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Spectroscopic Investigation of Lanthanide Nitrates

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Summary. The stability constants β_n of nitrato complexes of Pr, Nd, Sm, Ho, and Er were determined by UV/Vis spectroscopy. It was found that $\beta_1 = 0.87, 1.24, 1.94, 0.24, 0.11$ for $M\ (NO_3)^{2+}$ (M = Pr, Nd, Sm, Ho, Er) and $\beta_2 = 0.06, 0.04$ for $M\ (NO_3)_2^+$ (M = Pr, Nd) at 25 °C. Detailed inspection of the lanthanide spectra shows that increasing nitrate concentration in the solution results in a bathochromic shift of the f–f bands for Nd and Sm which provides evidence for the formation of inner sphere nitrato complexes.

Keywords. Lanthanide nitrates; Complexes.

Spektroskopische Untersuchung von Lanthanidennitraten

Zusammenfassung. Die Stabilitätskonstanten β_n der Nitratokomplexe von Pr, Nd, Sm, Ho und Er wurden UV/Vis-spektroskopisch bestimmt. Es ergaben sich Werte von 0.87, 1.24, 1.94, 0.24 und 0.11 für β_1 ($M(NO_3)^{2+}$, M = Pr, Nd, Sm, Ho, Er) und 0.06 und 0.04 für β_2 ($M(NO_3)_2^+$, M = Pr, Nd). Eine detaillierte Analyse der Lanthanidenspektren zeigt, daß steigende Nitratkonzentration in Lösung eine bathochrome Verschiebung der f–f-Banden von Nd und Sm bewirkt. Das weist auf die Bildung von *inner sphere* – Nitratokomplexen hin.

Introduction

New applications of the lanthanides, for example as biological probes or liquid lasers, require information on the composition and structure of complex species existing in the respective systems. Complexes of the lanthanides with simple counter ions, such as nitrates [1], chlorides [1], and perchlorates [2–5] have recently been investigated. Different methods were used; among them, UV/Vis spectroscopy is an effective tool for the evaluation of the change of the structure of the complexes and their stability in aqueous and nonaqueous solutions. The problem of the determination of the stability constants of the lanthanide complexes from the UV/Vis data [6] is very complicated with respect to the fact that structural absorption bands are either incompletely resolved or unresolved as a result of small ligand field stabilization [6]. Broadening, overlap, and band shifts require the use of instruments with high resolution.

From a mathematical viewpoint, the analysis of the UV/Vis data, based on the additivity of absorbance of different species in solution, is still in the course of refinement. Different researchers use different methods of the fit and their data are incompatible.

There are some papers concerning the use of UV/Vis spectrophotometrical methods for the evaluation of the stability constants of the lanthanide nitrato complexes, but the results presented differ to such an extent that in practice it is impossible to estimate the order of the stability constants or even to predict the trend of their values in the lanthanide series [7–12].

Having in mind the above mentioned doubts, we decided to repeat the measurement of the stability constants of $Ln(NO_3)_n^{3-n}$ complexes in aqueous solution, to compare them with the data of other authors and to get information about their character in the sense of their outer or inner sphere nature. We started our work from the lanthanides Pr, Nd, Sm, Ho, and Er which have pronounced bands in the visible range of the spectra of their salts.

Results and Discussion

Theory

The complexation of the lanthanides by nitrates proceeds according to Scheme 1.

$$Ln^{3+} + nNO_3^- \overset{\beta_n}{\rightleftarrows} Ln(NO_3)_n^{3-n} \qquad 1$$

The free uncomplexed ion Ln^{3+} and successive complexes from $Ln(NO_3)^{2+}$ to $Ln(NO_3)_n^{3-n}$ each have their own molar absorptivity coefficient: ε_0, ε_n. The absorbance A of the lanthanide nitrate solution at a selected wavelength is described by the well known equation 2 which results from *Lambert-Beer*'s law.

$$A = \frac{\varepsilon_0 + \varepsilon_1\beta_1[L] + \cdots \varepsilon_n\beta_n[L]^n}{1 + \beta_1[L] + \cdots \beta_n[L]^n}[Me]_T \qquad 2$$

Here, β_n refers to the overall stability constant of the lanthanide nitrato complex, $[L]$ is the molar ligand concentration, and $[Me]_T$ denotes the total molar concentration of the lanthanide ion in the solution.

