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

III. Extraction of Ytterbium(III) and Holmium(III) by *PAN* from Aqueous-Methanol Solutions

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The solvent extraction of Yb(III) and Ho(III) by 1-(2-pyridylazo)-2-naphthol (*PAN* or H*L*) in carbon tetrachloride from aqueous-methanol phase has been studied as a function of $pH^{\times}$ and the concentration of *PAN* or methanol (*Me*OH) in the organic phase. When the aqueous phase contains above ~ 25% *v/v* of methanol the synergistic effect was increased. The equation for the extraction reaction has been suggested as:

$$Ln\,(\mathrm{H_2O})^{3+}_{m(p)} + 3\,\mathrm{H}L_{(o)} + t\,Me\mathrm{OH}_{(o)} \overset{K_{ex}}{\rightleftharpoons}$$
$$LnL_3(Me\mathrm{OH})_{t(o)} + 3\,\mathrm{H}^+_{(p)} + m\,\mathrm{H_2O}$$

where: $Ln^{3+} = \mathrm{Yb, Ho}$;

$$t = 3 \text{ for } C_{Me\mathrm{OH}\,in.} \in (\sim 25 - 50)\%\ v/v;$$
$$t = 0 \text{ for } C_{Me\mathrm{OH}\,in.} \in (\sim 5 - 25)\%\ v/v.$$

The extraction equilibrium constants (K_{ex}) and the two-phase stability constants ($\beta_3^{\times}$) for the $LnL_3(Me\mathrm{OH})_3$ complexes have been evaluated.

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

Extraktion von Ionen der Seltenerdenmetalle mit 1-(2-Pyridilazo)-2-naphthol (PAN). III: Extraktion von Yb(III) *und* Ho(III) *aus Wasser—Methanol-Lösungen*

Die Extraktion von Yb(III) und Ho(III) mittels 1-(2-Pyridilazo)-2-naphthol (*PAN* oder H*L*) in Kohlenstofftetrachlorid aus Wasser—Methanol in Abhängigkeit vom $pH^{\times}$ sowie von der Konzentration von *PAN* oder Methanol (*Me*OH) in der organischen Phase wurde untersucht. Es wurde eine Zunahme der Extraktionsfähigkeit festgestellt, wenn die wässerige Lösung ~ 25% *v/v*

Methanol enthält. Die folgenden Gleichungen beschreiben die Extraktionsreaktion:

$$Ln(\mathrm{H_2O})^{3+}_{m(p)} + 3\,\mathrm{H}L_{(o)} + t\,Me\mathrm{OH}_{(o)} \overset{K_{ex}}{\rightleftharpoons}$$
$$LnL_3(Me\mathrm{OH})_{t(o)} + 3\,\mathrm{H}^+_{(p)} + m\,\mathrm{H_2O}$$

wobei: $Ln^{3+} = \mathrm{Yb, Ho}$;

$t = 3$ für $C_{Me\mathrm{OH}\,in.} \in (\sim 25 - 50)\%\ v/v$;
$t = 0$ für $C_{Me\mathrm{OH}\,in.} \in (\sim 5 - 25)\%\ v/v$.

Die Werte der Extraktions-Gleichgewichtskonstante (K_{ex}) sowie der zweiphasigen Beständigkeitskonstante ($\beta_3^{\times}$) für die Komplexe $LnL_3(Me\mathrm{OH})_3$ wurden berechnet.

Introduction

The extraction of Yb(III) by 1-(2-pyridylazo)-2-naphthol (*PAN* or H*L*) from aqueous and aqueous-ethanol solutions has been described in previous papers[1,2].

In the present paper the study of these type of systems is continued and the results of the investigation of the extraction of Ho(III) from aqueous phase and Yb(III) or Ho(III) from aqueous—methanol solutions with *PAN* in carbon tetrachloride are given.

Experimental

Procedure and Reagents

The distribution coefficient (D) of Ln(III) [Ln(III) = Yb, Ho] was obtained from extraction and reextraction experiments as:

$$D = \frac{[Ln]_{(o)}}{[Ln]_{(p)}} \tag{1}$$

where $[Ln]_{(o)}$, $[Ln]_{(p)}$ are the equilibrium concentrations of Ln(III) in the organic and the aqueous—methanol (polar) phase.

The experimental procedure and the calculations were described previously[1,2].

In the course of extracting Ho(III) with *PAN* solutions in carbon tetrachloride from aqueous phase a turbidity of this phase and the occurrence of a suspension at the phase boundary was observed. The extraction efficiency (%E) of Ho(III) was calculated from the following equation[3]:

$$\%E = \frac{q_{(o)} \cdot 100}{q}\,\% \tag{2}$$

where $q_{(o)}$ is the Ho(III) content in the organic phase in the state of equilibrium (μg) and q is the initial Ho(III) content in the aqueous (or polar) phase (μg).

