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Effect of the 18-Crown-6 and Benzo-18-Crown-6 on the Solvent Extraction and Separation of Lanthanide(III) Ions with 8-Hydroxyquinoline

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Abstract—The synergistic solvent extraction of 13 lanthanides with mixtures of 8-hydroxyquinoline (HQ) and the crown ethers (S) 18-crown-6 (18C6) or benzo-18-crown-6 (B18C6) in 1,2-dichloroethane has been studied. The composition of the extracted species has been determined as $LnQ_3 \cdot S$. The values of the equilibrium constant and separation factor have been calculated. Here, the effect of the synergistic agent (18C6 or B18C6) on the extraction process is discussed.

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The phenomenon in which two extractants taken together extract a metal ion species with a much higher efficiency as compared to the normal additive effect of these extractants separately is called synergism. Mixtures of chelating extractants and various crown ethers have often been used for the synergistic solvent extraction of metals using a variety of organic diluents and different ionic media and ionic strengths in the aqueous phase. Synergistic extraction of trivalent lanthanides [1–18], divalent transition metals, and alkali and alkaline earth metals [19–24] has been reported. It has been found that the metal ions can be extracted synergistically. Meguro et al. [9] have reported that the crown ethers as an adduct in the complexes $M(TTA)_3 \cdot S$ do not bind the central metal ion to form a structure in which the metal ion is grasped inside the cavity of the crown ether. Mathur and Khopkar [4] have accepted that not all oxygen atoms of the crown ether are coordinated to the metal. On the basis of thermodynamic studies [5], it is suggested that B15C5 is bound to the metal only through the three oxygen atoms and that $LnP_3 \cdot 2B15C5$ (P is 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazol-5-one) is a sandwich-type complex.

In most of the studies to date, the separation of the lanthanides has also been discussed, but little improvement in the selectivity for trivalent lanthanides has been achieved. However, Reddy et al. [11–13] reported an increase in both extractability and selectivity for the extraction of Nd, Eu, and Tm with acylpyrazolones and 18C6, DCH18C6, or DB18C6. In fact, very few investigations have covered the complete 4f- series [15].

A raview of crown-ether-containing extraction systems has recently been published [25]. Only a few papers have been referred dealing with the extraction of Co(II) with mixtures of 8-hydroxyquinoline and DB18C6 [26, 27].

No investigations, however, have been published for the extraction of the entire series of lanthanide elements using the extraction system HQ–18C6 (B18C6). Thus, the present work was undertaken to study the synergistic extraction of lanthanide metals (with the exception of Ce, because of its unstable trivalent state, and the radioactive Pm) with the above extraction systems, and to determine the possibilities for the separation of the metals. The conditions of the extraction experiment, the probable mechanism of the extraction process, as well as the composition of the metal complexes being transferred into the organic phase, are specified.

EXPERIMENTAL

Reagents

The commercial products 8-hydroxyquinoline (Riedel-de Haen, 99%), (HQ), 18-crown-6 (Fluka, >98%), and benzo-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.

Apparatus

A S–20 Spectrophotometer Boeco (Germany) was used for measuring absorbances. A pH 211 HANNA digital pH meter was used for the pH measurements.

Table 1. Values of the equilibrium constants K_Q, $K_{Q,S}$ and $\beta_{Q,S}$ for the extraction of lanthanide ios with HQ, and HQ–18C6(B18C6) systems in 1,2-dichloroethane

Ln^{3+}	$\log K_Q$	$\log K_{Q,S}$		$\log \beta_{Q,S}$	
		B18C6	18C6	B18C6	18C6
La	–15.95	–13.53	–13.14	2.16	2.81
Pr	–15.30	–12.87	–12.54	2.43	2.76
Nd	–15	–12.57	–12.03	2.43	2.97
Sm	–14.35	–11.92	–11.62	2.43	2.73
Eu	–14.12	–11.64	–11.24	2.48	2.88
Gd	–13.90	–11.37	–10.77	2.53	3.13
Tb	–13.60	–11.19	–9.98	2.41	3.62
Dy	–13.40	–10.99	–9.25	2.41	4.15
Ho	–13.15	–10.74	–8.64	2.41	4.51
Er	–12.98	–10.58	–7.97	2.40	5.01
Tm	–12.82	–10.42	–7.34	2.40	5.48
Yb	–12.64	–10.18	–6.69	2.46	5.95
Lu	–12.38	–9.95	–6.15	2.43	6.23

Note: Error limits in the range of ≤ ±0.05.

