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Study of Complexation in the $Nd^{3+} - SCN^-$ System

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Summary. A spectroscopic study of the association in the $Nd^{3+} - SCN^-$ system is presented. A characteristic change of the molar absorptivity of the solution with a plateau at 2–4 *M* [SCN^-] and an increase at 4–8 *M* [SCN^-] reflects the change from outer- to innersphere complexation.

Keywords. Neodymium thiocyanate; Overall stability constant; Outer sphere complexes; Inner sphere complexes.

Untersuchungen zur Komplexierung im $Nd^{3+} - SCN^-$-System

Zusammenfassung. Es wird eine spektroskopische Studie der Assioziationsverhältnisse im $Nd^{3+} - SCN^-$-System präsentiert. Die charakteristische Änderung in der molaren Absorption der Lösung mit einem Plateau bei 2–4 *M* [SCN^-] und ein Anstieg bei 4–8 *M* [SCN^-] ist auf einen Wechsel von außensphärischer zu innensphärischer Komplexierung zurückzuführen.

Introduction

The lanthanide thiocyanates play a significant role in the separation chemistry of these elements [1–5]. In 1981 Ceccaroli and Alstad [6] found an improvement of lanthanide separation in the solvent extraction process in the presence of thiocyanate anions in aqueous phase. For these reasons the detailed analysis of the complexation in the aqueous lanthanide thiocyanates is very important. First of all it is interesting to find out the change of the thiocyanates stability constants in the lanthanide series. Are these differences between stability constants enough to be used in the separation process? Is the behaviour of yttrium different in comparison with other lanthanides?

The values of the stability constants of lanthanide thiocyanates found by different authors [7–14] are incomparable and the decision to reinvestigate these complexes seems to be justified.

We used spectrophotometrical methods, which were successfully applied in the studies of lanthanide nitrates [15] and chlorides [16]. This method is based on the fact that the f–f transitions in the lanthanide ions slightly depend on the ligational environment of the central ion.

Experimental

$HClO_4$, NaOH, Nd_2O_3, NaSCN, K_2CrO_4, $AgNO_3$, all analytically pure, were provided by P.O.CH. Gliwice.

A specord M40 spectrophotometer (Carl Zeiss Jena production) was used for the registration of the spectra. Collected data, with 0.12 nm resolution, covered the complete visible range.

The neodymium perchlorates were prepared by dissolution of the weighted amount of Nd_2O_3 in perchloric acid and evaporation to dryness. The resulting salt was dissolved in NaSCN solution. Constant ionic strengths of a few different sets of mixtures were controlled by $NaClO_4$. All solutions had *pH* 5.5 to avoid partial hydrolysis of NaSCN.

Results and Discussion

Theory

The molar absorptivity of the solution is expressed by the following equation,

$$\varepsilon = (\varepsilon_0 + \varepsilon_1\beta_1[L] + \cdots + \varepsilon_n\beta_n[L]^n)/(1 + \beta_1[L] + \cdots + \beta_n[L]^n), \qquad (1)$$

where $\varepsilon, \varepsilon_0, \ldots, \varepsilon_n$ denote molar absorptivities of the solution and particular complex species with $\beta_1, \ldots, \beta_n$ overall stability constants.

If we do not know the range of the change of stability constants, we may at first use a more simplified form of this equation limited to one complex species only,

$$(\varepsilon - \varepsilon_0)/[L] = \beta_1\varepsilon_1 - \beta_1\varepsilon\ . \qquad (2)$$

From the straight line relationship of $(\varepsilon - \varepsilon_0)/[L]$ vs. $\beta_1\varepsilon$ we can easily find values of β_1 and ε_1, which can be used in Eq. (1) as the first approximation. The best values of $\varepsilon_1/\varepsilon_0, \ldots, \varepsilon_n/\varepsilon_0, \beta_1, \ldots, \beta_n$ can be found from the best fit, which obeys the following relationship,

$$r^2 = \sum\{(\varepsilon/\varepsilon_0)_{\text{exp.}} - (\varepsilon/\varepsilon_0)_{\text{calc.}}\}^2 / \sum\{(\varepsilon/\varepsilon_0)_{\text{exp.}} - (\varepsilon/\varepsilon_0)_{\text{av.}}\}^2,$$

where indexes exp., calc., av. refer to the experimental, calculated and average values of the relative molar absorptivities.

In the case when $r^2 < 0.01$ only 1% of the experimental values is outside of the model and the fit is satisfactory.

