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Extraction and separation of lanthanides from aqueous chloride and nitrate media using mixtures of binary extractants based on secondary and tertiary amines

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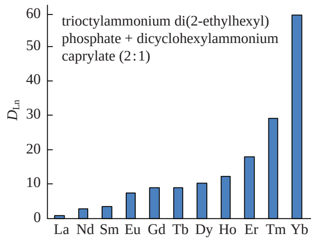
Mixtures of dicyclohexylammonium caprylate with dicyclohexylammonium di(2-ethylhexyl) phosphate and with trioctylammonium di(2-ethylhexyl) phosphate were evaluated as synergistic binary extractants for the recovery and separation of lanthanides. Heavy lanthanides can be effectively separated from the light ones using mixtures of binary extractants based on secondary and tertiary amines.



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Solvent extraction of rare earth elements (REEs) employs extractants of various classes, including organophosphorus cation-exchange ones, for example, 2-ethylhexyl 2-ethylhexylphosphonate (EHEHPA), bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) or di(2-ethylhexyl) phosphate (D2EHPA);[1–3] neutral extractants,[4–7] such as isopropyl 2-(diphenylphosphorylmethoxy)benzoate,[4] as well as functional ionic liquids (FILs) and/or binary extractants, which are salts of organic bases with organic acids.[8–22] The last type of compounds comprises coordination ligands that facilitate the extraction process through the solvation along with ion exchange mechanism. Binary extractants based on alkylamines and organic acids are characterized by simple preparation routes, compared with those based on quaternary ammonium salts, and are typically generated by blending the equimolar amounts of corresponding alkylamines with organic acids. Thus, mixtures of Cyanex 272 with tertiary amines like tri(C_8–C_{10} alkyl)amine (Alamine 336), trioctylamine (TOA), tri(2-ethylhexyl)amine were tested in the Pr and Nd extraction from chloride solutions, and the mixture with Alamine 336 demonstrated the best extraction ability and the maximum synergistic enhancement factors.[8] Extraction of La^{III} by the binary extractants based on *N*,*N*-dioctyldiglycolamic acid and various amines produced the extracted species with different composition, which depended on the initial aqueous medium, namely the chloride or nitrate one.[9] For the binary extractants based on D2EHPA, low-soluble compounds are typically formed in the organic phase, while the presence of salts derived from secondary and tertiary amines can improve the solubility of extracted species and the extraction selectivity.[10,11] For example, a synergistic effect for the system of 2-ethylhexyl 2-ethylhexylcarboxylate, dioctylammonium decanoate and trioctylammonium decanoate was pointed out.[11] In a mixture of two binary extractants, the selectivity of lanthanide extraction is governed by the one with higher individual extraction ability, therefore the search for new binary extractants and new their mixtures, including salts of secondary amines, for the extraction and separation of REEs is promising.

The aim of this work was to explore new binary extractants based on dicyclohexylamine (DCHA) salts with D2EHPA and caprylic acid (CA) in mixtures with TOA–D2EHPA in the extraction of lanthanides from chloride and nitrate aqueous solutions.

Our preliminary tests revealed that the extraction of La^{III} from the chloride and nitrate solutions using the DCHA salts dissolved in hexane led to the formation of poorly soluble extracted compounds. To improve their solubility, mixtures of DCHA–CA and TOA–D2EHPA of various compositions were explored.[†] As follows from Figure 1(*a*), the extraction of La^{III} with isomolar mixtures of TOA–D2EHPA and DCHA–CA in hexane enhances with an increase in the fraction of DCHA–CA. Moreover, no solid extracted species were detected in this system.

Then, mixtures of TOA–D2EHPA and DCHA–CA with a constant 2 : 1 ratio in hexane were examined in the extraction of lanthanides(III) from chloride and nitrate solutions [Figure 1(*b*)]. Total concentration of the binary extractants $C_{\text{extractant(total)}}$ in the mixture solution was calculated as follows:

$$C_{\text{extractant(total)}} = (C_{\text{extractant(1)}}V_1 + C_{\text{extractant(2)}}V_2)/V, \qquad (1)$$

[†] All chemicals were of reagent grade. Stock solutions of lanthanide chlorides and nitrates were prepared from their oxides (>99.9% purity) by dissolution in conc. HCl or HNO_3, respectively. The solutions were diluted to the desired lanthanide concentrations. The required concentrations of chloride and nitrate ions in the aqueous solutions were attained by addition of NaCl or $NaNO_3$.