Procedure

The experiments were carried out using 10-cm^3 volumes of aqueous and organic phases. The samples were shaken mechanically for 45 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 [28]. The acidity of the aqueous phase was measured by a pH meter with an accuracy of 0.1 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

Solvent Extraction of Ln^{3+} Ions with 8-Hydroxyquinoline or Crown Ethers Alone

A traditional and effective means of obtaining both the stoichiometric and equilibrium constant and information about the extraction processes, called "slope analysis," is based on an examination of the variation of *D*, the distribution ratio, as a function of the relevant experimental variables. A log–log plot of the extraction data in the form of *D* vs. [H$^+$] and [HQ] indicates the stiochiometry of the extractable complex, and thus leads to the derivation of a suitable equilibrium expression and then to the calculation of the equilibrium constant. The plots of log *D* vs. pH and log[HQ] were linear, with slopes close to three. (These plots are not shown in the figures.)

Thus, the extraction of Ln^{3+} ions can be described by the equation

$$Ln^{3+}_{(aq)} + 3HQ_{(o)} = LnQ_{3(o)} + 3H^{+}_{(aq)}, \qquad (1)$$

where Ln^{3+} denote lanthanides, and (aq) and (o) the aqueous and organic phases, respectively.

The formation of LnQ_3 when HQ and its derivatives are used as extractants was found in some other studies [29–32]. But in [33], extraction of self-adducts was reported for some metals of the 4f-series (Ho^{3+} and Er^{3+}).

As the partition of HQ towards the aqueous phase is very low [34], the relationship between the distribution coefficient D_Q and the equilibrium constant K_Q can be expressed as

$$\log K_Q = \log D - 3\mathrm{pH} - 3\log[\mathrm{HQ}]. \qquad (2)$$

The values of the equilibrium constant K_Q are given in Table 1. It is seen that they increase with increasing atomic number of the lanthanides, as expected from their decreasing atomic radii.

The experimental data showed that the lanthanides (Ln) extraction with both B18C6 and 18C6 alone is negligible under the experimental conditions of the present study.

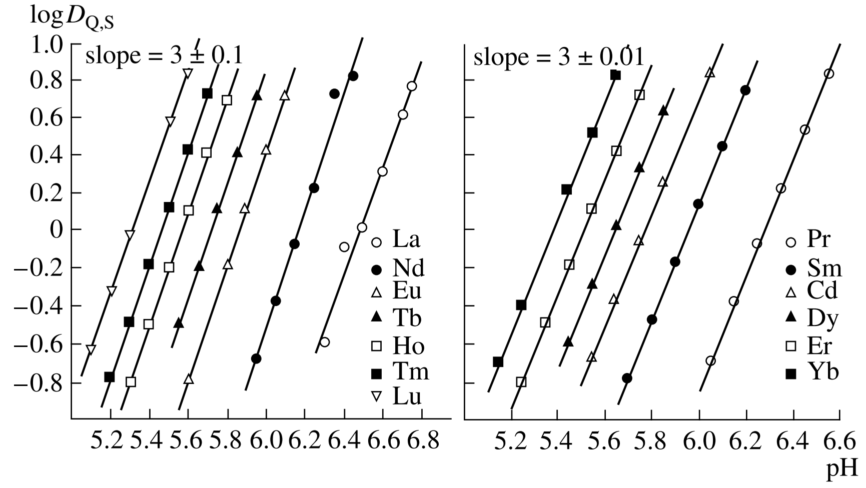

Fig. 1. $\log D_{Q,S}$ vs. pH for the extraction of lanthanide(III) ions with HQ–B18C6 mixture at [HQ] = 6×10^{-2} mol/dm^3 and [B18C6] = 5×10^{-3} mol/dm^3.

