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Solvent Extraction of Rare Earth Metal Ions with 1-(2-Pyridylazo)-2-naphthol (*PAN*)

IV. Extraction of Lutetium(III) and Erbium(III) by *PAN* from Aqueous Solutions

Bożena Kuźnik* and **Ewa Wójcik**

Institute of General Chemistry, Technical University, PL-90924 Łódź, Poland

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Extraction of lutetium(III) and erbium(III) with 1-(2-pyridylazo)-2-naphthol (*PAN* or H*L*) in carbon tetrachloride from aqueous solutions was examined. The composition of the complex extracted was determined and it was found that the extraction process can be described by the following equation (Ln^{3+} = Lu, Er):

$$Ln(H_2O)_m^{3+} + 3\,HL_{(0)} \overset{K_{ex}}{\rightleftharpoons} LnL_{3(0)} + 3\,H^+ + m\,H_2O$$

The extraction constants (K_{ex}) and two-phase stability constants ($\beta_3^\times$) for LnL_3 complexes have been evaluated.

[Keywords: Extraction; 1-(2-Pyridylazo)-2-naphthol; Rare earth complexes]

Extraktion von Seltenerdenmetall-Ionen mit 1-(2-Pyridilazo)-2-naphthol (PAN), IV. Extraktion von Lu*(III) und* Er*(III) aus wäßriger Lösung*

Die Extraktion von Lu(III) und Er(III) mittels 1-(2-Pyridilazo)-2-naphthol (*PAN* oder H*L*) in Kohlenstofftetrachlorid aus wäßriger Phase wurde untersucht. Die Zusammensetzung des extrahierten Komplexes wurde bestimmt und es wurde festgestellt, daß der Extraktionsprozeß durch die folgende Gleichung beschrieben wird (Ln^{3+} = Lu, Er):

$$Ln(H_2O)_m^{3+} + 3\,HL_{(0)} \overset{K_{ex}}{\rightleftharpoons} LnL_{3(0)} + 3\,H^+ + m\,H_2O$$

Die Werte der Extraktions-Gleichgewichtskonstante (K_{ex}) sowie der Zweiphasen-Beständigkeitskonstante ($\beta_3^\times$) für die Komplexe LnL_3 wurden berechnet.

Introduction

As a part of systematic research of the extraction of rare earth metal ions with 1-(2-pyridylazo)-2-naphthol (*PAN* or H*L*) we have studied and described the extraction of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Ho(III), and Yb(III) from aqueous or aqueous-alcoholic (methanol, ethanol) phases[1–4]. It was found that the extraction of Yb(III) and Dy(III) from aqueous phase with *PAN* in CCl_4 may be described as[1]:

$$Ln(\mathrm{H_2O})_m^{3+} + 3\,\mathrm{H}L_{(0)} \rightleftharpoons LnL_{3(0)} + 3\,\mathrm{H}^+ + m\,\mathrm{H_2O} \qquad (1)$$

where Ln^{3+} = Yb, Dy, and the subscript (0) denotes the organic phase.

In this paper the distribution equilibrium study of these types of systems is continued and the results of the extraction of Lu(III) and Er(III) with *PAN* in carbon tetrachloride are given.

Recently, the extraction of Tm(III), Lu(III), Yb(III), Ce(III), Sm(III), and Er(III) pyridylazonaphtholates with chloroform has been reported[5,6]. These investigations were performed at high *pH* of the aqueous phase (from ~ 6.8 to ~ 7.6) in the presence of chloric anion. The authors have suggested from spectrophotometric data that the extracted complex was LnL_2Cl.

Experimental

The experimental procedure, the calculations, equipment and materials such as 1-(2-pyridylazo)-2-naphthol, buffers, arsenazo-III, and carbon tetrachloride used have been described previously[1]. Stock solutions of $Lu(ClO_4)_3$ or $Er(ClO_4)_3$ were prepared by dissolving Lu_2O_3 or Er_2O_3 (Inter. Enzym. Limit. pure) in 3 *M* perchloric acid.

The concentration of Ln(III) in the aqueous phase was always 50 μg/cm^3, the concentration of *PAN* in the organic phase ($C_{\mathrm{H}L\,in.}$) varied from $1 \cdot 10^{-3}$ to $5 \cdot 10^{-2}$ *M*.

In all experiments the organic phase was back-extracted with 0.06 *M* perchloric acid. From the equilibrium concentrations of Ln(III) in the organic and the aqueous phase the distribution coefficient (*D*) was calculated. The balance of lanthanide in the both phases was 100 ± 2%.

