EXTRACTION OF RARE EARTH METALS FROM TRICHLOROACETATE SOLUTIONS IN THE PRESENCE OF LINEAR POLYOXONIUM COMPOUNDS

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Extraction of rare eath metals from lithium trichloroacetate solutions (1·20—2·88 mol l^{-1}) with solutions of the commercial nonionic surfactant Slovafol 909 (*p*-nonylphenylnonaethylene glycol) in chloroform and dichloromethane was investigated. The extraction constants as well as the Slovafol 909 distribution constants were determined in the water–dichloromethane and water–chloroform systems. The lanthanide distribution ratios decrease with their atomic numbers first rather rapidly (approximately to Sm): the separation factor $\alpha_{\mathrm{Sm}}^{\mathrm{La}} = 1{\cdot}54$ and 1·87 in dichloromethane and in chloroform, respectively; for lanthanides with higher atomic numbers the drop is less pronounced ($\alpha_{\mathrm{Lu}}^{\mathrm{La}} = 2{\cdot}42$ and 2·85 in the two solvents, respectively).

Lanthanides are mutually separated mainly by extraction employing classical extraction agents such as bis(2-ethylhexyl)phosphoric acid (D2EHPA) and tributylphosphate. The applicability of other extracting agents, e.g. linear and cyclic polyoxonium compounds (podands and crowns[1]) is being studied extensively. These are mostly neutral compounds whose complexes with the metal extracted can only pass into the organic phase together with a suitable, preferably hydrophobic anion. The picrate and, less frequently, the bis(1,2-dicarbollyl)cobaltate(III) anions are mostly used, extraction from solutions containing, e.g., nitrates in high concentrations being also feasible.

The extraction usually follows the pathway

$$\mathrm{M}_{\mathrm{aq}}^{3+} + 3\,\mathrm{A}_{\mathrm{aq}}^{-} + n\,\mathrm{L}_{\mathrm{org}} \rightleftarrows \mathrm{ML}_n\mathrm{A}_{3,\mathrm{org}} \qquad (A)$$

where M^{3+} is the ion extracted, A^- is the hydrophobic anion, L is the polyoxonium compound, and the subscripts aq and org refer to the aqueous and organic phases, respectively. The complex extracted, $\mathrm{ML}_n\mathrm{A}_{3,\mathrm{org}}$, can be completely or partially dissociated in the organic phase, so that if polar solvents are used, the reaction

$$\mathrm{M}_{\mathrm{aq}}^{3+} + 3\,\mathrm{A}_{\mathrm{aq}}^{-} + n\,\mathrm{L}_{\mathrm{org}} \rightleftarrows \mathrm{ML}_{n,\mathrm{org}}^{3+} + 3\,\mathrm{A}_{\mathrm{org}}^{-} \qquad (B)$$

is also feasible. Moreover, the distribution of the polyoxonium compound between the aqueous and organic phases

$$L_{aq} \rightleftarrows L_{org}, \qquad (C)$$

characterized by the distribution constant of the ligand K_D, must also be taken into account. Numerous other competitive reactions, such as extraction of the supporting electrolyte cation or of the H^+ ion present in the aqueous phase, can also occur.

In addition to advantages, the anions so far examined suffer also from some shortcomings. Common inorganic anions are not very hydrophobic, and so the distribution ratios attained are low even if the supporting electrolyte is used in high concentrations. The vast majority of organic anions, or the corresponding acids, have too low dissociation constants, so that the extraction should be performed at high pH, which, however, is not practicable due to the hydrolysis of the lanthanides. Bis(1,2-dicarbollyl)cobaltate(III) is relatively expensive, whereas the widely used picrates distribute between the two phases during the extraction.

