Monatshefte für Chemie 121, 585–592 (1990)

Monatshefte für Chemie
Chemical Monthly

Solvent Extraction of Lanthanide Ions with 1-Phenyl-3-Methyl-4-Benzoyl-Pyrazolone-5 (H*PMBP*), II. Extraction of Erbium(III), Ytterbium(III) and Lutetium(III) by H*PMBP* from Aqueous-Methanol Solutions

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Abstract. The solvent extraction of lanthanides(III) (Ln = Er, Yb, Lu) by 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (HL) in carbon tetrachloride from aqueous-methanol phase was investigated. The equilibrium constants for the extraction from aqueous – 50% (v/v) methanol phase (K_{ex}), two-phase stability constants of the complexes LnL_3 (β_3^*) and stability constants of complexes LnL^{2+}, LnL_2^+, LnL_3 (β_n) (Ln = Yb, Lu) were calculated. It was confirmed that the addition of methanol to the aqueous phase causes a synergistic effect. The influence of methanol on the dissociation constant of H*PMBP* (K_a) and the distribution constant of H*PMBP* ($p_{\mathrm{H}L}$) between carbon tetrachloride and water-methanol solutions was investigated.

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*), II. Extraktion von Er(III), Yb(III) und Lu(III) aus Wasser-Methanol-Lösungen

Zusammenfassung. Die Extraktion von Lanthaniden (Ln = Er, Yb, Lu) mittels 1-Phenyl-3-methyl-4-benzoyl-pyrazolon-5 (HL) in Kohlenstofftetrachlorid aus Wasser-Methanol Phase wurde untersucht. Die Werte der Gleichgewichtskonstante für Extraktion aus Wasser – 50% (v/v) Methanol-Phase (K_{ex}), der zweiphasigen Beständigkeitskonstante für die Komplexe LnL_3 (β_3^*), sowie der Stabilitätskonstante des Komplexes LnL^{2+}, LnL_2^+ und LnL_3 (β_n) (Ln = Yb, Lu), wurden berechnet. Es wurde festgestellt, daß die Zugabe von Methanol zur wäßrigen Phase einen synergistischen Effekt hat. Der Einfluß von Methanol auf die Dissoziationskonstante von H*PMBP* (K_a) und die Verteilungskonstante des H*PMBP* ($p_{\mathrm{H}L}$) zwischen organischer und wäßrig-methanolischer Phase wurde untersucht.

Introduction

This paper is a continuation of our studies on the complex and distribution equilibria of lanthanide(III) ions (Ln) with 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (H*PMBP* or HL). Previously [1] we have studied the partition of Er(III), Yb(III) and Lu(III) between aqueous phase and the solution of H*PMBP* in CCl_4.

Now particular attention is given to the influence of methanol (*Me*OH) in aqueous phase on the extraction of Er(III), Yb(III) and Lu(III) with H*PMBP*.

In spite of the interest in H*PMBP* little information is available on the formation constants of its chelates with lanthanide(III) ions as well in aqueous as aqueous-alcoholic solutions. For this reason the complex formation of Yb(III) and Lu(III) with H*PMBP* in CH_3OH-H_2O mixtures was studied by the extraction method.

Moreover, the dissociation constant of H*PMBP* (K_a) in different water-methanol mixtures and the distribution constant of H*PMBP* (p_{HL}) between CCl_4 and water-methanol solutions were examined.

Experimental Part

The materials used have been described previously [1]. Methanol (POCh-Gliwice p.a.) was purified by distillation. All other reagents were analytically pure (POCh-Gliwice).

Determination of Distribution Coefficients of Lanthanide(III)

The experimental procedure and the instruments were the same as reported earlier [1].

The concentration of *Ln*(III) in the aqueous-methanol (polar) phase was 50 µg/cm³. The initial concentration of H*PMBP* (C_{HL}) varied from $1.50 \cdot 10^{-3}$ to $1.50 \cdot 10^{-2} M$.