It was observed that the addition of methanol (MeOH) ($d = 0.791\ \mathrm{g/cm^3}$, POCh-Gliwice p.a.) to the aqueous phase during extraction with *PAN* in $\mathrm{CCl_4}$ causes an increase of the Yb(III) distribution coefficient (Fig. 1), prevents the precipitation and increases the efficiency of Ho(III) extraction (Fig. 2).

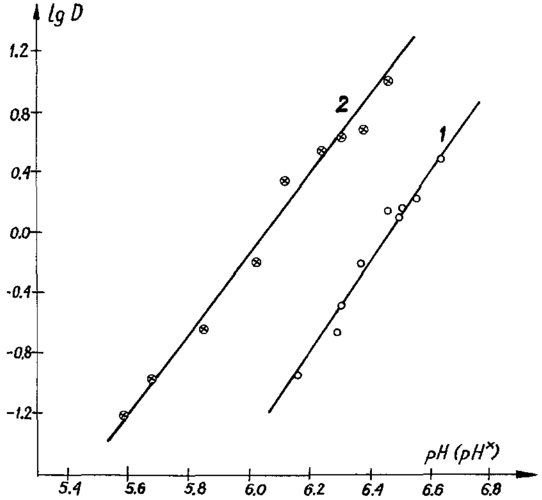

Fig. 1. Distribution coefficient of Yb(III) as a function of $pH^{\times}$ (or pH) of the polar phase. Curves: *1* extraction from aqueous phase[1], *2* from water—50% v/v methanol phase. $C_{\mathrm{Yb}\,in.} = 50\,\mu\mathrm{g/cm}^3$, $[\mathrm{H}L]_{(o)} = 1.00 \cdot 10^{-2}\,M$

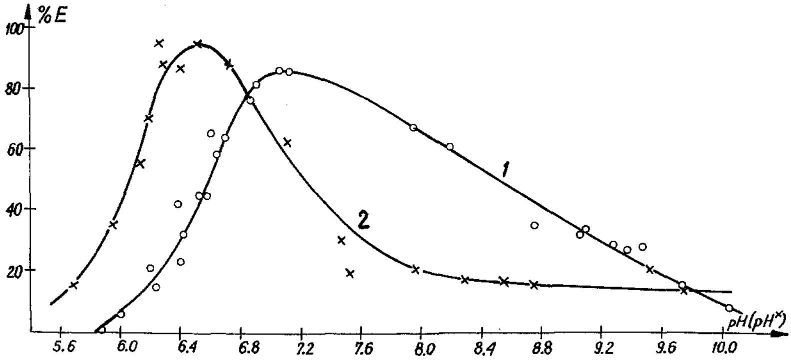

Fig. 2. The efficiency of Ho(III) extraction with PAN in CCl_4 from: *1* aqueous phase, *2* water—50% v/v methanol phase. $C_{\mathrm{Ho}\,in.} = 50\,\mu\mathrm{g/cm}^3$, $[\mathrm{H}L]_{(o)} = 1.00 \cdot 10^{-2}\,M$

It was confirmed that Yb(III) and Ho(III) do not extract with pure CCl_4 from water—methanol phase.

The concentration of Ln(III) in the aqueous or aqueous—methanol phase ($C_{Ln\,in.}$) was always $50\,\mu\mathrm{g/cm}^3$.

The initial concentration of methanol in the polar phase ($C_{MeOH\,in.}$) and PAN in the organic phase ($C_{\mathrm{HL}\,in.}$) varied from 5 to 50% v/v and from $2.50 \cdot 10^{-3}$ to $4.00 \cdot 10^{-2}\,M$, respectively.

The $pH^{\times}$ of the polar phase ($pH^{\times} = -\lg[H^+]$ in water—methanol solutions[4]) was adjusted with hexamethylenetetramine buffer[5] and was measured with an accuracy $\pm 0.02\, pH^{\times}$ division.

The constant ionic strength ($\mu = 0.1\,M$) was maintained by adding sodium perchlorate.

The changes of the polar and organic phases volumes at different concentrations of methanol in the polar phase were determined.

The distribution coefficients of Yb(III) and Ho(III) were determined according to eqn. (1) in three series of measurements:

a) with fixed *PAN* and *Me*OH concentrations, varied $pH^{\times}$,

b) with fixed $pH^{\times}$ and *PAN* concentration, varied *Me*OH concentration,

c) with fixed $pH^{\times}$ and *Me*OH concentration, varied *PAN* concentration.