For the extraction of lanthanides with a solution of 18-crown-6 in 1,2-dichloron methane, Samy and coworkers[2] employed the well-available trichloroacetate anios as the hydrophobic species; they used it in the form of an aqueous solution of it-lithium salt. This anion has also been applied to the extraction of lanthanides in the form of their hydrophobic complexes with α,α′-bipyridyl[3]. Trichloroacetic acid is a strong acid, and with respect to its hydrophobicity its anion can be classed roughly between inorganic and bulky organic anions[4].

The main drawback of cyclic polyethers (crowns) is their high price. Benešová and coworkers[5] used the inexpensive nonionic surfactant *p*-nonylphenylnonaethylene glycol, marketed under the commercial name Slovafol 909, for the extraction of lanthanides with bis(1,2-dicarbollyl)cobaltate(III). Other types of nonionic surfactants based on alkylphenylpolyethylene glycols (trade names Triton X-100 and Triton X-405) have been applied by Yoshida and coworkers[6] to the extraction of rare earth element picrates.

The aim of the present work was to examine the possibility of extracting lanthanides in a system containing inexpensive and well-available substances, viz. aqueous solution of lithium trichloroacetate as the aqueous phase and a solution of Slovafol 909 in dichloromethane or chloroform as the organic phase.

EXPERIMENTAL

Chemicals and Solutions

Oxides of rare earth metals of "extra pure" grade (Novosibirsk Precious Metals Plant, U.S.S.R.), scandium oxide of "Specpure" grade (Johnson, Matthey, U.K.) trichloroacetic acid ("pure" grade) and Slovafol (Chemical Works, Nováky, C.S.F.R.) were used as received. The other chemicals used were of reagent grade purity.

Stock solutions of metal nitrates in a concentration of 0·1 mol l^{-1} in nitric acid of a concentration of 0·1 mol l^{-1} were prepared by dissolving the metal oxides in calculated volumes of dilute (1 : 1) nitric acid and diluting with water.

The stock solution of lithium trichloroacetate (4·8 mol l^{-1}) was prepared by neutralization of a known amount of trichloroacetic acid with solid lithium hydroxide.

Procedure

Aqueous phase for the extraction was prepared by dilution from the stock solutions of the rare earth metal nitrates and of lithium trichloroacetate. Prior to the extraction, the pH was adjusted with trichloroacetic acid or with lithium hydroxide.

The distribution constants of Slovafol, viz. K_D 16·9 and 24·7 in the water–dichloromethane and water–chloroform systems, respectively, were determined by evaporating the solvent (or water) from the equilibrium organic (or aqueous) phase and weighing the remaining surfactant.

The extraction experiments were performed by agitating equal volumes of the aqueous and organic phases (5 or 3 ml) for 1 h; preliminary experiments gave evidence that this is a time sufficiently long for the equilibrium to establish. Concentrations of the rare earth metals in the solution before extraction and in the equilibrium aqueous phase were determined chelatometrically by titration with the disodium salt of diethylenetriaminopentaacetic acid (5 mmol l^{-1}) using xylenol orange as the indicator. The metal concentration in the reextract was also determined chelatometrically, using xylenol orange, after neutralization with 0·5M-NaOH. The mass balance of the metal extracted agreed to within a few percent.

The pH_e value of the equilibrium aqueous phase was measured with a Radelkis OP-0808P combined glass–silver chloride electrode interfaced to a Radelkis OP 211/1 pH-meter.

In the extraction of trichloroacetic acid alone (without metal), the concentration of the acid in the aqueous phase was determined by potentiometric titration with a carbonate-free NaOH solution; in the organic phase it was determined likewise after evaporation of the sample in air and its subsequent dissolution in water.

The concentration of lithium in the organic phase was determined after evaporation of the solvent and dissolution of the residue in water; the atomic absorption spectroscopy technique was used at the Central Laboratories of the Institute.

All experiments were performed at room temperature (23°C).

