Studies on azide complexes of neodymium(III)—Part XII

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Received 5 April 1994; revised and accepted 10 August 1994

The spectrophotometric measurements carried out in aqueous solutions containing Nd\(^{3+}\) and N\(_3^-\) ions, show the formation of a weak Nd(N\(_3\))\(^{2+}\) complex ion in 1:1 molar ratio. The stability constant of the complex has been measured at 25±1°C, pH = 5.0 and at an ionic strength = 2.0 M (NaCl\(_4\)), using both Scott and Dilution methods and the values are found to be (50.1±0.5) \times 10^{-2} and (49.9±1.6) \times 10^{-2} respectively. The molar absorptivity values of the complex are (33.24±0.31) and (36.3±0.6) at 575 nm.

Although the complexes of azide ions have been studied quite extensively by several authors\(^{1-3}\), there are comparatively few studies reported on the lanthanon complexes.

We have earlier reported the stability of the azide complexes of Pr(III)\(^4\) using radioactive Pr(143) and Sm(III)\(^5\). We have also studied the synthesis and characterization of solid azide complexes\(^6\) of the type Ln(OH)\(_2\)N\(_3\)H\(_2\)O, (where Ln = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb). In this note, the stability constant of Nd(III) azide complex at \(\mu = 2.0 \text{ M}\) and \(\text{pH} = 5.0\) has been determined using both Scott\(^7\) and dilution\(^8\) methods.

**Experimental**

A stock solution of neodymium perchlorate and sodium azide were prepared and standardized as previously reported. A stock solution of hydrazoic acid was prepared as described elsewhere\(^9\).

The spectrophotometric measurements in the UV/visible region were carried out using Unicam SP 8000 double beam recording spectrophotometer as well as manually operated Beckman DU 2 spectrophotometer. Silicon glass cells of 1 cm and 4 cm path lengths were used.

The \(\text{pH}\) measurements were carried out using Radiometer digital \(\text{pH}\) meter type 63 fitted with combined glass electrode. The KCl of the electrode was replaced by \(\text{NH}_4\text{Cl}\) to avoid blocking by KClO\(_4\).

**Results and discussion**

The addition of excess azide ions to neodymium perchlorate solution led to increase in colour intensity with slight red shift. This was taken as a criterion for the existence of azide complex of Nd(III). It was observed that the complex formation is dependent on the \(\text{pH}\) and temperature since precipitation of metal hydroxide readily takes place at \(\text{pH}\) higher than 5.5 and hydrazoic acid evolved as temperature increases.

The graphical method\(^10\) was used to determine the number of absorbing species present in solution. These methods depend on the criterion that the rank of the matrix of absorbance values of a series of solutions at several wavelengths gives the number of the species present. Linear plots are obtained by plotting \(A_{i}/A_{k}\) vs. \(A_{j}/A_{k}\) where \(A_{i}, A_{j}, A_{k}\) are the absorbances at the wavelengths i, j, and k for a given solution of composition x, compatible with the existence of two light absorbing species. This observation has been confirmed in Nd(III)-azide system (Fig. 1).

The Scott\(^7\) method as well as methods based on dilution were used to calculate the stability constants of the equilibria under investigation. A slight

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modification was made to suit the present situation where both metal ion and their azide complex absorb at a given wavelength.

The Scott method utilises the following equation

$$\frac{C_{\text{B}}[A]^n}{\Delta As} = \frac{[A]^n}{l \Delta \varepsilon_n} + \frac{1}{l \beta_n \Delta \varepsilon_n}$$

where $C_{\text{B}}$ is the analytic concentration of metal ion, $l$, the path length, $\Delta As = As - l \varepsilon_0 C_{\text{B}}$, $\Delta \varepsilon_n = \varepsilon_n - \varepsilon_0$ and $C_A$ is the concentration of the free azide ions which is calculated from the relationship

$$[N_3^-] = C_A \left[1 + \frac{[H^+]}{K_a}\right]^{-1}$$

where $C_A$ is the initial concentration of NaN$_3$, $[H^+]$ is the hydrogen ion concentration and $K_a$ is the dissociation constant of HN$_3$ at the same ionic strength and was found to be $1.66 \times 10^{-5} \pm 0.08$.

A plot of $C_{\text{B}}[A]^n/\Delta As$ vs $[A]^n$ should give a straight line of a slope $1/l \Delta \varepsilon_n$ and intercept $1/l \beta_n \Delta \varepsilon_n$. The data are represented graphically in Fig. 2 from which $\beta_1$ was found to be $(50.1 \pm 0.5) \times 10^{-2}$ and $\varepsilon_1$ (molar absorptivity of the complex) equal to $33.24 \pm 0.31$ at 575 nm.

In the dilution method (a method in which only a single solution is prepared), the effect of adding various amounts of the solvents upon the optical density was observed. It was also observed that $C_a \gg C_b$ (where $C_a$ and $C_b$ are the concentration of $N_3^-$ and Pr$^{3+}$, respectively). The ionic strength and pH were kept constant at the same values mentioned above. The equation used in such a case was,

$$V^n = \frac{l \beta_n \Delta \varepsilon_n m_n m_b^n}{V \Delta As} - \frac{\beta_n m_b^n}{V \Delta As}$$

where $V$ is the total volume and $m_n$ and $m_b$ are the number of moles of azide ions and of metal perchlorate, respectively. The $\beta$ values were derived from at least three determinations, applying the least square method, and were found to be $(49.9 \pm 1.6) \times 10^{-2}$ and $\varepsilon_1 = 36.3 \pm 0.6$ at 575 nm.

It is observed that, both the methods of calculation are in fairly good agreement within experimental error, and the azide complexes of lanthanons are rather weak if compared with those of $d$-group transition metal ions but have striking similarity with those of thiocyanate ions.

References
7. Scott R I, Recl Trav chim pays-Belg, 75 (1956) 787.