Solvent Extraction of Certain Rare Earth Metal Ions with 1-(2-Pyridylazo)-2-naphthol (*PAN*)
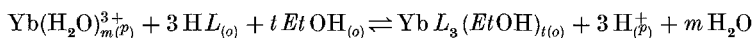
II. Extraction of Ytterbium(III) by *PAN* from Aqueous-Ethanol Solutions

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The solvent extraction of Yb(III) by 1-(2-pyridylazo)-2-naphthol (*PAN* or H L) in carbon tetrachloride from aqueous—ethanol phase has been investigated as a function of the $pH^{\times}$ of the polar phase and the concentrations of *PAN* or ethanol (*Et*OH) in the organic phase. It was confirmed that the addition of ethanol to the aqueous phase causes an increase of the Yb(III) distribution coefficient. The equation for the extraction reaction has been suggested as:
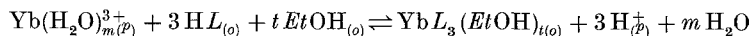
$$\text{Yb}(\text{H}_2\text{O})^{3+}_{m(P)} + 3\,\text{H}L_{(o)} + t\,Et\,\text{OH}_{(o)} \rightleftharpoons \text{Yb}\,L_3\,(Et\text{OH})_{t(o)} + 3\,\text{H}^+_{(P)} + m\,\text{H}_2\text{O}$$

where t changes from 0 to 3.

The extraction equilibrium constant (K_{ex}) and two-phase stability constants $(\beta_3^{\times})$ for the Yb $L_3\,(Et\,\text{OH})_3$ complex have been evaluated.

The formation of solvates Yb $L_3\,(Et\,\text{OH})_t$ is probably the main reason of the synergistic effect which was observed.

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

Extraktion von Seltenerdenmetall-Ionen mit 1-(2-Pyridilazo)-2-naphthol (PAN), II. Extraktion von Yb(III) aus wäßrig-ethanolischer Lösung

Die Extraktion von Yb(III) mittels 1-(2-Pyridilazo)-2-naphthol (*PAN* oder H L) in Kohlenstofftetrachlorid aus Wasser—Ethanol-Phase in Abhängigkeit vom $pH^{\times}$ der polaren Phase sowie von der Konzentration von *PAN* oder Ethanol (*Et*OH) in der organischen Phase wurde untersucht. Es wurde festgestellt, daß Zugabe von Ethanol zur wäßrigen Phase eine Erhöhung des Verteilungskoeffizienten von Yb(III) bedingt. Folgende Gleichung der Extraktionsreaktion wird vorgeschlagen:

$$\text{Yb}(\text{H}_2\text{O})^{3+}_{m(P)} + 3\,\text{H}L_{(o)} + t\,Et\text{OH}_{(o)} \rightleftharpoons \text{Yb}\,L_3\,(Et\text{OH})_{t(o)} + 3\,\text{H}^+_{(P)} + m\,\text{H}_2\text{O}$$

wobei t Werte von 0 bis 3 annimmt.

Die Werte der Extraktions-Gleichgewichtskonstante (K_{ex}), sowie der zweiphasigen Beständigkeitskonstante $(\beta_3^{\times})$ für den Komplex $\mathrm{Yb}L_3\,(EtOH)_3$ wurden berechnet.

Die Hauptursache des festgestellten synergistischen Effekts ist die Bildung der Solvate $\mathrm{Yb}L_3\,(EtOH)_t$.

Introduction

The presence of a miscible organic component in the aqueous (polar[1]) phase is usually found to have a big effect (either enhancing or depressing) on the extraction of the ions of many metals[2]. Such an effect is certainly valuable in analytical separations, since it adds an additional factor affecting extraction.

The influence of miscible organic components in the aqueous phase on the extraction of metal ions with amines and organophosphorus extrahents was investigated[2]. Relatively few papers are devoted to the studies of solvent extraction from aqueous-organic solutions by chelate forming agents. Refs.[3-6] describe only extensive studies on Hf(IV) extraction from mixed media by various chelate agents.

Extraction of Yb(III) and Dy(III) by 1-(2-pyridylazo)-2-naphthol from aqueous solutions has been discussed in an earlier paper[7]. The present paper reports the distribution equilibrium data for the extraction of Yb(III) in tracer concentration with 1-(2-pyridylazo)-2-naphthol (PAN or HL) in presence of ethanol in the aqueous phase. The solvent was carbon tetrachloride.