In series a) and b) the constant equilibrium concentration of *PAN* in the organic phase ($[\mathrm{H}L]_{(o)} = 1.00\cdot 10^{-2}\,M$) was maintained.

Taking into account the volume changes, the balance of *Ln*(III) in both phases ($100 \pm 2\%$) and the initial concentration of *PAN* ($C_{\mathrm{H}L\,in.}$) in series a) and b) were calculated.

The distribution constants ($p_{\mathrm{H}L}$) between carbon tetrachloride and water—methanol solutions ($\mu = 0.1\,M$) were obtained as previously[2].

The distribution constant of methanol ($p_{Me\mathrm{OH}}$) between carbon tetrachloride and water ($\mu = 0.1\,M$) was determined chromatographically. Investigations were carried out using the chromatograph GIDE GCHF 18.3. Detector flame-ionization gauge. Conditions of work: carrier gas—Ar, packing—10% skwalan on chromosorb W, column 3 m, temp. 90 °C. The measurements were done for the concentration of *Me*OH from 10 to 50% *v/v*.

Results

Fig. 3 shows the dependence of the *PAN* distribution coefficient ($D_{\mathrm{H}L}$) between CCl_4 and water—50% *v/v* methanol phase ($\mu = 0.1\,M$) vs. $pH^{\times}$ of this phase. As can be seen from Fig. 3 $D_{\mathrm{H}L}$ is constant at the $pH^{\times}$ range from ~ 3.5 to ~ 9.0 and allow to determine the value of the distribution constant of *PAN* ($\lg p_{\mathrm{H}L} = 2.16$).

The values of $p_{\mathrm{H}L}$ at the other concentrations of methanol in the polar phase (from 0 to 50% *v/v*) were obtained in the same way.

Fig. 4 shows the dependence of $\lg p_{\mathrm{H}L}$ on the methanol concentration in the polar phase. The distribution constant of *PAN* between CCl_4 and the water—methanol phase ($\mu = 0.1\,M$) decreases with the increase of the alcohol concentration in the polar phase.

It was shown previously[2] that the extraction of Yb(III) with *PAN* in CCl_4 from water—ethanol (*R*OH) solutions can be described by the following equation:

$$\mathrm{Yb(H_2O)}^{3+}_{m(p)} + (3+n)\mathrm{H}L_{(o)} + t\,R\mathrm{OH}_{(o)} \overset{K_{ex}}{\rightleftharpoons} \mathrm{Yb}L_3(\mathrm{H}L)_n(R\mathrm{OH})_{t(o)} + 3\,\mathrm{H}^+_{(p)} + m\,\mathrm{H_2O} \qquad (3)$$

where the subscripts (*p*) and (*o*) denote the polar and the organic phase, respectively; H*L* = *PAN*; and K_{ex} is the extraction constant.

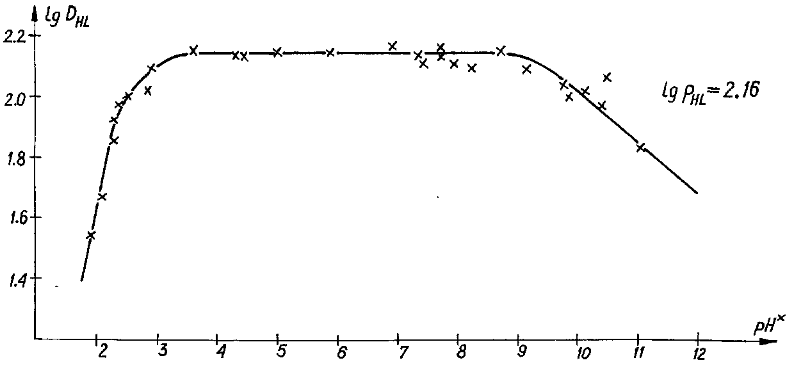

Fig. 3. The distribution coefficient of *PAN* (D_{HL}) between carbon tetrachloride and water—50% *v*/*v* methanol solution as a function of $pH^{\times}$ of the polar phase. $C_{HL\,in.} = 1.00 \cdot 10^{-2} M$, $\mu = 0.1\,M$

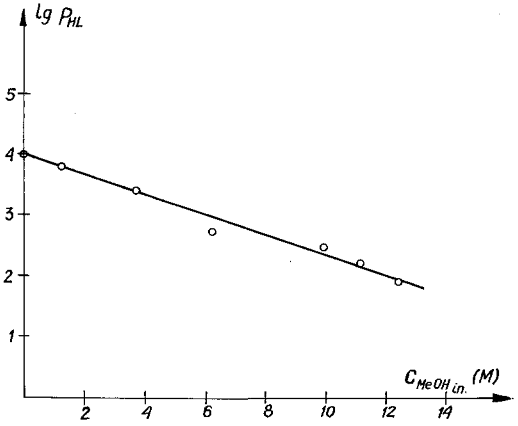

Fig. 4. The dependence of the *PAN* distribution constant (p_{HL}) between carbon tetrachloride and water—methanol phase. $C_{HL\,in.} = 1.00 \cdot 10^{-2} M$, $pH^{\times} = 6.39$, $\mu = 0.1\,M$

