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Crown Ethers as Synergistic Agents in the Solvent Extraction of Trivalent Lanthanoids with Thenoyltrifluoroacetone

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Abstract: The solvent extraction of trivalent lanthanoids (without Pm) with thenoyltrifluoroacetone (HTTA) and dibenzo-18-crown-6 (DB18C6) or dibenzo-24-crown-8 (DB24C8) has been studied. It was found that in the presence of a crown ether (S) the lanthanoids have been extracted as $Ln(TTA)_3 \cdot S$. On the basis of the experimental data, the values of the equilibrium constants have been calculated. It was established that the stability of the complexes involving DB24C8 is higher than those involving DB18C6. The influence of the synergistic agent on the extraction process has been discussed. The synergistic and separation factors have been determined too.

Keywords: Synergistic extraction, Thenoyltrifluoroacetone, Dibenzo-24-crown-8, Dibenzo-18-crown-6, Lanthanoids separation factors

INTRODUCTION

Since the last decades the synergistic solvent extraction of lanthanoids has become an extensively investigated field both from theoretical and practical points of view. Crown ethers have been used as synergistic agents in the extraction of trivalent lanthanoids and actinoids (1–16), divalent transition metals (17–19), U(VI) and Th(IV) (20) with various chelating extractants. A recent review (21) summarizes much of the studies dealing with the synergistic extraction of metals using crown ethers as synergistic agents. Although

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in such systems an increased extractability can be obtained, the selectivity is often not improved. However, an increase of both extractability and selectivity has been reported by Kitatsuji et al. (6) when lanthanoid (III) ions have been extracted with thenoyltrifluoroacetone (HTTA) and 18-crown-6 (18C6) or dicyclohexano-18-crown-6 (DCH18C6), as well as by Reddy et al. (11, 13, 14) for the extraction of Nd, Eu, and Tm with acylpyrazolones and 18C6, DCH18C6, or dibenzo-18-crown-6 (DB18C6).

The present work was undertaken in order to study the synergistic solvent extraction and the separation of the metals of the entire lanthanoid series (with exception of Pm) using thenoyltrifluoroacetone (HTTA) and dibenzo-18-crown-6 (DB18C6) or dibenzo-24-crown-8 (DB24C8) in 1,2-dichloroethane.

EXPERIMENTAL

Reagents

The commercial products thenoyltrifluoroacetone with purity greater than 99% (Fluka), dibenzo-24-crown-8 (Fluka, >98%), and dibenzo-18-crown-6 (Fluka, >98%) were used as received. The diluent was 1,2-dichloroethane (Merck, p.a.). Stock solutions of the metals were prepared from their oxides (Fluka, puriss.). Arsenazo III (Fluka) was of analytical grade purity as were the other reagents used.

Procedure

The experiments were carried out using 10 cm^3 volumes of aqueous and organic phases. The samples were shaken mechanically for 60 min at room temperature, which was sufficient to reach equilibrium. After the separation of the phases, the metal concentration in the aqueous phase was determined photometrically using Arsenazo III (22). The acidity of the aqueous phase was measured by a pH-meter with an accuracy of 0.01 pH unit. The ionic strength was maintained at 0.1 M with (Na, H)Cl. The initial concentration of the metals was 2.5×10^{-4} mol/dm^3 in all experiments.

RESULTS AND DISCUSSION

The lanthanoid (III) ions extraction with HTTA alone and with mixtures of HTTA and a crown ether was studied using the "slope analysis" method. Double logarithmic plots of D_T (the distribution coefficient due to the metal extraction with HTTA) or $D_{T,S}$ (the distribution coefficient due to the synergistic effect) vs. one of the variables $[H^+]$ and [HTTA] for the extraction with HTTA alone and $[H^+]$, [HTTA] and [DB24C8 or DB18C6 (S)] (for the synergistic extraction) keeping the other two constant indicate the stoichiometry and allows the calculation of the equilibrium constants. As the metal extraction with crown ether is negligible under the experimental conditions of the present study and the partition of HTTA (5) and S (15, 16) toward the aqueous phase is very low, the values of $D_{T,S}$ were calculated as $D-D_T$ ($D_{T,S}$ is the distribution coefficient obtained for the metal extraction with mixtures of HTTA and S, and D_T is the distribution coefficient obtained for the metal extraction with HTTA alone under the same experimental conditions).