The DCHA-derived binary extractants were prepared by dissolving equimolar amounts of DCHA (Aldrich, 99% purity) and D2EHPA (Aldrich, 97% purity) or CA (Acros Organics, 99% purity) in hexane. TOA–D2EHPA was prepared analogously by dissolution of equimolar amounts of TOA (Fluka, 97% purity) and D2EHPA in hexane.

Distribution coefficients *D* were calculated as ratios of the Ln^{III} concentration in organic phase to that in the aqueous phase. A separation factor for two lanthanides $\beta_{\text{Ln(2)/Ln(1)}}$ was calculated as a ratio of $D_{\text{Ln(2)}}$ to $D_{\text{Ln(1)}}$.

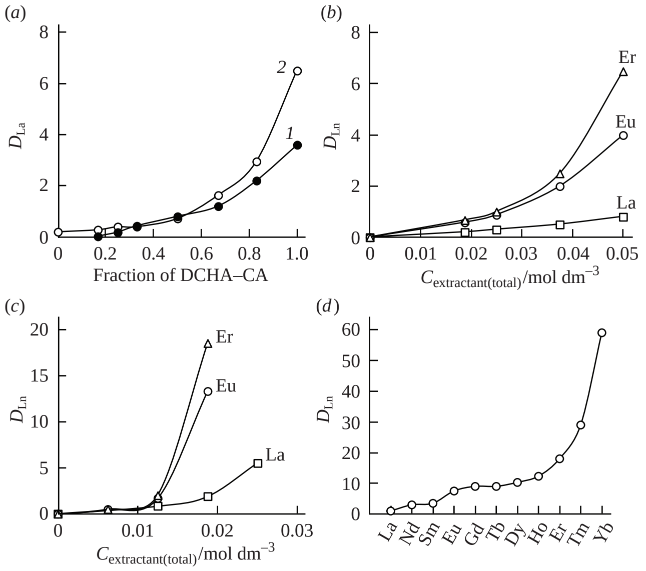

Figure 1 Distribution coefficients in extraction of lanthanides(III) from 0.5 M aqueous solutions of sodium salts at $C_{\mathrm{Ln(initial)}}$ = 0.015 mol dm^{-3}: (*a*) extraction of La$^{\mathrm{III}}$ from solutions of (*1*) NaCl and (*2*) $NaNO_3$ using isomolar mixtures of TOA–D2EHPA and DCHA–CA in hexane *vs.* molar fraction of DCHA–CA in the extractants mixture at $C_{\mathrm{extractant(total)}}$ = 0.02 mol dm^{-3}; (*b*) extraction of La$^{\mathrm{III}}$, Eu$^{\mathrm{III}}$ and Er$^{\mathrm{III}}$ from NaCl solution *vs.* total concentration of TOA–D2EHPA and DCHA–CA in their 2 : 1 mixture; (*c*) extraction of La$^{\mathrm{III}}$, Eu$^{\mathrm{III}}$ and Er$^{\mathrm{III}}$ from NaCl solution *vs.* total concentration of DCHA–D2EHPA and DCHA–CA in their 1 : 1 mixture and (*d*) extraction of different lanthanides(III) from NaCl solution with a 2 : 1 mixture of TOA–D2EHPA and DCHA–CA in hexane at $C_{\mathrm{extractant(total)}}$ = 0.05 mol dm^{-3}.

where $C_{\mathrm{extractant(1)}}$ and $C_{\mathrm{extractant(2)}}$ are the concentrations of the extractants, V_1 and V_2 are the corresponding volumes and V is total volume of the mixture solution. As follows from Figure 1(*b*), the distribution coefficients for Ln$^{\mathrm{III}}$ increase with elevation of the total concentration of binary extractants in the mixtures, while the extractability of lanthanides(III) enhances with their atomic number. The separation factors of lanthanides collected in Table 1 increase with elevation of the total binary extractants concentration in the mixtures. However, under conditions of extractants deficiency, when $C_{\mathrm{extractant(total)}} \leqslant C_{\mathrm{Ln(initial)}}$, the separation factors vary insignificantly, probably due to saturation of the organic phase.