In consideration of the side reactions in the polar phase, the distribution coefficient of Yb(III) (*D*) can be expressed as [2]:

$$\lg D + \lg (1 + \beta_1 [L^-]_{(p)}) = \lg K_{ex} + (3 + n) \lg [HL]_{(o)} + \\ + 3\,pH^{\times} + t \lg [ROH]_{(o)} \qquad (4)$$

where β_1 is the stability constant of the complex YbL^{2+}; $[L^-]_{(p)}$, $[HL]_{(o)}$ are the equilibrium concentrations of anionic and neutral species of *PAN* in the polar and organic phases, respectively; and $[ROH]_{(o)}$ is the equilibrium concentration of alcohol in the organic phase.

Taking into account the hydrogen ion concentration, volume changes of phases, the appropriate values of p_{HL} (Fig. 4), and the acid dissociation constants of *PAN* (K_a, K_p) in the aqueous—methanol solutions containing a suitable concentration of methanol[6,7], values of $[L^-]_{(p)}$ and $[HL]_{(o)}$ were calculated from equations given previously[1,2]. $[ROH]_{(o)}$ was calculated with the value of $p_{MeOH} = 1.74 \cdot 10^{-2}$.

By the spectrophotometric method of *Malinowska* and *Czakis-Sulikowska*[8] it was shown that Yb(III) and Ho(III) form with *PAN* in water—50% v/v methanol solutions the complexes of the type LnL^{2+} with the stability constants $\lg \beta_1 = 10.17$ for YbL^{2+} and $\lg \beta_1 = 9.56$ for HoL^{2+} complexes. These complexes were formed at the same conditions which exists in the extraction process in the polar phase.

As can be seen from eqn. (4) the plots of $\lg D\ (1 + \beta_1[L^-]_{(p)})$ vs. $pH^\times$ at constant $[HL]_{(o)}$ and $[ROH]_{(o)}$ or that of $\lg D\ (1 + \beta_1[L^-]_{(p)})$ vs. $\lg [HL]_{(o)}$ at a certain hydrogen ion concentration and at constant $[ROH]_{(o)}$ should be straight lines of slopes 3 and $(3 + n)$, respectively. At the same time, from distribution experiments performed at constant $pH^\times$ and $[HL]_{(o)}$ the value of t can be obtained from the slope of $\lg D$ $(1 + \beta_1[L^-]_{(p)})$ vs. $\lg [ROH]_{(o)}$.

Extraction as a Function of pH$^\times$ (Series "a")

Fig. 5 shows the dependence of $\lg D\ (1 + \beta_1[L^-]_{(p)})$ vs. $pH^\times$ of water—50% v/v methanol phase. The extraction process was investigated in the $pH^\times$ range from ~ 5.4 to ~ 6.7 for $[HL]_{(o)} = 3.00 \cdot 10^{-2}\,M$ [curve 1 for Yb(III)] and $[HL]_{(o)} = 1.00 \cdot 10^{-2}\,M$ [curves 2, 3 for Yb(III) and Ho(III), respectively]. As to be expected for trivalent cations the slopes of these plots are about 3. This indicates that in both cases three protons are lost. With increase of the initial concentration of *PAN* the extraction curves move towards lower values of $pH^\times$ (Fig. 5, curves 1 and 2).

Extraction as a Function of Methanol Concentration (Series "b")

In these series of measurements the distribution coefficient of Ln(III) at constant $pH^\times$ of the water—methanol phase [$pH^\times = 6.26$ and 6.34 for Yb(III), $pH^\times = 6.26$ for Ho(III)] and $[HL]_{(o)} = 1.00 \cdot 10^{-2}\,M$ was investigated. The initial concentration of methanol in the polar phase varied from 5 to 50% v/v.

Fig. 6 shows the results as the dependence of $\lg D\ (1 + \beta_1[L^-]_{(p)})$ vs. $\lg [MeOH]_{(o)}$ [curves 1, 2 for Yb(III), curve 3 for Ho(III)].

