Monatshefte für Chemie 119, 389—396 (1988)

Monatshefte für Chemie
Chemical Monthly

Solvent Extraction of Lanthanide Ions with 1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5 (H*PMBP*)

I. Extraction of Erbium(III), Ytterbium(III) and Lutetium(III) by H*PMBP* from Aqueous Solutions

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(Received 21 January 1987. Accepted 16 March 1987)

The solvent extraction of Er(III), Yb(III) and Lu(III) by 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (H*PMBP* or H*L*) in carbon tetrachloride has been studied as a function of the *pH* of the aqueous phase and the concentration of the extractant in the organic phase. The equation for the extraction reaction has been suggested as:

$$Ln^{3+} + 3\,\mathrm{H}L_{(0)} \rightleftharpoons LnL_{3(0)} + 3\,\mathrm{H}^{+} \; (Ln^{3+} = \mathrm{Er, Yb, Lu})$$

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

(Keywords: Extraction; 1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5; Rare earth complexes)

*Extraktion von Seltenerdmetall-Ionen mit 1-Phenyl-3-methyl-4-benzoyl-pyrazolon-5 (*H*PMBP), I. Extraktion von* Er(III), Yb(III) *und* Lu(III) *aus wäßriger Lösung*

Die Extraktion von Er(III), Yb(III) und Lu(III) mittels 1-Phenyl-3-methyl-4-benzoyl-pyrazolon-5 (H*PMBP* oder H*L*) in Kohlenstofftetrachlorid aus wäßriger Phase in Abhängigkeit vom *pH* der wäßrigen Phase sowie von der Konzentration von H*PMBP* in der organischen Phase wurde untersucht. Die folgende Gleichung beschreibt die Extraktionsreaktion:

$$Ln^{3+} + 3\,\mathrm{H}L_{(0)} \rightleftharpoons LnL_{3(0)} + 3\,\mathrm{H}^{+} \; (Ln^{3+} = \mathrm{Er, Yb, Lu})$$

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

Introduction

Previously [1–4] it was shown that the presence of methanol or ethanol in the aqueous phase causes a synergistic effect on the extraction of lanthanides(III) with 1-(2-pyridylazo)-2-naphthol. The studies of these problems were continued and the extraction of lanthanides(III) (*Ln*) with 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (H*PMBP* or H*L*) was investigated.

The extraction of rare-earth elements by H*PMBP* has been studied by many authors using a variety of organic solvents, various ionic media and ionic strength in the aqueous phase [5–22]. However, to our knowledge these extraction systems have been studied only occasionaly, except [6], and especially on the extraction with H*PMBP* in carbon tetrachloride systematic data are not available.

The composition of the complex extracted corresponds to a formula LnL_3 [6–12, 14, 16, 18, 20], $LnL_3 \cdot HL$ [8–10, 12, 13, 15–17, 21, 22] or $LnL_2X \cdot sHL$ [14, 15] (where X = anion Cl^- or NO_3^-). The extraction mechanism depends on the H*PMBP* concentration, the lanthanide ion, the kind of organic solvent in organic and anion in aqueous phases.

It is known that H*PMBP* extracts lanthanides(III) at a lower *pH* than the widely used 2-thenoyl-trifluoracetone (H*TTA*) [9, 10, 20, 23] under the same conditions. Moreover, the extraction of some lanthanides(III) with H*PMBP* increases at the presence of a solvent containing oxygen because complexes of the type $LnL_3 \cdot xS$ (where S = the molecule of solvent) are formed [19].

This paper reports a study of the extraction of Er(III), Yb(III) and Lu(III) by 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5. Carbon tetrachloride was chosen as solvent and sodium perchlorate as aqueous ionic medium. The influence of methanol will be described in the next paper.

Experimental

1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5 was prepared by a procedure of *Jensen* [24] (m.p. of the methanol-water recrystallized product was 121 °C, lit. 122 °C [24]). Stock solutions of H*PMBP* in carbon tetrachloride (POCh-Gliwice p.a.) were prepared by weighing and then diluted to the predetermined concentrations with solvent. All organic solutions of H*PMBP* were prepared the day before use. Initial solutions of $Ln(ClO_4)_3$ [*Ln*(III) = Er, Yb, Lu] were prepared by solving Er_2O_3, Yb_2O_3 or Lu_2O_3 (Fluka, 99.9% pure) in 3 *M* perchloric acid. The metal content was estimated by *EDTA* titration with xylenol orange as the indicator [25]. A 0.01% aqueous solution of the sodium salt of bis-2,7-(2-arsenobenzo-1-azo)-chromotropic acid (Arsenazo III) (Reachim p.a.) was used. All other chemicals (POCh-Gliwice) were analytically pure.

