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


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$_2$O$_3$, NaSCN, K$_2$CrO$_4$, 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$_2$O$_3$ 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,

\[
e = (e_0 + e_1 \beta_1[L] + \cdots + e_n \beta_n[L]^n)/(1 + \beta_1[L] + \cdots + \beta_n[L]^n),
\]

where $e$, $e_0$, ..., $e_n$ denote molar absorptivities of the solution and particular complex species with $\beta_1$, ..., $\beta_n$ 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,

\[
(e - e_0)/[L] = \beta_1 e_1.
\]

From the straight line relationship of $(e - e_0)/[L]$ vs. $\beta_1 e$ we can easily find values of $\beta_1$ and $e_1$, which can be used in Eq. (1) as the first approximation. The best values of $e_1/e_0$, ..., $e_n/e_0$, $\beta_1$, ..., $\beta_n$ can be found from the best fit, which obeys the following relationship,

\[
r^2 = \sum ((e/e_0)_{exp.} - (e/e_0)_{calc.})^2/\sum (e/e_0)_{exp.} - (e/e_0)_{av.})^2,
\]

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$$^{2+}$ ion outersphere pair. Similarly Kinnard and Choppin [10] concluded from their spectral data $\beta_1 = 0.70$ for Nd(SCN)$^{2+}$ outersphere species. It follows from our data that the second successive stability constant of the Nd(SCN)$_2$$^{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