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Crown ethers as synergistic agents in the solvent extraction of trivalent lanthanides with 8-hydroxyquinoline

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Abstract: The liquid extraction of the 13 lanthanides with mixtures of 8-hydroxyquinoline (HQ) and crown ethers (S) dibenzo-18-crown-6 (DB18C6) and dibenzo-24-crown-8 (DB24C8) in 1,2-dichloroethane as a diluent from chloride medium at constant ionic strength $\mu = 0.1$ was investigated. The composition of the extracted species was established as LnQ_3 with HQ alone and as $LnQ_3 \cdot S$ in the presence of a crown ether. The values of the equilibrium constants were calculated. The addition of DB18C6 to the metal chelate system improved the extraction efficiency, while a weak synergistic enhancement was found when the metals were extracted with mixtures of HQ–DB24C8. The parameters of the extraction process were determined and the separation factors between two adjacent lanthanides(III) were calculated.

Keywords: synergistic extraction; 8-hydroxyquinoline; dibenzo-24-crown-8; dibenzo-18-crown-6; lanthanides separation factors.

INTRODUCTION

The coordination chemistry of macrocyclic polyethers (commonly referred to as "crown" ethers) has been the subject of numerous investigations since the discovery of such compounds by Pedersen in 1967.[1] They are often used as synergistic additives to chelating, acidic or neutral extractants for the extraction of various metal ions. The synergistic solvent extraction of multi-charged transition ions,[2–4] lanthanide and actinide ions,[5–22] as well as alkali and alkaline earth metals[2–4] has been extensively studied using acidic chelating agents, *e.g.*, β-diketones and various crown ethers as synergists. It was found that the metal ions can be extracted synergistically. The formation of mixed adducts containing one or two crown ether molecules has been reported. In most cases, the separation of the lanthanides has also been discussed because of their chemical similarities, which makes their separation difficult. Reddy *et al.*[15–17] reported an increase of both

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the extractability and selectivity for the extraction of Nd, Eu and Tm with acylpyrazolones and 18C6, DCH18CH, or DB18C6.

A review of crown ether containing extraction systems has recently been published.[23] Only a few papers dealing with the extraction of Co(II) with mixtures of 8-hydroxyquinoline and DB18C6 have been published.[24,25] This provoked interest in extraction systems containing HQ, as a part of systematic studies of synergistic solvent extraction and the separation of lanthanide ions.

The aim of the present work was to study synergistic solvent extraction and separation of the metals of the entire lanthanide series (with the exception of Ce because of its unstable trivalent state and the radioactive Pm) using 8-hydroxyquinoline (HQ) and dibenzo-18-crown-6 (DB18C6) or dibenzo-24-crown-8 (DB24C8) in 1,2-dichloroethane. The conditions of the extraction experiment, the probable mechanism of extraction process, as well as the composition of the metal complexes transferred into the organic phase are specified.

EXPERIMENTAL

Reagents

The commercial products 8-hydroxyquinoline (Riedel-de Haen, 99 %), 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 employed reagents.

Apparatus

An S-20 spectrophotometer, Boeco (Germany) was used for measuring the absorbances. A pH 211 HANNA digital pH meter was used for the pH measurements.

Procedure

The experiments were performed using 10 cm^3 volumes of the aqueous and organic phases. The samples were shaken mechanically for 45 min at room temperature, which was sufficient for equilibrium to be attained. After the separation of the phases, the metal concentration in the aqueous phase was determined photometrically using Arsenazo III.[26] The acidity of the aqueous phase was measured by a pH-meter with an accuracy of 0.01 pH units. The ionic strength was maintained at 0.1 M with (Na,H)Cl. The initial concentration of the metals in all experiments was 2.5×10^{-4} mol dm^{-3}.

RESULTS AND DISCUSSION

Solvent extraction of Ln^{3+} ions with 8-hydroxyquinoline or crown ethers alone

The extraction behavior of the lanthanide ions using HQ in 1,2-dichloroethane was studied as a function of pH and [HQ]. The plots of log *D* (*D* is the distribution coefficient for the extraction with HQ alone) *vs.* pH and log [HQ] were linear, with slopes close to three (these plots are not shown).

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

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

where Ln denote a lanthanide and “aq” and “o”, the aqueous and organic phase, respectively.