The plots of $\log D_T$ vs. pH and log[HTTA] are linear with slopes close to 3 and 3 (they are not shown in the figures) and the plots of $\log D_{T,S}$ vs. pH, log[HTTA] and log[DB24C8 (DB18C6)] (Figs. 1–6) represent straight lines close to 3, 3, and 1, respectively. On the basis of slope analysis data the extraction of the metals can be represented by the following equations:

$$\mathrm{Ln}^{3+}_{(aq)} + 3\mathrm{HTTA}_{(o)} \overset{K_T}{\rightleftharpoons} \mathrm{Ln(TTA)}_{3(o)} + 3\mathrm{H}^{+}_{(aq)} \qquad (1)$$

$$\mathrm{Ln}^{3+}_{(aq)} + 3\mathrm{HTTA}_{(o)} + \mathrm{S}_{(o)} \overset{K_{T,S}}{\rightleftharpoons} \mathrm{Ln(TTA)}_{3} \cdot \mathrm{S}_{(o)} + 3\mathrm{H}^{+}_{(aq)} \qquad (2)$$

where Ln is the lanthanoid ion, and the subscripts aq and o denote aqueous and organic phases, respectively.

Ensor and Shah (1) and Reddy et al. (11–15) have also reported the involvement of one molecule of the crown ether in the mixed complex when trivalent lanthanoids have been extracted with chelating extractant (HTTA, acylpyrazolones, isoxazolones) and various crown ethers. On the other hand, Kitatsuji et al. (6) have found formation of an anionic complex

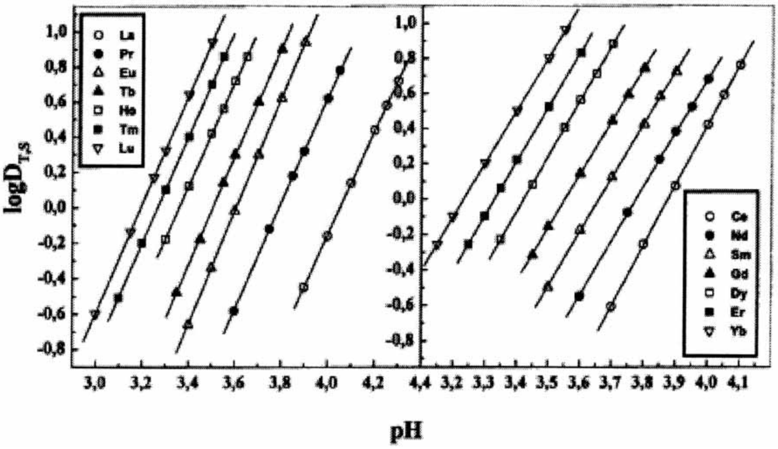

Figure 1. Log $D_{T,S}$ vs. pH for the extraction of lanthanoid elements with HTTA–DB24C8 mixture at $[\mathrm{HTTA}] = 6 \times 10^{-2}\,\mathrm{mol/dm^3}$ and $[\mathrm{DB24C8}] = 2.5 \times 10^{-3}\,\mathrm{mol/dm^3}$.

