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Comparison of Complexation in $Pr(NO_3)_3$ and $Pr(SCN)_3$ Solutions

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Summary. The UV-Vis spectral data for $Pr(SCN)_3$–NaSCN and $Pr(NO_3)_3$–$LiNO_3$ are reported for 17, 25, 35, 50, and 61.3 °C. The calculated absolute values of the stability constants for the Pr nitrato complexes are higher than those for thiocyanates. The equilibria in outer vs. inner sphere complexation in the system are discussed.

Keywords. Lathanide; Absorbance; Effective stability constant.

Vergleich der Komplexierung in $Pr(NO_3)_3$- und $Pr(SCN)_3$-Lösungen

Zusammenfassung. Es wurden die UV-Vis-Daten für $Pr(NO_3)_3$–$LiNO_3$ und $Pr(SCN)_3$–NaSCN bei 17, 25, 35, 50 und 61.3 °C aufgezeichnet. Die berechneten absoluten Stabilitätskonstanten für die Pr-Nitratokomplexe sind höher als die der Thiocyanatokomplexe. Es wird das Gleichgewicht zwischen äußerer gegenüber innerer Sphären-Komplexierung diskutiert.

Introduction

The stepwise complexation of the lanthanide tripositive ions with simple counter ions is still the subject of investigation for many authors with respect to the increased utility of the lanthanides as spectroscopic probes in biological systems. Nitrates and thiocyanates form weak ionic pairs [1–7] with lanthanide ions. The absolute values of the stability constants of these complexes reported by different authors differ so much that only conclusions about the qualitative nature of these species are common. The complexation proceeds through the replacement of water from the first coordination sphere of the lanthanide by ligands and the so-called outer sphere complexation passes to inner sphere. The question is at what ligand concentration this process occurs and what is happening with the equilibrium outer-inner sphere with increasing temperature.

In the two previous papers [6–7] we reported the values of stability constants of $Pr,Nd,Sm(SCN)^{2+}$ and $Pr,Nd,Sm(SCN)_2^+$ species. However, we limited ourselves to 25 °C. To cover the full thermodynamic scope of the complexation we decided to extend our investigations to other temperatures: 10, 17, 35, 50, and 61.3 °C. It would allow us to determine the change of thermodynamical functions following the complexation process. Lanthanide thiocyanato and nitrato complexes are classified as predominantly outer sphere type species. The aim of this paper is to show that there is some difference in the complexation mode in these two complexes. Starting this comparison from Pr we will extend it to other lanthanides as well.

Experimental

The Pr salt solutions were standardized from Pr_6O_{11} (Merck). A UV-vis M1 spectrophotometer (Carl Zeiss Jena) connected with a thermostat was used. The absorption of Pr at 444 nm was recorded. As reference samples we used solutions of NaSCN or $LiNO_3$. The ionic strength was maintained at 4 M for $NaClO_4$ and $HClO_4$. We used the Sigma Plot program (Jandel Scientific Corporation 1988–90). to determine the values of molar absorptivity coefficients and stability constants of the different species from the absorbance readings. The program minimizes the least square sum: $(A_{exp} - A)^2$, where A_{exp} are the absorbance readings from the experiments and A is the absorbance from the model defined as:

$$A = \frac{(\varepsilon_0 + \varepsilon_1\beta_1L + \cdots \varepsilon_n\beta_nL^n)c_t}{(1 + \beta_1L + \cdots \beta_nL^n)}. \tag{1}$$

Different models for different number of species in the solution with the molar absorptivities ε_n and stability constants β_n were checked until the best "fit" between the A_{exp} and A was obtained. All measurements were carried out at a constant total Pr concentration $c = 0.049M$.

Results and Discussion

$Pr(SCN)_3$–NaSCN *System*

There is a marked increase of the Pr absorbance readings with the SCN^- concentration increase (Fig. 1). The values of the stability constants for the different

