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Extraction studies on the formation of La(III), Gd(III) and Lu(III) species with 5,7-dihalogeno derivatives of 8-hydroxyquinoline

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Abstract

The nature of species formed in the extraction of Ln(III) (where Ln(III)=La, Gd, Lu) with 5,7-dibromo-8-hydroxyquinoline (5,7(Br)HO*x*) in $CHCl_3$ from water phase and La(III) with 5,7-dichloro-8-hydroxyquinoline (5,7(Cl)HO*x*) in $CHCl_3$ from water and water–methanol phases was examined. It was stated that during the extraction from water phase the six-coordinated chelates were extracted. In the presence of methanol in the water phase eight-coordinated mixed ligand adducts were observed. The parameters of the extraction process and separation factors of La–Gd, Gd–Lu and La–Lu pairs were calculated. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Lanthanum(III); Gadolinium(III); Lutetium(III); Extraction; 5,7-Dihalogeno-8-hydroxyquinoline derivatives

1. Introduction

The nature of species formed in the extraction of Y(III), Gd(III) [1], Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III) [2] and Lu(III) [3] with 5,7-dichloro-8-hydroxyquinoline (5,7(Cl)HO*x*) and Y(III), La(III), lanthanides(III) from Pr to Lu (except Pm) [4] with 8-hydroxyquinoline (HO*x*) was described previously. The literature data concerning extraction of rare earth elements with 5,7-dibromo-8-hydroxyquinoline (5,7(Br)HO*x*) are scarce and contradictory. It was stated that Nd(III) [5], Pr(III), Eu(III) and Yb(III) [6–8] can be extracted as simple chelates and self adducts containing one molecule of 5,7(Br)HO*x*. Now, the nature of species extracted into organic phase and the equilibrium extraction constants in the systems Ln(III)-H_2O-5,7(Br)HO*x*-$CHCl_3$ (Ln(III)=La, Gd, Lu); La(III)-H_2O-5,7(Cl)HO*x*-$CHCl_3$ and La(III)-H_2O-MeOH-5,7(Cl)HO*x*-$CHCl_3$ (MeOH=CH_3OH) were determined. Moreover, the separation factors (*S*) of investigated pairs of rare earth elements were calculated.

2. Experimental

The solution of $Ln(ClO_4)_3$ was obtained by dissolving the appropriate 99.9% pure: La_2O_3, Lu_2O_3 (Fluka) and Gd_2O_3 (Koch & Ligh Lab.) in small quantity of hot 3 mol l^{-1} perchloric acid and diluting with water. 5,7-Dibromo-8-hydroxyquinoline and 5,7-dichloro-8-hydroxyquinoline (99.9% Aldrich Chemical) solutions in chloroform were used. The remaining reagents, experimental procedure and apparatus were described earlier [1].

The values of Ln(III) distribution coefficient (*D*) were determined by varying one of the parameters: pH or pH* (pH*$=-\log [H^+]$ in the water–methanol solution), concentration of extractant (HL=5,7(Br)HO*x* or 5,7(Cl)HO*x*) or methanol. Experiments were carried out at $C_{Ln}=2.50\cdot 10^{-4}$ mol l^{-1}, $C_{HL}\in(0.15–2.40)\cdot 10^{-2}$ mol l^{-1} for 5,7(Br)HO*x*; $C_{Ln}=50$ μg ml^{-1}, $C_{HL}\in(0.15–3.00)\cdot 10^{-2}$ mol l^{-1}, $C_{MeOH}\in(5–50)$% (v/v) for 5,7(Cl)HO*x*; $\mu=0.1$ mol l^{-1} ($NaClO_4$), temp. 21±1°C.

3. Results and discussion

The overall reactions for the extraction of Ln(III) with HL from water and water–methanol phase are as follows:

$$Ln(H_2O)_y^{3+} + (3+n)HL_{(o)} \overset{K_{ex}}{\rightleftharpoons} LnL_3\cdot nHL_{(o)} + yH_2O + 3H^+ \quad (1)$$

$$Ln(H_2O)_m^{3+} + (3+n)HL_{(o)} + tMeOH_{(o)} \overset{K^*_{ex}}{\rightleftharpoons} LnL_3\cdot nHL\cdot tMeOH_{(o)} + mH_2O + 3H^+ \quad (2)$$