RESULTS AND DISCUSSION

The extraction of rare earth elements (La – Lu, Y, Sc) from a lithium trichloroacetate solution (2·70 mol l^{-1}) with dichloromethane–chloroform solutions of Slovafol 909 was examined via the distribution ratios D_M, which are summarized in Table I. At least two measurements, which agreed to within a few relative per cent, were carried out for each metal. The rare earth metal distribution ratios were found to be independent of their concentration at least up to c_M = 0·017 mol l^{-1} and, for trivalent lanthanide ions, to roughly decrease with their atomic number. To a degree, lanthanum is an exception, its distribution ratios for the two solvents being lower than those of cerium; another exception is ytterbium, which extracts to a lesser degree than lutetium. A similar behaviour has been observed during the extraction of lanthanides from nitrate solutions with bis(1,2-dicarbollyl)cobaltate(III) solutions in nitrobenzene[9].

The separation factors, $\alpha_{\mathrm{Lu}}^{\mathrm{La}} = 2{\cdot}42$ for dichloromethane and $\alpha_{\mathrm{Lu}}^{\mathrm{La}} = 2{\cdot}85$ for chloroform, are low, considerably lower than in other systems; this also applies to the Ce–Yb pair ($\alpha_{\mathrm{Yb}}^{\mathrm{Ce}} = 2{\cdot}59$ and 3·34, respectively). Noteworthy, on the other hand, is the fact that the highest separation factors are attained for the Pr–Nd pair: $\alpha_{\mathrm{Nd}}^{\mathrm{Pr}} = 1{\cdot}25$ and 1·45 in the two solvents, respectively. These values are even higher than in the case of D2EHPA, employed on an industrial scale. The order of extraction of Pr–Nd is here reverse with respect to the order of stability constants of these ions with conventional masking agents, so that this extraction may be of practical importance.

Scandium is extracted considerably better than any heavy lanthanide, although the reverse is true of the extraction with bis(1,2-dicarbollyl)cobaltate(III) in nitro-

TABLE I

Distribution ratios and extraction constants of rare earth metal ions in the extraction with solutions of Slovafol 909 (L) in dichloromethane or chloroform from aqueous solution of lithium trichloroacetate (A^-)[a]

M^{3+}	r[b]	Dichloromethane		Chloroform	
		D_M	K_{ex}[c]	D_M	K_{ex}[c]
La	0·119	4·86	1·69	2·10	0·710
Ce	0·115	4·99	1·75	2·17	0·738
Pr	0·114	4·24	1·48	1·73	0·586
Nd	0·112	3·40	1·19	1·19	0·402
Sm	0·110	3·12	1·08	1·02	0·342
Eu	0·109	3·01	1·05	0·992	0·334
Gd	0·108	2·92	1·02	0·826	0·278
Tb	0·106	2·52	0·879	0·907	0·305
Dy	0·105	2·46	0·858	0·892	0·301
Ho	0·104	2·39	0·835	0·895	0·302
Er	0·103	2·30	0·803	0·860	0·290
Tm	0·102	2·26	0·787	0·803	0·270
Yb	0·101	1·93	0·671	0·650	0·218
Lu	0·100	2·01	0·701	0·738	0·248
Y	0·106	2·13	0·742	0·776	0·261
Sc	0·083	3·67	1·27	1·68	0·563

[a] $c_M = 0{\cdot}01\ \mathrm{mol\,l^{-1}}$, $c_A = 2{\cdot}70\ \mathrm{mol\,l^{-1}}$, $c_L = 0{\cdot}169\ \mathrm{mol\,l^{-1}}$, $\mathrm{pH_e}$ 3·66 (dichloromethane), 3·35 (chloroform); [b] ref.[7] (for Y^{3+} and Sc^{3+}, ref.[8]); [c] the values of $K_D = 16{\cdot}9$ and 24·7 were used for the water–dichloromethane and water–chloroform systems, respectively.

