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Study of Nd-Nitrato Complexes in Aqueous-Methanol Solutions

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The stability constants $K_1 = 3.6$ and $K_2 = 1$ of $Nd(MeOH)_xNO_3^{2+}$ and $Nd(MeOH)_x(NO_3)_2^{+}$ complexes were determined spectrophotometrically. On the basis of an analysis of the stepwise stability constants ratio it was found that these are inner sphere complexes.

(Keywords: Neodymium nitrate; Formation degree; Overall stability constant; Stepwise stability constant)

Untersuchungen von Nd-Nitratokomplexen in wäßrig-methanolischen Lösungen

Es wurden die Stabilitätskonstanten $K_1 = 3.6$ und $K_2 = 1$ der Komplexe $Nd(MeOH)_xNO_3^{2+}$ und $Nd(MeOH)_x(NO_3)_2^{+}$ spektrophotometrisch bestimmt. Basierend auf einer Analyse der stufenweisen Stabilitätskonstanten wurde festgestellt, daß es sich um Komplexe der inneren Sphäre handelt.

Introduction

The determination of the structure and stability of lanthanide complexes using spectrophotometrical methods is based on the intensity change of the bands corresponding to the f-f transitions during replacement of the water in the hydratation shell of the lanthanide ion by other ligands. In the case of such ligands as NO_3^-, Cl^-, SCN^-, SO_4^{2-} this change is small due to small values of the stability constants. Some papers concerning the spectroscopic studies of the lanthanide nitrato complexes should be mentioned [1–11].

Choppin, Henrie and *Buijs* [1] compared the absorption band corresponding to the "hypersensitive" transition $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^4G_{7/2}$ in Nd^{3+} for $Nd(NO_3)_3$, $NdCl_3$ and $Nd(ClO_4)_3$. The completely different shape of the band in the case of the nitrates is explained by the authors by the occurence of the inner sphere nitrato complexes.

Katzin [2] investigated the spectra of: $Pr(NO_3)_3$, $Nd(NO_3)_3$, $Er(NO_3)_3$ solutions in *TBP* and concluded the formation of covalent bonds between NO_3^- and Ln^{3+} ions.

Abrahamer and *Marcus* [3] found on the basis of absorption spectra of the lanthanide nitrates that the bonds Ln^{3+}-NO_3^-, Ln^{3+}-H_2O, Ln^{3+}-*TBP* have similar strengths. Additional studies of the absorption spectra of the lanthanide nitrates on tri-isooctylamine showed the possibility of taking two coordination places in the coordination sphere of the lanthanide ion by the NO_3^- ion.

Barinow and *Tebieliew* [8] observed the influence of HNO_3 concentration and some of its salts on the absorption spectrum of $Nd(NO_3)_3$ in the region correspondent to the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition. Apart from the 4273 Å band, which in perchlorates solutions is attributed to the Nd^{3+} aquaion, the bands 4277 Å, 4284 Å corresponding to the $NdNO_3^{2+}$ and $Nd(NO_3)_2^+$ ions were observed in the nitrates solutions.

The aim of this paper was the determination of the stability constants of the neodymium nitrato complexes: $Nd(MeOH)_xNO_3^{2+}$, $Nd(MeOH)_x(NO_3)_2^+$ on the basis of the absorption spectra. Very detailed studies of this type have been conducted recently by *Hamze* [12] and coworkers.

Experimental

$HClO_4$ (analytically pure), $LiNO_3$ (pure), Nd_2O_3 (99.9% purity), methanol (pure), *EDTA* (analytically pure) and xylenol orange (pure) were obtained from Polskie Odczynniki Chemiczne.

Two sets of the binary mixtures were prepared with the following compositions:

1. $Nd(ClO_4)_3$ 0.0165 *M*, $LiNO_3$ 0–2.4 *M*.
2. $Nd(ClO_4)_3$ 0.0400 *M*, $LiNO_3$ 0–2.4 *M*.

The solutions of $Nd(ClO_4)_3$ were prepared by the dissolution and evaporation to dryness of a weighted amount of Nd_2O_3 in $HClO_4$. The concentration of Nd^{3+} was determined complexometrically by *EDTA*, using xylenol orange as an indicator.

The measurements were done using a PYE UNICAM SP-8-100 spectrophotometer. Absorption bands in the UV and visible regions were examined for each $Nd(NO_3)_3$ solution.