We tested different models of lanthanide complexation, taking into account the least square sum $(A_{exp} - A_{fit})^2$ where A_{exp} and A_{fit} refer to the values of the absorbance from the experiment and from the fit. The procedure of the fitting was checked by the Simplex method [13] using the commercial Tech-Plot program. It was possible to analyze the absorbance readings at maximally eight wavelengths, based on equation 2.

Spectra of the Lanthanide Nitrates

The experimental spectra of Pr, Nd, Sm, Ho, and Er nitrates are presented in Fig. 1. We have chosen the bands which are sensitive to NO_3 addition. It is obvious that only in the case of Nd and Sm the red shift of the bands resulting from f–f transitions occurs to a remarkable extent with increasing NO_3^- concentration. The summary of the band shifts is given in Fig. 2. For the rest of the lanthanides, the position of the f–f bands does not change with NO_3^- addition. Only in the case of Ho a slight hypsochromic shift of the corresponding band appears. To our opinion, the change

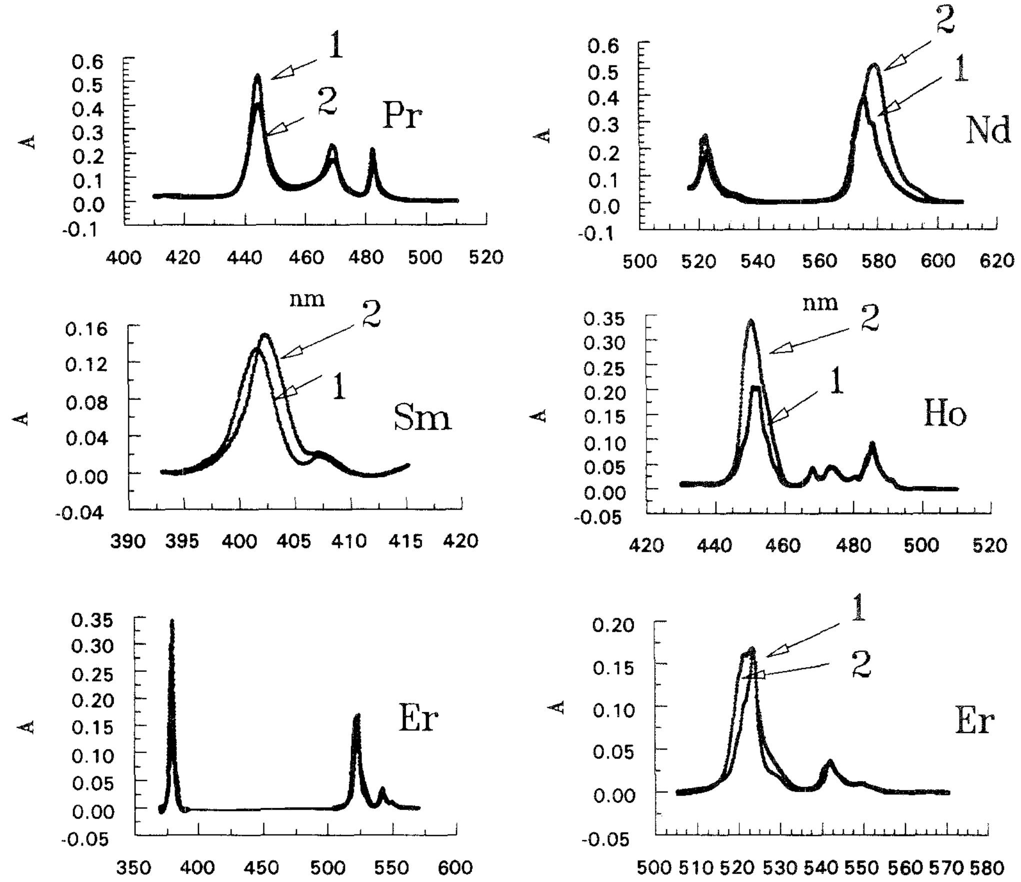

Fig. 1. Change in the spectra of the lanthanides upon increasing NO_3^- concentration (1: 0.05 *M* *Ln*$(ClO_4)_3$ + 3.6 *M* $HClO_4$; 2: 0.05 *M* *Ln*$(ClO_4)_3$ + 3.6 *M* $LiNO_3$; temperature: 25 °C; path length: $d = 1$ cm)

in position of these bands for Nd and Sm results from the change in the symmetry of the ligational environment around the central ion upon complexation.

It was mentioned by *Spedding* and coworkers [14–18] that the amount of inner sphere complexation in the lanthanide nitrates increases with shrinking lanthanide ionic radius in the region of La–Sm. We suppose that the coordination number of the lanthanide ion is lowered during the formation of the $Ln(H_2O)_xNO_3^{2+}$ inner sphere species when water is replaced by nitrate. This is the only explanation for the simultaneous red shift and intensification of the f–f bands for Nd and Sm. For the remaining lanthanides, we can observe only the pronounced intensification of these bands, which in our opinion results from the formation of outer sphere species in which NO_3^- anions are separated from the lanthanide ions by water molecules. The so-called "oscillator strength" (theory of f–f transition) increases during complex formation [6] in the sense of a simultaneous increase of the amplitude oscillations and a decrease of their frequency with decreasing coordination number of the lanthanide in the complex.