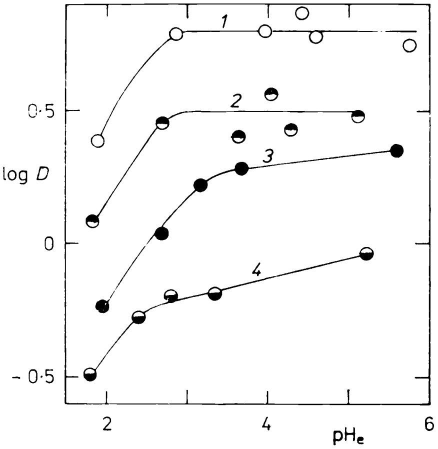
benzene[9], which is consistent with the ionic radius of Sc^{3+} being smaller than that of lanthanides (Table I). This can apparently be ascribed to the fact that during the solvation of scandium with a molecule of *p*-nonylphenylnonaethylene glycol, when the molecules of water solvating the Sc^{3+} ion are substituted by oxygen atoms of the ethylene glycol groups, the hydrophobicity increases to a higher extent than in the case of lanthanide ions, because a lower number of water molecules remain for solvation of the Sc–Slovafol complex. This effect has also been observed during the extraction of some lanthanides and Sc with Slovafols with lower ($n = 6$) and higher ($n = 10$) numbers of ethylene glycol groups in the molecules[10].

The dependence of the extraction of La and Yb on pH_e is shown in Fig. 1, demonstrating that over the regions of pH 2·8 – 5·8 for dichloromethane and pH 2·9 – 5·1 for chloroform, the extraction of La with Slovafol 909 is virtually independent of the aqueous phase acidity; if, however, the acidity is further increased, the extraction grows poorer, probably due to a competition of H^+ ions and, to an extent, of Li^+ ions. The dependence of the extraction of H^+ and Li^+ ions from lithium trichloroacetate on the aqueous phase pH (Table II) demonstrates that this competition manifests itself to a lower degree than as corresponds to the concentration of the acid extracted; on the other hand, for the highest acidity the decrease is higher than as corresponds to the concentration of lithium in the organic phase (for extraction into chloroform at least). For ytterbium, the distribution ratio is not entirely pH-independent, the dependence, however, is not too marked at pH $\geqq$ 3·4 (dichloromethane) or at pH $\geqq$ 2·5 (chloroform).

According to Sukhan and Nazarenko[11], the extraction of trichloroacetic acid with chloroform alone is very low ($K_{D,HA} = 0{\cdot}07$). Our experiments show that in the case of aqueous phase constituted by lithium trichloroacetate at a concentration of

FIG. 1

Dependence of the distribution ratios of La^{3+} and Yb^{3+} on pH for the extraction with solutions of Slovafol 909 from aqueous solutions of lithium trichloroacetate at 23°C; for La^{3+}, $c_A = 2{\cdot}88$ mol l^{-1}, $c_L = 0{\cdot}133$ mol l^{-1}; for Yb^{3+}, $c_A = 2{\cdot}66$ mol . l^{-1}, $c_L = 0{\cdot}170$ mol l^{-1}. *1* La^{3+}, dichloromethane; *2* La^{3+}, chloroform; *3* Yb^{3+}, dichloromethane; *4* Yb^{3+}, chloroform



2·88 mol l^{-1}, the distribution constant in the extraction with dichloromethane and with chloroform is roughly the same, viz. $K_{D,HA} = 0·4$. The extraction of trichloroacetic acid, which is present in an overstoichiometric quantity with respect to Slovafol, thus cannot be regarded as the distribution of the acid itself, which is very low at pH > 2; rather, a molecule of Slovafol in the organic phase solvates more than one molecule of the acid.