Extraction Procedure

In all extraction experiments the concentration of Ln(III) in the aqueous phase was 50 μg/cm^3. The *pH* of this phase within the region 2.5–6.5 was adjusted by means of $HClO_4$, $NaClO_4$ or NaOH solutions to obtain the final ionic strength $\mu = 0.1$. The initial concentration of H*PMBP* in the organic phase (C_{HL}) varied from $1.75 \cdot 10^{-2}$ to $1.50 \cdot 10^{-3}$ *M*.

Equal volumes of the aqueous and organic phases (20 cm^3) were agitated on a shaking machine in a glass vial at the temperature 21 ± 1 °C. The shaking duration was established by preliminary experiments as 45 min. After the extraction and phase separation the *pH* value of the aqueous phase was measured by using a *pH*-meter N-517 type with an accuracy ± 0.02 *pH* division. The concentration of Ln(III) in the aqueous phase was determined colorimetrically be means of Arsenazo III [26]. The absorbance was measured at $\lambda = 660$ nm on a spectral colorimeter in a 1 cm cell.

In all experiments the organic phase was back-extracted with 0.2 *M* perchloric acid. It was confirmed by preliminary investigations that such acid concentrations were sufficient to assure the balance of lanthanide ion in both phases (100 ± 2%) in one-step reextraction (the time of reextraction is 1 h).

After the phase separation the aqueous phase was alkalized with 0.1 *M* NaOH and the concentration of Ln(III) was determined as above.

From the Ln(III) equilibrium concentrations in the organic and in the aqueous phase the distribution coefficient (*D*) was calculated. The extent of extraction (%*E*) was obtained as earlier [1].

Results and Discussions

The time required to reach equilibrium was determined by measuring the concentration of lanthanide(III) in the aqueous phase as a function of time. The results for the extraction of Yb(III) with $1.00 \cdot 10^{-2}$ *M* H*PMBP* in CCl_4 ($pH = 3.30$) are shown in Fig. 1. The equilibrium was established after 30 min and in further experiments 45 min was accepted as the optimal time of extraction. The same results were obtained for Er(III) and Lu(III).

The *pH* range for the extraction of Er(III), Yb(III) and Lu(III) with H*PMBP* solutions in CCl_4 was determined. The data of the dependence of the extraction extent (%*E*) vs. *pH* are given in Fig. 2. The extraction of these lanthanides(III) starts at $pH \sim 2.8$. The influence of *pH* on Yb(III) and Lu(III) extraction is the same. The efficiency of Yb(III) and Lu(III) extraction is higher than for Er(III) extraction. In further calculations only the linear ascending parts of the extraction curves were examined.

On the basis of the literature data [8, 27, 28] the influence of the side-reactions in the aqueous phase on the extraction process in the range of $pH\, 2 \div 4$ was estimated. It was stated that in the extraction equation the expressions reflecting the formation of Ln(III) complexes with OH^-, ClO_4^- or H*PMBP* anion can be neglected. Thus, the composition of the complexes in the organic phase and the equilibrium constants of the extraction reaction were determined from lg-lg plots of *D* vs. $[H^+]$ or H*PMBP* concentrations.

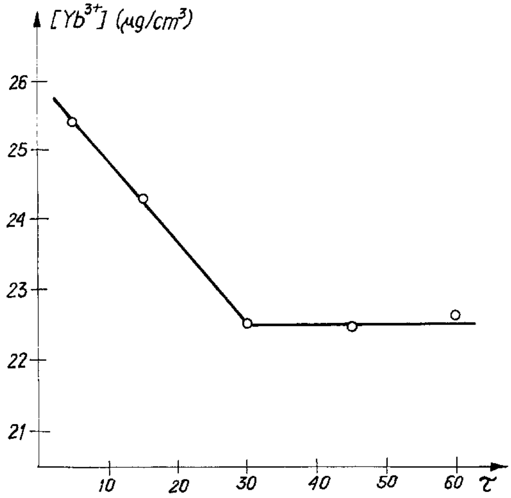

Fig. 1. The concentration of Yb(III) in the aqueous phase as a function of time of extraction. $pH = 3.30$, $C_{\mathrm{Yb}} = 50\,\mu\mathrm{g/cm}^3$, $C_{HPMBP} = 1.00 \cdot 10^{-2}\,M$