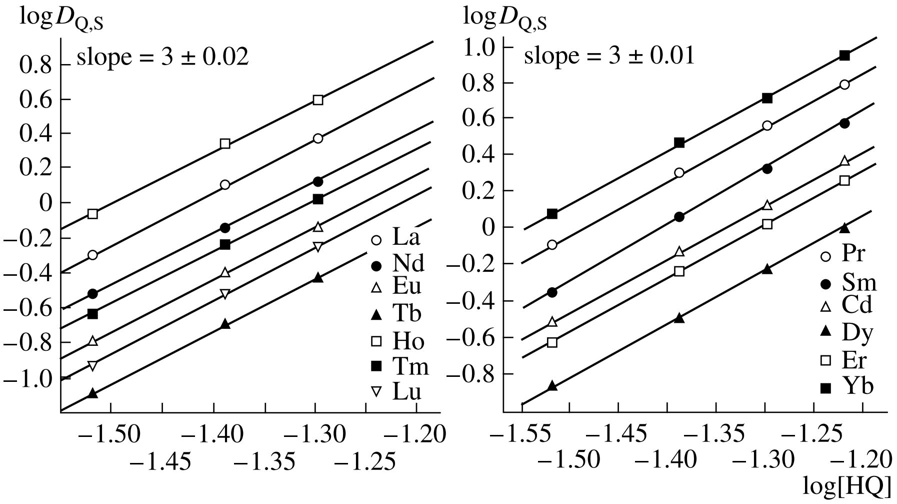

Fig. 2. $\log D_{Q,S}$ vs. $\log[HQ]$ for the extraction of lanthanide(III) ions with mixture HQ–B18C6 at [B18C6] = 5×10^{-3} mol/dm^3. (La, pH = 6.70; Nd, pH = 6.30; Eu, pH = 5.90; Tb, pH = 5.65; Ho, pH = 5.85; Tm, pH = 5.55; Lu, pH = 5.30; Pr, pH = 6.55; Sm, pH = 6.15; Gd, pH = 5.90; Dy, pH = 5.65; Er, pH = 5.60; Yb, pH = 5.70.)

Solvent Extraction of Ln^{3+} Ions with Mixtures of HQ and B18C6 or 18C6

The synergistic solvent extraction of Ln^{3+} ions with mixtures of HQ and B18C6 or 18C6 (S) can be expressed by the equation

$$\mathrm{Ln}^{3+}_{(aq)} + m\mathrm{HQ}_{(o)} + n\mathrm{S}_{(o)} = \mathrm{LnQ}_m \cdot \mathrm{S}_{n(o)} + m\mathrm{H}^+_{(aq)}. \quad (3)$$

It may be shown easily that

$$\log D_{Q,S} = \log K_{Q,S} + m\log[\mathrm{HQ}] + n\log[S] + mp\mathrm{H}, (4)$$

where $D_{Q,S}$ is the distribution coefficient due to the synergistic effect.

As the lanthanide extraction with the crown ether is negligible under the experimental conditions of the present study, the value of the distribution coefficient D obtained experimentally is the sum of $D_{Q,S}$ and D_Q. Thus, the values of $D_{Q,S}$ can be calculated as $D - D_Q$.

If the hydrolysis and complexation in the aqueous phase and the polymerization in the organic phase occur to a negligible extent only, then the double logarithmic plots of $D_{Q,S}$ vs. one of the variables [HQ], [B18C6 (18C6)] and [H$^+$], keeping the other two constant, will be linear, and their slopes will give the number of the ligands participating in the formation of the adduct.

