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Nitrate Ion Association with Nd^{3+}

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The overall stability constants K_1 and K_2 of $NdNO_3^{2+}$ and $Nd(NO_3)_2^+$ complexes were determined ($K_1 = 1.77$; $K_2 = 1.28$) using an extraction method with tri-*n*-butyl phosphate as the extractant. The ratio β_1/β_2 of the stepwise stability constants is discussed. It was established that the $Nd(NO_3)_2^+$ complex was an outer-sphere ion pair.

(Keywords: Lanthanide nitrato complexes; Neodymium nitrate, Tri-n-butyl phosphate; Stepwise stability constants, Formation degree; Coordination polyhedron)

Die Assoziation von Nitrat-Ion mit Nd^{3+}

Mittels einer Extraktionsmethode wurden die Stabilitätskonstanten K_1 und K_2 von $NdNO_3^{2+}$- und $Nd(NO_3)^+$-Komplexen bestimmt ($K_1 = 1.77$; $K_2 = 1.28$; Tri-*n*-butylphosphat als Extraktionsmittel). Das Verhältnis β_1/β_2 der stufenweisen Stabilitätskonstanten wird diskutiert. Es stellte sich heraus, daß der $Nd(NO_3)^+$-Komplex als ein „Outer-Shere"-Ionenpaar vorliegt.

Introduction

Apart from the theoretical importance, the knowledge of the stability constants of the lanthanide nitrato complexes is also of great practical importance. The lanthanide nitrates are starting material in the separation extraction process of these elements. The distribution coefficients and the separation factors of the lanthanides are connected with the stability constants of complexes present in the aqueous phase.

It was confirmed long time ago that lanthanide ions formed complexes with nitrate ions[1]. The complexes $LnNO_3^{2+}$ were the only which were examined accurately[2—5]. *Choppin* and *Strazik*[2] measured the stability constants of mononitrato lanthanide complexes. The enthalpy and entropy data for $Ln\mathrm{NO}_3^{2+}$ indicated that these were outer sphere ion pairs. The stability of the higher complexes is so little that it is very difficult to record their presence in the solution. *Sokołowska* and *Siekierski*[6] found (using an extraction method) that higher nitrato complexes ($Ln:\mathrm{NO}_3 = 1:4$, $1:5$) were inner-sphere ion pairs.

We decided to measure stability constants of $Ln(\mathrm{NO}_3)_2^+$ complexes because of discrepancies in data obtained by different authors[7—15], beginning our work from Nd.

We applied the extraction method, using tri-*n*-butyl phosphate. The equation of the extraction reaction in the case of lanthanide nitrates is the following[16] (*aq*—aqueous phase; *o*—organic phase):

$$Ln_{aq}^{3+} + 3\,\mathrm{NO}_{3o}^- + 3\,TBP_o \leftrightharpoons Ln(\mathrm{NO}_3)_3\,3\,TBP_o \tag{1}$$

The expression for the lanthanide distribution coefficient D (neglecting the activity coefficients) assumes the form:

$$D = \frac{[TBP]^3\,[\mathrm{NO}_3^-]^3}{K^{-1} + K_1 K^{-1}[\mathrm{NO}_3^-] + K_2 K^{-1}[\mathrm{NO}_3^-]^2} \tag{2}$$

In this expression K is the equilibrium constant of reaction (1), K_1 and K_2 are the stability constants of $Ln\mathrm{NO}_3^{2+}$ and $Ln(\mathrm{NO}_3)_2^+$ complexes. The equation (2) can be easily transformed into the form (3), more convenient for calculations:

$$W = \frac{1}{K} + \frac{K_1}{K}[\mathrm{NO}_3^-] + \frac{K_2}{K}[\mathrm{NO}_3^-]^2 \tag{3}$$

where: $W = \dfrac{[TBP]^3 \cdot [\mathrm{NO}_3^-]^3}{D}$.

Experimental

Reagents

Tri-*n*-butyl phosphate produced by Merck, analytically pure; $\mathrm{NH_4NO_3}$, Arsenazo III, $\mathrm{Nd_2O_3}$, and $\mathrm{HNO_3}$ were obtained from Polskie Odczynniki Chemiczne (all analytically pure, $\mathrm{Nd_2O_3}$ of 99.9% purity).

Procedure

The distribution coefficients of Nd were determined by shaking equal volumes of aqueous and organic phases in the separatory funnel at $25 \mp 0.5\,°\mathrm{C}$. The equilibrium was established in 10 min. The mixture of $\mathrm{Nd(NO_3)_3}$ and $\mathrm{NH_4NO_3}$ ($\mathrm{Nd^{3+}} = 10^{-4}\,M$, $\mathrm{NH_4NO_3} = 0.1$–$2.74\,M$) was used as an aqueous phase. The undiluted *TBP* (3,66 *M*) was used as an organic phase. The Nd concentration was determined spectrophotometrically using Arsenazo III[17]. 5 ml of aqueous phase was transferred to a 50 ml flask and then 10 ml of 0.01% Arsenazo III was added.

The volume of 50 ml was adjusted by HNO_3 with $pH = 2.6$. The reextraction of the organic phase was carried out using Arsenazo III solution. The absorbance was recorded at 665 nm, in the presence of Arsenazo III as a reference.