Experimental

Procedure and Reagents

The extraction and reextraction experiments for the determination of the distribution coefficient (D) were carried out as described before[7]. The aqueous phase contained a definite volume of ethanol ($d = 0.7894\,\mathrm{g/cm^3}$, POCh-Gliwice p.a.) (further this phase is called the polar phase).

The concentration of Yb(III) in the polar phase was always $50\,\mu\mathrm{g/cm^3}$. The initial concentration of ethanol in the polar phase and PAN in the organic phase varied from 0 to 50% v/v and from $\sim 1\cdot 10^{-3}$ to $\sim 5\cdot 10^{-2}\,M$, respectively.

In all investigations the $pH^{\times}$ ($pH^{\times} = -\lg[\mathrm{H}^+]$ in water-ethanol solutions[8]) was adjusted with hexamethylenetetramine buffer[9] and the organic phase was back-extracted. The $pH^{\times}$ of the polar phase was measured with an accuracy $\pm\, 0.02\,pH^{\times}$ division.

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

The distribution coefficient of Yb(III) (D) was obtained as:

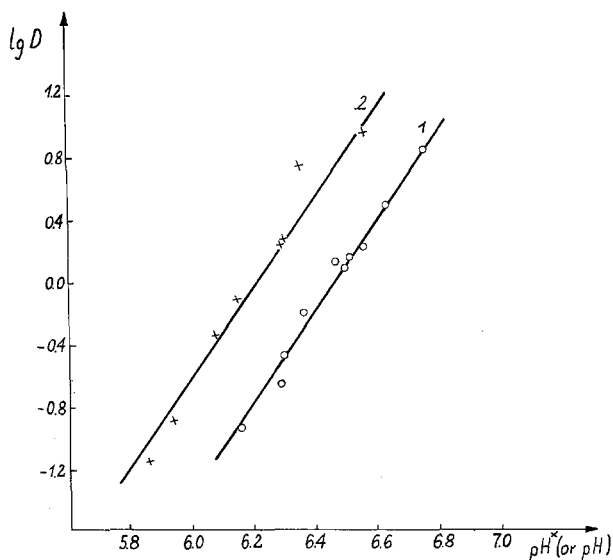$$D = \frac{[\mathrm{Yb}]_{(o)}}{[\mathrm{Yb}]_{(p)}} \tag{1}$$

Fig. 1. Distribution coefficient (D) of Yb(III) as a function of $pH^{\times}$ (or pH) of the polar phase. 1—extraction from aqueous-solutions[7]; 2—from water-50% v/v ethanol solution, $C_{Yb\,in.} = 50\,\mu g/cm^3$, $[HL]_{(o)} = 1.00 \cdot 10^{-2}\,M$

where $[Yb]_{(o)}$, $[Yb]_{(p)}$ are the equilibrium concentrations of Yb(III) in the organic and the polar phases, respectively.

Three series of measurements were performed:

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

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

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

In series a) and c) the constant equilibrium concentration of PAN in the organic phase ($[HL]_{(o)} = 1.00 \cdot 10^{-2}\,M$) was maintained. Taking into account the volume changes, the balance of ytterbium in both phases ($100 \pm 2\%$), the equilibrium concentrations of PAN or ethanol and the initial concentration of PAN in series a) and c) were calculated.

In preliminary investigations it was observed that the addition of ethanol to the aqueous phase causes an increase of the Yb(III) distribution coefficient (Fig. 1). Moreover, it was confirmed that Yb(III) does not extract with pure carbon tetrachloride from water-ethanol phase.

Determination of PAN (HL) Distribution Constants (p_{HL}) Between Carbon Tetrachloride and Water-Ethanol Solutions

20 cm³ of water-ethanol phase which contains a definite volume of alcohol was shaken with 20 cm³ of PAN solution in carbon tetrachloride for 3 h. The initial concentration of PAN ($C_{HL\,in.}$) was $3.00 \cdot 10^{-2}\,M$ and the initial concentration of ethanol in the polar phase varied from 5 to 50% v/v. The $pH^{\times}$ of the polar phase was adjusted with perchloric acid, acetic acid, ammonium hydroxide, sodium hydroxide and hexamethylenetetramine buffer solutions.