In order to enable logarithmic analysis in its conventional form, i.e. by plotting the log D vs log c_A and log c_L dependences, to be applied to the determination of the composition of the extracted species, the requisite conditions must be satisfied; that is, we must have $[A]_{aq} = c_A$, $[L]_{org} = c_L$ (or $[L]_{org} = c_L \,.\, K_D/(1 + K_D)$) and, unless the entire log D vs log c_A or log D vs log c_L has been measured at a constant pH$_e$, the distribution ratios must be pH-independent. In view of the facts that over region applied the distribution ratios are independent of the aqueous phase acidity and that the concentration of the coextracted H^+ and Li^+ ions is low at pH > 5 (dichloromethane) or at pH > 3 (chloroform), and since we have $[M^{3+}]_{org} \ll [L]_{org}$, the above assumptions can be considered satisfied.

The dependences of log D_{La} and log D_{Yb} on the logarithm of concentration of lithium trichloroacetate in the aqueous phase (log c_A) were plotted at a constant

Table II

Extraction of H^+ and Li^+ ions from lithium trichloroacetate (2·88 mol l^{-1}) and trichloroacetic acid solutions with Slovafol 909 in dichloromethane or chloroform at 23°C[a]

c_A^0 mol l^{-1}	c_H^0 mol l^{-1}	pH$_e$	$c_{H,aq}$ mol l^{-1}	$c_{H,org}$ mol l^{-1}	$c_{Li,org}$ mol l^{-1}
Dichloromethane (c_L = 0·133 mol l^{-1})					
3·29	0·413	1·88	0·0861	0·308	0·0708
3·05	0·165	2·50	0·0301	0·136	—[b]
2·96	0·083	3·00	0·0168	0·0614	—
2·92	0·041	5·01	0·0051	0·0362	0·0358
2·88	~10^{-4}	6·26	—[b]	0	0·0269
Chloroform (c_L = 0·134 mol l^{-1})					
3·29	0·413	1·85	0·0928	0·288	0·0413
3·05	0·165	2·36	0·0372	0·128	—
2·96	0·083	2·77	0·0224	0·0649	—
2·92	0·041	3·10	0·0150	0·022	0·0154
2·88	~10^{-4}	4·29	—[b]	0	0·0118

[a] c^0 are the starting concentrations in the aquous phase, charges are omitted for simplicity; [b] not determined.

concentration of Slovafol, viz. 8% (v/v); the dependences of log D_{La} and log D_{Yb} (and, for the extraction with Slovafol solutions in chloroform, also of log D_{Eu}) on the logarithm of concentration of Slovafol (log c_L) were plotted at a constant concentration of lithium trichloroacetate in the aqueous phase. The results are summarized in Figs 2 and 3.

For the log D vs log c_A dependences, the slopes (tg γ) are 3·6 for dichloromethane as the solvent and 3·2–3·4 for chloroform as the solvent.

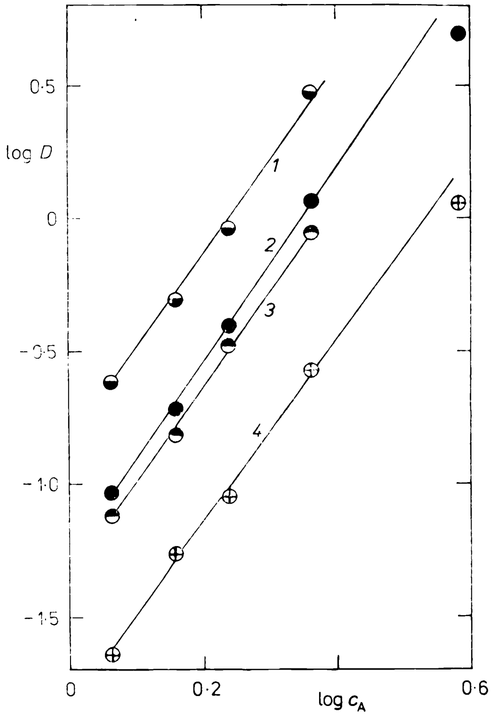


FIG. 2

Dependence of the distribution ratios of La^{3+} and Yb^{3+} on the lithium trichloroacetate concentration in the aqueous phase at 23°C for the extraction with Slovafol 909; c_L = 0·133 mol l^{-1}. *1* La^{3+}, dichloromethane; *2* La^{3+}, chloroform; *3* Yb^{3+}, dichloromethane; *4* Yb^{3+}, chloroform