$_{(o)}$-organic phase

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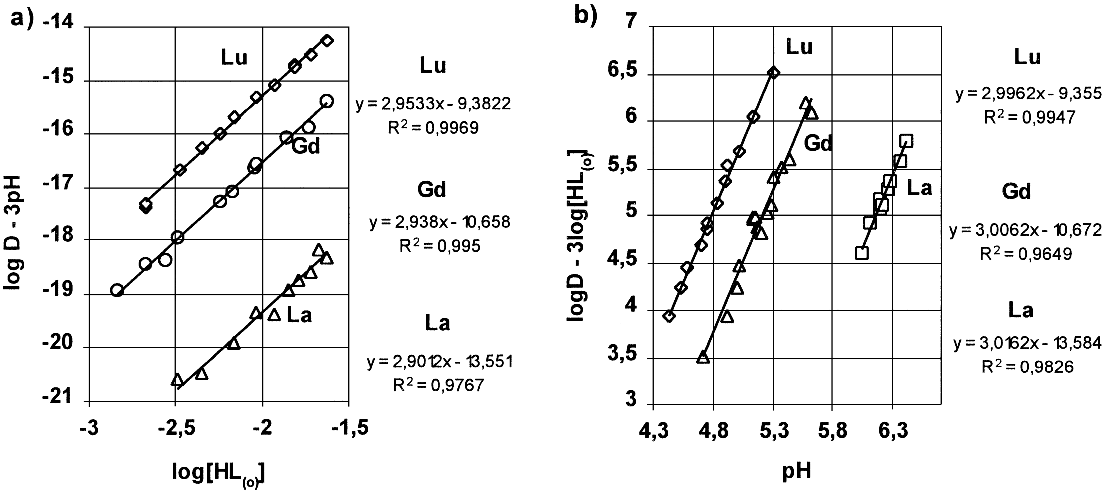

Fig. 1. Systems Ln(III)-H_2O-5,7(Br)HO*x* in $CHCl_3$. Dependencies: (a) log D-3pH$=f$(log $[HL_{(o)}]$) at pH~$pH_{0.5}$, $C_{HL}\in(0.15–2.40)\cdot 10^{-2}$ mol l^{-1}; (b) log $D-3$ log $[HL_{(o)}]=f$(pH) at $C_{HL}=2.40\cdot 10^{-2}$ mol l^{-1} (R^2, the correlation coefficient).