The constant ionic strength ($\mu = 0.1\,M$) was maintained by adding sodium perchlorate. After shaking the solutions were centrifuged, the $pH^{\times}$ of the polar phase was measured and the equilibrium concentration of PAN in the polar phase ($[HL]_{(p)}$) was determined colorimetrically ($pH^{\times} \sim 2.0$, $\lambda = 440\,\mathrm{nm}$, 1 cm cell)[10]. The calibration curve was used for calculation the reagent concentration in the polar phase. Taking into account the initial concentration of PAN and the volume changes, the distribution coefficient of PAN (D_{HL}) was obtained as:

$$D_{\mathrm{HL}} = \frac{C_{\mathrm{HL}in.} - [HL]_{(p)}}{[HL]_{(p)}} \tag{2}$$

Results and Discussion

Fig. 2 shows the dependence of the PAN distribution coefficient (D_{HL}) between carbon tetrachloride and water-50% v/v ethanol phase vs. $pH^{\times}$ of the polar phase. Fig. 2 indicates that the reagent distribution coefficient is constant at the $pH^{\times}$ range from ~ 3.5 to ~ 8.5 and allows to determine the value of the distribution constant of PAN (p_{HL}).
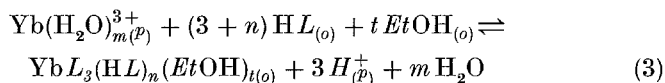
The values of the distribution constants of PAN at the other concentrations of ethanol in the polar phase were obtained in the same way.

Fig. 3 shows the dependence of $\lg p_{\mathrm{HL}}$ on the ethanol concentration in the polar phase. The distribution constant of PAN between carbon tetrachloride and water-ethanol phase decreases with the increase of the alcohol concentration in the polar phase.

According to *Yatsimirskii* and *Davidenko*[11], ions of lanthanides(III) exist in aqueous-alcoholic solutions containing less than 80–85% v/v of alcohol as aquo-ions (spectrophotometric data). *Abrahamer* and *Marcus*[12] have obtained the following affinity series of ligands and solvents for lanthanide(III) ions:

$$DMF > TBP > NO_3^- \sim H_2O > C_2H_5OH > \text{dioxane}.$$

Thus, in consideration of the data obtained before[7], the extraction of Yb(III) by PAN from aqueous-alcoholic medium can be generally expressed as:

$$\mathrm{Yb}(H_2O)^{3+}_{m(P)} + (3 + n)\,HL_{(o)} + t\,EtOH_{(o)} \rightleftharpoons$$
$$\mathrm{Yb}L_3(HL)_n(EtOH)_{t(o)} + 3\,H^+_{(P)} + m\,H_2O \tag{3}$$

where the subscripts (p) and (o) correspond to the polar and organic phases, respectively; $HL = PAN$, $EtOH = C_2H_5OH$.

The extraction constant (K_{ex}) is given by:

$$K_{ex} = \frac{[\mathrm{Yb}L_3(HL)_n(EtOH)_t]_{(o)}\,[H^+]^3_{(P)}}{[\mathrm{Yb}(H_2O)^{3+}_m]_{(p)}\,[HL]^{3+n}_{(o)}\,[EtOH]^t_{(o)}} \tag{4}$$
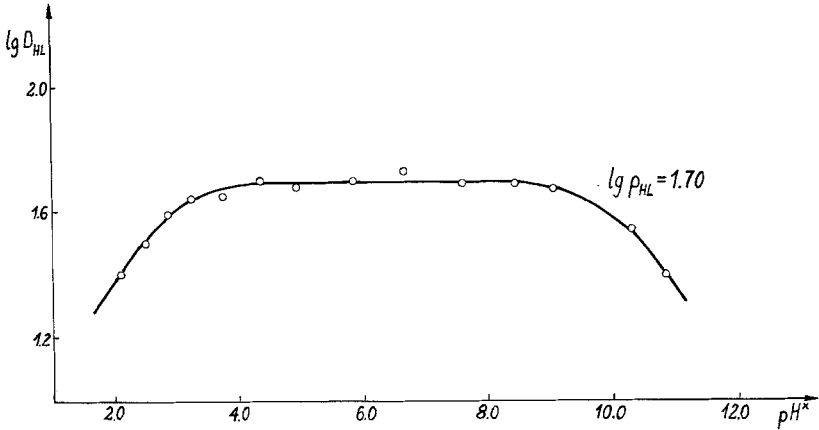
Fig. 2. The dependence of the *PAN* distribution coefficient (D_{HL}) between carbon tetrachloride and water-50% *v/v* ethanol phase vs. $pH^{\times}$ of the polar phase, $C_{HLin.} = 3.00 \cdot 10^{-2} M$
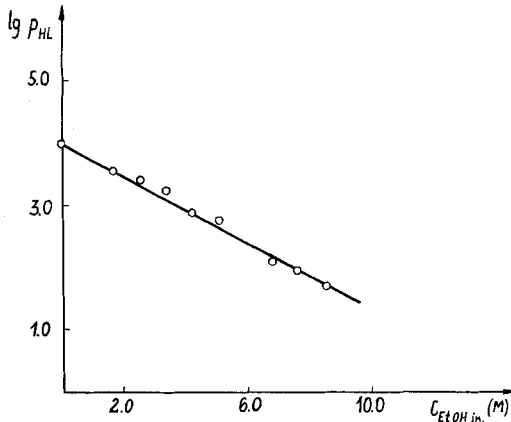