The *pH* range for the extraction of Lu(III) or Er(III) with *PAN* solutions in CCl_4 was determined. The data, presented in the form of dependence of the extraction extent (% *E*)[1] vs. *pH* are shown in Fig. 1. From this Figure it follows that the extraction of Lu(III) or Er(III) with $1.00 \cdot 10^{-2}$ *M* PAN solution in CCl_4 starts at *pH* ~ 6.0. Above *pH* ~ 7.5 a turbidity of the aqueous phase and the occurrence of a suspension at the phase boundary is observed. Further investigations were limited only to the *pH* range ~ 6.0–7.0 (for $1.00 \cdot 10^{-2}$ *M PAN*) and 5.4–6.4 (for $5.00 \cdot 10^{-2}$ *M PAN*). Taking into account solubility products of $Ln(OH)_3$[7] and concentrations of lanthanides in the aqueous phase ($C_{\mathrm{Lu(III)}} = 2.86 \cdot 10^{-4}\,M$ and $C_{\mathrm{Er(III)}} = 2.90 \cdot 10^{-4}\,M$) precipitation of $Lu(OH)_3$ or $Er(OH)_3$, without any complexing factors, should take place at *pH* ~ 7.4 and ~ 7.7, respectively.

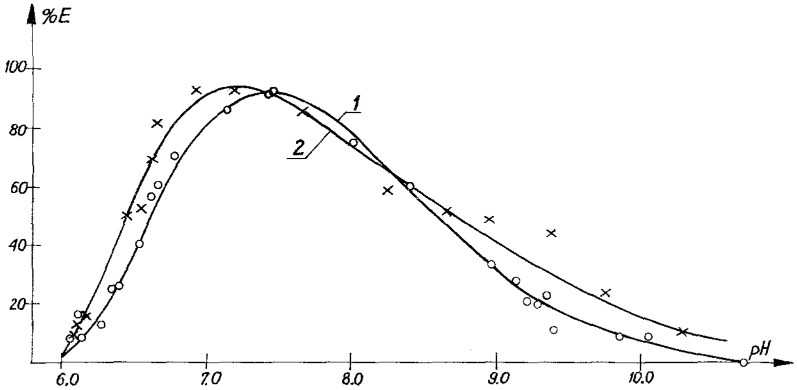

Fig. 1. Plot of the extent of Lu(III) (curve 1) and Er(III) (curve 2) extraction vs. *pH* of the aqueous phase. $C_{Ln\,in.} = 50\,\mu g/cm^3$, $C_{PAN\,in.} = 1.00 \cdot 10^{-2}\,M$ in carbon tetrachloride

Equilibrations were made using variable *pH* of the aqueous phase and constant *PAN* concentration in the organic phase or variable *PAN* concentration and constant *pH*.

Results and Discussions

Similarly as in the extraction of Yb(III) and Dy(III) with *PAN* from aqueous phase the influence of hydrolysis of Lu(III) [$\lg \beta_{Lu(OH)^{2+}} = 5.83$][8] or Er(III) [$\lg \beta_{Er(OH)^{2+}} = 5.74$][8] within the investigated *pH* range, the presence of their complexes with *PAN*, molecules of NH_3, hexamethylenetetramine, and ions ClO_4^- can be neglected. Thus, as it was shown previously[1] the extraction of Lu(III) or Er(III) with *PAN* from aqueous phase may be described by the equations:

$$Ln(H_2O)_m^{3+} + (3+n)\,HL_{(0)} \overset{K_{ex}}{\rightleftharpoons} LnL_3(HL)_{n(0)} + 3\,H^+ + m\,H_2O \quad (2)$$

and

$$\lg D = \lg K_{ex} + 3\,pH + (3+n) \lg C_{HL} \quad (3)$$

where Ln^{3+} = Lu, Er.

A lg—lg plot of the extraction data in the form of *D* vs. concentration of H^+ or H*L* indicates the stoichiometry of the formation of the extractable complex and thus leads to the derivation of a suitable equilibrium expression and then to the calculation of equilibrium constants.

The slopes of the lg *D* vs. *pH* plots are 2.8 [for Lu(III)] and 2.6 [for Er(III)] (Fig. 2). This indicates that in both cases three protons are lost.