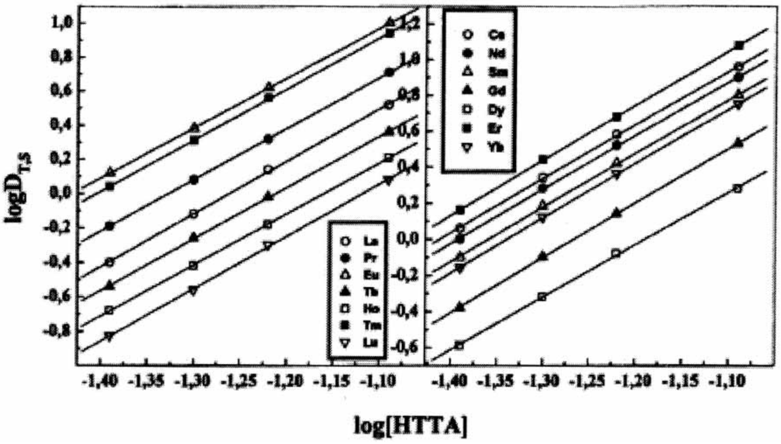

Figure 2. Log $D_{T,S}$ vs. log[HTTA] for the extraction of lanthanoid elements with mixture HTTA–DB24C8 at $[DB24C8] = 2.5 \times 10^{-3}$ mol/dm^3. (La, pH = 4.10; Pr, pH = 3.90; Eu, pH = 3.80; Tb, pH = 3.50; Ho, pH = 3.30; Tm, pH = 3.45; Lu, pH = 3.10. Ce, pH = 4.05; Nd, pH = 3.95; Sm, pH = 3.80; Gd, pH = 3.60; Dy, pH = 3.35; Er, pH = 3.55; Yb, pH = 3.35).

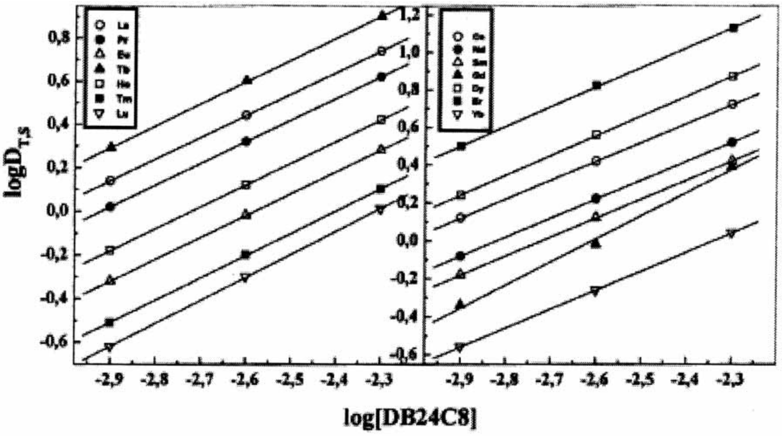

Figure 3. Log $D_{T,S}$ vs. log[DB24C8] for the extraction of lanthanoid elements with HTTA–DB24C8 mixture at $[HTTA] = 6 \times 10^{-2}$ mol/dm^3. (La, pH = 4.20; Pr, pH = 3.90; Eu, pH = 3.60; Tb, pH = 3.70; Ho, pH = 3.40; Tm, pH = 3.20; Lu, pH = 3.10. Ce, pH = 4.00; Nd, pH = 3.85; Sm, pH = 3.70; Gd, pH = 3.55; Dy, pH = 3.60; Er, pH = 3.60; Yb, pH = 3.15).

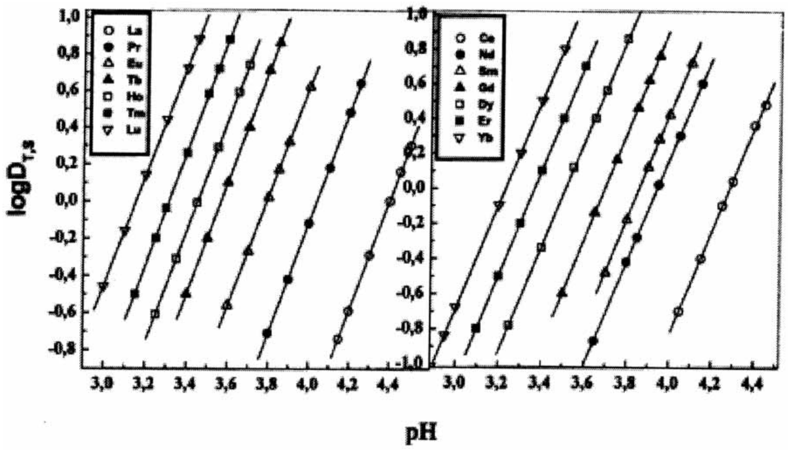

Figure 4. Log $D_{T,S}$ vs. pH for the extraction of lanthanoid elements with HTTA–DB18C6 mixture at [HTTA] = 8×10^{-2} mol/dm^3 and [DB18C6] = 2.5×10^{-3} mol/dm^3.