Fig. 3. The dependence of the *PAN* distribution constant (p_{HL}) vs. ethanol concentration in the polar phase, $C_{HLin.} = 3.00 \cdot 10^{-2} M$, $pH^{\times} = 6.39$

Assuming that only the complex $Yb L_3 (HL)_n (EtOH)_t$ is soluble in the organic phase, the distribution coefficient of Yb(III) is given by:

$$D = \frac{[Yb L_3 (HL)_n (EtOH)_t]_{(o)}}{[Yb]_{tot.(p)}} \tag{5}$$

where $[Yb]_{tot.(p)}$ is the equilibrium total concentration of Yb(III) in the polar phase[7].

Taking into account the presence in the polar phase of ions and molecules $(\text{OH}^-, \text{ClO}_4^-, L^-,$ hexamethylenetetramine, $Et\text{OH})$ which can form non-extractable complexes and the possibility of side reactions in this phase, the distribution coefficient of Yb(III) can be expressed by the following equation[7]:

$$\lg D + \lg\left(1 + \sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{q=1}^{3}\beta_{ijq}[\text{OH}^-]^i[L^-]^j[X]^q\right) =$$

$$= \lg K_{ex} + 3\,pH^\times + (3+n)\lg[HL]_{(o)} + t\lg[Et\text{OH}]_{(o)} \qquad (6)$$

where β_i, β_j, β_q are the stability constants of Yb(OH)_i^{3-i}, $\text{Yb}L_j^{3-j}$ and $\text{Yb}X_q^{3-q}$ complexes, and $X = \text{ClO}_4^-$, hexamethylenetetramine.

When the initial and the equilibrium volumes of phases were introduced, the concentrations of $[L^-]_{(p)}$ and $[HL]_{(o)}$ were calculated as before[7]. The following equations were obtained:

$$[L^-]_{(p)} = \frac{C_{\text{H}Lin.}\,V_{(o)in.}}{\left\{\dfrac{[\text{H}^+]}{K_a}\left(V_{(p)} + p_{\text{HL}}\,V_{(o)} + \dfrac{[\text{H}^+]\,V_{(p)}}{K_p}\right) + V_{(p)}\right\}} \qquad (7)$$

and

$$[HL]_{(o)} = \frac{C_{\text{H}Lin.}\,V_{(o)in.}}{\left\{V_o + \dfrac{V_{(p)}}{p_{\text{HL}}}\left(1 + \dfrac{K_a}{[\text{H}^+]} + \dfrac{[\text{H}^+]}{K_p}\right)\right\}} \qquad (8)$$

where $C_{\text{H}Lin.}$ is the initial concentration of $PAN\,(M)$, p_{HL} is the distribution constant of PAN between carbon tetrachloride and an aqueous-ethanol phase containing suitable concentration of alcohol,

K_a, K_p are the acid dissociation constants of PAN in an aqueous-ethanol solution containing suitable concentration of alcohol,

$V_{(o)in.}$, $V_{(p)}$, $V_{(o)}$ are the initial and the equilibrium volumes of phases (cm³).

The equilibrium concentration of ethanol in the organic phase $[Et\text{OH}]_{(o)}$ may be calculated from the following equation based on $Et\text{OH}$ balance:

$$[Et\text{OH}]_{(o)} = \frac{C_{Et\text{OH}in.}\,V_{(o)in.}}{\left(\dfrac{V_{(p)}}{p_{Et\text{OH}}} + V_{(o)}\right)} \qquad (9)$$

where $C_{Et\text{OH}in.}$ is the initial concentration of ethanol in the polar phase (M) and $p_{Et\text{OH}}$ is the distribution constant of ethanol between carbon tetrachloride and water, $p_{Et\text{OH}} = 2.4 \cdot 10^{-2}$ [13].

