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STUDY ON SPECIES OF HEAVY LANTHANIDES(III) CHELATES EXTRACTED INTO ORGANIC PHASE WITH 5,7-DICHLORO-8-HYDROXYQUINOLINE

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The nature of species formed in the extraction of lanthanides Ln(III) (where Ln = Tb, Dy, Ho, Er, Tm and Yb) with 5,7-dichloro-8-hydroxyquinoline (HIL) in CHCl_3 from water or water-methanol phase was examined. It was stated that during the extraction from water phase the chelates LnL_3 (Tb, Tm), seven-coordinated self-adducts $\text{LnL}_3 \div \text{HIL}$ (Er, Ho) or both types of these species (Dy, Yb) were extracted. In the presence of methanol (MeOH) in the aqueous phase the eight-coordinated mixed species of the type $\text{LnL}_3 \cdot 2\text{MeOH}$ were observed.

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1. Introduction

The study of the nature of species formed in the extraction of lanthanide ions have been the subject of extensive investigations during the last few years [1, 2]. However, there is scanty information on the species of the lanthanide chelates extracted into organic phase with different N,O or O,O donor extractants [3-5]. 8-Hydroxyquinoline (HIOx) and its derivatives are one of the most important and interesting of these extractants, since they form not only simple chelates but also self-adducts and mixed ligand adducts in the presence of other neutral ligands [4, 6, 7].

Now, particular attention is given to the extraction of heavy lanthanides with 5,7-dichloro-8-hydroxyquinoline (HIL or 5,7(Cl)HIOx) which may be preferable to 8-hydroxyquinoline as a reagent for solvent extraction [6]. The nature of species extracted into organic phase in the systems $\text{Ln(III)}-\text{H}_2\text{O}-\text{HIL}-\text{CHCl}_3$ and $\text{Ln(III)}-\text{H}_2\text{O}-\text{MeOH}-\text{HIL}-\text{CHCl}_3$ (where $\text{Ln(III)} = \text{Tb, Dy, Ho, Er, Tm, Yb}$; MeOH — methanol) was investigated.

2. Experimental

The solutions of $\text{Ln}(\text{ClO}_4)_3$ ($\text{Ln}(\text{III}) = \text{Tb, Dy, Ho, Er, Tm}$ and Yb) were prepared from the corresponding Ln_2O_3 (99.9% Fluka). 5,7-Dichloro-8-hydroxyquinoline (99.9% Aldrich Chemical) solutions in chloroform were used. The experimental procedure, apparatus and other reagents used have been described previously [5].

Studies on the extraction of lanthanides(III) from water phase were carried out at varying $C_{\text{IIL}(\text{o})}$ ($1.5 \times 10^{-3} \div 3.00 \times 10^{-2}$ mol/l, (o) — denotes the organic phase) and $\text{pH} \approx 4 \div 5.5$. Two series of experiments:

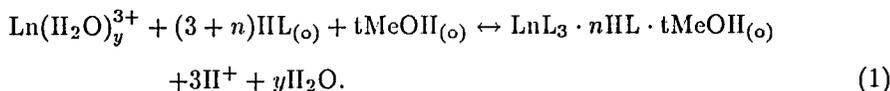
— at varying $C_{\text{IIL}(\text{o})}$ ($1.5 \times 10^{-3} \div 3.00 \times 10^{-2}$ mol/l) and $C_{\text{MeOH}} = 50\%(\text{V/V})$,

— at varying C_{MeOH} ($5 \div 50\%(\text{V/V})$) and $C_{\text{IIL}(\text{o})} = 3.00 \times 10^{-2}$ mol/l,

during the extraction from water-methanol phase ($\text{pH}^* \approx 3.5 \div 5$ where $\text{pH}^* = -\log[\text{H}^+]$ in water-methanol solutions [8]) were performed. In all series of measurements the concentration of $\text{Ln}(\text{III})$ was $50 \mu\text{g/ml}$. Experiments were carried out at $21 \pm 1^\circ\text{C}$ and at constant ionic strength ($\mu = 0.1$ mol/l).

3. Results and discussion

The overall reaction for the extraction of investigated ions with 5,7-dichloro-8-hydroxyquinoline can be represented by equation



As can be seen from Eq. (1) the extraction behaviour of the lanthanides may be evaluated from a log-log plot of the distribution coefficient (D) vs. equilibrium concentration of IIL or MeOH in the organic phase. Taking into account the hydrogen ion concentration, volume changes of phases, the IIL and H_2L^+ acid dissociation constants and the IIL distribution constants, the equilibrium concentration ($[\text{IIL}(\text{o})]$) was calculated [9, 10]. Equilibrium concentration of methanol in organic phase ($[\text{MeOH}(\text{o})]$) in relation to its initial concentrations in water-methanol solutions, were determined chromatographically [11].

Examples of the results of investigations are shown in Figs. 1 and 2 whereas data concerning the species extracted into organic phase are compiled in Table. Plots of $\log-3\text{pH}$ vs. $\log[\text{IIL}(\text{o})]$ (for the extraction from water phase) indicated linear relationships with slopes ≈ 3 (Tb, Tm) and ≈ 4 (Ho, Er). In contrast, slopes intermediate between 3 and 4 for Dy and Yb were observed. Finally, it was stated that during the extraction from water phase the chelates LnL_3 , seven-coordinated self-adducts $\text{LnL}_3 \cdot \text{IIL}$ or both types of these species are formed. Previously [5], it was shown that in the extraction of Tb, Dy, Ho, Er, Tm and Yb with 8-hydroxyquinoline in CHCl_3 from water phase only six-coordinated species of the type LnOx_3 were extracted. Oxine did not form self-adducts in these systems. It may be caused by smaller value of HOx than 5,7(Cl)HOx distribution constant [5, 9].