The formation of chelates was found in some other studies.[27] It was stated that all the investigated Ln(III) ions were extracted with HQ, as well as with Hdbq (5,7-dibromo-8-hydroxyquinoline) as simple 1:3 chelates into chloroform.[28] However, Ho^{3+} and Er^{3+} were extracted with Hdcq (5,7-dichloro-8-hydroxyquinoline) as self-adducts of the type $Ln(dcq)_3·Hdcq$.[29] Moreover, in the extraction of Gd^{3+} with HQ, as well as Pr^{3+}, Dy^{3+} and Yb^{3+} with Hdcq,[30] the existence of both of the chelates (GdQ_3 or $Ln(dcq)_3$) and the self-adducts ($GdQ_3·HQ$ or $Ln(dcq)_3·Hdcq$) were observed. It is further reported[31] that Nd^{3+} is extracted as $Nd(dbq)_3$, as are other Ln^{3+} (La, Gd and Lu) as $Ln(dbq)_3$ into $CHCl_3$.

As the partition of HQ towards the aqueous phase is very low,[32] the relationship between the distribution coefficient D_Q and the equilibrium constant K_Q can be expressed as:

$$\log K_Q = \log D_Q - 3\text{pH} - 3\log [\text{HQ}] \qquad (2)$$

The values of the equilibrium constant K_Q are given in Table I. It can be seen that they increase with decreasing radius of the Ln^{3+} ion. The increase in the extractability along the lanthanide series can be due to the increase in electrostatic interaction between the cation and the ligand with decreasing ionic radius.[22]

The experimental data show that the extraction of the lanthanides(III) with both DB18C6 and DB24C8 alone was negligible under the experimental conditions employed in the present study.

TABLE I. Values of the equilibrium constants $K_{Q,S}$ and $\beta_{Q,S}$ for the extraction of lanthanide metals with HQ–DB24C8 and HQ–DB18C6 mixtures in 1,2-dichloroethane

Ln^{3+}	$\log K_Q$	$\log K_{Q,S}$		$\log \beta_{Q,S}$	
		DB24C8	DB18C6	DB24C8	DB18C6
La	–15.95	–13.52	–13.42	2.35	2.53
Pr	–15.30	–12.74	–12.54	2.56	2.76
Nd	–15.00	–12.58	–11.96	2.42	3.04
Sm	–14.35	–11.96	–11.30	2.39	3.05
Eu	–14.12	–11.60	–10.58	2.60	3.54
Gd	–13.90	–11.36	–10.06	2.54	3.84
Tb	–13.60	–11.02	–9.82	2.58	3.78
Dy	–13.40	–10.83	–9.56	2.57	3.84
Ho	–13.15	–10.64	–9.28	2.51	3.87
Er	–12.98	–10.44	–8.84	2.54	4.14
Tm	–12.82	–10.24	–8.44	2.58	4.38
Yb	–12.64	–10.11	–8.06	2.53	4.58
Lu	–12.38	–9.87	–7.70	2.51	4.68

Solvent extraction of Ln^{3+} ions with mixtures of HQ and DB18C6 or DB24C8

The synergistic solvent extraction of Ln^{3+} ions with mixtures of HQ and DB18C6 or DB24C8 (S) can be expressed by the equation:

$$Ln^{3+}_{(aq)} + m\mathrm{HQ}_{(o)} + n\mathrm{S}_{(o)} \rightleftarrows \mathrm{LnQ}_{m}\cdot \mathrm{S}_{n(o)} + m\mathrm{H}^{+}_{(aq)} \qquad (3)$$

It may be shown easily that:

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

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

As the lanthanide extraction with the crown ethers was negligible under the experimental conditions employed in the present study, the values of the experimentally obtained distribution coefficient D is the sum of $D_{Q,S}$ and D_{Q}. Hence, the values of $D_{Q,S}$ can be calculated as $D - D_{Q}$. If hydrolysis and complexation in the aqueous phase, as well as 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 $[H^{+}]$, [HQ] or [DB18C6(DB24C8)], keeping the other two constant, should be linear and the slopes will give the number of the ligands participating in the formation of the adduct.