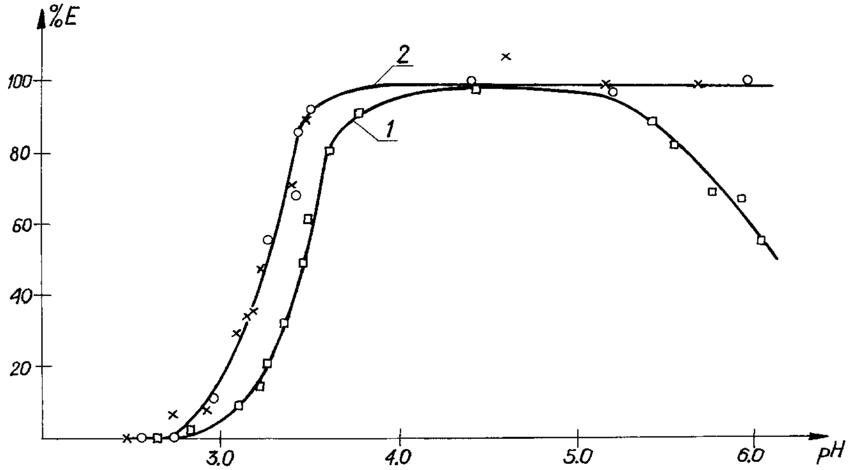

Fig. 2. Plot of the extent of Er(III) (*1* □), Yb(III) (*2* ○) and Lu(III) (*2* ×) extraction vs. pH of the aqueous phase. $C_{Ln} = 50\,\mu\mathrm{g/cm}^3$, $C_{HPMBP} = 1.00 \cdot 10^{-2}\,M$

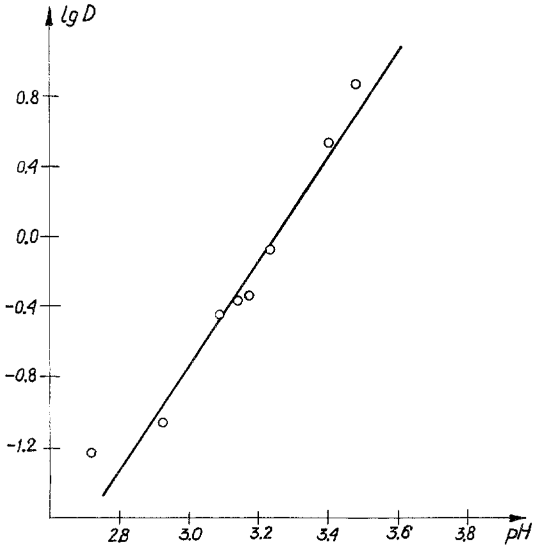

Fig. 3. Effect of the hydrogen ion concentration on the Lu(III) distribution between the aqueous phase and solutions of H*PMBP* in carbon tetrachloride. $C_{\text{Lu}} = 50\,\mu\text{g/cm}^3$, $C_{\text{H}PMBP} = 1.00 \cdot 10^{-2}\,M$

The lg D dependence on the pH of the aqueous phase within the range 2.70–3.70, at constant H*PMBP* concentration ($1.00 \cdot 10^{-2}\,M$) for the Lu(III) extraction is linear with a slope of 3 (Fig. 3). Analogous dependences were obtained for the extraction of Yb(III) (slope 3.2) and Er(III) (slope 3.2). It indicates that three protons per metal ion are released.

These results suggest that the $LnL_3 \cdot n\text{H}L$ complex can be extracted and the extraction may be expressed by the equation:

$$Ln^{3+} + (3+n)\,\text{H}L_{(0)} \rightleftharpoons LnL_3 \cdot n\text{H}L_{(0)} + 3\,\text{H}^+ \tag{1}$$

where Ln^{3+} = Er, Yb, Lu; (0) denotes the organic phase.

