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Solvent Extraction of Lanthanide Ions with 1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5 (*HPMBP*), III: Extraction of Gadolinium(III), Terbium(III), Dysprosium(III), Holmium(III), and Thulium(III) by *HPMBP* from Aqueous Solutions

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Summary. The solvent extraction behaviour of Gd(III), Tb(III), Dy(III), Ho(III), and Tm(III) has been investigated using 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (*HPMBP* or H*L*) in carbon tetrachloride as the extractant. Depending on the concentration of *HPMBP* in the organic phase the chelates LnL_3 [Ln(III) = Gd, Tb, Dy, Ho, Tm] and adducts $LnL_3 \cdot HL$ [Ln(III) = Gd, Tb, Dy, Ho] were extracted. The extraction equilibrium constants (K_{ex3} or K_{ex4}) for the formation of LnL_3 or $LnL_3 \cdot HL$ and the two-phase stability constants of the chelates or adducts (β_3^x, β_4^x) 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-prazolon-5 (*HPMBP*), 3. Mitt.: Extraktion von Gd(III), Tb(III), Dy(III), Ho(III), und Tm(III) aus wäßrigen Lösungen

Zusammenfassung. Die Extraktion von Gd(III), Tb(III), Dy(III), Ho(III), und Tm(III) mittels 1-Phenyl-3-methyl-4-benzoyl-pyrazolon-5 (*HPMBP* oder H*L*) in Kohlenstofftetrachlorid wurde untersucht. In Abhängigkeit von der Konzentration an *HPMBP* in der organischen Phase bildeten sich Chelate vom Typ LnL_3 [Ln(III) = Gd, Tb, Dy, Ho, Tm] and Addukte vom Typ $LnL_3 \cdot HL$ [Ln(III) = Gd, Tb, Dy, Ho]. Die Werte der Extraktions-Gleichgewichtskonstanten (K_{ex3} oder K_{ex4}) für LnL_3 oder $LnL_3 \cdot HL$, sowie die Zweiphasen-Beständigkeitskonstanten (β_3^x, β_4^x) der Chelate oder Addukte wurden berechnet.

Introduction

Previously it was shown that the heavy lanthanides (*Ln*) are extracted by 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (*HPMBP* or H*L*) solutions in CCl_4 as LnL_3 complexes [Ln(III) = Er, Yb, Lu] [1] and that the addition of methanol to the aqueous phase causes a synergistic effect [2] which is related to the formation of adduct complexes with molecules of methanol.

In continuation of our studies on the extraction equilibria of lanthanide(III) ions by means of *HPMBP* we present now the results of the Gd(III), Tb(III), Dy(III), Ho(III), and Tm(III) extraction from aqueous phase.

Experimental Part

Initial solutions of $Ln(ClO_4)_3$ [Ln(III) = Gd, Tb, Dy, Ho, and Tm] were prepared by solving Gd_2O_3 (Koch Light Lab., 99.9% pure), Tb_4O_7 (Rare Earth Products Limit., 99.9%), Dy_2O_3, Ho_2O_3 (Fluka 99.9% pure), Tm_2O_3 (Johnson Matthey, Chemicals Ltd, specpure) in $3M$ perchloric acid. The metal content was estimated by *EDTA* titration with xylenol orange as indicator [3]. All other materials used have been described previously [1].

The experimental procedure, the method of metal determination, and the instruments were the same as reported earlier [1].

The distribution coefficients (D) of Gd(III), Tb(III), Dy(III), Ho(III), and Tm(III) were determined in two series of measurements:

(i) with fixed *HPMBP* concentration ($C_{HL} = 1.00 \cdot 10^{-2} M$, $2.00 \cdot 10^{-2} M$, $3.00 \cdot 10^{-2} M$, $4.00 \cdot 10^{-2} M$) and varied pH (from ~ 2.2 to ~ 3.8);

(ii) with varied *HPMBP* concentration (C_{HL} from $1.0 \cdot 10^{-3} M$ to $4.00 \cdot 10^{-2} M$) and varied pH.

In all extraction experiments the concentration of the lanthanide in the aqueous phase was $2.5 \cdot 10^{-4} M$.

Results and Discussion

The pH range for the extraction of the lanthanides with *HPMBP* solutions in CCl_4 was determined. The data of the dependence of the extraction extent (%E) vs. pH for Gd(III) and Tm(III) are given in Fig. 1. The influence of pH on Tb(III), Dy(III) and Ho(III) extraction is the same and the extraction curves of these ions are between the curves for Gd(III) and Tm(III), respectively.