$Ln(TTA)_2S^+$ for lighter lanthanoids (La–Gd) and $Ln(TTA)_3 \cdot S$ for heavier lanthanoids (Ho–Lu).

The equilibrium constants K_T and $K_{T,S}$ can be determined by the equations:

$$\log K_T = \log D_T - 3\log[HTTA] - 3\,pH \tag{3}$$

$$\log K_{T,S} = \log D_{T,S} - 3\log[HTTA] - \log[S] - 3\,pH \tag{4}$$

The formation of mixed adducts in the organic phase can be expressed by the equation:

$$Ln(TTA)_{3(o)} + S_{(o)} \rightleftharpoons Ln(TTA)_3 \cdot S_{(o)} \tag{5}$$

The equilibrium constant $\beta_{T,S}$ for the organic phase reaction can be determined as:

$$\log \beta_{T,S} = \log K_{T,S} - \log K_T \tag{6}$$

The values of $\log K_T$, $\log K_{T,S}$, and $\beta_{T,S}$ are given in Table 1. The equilibrium constants measured in this work are concentration constants, and they are based on the assumption that the activity coefficients of the species do not change significantly during the reaction.

The data in Table 1 show that the values of $\log K_{T,S}$ increase with increasing atomic number of the metals. A similar trend has been observed by Reddy et al. (14, 15) in the extraction of lanthanoid (III) ions with mixtures of 1-phenyl-3-methyl-4-pyvaloyl-5-pyrazolone or

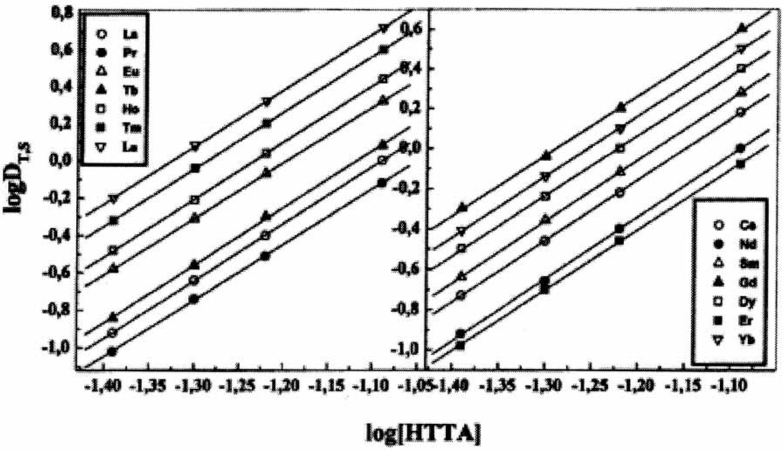

Figure 5. Log $D_{T,S}$ vs. log[HTTA] for the extraction of lanthanoid elements with HTTA–DB18C6 mixture at [DB18C6] $= 2.5 \times 10^{-3}$ mol/dm^3. (La, pH = 4.50; Pr, pH = 4.10; Eu, pH = 4.00; Tb, pH = 3.70; Ho, pH = 3.70; Tm, pH = 3.60; Lu, pH = 3.50. Ce, pH = 4.45; Nd, pH = 4.05; Sm, pH = 4.05; Gd, pH = 4.00; Dy, pH = 3.75; Er, pH = 3.45; Yb, pH = 3.50).