The experimental data for the extraction of the lanthanides with mixtures of HQ and DB18C6 or DB24C8 are shown in Figs. 1–6. The plots of log $D_{Q,S}$ *vs.* pH and log [HQ] are linear with slopes of three while the plots of log $D_{Q,S}$ *vs.* [S] exhibit slopes equal to one. On the basis of the analysis of the slope data, the synergistic extraction of lanthanides can be described by the following reaction:

$$Ln^{3+}_{(aq)} + 3\mathrm{HQ}_{(o)} + \mathrm{S}_{(o)} \rightleftarrows \mathrm{LnQ}_{3}\cdot \mathrm{S}_{(o)} + 3\mathrm{H}^{+}_{(aq)} \qquad (5)$$

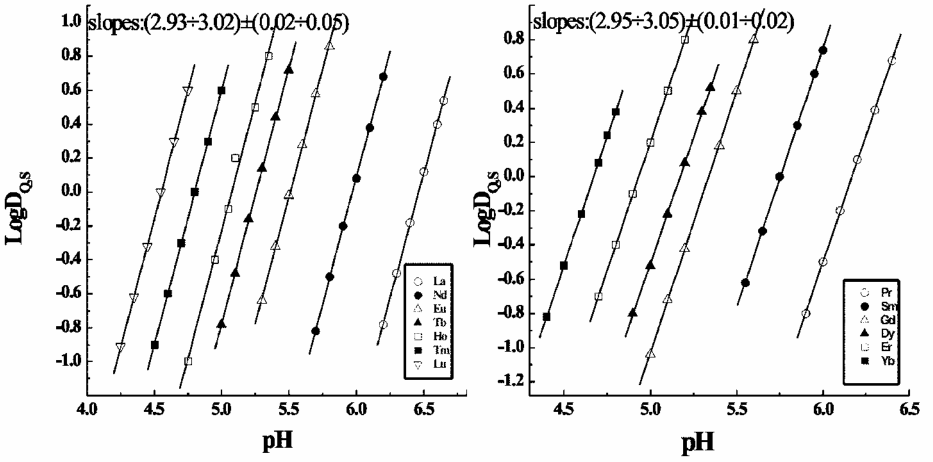

Fig. 1. log $D_{Q,S}$ *vs*. pH for the extraction of lanthanide(III) ions with HQ–DB18C6 mixture at $[\mathrm{HQ}] = 6\times10^{-2}$ mol dm^{-3} and $[\mathrm{DB18C6}] = 5\times10^{-3}$ mol dm^{-3}.

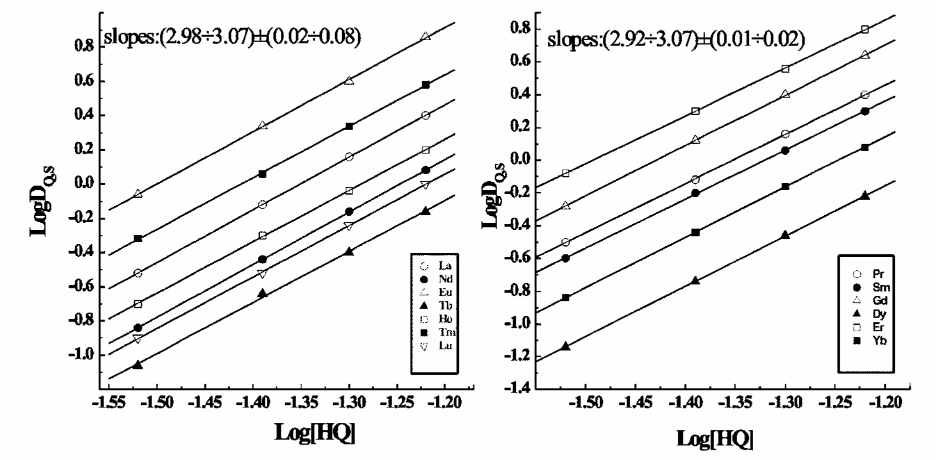

Fig. 2. log $D_{Q,S}$ *vs.* log [HQ] for the extraction of lanthanide(III) ions with the mixture HQ–DB18C6 at [DB18C6] = 5×10^{-3} mol dm^{-3} (La, pH 6.60; Nd, pH 6.00; Eu, pH 5.80; Tb, pH 5.20; Ho, pH 5.15; Tm, pH 5.00; Lu, pH 4.55; Pr, pH 6.30; Sm, pH 5.85; Gd, pH 5.55; Dy, pH 5.10; Er, pH 5.20; Yb, pH 4.70).