The overall reaction for the extraction of Gd(III), Tb(III), Dy(III), Ho(III), and Tm(III) with *HPMBP* can be represented by Eq. (1) where the subscript (0) refers to the organic phase:

$$Ln(H_2O)_m^{3+} + (3+n)HL_{(0)} \rightleftharpoons LnL_3 \cdot n\,HL_{(0)} + 3\,H^+ + m\,H_2O \qquad (1)$$

Similarly, as in the extraction of Er(III), Yb(III), and Lu(III) with *HPMBP* [1] the influence of side reaction in the aqueous phase in the given pH range can

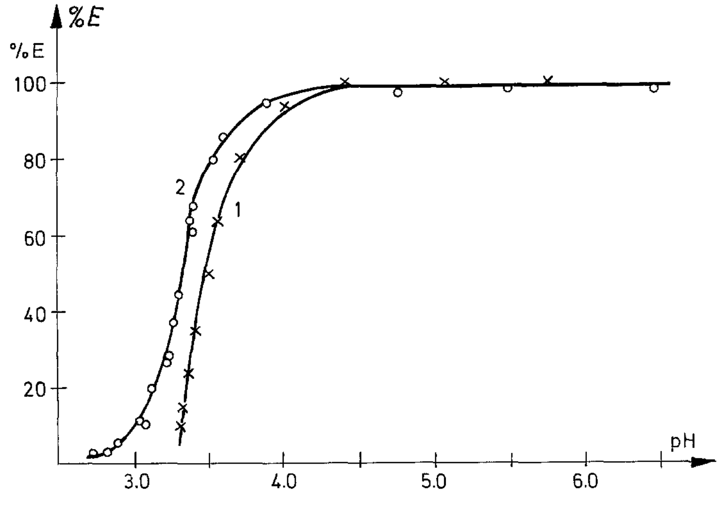

Fig. 1. The efficiency of Gd(III) (curve *1*) and Tm(III) (curve *2*) extraction with *HPMBP* in CCl_4 from aqueous phase; $C_{Ln} = 2.5 \cdot 10^{-4} M$, $C_{HL} = 1.00 \cdot 10^{-2} M$

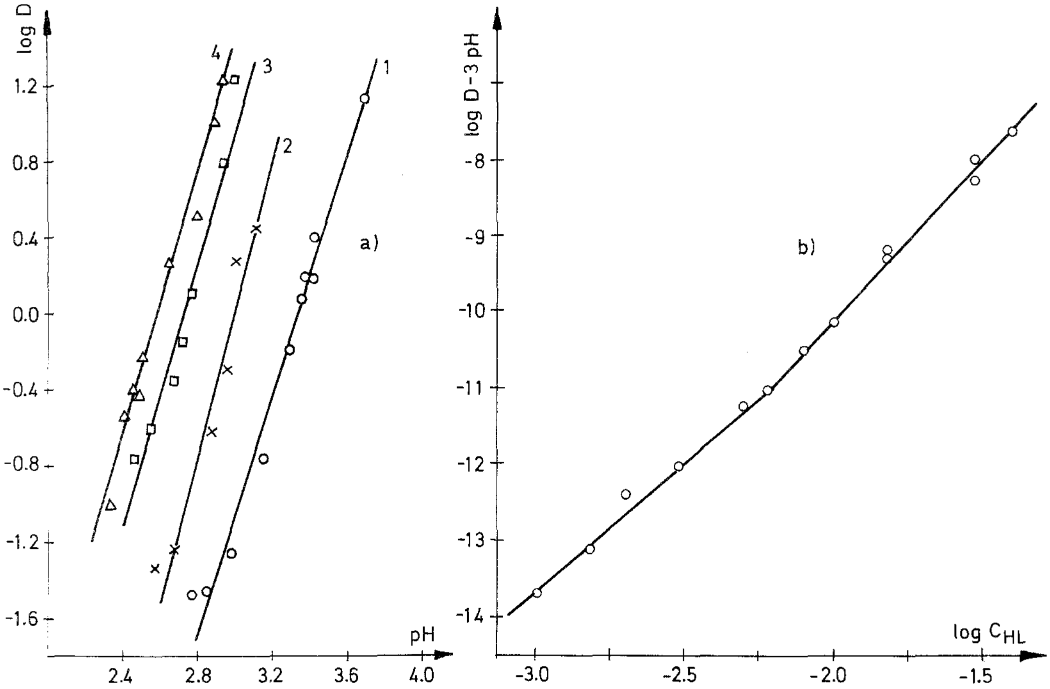

Fig. 2. Extraction of Ho(III) with *HPMBP* in CCl_4, $C_{Ho} = 2.5 \cdot 10^{-4} M$. **a** Plots of $\lg D$ vs. *pH* of aqueous phase for *HPMBP* variation: curve *1*: $1.00 \cdot 10^{-2} M$, *2*: $2.00 \cdot 10^{-2} M$, *3*: $3.00 \cdot 10^{-2} M$, *4*: $4.00 \cdot 10^{-2} M$. **b** Plots of ($\lg D - 3pH$) vs. $\lg C_{HL}$

be neglected. Moreover, the equilibrium concentration of *HPMBP* in the organic phase is assumed to be equal to its initial concentration in this phase [1].