The influence of MeOH on the nature of the species extracted is shown in Fig. 2 on the example of Tm(III) extraction. Plots of $\log D - 3\text{pH}^*$ vs. $\log[\text{IIL}(\text{o})]$ and $\log D - 3\text{pH}^* - 3\log[\text{IIL}(\text{o})]$ vs. $\log[\text{MeOH}(\text{o})]$ are always linear with slopes ≈ 3 and ≈ 2 , respectively. These findings would lead to the conclusion that in the presence of methanol in the aqueous phase mixed ligand adducts of the type

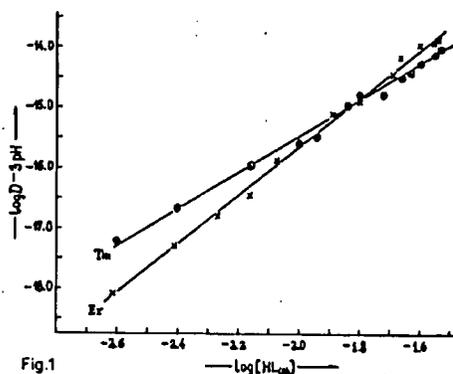


Fig.1

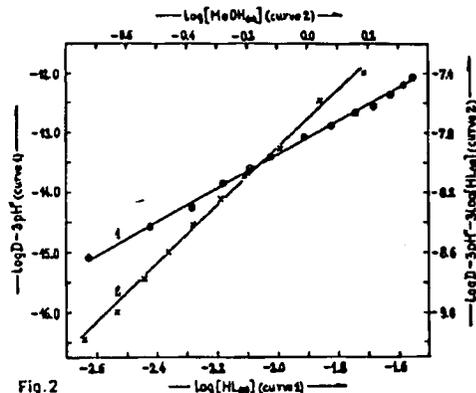


Fig.2

Fig. 1. Extraction of Er(III) and Tm(III) with 5,7(Cl)HOx in chloroform from the water phase. Plots of $\log D - 3pH$ vs. $\log [HL_{(o)}]$.

Fig. 2. Extraction of Tm(III) with 5,7(Cl)HOx in chloroform from the water-methanol phase. Curves: 1 — plot of $\log D - 3pH^*$ vs. $\log [HL_{(o)}]$ at $C_{MeOH} = 50\%(V/V)$; 2 — plot of $\log D - 3pH^* - 3\log [HL_{(o)}]$ vs. $\log [MeOH_{(o)}]$ at $C_{HL(o)} = 3.00 \times 10^{-2}$ mol/l and $C_{MeOH} = 5 \div 50\%(V/V)$.

TABLE

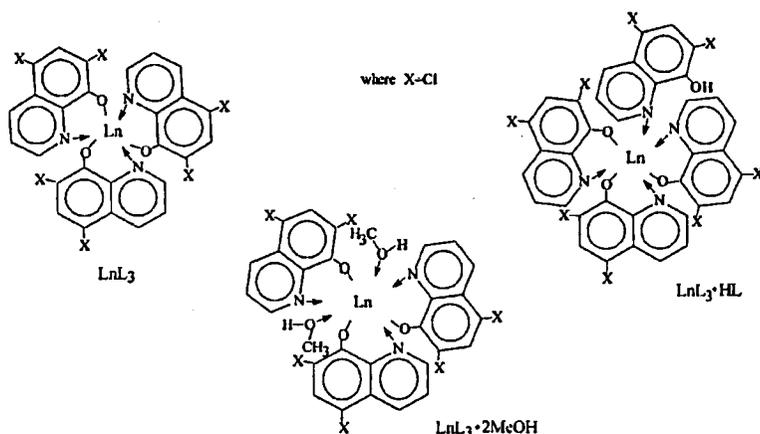
The species extracted into organic phase with 5,7-dichloro-8-hydroxyquinoline; $C_{HL(o)}$ from 1.5×10^{-3} to 3.00×10^{-2} mol/l; $C_{Ln} = 50$ $\mu\text{g/ml}$; temperature = $21 \pm 1^\circ\text{C}$; $\mu = 0.1$ mol/l.

System	Ln(III)	Predominant species
Ln(III)-H ₂ O-HL-CHCl ₃	Tb, Tm	LnL ₃
	Ho, Er	LnL ₃ · HL
	Dy, Yb	LnL ₃ and LnL ₃ · HL ^a
	Lu [2]	
Ln(III)-H ₂ O-MeOH-HL-CHCl ₃	Tb, Dy, Ho, Er, Tm, Tb	LnL ₃ · 2MeOH

^aIn great part at $C_{HL(o)} > 1.5 \times 10^{-2}$ mol/l.

LnL₃ · 2MeOH are formed. Similar adducts were also observed in the extraction of heavy lanthanides with HOx [5]. The formation of eight-coordinated adducts with two molecules of MeOH is combined with greater lanthanides(III) affinity to O-donor atom than to N-donor atom as well as with steric factor.

A possible structures of the species extracted into the organic phase with 5,7-dichloro-8-hydroxyquinoline are:



The increase in coordination number from 6 (or 7) to 8 for species extracted with 5,7(Cl)HOx as well as with HOx can explain the synergism observed in the extraction of lanthanides(III) from water-methanol phase.

The study of the extraction parameters in investigated systems will be the matter of our next paper.

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