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Nitrate Ion Association with Sm^{3+} Ion

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A solvent extraction method with *TBP* as an extractant was used for the determination of the stability constants K_1° for the $SmNO_3^{2+}$ complex, for different least approach distances $\mathring{a}$ of ions. It was established that $\mathring{a} = 6.5$ Å for $SmNO_3^{2+}$.

(Keywords: Samarium nitrate; Activity coefficient; Least approach distance of ions; Overall thermodynamic stability constant)

Zur Assoziation von Nitrat-Ion mit Sm^{3+}

Die Stabilitätskonstanten K_1° für den $SmNO_3^{2+}$-Komplex bei verschiedenen Mindestannäherungsdistanzen $\mathring{a}$ der Ionen wurden mittels einer Lösungsmittelextraktionsmethode mit *TBP* ermittelt. Der beste Wert für $\mathring{a}$ war 6.5 Å.

Introduction

This work is the continuation of our lanthanide nitrate stability constants studies. The previous work[1] presented a method to calculate the stability constants by applying extraction data in the $Nd(NO_3)_3$—NH_4NO_3—*TBP* system:

$$W = \frac{1}{K} + \frac{K_1}{K}[NO_3^-] + \frac{K_2}{K}[NO_3^-]^2 \tag{1}$$

If we introduce activity coefficients Eq. (1) will obtain the form:

$$W\frac{y_\pm^4}{y_{TBP}^3} = \frac{1}{K^\circ} + \frac{K_1^\circ}{K^\circ}\pi_1[NO_3^-] + \frac{K_2^\circ}{K^\circ}\pi_2[NO_3^-]^2 \tag{2}$$

where $y_\pm$ is the mean molar activity coefficient of the lanthanide nitrate in NH_4NO_3 solution, π_1, π_2 express the activity coefficient change of the Ln^{3+} ion during complex formation, y_{TBP} represents the molar activity coefficient of tri-*n*-butyl phosphate (in the case of undiluted *TBP*

$y_{TBP} = 1$), K° is the thermodynamic equilibrium constant of the extraction reaction, and K_1°, K_2° are the overall thermodynamic stability constants of the $Ln\mathrm{NO}_3^{2+}$, $Ln(\mathrm{NO}_3)_2^+$ complexes.

Experimental

Undiluted *TBP* was used as an organic phase and the mixture of $\mathrm{Sm(NO_3)_3}$ and $\mathrm{NH_4NO_3}$, $[\mathrm{Sm(NO_3)_3}] = 2 \cdot 10^{-4}\,M$, $[\mathrm{NH_4NO_3}] = 0.1$–$2.74\,M$, as an aqueous phase. The spectrophotometrical determination of Sm in both phases, using Arsenazo III, was the same as in a previous work[1].

Results and Discussion

Table 1 contains the values of the extraction coefficients *D* and the *W* values which increase with increased $\mathrm{NO_3^-}$ concentration [see Eq. (1)].

The Eq. (2) parameters: $y_\pm^4$ *W*, π_1 $[\mathrm{NO_3^-}]$ are given in Table 2. The values of $y_\pm^4$ were calculated based on the *Rosen* equation[2]:

$$\lg \gamma_\pm = \frac{-0.5091\, Z_1 Z_2 \sqrt{I}}{1 + 0.3286\, \mathring{a} \sqrt{I}} - \frac{n_M}{v} \lg a_{\mathrm{H_2O}} - \lg[1 - 0.018\,(n_S - v)\, m_S] \quad (3)$$

where $\gamma_\pm$ is the mean molal activity coefficient of $Ln(\mathrm{NO_3})_3$, Z_1, Z_2 are the charges of the cation and the anion, I is the molal ionic strength, $\mathring{a}$ is the least approach distance of the ions (in Å), n_M is the hydration number of the extracted ion (we assumed that $n_M = 9$ for $\mathrm{Sm^{3+}}$), v is the number of ions formed during the dissociation of the extracted compound [$v = 4$ for $Ln(\mathrm{NO_3})_3$], $a_{\mathrm{H_2O}}$ is the water activity (see Table 3), n_S is the hydration

Table 1. *The extraction coefficients D of Sm (the mean values of D were taken from three experiments; temp. 25 °C ± 0.5 °C)*