Analysis of the Spectra

Fig. 1 shows the spectra of the mixtures of $Nd(ClO_4)_3$ and $Nd(ClO_4)_3 + NaSCN$ at the same total Nd concentration. The high concentration of SCN^- in the second mixture creates conditions for the maximum association of Nd^{3+} with SCN^- ions. We can notice the shift of the absorption maxima in the direction of the long wavelength range, as well as an increase of the band intensity. This fact is consistent with the formation of thiocyanato complexes.

The set of the stability constant values for different ionic strengths is presented in Table 1. Our results are comparable with those of Coward [15], who found $\beta_1 = 0.77$ for the $Nd(NO_3)^{2+}$ ion outersphere pair. Similarly Kinnard and Choppin [10] concluded from their spectral data $\beta_1 = 0.70$ for $Nd(SCN)^{2+}$ outersphere species. It follows from our data that the second successive stability constant of the $Nd(SCN)_2{}^+$ species is higher than the first one (take for example the first pair of the data: $\beta_1 = 0.33$, $\beta_2 = 0.41$, $K_2 = 1.24$), which is a very rare case in the lanthanide coordination chemistry.

Fig. 2 reveals the influence of the SCN^- concentration on the change of the

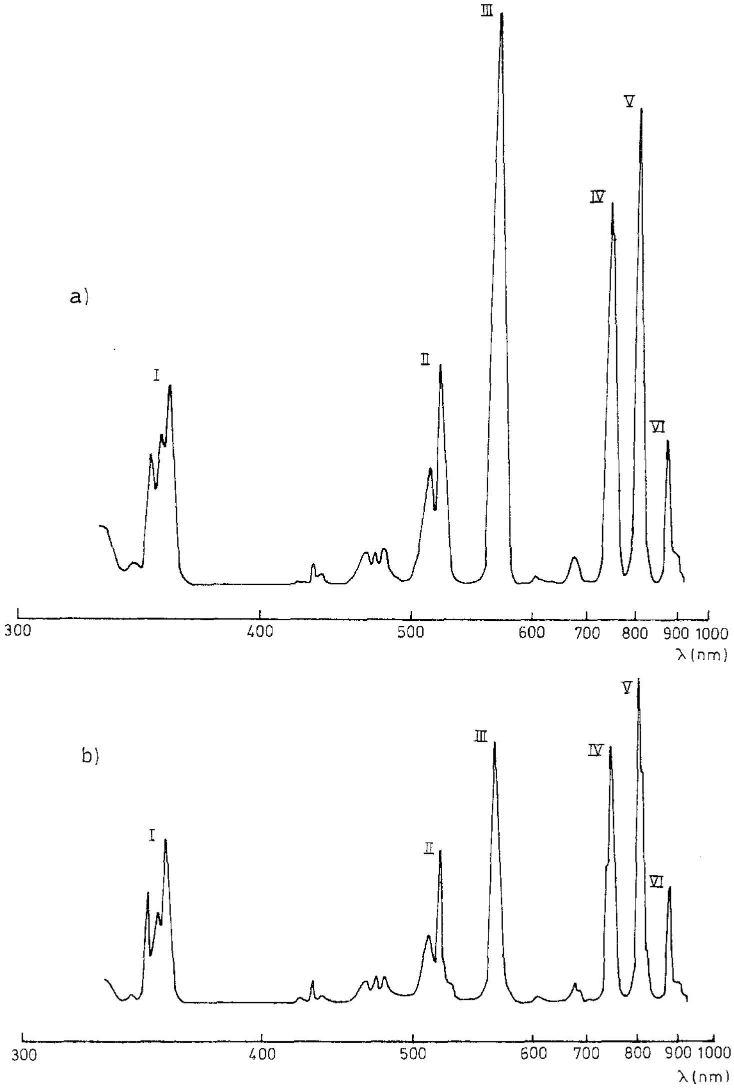

Fig. 1. The spectra of Nd (path length $d = 1$ cm, temp. 25°C; *a* and *b* refer to $8M$ NaSCN and water; the absorbances and wavelengths for different peaks are as follows: I(*a*) − 0.2584, 355.3 nm ($^4D_{1/2,5/2,3/2} - {}^4I_{9/2}$), II(*a*) − 0.2888, 523.5 nm ($^4G_{7/2} - {}^4I_{9/2}$), III(*a*) − 0.7983, 580.6 nm, ($^4G_{5/2} - {}^4I_{9/2}$), IV(*a*) − 0.5, 742.3 nm ($^4F_{7/2} - {}^4I_{9/2}$), V(*a*) − 0.6244, 799.2 nm ($^2H_{9/2} - {}^4I_{9/2}$), VI(*a*) − 0.1907, 869.3 nm ($^4F_{9/2} - {}^4I_{9/2}$), I(*b*) − 0.2069, 354.3 nm, II(*b*) − 0.1973, 522.4 nm, III(*b*) − 0.3438, 575.3 nm, IV(*b*) − 0.3334, 740.6 nm, V(*b*) − 0.4305, 794.7 nm, VI(*b*) − 0.1494, 866.3 nm)