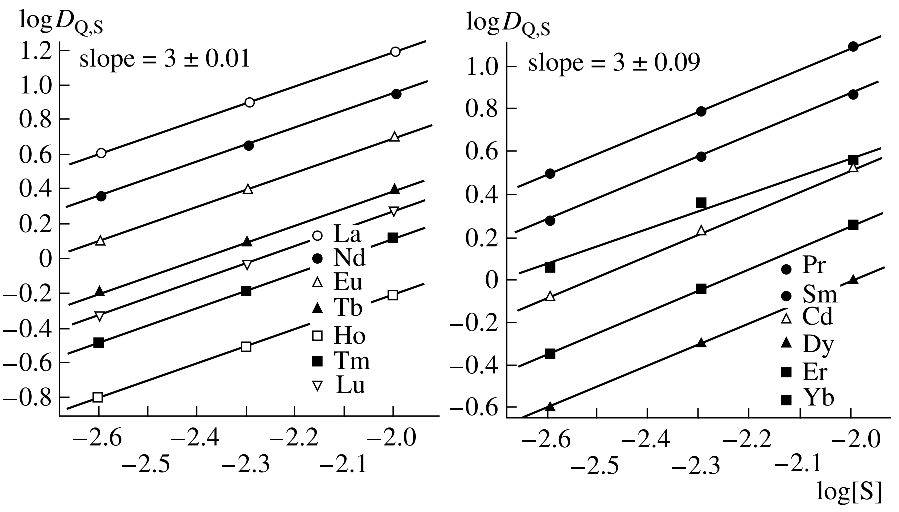

Fig. 3. $\log D_{Q,S}$ vs. $\log[B18C6]$ for the extraction of lanthanide(III) ions with mixture HQ–B18C6 at [HQ] = 6×10^{-2} mol/dm^3. (La, pH = 6.80; Nd, pH = 6.40; Eu, pH = 6.00; Tb, pH = 5.75; Ho, pH = 5.40; Tm, pH = 5.40; Lu, pH = 5.30; Pr, pH = 6.55; Sm, pH = 6.15; Gd, pH = 5.85; Dy, pH = 5.55; Er, pH = 5.50; Yb, pH = 5.50.)

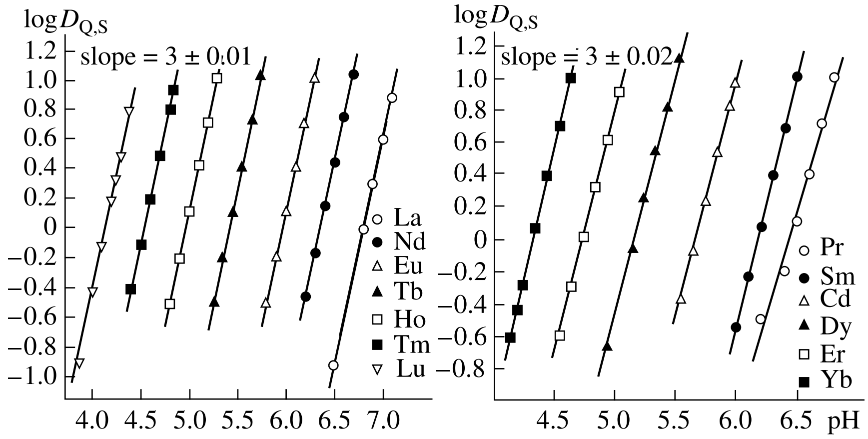

Fig. 4. $\log D_{Q,S}$ vs. pH for the extraction of lanthanide(III) ions with HQ–18C6 mixture at [HQ] = 6×10^{-2} mol/dm^3 and [18C6] = 5×10^{-3} mol/dm^3.

The experimental data for the extraction of the lanthanides with mixtures of HQ and B18C6 and 18C6 are shown in Figs. 1–6. The plots of $\log D_{Q,S}$ vs. pH and $\log[HQ]$ are linear with slopes 3, and the plots of $\log D_{Q,S}$ vs. [S] exhibit slopes equal to 1. On the basis of the slope analysis data, the synergistic extraction of the lanthanides can be described by the following reaction:

$$\mathrm{Ln}^{3+}_{(aq)} + 3\mathrm{HQ}_{(o)} + \mathrm{S}_{(o)} = \mathrm{LnQ_3} \cdot \mathrm{S}_{(o)} + 3\mathrm{H}^{+}_{(aq)}. \quad (5)$$

Similar synergistic complexes, Ln(TTA)$_3$ · S, have been found in our previous study for the extraction of trivalent lanthanides from chloride solutions with HTTA in the presence of DB18C6 and DB24C8 into 1,2-dichloroethane [15]. Reddy et al. [11–13, 16, 18], Dukov et al. [6], and Ensor and Shah [35] have also reported the involvement of one molecule of the crown ether in the synergistic species when trivalent lanthanides were extracted with chelating extractants and various crown ethers.