The distribution coefficients (*D*) of *Ln*(III) were determined as a function of pH^* of the polar phase ($pH^* = -\lg[H^+]$ in water methanol solutions [2]) and the concentration of H*PMBP* in the organic phase at 50% (*v*/*v*) of *Me*OH in the polar phase. The influence of methanol on the distribution coefficient of Er(III), Yb(III) and Lu(III) in the range of concentration 5 to 50% (*v*/*v*) *Me*OH in the polar phase was investigated. In these series the initial concentration of H*PMBP* was purposely matched so that its equilibrium concentration in the organic phase would be constant $[HL_{(0)}] = 1.00 \cdot 10^{-2} M$.

By employing the appointed values of *D*, the equilibrium constants of reaction extraction (K_{ex}) and the stability constants (β_n) of Yb(III) and Lu(III) complexes with H*PMBP* were calculated.

Determination of the Acid Dissociation Constant of H*PMBP* *(*pK_a*) in Water-Methanol Mixtures*

The molecule of H*PMBP* (H*L*) may dissociate to form anionic species (L^-). The acid dissociation constant of H*PMBP* in 25, 50 and 75% (*v*/*v*) methanol-water medium were determined spectrophotometrically (λ = 340 and 350 nm, 1 cm cell). The initial concentration of H*PMBP* in methanol-water mixtures was $2.50 \cdot 10^{-4} M$. The pH^* was changed from ~ 1.7 to ~ 10.5. The pK_a values were calculated from the equation

$$pK_a = \lg\frac{A_L - A}{A - A_{HL}} + pH^*, \tag{1}$$

where A_L and A_{HL} are the absorbance of anionic or neutral form of H*PMBP*, *A* is the absorbance of the solution containing both species.

Determination of the H*PMBP* *Distribution Constant (*p_{HL}*) Between Carbon Tetrachloride and Water-Methanol Solutions*

Equal volumes of the aqueous-methanol and organic phase were stirred for 2 hours. This time had been found sufficient for the establishment of an extraction equilibrium. The initial concentrations of H*PMBP* in CCl_4 were $1.00 \cdot 10^{-2} M$, $2.50 \cdot 10^{-2} M$ and $5.00 \cdot 10^{-2} M$. The p_{HL} for 0, 10, 20, 30, 40 and 50% (*v*/*v*) *Me*OH in the aqueous phase were examined. The pH^* of the polar phase in the range from ~ 1.7 to ~ 10.5 was changed. After the separation of the phases, the pH^* of the polar phase was measured and the equilibrium concentration of H*PMBP* in this phase was determined spectrophotometrically in the presence of 0.1 *M* NaOH (λ = 370 nm, 1 cm or 5 cm cell). The calibration curves were prepared at the same conditions. It was stated that the absorbance of H*PMBP* in 0.1 *M* NaOH is not influenced by *Me*OH. The distribution coefficient of H*PMBP* at different *pH** from the initial and equilibrium concentration of H*PMBP* in the polar phase was calculated.

Results and Discussion

The influence of *pH** on the absorbance of H*PMBP* in water 50% (*v*/*v*) methanol solution is shown in Fig. 1.

The found values of the acid dissociation constant (pK_a) and the distribution constant of reagent (p_{HL}) at different concentration of methanol are given in Table 1.

The dependences of pK_a or lg p_{HL} vs. concentration of *Me*OH in the polar phase are linear (Fig. 2).

Table 1. The values of the acid dissociation constant of H*PMBP* (K_a) in water-methanol mixtures and the distribution constant of H*PMBP* (p_{HL}) between CCl_4 and water-methanol solutions at 21 ± 1 °C, $\mu = 0.1\,M$ ($NaClO_4$)

% (*v*/*v*) of *Me*OH in the polar phase	pK_a (±0.02)	lg p_{HL} (±0.05)
0	4.11 [3]	2.52 [4]
0		3.10
10		2.84
20		2.55
25	4.27	
30		2.43
40		2.31
50	4.45	2.00
75	4.63	