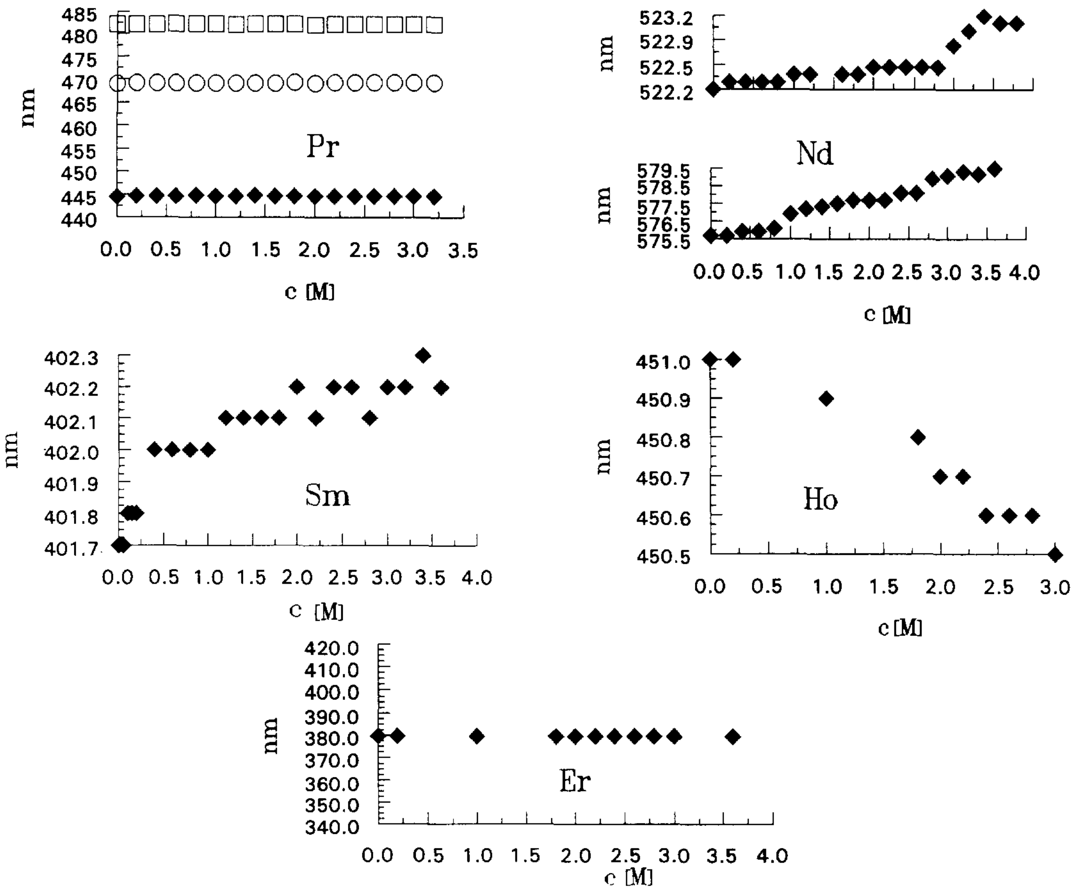

Fig. 2. Band shifts in the spectra of the lanthanide nitrates for NO_3^- concentrations ranging from 0 to 3.6 *M* (temperature 25 °C, $d = 1$ cm)

Stability Constants

The stability constants of $Ln(NO_3)^{3-n}$ complexes are given in Table 1. They were calculated based on experimental data which comprise the absorbance readings for different wavelengths. An exemplary set of the change of absorbance with ligand concentration increase for 17 °C is given in Fig. 3.

We tested different models of complexation with varying NO_3^- concentration based on equation 1. We found the best fit of the data for the simultaneous occurence of 1:1 and 1:2 complexes in the case of Pr and Nd and 1:1 complexes in the case of Sm, Ho, and Er. The values of stability constants for Pr are the same as those found previously [19] from one-wavelength absorbance measurements.