The overall equilibrium constant $K_{Q,S}$ can be determined by the equation

$$\log K_{Q,S} = \log D_{Q,S} - 3\log[\mathrm{HQ}] - \log[S] - 3\mathrm{pH}. \quad (6)$$

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

$$\mathrm{LnQ}_{3(o)} + \mathrm{S}_{(o)} = \mathrm{LnQ_3} \cdot \mathrm{S}_{(o)}. \quad (7)$$

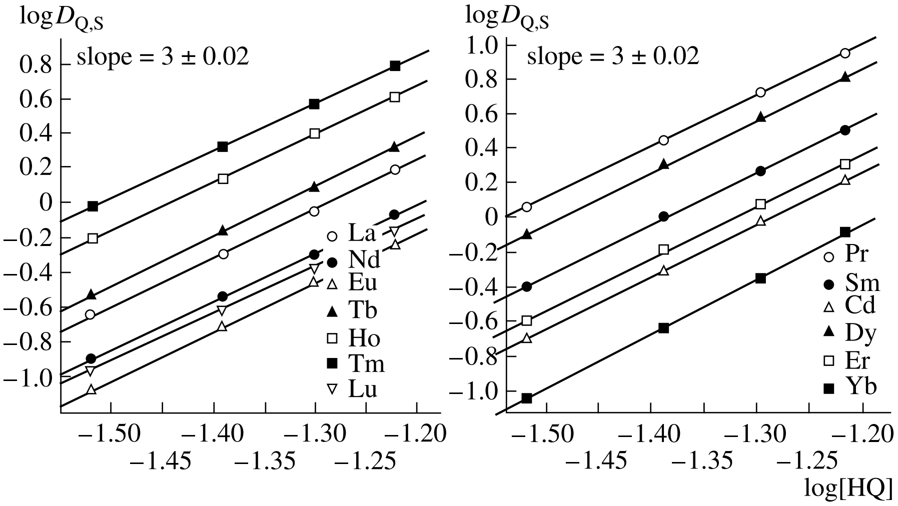

Fig. 5. $\log D_{Q,S}$ vs. log[HQ] for the extraction of lanthanide(III) ions with mixture HQ–18C6 at [18C6] = 5×10^{-3} mol/dm^3. (La, pH = 6.95; Nd, pH = 6.40; Eu, pH = 5.95; Tb, pH = 5.60; Ho, pH = 5.25; Tm, pH = 4.90; Lu, pH = 4.15; Pr, pH = 6.80; Sm, pH = 6.35; Gd, pH = 5.75; Dy, pH = 5.45; Er, pH = 4.85; Yb, pH = 4.30).

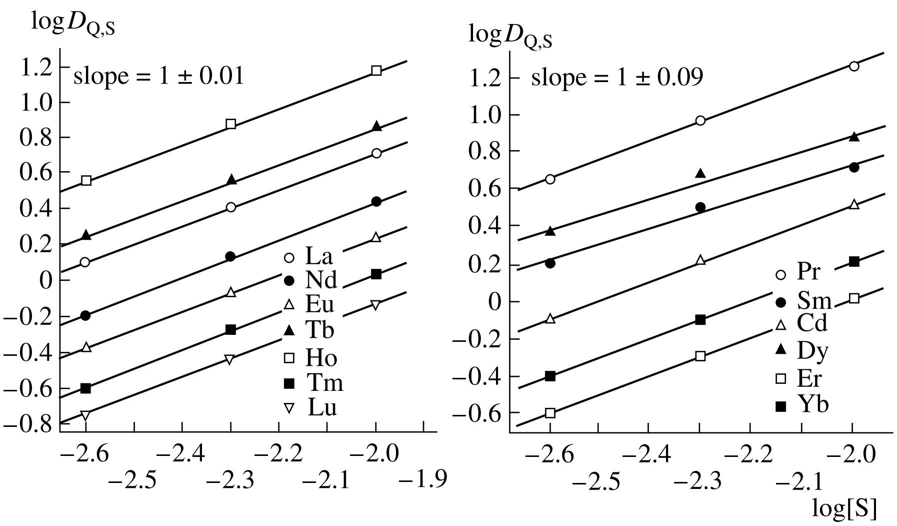

Fig. 6. $\log D_{Q,S}$ vs. $\log[18C6]$ for the extraction of lanthanide(III) ions with mixture HQ–18C6 at [HQ] = 6×10^{-2} mol/dm^3. (La, pH = 6.95; Nd, pH = 6.40; Eu, pH = 5.95; Tb, pH = 5.60; Ho, pH = 5.25; Tm, pH = 4.45; Lu, pH = 4.00; Pr, pH = 6.80; Sm, pH = 6.35; Gd, pH = 5.75; Dy, pH = 5.40; Er, pH = 4.65; Yb, pH = 4.30).