The values of K_a and K_p of PAN in solutions containing variable concentrations of ethanol were calculated from [14]:

$$pK_a = 14.07 - 0.026\,\varepsilon - B \text{ for } \varepsilon = 50\text{--}75 \qquad (10)$$

and

$$pK_p = 1.12 + 0.0175\,\varepsilon - B \text{ for } \varepsilon = 35\text{--}75 \qquad (11)$$

where ε is the dielectric constant of solution at $t = 20\,^\circ C$[15] and $B = \dfrac{\sqrt{\mu}}{1 + \sqrt{\mu}}$ for the ionic strength $\mu = 0.1\text{--}0.5$.

The complexes of lanthanides with ClO_4^- ion and hexamethylene-tetramine are thermodynamically unstable under the investigated conditions [16]. Thus in eqn. (6) the expression $\sum\limits_{q=1}^{3} \beta_q [L]^q$ can be neglected.

It was shown previously [7] that for the extraction from aqueous solutions the expression $\sum\limits_{i=1}^{3} \beta_i [\text{OH}^-]^i$ reflecting the hydrolysis of Yb(III) can also be neglected. Thus, this expression can be omitted for the extraction of Yb(III) from aqueous-alcoholic solutions as well.

By the spectrophotometric method *Malinowska* and *Czakis-Sulikowska*[17] showed that Yb(III) forms with PAN in water-50% v/v ethanol solution the complex of the type YbL^{2+} with the stability constant $\lg \beta_1 = 10.03$. The YbL^{2+} complex was formed at the same conditions (the concentration of Yb(III) and $[\text{L}^-]_{(p)}$, $pH^\times$) which exist in the extraction process in the polar phase.

Thus, taking together these facts, it may be accepted that for the extraction of Yb(III) with solutions of PAN in carbon tetrachloride from water-ethanol solutions, at the polar phase exists the complex YbL^{2+} with the stability constant mentioned above.

Based on above data eqn. (6) can be simplified as follows:

$$\lg D + \lg(1 + \beta_1 [L^-]_{(p)}) = \lg K_{ex} + (3 + n)\lg[HL]_{(o)} + $$
$$+ 3\,pH^\times + t\lg[Et\text{OH}]_{(o)} \qquad (12)$$

With predetermined PAN and EtOH concentrations in the organic and the polar phases, the relationship

$$\lg D + \lg(1 + \beta_1 [L^-]_{(p)}) = f(pH^\times) \qquad (13)$$

should give a straight line of slope 3. On the other hand, at a predetermined $pH^\times$ of the polar phase and EtOH concentration in this phase, the relationship

$$\lg D + \lg(1 + \beta_1 [L^-]_{(p)}) = f(\lg[HL]_{(o)}) \qquad (14)$$
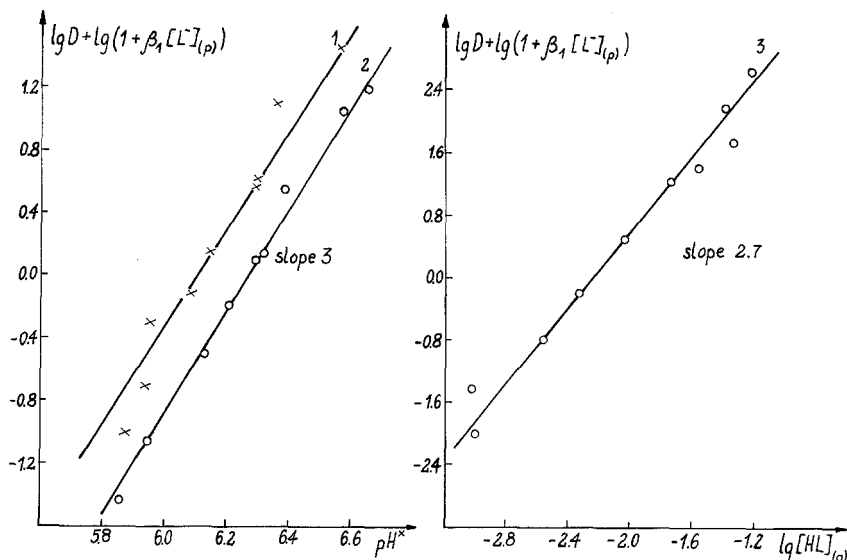
should yield a straight line of slope $(3 + n)$.

