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 (HL) in CHCl3 from water or water-methanol phase was examined. It was stated that during the extraction from water phase the chelates LnL3 (Tb, Tm), seven-coordinated self-adducts LnL2 + HL (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 LnL3 • 2MeOH 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 (HOOx) 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 (HII or 5,7(Cl)HOOx) 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 Ln(III)–H2O–HL–CHCl3 and Ln(III)–H2O–MeOH–HL–CHCl3 (where Ln(III) = Tb, Dy, Ho, Er, Tm, Yb; MeOH — methanol) was investigated.
2. Experimental

The solutions of Ln(ClO₄)₃ (Ln(III) = Tb, Dy, Ho, Er, Tm and Yb) were prepared from the corresponding Ln₂O₃ (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 C₁₁L(0)(1.5 x 10⁻³ – 3.00 x 10⁻² mol/l, (o) — denotes the organic phase) and pH ≈ 4 – 5.5. Two series of experiments:
— at varying C₁₁L(0)(1.5 x 10⁻³ – 3.00 x 10⁻² mol/l) and C₅₆₇₈₉₀ = 50% (V/V),
— at varying C₅₆₇₈₉₀ (5– 50% (V/V)) and C₁₁L(0) = 3.00 x 10⁻² mol/l, during the extraction from water–methanol phase (pH* ≈ 3.5 ÷ 5 where pH* = -log[H⁺] in water–methanol solutions [8]) were performed. In all series of measurements the concentration of Ln(III) was 50 μg/ml. Experiments were carried out at 21 ± 1°C and at constant ionic strength (μ = 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

$$\text{Ln}(\Pi₂O)₃^{3+} + (3 + n)\Pi₃L(0) + \text{tMeOII(0)} \leftrightarrow \text{LnL₃} \cdot n\Pi₃L \cdot \text{tMeOII(0)}$$

$$+3\Pi^{2+} + y\Pi₂O.$$  (1)

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 IIIL or MeOII in the organic phase. Taking into account the hydrogen ion concentration, volume changes of phases, the IIIL and II₂L⁺ acid dissociation constants and the IIIL distribution constants, the equilibrium concentration ([IIIL(0)]) was calculated [9, 10]. Equilibrium concentration of methanol in organic phase ([MeOII(0)]) 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–3pH vs. log[IIIL(0)] (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 LnL₃, seven-coordinated self-adducts LnL₃ • IIIL 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 CIICl₃ from water phase only six-coordinated species of the type LnOx₃ 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 MeOII on the nature of the species extracted is shown in Fig. 2 on the example of Tm(III) extraction. Plots of logD–3pH* vs. log[IIIL(0)] and logD–3pH*–3log[IIIL(0)] vs. log[MeOII(0)] 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
LnL₃ and 2MeOII are formed. Similar adducts were also observed in the extraction of heavy lanthanides with HIOx [5]. The formation of eight-coordinated adducts with two molecules of MeOII 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:

**TABLE**

<table>
<thead>
<tr>
<th>System</th>
<th>Ln(III)</th>
<th>Predominant species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ln(III)–II₂O–III–CHCl₃</td>
<td>Tb, Tm</td>
<td>LnL₃</td>
</tr>
<tr>
<td></td>
<td>Ho, Er</td>
<td>LnL₃·III</td>
</tr>
<tr>
<td></td>
<td>Dy, Yb</td>
<td>LnL₃ and LnL₃·III&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Lu [2]</td>
<td></td>
</tr>
<tr>
<td>Ln(III)–II₂O–MeOII–III–CHCl₃</td>
<td>Tb, Dy, Ho, Er, Tm, Tb</td>
<td>LnL₃·2MeOII</td>
</tr>
</tbody>
</table>

<sup>a</sup> In great part at C<sub>III(o)</sub> > 1.5 × 10⁻² mol/l.
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.

References