It is seen from Fig. 6 that the extraction curves have two asymptotes, one of slope 0 (up to the initial concentration of $MeOH$ in the polar phase ~ 25% v/v) and the other of slope ~ 3 (above ~ 25% v/v of the

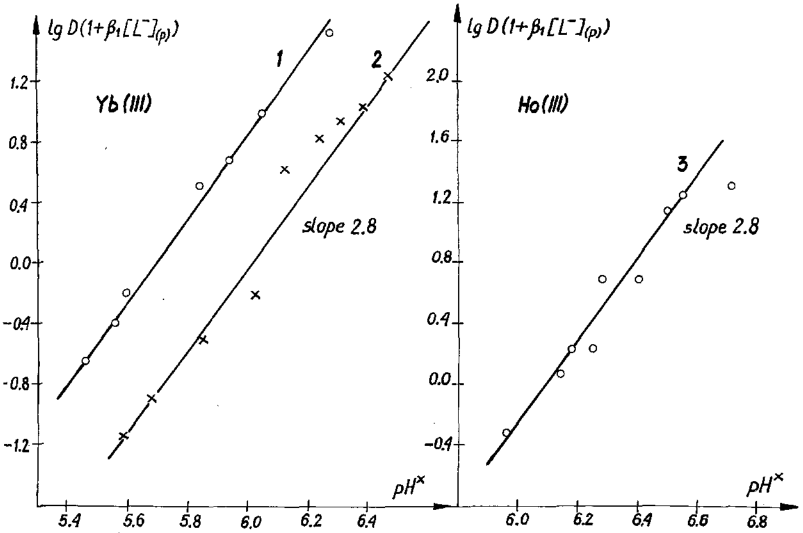

Fig. 5. The dependence of lg D $(1 + \beta_1[L^-]_{(p)})$ vs. $pH^\times$ of water—50% v/v methanol phase. Curves: *1* extraction of Yb(III) at $[\mathrm{H}L]_{(o)} = 3.00 \cdot 10^{-2} M$, *2* extraction of Yb(III) at $[\mathrm{H}L]_{(o)} = 1.00 \cdot 10^{-2} M$, *3* extraction of Ho(III) at $[\mathrm{H}L]_{(o)} = 1.00 \cdot 10^{-2} M$. $C_{Ln\,in.} = 50\,\mu g/cm^3$

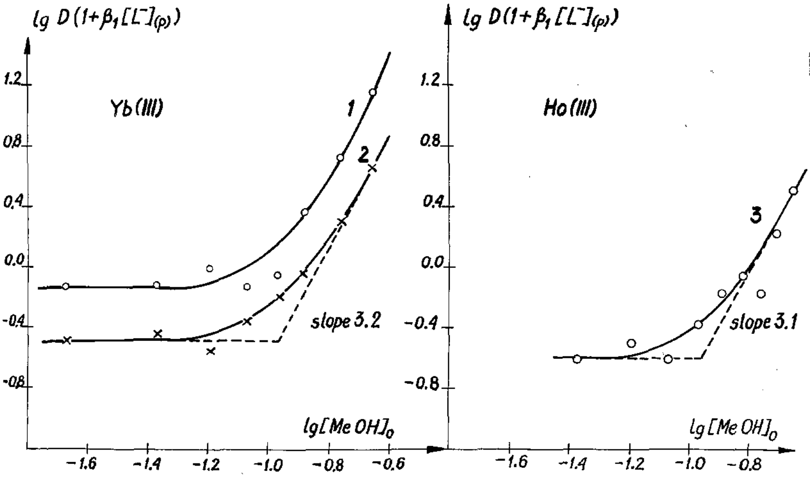

Fig. 6. The dependence of lg D $(1 + \beta_1[L^-]_{(p)})$ vs. lg $[Me\mathrm{OH}]_{(o)}$ at $[\mathrm{H}L]_{(o)} = 1.00 \cdot 10^{-2} M$. Curves: *1*, *2* for the extraction of Yb(III) at $pH^\times = 6.34$ and 6.26, respectively, *3* for the extraction of Ho(III) at $pH^\times = 6.26$. $C_{Ln\,in.} = 50\,\mu g/cm^3$

initial concentration of methanol). Thus, the extraction in the lower $[MeOH]_{(o)}$ region is independent of the concentration of methanol in the polar phase. In the higher region of $[MeOH]_{(o)}$, on the other hand, the extraction is dependent on the third order of $[MeOH]_{(o)}$. This indicates that in the extraction process of Yb(III) and Ho(III) from water—methanol phase at the initial concentration of methanol in the polar phase from ~ 25 to 50%₀ v/v participate 3 molecules of MeOH [$t = 3$ in eqn. (4)]. When the initial concentration of methanol in the polar phase is lower than ~ 25%₀ v/v t in eqn. (4) is equal O.