Fig. 4. The dependence of $\lg D + \lg(1 + \beta_1 [L^-]_{(p)})$ vs. $pH^\times$ (curves 1 and 2) or vs. $\lg[HL]_{(o)}$ (curve 3). 1—water-50% v/v ethanol phase, $[HL]_{(o)} = 1.00 \cdot 10^{-2} M$; 2—water-30% v/v ethanol phase, $[HL]_{(o)} = 1.00 \cdot 10^{-2} M$; 3—water-50% v/v ethanol phase, $pH^\times = 6.34$, $C_{\mathrm{Yb}in.} = 50 \,\mu g/cm^3$

From distribution experiments performed at constant $pH^\times$ of the polar phase and $[HL]_{(o)}$ concentration in the organic phase the value of t can be obtained from the slope of

$$\lg D + \lg(1 + \beta_1 [L^-]_{(p)}) = f(\lg[EtOH]_{(o)}) \qquad (15)$$

Extraction as a Function of $pH^\times$

In these series of measurements the distribution coefficient of Yb(III) was investigated at $[HL]_{(o)} = 1.00 \cdot 10^{-2} M$, ethanol concentrations in the polar phase 30 or 50% v/v and at a $pH^\times$ range of 5.8—6.7.

Fig. 4 shows the dependence of $\lg D + \lg(1 + \beta_1 [L^-]_{(p)})$ vs. $pH^\times$ of water-50% v/v (curve 1) or water-30% v/v (curve 2) ethanol phase. The concentration of $[L^-]_{(p)}$ was calculated from eqn. (7).

In both cases three protons are lost (slopes of the obtained dependences are 3) and with increase of the initial concentration of ethanol in the polar phase the extraction curves move towards lower values of $pH^\times$.

Extraction as a Function of PAN Concentration

The distribution coefficient of Yb(III) at constant $pH^{\times}$ of water-50% v/v ethanol phase ($pH^{\times} = 6.34$) and varied initial concentration of PAN in the organic phase (from $1.00 \cdot 10^{-3}$ to $5.00 \cdot 10^{-2} M$) was measured.

Fig. 4 (curve 3) shows the results as the dependence of $\lg D + \lg(1 + \beta_1 [L^-]_{(p)})$ vs. $\lg [HL]_{(o)}$. The concentration of $[L^-]_{(p)}$ and $[HL]_{(o)}$ were calculated from eqns. (7) and (8).

The relationship $\lg D + \lg(1 + \beta_1 [L^-]_{(p)}) = f(\lg [HL]_{(o)})$ is straight line of slope 2.7. This value indicates that three molecules of ligand participate in the extraction process.

Extraction as a Function of EtOH Concentration

The influence of EtOH concentration on the Yb(III) extraction at constant $pH^{\times}$ of the water-ethanol phase ($pH^{\times} = 6.31, 6.40$ and 6.61) at constant PAN concentration in the organic phase ($[HL]_{(o)} = 1.00 \cdot 10^{-2} M$) and varied initial concentration of ethanol in the polar phase (from 5 to 50% v/v) have been investigated.
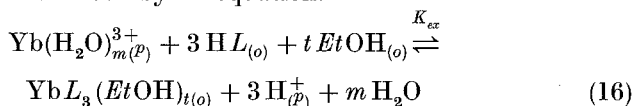
The stability constant values for YbL^{2+} complex in water-ethanol solutions depend to an inconsiderable degree on the concentration of alcohol up to 50% v/v[18]. Thus, for calculation of expression values $\lg D + \lg(1 + \beta_1 [L^-]_{(p)})$, the $\lg \beta_1$ value stated in water-50% v/v ethanol solution was accepted.

Using the values of p_{HL} (Fig. 3), K_a (eqn. 10) and K_p (eqn. 11), the concentration of $[L^-]_{(p)}$ was determined from eqn. (7). The concentration of $[EtOH]_{(o)}$ was calculated from eqn. (9).

Fig. 5 shows the results as the dependence of $\lg D + \lg(1 + \beta_1 [L^-]_{(p)})$ vs. $\lg [EtOH]_{(o)}$.

From Fig. 5 it is evident that in the extraction process of Yb(III) from water-ethanol solutions a variable number of alcohol molecules participate (t in eqn. 3). The number of ethanol molecules increases with increasing alcohol concentration in the organic phase and at the initial concentrations of ethanol in the polar phase above $\sim 40\%$ v/v reaches the value 3 (slopes of the asymptotes drawn to the obtained curves at these concentrations of ethanol).