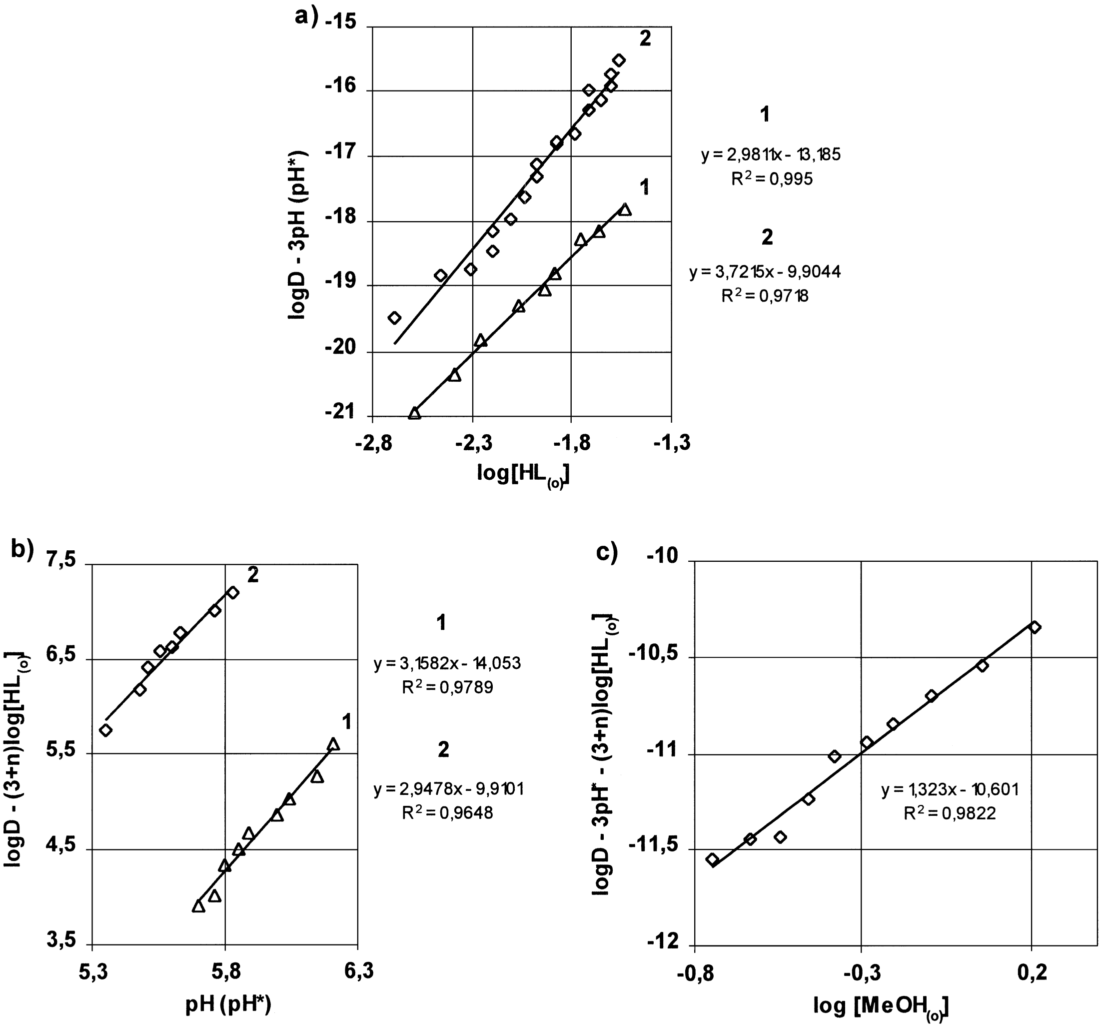

Fig. 2. Extraction of La(III) with 5,7(Cl)HO*x* in $CHCl_3$. Dependencies: (a) log $D-$3pH(or pH*)$=f$(log $[HL_{(o)}]$) at pH(pH*)~$pH_{0.5}(pH^*_{0.5})$, $C_{HL}\in(0.15–3.00)\cdot 10^{-2}$ mol l^{-1}; (b) log $D-(3+n)$log $[HL_{(o)}]=f$(pH)(or pH*) at $C_{HL}=3.00\cdot 10^{-2}$ mol l^{-1}, curves: 1, from water phase; 2, from water –50% (v/v) methanol phase; (c) log $D-3pH^*-(3+n)$log $[HL_{(o)}]=f$(log $[MeOH_{(o)}]$) at pH*~$pH^*_{0.5}$, $C_{HL}=3.00\cdot 10^{-2}$ mol l^{-1}, $C_{MeOH}\in(5–50)\%$ (v/v).

The stoichiometric coefficients in Eqs. (1) and (2) were determined from plots of log $D-3$pH or (pH*)$=f$(log [$HL_{(o)}$]), log $D-(3+n)$log [$HL_{(o)}$]$=f$(pH) or (pH*) and log $D-3$pH*$-(3+n)$log [$HL_{(o)}$]$=f$(log [$MeOH_{(o)}$]) for the extraction from water and the water–methanol phase, respectively (Figs 1 and 2). The extracted data were analyzed using the linear regression computer program Excel 7.0 [3]. From the suitable equations of the above-mentioned dependencies it was stated that during the extraction of La(III), Gd(III) and Lu(III) with 5,7(Br)HO*x* and La(III) with 5,7(Cl)HO*x* from water phase only six-coordinated species of the type LnL_3 (Table 1) are extracted:

$$Ln(H_2O)_y^{3+} + 3HL_{(o)} \overset{K_{ex}}{\rightleftharpoons} LnL_{3(o)} + yH_2O + 3H^+ \qquad (3)$$

Analogous type of species LnL_3 in the extraction of Gd(III) and Lu(III) with 5,7(Cl)HO*x* from water phase were described [1,3]. However, in the extraction of Gd(III) with HO*x* from water phase the chelates Gd(O*x*)$_3$ and seven-coordinated adducts Gd(O*x*)$_3$·HO*x* were formed. The extraction behaviour of La(III) and Lu(III) with HO*x* was quite distinct. In this case the existence of the third phase was observed [4].

In the extraction of La(III) with 5,7(Cl)HO*x* from water–methanol phase the formation of eight-coordinated mixed ligand adducts (Table1) takes place:

$$La(H_2O)_m^{3+} + 4HL_{(o)} + MeOH_{(o)} \overset{K_{ex}^*}{\rightleftharpoons} LaL_3 \cdot HL \cdot MeOH_{(o)} + mH_2O + 3H^+ \qquad (4)$$

Previously, it was stated that during the extraction of Gd(III) and Lu(III) with 5,7(Cl)HO*x* from water–methanol phase adducts of the type $LnL_3\cdot 2MeOH$ were extracted [1,3]. We reported [4], that Gd(III) in the extraction with HO*x* from water–methanol phase got extracted as mixed ligand adducts Gd(O*x*)$_3$·2MeOH, while La(III) was extracted as seven-coordinated adducts La(O*x*)$_3$·HO*x*. Lu(III) was not extracted in this system.