Figure 1(*c*) illustrates the effect of the total concentration of DCHA–D2EHPA and DCHA–CA in a mixture with a constant 1 : 1 ratio on the distribution coefficients of lanthanides(III) during extraction from a 0.5 M NaCl solution. In contrast to the extraction of Ln$^{\mathrm{III}}$ with a 2 : 1 mixture of TOA–D2EHPA and DCHA–CA [see Figure 1(*b*)], here the distribution coefficients of Ln$^{\mathrm{III}}$ are significantly larger. At the total extractants concentration of 0.0187 mol dm^{-3} in hexane, the separation factors are the following: $\beta_{\mathrm{Eu/La}}$ = 7.0, $\beta_{\mathrm{Er/La}}$ = 9.74 and $\beta_{\mathrm{Er/Eu}}$ = 1.40. Thus, using the mixture of DCHA–D2EHPA and DCHA–CA, the representatives of heavy and medium lanthanides can be effectively separated from the light ones.

Table 1 Separation factors of lanthanides(III) during extraction from 0.5 M solutions of NaCl and $NaNO_3$ with a 2 : 1 mixture of TOA–D2EHPA and DCHA–CA in hexane.

$C_{\mathrm{extractant(total)}}$/mol dm^{-3}	$C_{\mathrm{Ln(initial)}}$/mol dm^{-3}	$\beta_{\mathrm{Eu/La}}$	$\beta_{\mathrm{Er/La}}$	$\beta_{\mathrm{Er/Eu}}$
	Cl^- solutions			
0.0187	0.015	2.9	3.35	1.16
0.025		2.92	3.33	1.14
0.0375		4.0	5.0	1.25
0.050		5.0	8.13	1.63
	NO_3^- solutions			
0.0187	0.015	1.53	2.19	1.43
0.025		1.69	2.56	1.51
0.0375		2.42	7.02	2.90
0.050		3.88	24.3	6.27
0.0187	0.03	1.59	2.18	1.37
0.025		1.28	1.94	1.51
0.0313		1.42	–	–

Since the extraction investigated proceeds through cation-exchange and solvation mechanism (see above), it can be assumed that for the binary extractants based on secondary and tertiary amines, represented generally as R_2NH–HA and R_3N–HA, respectively, the process is accompanied by the formation of extracted species of various composition in the organic phase, for example, LnA_3, $LnA_3 \cdot nR_2NHHA$, $LnA_3 \cdot nR_3NHA$, $LnCl_3 \cdot nR_2NHHA$, $LnCl_3 \cdot nR_3NHA$, $Ln(NO_3)_3 \cdot nR_2NHHA$, $Ln(NO_3)_3 \cdot nR_3NHA$, where HA is an organic acid and n is the number of solvated molecules.

To study the different lanthanides(III) selectivity, a 2 : 1 mixture of TOA–D2EHPA and DCHA–CA was tested, the data obtained for trivalent light (La, Nd), medium (Sm, Eu and Gd) and heavy (Tb–Yb) lanthanides during the extraction from a 0.5 M NaCl solution are collected in Figure 1(*d*). The results indicate that an effective separation of heavy lanthanides from the medium and light ones can be achieved in the system proposed.

Stripping of La$^{\mathrm{III}}$ from the loaded organic phase after extraction with mixtures of binary extractants, namely TOA–D2EHPA/DCHA–CA and DCHA–D2EHPA/DCHA–CA, was explored as a function of HCl concentration. It was demonstrated that the stripping of La at $C_{\mathrm{La(organic)}}$ = 0.016 mol dm^{-3} increased with elevation of the HCl amount. La$^{\mathrm{III}}$ was completely recovered from the organic phase using 0.25 M solution of HCl.

Thus, in systems involving mixtures of TOA–D2EHPA and DCHA–CA as well as DCHA–D2EHPA and DCHA–CA, lanthanides(III) can be readily stripped from the organic phase with dilute hydrochloric acid.

In summary, heavy lanthanides can be efficiently separated from the light ones using systems with mixtures of binary extractants based on secondary and tertiary amines. In these extraction systems lanthanides can be effectively stripped from the organic phase with dilute hydrochloric acid. Therefore, the mixtures of binary extractants are promising for the development of new extraction systems and related counter-current chromatographic methods.[23,24]

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