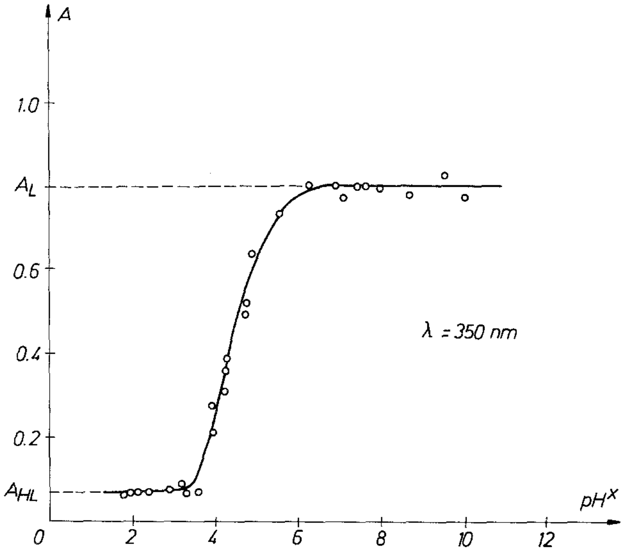

Fig. 1. Absorbance of H*PMBP* vs. *pH** in water − 50% (*v*/*v*) methanol solution at 350 nm ($C_{HL} = 2.50 \cdot 10^{-4} M$, 1 cm cell)

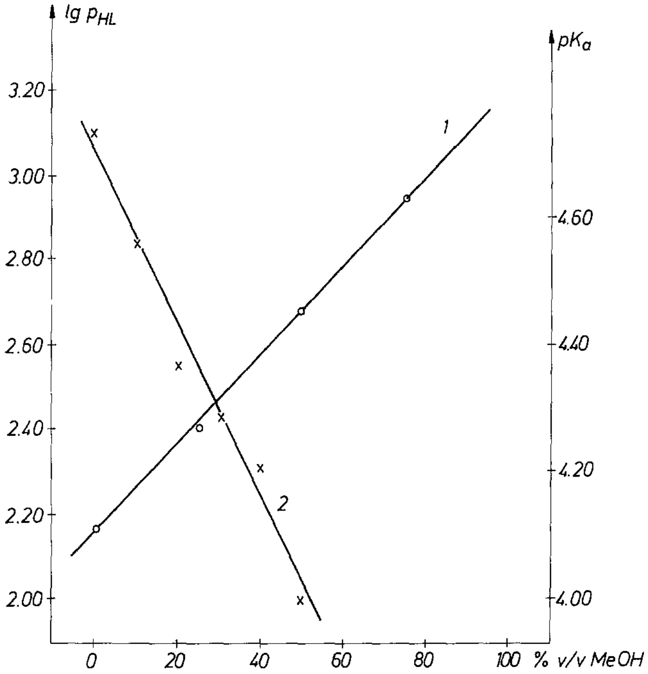

Fig. 2. The dependence of the acid dissociation constant (pK_a) (*1*) and the distribution constant (lg p_{HL}) of H*PMBP* (*2*) vs. the concentration of methanol

The literature data of pK_a [3] and p_{HL} [4] for aqueous solution are also shown in Table 1. The value of lg p_{HL} at 0% (*v*/*v*) *Me*OH obtained by us is greater than this presented by Navratil and Malach [4]. These authors determined the values of p_{HL} from the equilibrium concentration of H*PMBP* in the aqueous phase after reextraction this phase with pure CCl_4.

