nd mixture precipitate.

The system we studied is analogous (in some aspects) to the one investigated in Ref. 10. Those authors dissolved previously prepared LnA_3 complexes in HNO_3. Under those conditions, $LnA(NO_3HA)_2$ complexes were formed. Precipitation of LnA_3 occurred when water was added.

By using HA (instead of solely NaA) as a reactant for LnA_3 preparation, we are also ensuring the presence of HNO_3 in the system. Accordingly, the behavior of PrA_3 and ErA_3 could be expected from the results (10). The enrichment (coefficient of enrichment 3.1) of the precipitate with erbium is of the expected order. It is hard to explain this effect with the formation of longer and less soluble polymer chains by the heavier RE, as was supposed (10). The only data for the degree of polymerization (7) show that for $(PrA_3)_n$, $n \approx 7000$, which is higher than for the rest of the $(LnA_3)_n$ investigated. It is hardly probable that ErA_3 (for which no data exist) forms longer chains. Indeed, when the complexes are precipitated from HNO_3 solution, the chain lengths could be rather different. For the time

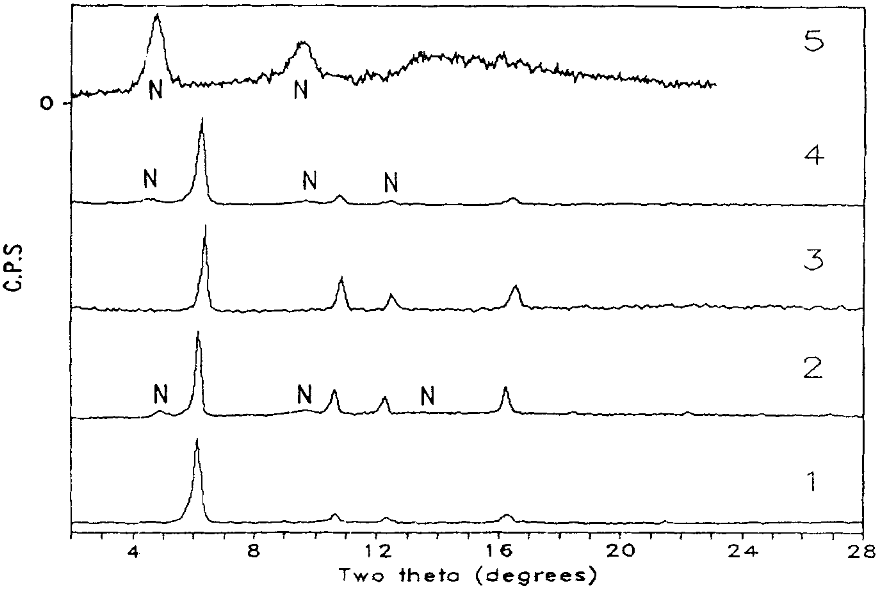

FIG. 5 Diffractograms of PrA_3 (1), $Pr_{0.28}Er_{0.72}A_3$ (2), [$0.0006La(HA')_3$ + $0.9994NdA_3$] (3), [$0.036La(HA')_3$ + $0.964NdA_3$] (4), and $La(HA')_2NO_3 \cdot 1.5H_2O$ (5); *N*-amorphous or nanocrystalline phase.

being, there is no experimental proof for such an assumption. It has been suggested (8) that structure factors play an important role in the separation of europium from other REs.

Along with these hypotheses, we assume that the observed enrichment is connected with the established fact (10) and confirmed by us that decreasing stability of the $LnA(NO_3HA)_2$ complexes occurs with increasing lanthanide atomic number.

The separation factors for La–Nd (Table 2) are much higher than the ones reported for Eu–Ln(III) (10). In the system studied in the present paper, HNO_3 is produced in an amount more than sufficient for the complete destruction of the LaA_3 produced by the reaction $LaA_3 + 3HNO_3 \rightarrow La(NO_3)_3 + 3HA$. However, such a reaction takes place only with LaA_3; much more HNO_3 is needed for the analogous reaction with the other LnA_3 (10). In the system we studied, Nd^{3+} stays mainly in the form of $NdA(NO_3HA)_2$.