Taking into account the acid dissociation constants of H*PMBP* (K_a and K_p) and the distribution coefficient of the molecular form of reagent ($p_{\text{H}L}$), the equilibrium concentration of H*PMBP* in the organic phase ($[\text{H}L]_0$) may be calculated [1]:

$$[\text{H}L]_0 = \frac{C_{\text{H}L}}{1 + \frac{1}{p_{\text{H}L}}\left(1 + \frac{K_a}{[\text{H}^+]} + \frac{[\text{H}^+]}{K_p}\right)} \tag{2}$$

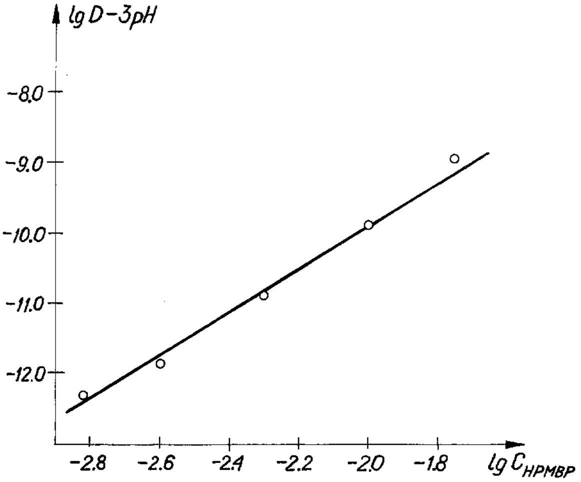

Fig. 4. Effect of the initial concentration of H*PMBP* on the Yb(III) distribution between the aqueous phase and solutions of H*PMBP* in carbon tetrachloride. $C_{\mathrm{Yb}} = 50\,\mu\mathrm{g/cm^3}$

From Eq. (2) it follows that at $\lg K_a = -4.11$, $\lg K_p = -0.28$ [29] and $\lg p_{\mathrm{H}L} = 3.10$ [30] $[\mathrm{H}L]_0 \cong C_{\mathrm{H}L}$ for $1 < pH < 4$ within experimental error (i.e. $[\mathrm{H}L]_0/C_{\mathrm{H}L}$ for $pH = 2$ and $pH = 4$ is 0.9992 and 0.9986, respectively). So, the equilibrium concentration of H*PMBP* in the organic phase was assumed to be equal to its initial concentration in this phase.

To determine the number of H*PMBP* molecules participating in the extraction process, $\lg D$ as a function of the inital concentration of H*PMBP* in the organic phase at constant *pH* of the aqueous phase was measured. The concentration of H*PMBP* changed in the range $1.75 \cdot 10^{-2} - 1.50 \cdot 10^{-3}\,M$. The distribution coefficient was corrected for small changes in hydrogen ion concentration. The dependences of ($\lg D - 3\,pH$) vs. $\lg C_{\mathrm{H}PMBP}$ are straight lines with slopes 3 for Yb(III) (Fig. 4), 2.7 for Lu(III), and 3.2 for Er(III).

These results show that the extraction process of ytterbium, lutetium and erbium with a solution of 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 in carbon tetrachloride (in the mentioned H*PMBP* concentration) may be described by the following equation:

$$Ln^{3+} + 3\,\mathrm{H}L_{(0)} \overset{K_{ex}}{\rightleftharpoons} LnL_{3(0)} + 3\,\mathrm{H}^+ \qquad (3)$$

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

The extraction constants (K_{ex}) calculated from the experimental data maintain satisfactory constancy when the pH and the concentration of the extractant change. The $\lg K_{ex}$ values were calculated by a least square procedure and are given in Table 1.

Table 1. *Extraction parameters for the formation of LnL_3 complexes* (at 21 ± 1 °C, ionic strength 0.1 M; $C_{HPMBP} = 1.00 \cdot 10^{-2}\,M$)

Parameters	Er^{3+}	Yb^{3+}	Lu^{3+}
$\lg K_{ex}$ ($\pm$ 0.03)	-4.22	-3.76	-3.65
$\lg \beta_3^{\times}$	17.41	17.87	17.98
$pH_{0.5}$	3.43	3.23	3.25

From the data for K_{ex} and the values of K_a and p_{HL}, the two-phase stability constants ($\beta_3^{\times}$) for the LnL_3 complexes were calculated as [1]:

$$\lg \beta_3^{\times} = \lg K_{ex} + 3\,pK_a + 3\lg p_{HL} \qquad (4)$$

The results are given in Table 1.

The extraction constants (Table 1) are greater than those for the extraction of Er(III), Yb(III) and Lu(III) with H*PMBP* in chloroform [6] (at 25 ± 1 °C, ionic strength 0.1 *M*). These values are also considerable greater than the extraction constants obtained by *Alstad* and coworkers [23] when H*TTA* in carbon tetrachloride as extractant was used.

Acknowledgements

This paper was included in the problem RP.I.-08 and supported by the Ministry of Science, Higher Education and Technology and the Polish Academy of Sciences.

Some experimental data were obtained by *Anna Kosińska*, undergraduate.

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