relative molar absorptivity $\varepsilon/\varepsilon_0$ of the $Nd(SCN)_3$ solutions. There is an increase of the molar absorptivity up to $2M$ concentration range, its plateau in the 2–4 *M* range and an increase in the 4–8 *M* range. We can presume the formation of $Nd(SCN)^{2+}$ and $Nd(SCN)_2{}^+$ species in the 0–4 *M* range. The plateau in the 2–4 *M* range reflects the "saturation" of the solution by the second complex. At higher SCN^- concentrations the formation of the innersphere complexes with the penetration of the hydration sphere of the central ion by ligand is possible. The resulting change of the symmetry of the ligational environment around the central ion causes the increase of the f − f transitions intensity. No conclusions concerning the co-

Table 1. The stability constants of Nd thiocyanates (the numbers in parentheses denote the standard deviation; $[\mathrm{Nd}]_t$ denotes the total Nd concentration in [*M*]; *I* is the ionic strength; the intensities of the 575 nm band were taken for calculation)

β_1	β_2	$\varepsilon_1/\varepsilon_0$	$\varepsilon_2/\varepsilon_0$	*I*	$[\mathrm{Nd}]_t$
0.33 (0.09)	0.41 (0.08	1.48 (0.1)	1.55 (0.07)	1	0.025
0.45 (0.05)	0.45 (0.05)	1.35 (0.05)	1.40 (0.0)	2	0.025
0.39 (0.1)	0.32 (0.14)	1.47 (0.11)	1.46 (0.10)	2	0.05
0.37 (0.05)	0.23 (0.07)	1.53 (0.07)	1.57 0.04)	2.5	0.05
0.5 (0.08)	0.34 (0.05)	1.33 (0.04)	1.63 (0.04)	3.0	0.05
0.4 (0.08)	0.23 (0.05)	1.57 (0.09)	1.73 (0.05)	4.0	0.05

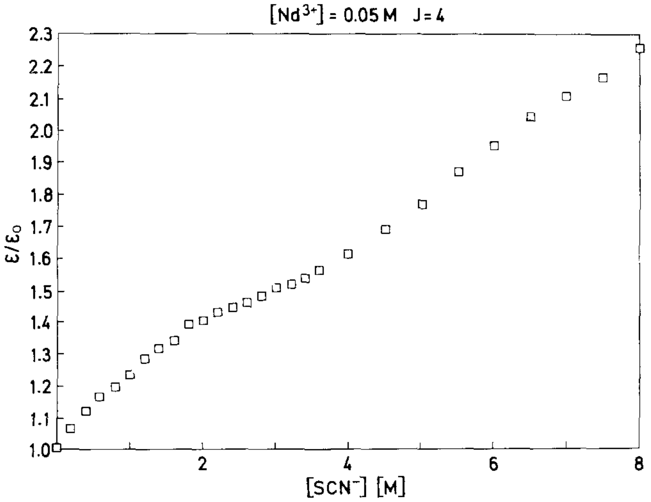

Fig. 2. The change of the relative molar absorptivity of Nd with increasing $[\mathrm{SCN}^-]$ concentration (the peak 575 nm was taken for observation, $[\mathrm{Nd}]_t = 0.05$ *M*); points in the range 0–4 *M* refer to the constant ionic strength $I=4$

ordination numbers of Nd^{3+} in these species are possible. The shift of the absorption maximum (575–580 nm) is comparable with that found by Hamze [16] (579–586 nm) for the species $\mathrm{NdCl}_2{}^+$ formed in methanol, which due to a decrease of the dielectric constant of the solution is probably of innersphere character.

Conclusions

Our results are consistent with the conclusion about the equilibrium in the inner versus outersphere formation in $\mathrm{Nd(SCN)}_3$ solutions. Complementary research should be continued based on the application of the extraction method. We cannot preclude that at lower *pH* values completely different species would be formed with coordination of the lanthanide ions by undissociated HSCN molecules.

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