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Nitrate Ion Association with La^{3+}, Gd^{3+}, and Dy^{3+}

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Using the solvent extraction method it was found that the stability constants $K_1{}^0$ of the La, Gd, $DyNO_3{}^{2+}$ complexes are 41, 39, 21, respectively. The change of stability constants of $LnNO_3{}^{2+}$ complexes in the lanthanide series was related to the change of the amount of "inner sphere complexation".

(Keywords: Outer sphere complexes; Inner sphere complexes; Stability constant; Closest approach distance; Lanthanide ion)

Zur Assoziation von Nitrationen mit La^{3+}, Gd^{3+} *und* Dy^{3+}

Mittels der Lösungsmittelextraktionsmethode wurden die Stabilitätskonstanten $K_1{}^0$ von La, Gd und $DyNO_3{}^{2+}$ zu 41, 39 und 21 bestimmt. Der Unterschied der Stabilitätskonstanten der $LnNO_3{}^{2+}$-Komplexe innerhalb der Lanthanidenserie wurde mit dem Wechsel der „Inneren-Sphären-Komplexierung" verknüpft.

Introduction

We emphasized in the previous papers [1–2] that the nitrato lanthanide complexes are of the outer-sphere type in their ion-ligand bond character. There are some experimental data which confirm the existence of small amounts of inner-sphere complexation in lanthanide nitrates. Electrical conductance data [3–4] show that "the amount of inner-sphere complexation" decreases from La to Lu for concentrations greater than 0.9 *M*; the same is the case with the average ligand number. It results from NMR [5–6], *Raman* [7–9] and ultrasound absorption data [10] that inner-sphere complexes dominate in the solution at higher concentrations.

The aim of this paper is to determine stability constants of $LaNO_3{}^{2+}$, $GdNO_3{}^{2+}$, $DyNO_3{}^{2+}$ complexes as well as the closest approach distances of the ions. If some "amount of inner-sphere complexation" exists in lanthanide nitrates it should be seen in the change of stability constants values and in the values of the closest approach distances.

Experimental

Reagents: Tri-*n*-butyl phosphate (Merck, analytically pure); NH_4NO_3, Arsenazo III (Polskie Odczynniki Chemiczne, analytically pure); La_2O_3, Gd_2O_3, Dy_2O_3 (Koch Light Laboratory, 99.9% purity).

Procedure: The determination of the lanthanide distribution coefficients was given earlier [1]; undiluted *TBP* was used as an organic phase and the solutions of NH_4NO_3 as an aqueous phase. The concentrations of the lanthanides in both phases were determined spectrophotometrically using Arsenazo III.

Results and Discussion

The mean distribution coefficients of the lanthanides are given in Table 1. The following equation determines the distribution coefficient of the lanthanide during the extraction using *TBP*.

$$D = \frac{[TBP]^3[NO_3^-]^3}{K^{-1} + K^{-1}\beta_1[NO_3^-] + K^{-1}\beta_2[NO_3^-]^2}$$

If the activity coefficients are neglected it can be found that $K = 0.01$, $\beta_1 = 0.2$, and $\beta_2 = 0.2$ for La extraction. Table 2 includes the values of empirical distribution coefficients and those calculated. In the case of the model with the activity coefficients (all details which refer to this model are given in [2]) correlation between $D_{\text{calc.}}$ and $D_{\text{emp.}}$ is better. It has been found that in the case of the model neglecting the activity coefficients, the mean difference between $D_{\text{calc.}}$ and $D_{\text{emp.}}$ for the whole concentration

Table 1. *Distribution coefficients D of the lanthanides with standard deviations s (temp. 25 °C; volume phase ratio = 1; time of extraction = 10 min)*

$c_{\text{aqu. phase}}$ $[NO_3^-]$	D(La)	s	D(Gd)	s	D(Dy)	s
0.1	0.012	0.002	0.012	0.001	0.014	0.002
0.21	0.016	0.001	0.025	0.001	0.026	0.004
0.34	0.042	0.002	0.053	0.002	0.048	0.003
0.49	0.087	0.008	0.107	0.002	0.09	0.003
0.66	0.160	0.011	0.198	0.003	0.157	0.001
0.85	0.231	0.016	0.320	0.016	0.265	0.006
1.06	0.382	0.011	0.472	0.028	0.438	0.002
1.29	0.598	0.060	0.717	0.023	0.71	0.036
1.54	0.975	0.091	1.00	0.040	1.02	0.050
1.81	1.41	0.038	1.43	0.047	1.65	0.090
2.1	1.95	0.15	2.09	0.037	2.33	0.090
2.41	2.80	0.23	2.85	0.098	3.19	0.060
2.74	3.19	0.10	3.97	0.170	4.12	0.200

Table 2. *Comparison of $D_{calc.}$ with $D_{emp.}$ for La (all calculations were performed using the computer Amstrad CPC 6128)*

$c_{\text{aqu. phase}}$ $[NO_3^-]$	$D_{\text{calc.}}$ model without activity coefficients	$D_{\text{calc.}}$ model with activity coefficients	$D_{\text{emp.}}$
0.1	0.0005	0.003	0.0012
0.21	0.004	0.016	0.016
0.34	0.018	0.043	0.042
0.49	0.050	0.090	0.087
0.66	0.115	0.163	0.160
0.85	0.229	0.273	0.231
1.06	0.406	0.429	0.382
1.29	0.661	0.643	0.598
1.54	1.00	0.936	0.975
1.81	1.44	1.33	1.41
2.1	1.97	1.85	1.95
2.41	2.59	2.54	2.80
2.74	3.31	3.49	3.19

Table 3. *Stability constants of $Ln\text{NO}_3^{2+}$ complexes extrapolated to zero ionic strength (K_1^0 refers to the extraction constant, β_1 and β_2 denote the overall stability constants)*

K_1^0 $[M^{-1}]$	K^0 $[M^{-6}]$	$\mathring{a}$ [A]	*Ln*
41	1.2	12.5	La
188	21	6.0	Nd
152	18.5	6.5	Sm
38.7	2.4	8.5	Gd
21	0.8	12.5	Dy

Table 4. *Concentration stability constants of $Ln\text{NO}_3^{2+}$ complexes (K refers to the extraction constant)*

β_1	β_2	*K*	*Ln*
0.2	0.2	0.01	La
1.77	1.28	0.05	Nd
0.51	0.70	0.02	Sm
0.29	0.30	0.01	Gd
0.27	0.29	0.01	Dy

range of NH_4NO_3 is 21.6% and in the case of the second model this difference equals only 3.3%. The values of the closest approach distances of ions $\mathring{a}$ are given in Table 3. It is probable that decrease of $\mathring{a}$ values going from La to Nd, Sm is connected with the increase of "the amount of inner-sphere complexation". For the heavy lanthanides, the values of $\mathring{a}$ increase which would be explained as a result of stronger interaction of lanthanide-water compared to lanthanide-nitrate. The arrangement of water molecules around the central ion refers to the tricapped trigonal prisma for the lanthanides La-Pm [11] and to the square antiprisma for the lanthanides Tb-Lu. This difference in the shape of coordination polyhedrons may determine the equilibrium inner versus outer-sphere complexation. In the case of the tricapped trigonal prisma, water molecules are bonded more loosely with the central ion and therefore their replacement by nitrate ions is easier than in the case of square antiprisma.

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