$[\mathrm{NO_3^-}]$ [*M*]	*D*	$W = \dfrac{[TBP]^3 [\mathrm{NO_3^-}]^3}{D}$
0.1	0.045	1.089
0.21	0.066	6.88
0.34	0.113	17.05
0.49	0.179	32.22
0.66	0.309	45.61
0.85	0.435	69.22
1.06	0.707	82.59
1.29	0.960	109.63
1.54	1.27	140.99
1.81	1.92	151.42
2.1	2.72	166.93
2.41	3.51	192.52
2.74	5.15	195.83

Table 2. *The parameters, for Eq. (2), calculated for an å value of 6.5 Å giving the best fit*

$\pi_1 [NO_3^-]$	$y_\pm^4 W_{exp.}$	$y_\pm^4 W_{calc.}$
0.0268	0.0783	0.2732
0.0366	0.2775	0.3534
0.0565	0.4706	0.5162
0.0711	0.6798	0.6357
0.0865	0.7853	0.7611
0.1031	1.0177	0.8975
0.121	1.0818	1.044
0.1411	1.3041	1.2085
0.1622	1.5729	1.3811
0.1862	1.6247	1.5775
0.213	1.7501	1.7968
0.2435	2.0644	2.0464
0.2783	2.1163	2.3311

Table 3. *The osmotic coefficients and the derived water activities of the* NH_4NO_3 *solutions*[3] *at 25 °C; m... molal concentration of the solution;* φ... *osmotic coefficient;* $\varphi = -\frac{2\,303 \lg a_{H_2O}}{v m M_1}$, *where* M_1 *is the molecular weight of the solvent* ($M_1 = 18$) *and* v *is the number of ions after dissociation of the electrolyte* ($v = 2$)

m	φ	$-\lg a_{H_2O}$
0.1	0.911	0.0014
0.2	0.890	0.0028
0.3	0.876	0.0041
0.4	0.864	0.0054
0.5	0.855	0.0067
0.6	0.847	0.0079
0.7	0.840	0.0092
0.8	0.834	0.01
0.9	0.829	0.0117
1.0	0.823	0.0129
1.2	0.813	0.0153
1.4	0.803	0.0176
1.6	0.793	0.0198
1.8	0.785	0.0221
2.0	0.776	0.0243
2.5	0.758	0.0296
3.0	0.743	0.0348
3.5	0.728	0.0399

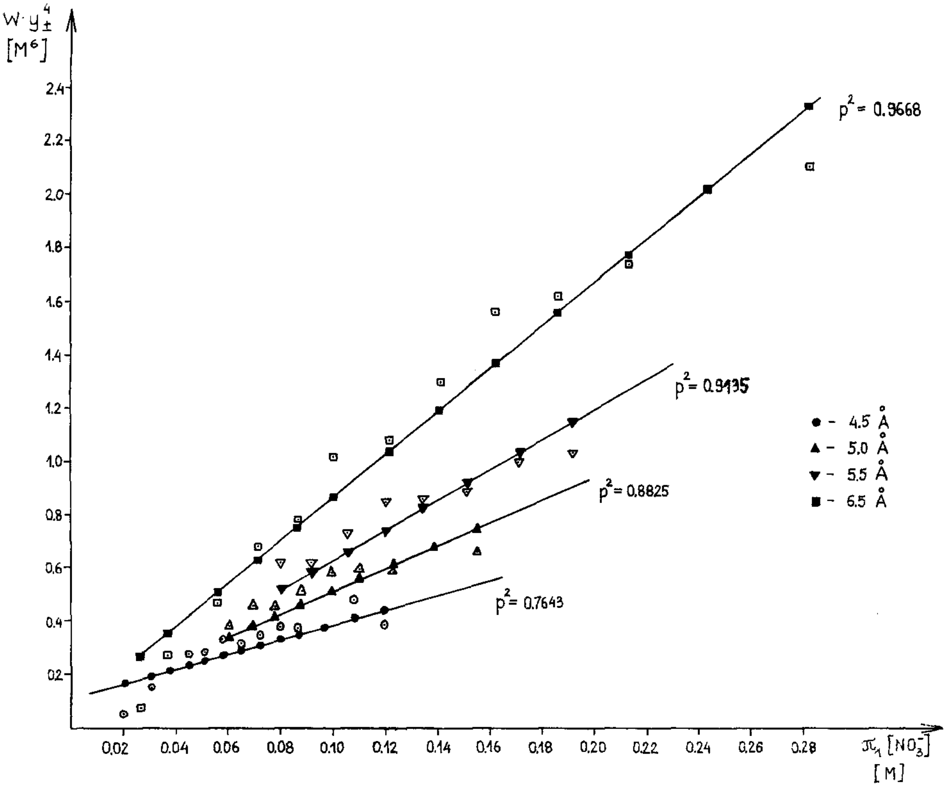

Fig. 1. The straight lines $y_{\pm}^4 W = b + a\pi_1[NO_3^-]$ for different $\mathring{a}$ values (open marks $y_{\pm}^4 W_{exp.}$, full marks $y_{\pm}^4 W_{calc.}$)

number of the salting-out ion (according to *Harned*[4] $n_S = 0$ for NH_4^+ in NH_4NO_3 solution), and m_S is the molality of the salting-out agent solution.

