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Complex Formation of Certain Rare Earth Metals 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) = Pr, Nd, Sm, Eu, Gd, Tb, alcohol = ethanol and *Ln*(III) = Eu, alcohol = *n*-propanol, isopropanol] 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+} are reported.

(Keywords: Complexes; Lanthanides; 1-(2-Pyridylazo)-2-naphthol; Stability constants)

Komplexbildung einiger Seltenerdmetalle 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) = Pr, Nd, Sm, Eu, Gd, Tb, Alkohol = Ethanol und *Ln*(III) = Eu, Alkohol = *n*-Propanol, Isopropanol] 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

Previously we described the complex formation of 1-(2-pyridylazo)-2-naphthol with Y(III) and all lanthanides(III) (with the exception Pm) in methanol—water [1-3] and Dy(III), Ho(III), Er(III), Yb(III), Lu(III), Y(III) in ethanol—water or *n*-propanol—water and isopropanol—water solutions [2, 4, 5].

This report is a continuation of the investigation of complex formation between lanthanide and *PAN* in ethanol—water solution. At present the process of complexing in the systems *Ln*(III)—*PAN*—ethanol—water

[*Ln*(III) = Pr, Nd, Sm, Eu, Gd, Tb] was studied by a spectrophotometric method. Moreover, the complex of Eu(III) with *PAN* in *n*-propanol—water and isopropanol—water medium was investigated.

Experimental

The solutions of lanthanide perchlorates were obtained by dissolving appropriate oxides (99.9% pure—Pr_6O_{11}, Tb_4O_7—Rare Earth Products Ltd., Sm_2O_3, Eu_2O_3—Serva, Nd_2O_3, Gd_2O_3—Koch Light Lab.) in 3 mol/dm^3 perchloric acid and then diluting with water. The concentration of lanthanide in these solutions was determined complexometrically [6]. Stock solutions of *PAN* (POCh—Gliwice p.a.) were prepared by dissolving solid *PAN* in appropriate alcohols. Ethanol, n-propanol, isopropanol (POCh—Gliwice p.a.) were purified by distillation.

The experimental procedure, the instruments, the calculations and other reagents were the same as in earlier publications [1, 2].

At variable concentration of metal ions (series 1) or *PAN* (series 2) and $pH^\times$ = constant ($pH^\times = -\lg[H^+]$ in aqueous-alcohol solution [7]) absorption spectra of the system *Ln*(III)—*PAN*—alcohol—water were determined. The concentration of alcohol was 50 and 75% *v*/*v*. The solutions were prepared as described previously. The ionic strength of the solutions was 0.1 mol/dm^3 ($NaClO_4$). The measurement were performed at 21 ± 1 °C.

Results and Discussion

Absorption spectra of *Ln*(III)—*PAN*—alcohol—water systems showed the formation of red complexes in the $pH^\times$ range ~ 5.5–7. The absorption spectra of all systems with the exception of Pr(III) were similar in appropriate series. Figure 1 gives, as an example, the absorption spectra for the system Tb(III)—*PAN*—75% *v*/*v* ethanol (series 1). The isosbestic point was observed (at $\lambda = 495$ nm) in the absorption spectra of *PAN* at different concentrations of lanthanide ions (series 1) in all cases. For Pr(III) (series 1) absorption curves were not well separated. Therefore this system was not investigated further.

The molar ratio in the reaction of metal and *PAN* was determined by the straight line method [8]. The results show the formation of 1:1 complexes LnL^{2+} in all investigated systems.

The equilibrium constants (*K*) of the reaction:

$$Ln^{3+} + HL \rightleftharpoons LnL^{2+} + H^+ \tag{1}$$

were obtained by the *Watters* method [9]. The calculations of *K* were performed by the method of least-squares. Figure 2 shows, as an example, the graphic determination of equilibrium constants (*K*) from the plot $[Ln^{3+}] \cdot 10/[H^+](\bar{\varepsilon} - \varepsilon_1)$ vs. $[Ln^{3+}] \cdot 10^{-3}/[H^+]$ ($\bar{\varepsilon}$: mean absorption coefficient: ε_1: absorption coefficient of *PAN*). The stability constants (β) of complexes were evaluated using the equation $\beta = K/K_{OH}$ (K_{OH} is the

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

Ln(III)	*pK*	Δ_{pK}	lg β	*pK*	Δ_{pK}	lg β
	50% *v/v* ethanol			75% *v/v* ethanol		
Nd	2.71	0.96	10.06	2.44	0.97	10.96
Sm	2.75	0.96	10.02	2.13	0.96	11.27
Eu	3.45	0.97	9.32	2.98	0.98	10.42
Gd	3.48	0.96	9.29	3.06	0.97	10.34
Tb	3.56	0.97	9.21	3.31	0.98	10.09
	50% *v/v* *n*-propanol			75% *v/v* *n*-propanol		
Eu	2.85	0.96	8.60	2.47	0.97	9.13
	50% *v/v* isopropanol			75% *v/v* isopropanol		
Eu	2.86	0.97	9.24	2.22	0.98	10.53