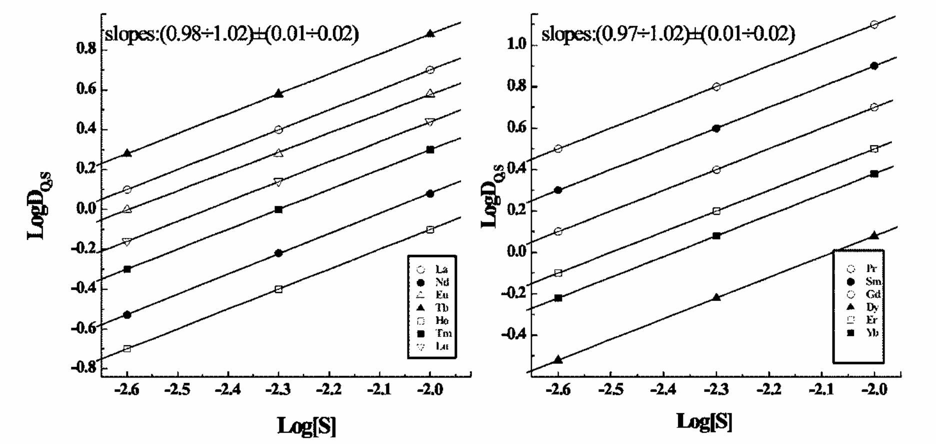

Fig. 3. log $D_{Q,S}$ *vs.* log [DB18C6] for the extraction of lanthanide(III) ions with the mixture HQ–DB18C6 at [HQ] = 6×10^{-2} mol dm^{-3} (La, pH 6.60; Nd, pH 5.90; Eu, pH 5.60; Tb, pH 5.45; Ho, pH 4.95; Tm, pH 4.80; Lu, pH 4.60; Pr, pH 6.30; Sm, pH 5.95; Gd, pH 5.60; Dy, pH 5.10; Er, pH 5.00; Yb, pH 4.70).

The same type of mixed adduct complexes ($Ln(TTA)_3\cdot S$) was established for the synergistic solvent extraction of metals of entire 4f-series with the chelating extractant HTTA and the crown ethers DB18C6 and DB24C8.[19] Reddy *et al.*,[15–17,20,22] Dukov *et al.*[10] and Ensor and Shah[33] 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.

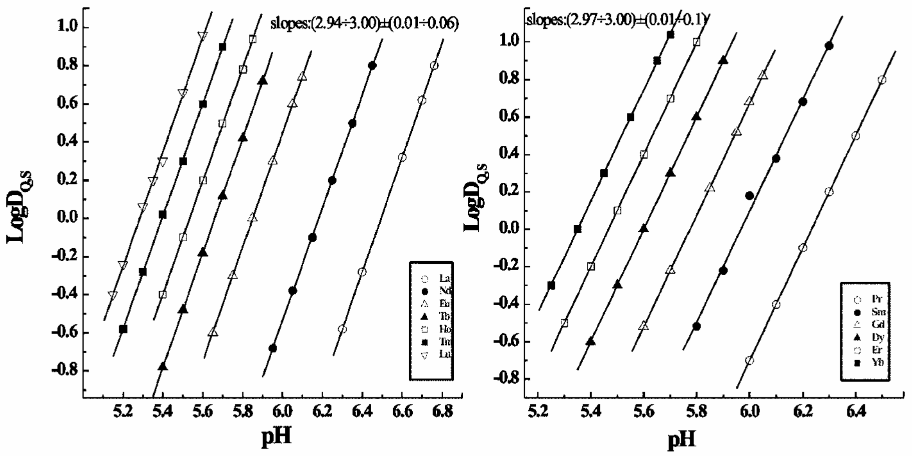

Fig. 4. log $D_{Q,S}$ *vs*. pH for the extraction of lanthanide(III) ions with the HQ–DB24C8 mixture at [HQ] = 6×10^{-2} mol dm^{-3} and [DB24C8] = 5×10^{-3} mol dm^{-3}.