The composition, the stability and the distribution constants of Yb(III) and Lu(III) complexes with H*PMBP* in water – 50% (*v*/*v*) methanol mixtures were determined from the dependence lg *D* vs. lg $[L^-_{(p)}]$ by the Dyrssen and Sillen method of two-parameters [5]. The concentration of anionic form of H*PMBP* $[L^-_{(p)}]$ in the polar phase was calculated from

$$[L^-_{(p)}] = \frac{C_{HL} \cdot V_{(o)\,in} - 3\,[Ln_{(o)}] \cdot V_{(o)}}{\frac{[H^+]}{K_a}\,(V_{(p)} + p_{HL} \cdot V_{(o)}) + V_{(p)}}, \qquad (2)$$

where (*p*), (*o*) the polar and organic phase, $V_{(o)in}$, $V_{(o)}$, $V_{(p)}$ the initial and the equilibrium volumes of organic or polar phase, respectively, $[Ln_{(o)}]$ the equilibrium concentration of lanthanide ion in the organic phase, K_a the dissociation constant of H*PMBP* in water – 50% (*v*/*v*) *Me*OH mixtures, p_{HL} the distribution constant of H*PMBP* between carbon tetrachloride and water – 50% (*v*/*v*) *Me*OH phase.

The presence of LnL^{2+}, LnL_2^+ and LnL_3 (*Ln*(III) = Yb, Lu) complexes in water – 50% (*v*/*v*) methanol solution was confirmed. The stability constants (β_n) of the complexes, the distribution constant (χ_3) of the extracted complex LnL_3 and its two-phase stability constant (β_3^*) are presented in Table 2. The β_3^* for YbL_3 and LuL_3 complexes were calculated from

$$\beta_3^* = \chi_3 \cdot \beta_3. \qquad (3)$$

The obtained values for Yb and Lu complexes in 50% (*v*/*v*) *Me*OH differ slightly.

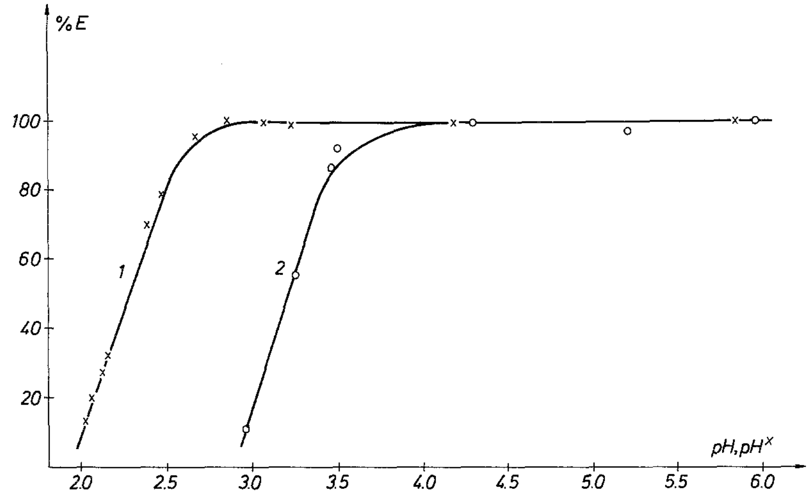

Fig. 3. The efficiency of Yb(III) extraction with H*PMBP* in CCl_4 from: *1* water – 50% (*v*/*v*) methanol phase; *2* aqueous phase [1]. $C_{Yb} = 50\,\mu g/cm^3$, $C_{HL} = 1.00 \cdot 10^{-2} M$

The results for Er(III), Yb(III) and Lu(III) extraction with H*PMBP* solutions in CCl_4, within the region of *pH** from ~ 2 to ~ 6 show that these lanthanide ions are efficiently extracted when the aqueous phase contains methanol. Fig. 3 shows, as an example, the influence of 50% (*v*/*v*) *Me*OH on the extraction of Yb(III) with $1.00 \cdot 10^{-2} M$ H*PMBP* in CCl_4. The values of $pH^*_{0.5}$ (Table 3) are higher about one unit than appropriate values of $pH_{0.5}$ [1].

In order to identify the species extracted, the distribution coefficients were measured at different concentration of hydrogen ion, initial concentration of H*PMBP* in the organic phase, and initial concentration of *Me*OH in the polar phase.

