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Complex Formation Studies on Ho(III) and Lu(III) with 1-(2-Pyridylazo)-2-naphthol (*PAN*) in Alcohol—Water Solutions

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The formation of *PAN* complexes in the systems *Ln*(III)—*PAN*—alcohol—water (where: *Ln*(III) = Ho, Lu and alcohol = ethanol, *n*-propanol, *iso*-propanol) was investigated by a spectrophotometric method. Equilibrium constants for the reaction $Ln^{3+} + HL \rightleftharpoons LnL^{2+} + H^+$ ($HL = PAN$) and stability constants of complexes LnL^{2+} were calculated.

(Keywords: Complexes; Holmium(III); Lutetium(III); 1-(2-Pyridylazo)-2-naphthol; Stability constants)

Untersuchungen zur Komplexbildung von Ho(III) *und* Lu(III) *mit 1-(2-Pyridylazo)-2-naphthol (PAN) in alkoholisch—wäßrigen Lösungen*

Die Bildung der Komplexe von *PAN* in den Systemen *Ln*(III)—*PAN*—Alkohol—Wasser (*Ln*(III) = Ho, Lu; Alkohol = Ethanol, *n*-Propanol, *iso*-Propanol) wurde mit einer spektrophotometrischen Methode untersucht. Die Gleichgewichtskonstanten der Reaktionen $Ln^{3+} + HL \rightleftharpoons LnL^{2+} + H^+$ ($HL = PAN$) und die Stabilitätskonstanten der Komplexe LnL^{2+} wurden berechnet.

Introduction

In earlier publications we have reported the complex formation of 1-(2-pyridylazo)-2-naphthol with lanthanide(III) (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Y) in methanol—water solutions[1] and with Y(III), Er(III), Yb(III) in ethanol—water, *n*-propanol—water, *iso*-propanol—water mixtures[2].

The present communication is a continuation of spectrophotometric studies on the complex formation of *PAN* with lanthanide in alcohol—water solutions. The equilibrium constants for complexing reactions and stability constants of complexes Ho(III) and Lu(III) with *PAN* in ethanol—water, *n*-propanol—water, *iso*-propanol—water solutions are given.

Experimental

Reagents

The solutions of lanthanide perchlorates were obtained by dissolving the oxides [99.9% pure—Ho_2O_3, Lu_2O_3 (Koch. Light Lab.)] in 3 mol/dm^3 perchlorate acid and then diluting with water. The metal concentration was determined complexometrically[3]. Stock solutions of *PAN* (POCh—Gliwice p.a.) in the appropriate alcohols were prepared by dissolving *PAN* in these alcohols. Alcohols (POCh—Gliwice p.a.) were purified by distillation. Other reagents were analytically pure (NaOH—POCh Gliwice, $HClO_4$—Hoping Williams, $NaClO_4$—Reachim).

The instruments and calculations were the same as reported earlier[1,2]. The hydrogen ion concentration in the alcohol-aqueous solution (where $pH^X = -\log[H^+]$[4,5]) was determined with a *pH*-meter. The *pH*-meter was calibrated with standardized hydrochloric acid in water—alcohol mixtures[6].

Procedure

The absorption spectra in the following series of solutions were studied:

1. Constant concentration of metal ions and constant concentration of *PAN* at different pH^X;
2. Constant concentration of *PAN* and constant pH^X and varying the concentration of metal ions;
3. Constant concentration of metal ions and constant pH^X and varying the concentration of *PAN*.

In series 1 the concentrations of *PAN* (C_{PAN}) and metal ions (C_{Ln}) were $3.5 \cdot 10^{-5}$ mol/dm^3 and $8 \cdot 10^{-4}$ mol/dm^3, respectively. In series 2 C_{PAN} was $3.5 \cdot 10^{-5}$ mol/dm^3, the range of concentration of metal ions from $1 \cdot 10^{-4}$ mol/dm^3 to $4 \cdot 10^{-3}$ mol/dm^3. In series 3 C_{Ln} was $5 \cdot 10^{-4}$ mol/dm^3 and the range of concentration of *PAN* from $0.7 \cdot 10^{-5}$ mol/dm^3 to $5 \cdot 10^{-5}$ mol/dm^3. The concentration of alcohol was 50% or 75% (*v*/*v*). The solutions were prepared as described previously[1]. The ionic strength of all solutions was $\mu = 0.1$ mol/dm^3 ($NaClO_4$). The measurements were carried out at 21 ± 1 °C.

Results and Discussion

The absorption spectra of all studied systems are similar in appropriate series. Absorption spectra of *Ln*(III)—*PAN*—alcohol—water systems showed the formation of the complexes in the pH^X range ~ 5.5–7. The isosbestic point was observed in the absorption spectra of *PAN* at different concentration of metal ions (series 2), for all investigated alcohol—water solution. Fig. 1 shows, as an example, the absorption spectra for the system Lu(III)—*PAN*—50% (*v*/*v*) *n*-propanol. The absorption curve of the free ligand passes through this isosbestic point.