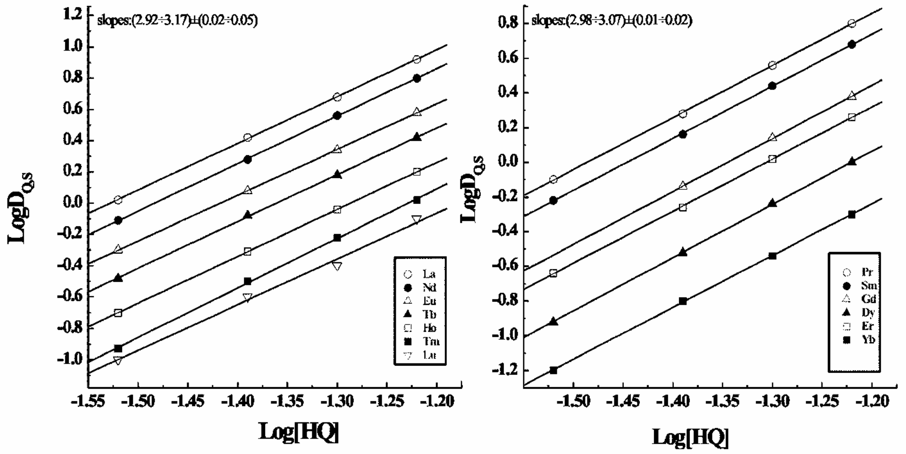

Fig. 5. log $D_{Q,S}$ *vs*. log [HQ] for the extraction of lanthanide(III) ions with the mixture HQ–DB24C8 at [DB24C8] = 5×10^{-3} mol dm^{-3} (La, pH 6.80; Nd, pH 6.45; Eu, pH 6.05; Tb, pH 5.80; Ho, pH 5.60; Tm, pH 5.40; Lu, pH 5.25; Pr, pH 6.50; Sm, pH 6.20; Gd, pH 5.90; Dy, pH 5.60; Er, pH 5.55; Yb, pH 5.25).

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

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

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

$$LnQ_{3(o)} + S_{(o)} \rightleftarrows LnQ_3{\cdot}S_{(o)} \qquad (7)$$

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

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

Since the partition coefficient of the employed crown ether ($\log K_D$, DB18C6 = 4.0) are known to be quite large, no correction is necessary for the partitioning of this crown ether in the aqueous phase.[16] It was assured that this is also true for DB24C8. The values of $\log K_{Q,S}$ and $\log \beta_{Q,S}$ (together with the values of $\log K_Q$) are given in Table I.

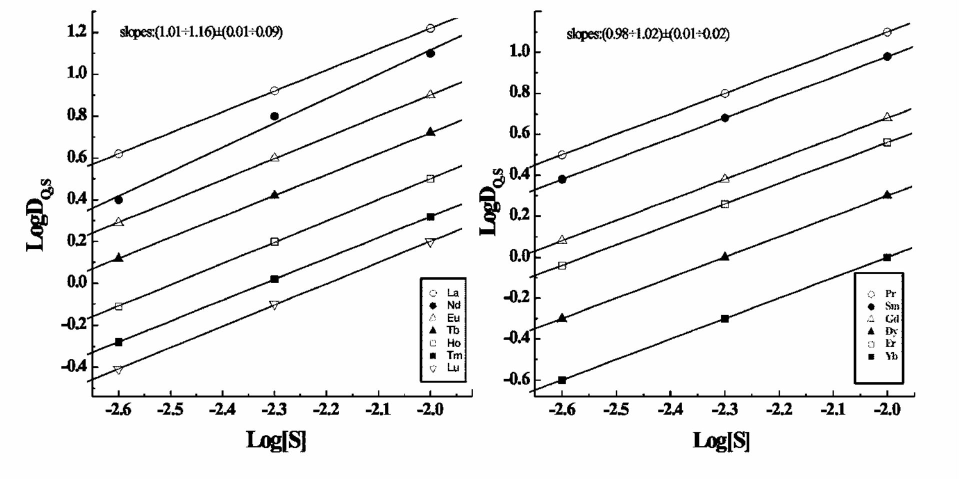

Fig. 6. $\log D_{Q,S}$ *vs*. log [DB24C8] for the extraction of lanthanide(III) ions with the mixture HQ–DB24C8 at [HQ] = 6×10^{-2} mol dm^{-3}. (La, pH 6.80; Nd, pH 6.45; Eu, pH 6.05; Tb, pH 5.80; Ho, pH 5.60; Tm, pH 5.40; Lu, pH 5.25; Pr, pH 6.50; Sm, pH 6.20; Gd, pH 5.90; Dy, pH 5.60; Er, pH 5.55; Yb, pH 5.25).