Results and Discussion

Concerning equation (3) we should notice that if the complexes are absent in the solution, the expression for W should be constant. In our experiment (see Tab. 1) W changes, therefore complexes of Nd exist in the solution. The stability constants K_1 and K_2 were determined using the curve-linear regression analysis technique[18]. The least square criterion was used to minimize the sum of the squares of the vertical distances between the data points and the appriopriate curve. The curve which minimizes this sum is the least square regression curve, which represents the best fit. The correlation coefficient reflects the goodness of the fit and is defined as

Table 1. *Extraction data for the* $Nd(NO_3)_3$—NH_4NO_3—*TBP system*

$[NO_3^-]/M$	Distribution coefficient of Nd D	W exp.	W from regression curve
0.1	0.016	3.08	23.14
0.21	0.048	9.46	27.78
0.34	0.082	23.5	34.04
0.49	0.135	42.72	42.29
0.66	0.28	50.34	53.01
0.85	0.38	79.23	66.68
1.06	0.60	97.32	83.87
1.29	0.81	129.93	105.21
1.54	1.15	155.7	131.4
1.81	1.79	162.41	163.17
2.1	2.44	186.1	201.3
2.41	2.82	243.35	246.71
2.74	3.41	295.76	300.78

$$R^2 = \frac{\text{sum of squares due to regression}}{\text{total (corrected) sum of squares}}$$

In our case the equation for the least square curve assumes the following expression:

$$W = 19.45 + 34.45\,[NO_3^-] + 24.83\,[NO_3^-]^2 \qquad (4)$$

The correlation coefficient R^2 approaches 1 ($R^2 = 0.9571$), the quality of the fit is good.

The degree of formation, as defined by *Bjerrum*[19], for the formation of individual complexes is given by the equation:

$$\alpha_n = \frac{K_n[A]^n}{1 + \sum_1^N K_n[A]^n} \tag{5}$$

where K_n are the overall stability constants (in our case $K_1 = 1.77$ and $K_2 = 1.28$) and A is the ligand concentration.

The calculated degrees of formation of free Nd^{3+} and its complexes are given in the Table 2.

Table 2. *Degrees of formation for* Nd^{3+}, $NdNO_3^{2+}$, *and* $Nd(NO_3)_2^+$

$[NO_3^-]/M$	$\alpha_{Nd^{3+}}$	$\alpha_{NdNO_3^{2+}}$	$\alpha_{Nd(NO_3)_2^+}$
0.1	0.84	0.15	0.01
0.21	0.70	0.26	0.04
0.34	.0.57	0.34	0.08
0.49	0.46	0.40	0.14
0.66	0.37	0.43	0.20
0.85	0.29	0.44	0.27
1.06	0.23	0.43	0.33
1.29	0.18	0.42	0.39
1.54	0.15	0.40	0.45
1.81	0.12	0.38	0.49
2.1	0.10	0.36	0.54
2.41	0.08	0.33	0.58
2.74	0.06	0.31	0.62

A separate discussion has to be devoted to the ratio β_1/β_2 of the stepwise stability constants ($\beta_1 = K_1$; $\beta_2 = K_2/K_1$). *Bjerrum*[19] proposed the following equation for the ratio of the stepwise stability constants:

$$\beta_1/\beta_2 = S \cdot T \tag{6}$$

where S is the statistical factor, which is readily calculated, when we know the number of ligand groups and the coordination number of central ion, and T is the work done in bringing a second ligand from infinity to its equilibrium position in the ML_2 complex, connected with the overcoming of repulsion invoked by the already bound ligand. Factor T is determined by the equation:

$$\lg T = \frac{1}{2.303} \cdot \frac{e^2}{Dr} \cdot \frac{1}{kK} \tag{7}$$

Table 3. β_1/β_2, *S, T values for the* $Nd(NO_3)_2^+$ *complex*

	monodendate NO_3^-	bidendate NO_3^-
β_1/β_2	2.46	2.46
S	2.2	3.5
T	1.1	0.7

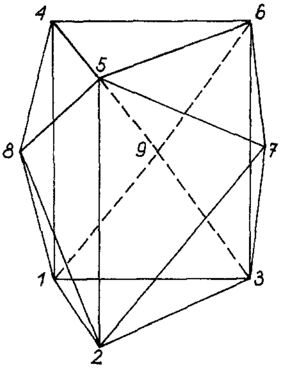

Fig. 1. Illustration of the tricapped trigonal prisma

where e is the electronic charge, D the dielectric constant, r the separation of the charged ligands in the ML_2 complexes, k the *Boltzmann* constant, and K the absolute temperature. According to *Manning*[20], the value $T = 1.4$ should be a lower limit for the lanthanide complexes and $T = 1.1$ should correspond with ion pairs.

The values P, determined experimentally, and values S calculated for mono- and bidendate NO_3^- ions together with T values are given in Table 3. It was assumed that Nd^{3+} ion was nonacoordinated[21]. The coordination polyhedron posses the shape of a tricapped trigonal prisma (Fig. 1). If the NO_3^- ion is bidendate, then the first ligand can take up 21 different positions while forming the $NdNO_3^{2+}$ complex, and the second ligand can take up 12positions during formation of the $Nd(NO_3)_2^+$ complex, if we preclude simultaneous occurence of: 25.56; 25.23; 25.45; 25.12; 25.57; 25.58; 25.28; 25.27 positions with increased ligand repulsion. Since the tendency to split off is proportional to the number of ligands taken up, it follows from this that 2 stepwise constants must have ratios proportional to the fractions: 21/1 : 12/2.

The value $S = 3.5$ will be connected with $T = 0.7$. This model cannot be accepted since $T \nless 1$. The value $T = 1.1$ corresponding with unidendate NO_3^- ions reflects the existence of a $Nd(NO_3)_2^+$ ion pair, the Nd^{3+} ion being separated from the NO_3^- ions by water molecules.

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