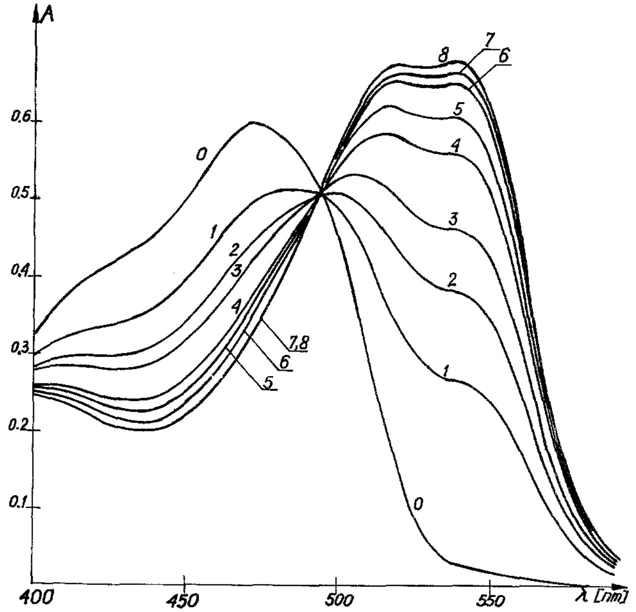

Fig. 1. Absorption spectra of *PAN* in the presence of Tb(III) in 75% *v/v* ethanol. Concentration of *PAN* $3.5 \cdot 10^{-5}$ mol/dm^3, Tb(III) concentration $C_{Tb} \cdot 10^4$ mol/dm^3 for curves: *0* 0.00; *1* 2.16; *2* 2.88; *3* 3.60; *4* 5.40; *5* 7.20; *6* 10.80; *7* 18.00; *8* 28.80; $pH^{\times} = 6.18$

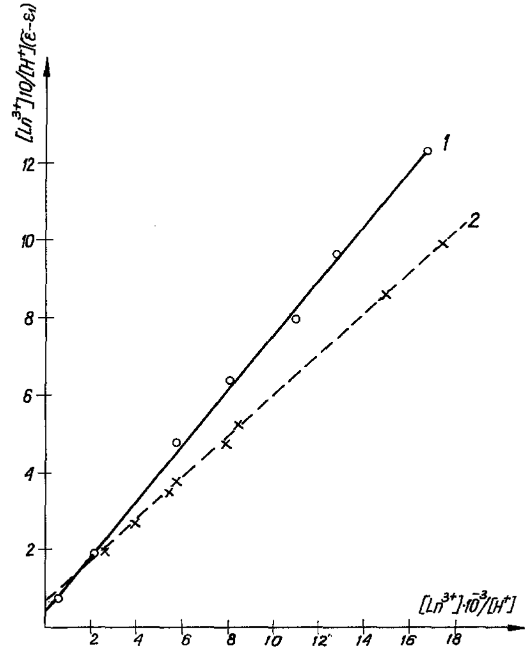

Fig. 2. *Watter*'s plot of $[Ln^{3+}]\cdot 10/[H^+](\bar{\varepsilon}-\varepsilon_l)$ vs. $[Ln^{3+}]\cdot 10^{-3}/[H^+]$ for the systems: *1* Eu(III)—*PAN*—50% *v*/*v* *n*-propanol; *2* Gd(III)—*PAN*—75% *v*/*v* ethanol

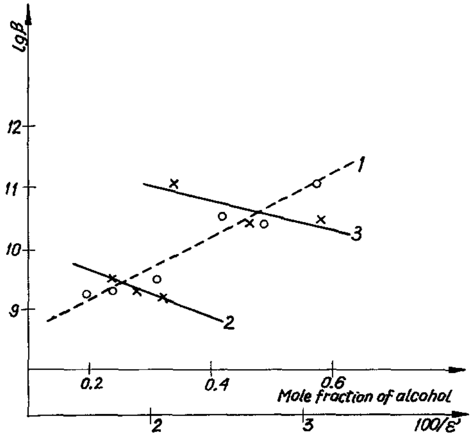

Fig. 3. Dependence of lg β vs. mole fraction of alcohol for the complex EuL^{2+} in alcohol—water solutions (*1*). Dependence of lg β vs. $100/\varepsilon'$ for the complex EuL^{2+} (*2*, *3*). Ranges of the mole fraction of alcohol for *2* and *3* are 0.191–0.308 and 0.414–0.572, respectively

dissociation constant of *PAN* in alcohol—water solution [2]). The values of constants K and β are reported in Table 1. The determined stability constants β are conditional stability constants.

As in previous papers [1–5], an increase in the stability constants of the complexes LnL^{2+} by increasing the concentration of alcohols was observed in all studied systems. The changes in the stability of complexes in the group Eu—Gd—Tb were slight.

For the complex EuL^{2+} we obtained linear relations $\lg\beta$ vs. mole fraction of alcohol (Fig. 3, curve 1) and $\lg\beta$ as a function of the inverse of the dielectric constant ($100/\varepsilon'$) of the medium (Fig. 3, curve 2 and 3) in alcohol—water solutions (alcohol = methanol [1], ethanol, isopropanol; values of ε' [10]). Analogous dependences we found previously for the complexes LnL^{2+}, where *Ln*(III) = Ho, Er, Yb, Lu and Y [2, 5]. The values of stability constants of the complex EuL^{2+} in the system ethanol—water and isopropanol—water are very similar. In *n*-propanol—water solutions a decrease of the stability constants of the complex EuL^{2+} is observed. A similar dependence was stated previously for the complexes HoL^{2+} and LuL^{2+} [5].

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