The equilibrium given by the Eq. (1) is quantitatively described by Eq. (2),

$$\lg D = \lg K_{ex} + 3pH + (3 + n) \lg C_{HL} . \tag{2}$$

Plots of $\lg D$ vs. *pH* for the extraction of Ho(III) and Tm(III) (as an example) are presented in Figs. 2 a and 3 a. The third order *pH* dependences for Ho(III), Tm(III) and at the same time for Gd(III), Tb(III) and Dy(III) extraction were obtained.

In Figs. 2 b and 3 b the plots of ($\lg D - 3pH$) vs. $\lg C_{HL}$ for Ho(III) and Tm(III) are shown. For the extraction of Tm(III) the slope of this dependence is about 3 in the whole investigated range of the extractant concentration. This indicates that in the extraction process of Tm(III) with *HPMBP* 3 molecules of extractant are involved and the chelate TmL_3 is formed. In the case of Ho(III), similarly as for Gd(III), Tb(III), and Dy(III), the experimental points on the plots ($\lg D - 3pH$) vs. $\lg C_{HL}$ curves with the slope ~ 3 and ~ 4 for the lower and higher concentration of *HPMBP*, respectively.

Such results show that – depending on the concentration of extractant – the chelates LnL_3 [Ln(III) = Gd, Tb, Dy, Ho, Tm] and adducts $LnL_3 \cdot HL$ [Ln(III) = Gd, Tb, Dy, Ho, Tm] are extracted into the organic phase.

Thus, the processes of extraction of the investigated lanthanide ions can be

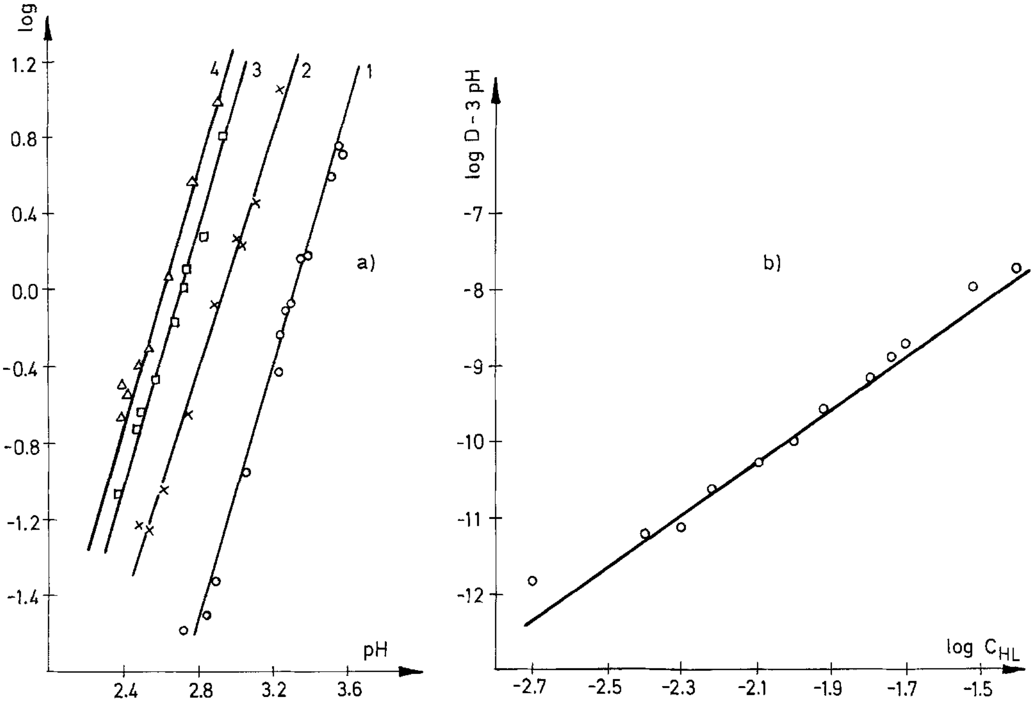

Fig. 3. Extraction of Tm(III) with *HPMBP* in CCl_4, $C_{Tm} = 2.5 \cdot 10^{-4}\,M$. **a** Plots of $\lg D$ vs. pH of aqueous phase for *HPMBP* variation: curve *1*: $1.00 \cdot 10^{-2}\,M$, *2*: $2.00 \cdot 10^{-2}\,M$, *3*: $3.00 \cdot 10^{-2}\,M$, *4*: $4.00 \cdot 10^{-2}\,M$. **b** Plots of $(\lg D - 3pH)$ vs. $\lg C_{HL}$