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

$$\log\beta_{Q,S} = \log K_{Q,S} - \log K_Q. \quad (8)$$

Since the partition coefficient of the crown ether B18C6 used is known to be quite large, no correction is necessary for the partitioning of those crown ethers in the aqueous phase [18]. But the equilibrium concentration of 18C6 was calculated using the partition coefficient ($\log K_D$ = –0.04) taken from the literature [12].

$$[S]_{in} = [S]_{(o)} + [S]_{(aq)}$$

$$K_D = [S]_{(o)}/[S]_{(aq)} \text{ and } [S]_{(o)} = [S]_{in} - [S]_{(o)}/K_D$$

$$\text{So, } [S]_{in} = \frac{[S]_{(o)}}{1 + \frac{1}{K_D}}.$$

The equilibrium constants $\log K_{Q,S}$ obtained with mixture HQ–18C6 can be determined by the equation (6), taking into account the correction of [S].

The values of $\log K_{Q,S}$ and $\beta_{Q,S}$ (along with the values of $\log K_Q$) are given in Table 1.

The equilibrium constants are based on the assumption that the activity coefficients of the species do not change significantly under the experimental conditions. The data in Table 1 show that the values of $\log K_{Q,S}$ increase from La to Lu. The difference of $\log K_{Q,S}$ values for the extraction of a particular lanthanide metal with HQ–18C6 and HQ–B18C6 also increases from La to Lu. The variation of the equilibrium constants K_Q and $K_{Q,S}$ versus the atomic number Z of the lanthanides is given in Fig. 7. It is seen that the two curves (HQ and HQ–B18C6) vary practically in the same manner. The same was true for the system HQ–18C6 but for the heavier metal ions (Gd–Lu), the values of $K_{Q,S}$ increase very fast.

The noticeable decrease of the $\log K_{Q,S}$ values especially for heavier lanthanide ions from 18C6 to B18C6 mostly reflects increasing steric effects and decreasing basicity. A similar trend was observed by Reddy et al. [18] and Mathur and Choppin [36].

The synergistic enhancement obtained for the combination of two extractants can be evaluated by calculating the synergistic coefficients (SC) [38]:

$$SC = \log(D_{1,2}/D_1 + D_2),$$

where $D_{1,2}$, D_1, and D_2 denote the distribution coefficients of a metal ion using a mixture of extarctants ($D_{1,2}$) and using the same extractants separately (D_1 and D_2).

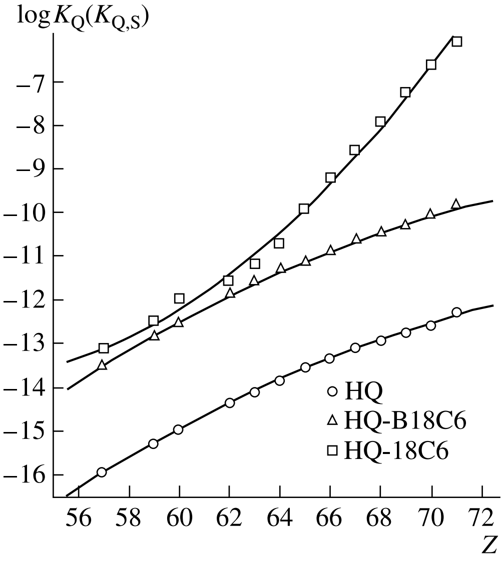

Fig. 7. $\log K_Q(K_{Q,S})$ vs. Z.