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 I show that the value of $\log K_{Q,S}$ increases from La to Lu with decreasing ionic radius of the metal ion. The variation of the equilibrium constants K_Q and $K_{Q,S}$ *vs.* the atomic number Z of the lanthanide is given in Fig. 7, from which it can be seen that the three curves vary practically in the same manner.

The strength of the complexation of trivalent lanthanides follows the order: DB18C6 > DB24C8. DB24C8 is too large (4.5 to 5.6 Å)[34] to form a stable complex with HQ and maybe the decrease of the complexation reflects increasing steric effects.

Comparison of these results with the data found in a recent study[19] for the system HTTA–DB18C6 (DB24C8) showed the opposite tendency. The values of the equilibrium constants, as well as those of the synergistic coefficient were higher when DB24C8 was used as the synergistic agent but the difference between these values for the two crown ethers decreased with increasing atomic number. This fact can be explained taking into account that HQ is a weaker acid (pK_a = 9.65)[32] than HTTA (pK_a = 6.2).[35] It is well known that the acidity of the extractant is one of the predominant factors governing extractability, *i.e.*, the lower the pK_a value, the larger is log K_{exc}. Torkestani *et al.*,[36] Sekine *et al.*,[37] and Reddy and coworkers[22] stated that the interaction between the chelating agent and a neutral oxo-donor in $CHCl_3$ are, in general, weaker when the diluent itself has strong interaction with the oxo-donor. However, the difference in the polarity of the diluents is higher (dielectric constant of chloroform = 4.9, 1,2-dichloroethane = 10.4). Hence, the present results demonstrate that steric effects are significant (cavity size and the properties of the extractant).

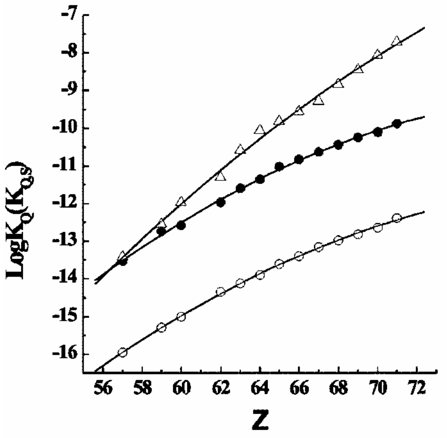

Fig. 7. log K_Q($K_{Q,S}$) *vs.* Z (open circles: HQ; solid circles: HQ–DB24C8; triangles: HQ–DB18C6).

The synergistic enhancement obtained for the combination of two extractants can be evaluated 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 coefficient of a metal ion using a mixture of extractants ($D_{1,2}$) and using the same extractants individually (D_1 and D_2). The values of the synergistic coefficients of the lanthanide ions when DB18C6 and DB24C8 were used as synergistic agents in combination with HQ are given in Table II. The synergistic enhancement increased from La to Lu for the HQ–DB18C6 mixture, while the values of the *SC* obtained for the HQ–DB24C8 mixture are almost the same. Reddy *et al.*[22] also reported that the synergistic constant increased from Nd^{3+}, Eu^{3+} to Tm^{3+} in their extraction with mixtures of 3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone and various crown ethers.

The separation factors between the lanthanides, defined as the ratios of the respective equilibrium constants $K_{Q,S}$ are also listed in Table II. The addition of DB18C6 to the Ln^{3+}–HQ system improves the separation. Thus, the synergistic mixtures, used in the present study, combine extraction efficiency with improved selectivity as compared to HQ. It can be seem from Table II that the separation factors obtained for the extraction of the lanthanide ions with HQ alone and those with the HQ–DB24C8 combination do not differ to a large extent.

