

Complexation of Lanthanide Nitrates

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Summary. The change of the stability constants K_1^0 of the lanthanide nitrate complexes in the lanthanide series is presented and discussed from the viewpoint of the interaction between the first and second hydration sheath of lanthanide ions.

Keywords. Stability constants; Distribution coefficient; Coordination number; Hydration sheath.

Komplexierung bei Lanthaniden-Nitraten

Zusammenfassung. Es wird der Verlauf der Stabilitätskonstanten K_1^0 von Nitrate-Komplexen in der Lanthanidenreihe vorgestellt und auf Basis von Wechselwirkungen zwischen der ersten und zweiten Hydrat-Schicht der Lanthaniden-Ionen diskutiert.

Introduction

The number of papers concerning the stability and structure of the lanthanide ionic pairs still increases [1–4]. Recently Silber and coworkers [5] published the results of the complexation in some lanthanide nitrates in aqueous-methanol solutions. They suggested the existence of higher complexes with the stability much lower than the first complex. In aqueous solutions only one species with metal:ligand ratio equal 1 was detected.

In this paper we present our data for complexation of Eu, Tb, Er, Lu nitrates, and together with previous data we try to explain the change of the stability constants of lanthanide nitrates from the viewpoint of the attractions between the first and second hydration sheath of the lanthanide ion. The role of the polarization of the first hydration sheath by the central ion was discussed by Manning [6] during the study of the complexation of lanthanide acetates.

Experimental Part

NH_4NO_3 analytically pure (Gliwice); *TBP* analytically pure (Merck); Ln_2O_3 of 99.9% purity (Merck); Arsenazo III analytically pure (POCH, Gliwice); HNO_3 analytically pure (POCH, Gliwice).

The use of *TBP* as an extractant (determination of the distribution coefficients) was described previously [7].

Results and Discussion

The values of the distribution ratios D in the $Ln(NO_3)_3$ - NH_4NO_3 - TBP system are described by Eq. (1)

$$D = \frac{(TBP)^3 (NO_3^-)^3 K^0 y_{\pm}^4}{[1 + K_i^0 \pi_i (NO_3^-)^i]} \quad (1)$$

where y_{\pm} denotes the mean molar activity coefficient of $Ln(NO_3)_3$, K^0 is the extraction constant and K_i^0 refers to the overall thermodynamic stability constants of the lanthanide nitrato complexes. The unknown values of the stability constants

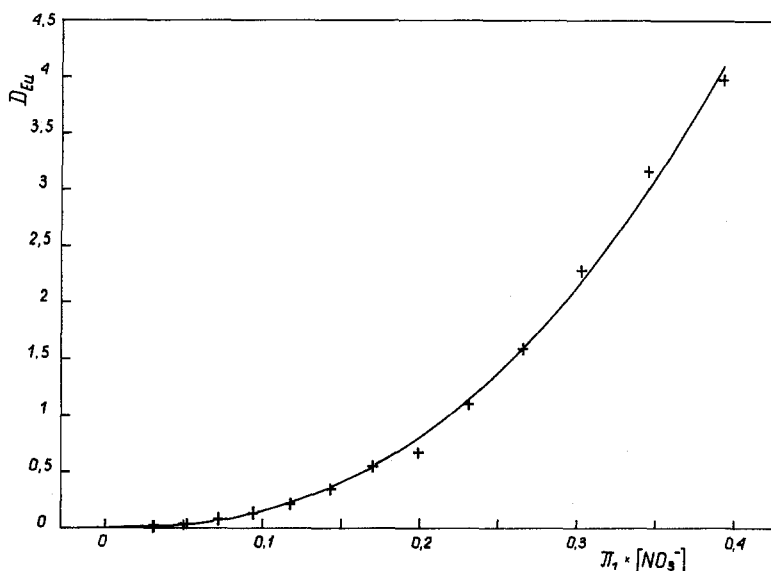


Fig. 1. The change of D_{Eu} with NH_4NO_3 concentration (temperature 25°C, o/aq. = 1)