The average values of the equilibrium extraction constants were calculated as previously [3] with data presented in Figs. 1 and 2. As can be seen from the extraction parameters given in Table 1, 5,7-dihalogeno derivatives of 8-hydroxyquinoline show better extraction properties in respect to La(III), Gd(III) and Lu(III) than 8-hydroxyquinoline.

The addition of methanol to the water phase causes an increase of the extraction constants and decrease of $pH_{0.5}$ (Table 1). The observed synergistic effect may be connected with the increase of coordination number for species extracted with 5,7(Cl)HO*x*, as well as, with HO*x* [1,4].

The separation factors (*S*) of La–Gd, Gd–Lu and La–Lu pairs were calculated (at pH$=$5.5) from efficiency of

Table 1
Extraction parameters and the species extracted into organic phase with 8-hydroxyquinoline or its 5,7-dihalogeno derivatives; $\mu=0.1$ mol l^{-1}, temp. 21±1°C

	La(III)	Gd(III)	Lu(III)
System Ln(III)-H_2O-5,7(Br)HOx-$CHCl_3$			
Species	LaL_3	GdL_3	LuL_3
$pH_{0.5}$ [a]	6.15	5.18	4.76
$-\log K_{ex}$	13.57	10.67	9.37
System Ln(III)-H_2O-5,7(Cl)HOx-$CHCl_3$			
Species	LaL_3	GdL_3 [1]	LuL_3 [3]
$pH_{0.5}$ [b]	5.90	4.94	5.96
$-\log K_{ex}$	13.28	10.24	12.78
System Ln(III)-H_2O-HOx-$CHCl_3$			
Species	not extracted	Gd(O*x*)$_3$, (Gd(O*x*)$_3$·HO*x*) [4]	Not extracted
$pH_{0.5}$ [c]		5.78	
$-\log K_{ex}$		13.32, (11.99)	
System Ln(III)-H_2O-MeOH-5,7(Cl)HOx-$CHCl_3$			
Species	$LaL_3\cdot HL\cdot MeOH$	$GdL_3\cdot 2MeOH$ [1]	$LuL_3\cdot 2MeOH$ [3]
$pH^*_{0.5}$ [b]	5.45	4.34	5.32
$-\log K^*_{ex}$	10.28	8.67	11.56
System Ln(III)-H_2O-MeOH-HOx-$CHCl_3$			
Species	La(O*x*)$_3$·HO*x* [4]	Gd(O*x*)$_3$·2MeOH [4]	Not extracted
$pH^*_{0.5}$ [c]	6.18	5.20	
$-\log K^*_{ex}$	13.14	12.02	

[a] $C_{HL}=2.40\cdot 10^{-2}$ mol l^{-1}.
[b] $C_{HL}=3.00\cdot 10^{-2}$ mol l^{-1}.
[c] $C_{HOx}=5.00\cdot 10^{-2}$ mol l^{-1}.

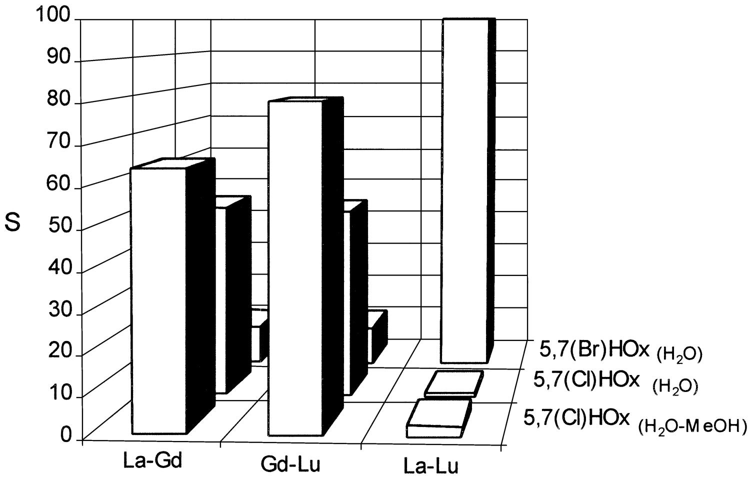

Fig. 3. The separation factors (*S*) of La–Gd, Gd–Lu and La–Lu pairs during the extraction with 5,7(Cl)HO*x* or 5,7(Br)HO*x* from water phase and with 5,7(Cl)HO*x* from water–50% (v/v) methanol phase.

Ln(III) extraction [9] and presented in Fig. 3. The highest value of *S* for La–Lu pair in the extraction with 5,7(Br)HO*x* from water phase was obtained ($S_{\mathrm{La-Lu}} = 100$). The addition of methanol in the extraction with 5,7(Cl)HO*x* causes the increase of the separation factors of investigated pairs (for an example $S_{\mathrm{Gd-Lu}}$ changes from 49 to 80).

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