Results and Discussion

If the complexes exist in the metal salt solution, the absorbance A of the solution may be expressed as the sum of the absorbances of the particular complexes, according to the equation:

$$A = \alpha_0 A_0 + \alpha_1 A_1 + \ldots \alpha_n A_n \tag{1}$$

where α_0, α_1, α_n are the formation degrees of M and the ML, ... ML_n complexes, A_0, A_1, ... A_n are the absorbances corresponding to particular complexes.

This equation may be rearranged to a form more convenient for the calculations:

$$A/A_0 = \alpha_0 + (A_1/A_0)\cdot\alpha_1 + \ldots (A_n/A_0)\cdot\alpha_n \tag{2}$$

If we introduce the values of the stability constants, we will obtain:

$$\begin{aligned} A/A_0 = (1 + K_1(A_1/A_0)[L] + \\ + \ldots K_n(A_n/A_0)[L]^n)/(1 + K_1[L] + \ldots K_n[L]^n) \end{aligned} \tag{3}$$

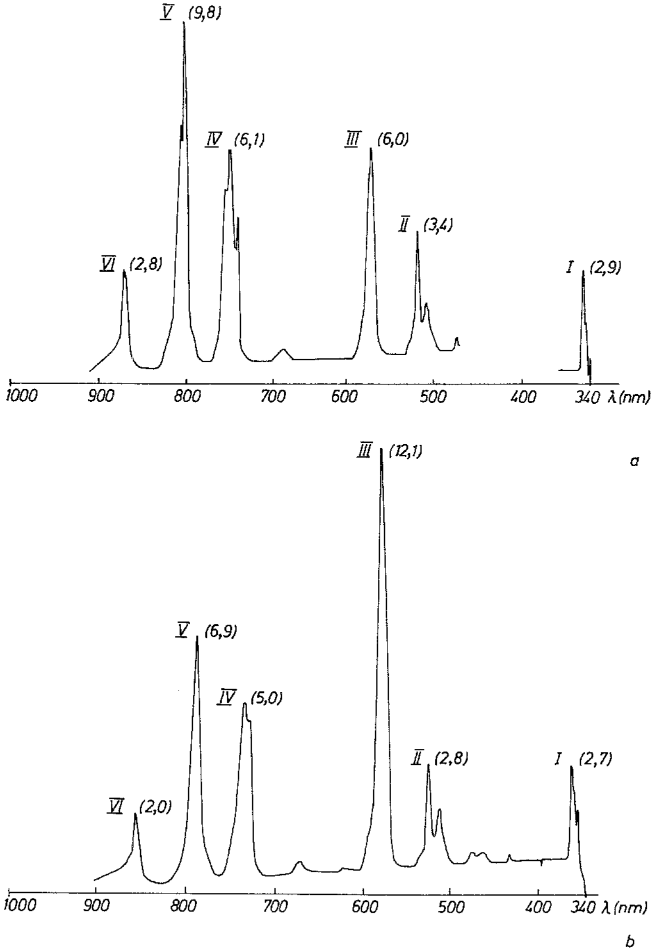

Fig. 1. Absorption spectra of the $Nd(Cl_4)_3$ methanolic solutions; *a* $Nd(ClO_4)_3 = 0.04\,M$, $LiNO_3 = 0$, $MeOH:H_2O = 90:10$, $l = 1$ cm; *b* $Nd(ClO_4)_3 = 0.04\,M$, $LiNO_3 = 1.8\,M$, $MeOH:H_2O = 90:10$, $l = 1$ cm

where $K_1, \ldots K_n$ are the overall stability constants of ML_n complexes and $[L]$ the ligand concentration.

Spectra Observations

The absorption spectra of $Nd(NO_3)_3$ methanol-water (90:10) solutions are shown in Fig. 1. We may notice six sharp peaks (the transitions corresponding to the particular peaks are given in Table 1). In the visible region the intensities of the bands II, IV, V, VI decrease and the intensity of the band III increases with the $LiNO_3$ concentration increase. The band III shows the most pronounced changes, therefore we chose it for the qualitative treatment. The intensity changes of the band III with the $LiNO_3$ concentration increase are given in Table 2.