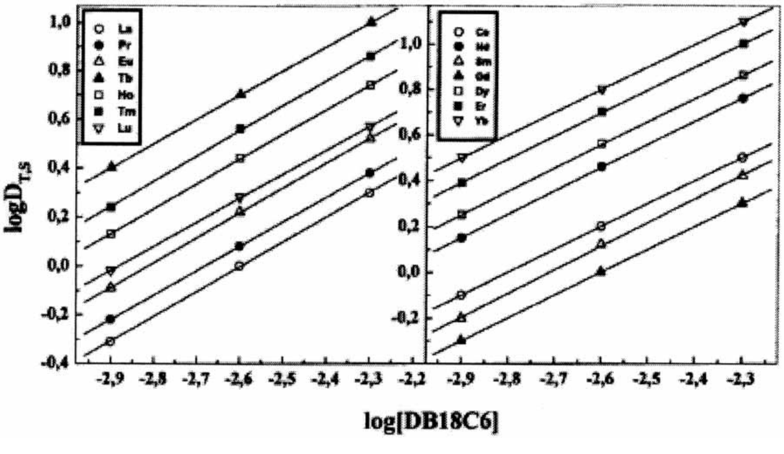

Figure 6. Log $D_{T,S}$ vs. log[DB18C6] for the extraction of lanthanoid elements with HTTA–DB18C6 mixture at [HTTA] $= 8 \times 10^{-2}$ mol/dm^3. (La, pH = 4.40; Pr, pH = 4.10; Eu, pH = 3.90; Tb, pH = 3.80; Ho, pH = 3.60; Tm, pH = 3.50; Lu, pH = 3.25. Ce, pH = 4.35; Nd, pH = 4.10; Sm, pH = 3.90; Gd, pH = 3.70; Dy, pH = 3.70; Er, pH = 3.60; Yb, pH = 3.50).

Table 1. Values of the equilibrium constants $K_{T,S}$ and $\beta_{T,S}$ for the extraction of lanthanoid metals with HTTA–DB24C8 and HTTA–DB18C6 mixtures in 1,2-dichloroethane

		log $K_{T,S}$		log $\beta_{T,S}$	
Metal	log K_T	HTTA–DB24C8	HTTA–DB18C6	HTTA–DB24C8	HTTA–DB18C6
La	−9.86	−5.90	−6.98	3.96	2.88
Ce	−9.25	−5.32	−6.51	3.93	2.74
Pr	−9.02	−5.12	−6.23	3.90	2.79
Nd	−8.74	−5.07	−5.85	3.67	2.89
Sm	−8.36	−4.72	−5.45	3.64	2.91
Eu	−8.04	−4.55	−5.28	3.49	2.76
Gd	−7.82	−4.40	−5.01	3.42	2.81
Tb	−7.61	−4.25	−4.81	3.36	2.80
Dy	−7.40	−4.00	−4.65	3.40	2.75
Ho	−7.30	−3.82	−4.47	3.48	2.83
Er	−7.19	−3.72	−4.21	3.47	2.98
Tm	−7.03	−3.54	−4.05	3.49	2.98
Yb	−6.79	−3.44	−3.81	3.35	2.98
Lu	−6.56	−3.32	−3.57	3.24	2.99

Notes: Error limits in the range of $\leq \pm 0.05$.

3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone and 18C6, DCH18C6, and DB18C6 but an apposite tendency has been reported by Kitatsuji et al. (6) for the lighter lanthanoids.

The comparison of $K_{T,S}$ values obtained for HTTA–DB24C8 and HTTA–DB18C6 combinations shows that the stability of the complexes involving DB24C8 is higher than those involving DB18C6. It could be explained by the fact that the electron density at the oxygen atoms adjacent to the benzene rings is less than those at the other oxygens (16). The author has noted that the oxygen atoms with higher electron density can come nearer to the metal ion and result in a stronger bonding. As the number of such oxygen atoms in DB24C8 is greater, the stability of the complex with its participation have to be greater too. However, the data in Table 1 show that the difference of the equilibrium constants $K_{T,S}$ for the extraction of a particular metal with HTTA–DB24C8 and HTTA–DB18C6 decreases from La to Lu. It is probably a result of sterical hindrances due to the decreasing lanthanoid radii.

The values of the synergistic enhancement factors of the lanthanoid ions calculated as $D_{T,S}/D_T + D_S$ for both DB24C8 and DB18C6 as synergistic agents in combination with HTTA are given in Table 2. For a particular lanthanoid ion the synergistic factor is larger for DB24C8. The data

Table 2. Values of the synergistic factors ([HTTA] $= 6 \times 10^{-2}$ mol/dm^3, [DB24C8(DB18C6)] $= 2.5 \times 10^{-3}$ mol/dm^3, pH $= 3.80$) and the separation factors for the lanthanoid extraction with HTTA alone, HTTA–DB24C8 and HTTA–DB18C6 in 1,2-dichloroethane