The obtained data show that the extraction of ytterbium with 1-(2-pyridylazo)-2-naphthol in carbon tetrachloride from water-ethanol solutions may be described by an equation:

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

$$\mathrm{Yb}L_3(Et\mathrm{OH})_{t(o)} + 3\,\mathrm{H}_{(p)}^+ + m\,\mathrm{H_2O} \qquad (16)$$

where t changes from 0 to 3.

Thus, the increase of the Yb(III) distribution coefficient at the presence of ethanol in the aqueous phase is probably caused by the formation of solvate $YbL_3(EtOH)_t$ with variable number of ethanol molecules.

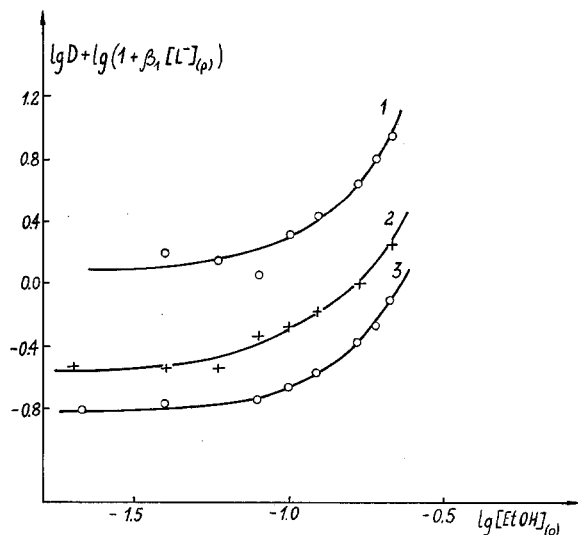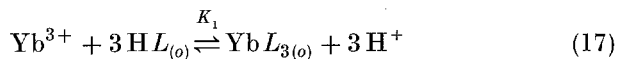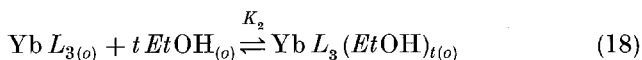The values of $\lg K_{ex}$ calculated from eqn. (12) (in which $n = 0$ and $t = 3$) are given in Tab. 1.

Fig. 5. The dependence of $\lg D + \lg(1 + \beta_1[L^-]_{(p)})$ vs. $\lg[EtOH]_{(o)}$ at $[\overline{H}L]_{(o)} = 1.00 \cdot 10^{-2}\,M$ and $pH^\times = 6.61$ (curve 1), $pH^\times = 6.40$ (curve 2), $pH^\times = 6.31$ (curve 3), $C_{Ybin.} = 50\,\mu g/cm^3$

The formation of solvate in the organic phase may also be given as a two-step reaction:

$$Yb^{3+} + 3\,HL_{(o)} \overset{K_1}{\rightleftharpoons} YbL_{3(o)} + 3\,H^+ \tag{17}$$

and

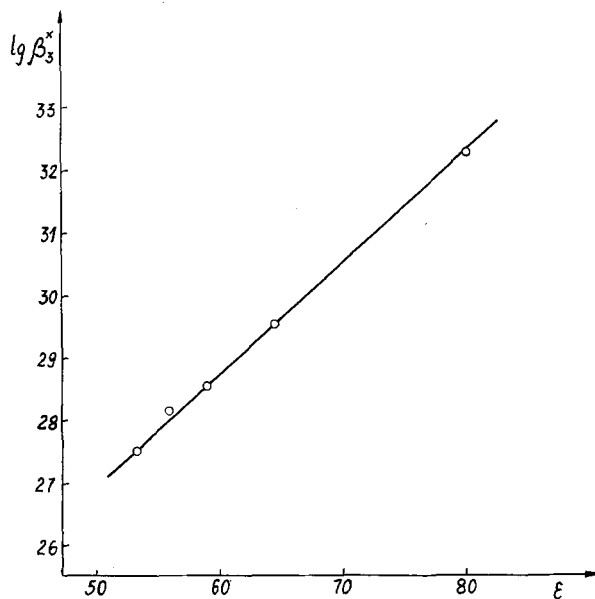$$YbL_{3(o)} + t\,EtOH_{(o)} \overset{K_2}{\rightleftharpoons} YbL_3(EtOH)_{t(o)} \tag{18}$$