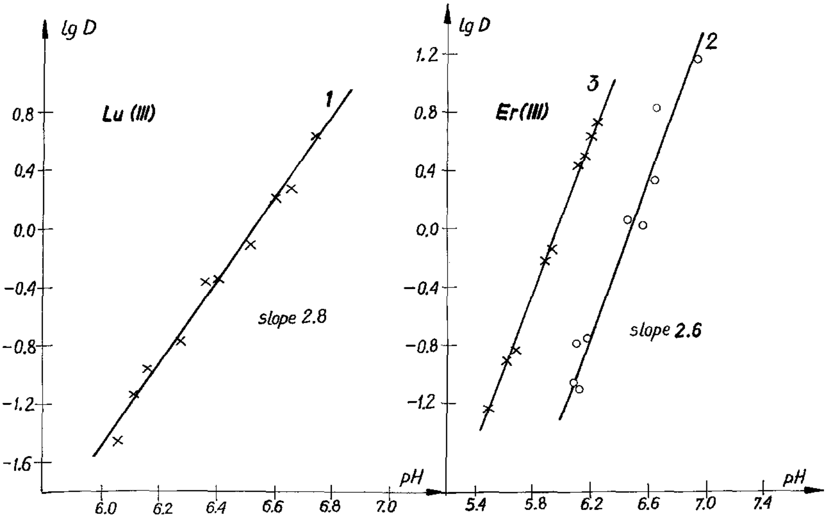

Fig. 2. Effect of the hydrogen ion concentration on Lu(III) (curve 1) and Er(III) (curves 2, 3) distribution between the aqueous phase and the solution of *PAN* in carbon tetrachloride. Curves 1, 2: $1.00 \cdot 10^{-2}\,M$ *PAN*; 3: $5.00 \cdot 10^{-2}\,M$ *PAN*, $C_{Ln\,in..} = 50\,\mu g/cm^3$

From the distribution experiment performed at constant *pH* and variable concentration of *PAN* in the organic phase the number of ligand molecules participating in the extraction process was obtained. The distribution coefficient was corrected for small changes in hydrogen ion concentration. Fig. 3 shows the results as a dependence of ($\lg D$—$3\,pH$) vs. $\lg C_{HL}$. For the extraction of Lu(III) the experimental points give a straight line with a slope of 3 in the whole area of investigated *PAN* concentrations. In the case of the Er(III) extraction a straight line with a slope 2.8 for the concentration of *PAN* from $\sim 1 \cdot 10^{-3}\,M$ to $\sim 3 \cdot 10^{-2}\,M$ was obtained.

The present results show that the extraction process of lutetium or erbium with a solution of 1-(2-pyridylazo)-2-naphthol in carbon tetrachloride may be described by Eq. (1) (where $Ln^{3+} = \mathrm{Lu, Er}$).

The extraction constants (K_{ex}) and the two-phase stability constants (β_3^x) of the complexes $\mathrm{Lu}L_3$ and $\mathrm{Er}L_3$ were calculated as previously[1]. The obtained constants and $pH_{0.5}$ values at $C_{HL} = 1.00 \cdot 10^{-2}\,M$ are given in Table 1.

The complexes of Lu(III) and Er(III) with *PAN* and those of Yb(III) and Dy(III)[1] are characterized by similar extraction parameters.

On the other hand, the addition of methanol (*Me*OH) or ethanol

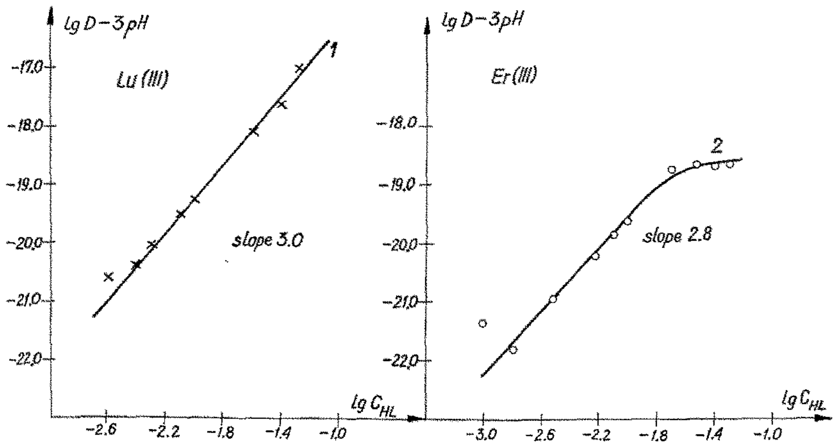

Fig. 3. Effect of the initial concentration of *PAN* on Lu(III) (curve 1) and Er(III) (curve 2) distribution between the aqueous phase and solutions of *PAN* in carbon tetrachloride, $C_{Ln\,in.} = 50\,\mu g/cm^3$

Table 1. *Extraction parameters for the formation of* LnL_3 *complexes (at 21 ± 1 °C, ionic strength 0.1 M)*

Parameter	Er^{3+}	Lu^{3+}
$\lg K_{ex}\,(\pm 0.03)$	—13.57	—13.41
$\lg \beta_3^x$	32.02	32.19
$pH_{0.5}$ at $C_{PAN} = 1.00 \cdot 10^{-2}\,M$	6.46	6.53

(*Et*OH) to the aqueous phase (above ~25% *v/v*) causes an increase of $\lg K_{ex}$(Lu) in the following order (compare Ref.[7]):

$$\begin{array}{ccccc} \lg K_{ex}(\mathrm{Lu})_{aq\text{-}MeOH} & & \lg K_{ex}(\mathrm{Lu})_{aq\text{-}EtOH} & & \lg K_{ex}(\mathrm{Lu})_{aq} \\ -9.86 & > & -11.00 & > & -13.41 \end{array}$$

The values of $\lg K_{ex}$ for the extraction of Lu(III) and Er(III) pyridylazonaphtholates with chloroform in the presence of chloride anions presented in[5,6] are much greater than those obtained in this paper.

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