Table 1. *Characterization of the absorption maxima of the* Nd *solvate*

Band	Transition
I	$^4D_{1/2,5/2,3/2} \longleftarrow {}^4I_{9/2}$
II	$^4G_{7/2} \longleftarrow {}^4I_{9/2}$
III	$^4G_{5/2} \longleftarrow {}^4I_{9/2}$
IV	$^4F_{7/2} \longleftarrow {}^4I_{9/2}$
V	$^2H_{9/2} \longleftarrow {}^4I_{9/2}$
VI	$^4F_{3/2} \longleftarrow {}^4I_{9/2}$

Table 2. *Intensity change of the band III with the increase of the* $LiNO_3$ *concentration* (the values a^* are for solutions with $[Nd^{3+}] = 0.04\,M$ and b^* for $Nd^{3+} = 0.0165\,M$)

$[LiNO_3]$ $[M]$	Intensity change = A/A_0	
	a^*	b^*
0.0	1.00	1.00
0.2	1.38	1.45
0.4	1.50	1.54
0.6	1.61	1.64
0.8	1.65	1.73
1.0	1.69	1.73
1.2	1.77	1.82
1.4	1.81	1.82
1.6	1.88	1.91
1.8	1.92	1.91
2.0	2.00	1.91
2.2	2.08	1.91
2.4	2.08	2.00

Table 3. *Parameters of Eq. (3) for different models of complexation* ($a = A_1/A_0$, $b = A_2/A_0$, $c = A_3/A_0$; these parameters were found using a least-squares method)

a	b	c	K_1	K_2	K_3	fit	
2.0			3.4			0.9269	model with one complex
1.7	2.8		3.6	1.0		0.9550	model with two complexes
1.5	2.5	4.4	4.6	1.6	0.1	0.9400	model with three complexes

Table 4. *β_l/β_2, S, T values for the* $Nd(MeOH)_x(NO_3)_2^+$ *complex* (concerning the S and T values denoting the entropy and electrostatic terms of the ratio β_1/β_2 see Ref. [13])

$\beta_1/\beta_2 = 12.8$	monodendate NO_3^-	bidendate NO_3^-
S	2.2	3.5
T	5.8	3.8

Table 5. *Formation degrees for the different* $LiNO_3$ *concentrations*

$[LiNO_3]$ $[M]$	$[Nd(ClO_4)_3]$ $[M] = 0.04$			$[Nd(ClO_4)_3]$ $[M] = 0.0165$		
	α_0	α_1	α_2	α_0	α_1	α_2
0.0	1.00	0.00	0.00	1.00	0.00	0.00
0.2	0.59	0.40	0.01	0.58	0.40	0.02
0.4	0.40	0.55	0.05	0.39	0.55	0.06
0.6	0.29	0.61	0.10	0.29	0.61	0.10
0.8	0.22	0.64	0.14	0.22	0.64	0.14
1.0	0.18	0.64	0.18	0.18	0.64	0.18
1.2	0.15	0.64	0.21	0.15	0.64	0.21
1.4	0.12	0.63	0.24	0.12	0.63	0.24
1.6	0.11	0.62	0.27	0.11	0.62	0.27
1.8	0.09	0.60	0.30	0.09	0.60	0.30
2.0	0.08	0.59	0.33	0.08	0.59	0.33
2.2	0.07	0.57	0.35	0.07	0.57	0.35
2.4	0.06	0.56	0.37	0.06	0.56	0.37

The results of the stability constants calculations are given in Table 3. We assumed the existence of one, two and three complexes in the solution. The model with two complexes is the most probable (best fit of data).

If we take into account the ratio β_1/β_2 of stepwise stability constants we will come to the conclusion that the complexes $Nd(MeOH)_xNO_3^{2+}$, $Nd(MeOH)_x(NO_3)_2^+$ are of the inner sphere type (Table 4).

The formation degrees of the particular complexes are given in Table 5. During calculation of these values (and the stability constants values) a correction to the free ligand concentration was introduced according to the equation:

$$c_T = [L] + \{K_1[L]/(1 + K_1[L] + K_2[L]^2)\} \cdot c_{0(M)} + \\ + \{K_2[L]^2 \cdot 2/(1 + K_1[L] + K_2[L]^2)\} \cdot c_{0(M)} \tag{4}$$

where L is the free ligand concentration, the second term in the equation refers to the concentration of the ML complex and the third term denotes the concentration of the ML_2 complex. This is the reason we have different values α_0, α_1, α_2 for the 0–0.6 M region of $LiNO_3$ concentration for the different $Nd(ClO_4)_3$ concentrations.

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