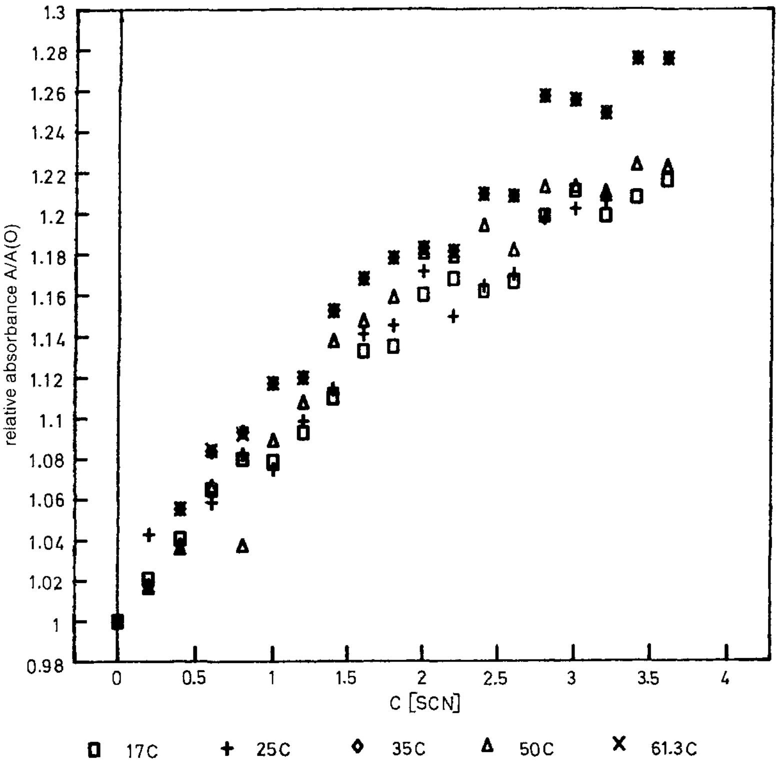

Fig. 1. The change of the absorbance of Pr for the $Pr(SCN)_3$–NaSCN system; constant ionic strength $I = 4$ ($\lambda_{max} = 444.2$ nm, path length $d = 1$ cm, $c_{NaSCN} = 0–4$ M); A/A(O) vs. c[SCN]

Table 1. Equilibrium data for the Pr^{3+}–SCN^- system (constant ionic strength $I = 4$, temperatures: 17, 25, 35, 50, and 61.3 °C)

Temperature K	β_1 $1/M\,dm^{-3}$	ΔH kJ/M	ΔG kJ/M	ΔS J/M K	ε_0	ε_1
290.16	0.2069	2.25	0.91	4.63	9	14
298.16	0.30	1.41	0.71	2.35	10.3	12.4
308.16	0.209	2.29	0.96	−2.36	9	14.7
323.16	0.263	−1.87	0.86	−8.42	8.7	13.2
334.16	0.204	−3.66	1.05	−14.1	10.1	15.3

The value of β_1 for 25 °C was taken from Ref. [7]

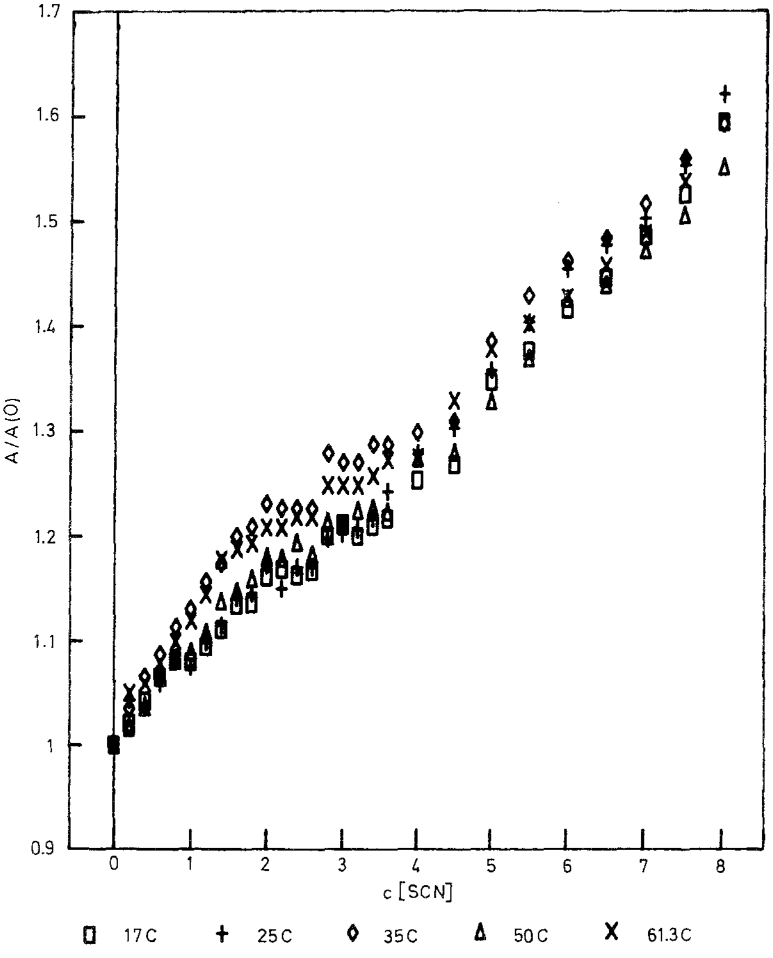

Fig. 2. The change of absorbance of Pr for the Pr(SCN)$_3$–NaSCN system; varied ionic strength ($\lambda_{max} = 444.2$–444.6 nm, $d = 1$ cm); A/A(O) vs. c[SCN]

temperatures are given in Table 1. We estimated the change of the thermodynamic functions following the formation of $Pr(SCN)^{2+}$ species based on the equations (2–4), where a, b, c denote the empirical parameters describing the changes of the stability constants β_n with the temperature T and $\Delta H, G, S$ denote the changes of the enthalpy, free energy, and entropy of the complexation.