The presence of H_2A' and $NaHA'$ in our system ensures the formation of $Ln(HA')_3 \cdot nH_2O$ [or $Ln(HA')_x(NO_3)_{3-x} \cdot nH_2O$] (12). As was experimentally proven in the same work, La complexes with mono-(2-eth-

TABLE 3
X-Ray Powder Diffraction Data

No.	2Θ°	Interlayer distance (d), $n10^{-10}$ m	d^{-2} Found	d^{-2} Calcd	h	k	l	Relative intensity (I/I_0), %
			$Pr_{0.28}Er_{0.72}A_3$					
1	6.03	17.0180	0.035	0.036	0	0	1	100
2	10.60	9.6904	0.0106	0.0108	0	0	1	30.0
3	12.20	8.4234	0.0141	0.0142	0	0	2	22.2
4	16.25	6.3334	0.0249	0.0250	2	0	2	33.3
5	18.45	5.5839	0.0321	0.0320	0	0	3	6.1
6	24.65	4.1934	0.0567	0.0568	3	2	1	1.9
			La–Nd–Precipitate (Exp. 2, Table 2)					
1	6.36	16.1283	0.0038	0.0037	0	0	1	100
2	10.86	9.4582	0.0112	0.0112	0	1	0	44.5
3	12.53	8.2005	0.0149	0.0149	0	0	2	21.5
4	16.55	6.2189	0.0259	0.0259	2	0	2	37.3
			La–Nd–Precipitate (Exp. 4, Table 2)					
1	6.25	16.4196	0.0037	0.0037	0	0	1	100
2	10.81	9.5062	0.0111	0.0111	0	1	0	11.3
3	12.42	8.2768	0.0146	0.0146	0	0	2	5.9
4	16.44	6.2614	0.0255	0.0255	2	0	2	7.6

ylhexyl) phosphoric acid are more stable against HNO relative to the complexes of the same element with the diester (HA). At the same time, the complexes with $(HA')^-$ ligands are more soluble in acetone–H_2O solution, which is due to the presence of OH (and NO_3^- in mixed ligand complexes) as well as to the formation of shorter polymer chains (12).

Therefore, when the desalting agent was added, the precipitation of NdA_3 started first. With an increase in the amount of this agent (i.e., increasing the RE yield in the precipitate), $Ln(HA')_x(NO_3)_{3-x}\cdot nH_2O$ also started to precipitate. Its presence in the precipitate is shown in the IR spectra and in the diffractograms. Due to the precipitation of La complexes with H_2A', the separation factor will obviously decrease as the yield increases. This effect is clearly expressed in Table 2. [Traces of the same type of complexes of praseodymium and/or erbium have been coprecipitated with LnA_3. They have caused amorphous regions in the relative diffractogram (Fig. 5.2)].

If H_2A' or $NaHA'$ is not present in the system, the lanthanum will exist mainly in the form of La^{3+} and will be coprecipitated with NdA_3. The H_2A' present acts as a "masking" agent for La^{3+}, binding it into complexes which are less coprecipitable with NdA_3, thus increasing the separation factor.

CONCLUSION

This study shows that the solid phase formed in the system HA–NaA–H_2A'–NaHA'–acetone–$Ln(NO_3)_3$–$Ln'(NO_3)_3$–H_2O (with specific ratios of the components) is enriched with heavier lanthanide. This is probably due to the decreasing stability of LnA_3 against HNO_3. The precipitate formed by the coexistence of $Pr(NO_3)_3$ and $Er(NO_3)_3$ represents a solid solution, most probably crystallizing in an orthorombic symmetry. Much higher separation factors (decreasing with an increase of the yield of lanthanides in the precipitate) are found for La–Nd. They are probably of the same order for the separation of lanthanum from other Ln(III). The higher separation of La is caused by the qualitatively different behavior of LaA_3 in HNO_3-containing system in comparison with other LnA_3. The H_2A' present plays the role of a "masking" agent for La^{3+}, forming a relatively soluble $La(HA')_x(NO_3)_{3-x}\cdot nH_2O$, and thus decreasing La^{3+} coprecipitation with NdA_3.

The relatively high separation factors obtained, which are accompanied with satisfactory yield, are encouraging for continuing studies of the system because of its potential use in the separation of lanthanides.

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