The values of the synergistic coefficients of the lanthanide ions for B18C6 and 18C6 used as synergistic agents in combination with HQ are given in Table 2. The synergistic enhancement increases from La to Lu

Table 2. Values of the synergistic factors ([HQ] = 6×10^{-2} mol/dm^3, [18C6(B18C6)] = 5×10^{-3} mol/dm^3, pH = 5.50) and the separation factors for the lanthanide extraction with HQ alone, HQ–18C6 and HQ–B18C6 in 1,2-dichloroethane

Ln^{3+}	S.C.		S.F.			
	B18C6	18C6		HQ	B18C6	18C6
La	0.12	0.19	Pr/La	4.46	4.57	3.98
Pr	0.13	0.14	Nd/Pr	1.99	1.99	3.24
Nd	0.13	0.35	Sm/Nd	4.46	4.46	2.57
Sm	0.13	0.14	Eu/Sm	1.69	1.90	2.39
Eu	0.10	0.26	Gd/Eu	1.65	1.86	2.95
Gd	0.23	0.51	Tb/Gd	1.99	1.52	6.16
Tb	0.11	1	Dy/Tb	1.58	1.58	5.37
Dy	0.11	1.53	Ho/Dy	1.77	1.77	4.07
Ho	0.11	1.89	Er/Ho	1.47	1.44	5.35
Er	0.10	2.39	Tm/Er	1.44	1.44	4.57
Tm	0.10	2.86	Yb/Tm	1.52	1.74	4.53
Yb	0.16	3.33	Lu/Yb	1.82	1.74	3.47
Lu	0.13	6.2				

for the HQ–18C6 mixture, while the values of SC obtained for HQ–B18C6 are almost the same. Reddy et al. [18] have also reported that the synergistic constant increases from Nd^{3+} to Tm^{3+} in their extraction with mixtures of 3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone and various crown ethers. The lanthanide contraction and steric effects are probably significant in establishing the different synergism.

The metal separation can be assessed using separation factors. The separation factors of the pairs were calculated as a ratio of the overall equilibrium constant $K_{Q,S}$ values of every pair as the metals form complexes of the same type when they are extracted with HQ–B18C6 (18C6) mixtures. The values of the separation factors are given in Table 2. The data show that the separation factors between adjacent metal ions for the lanthanides extracted with the mixture HQ–18C6 are rather high. It is seen that the separation factors decrease in the order HQ–18C6 > HQ–B18C6, and that the lanthanide extraction decreases in the same order. It is interesting to note that the synergistic agent 18C6 exhibits a separation for the heavier lanthanides two times higher than those obtained when B18C6 is used. The separation factor between Tm/Eu obtained when the HQ–18C6 mixture is used is rather high, 7.9×10^3, which is somewhat higher than those obtained by Reddy et al. [11–13, 18] for some lanthanide pairs with various chelating extractants (4-acylpyraolones and isoxazolones) and DB18C6. It is interesting to note that HQ, which is a much poorer extractant for lanthanides than β-diketones (the values of the equilibrium constants are some orders of magnitude lower), exhibits a separation for the pair Tm/Eu, which is 1000 times higher. But very high separation factors 1×10^3 and 2×10^3 have been observed between U(VI) and Th(VI) by Reddy et al. [37] when they are extracted into chloroform from nitric acid solutions using 3-phenyl–4-benzoyl–5-isoxazolone, which is a strong acidic extractant with pKa = 1.23, and DB18C6 and B15C5 respectively.

Although HQ was found to be a poorer extractant for trivalent lanthanides, the addition of a crown ether to the metal chelate system improves the selectivity among lanthanide pairs. Hence, such a system would be of practical value in their separation from weak acidic solutions.

CONCLUSIONS

The synergistic solvent extraction of thirteen lanthanoid metals with HQ–B18C6(18C6) in 1,2-dichloroethane has been studied. The experimental data showed that $LnQ_3 \cdot S$ are formed. The addition of a crown ether increases the extraction efficiency in the sequence 18C6 > B18C6. The values of the overall equilibrium constant $K_{Q,S}$ increase with increasing atomic number of the metals, and the difference of these values for the extraction of a particular lanthanide metal with HQ–18C6 and HQ–B18C6 increases from La to Lu as well. The synergistic enhancement factors are larger when 18C6 is used in combination with HQ. Their values increase with increasing atomic number of the lanthanides. But such a tendency was not found for the extraction with HQ–B18C6.

The SF between the adjacent metals are high for the system HQ–18C6. Still, their values are much larger for the heavier lanthanides.

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