Alike as previously [1], on the basis of the literature data and the values of lg β_n for Yb(III) and Lu(III) found in this work, it was stated that in the range of *pH** 2.0–2.7 the side reactions in the polar phase can be neglected. Thus, in general equation for the extraction process of lanthanide ions with H*PMBP* the term

$$\lg\left(1 + \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{q=1}^{n} \beta_{ijq} \cdot [OH^-]^i [L^-]^j [ClO_4^-]^q\right)$$

Table 2. The values of the stability constants (lg β_n) of the complexes LnL_n^{3-n}, the distribution constants (lg χ_3) and two-phase stability constants (lg β_3^*) for the complexes LnL_3 at 21 ± 1 °C, $\mu = 0.1\,M$ ($NaClO_4$)

Constant	Yb(III)	Lu(III)
lg β_1 (±0.08)	5.56	5.21
lg β_2 (±0.08)	11.21	11.01
lg β_3 (±0.08)	16.95	17.40
lg β_3^* (±0.08)	18.62	19.06
lg χ_3 (±0.05)	1.67	1.66

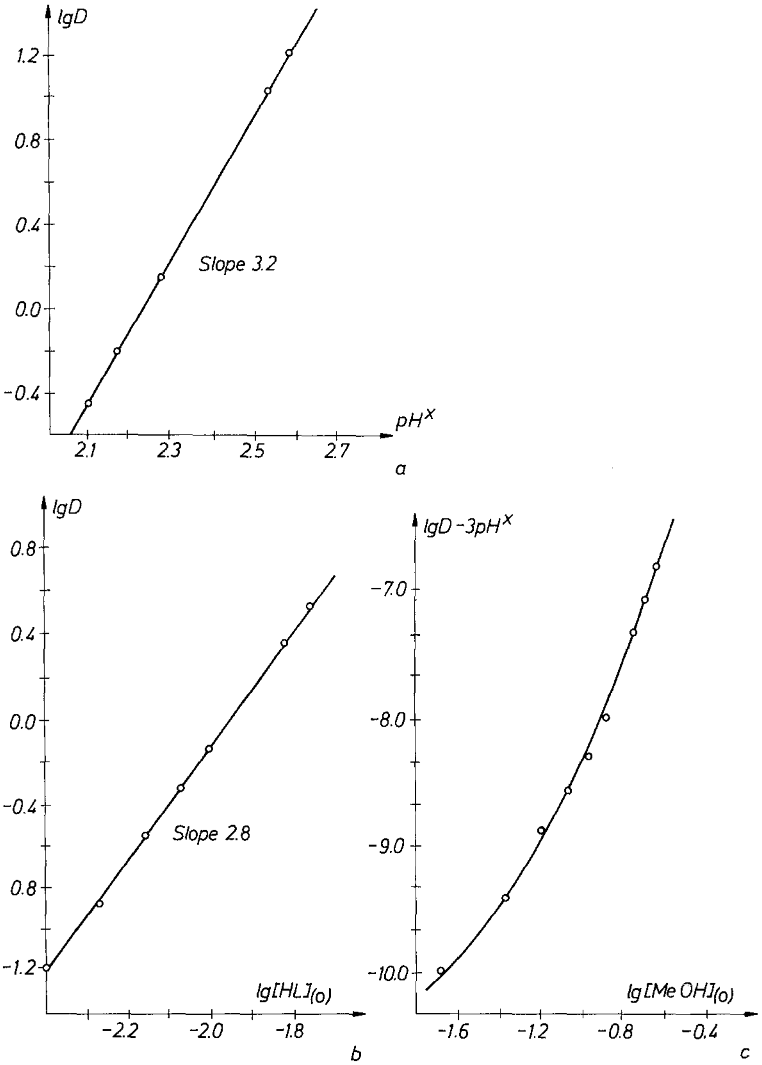

Fig. 4. Extraction of Lu(III) with H*PMBP*: **a** from aqueous – 50% (v/v) methanol phase at $[\mathrm{H}PMBP_{(o)}] = 1.00 \cdot 10^{-2} M$; **b** from aqueous – 50% (v/v) methanol phase at $pH^* = 2.23$; **c** from aqueous-methanol phase at $[\mathrm{H}PMBP_{(o)}] = 1.00 \cdot 10^{-2} M$. $C_{\mathrm{Lu}} = 50\ \mu\mathrm{g/cm}^3$

(where β_i, β_j, β_q are the stability constants of Ln(III) complexes with OH^-, L^- or CLO_4^-) can be omitted. Assuming that the differences in the stability constants of the investigated complexes are not too high, the same simplification may be taken for Er(III).

