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The Influence of the Temperature on the Formation of Samarium Nitrato Complexes

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The stability constants of the $Sm(NO_3)^{2+}$ complex were determined at three temperatures, using the solvent extraction method. It was found that: $K_1^0 = 63.6$ at 17 °C, 30.3 at 35 °C, 20.1 at 50 °C. This corresponds with the formation of a $Sm(H_2O)(NO_3)^{2+}$ complex at 17 °C and a $Sm(H_2O)_2(NO_3)^{2+}$ complex at 50 °C.

(Keywords: Samarium nitrate; Enthalpy change; Entropy change)

Der Einfluß der Temperatur auf die Bildung von Samarium Nitrato Komplexen

Die Stabilitätskonstanten von $Sm(NO_3)^{2+}$ Komplexen wurden mittels der Lösungsmittelextraktionsmethode bei drei Temperaturen bestimmt. Dabei ergab sich $K_1^0 = 63.6$ bei 17 °C, 30.3 bei 35 °C und 20.1 bei 50 °C. Das entspricht der Bildung eines $Sm(H_2O)(NO_3)^{2+}$ Komplexes bei 17 °C und eines $Sm(H_2O)_2(NO_3)^{2+}$ Komplexes bei 50 °C.

Introduction

The previous paper [1] presented the way of calculating the stability constants by applying extraction data in the $Sm(NO_3)_3$-NH_4NO_3-*TBP* system. We haven't taken into account the possibility of the existence of hydroxocomplexes $Sm(OH)^{2+}$, $Sm(OH)_2^+$, and $Sm(OH)_3$, which under our experimental conditions ($pH = 5$) can be formed in small amounts. The equation describing the equilibrium in the extraction process will have the form:

$$Wy_{\pm}^4 = \frac{1}{K^0} + \frac{K^0{}_1}{K^0}\pi_1[NO_3^-] + \frac{\beta_1}{K^0}\pi_1[H^+]^{-1} + \frac{\beta_2}{K^0}\pi_2[H^+]^{-2} + \frac{\beta_3}{K^0}\pi_3[H^+]^{-3}$$

where W, $y_{\pm}^4$, n, K^0, K_1^0 are the quantities explained previously [1]. b are

Table 1. *Extraction coefficients of* Sm *at different temperatures*

Concentration of $NH_4NO_3[M]$	Extraction Coefficient D		
	17°	35°	50°
0.1	0.022	0.020	0.022
0.21	0.053	0.051	0.027
0.34	0.156	0.084	0.073
0.49	0.260	0.151	0.113
0.66	0.370	0.316	0.194
0.85	0.576	0.434	0.273
1.06	0.974	0.751	0.452
1.29	1.378	1.064	0.561
1.54	2.194	1.788	1.017
1.81	2.690	2.216	2.112
2.1	3.553	3.083	2.176
2.41	4.773	4.004	2.791
2.74	6.100	5.173	4.024

Table 2. *Stability constants of* $Sm(NO_3)^{2+}$ *complex at different temperatures* ($å$ is the least approach distance of the ions, K^0 denotes the stability of the equilibrium of the extraction reaction, K_1^0 denotes the stability constant of the complex, and p^2 is the "fit"-correlation coefficient)

$K^0 [M^{-6}]$	$K_1^0 [M^{-1}]$	$å$ [Å]	p^2	Temp. [°C]
9.9	28.7	5.0	0.9455	17
11.3	44.3	5.5	0.9970	17
12.8	63.6	6.0	0.9979	17
7.2	24.4	5.0	0.7544	35
5.6	23.8	5.5	0.9133	35
5.5	30.3	6.0	0.9507	35
5.6	38	6.5	0.9670	35
7.2	67.7	7.5	0.9809	35
3.3	13.3	5.0	0.5873	50
3.1	17.2	5.5	0.7223	50
2.8	20.1	6.0	0.7981	50
2.6	22.8	6.5	0.8418	50
2.4	29.4	7.5	0.8869	50

the stability constants of the hydroxocomplexes (taken from Ref. [2, 3]) and are defined as:

$$\frac{M_p(\mathrm{OH})_q}{[M]^p}[\mathrm{H}^+]^q = \beta_{q,p}$$

Table 3. *The change of the thermodynamic functions following the extraction of* Sm

$\Delta H^0 [\mathrm{J}\, M^{-1}]$	$\Delta G^0 [\mathrm{J}\, M^{-1}]$	$-T\Delta S [\mathrm{J}\, M^{-1}]$
—38 314	—6 050	+ 32 264

Experimental

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

Results and Discussion

Table 1 includes the values of the extraction coefficients *D* at 17°, 35° and 50°. For all concentrations of NH_4NO_3 we can notice the decrease of *D* with the increase of the temperature. Table 2 contains the values of stability constants K_1^0 calculated for the different least approach distances of ions. We have found the best "fit" of the data for 6.0 Å at 17 °C and 7.5 Å at 50 °C. This means that the equilibrium of the complexation is shifted from inner to outer sphere type complexes during the increase of the temperature. If we take into account the values of Sm^{3+} ion and water molecule radii, we will find that we have the species $Sm(H_2O)(NO_3)^{2+}$ at 17 °C and $Sm(H_2O)_2(NO_3)^{2+}$ at 50 °C.

The change of the thermodynamic functions following the extraction process is described by the following equations:

$$-1/R \cdot \Delta H^0 = \frac{\mathrm{d} \ln K^0}{\mathrm{d}(1/T)}, \quad T\Delta S^0 = \Delta H^0 - \Delta G^0, \quad \text{and} \quad \Delta G^0 = -RT \ln K^0$$

where ΔH^0, ΔS^0, ΔG^0 are enthalpy, entropy, and free enthalpy of extraction in their standard state [as standard state we used 298 °K and infinite dilution of $Sm(NO_3)_3$].

The entropy change (see Table 3) is negative, which is typical for the formation of outer sphere complexes [4, 5], indicating that $Sm(NO_3)_3 \cdot 3$ *TBP* is an outer sphere complex with respect to *TBP*. This is in the contrast with the presumption of *Marcus* and *Abrahamer* [6], who have found that *TBP* has a stronger donor-ability than the NO_3^- ion. They have proposed the following series of the donor-ability:

$$DMF > TBP > NO_3^- > H_2O > C_2H_5OH > \text{dioxane}.$$

According to *Karraker* [7] coordination numbers of Nd^{3+} and Er^{3+} in the above mentioned complex are 8 and 6, respectively. Three places in the coordination sphere are taken by *TBP* and the remaining of by nitrate ions.

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