Extraction as a Function of PAN Concentration (Series "c")

The influence of *PAN* concentration on the *Ln*(III) extraction at constant initial concentration of *Me*OH in the polar phase (50% v/v) and the variation of the initial concentration of *PAN* in the organic phase (from $2.50 \cdot 10^{-3}$ to $4.00 \cdot 10^{-2}$ M) have been investigated.

The distribution coefficient was corrected for small changes in hydrogen ion concentration by multiplying $D(1 + \beta_1[L^-]_{(p)})$ by $[H^+]^3$ [9]. The plots of $\lg D\ (1 + \beta_1[L^-]_{(p)})\ [H^+]^3$ vs. $\lg [HL]_{(o)}$ [Fig. 7, curve 1 for Yb(III), curve 2 for Ho(III)] are straight lines of slope about 3. These values indicate that three molecules of *PAN* participate in the extraction of Yb(III) or Ho(III) from water—methanol phase.

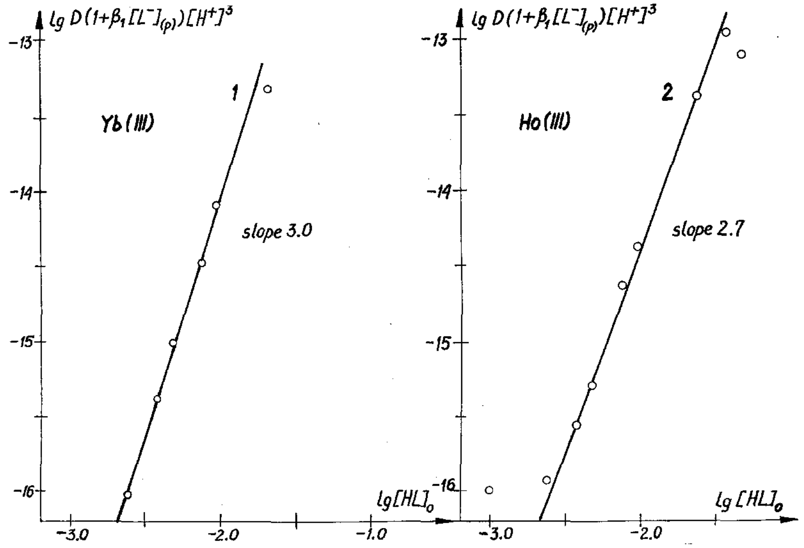

Fig. 7. The dependence of $\lg D\ (1 + \beta_1[L^-]_{(p)})\ [H^+]^3$ vs. $\lg [HL]_{(o)}$ for the extraction of Yb(III) (curve *1*) and Ho(III) (curve *2*) from water—50%₀ v/v methanol phase. $C_{Ln\,in.} = 50\ \mu g/cm^3$

Discussion

The obtained data show that the extraction of ytterbium or holmium with 1-(2-pyridylazo)-2-naphthol in carbon tetrachloride from water—methanol solutions may be described as:

$$Ln(\mathrm{H_2O})^{3+}_{m(p)} + 3\,\mathrm{H}L_{(o)} + t\,Me\mathrm{OH}_{(o)} \overset{K_{ex}}{\rightleftharpoons} LnL_3(Me\mathrm{OH})_{t(o)} + 3\,\mathrm{H}^+_{(p)} + m\,\mathrm{H_2O} \qquad (5)$$

where $Ln(\mathrm{III}) = \mathrm{Yb}$, Ho; $t = 3$ for $C_{Me\mathrm{OH}\,in.} \in (\sim 25 - 50)\%\,v/v$; and $t = 0$ for $C_{Me\mathrm{OH}\,in.} \in (\sim 5 - 25)\%\,v/v$.

Thus, the increase of Yb(III) or Ho(III) distribution coefficients at the presence of methanol in the aqueous phase (from ~ 25 to 50% v/v) is caused by the formation of solvates $LnL_3(Me\mathrm{OH})_3$. At lower MeOH concentration in the polar phase (from 5 to ~ 25% v/v) the chelates LnL_3 are extracted.

The values of $\lg K_{ex}$ of Yb(III) and Ho(III) reaction extraction at $C_{Me\mathrm{OH}\,in.}$ from ~ 25 to 50% v/v, calculated from eqn. (4) (in which $n = 0$, $t = 3$) are given in Table 1. The K_{ex} values were calculated by a least square procedure.