$$\log \beta = a + b\,T + c\,T^2 \tag{2}$$

$$d(\log \beta)/dT = b + 2c\,T = \Delta H/2.303\,RT^2 \tag{3}$$

$$\Delta S = (\Delta H - \Delta G)/T. \tag{4}$$

The small near zero enthalpy and negative entropy changes result rather from the formation of the outer sphere complexes in this range of ligand concentrations.

The case with varied ionic strength presented in Fig. 2 confirms our previous results for 25 °C [7]. We can observe an increase of the Pr absorbance for the concentration in the range 0–2 M SCN^-, then the absorbance curve preserves a "plateau" character up to 4 M SCN^- and at last, for higher concentration, absorption increases again. What is new: the nonmonotonic character of the absorbance curve is preserved for all temperatures. The stepwise replacement of the water from the first coordination sphere of Pr^{3+} ion with the formation of inner sphere thiocyanato complexes is marked also for temperatures higher than 25 °C. The formation of the higher species $Ln(SCN)_n^{3-n}$ is also probable, especially if we take into account the significant shift of λ_{max} from 444.2 nm (no presence of SCN^-) to 446.6 nm (8 M SCN^-).

$Pr(NO_3)_3$–$LiNO_3$ *System*

Contrary to the thiocyanate system there is a marked decrease of Pr absorbance with increasing ligand concentration (Fig. 3). It seems that the formation of a complex with higher symmetry of the ligand field is possible, compared to the aquocomplex.

For the qualitative estimation of the data at varied ionic strength we applied the idea of "effective stability constant" introduced by Marcus [8–11].

$$\beta_n^* = [ML_n^{3-n}]/[M^{3+}][a_L]^n. \tag{5}$$

The ligand concentration is replaced by the activity, which in the case of $LiNO_3$ can be easily calculated from the activity [12] and density data of $LiNO_3$ [13]. The values of the effective stability constants of $Pr(NO_3)^{2+}$ and $Pr(NO_3)_2^+$ for different temperatures are given in Tables 2–3. If we compare the absolute values of β_1 and β_1^* with the value of the thermodynamic stability constant K_1^0 (K_1^0 for La and Nd equals 41 and 188; see Ref. [14]) we can note that they are much lower. This fact is justified if we take into account the change of the activity coefficients according to the equation reported by Darbari [15]:

$$\pi_f = \frac{y_{Ln}\,y_{NO_3}}{y_{LnNO_3}} = \frac{y_\mp^4\,(3{:}1)}{y_\mp^3\,(2{:}1)} \tag{6}$$

where y denotes the activity coefficients of the complex, free ion Ln^{3+} and NO_3^-. The change of the activity coefficient of the free ion y_{Ln} during complexation was

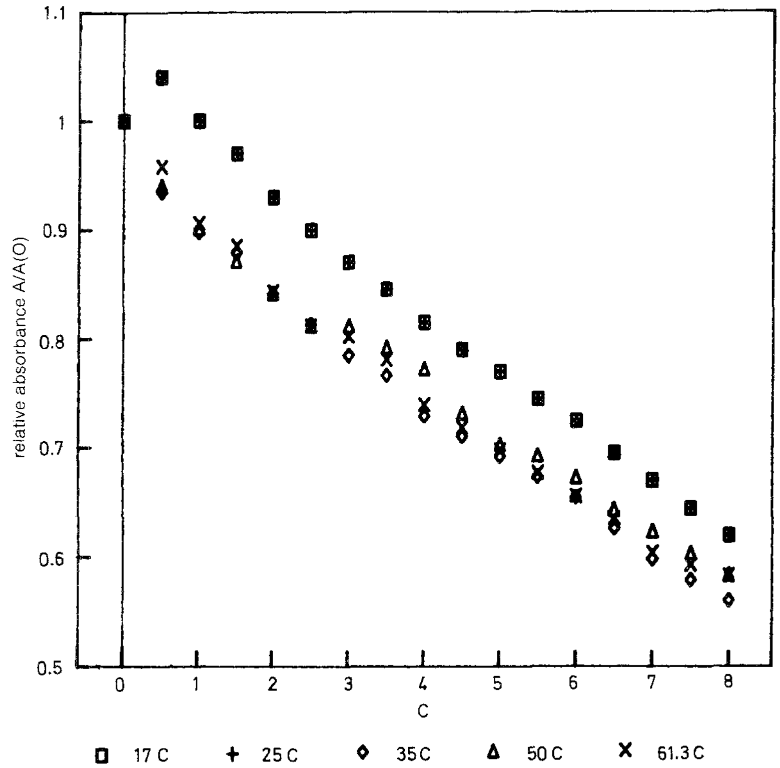

Fig. 3. The change of the absorbance of Pr for the Pr(NO$_3$)$_3$–LiNO$_3$ system: varied ionic strength: $c_{LiNO_3} = 0$–$8\,M$ ($\lambda_{max} = 444.2$ nm, $d = 1$ cm); A/A(O) vs. c