We did not find any substantial temperature dependence of the stability constant values; this is evident for β_1 values, but not in the case of β_2 values where the standard deviations are very high. This is in contrast with observations from solvent extraction data [20]. The pronounced change of the stability constants found in the case of the solvent extraction method provides evidence that different species are taken into consideration by the two different methods solvent extraction and spectrophotometry. In the case of solvent extraction, it is more probable that inner

Table 1. Stability constants of $Ln(NO_3)^{2+}$ and $Ln(NO_3)_2^+$ complexes at different temperatures

Ln	β_1					β_2				
	17 °C	25 °C	35 °C	50 °C	61 °C	17 °C	25 °C	35 °C	50 °C	61 °C
Pr	0.84 ± 0.14	0.87 ± 0.20	0.75 ± 0.06	0.69 ± 0.26	0.70 ± 0.02	0.06 ± 0.14	0.06 ± 0.25	0.06 ± 0.03	0.04 ± 0.51	0.05 ± 0.06
Nd	0.99 ± 0.07	1.24 ± 0.17	1.16 ± 0.21	0.95 ± 0.18	0.96 ± 0.14	0.05 ± 0.12	0.04 ± 0.03	0.05 ± 0.46	0.04 ± 0.05	0.05 ± 0.24
Sm	1.83 ± 0.02	1.94 ± 0.01	2.11 ± 0.04	1.58 ± 0.27	1.81 ± 0.05					
Ho	0.24 ± 0.07	0.27 ± 0.02	0.20 ± 0.02	0.25 ± 0.01	0.24 ± 0.07					
Er	0.10 ± 0.01	0.11 ± 0.01	0.10 ± 0.01							