The values of $\lg \gamma_{\pm}$ were converted to $\lg y_{\pm}$ based on the *Harned* equation[4]:

$$\lg \gamma_{\pm} = \lg y_{\pm} + \lg(d/d_0 - cM_2/1\,000\, d_0) \quad (4)$$

where d is the density of the electrolyte solution (the densities of NH_4NO_3 solutions were taken from[5]), d_0 is the density of the solvent (in our case $d_0 = 1$), c is the molar concentration of the electrolyte solution, and M_2 is the molecular mass of the solute ($M_2 = 80$).

The values of π_1 determining the activity coefficient changes of Ln^{3+} during complex formation were calculated according to formula:

$$\pi_n = \frac{-0.5091\,\Delta Z^2 \sqrt{I}}{1 + 0.3286\,\mathring{a}\sqrt{I}} - \frac{n_M}{v} \lg a_{H_2O} - \lg[1 - 0.018\,(n_S - v)\,m_S] \quad (5)$$

Table 4. *The å values for* $SmNO_3^{2+}$

å (experimental)	$å = r_{Sm^{3+}} + r_{N—O} + d_{H_2O}$	$å = r_{Sm^{3+}} + r_{N—O} + 2\, d_{H_2O}$
6.5 Å	4.94 Å	7.70 Å

Table 5. *The* **a** *and* **b** *coefficients of the equations* $y_\pm^4\ W_{calc.} = b + a\pi_1 [NO_3^-]$ *together with* $K°$ *and* $K_1°$ *values*

a	b	$K° [M^{-6}]$	$K_1° [M^{-1}]$	$å [Å]$	p^2
2.8508	0.1068	9.4	27	4.5	0.7643
4.3025	0.0876	11.4	49	5.0	0.8825
5.5653	0.0798	12.5	70	5.5	0.9135
6.6715	0.0862	11.6	77	6.0	0.9394
8.1828	0.0539	18.5	152	6.5	0.9668
	negative			7.5	

where ΔZ^2 is the change of the ion charge square calculated according to:

$$Ln^{3+} + n\,NO_3^- \rightleftharpoons Ln(NO_3)_n^{3-n}$$

$$\Delta Z^2 = 3^2 + n \cdot 1 - (3-n)^2;\ \Delta Z^2 = 6;\ 10 \text{ for } n = 1;\ 2$$

The $y_\pm^4\ W_{exp.}$ quantities, which were found from experimental data, are close to the fitted values $y_\pm^4\ W_{calc.}$ (found on the base of a least square linear regression[6]).

The plots $y_\pm^4\ W_{calc.}$ vs. $\pi_1 [NO_3^-]$ were tested for different least approach distances å. The p^2 values reflecting the goodness of the fit increase with the rise of å. Therefore a reasonable value for å for $SmNO_3^{2+}$ is 6.5 Å (see Table 2). If we compare the sum of the Sm^{3+} radius ($r_{Sm^{3+}} = 0.96$ Å according to *Shannon*[7]), the water molecule diameter ($d_{H_2O} = 2.76$ Å according to *Morgan*[8]), and the length of the N—O bond in the NO_3^- ion[9] ($r_{N—O} = 1.22$ Å), we will notice (see Table 4) that our å value corresponds with å values of the $SmNO_3^{2+}$ complex possessing one or two water molecules between the central ion and the ligand. Probably both kinds of complexes are present in the solution and their population depends on the NO_3^- ion concentration. Table 5 contains the values of $K_1°$ and $K°$. These values were found on the base of a and b coefficients of equations: $y_\pm^4\ S_{calc.} = b + a\pi_1 [NO_3^-]$ describing the straight lines of Fig. 1.

The stability constant values reported in this work seem reasonable presuming one complex in the solution; the models with two or more complexes were unreasonable due to the negative values for the stability constants.

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