The formation of $\mathrm{Yb}L_3(Me\mathrm{OH})_t$ in the organic phase may also be given as a two-step reaction:

$$\mathrm{Yb}^{3+} + 3\,\mathrm{H}L_{(p)} \overset{K_1}{\rightleftharpoons} \mathrm{Yb}L_{3(o)} + 3\,\mathrm{H}^+ \qquad (6)$$

and

$$\mathrm{Yb}L_{3(o)} + t\,Me\mathrm{OH}_{(o)} \overset{K_2}{\rightleftharpoons} \mathrm{Yb}L_3(Me\mathrm{OH})_{t(o)} \qquad (7)$$

It is evident, that

$$K_{ex} = K_1 \cdot K_2 \qquad (8)$$

as it was shown previously[2]:

$$K_{ex} = \frac{K_1\left(\dfrac{D}{D_1} - 1\right)(1 + \beta_1[L^-]_{(p)})}{[Me\mathrm{OH}]^t_{(o)}} \qquad (9)$$

where $\lg K_1 = -13.30^1$; D_1 is the distribution coefficient of Yb(III) from aqueous phase obtained at the same conditions as D^1.

The average value of the equilibrium constant of the Yb(III) reaction extraction obtained from eqn. (9) (for $t = 3$) is $\lg K_{ex}(\mathrm{Yb}) = -10.11$. This value is in a fair agreement with the one calculated from eqn. (4) [$\lg K_{ex}(\mathrm{Yb}) = -10.04$, Tab. 1].

Table 1. *The equilibrium constants* ($\lg K_{ex}$) *of* Yb(III) *and* Ho(III) *reaction extraction [eqn. (4) with* $n = 0$, $t = 3$*] with PAN in* CCl_4 *from water—methanol solutions for* $C_{MeOH\,in.} > 25\%\,v/v$ *(at* $21 \pm 1\,°C$*, ionic strength* $0.1\,M$*)*

Conditions of measurements			
Variable	Constant		$\lg K_{ex}$
System: Yb(III)—(water-methanol)—*PAN* in CCl_4			
$pH^{\times}$ $5.40 \div 6.50$	$50\%\ v/v$ of $MeOH$	$[HL]_{(o)} = 1.00 \cdot 10^{-2}\,M$	-9.98
		$[HL]_{(o)} = 3.00 \cdot 10^{-2}\,M$	-10.00
$C_{HL\,in.}$ $2.50 \cdot 10^{-3}\,M \div$ $2.50 \cdot 10^{-2}\,M$	$50\%\ v/v$ of $MeOH$	$pH^{\times} = 6.20 \div 6.30$	-10.14
$C_{MeOH\,in.}$ $25 \div 50\%\ v/v$	$pH^{\times} = 6.26$	$[HL]_{(o)} = 1.00 \cdot 10^{-2}\,M$	-10.10
	$pH^{\times} = 6.34$		-10.05
	Average $\lg K_{ex}$(Yb) ($\pm$ 0.03)		-10.04
System: Ho(III)—(water-methanol)—*PAN* in CCl_4			
$pH^{\times}$ $5.90 \div 6.70$	$50\%\ v/v$ of $MeOH$	$[HL]_{(o)} = 1.00 \cdot 10^{-2}\,M$	-10.29
$C_{HL\,in.}$ $2.50 \cdot 10^{-3}\,M \div$ $4.00 \cdot 10^{-2}\,M$	$50\%\ v/v$ of $MeOH$	$pH^{\times} = 6.15 \div 6.21$	-10.26
$C_{MeOH\,in.}$ $25 \div 50\%\ v/v$	$pH^{\times} = 6.26$	$[HL]_{(o)} = 1.00 \cdot 10^{-2}\,M$	-10.36
	Average $\lg K_{ex}$(Ho) ($\pm$ 0.03)		-10.30

Unfortunately the equilibrium constant of the Ho(III) reaction extraction with *PAN* from aqueous—methanol phase [$\lg K_{ex}$(Ho)] cannot be calculated in this manner because the extraction of Ho(III) from aqueous solution is connected with formation of a third phase [D_1 in eqn. (9) cannot be determined].

According to eqn. (5) for the initial concentration of methanol in the polar phase from 5 to $\sim 25\%\ v/v$ the chelates LnL_3 are extracted. Thus, from eqn. (4) for $n = 0$ and $t = 0$ the value of $\lg K_{ex} = \lg K_1$ can be calculated. The average value of $\lg K_1$ of the Yb(III) reaction extraction is $\lg K_1(Yb) = -13.13$. Previously, from the data of Yb(III) extraction with *PAN* from aqueous phase[1] the value of $\lg K_1(Yb) = -13.30$ was obtained.