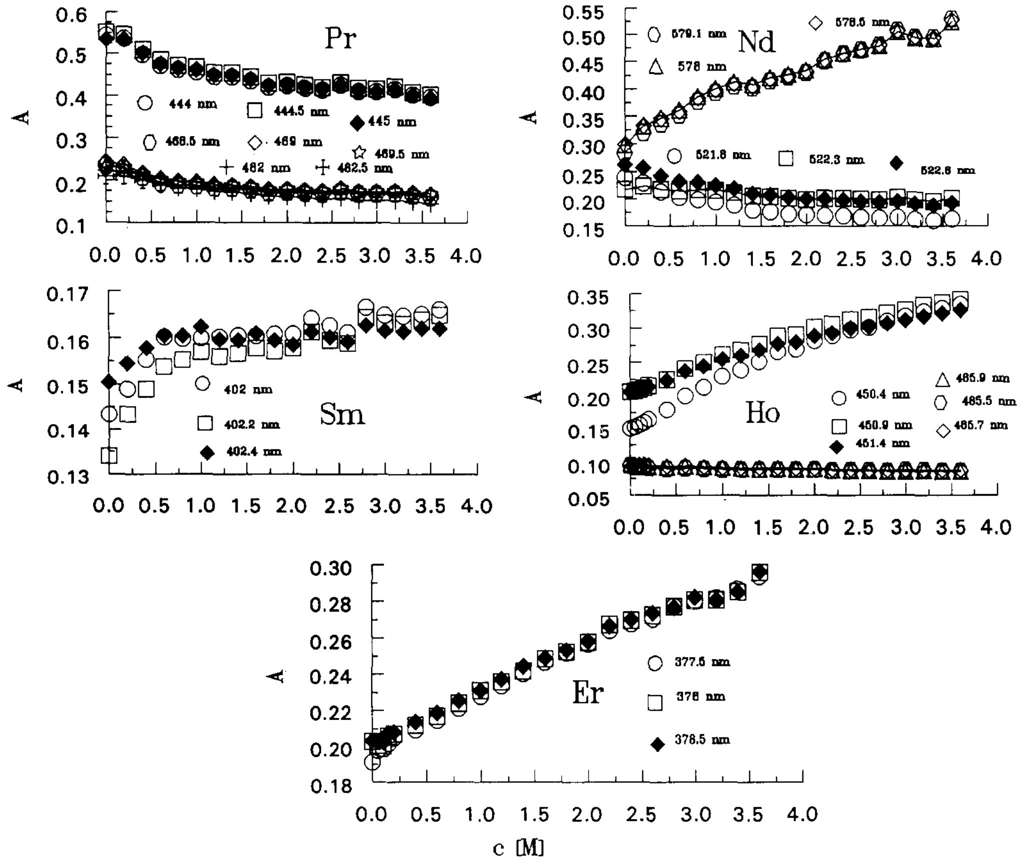

Fig. 3. Change of the absorptivity of the lanthanide nitrates at selected wavelengths with increasing NO_3^- concentration (temperature: 17 °C, path length: $d = 1$ cm); molar absorptivities of the respective complex species:

$$\varepsilon_{Pr^{3+}}^{444.5\,nm} = 11; \varepsilon_{Pr^{3+}}^{469\,nm} = 4.64; \varepsilon_{Pr^{3+}}^{482\,nm} = 4.46; \varepsilon_{Pr^{3+}}^{482.5\,nm} = 4.20; \varepsilon_{Nd^{3+}}^{521.8\,nm} = 4.20; \varepsilon_{Nd^{3+}}^{522.3\,nm} = 5; \varepsilon_{Nd^{3+}}^{578\,nm} = 5.8; \varepsilon_{Nd^{3+}}^{578.5\,nm} = 5.8; \varepsilon_{Sm^{3+}}^{402\,nm} = 2.96; \varepsilon_{Sm^{3+}}^{402.2\,nm} = 2.96; \varepsilon_{Sm^{3+}}^{402.4\,nm} = 2.68; \varepsilon_{Ho^{3+}}^{450.4\,nm} = 2.9; \varepsilon_{Ho^{3+}}^{450.9\,nm} = 4; \varepsilon_{Ho^{3+}}^{451.4\,nm} = 4; \varepsilon_{Ho^{3+}}^{485.5\,nm} = 1.9; \varepsilon_{Ho^{3+}}^{485.7\,nm} = 1.9; \varepsilon_{Pr(NO_3)^{2+}}^{444.5\,nm} = 7.2; \varepsilon_{Pr(NO_3)^{2+}}^{469\,nm} = 2.64; \varepsilon_{Pr(NO_3)^{2+}}^{482\,nm} = 2.56; \varepsilon_{Pr(NO_3)^{2+}}^{482.5\,nm} = 3.26; \varepsilon_{Nd(NO_3)^{2+}}^{521.8\,nm} = 2.84; \varepsilon_{Nd(NO_3)^{2+}}^{522.3\,nm} = 3.71; \varepsilon_{Nd(NO_3)^{2+}}^{578\,nm} = 8.65; \varepsilon_{Nd(NO_3)^{2+}}^{578.5\,nm} = 8.29; \varepsilon_{Sm(NO_3)^{2+}}^{402\,nm} = 3.18; \varepsilon_{Sm(NO_3)^{2+}}^{402.2\,nm} = 3.26; \varepsilon_{Sm(NO_3)^{2+}}^{402.4\,nm} = 3.23; \varepsilon_{Ho(NO_3)^{2+}}^{450.4\,nm} = 11.1; \varepsilon_{Ho(NO_3)^{2+}}^{450.9\,nm} = 10.2; \varepsilon_{Ho(NO_3)^{2+}}^{451.4\,nm} = 9.3; \varepsilon_{Ho(NO_3)^{2+}}^{485.5\,nm} = 1.6; \varepsilon_{Ho(NO_3)^{2+}}^{485.7\,nm} = 1.5; \varepsilon_{Pr(NO_3)_2^{2+}}^{444.5\,nm} = 7.83; \varepsilon_{Pr(NO_3)_2^{2+}}^{469\,nm} = 4.29; \varepsilon_{Pr(NO_3)_2^{+}}^{482\,nm} = 2.52; \varepsilon_{Pr(NO_3)_2^{+}}^{482.5\,nm} = 2.45; \varepsilon_{Nd(NO_3)_2^{+}}^{521.8\,nm} = 2.70; \varepsilon_{Nd(NO_3)_2^{+}}^{522.3\,nm} = 1.71; \varepsilon_{Nd(NO_3)_2^{+}}^{578\,nm} = 27.12; \varepsilon_{Nd(NO_3)_2^{+}}^{578.5\,nm} = 30; \varepsilon_{Ho^{3+}}^{485.9\,nm} = 1.9; \varepsilon_{Er^{3+}}^{377.5\,nm} = 3.9; \varepsilon_{Er^{3+}}^{378\,nm} = 4; \varepsilon_{Er^{3+}}^{378.5\,nm} = 4; \varepsilon_{Ho(NO_3)^{2+}}^{485.9\,nm} = 1.5; \varepsilon_{Er(NO_3)^{2+}}^{377.5\,nm} = 11.1; \varepsilon_{Er(NO_3)^{2+}}^{378\,nm} = 10.5; \varepsilon_{Er(NO_3)^{2+}}^{378.5\,nm} = 10.9$$

sphere species, which appear in the organic phase, affect the calculations of stability constants. Spectrophotometry provides information on the sum of inner and outer sphere species in the solution; the lacking temperature dependence of the stability constants of $Ln(NO_3)^{3-n}$ species proves their outer sphere character.