It is evident, that $K_{ex} = K_1 \cdot K_2$. $\tag{19}$

Table 1. *The equilibrium constant* ($\lg K_{ex}$) *of the Yb(III) extraction (eqn. 16 in which t = 3) with PAN from water-ethanol solutions*

The conditions of measurements		$\lg K_{ex}$
variable	constant	
$pH^\times$	50% v/v of *Et*OH $\quad$ $[\mathrm{H}L]_{(o)} = 1.00 \cdot 10^{-2}\,M$	-10.16
5.80–6.70	30% v/v of *Et*OH	-10.11
C_{HL} $1.00 \cdot 10^{-3}\,M-$ $5.00 \cdot 10^{-2}\,M$	50% v/v of *Et*OH $\qquad$ $pH^\times = 6.34$	-10.17
$C_{Et\mathrm{OH}}$ 30–50% v/v	$pH^\times = 6.31$	-10.13
	$pH^\times = 6.40$ $\quad$ $[\mathrm{H}L]_{(o)} = 1.00 \cdot 10^{-2}\,M$	-10.11
	$pH^\times = 6.61$	-10.16
	The average $\lg K_{ex}\,(\pm\,0.03)$	-10.14

Fig. 6. Two-phase stability constant of the Yb $L_3\,(Et\mathrm{OH})_3$ complex ($\beta_3^\times$) as a function of the dielectric constant (ε) of the polar phase

20*

The distribution coefficient of Yb(III) from aqueous-ethanol phase may be written as:

$$D = \frac{[\mathrm{Yb}L_3]_{(o)} + \sum\limits_{t=1}^{t=3} [\mathrm{Yb}L_3(Et\mathrm{OH})_t]_{(o)}}{[\mathrm{Yb}^{3+}]_{(p)tot.}} =$$
$$= D_1\left(1 + \frac{K_2[Et\mathrm{OH}]_{(o)}^t}{1 + \beta_1[L^-]_{(p)}}\right) \tag{20}$$

where D_1 is the distribution coefficient of Yb(III) from aqueous phase obtained at the same conditions as D[7].

From eqns. (19) and (20) we obtain:

$$K_{ex} = \frac{K_1\left(\dfrac{D}{D_1} - 1\right)(1 + \beta_1[L^-]_{(p)})}{[Et\mathrm{OH}]_{(o)}^t} \tag{21}$$

where $\lg K_1 = -13.30$[7].

The average value of $\lg K_{ex}$ obtained from eqn. (21) (for $t = 3$) is $\lg K_{ex} = -10.38$. This is in good agreement with the one calculated from eqn. (12) ($\lg K_{ex} = -10.14$).

The two-phase stability constant of the complex $\mathrm{Yb}L_3(Et\mathrm{OH})_3$ ($\lg \beta_3^\times$) may be calculated from the following relation:

$$\lg \beta_3^\times = \lg(\beta_3 \cdot p_{\mathrm{Yb}L_3(Et\mathrm{OH})_3}) = \lg K_{ex} + 3pK_a + +3\lg p_{HL} + 3\lg p_{Et\mathrm{OH}} \tag{22}$$

where β_3 and $p_{\mathrm{Yb}L_3(Et\mathrm{OH})_3}$ are the overall formation constant in the polar phase and the distribution constant of the chelate complex, respectively.

It is evident from eqn. (22) that the value of the two-phase stability constant of complex $\mathrm{Yb}L_3(Et\mathrm{OH})_3$ depends on the value which change with the ethanol concentration in the polar (or the organic) phase ($\lg p_{HL}$ decreases and pK_a increases with increasing ethanol concentration).

The obtained values of $\lg \beta_3^\times$ are: 27.51, 28.14, 28.53 and 29.55 for 50, 45, 40 and 30% v/v of the initial ethanol concentration in the polar phase, respectively. These values are lower than the two-phase stability constant of complex $\mathrm{Yb}L_3$[7]. The decrease of $\lg \beta_3^\times$ values with increasing ethanol concentration (or with decreasing the dielectric constant of the polar phase) (Fig. 6) may be probably due to a decrease of the distribution constant of the chelate, because this one changes analogously with that of the chelating agent[19].

Acknowledgements

I wish to thank Prof. *D. M. Czakis-Sulikowska* for useful discussions. Some experimental data were obtained by *Teresa Michoń,* undergraduate. This paper was included in the problem MR-I-14 and supported by the Ministry of Science, Higher Education and Technology and Polish Academy of Sciences.

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