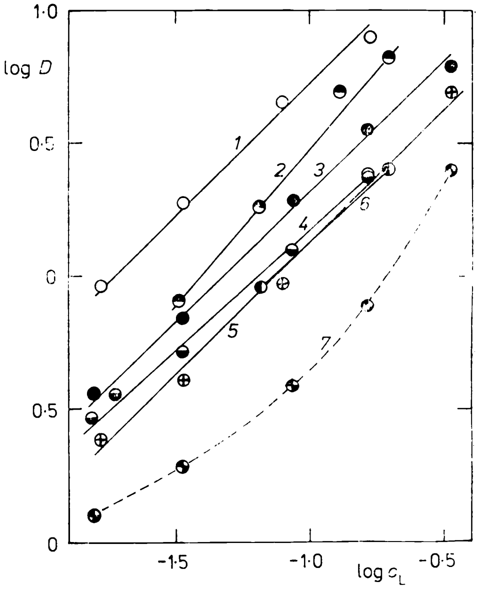


FIG. 3

Dependence of the distribution ratios of La^{3+}, Eu^{3+} and Yb^{3+} on the concentration of Slovafol 909 in the organic phase at 23°C for the extraction from aqueous solutions of lithium trichloroacetate; c_A = 2·88 (La^{3+}, 1, 3), 2·40 (La^{3+}, 2, 6), 3·58 (Eu^{3+}) and 2·88 mol l^{-1} (Yb^{3+}). *1* La^{3+}, dichloromethane; *2* La^{3+}, dichloromethane; *3* La^{3+}, chloroform; *4* Eu^{3+}, chloroform; *5* Yb^{3+}, dichloromethane; *6* La^{3+}, chloroform; *7* Yb^{3+}, chloroform

The log D_M vs log c_L plots for La and the two organic solvents and for Yb and dichloromethane as the solvent are linear, their slopes approaching unity. For Yb and chloroform as the solvent the dependence deviates from linearity, the average slope value, however, approaches unity also in this case.

It should be noted that these dependences are obeyed over the concentration region examined. For the extraction with Slovafol solutions in dichloromethane, the log D vs log c_A dependences depart from linearity at $c_A > 3 \text{ mol l}^{-1}$ (the slope is lower than the theoretical value of 3), and the log D vs log c_L plot departs from linearity at $c_L > 0{\cdot}17 \text{ mol l}^{-1}$ (the slope is lower than the theoretical value of 1).

When solutions of Slovafol 909 in benzene and in a tetrachloromethane–nitrobenzene 2 : 3 (v/v) mixture were used, the dependences of the distribution ratios on c_L and on c_A were little marked[10].

As mentioned above, the slopes of the log D vs log c_A dependences are higher than the theoretical value of 3, viz. 3·6 for dichloromethane and 3·2 – 3·4 for chloroform. The differences observed for La^{3+} and Yb^{3+} are similar, they depend, however, on the solvent. Although this departure can be ascribed to changes in the activity coefficients of the ion extracted in the aqueous phase associated with the increase in concentration of lithium trichloroacetate (from 1·2 to 3·8 mol l^{-1}), the difference occurring on replacing dichloromethane with chloroform remains unexplained. The data measured are insufficient to enable this problem to be solved.

In conclusion, with a simplification the extraction can be described by Eq. (*A*) with $n = 1$. The extraction constants $K_{ex} = [MLA_3]_{org}/[M]_{aq}[L]_{org}[A]^3_{aq}$ for lanthanides in the system of an aqueous solution of lithium trichloroacetate and a solution of Slovafol 909 in dichloromethane or in chloroform are given in Table I.

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