We compared our stability constant values with those found by *Koward* [10], *Anagnastopoulos* [11], and *Silber* [7] (Fig. 4). The data of *Horrocks* for Eu [12] were also included. For the light lanthanides, the trend of the stability constant found by different authors is consistent with the hypothesis that in the middle of the lanthanide series a maximum in ln β should appear. This fact results from the change in the equilibrium inner *vs.* outer sphere complexation in lanthanide nitrates. The

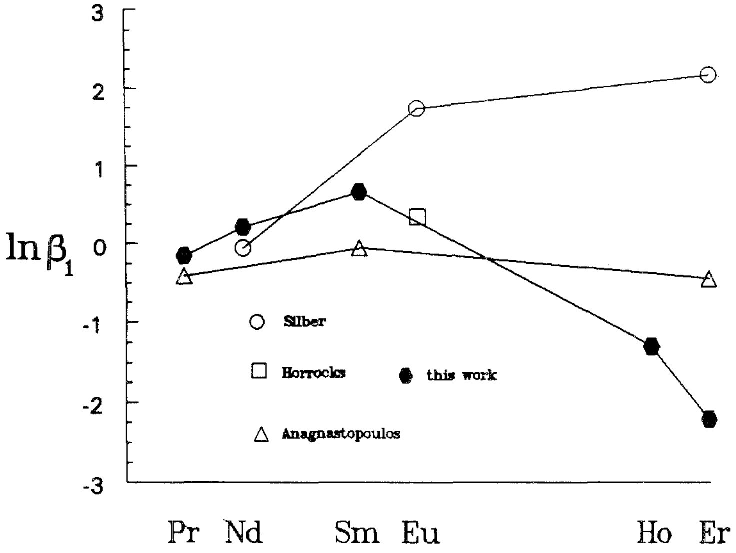

Fig. 4. Comparison of the stability constants of $Ln(NO_3)^{2+}$ complexes found by different authors

very high value of β_1 for $Er(NO_3)^{2+}$ found by Silber for the ionic medium $LiClO_4$–$LiNO_3$ requires discussion. It results from solvent extraction data, that the maximum in the values of stability constants is between Nd and Sm [1]. Hydration of the heavy lanthanides is much stronger than that of the light ones; therefore, complexation by nitrate decreases for the lanthanides heavier than Sm. However, the position of this maximum may be shifted to the heavy lanthanides. To our opinion it depends on the water activity in the medium, which affects the equilibrium of inner and outer sphere complexation in the lanthanide nitrates.

Conclusions

1. The bathochromic shift of the corresponding bands in Nd and Sm spectra provides evidence for inner sphere complexes in the nitrates of these elements.
2. The use of the spectrophotometrical method for the determination of the stability constants of the lanthanides provides the information on the sum of outer and inner sphere complexation in solution.

Experimental

Reagents

The solutions of the rare earth nitrates were prepared by dissolution of the respective oxides (Koch-Light) in nitric acid. The resulting nitrates, after evaporation to dryness, were dissolved in a mixture of $LiNO_3$ and $HClO_4$ (POCH-Gliwice) at constant ionic strength ($I = 4$). This solution was standardized with *EDTA* at *pH* 5 (acetate buffer) in the presence of xylenol orange as indicator.

Measurements

The investigated solutions of lanthanide nitrates had a constant $Ln(ClO_4)_3$ concentration of 0.05 *M* and a varying NO_3^- concentration from 0 to 3.6 *M*. Individual reference solutions of a $LiNO_3/HClO_4$

mixture were used to avoid small absorptions arising from the ionic medium. Spectra of the lanthanides were recorded using a UV/Vis M-40 spectrophotometer (Carl-Zeiss Jena). The data were obtained at 0.1 nm intervals. The comparative spectrophotometric method was used. Selected wavelength ranges in the visible region were investigated for Pr, Nd, Sm, Ho, and Er (Pr: 444, 444.5, 445, 468.5, 469, 469.5, 482, 482.5 nm; Nd: 521.8, 522.3, 522.8, 578, 578.5, 579.1 nm; Sm: 402, 402.2, 402.4 nm; Ho: 450.4, 450.9, 451.4, 485.5, 485.7, 485.9 nm; Er: 377.5, 378, 378.5 nm).

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