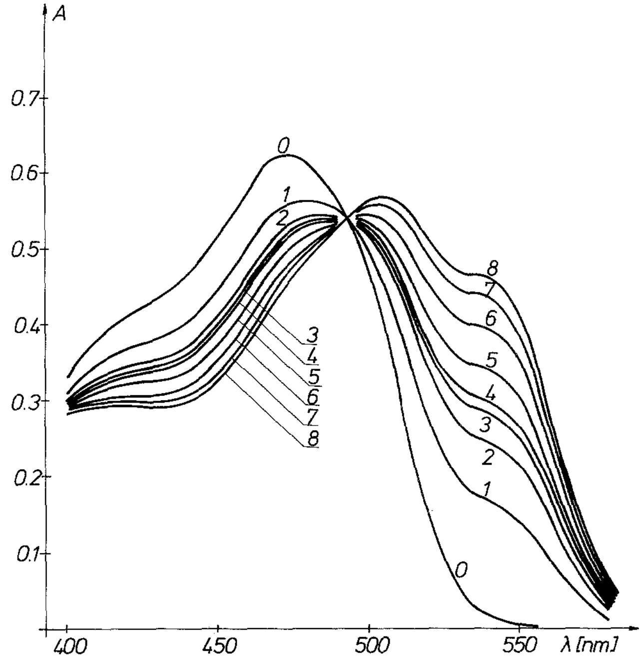

Fig. 1. Absorption spectra of *PAN* in the presence of Lu(III) in 50% (*v*/*v*) *n*-propanol. Concentration of *PAN* $3.5 \cdot 10^{-5}$ mol/dm^3, Lu(III) concentration $C_{\mathrm{Lu}} \cdot 10^4$ mol/dm^3 for curves 0–8 are: *0* 0, *1* 2.9; *2* 3.9; *3* 4.7; *4* 5.9; *5* 7.8; *6* 9.8; *7* 11.8; *8* 15.7, $pH^{\mathrm{x}} = 6.10$

This fact indicates that only one kind of complex and ligand in equilibrium is present over the appropriate range of conditions. The composition of the complexes was examined by the straight line method[7]. In the investigated alcohol—water mixtures Ho(III) and Lu(III) form with *PAN* the complexes $\mathrm{Ho}L^{2+}$ and $\mathrm{Lu}L^{2+}$.

The equilibrium constants K of the reaction: $Ln^{3+} + \mathrm{H}L \rightleftharpoons LnL^{2+} + \mathrm{H}^+$ were calculated using the *Watters* method[8]. The calculations of K were performed by the method of least squares. Stability constants β were evaluated using the expression:

$\beta = K/K_{\mathrm{OH}}$ (where K_{OH} is the dissociation constant of *PAN* in alcohol—water solution[2,9]). The values of the constants K and β are given in Table 1. The determined stability constants are conditional stability constants.

An increase in the stability constants of the complexes $\mathrm{Ho}L^{2+}$ and $\mathrm{Lu}L^{2+}$ by increasing the concentration of all alcohols in solution was found. The changes of stability constants for the studied complexes are the

Table 1. *Equilibrium constants K of the complexation reaction and stability constants* $\log\beta$ *of the complexes* LnL^{2+} ($L^- = PAN^-$) *in alcohol—water systems at* $21 \pm 1\,°C$, $\mu = 0.1$ ($NaClO_4$); Δ_{pK} *correlation coefficient*

Alcohol % (v/v)	Mole fraction of alcohol	Ho(III)			Lu(III)		
		pK	Δ_{pK}	$\log\beta$	pK	Δ_{pK}	$\log\beta$
ethanol							
50%	0.236	3.11	0.97	9.66	3.03	0.96	9.73
75%	0.484	2.92	0.98	10.48	2.56	0.97	10.84
n-propanol							
50%	0.194	3.45	0.96	8.00	2.75	0.97	8.70
75%	0.420	2.86	0.97	8.74	2.33	0.97	9.27
iso-propanol							
50%	0.191	3.55	0.96	8.48	2.53	0.97	9.57
75%	0.414	3.45	0.96	9.30	2.01	0.98	10.75

same and their values decrease in the following order: methanol > > ethanol > *iso*-propanol > *n*-propanol [excepted 50% (*v*/*v*) methanol and ethanol for HoL^{2+}]. This trend and an increase of $\log\beta$ with increasing the contents of all alcohols are caused by the change of the dielectric constant of solution (ε) with the exception of *n*-propanol. The supposition of the important influence of the dielectric constant of the

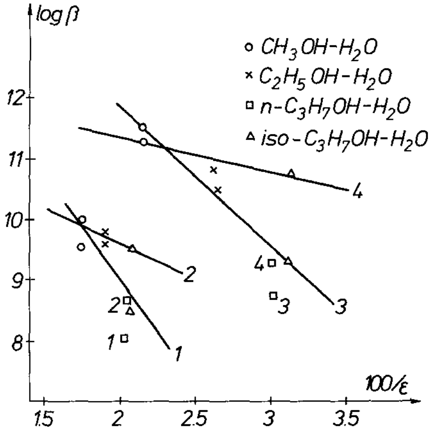

Fig. 2. Dependence of $\log\beta$ vs. 100/ε for the complexes LnL^{2+} in alcohol—water solution. Curves: *1* HoL^{2+}; *2* LuL^{2+} in 50% (*v*/*v*) alcohol; *3* HoL^{2+}; *4* LuL^{2+} in 75% (*v*/*v*) alcohol

solution on the stability constant is supported by the linear relation between $\log\beta$ and $100/\varepsilon$ (Fig. 2, values for the dielectric constants are taken from Ref.[10]).

The diversification of dependence $\log\beta$ vs. $100/\varepsilon$ in certain ranges of mole fraction of alcohol is most probably caused by the change of the solvation sphere of the metal ion with increasing alcohol concentration[11,12]. Similar dependences were observed previously for the complexes LnL^{2+} [Ln = Y(III), Er(III) and Yb(III)][2].

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