expressed as the function of the mean molar activity coefficient of the electrolytes 2:1 and 3:1. If we additionally take into account Davies [16] equation:

$$\log y_{\mp} = -0.50(Z_+ Z_-)\left(\frac{I^{0.5}}{1+I^{0.5}} - 0.3I\right)$$

Table 2. Equilibrium data for the Pr^{3+}–NO$_3^-$ system (constant ionic strength, temperature 17, 25, 35, 50 and 61.3 °C)

Temperature K	β_1	β_2 1/M dm^{-3}	ΔH_1 kJ/M	ΔG_1	ΔS_1 J/MK	ΔH_2 kJ/M	ΔG_2	ΔS_2 J/MK
290.16	0.84	0.06	−1.45	0.100	−5.33	−1.94	1.62	−12.3
298.16	0.87	0.06	−1.31	0.082	−4.68	−1.76	1.67	−11.5
308.16	0.75	0.06	−1.12	0.176	−4.20	−1.51	1.72	−10.5
323.16	0.69	0.04	−0.76	0.238	−3.09	−1.05	2.07	−9.6
334.16	0.70	0.05	−0.44	0.236	−2.04	−0.64	1.99	−7.9

Temp. K	290.16	298.16	308.16	323.16	334.16
e$_0$	11.1	10.6	10.3	9.6	9.4
e$_1$	7.2	7	7	6.5	6.4
e$_2$	8.3	7.9	7.9	8.9	6.8

Table 3. Equilibrium data for the Pr^{3+}–NO_3^- system (varied ionic strength, temperature 17, 25, 35, 50 and 61.3 °C)

Temperature K	β_1 1/M dm^{-3}	β_2	ΔH_1 kJ/M	ΔG_1	ΔS_1 J/MK	ΔH_2 kJ/M	ΔG_2	ΔS_2 J/MK
290.16	2.1	0.38	3.02	−0.41	11.8	−0.709	0.557	−4.3
298.16	2.3	0.42	1.99	−0.49	8.3	−0.63	0.514	−3.8
308.16	2.4	0.39	0.53	−0.3	3.4	−0.515	0.576	−3.6
323.16	2.4	0.33	−2.10	−0.7	−4.6	−0.305	0.712	−3.1
334.16	1.9	0.38	−4.30	−0.44	−11.4	−0.121	0.642	−2.3

(where Z denotes the charges of cation and anion and I refers to the ionic strength) we can find from calculation $\pi_f = 0.25$ for $I = 1$. This means that the value of K_1^0 should be a few times higher than β_1 due to the change of activity coefficients.

The changes of the effective stability constant β^* with the temperature are minor. The same is the case with the stability constant β measured for constant ionic strength. The thermodynamical parameters of the complexation are presented in Table 3. The small negative enthalpy changes result from the formation of outer sphere complexes: $Pr(NO_3)^{2+}$ and $Pr(NO_3)_2^+$.

We cannot neglect the existence of the inner sphere complexes if we take into account the small positive entropy changes (Table 3). The percentage of the inner sphere complexes in $Pr(NO_3)_3$ solutions is in our opinion higher than in the case of $Pr(SCN)_3$. If we compare the absolute values of stability constants, we can note that nitrato complexes of Pr are more stable, which is understandable in respect to the mono- and bi-and tridendate character of nitrates [17] and the exclusively monodendate character of thiocyanates.

The fact of gradual decrease of the Pr absorbance with the $[NO_3^-]$ increase is evidence for the formation of species with high symmetry. The ε_2 for the second symmetrical complex $Pr(NO_3)_2^+$ is lower than ε_0 for the aquion. The second complex is probably of outer sphere type if we take into account the reduction of the central ion charge during formation of the first complex and the decrease of the interaction in the $Pr(NO_3)^{2+}$ (NO_3^-) ion pair.

Conclusions

1. An equilibrium inner vs. outer sphere complexation exists in nitrato and thiocyanato complexes of the lanthanides.

2. The evidently lower stability of thiocyanato lanthanide complexes in comparison with nitrates results from the monodendate character of SCN^- as ligand.

3. The first complex $Pr(NO_3)^{2+}$ possesses more inner sphere character than $Pr(NO_3)_2^+$.

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