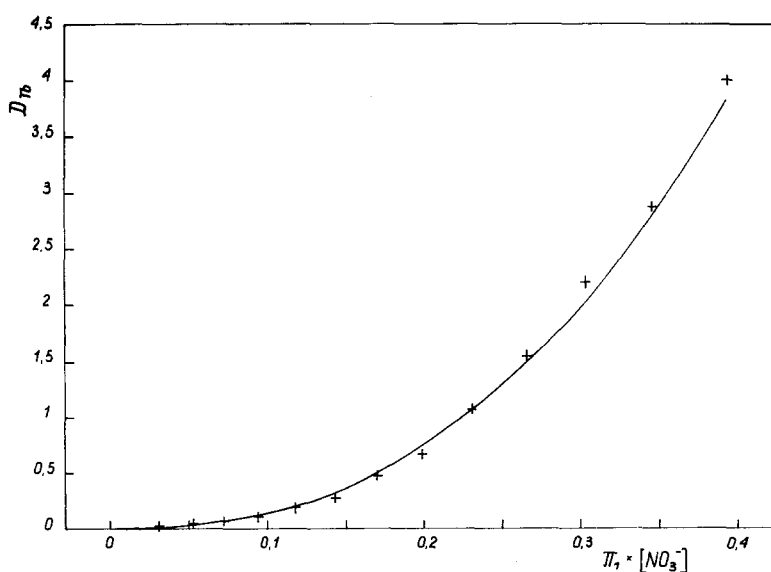


Fig. 2. The change of D_{Tb} with NH_4NO_3 concentration (temperature 25°C, o/aq. = 1)

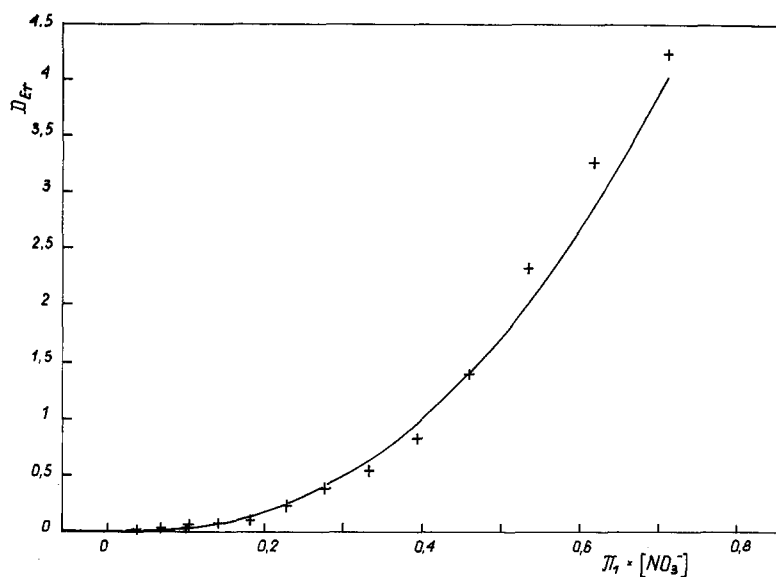


Fig. 3. The change of D_{Er} with NH_4NO_3 concentration (temperature 25°C , $o/aq. = 1$)

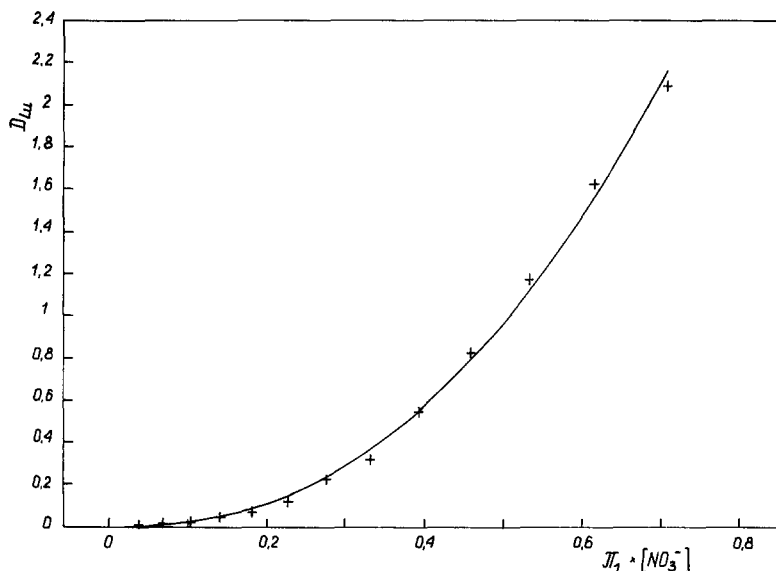


Fig. 4. The change of D_{Lu} with NH_4NO_3 concentration (temperature 25°C , $o/aq. = 1$)

K_i^0 can be found using a linear regression analysis comparing D_{exp} and D_{fit} (D from experiment and fit).