TABLE II. Values of the synergistic coefficients ([HQ] = 6×10^{-2} mol dm^{-3}, [S] = 5×10^{-3} mol dm^{-3}, pH = 5.50) and separation factors for the lanthanide extraction with HQ alone, as well as with HQ–DB24C8 or HQ–DB18C6 in 1,2-dichloroethane

Ln^{3+}	*SC*			*SF*		
	DB24C8	DB18C6		HQ	HQ–DB24C8	HQ–DB18C6
La	0.13	0.22	Pr/La	4.46	7.24	7.58
Pr	0.26	0.46	Nd/Pr	1.99	1.44	3.80
Nd	0.12	0.73	Sm/Nd	4.46	4.16	4.57
Sm	0.10	0.74	Eu/Sm	1.69	2.29	5.24
Eu	0.22	1.32	Gd/Eu	1.65	1.74	3.31
Gd	0.24	1.54	Tb/Gd	1.99	2.18	1.74
Tb	0.28	1.78	Dy/Tb	1.58	1.54	1.82
Dy	0.27	1.54	Ho/Dy	1.77	1.54	1.90
Ho	0.21	1.57	Er/Ho	1.47	1.58	2.75
Er	0.24	1.56	Tm/Er	1.44	1.58	3.63
Tm	0.28	2.08	Yb/Tm	1.52	1.35	2.90
Yb	0.23	2.28	Lu/Yb	1.82	1.74	2.49
Lu	0.21	2.38				

It is interesting to compare the separation factors obtained for the extraction of lanthanides with various chelating extractants and DB18C6. Reddy *et al.*[15–17,20,22] published data for the separation factors of the pairs Eu/Nd and Tm/Eu for various chelating extractants, *viz.* 4,4,4-trifluoro-1-phenyl-1,3-butanedione (HBTFA), 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone (HPMTFP), 1-phenyl-3-methyl-4-pivaloyl-5-pyrazolone (HPMPP), 3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone (HFBPI) and 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) with DB18C6. The separation factors for these systems are listed in Table III, together with the data obtained in the study,[19] from which it can be seen that HQ, which is a much poorer extractant for lanthanides than β-diketones, exhibits a quite high separation factor for the pairs Eu/Nd and Tm/Eu.

TABLE III. Values of the separation factors for the pairs Eu/Nd and Tm/Eu

Extractants	Eu/Nd	Tm/Eu
HQ–DB18C6	23.98	138.04
HTTA–DB18C6[19]	3.7	17.0
HPMTFP–DB18C6[15]	21.4	3.6
HPBI–DB18C6[20]	25.1	1.2
HBTFA–DB18C6[16]	20.2	5.1
HPMPP–DB18C6[17]	47.9	13.4
HFBPI–DB18C6[22]	4.78	1.75

CONCLUSION

The extraction equilibriums of trivalent lanthanides with 8-hydroxyquinoline and with mixtures of HQ and DB18C6 or DB24C8 were investigated. The experimental data show that the Ln^{3+} ions were extracted as LnQ_3 and LnQ_3–S. The equilibrium constants of the synergistic species were found to increase monotonically with decreasing ionic radii of the metal ions. The synergistic enhancement factors, as well as the separation factors between adjacent metal ions, were large when DB18C6 was used as the synergistic agent in combination with HQ.

ИЗВОД

КРУНСКИ ЕТРИ КАО СИНЕРГИСТИЧКИ ЧИНИОЦИ ПРИ ЕКСТРАКЦИЈИ ТРОВАЛЕНТНИХ ЛАНТАНИДА 8-ХИДРОКСИХИНОЛИНОМ

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Испитивана је екстракција у течној фази 13 лантанида смешом 8-хидроксихинолина (HQ) и крунских етара (S), дибензо-18-круна-6 (DB18C6) и дибензо-24-круна-8 (DB24C8), у 1,2-дихлороетану као разблаживачу, из хлоридне средине и при јонској јачини μ = 0,1. За врсте екстраховане са HQ установљен је састав LnQ_3, а LnQ3·S у присуству крунских етара. Израчунате су вредности константи равнотеже. Додавање DB18C6 метал–хелатном систему побољшава ефикасност екстракције, док су слаба синергистичка побољшања добијена уколико се метали екстрахују смешом HQ–DB24C8. Одређени су параметри процеса екстракције и израчунати сепарациони фактори суседних тровалентних лантанида.

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