The experimental data are presented as plots of lg D against pH^*, $\lg[\mathrm{H}L_{(o)}]$ or $\lg[Me\mathrm{OH}_{(o)}]$.

Considering the values of pK_a and $P_{\mathrm{H}L}$ determined, the value of the distribution constant of *Me*OH between CCl_4 and water-methanol [6] and the changes in phase volumes, the equilibrium concentration of H*L* ($[\mathrm{H}L_{(o)}]$) and *Me*OH ($[Me\mathrm{OH}_{(o)}]$) in the organic phase were calculated [7].

Plots of $\lg D$ vs. pH^* for the extraction of Er(III), Yb(III) and Lu(III) with H*PMBP* from water – 50% (v/v) *Me*OH phase all had a slope ~ 3, indicating the

Table 3. Extraction parameters for the extraction of Er(III), Yb(III) and Lu(III) from water – 50% (*v*/*v*) methanol phase with H*PMBP* in CCl_4 at 21 ± 1 °C, $\mu = 0.1$ *M* ($NaClO_4$)

Constant	Er(III)	Yb(III)	Lu(III)
$\lg K_{ex}$ (± 0.03)	−0.79	−0.68	−0.50
$\lg \beta_3^*$ (± 0.03)	18.56	18.67	18.85
$pH_{0.5}^*$ (± 0.02)	2.34	2.30	2.22

release of three protons per metal ions extracted (as an example, Fig. 4 a for Lu(III)). Within the investigated concentration range of H*PMBP*, the dependence of $\lg D$ vs. $\lg [HL_{(o)}]$ are straight lines of slope ~ 3 for all of the ions (as an example Fig. 4 b for Lu(III)).

The results obtained show that the extraction processes of Ln(III) from aqueous-methanol phase with H*PMBP* in CCl_4 may be described as

$$Ln(H_2O)_y^{3+} + 3\,HL_{(o)} \rightleftharpoons LnL_{3\,(o)} + 3\,H^+ + y\,H_2O. \tag{4}$$

The equilibrium constants (K_{ex}) for the extraction from water – 50% (*v*/*v*) methanol phase and two-phase stability constants of the complexes LnL_3 (β_3^*) were calculated from

$$\lg K_{ex} = \lg D - 3\lg p_{HL} - 3pK_a - 3\lg[L_{(p)}^-], \tag{5}$$

$$\lg \beta_3^* = \lg K_{ex} + 3pK_a + 3\lg p_{HL}, \tag{6}$$

and are given in Table 3. The concentration $[L_{(p)}^-]$ was calculated according to Eq. (2).

The presence of methanol in the polar phase causes the increase of K_{ex} and β_3^* [1]. The values of the two-phase stability constants of LnL_3 complexes calculated from Eqs. (3) and (6) are in a fair agreement.

The changes in the distribution coefficient of *Ln*(III) with the methanol concentration in the organic phase show, as an example, Fig. 4 c. Similar dependences were obtained for Er(III) and Yb(III). From Fig. 4 c may be concluded that the LuL_3 chelate seems to be able to add molecules of *Me*OH to form $LuL_3 \cdot (MeOH)_t$ adduct complexes. The composition of these adducts depends on the concentration of *Me*OH in the organic phase. This coordination of unsaturated LnL_3 chelates in the organic phase is characteristic for lanthanide ions of high coordination number. Moreover, it may be assumed that the synergistic effect observed in the investigated systems is related to the formation of these adducts [8].

Acknowledgements

This paper was included in the problem RP. I.08. Some experimental data were obtained by Halina Dziuba, undergraduate.

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Received October 16, 1989. Accepted February 26, 1990