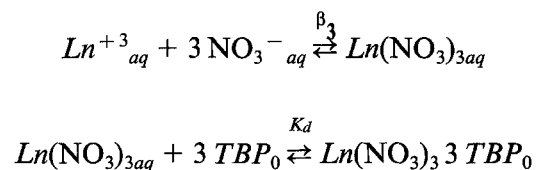
The typical paraboloidal change of the distribution coefficients of the lanthanides are given in Figs. 1 – 4. The solid lines refer to the D values based on Eq. (1). For the investigated lanthanides the change of D is similar and the “fit” is better than 99%. The values of the thermodynamic stability constants together with the least approach distances of the ions \AA are given in Table 1. The absolute values of K_i^0 have the same order as these found using the Munze equation [8]. There is an increase of the stability constants in the La-Nd, Sm range and a decrease for

Table 1. Stability constants of $Ln(NO_3)^{2+}$ complexes extrapolated to zero ionic strength (K^0 refers to the extraction constant, the values for La, Nd, Sm, Gd, Dy were taken from [11])

Ln^-	$K^0_1 [M^{-1}]$	$K^0 [M^{-6}]$	$\dot{a} [\text{\AA}]$
La	41	1.2	12.5
Nd	188	21	6.0
Sm	152	18.5	6.5
Eu	147	8.6	8.5
Gd	38.7	2.4	8.5
Tb	23.7	1.7	8.5
Dy	21	0.8	12.5
Er	9	0.4	12.5
Lu	24	0.4	12.5

the heavy lanthanides. The increase of $\log K^0_1$ for the light lanthanides can be explained as the consequence of the increase of the "inner-sphere complexation" [9]. Further decrease of ionic radius results in stronger polarization of the water protons from the first coordination sphere and therefore in increase of attraction between the first and the second coordination sphere through hydrogen bond. This is especially pronounced for the lanthanides heavier than Nd, which possess lower coordination numbers in aquoions, and the different geometry of coordination polyhedrons, which allows them to attract strongly the molecules from the second hydration sphere. Therefore the replacement of H_2O by NO_3^- is hindered and we observe a drop of $\log K^0_1$ in the Nd-Er range. A similar case was noticed by Manning [6] for the rare earth acetato complexes: an increase of the stability constants in La-Sm range, a decrease from Sm to Er and then a slight increase in the Er-Lu range, similar to our case where $K^0_1(Lu) > K^0_1(Er)$. We cannot find a satisfactory explanation for this fact. We can only presume that after the completed change in coordinating the water a further decrease of the lanthanide ionic radius results in further polarization of water protons, and increasing $H_2O-NO_3^-$ interaction through the hydrogen bond starts to determine the K^0_1 values. Therefore we can presume that competition between NO_3^- and H_2O exists not only in the first but also in the second coordination sphere of the lanthanide.

The extraction of the lanthanide nitrates by *TBP* is completed through the following stages:



If we take into account these two reactions and Eq. (1), we can easily formulate the following relationship (having in mind the fact that the distribution ratio results

from the ratio of the concentrations of species appearing in aqueous and organic phases):

$$K^0 = \beta_3 K_d$$

The K_d value is the distribution constant of the neutral complex $Ln(NO_3)_3$ from aqueous to the organic phase with the formation of the adduct $Ln(NO_3)_3 \cdot 3 TBP$. Recently Albinsson and Rydberg [10] found that the partition constant for the neutral lanthanide acetyl-acetonates between benzene and water, P_3 , increases in the lanthanide series. If we assume that this is also true in our case, the decrease of K^0 means the decrease of the β_3 value. In our case K^0 decreases in the range Nd, Sm-Lu. It is almost sure that β_3 changes in the same direction in this region of the lanthanide series which is not surprising. The species $Ln(NO_3)_2^+$ is highly hydrophilic. Water is strongly held, not only by the central ion, but also by the oxygens of NO_3^- through the hydrogen bond and this strength increases in the lanthanide series due to the polarization of H_2O . Therefore a replacement of the water from the first and from the second coordination sphere during formation of outer or inner sphere species $Ln(NO_3)_3$ will be much more difficult for the higher lanthanides than for the light ones.

Conclusions

The stability constants of the mononitrato lanthanide complexes possess a maximum in the middle of the lanthanide series. We can presume that in each case of outer sphere ionic pairs, for polarization of the water from the first or from the second coordination sphere this change of $\log K_1$ with lanthanide number will be similar. In the next papers we will present studies with $Ln(SCN)^{+2}$.

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