	Synergistic factors			Separation factors		
Metal	HTTA–DB24C8	HTTA–DB18C6		HTTA	HTTA–DB24C8	HTTA–DB18C6
La	22.9	1.9	Ce/La	4.07	3.80	2.97
Ce	21.4	1.38	Pr/Ce	1.70	1.58	1.90
Pr	19.9	1.54	Nd/Pr	1.91	1.12	2.40
Nd	11.8	1.55	Sm/Nd	2.40	2.23	2.51
Sm	11	2.04	Eu/Sm	2.09	1.47	1.48
Eu	7.8	1.45	Gd/Eu	1.67	1.41	1.86
Gd	6.1	1.62	Tb/Gd	1.62	1.41	1.59
Tb	5.75	1.58	Dy/Tb	1.62	1.77	1.44
Dy	6.3	1.41	Ho/Dy	1.26	1.52	1.52
Ho	7.6	1.70	Er/Ho	1.29	1.25	1.82
Er	7.4	2.40	Tm/Er	1.45	1.52	1.44
Tm	7.75	2.40	Yb/Tm	1.74	1.25	1.73
Yb	5.6	2.40	Lu/Yb	1.70	1.32	1.74
Lu	4.4	2.45				

in Table 2 show that the difference of the synergistic factors for the two crown ethers decreases with the increase of the atomic number of the lanthanoids (as the values of $K_{T,S}$ discussed above). Similar values of the synergistic enhancement have been observed by Reddy et al. (11–15) for the extraction of Nd, Eu, and Tm with acylpyrazolones and isoxazolones and DB18C6.

The separation factors between the lanthanoids defined as the ratios of the respective equilibrium constants $K_{T,S}$ are also listed in Table 2. It is seen that the separation factors obtained for the extraction with HTTA alone are similar to those obtained for the extraction with HTTA–DB24C8 or HTTA–DB18C6 mixtures. However, if both the extraction efficiency and the metal separation are taken into account, the synergistic combinations of HTTA and crown ether show some advantages in comparison with HTTA alone because in their presence the extraction process could be carried out at lower pH values (at equal conditions the values of the distribution coefficient $D_{T,S}$ are much larger than those of D_T).

It is interesting to compare the separation factors obtained for the extraction of lanthanoids with various chelating extractants and crown ethers. Reddy et al. (11–14) have published data for the separation factors of the pairs Eu/Nd and Tm/Eu for various chelating extractants

Table 3. Values of the separation factors of the pairs Eu/Nd and Tm/Eu

Extractants	Eu/Nd	Tm/Eu
HTTA–DB24C8	3.3	10.2
HTTA–DB18C6	3.7	17.0
HPMTFP–DB18C6 (11)	21.4	3.6
HPBI–DB18C6 (12)	25.1	1.2
HBTFA–DB18C6 (13)	20.2	5.1
HPMPP–DB18C6 (14)	47.9	13.4
HFBPI–DB18C6 (15)	4.78	1.75

viz. 4, 4, 4-trifluoro-1-phenyl-1, 3-butanedione (HBTFA), 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5 (HPMTFP), 1-phenyl-3-methyl-4-pivaloyl-5-pyrazolone (HPMPP) or 3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone (HFBPI) or 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) and DB18C6. The separation factors for these systems are listed in Table 3 along with the data obtained in the present study. The data in the table show that there is an opposite trend in the separation of the two pairs for the synergistic systems studied by Reddy et al. and those in the present study.

CONCLUSION

The experimental data show that the trivalent lanthanoids have been extracted as $Ln(TTA)_3 \cdot S$. The addition of a crown ether increases the extraction efficiency in the sequence DB24C8 > DB18C6. The values of the overall equilibrium constant $K_{T,S}$ increase with increasing atomic number of the metals. But the difference of these values for the extraction of a particular lanthanoid metal with HTTA–DB24C8 and HTTA–DB18C6 decreases from La to Lu. The synergistic enhancement factors are larger when DB24C8 is used in combination with HTTA. Their values decrease with increasing atomic number of the lanthanoids. Such a tendency was not found for the extraction with HTTA and DB18C6.

The values of the separation factors obtained for the lanthanoid extraction with HTTA alone and with mixtures of HTTA and DB24C8 or DB18C6 are similar.

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