The equilibrium constants of Yb(III) reactions extraction with *PAN* from aqueous and aqueous-(~ 25–50)% *v*/*v* of *R*OH solution (*R*OH = methanol, ethanol) change in the order:

$$\begin{array}{ccccc} \lg K_{ex}(\mathrm{Yb})_{aq\text{-}MeOH} & \sim & \lg K_{ex}(\mathrm{Yb})_{aq\text{-}EtOH} & > & \lg K_{ex}(\mathrm{Yb})_{aq} \\ -10.04 & \sim & -10.14\,[2] & > & -13.30\,[11] \end{array}$$

It is seen that the addition of *Me*OH or *Et*OH to the aqueous phase (above ~ 25% *v*/*v* of *R*OH) causes considerable displacement of the reaction extraction equilibrium. This fact explains the increase of extractability when the aqueous phase contains above ~ 25% *v*/*v* of methanol (Figs. 1 and 2) or ethanol[2].

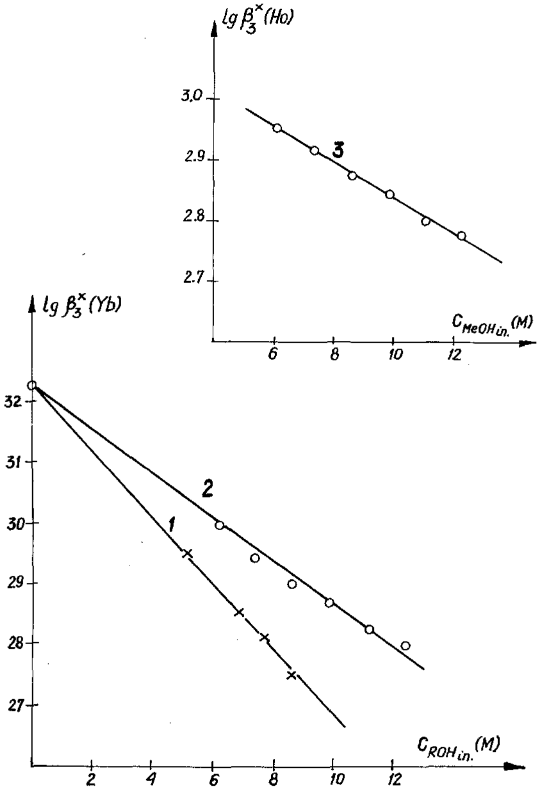

Fig. 8. $\lg \beta_3^x$ as a function of the initial concentration of *R*OH in the polar phase. Curves: *1* extraction of Yb(III) from aqueous—ethanol phase[2], *2* extraction of Yb(III) from aqueous—methanol phase, *3* extraction of Ho(III) from aqueous—methanol phase

On the other hand, the small difference in the values of $\lg K_{ex}(\mathrm{Yb})$ from aqueous—methanol and aqueous—ethanol solutions have been observed. Both alcoholes cause a similar synergistic effect.

As can be seen from Table 1

$$\begin{array}{ccc} \lg K_{ex}(\mathrm{Yb})_{aq\text{-}Me\mathrm{OH}} & \sim & \lg K_{ex}(\mathrm{Ho})_{aq\text{-}Me\mathrm{OH}} \\ -10.04 & \sim & -10.30 \end{array}$$

Small difference in the values of $\lg K_{ex}$ of Yb(III) and Ho(III) reaction extraction from aqueous—methanol phase is probably caused by the double-double effect[8, 10–12].

Two-phase stability constants of the complexes $LnL_3(Me\mathrm{OH})_3$ ($\lg \beta_3^{\times}$) may be calculated from:

$$\lg \beta_3^{\times} = \lg (\beta_3 \cdot p_{LnL_3(Me\mathrm{OH})_3}) = \lg K_{ex} + 3pK_a + \\ + 3 \lg p_{\mathrm{H}L} + 3 \lg p_{Me\mathrm{OH}} \qquad (10)$$

where β_3 and $p_{LnL_3(Me\mathrm{OH})_3}$ are the overall formation constant in the polar phase and the distribution constant of the chelate complex, respectively.

Fig. 8 shows the obtained values of $\lg \beta_3^{\times}$ of Yb(III) and Ho(III) solvates as a function of the initial concentration of ROH in the polar phase. A straight line relationship was found. Curves 1 and 2 in Fig. 8 represent the values of $\lg \beta_3^{\times}$ for the extraction of Yb(III) from aqueous—ethanol[2] (curve 1) and aqueous—methanol (curve 2) phase. Both straight lines intersect the abscissa ($C_{R\mathrm{OH}\,in.} = 0$) at the value of two-phase stability constant of YbL_3 chelate [$\lg \beta_3^{\times}(\mathrm{Yb}L_3) = 32.3$[1]].

The difference in the values of $\lg \beta_3^{\times}$ for $\mathrm{Yb}L_3(Me\mathrm{OH})_3$ and $\mathrm{Yb}L_3(Et\mathrm{OH})_3$ solvates increases with the increase of the initial concentration of alcohol in the polar phase. This is due to the changes in pK_a and $p_{\mathrm{H}L}$ values.

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