written as

$$Ln(H_2O)_m^{3+} + 3\,HL_{(0)} \overset{K_{ex3}}{\rightleftharpoons} LnL_{3(0)} + 3\,H^+ + m\,H_2O \tag{3}$$

for Tm(III) at C_{HL} from $1.0 \cdot 10^{-3}\,M$ to $4.00 \cdot 10^{-2}$ M and Gd(III), Tb(III), Dy(III), Ho(III) at C_{HL} from $1.0 \cdot 10^{-3}\,M$ to about $1.00 \cdot 10^{-2}\,M$ and

$$Ln(H_2O)_m^{3+} + 4\,HL_{(0)} \overset{K_{ex4}}{\rightleftharpoons} LnL_3 \cdot HL_{(0)} + 3\,H^+ + m\,H_2O \tag{4}$$

for Gd(III), Tb(III), Dy(III), Ho(III) at C_{HL} from about $1.00 \cdot 10^{-2}\,M$ to $4.00 \cdot 10^{-2}\,M$.

The extraction constants (K_{ex3} and K_{ex4}) were calculated from Eq. (2) for $n=0$ and $n=1$, respectively. The two-phase stablility constants (β_3^x and β_4^x) of the complexes LnL_3 and $LnL_3 \cdot HL$ were estimated as

$$\lg \beta_3^x = \lg K_{ex3} + 3pK_a + 3\lg p_{HL}, \tag{5}$$

$$\lg \beta_4^x = \lg K_{ex4} + 3pK_a + 4\lg p_{HL}, \tag{6}$$

where K_a is the dissociation constant of *HPMBP* [4] and p_{HL} is the distribution constant of *HPMBP* [2].

Table 1 lists the equilibrium constants ($\lg K_{ex3}$, $\lg K_{ex4}$), the two-phase stability constants ($\lg \beta_3^x$, $\lg \beta_4^x$), and the values of $pH_{0.5}$.

The values of $\lg K_{ex3}$ increase with the increase the atomic number of the rare earth ions. A linear dependence is observed.

Table 1. Extraction parameters for the extraction of Gd(III), Tb(III), Dy(III), Ho(III), and Tm(III) from aqueous phase with *HPMBP* in CCl_4 at 21 ± 1°C, $\mu = 0.1\,M$ ($NaClO_4$)

Constant	Gd(III)	Tb(III)	Dy(III)	Ho(III)	Tm(III)
lg K_{ex3} (± 0.03)	-4.42	-4.66	-4.03	-4.43	-3.78
lg K_{ex4} (± 0.03)	-2.14	-2.27	-1.56	-2.10	
lg β_3^x (± 0.03)	17.21	16.97	17.60	17.20	17.85
lg β_4^x (± 0.03)	22.59	22.46	23.17	22.63	
$pH_{0.5}$ (± 0.02) (at $C_{HL} = 1.00 \cdot 10^{-2} M$)	3.53	3.44	3.41	3.34	3.36

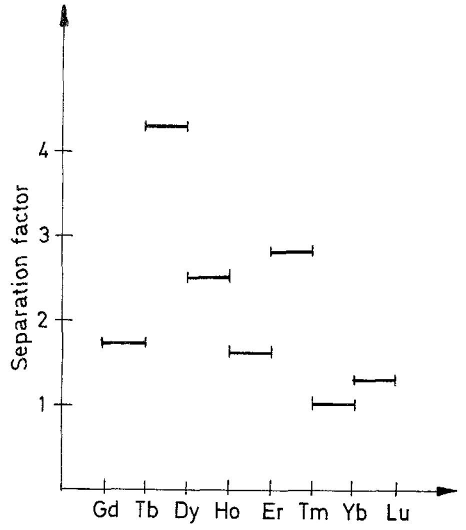

Fig. 4. Variation of the separation factor as a function of the adjacent rare earth pair

In order to characterize the possibilities of separation of *Ln*(III) with *HPMBP* in CCl_4, the separation factors of particular pairs of heavy lanthanide(III) ions during the extraction from aqueous and aqueous − 50% vol. methanol phase were calculated and the influence of methanol was estimated [5]. The separation factors (*S*) between the adjacent pair of lanthanides in the subgroup Gd − Lu are presented in Fig. 4. The value of *S* varies within this series being the largest for the Tb − Dy pair ($S_{Tb-Dy} = 4.3$) and the lowest for the Tm − Yb ($S_{Tm-Yb} = 1.0$) and Yb − Lu ($S_{Yb-Lu} = 1.3$) pairs.

These values are comparable with the ones reported by Alstad et al. [6] for the extraction of lanthanide(III) ions with *HTTA* in CCl_4 and by Roy and Nag [7] for *HPMBP* in $CHCl_3$.

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