Partial Ion-Association Constant for Contact Ion-Pairs in Aqueous $[Co(NH_3)_6]^{3+}$-I^- Systems

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It has been known for many years that ion-pairs can be classified into several classes with different structures and properties; partial ion-association constants for each class of ion-pairs have been reported only in rare cases.[1] Classifying the ion-pair $[Co(NH_3)_6]^{3+}I^-$ into two classes, *contact ion-pairs* and *separated ion-pairs* (those separated by *one or more* solvent molecules), we give partial ion-association constants for each class of ion-pairs.

The spectrophotometric study was made at 25.0± 0.1°C on aqueous systems of a constant ionic strength of 0.062 containing $[Co(NH_3)_6](ClO_4)_3$, KI, and $NaClO_4$. An absorption band which appears near 37 kK on the addition of iodide to an aqueous solution of hexamminecobalt(III) perchlorate is known to be due to the $[Co(NH_3)_6]^{3+}I^-$ ion-pair.[2] Except for the iodide ion (hydrated) and the metal complex ion, no other species absorb light in the wave number range of interest (30—45 kK). The absorbance, D, of the solution can thus be expressed as:

$$D = \varepsilon_M[M]+\varepsilon_A[A]+\varepsilon_{M\cdot\cdot A}[M\cdot\cdot A]+\varepsilon_{M\cdot A}[M\cdot A] \quad (1)$$

where ε symbolizes the molar extinction coefficient and where M, A, M··A, and M·A represent the metal complex ion, the anion (iodide ion), the separated ion-pair, and the contact ion-pair respectively. Equation (1) can be modified to give:

$$\varDelta D = (\varepsilon_{M\cdot A(CT)}-\varepsilon_A)[M\cdot A] \quad (2)$$

with $\varDelta D = D-\varepsilon_M c_M-\varepsilon_A c_A$, if the following assumptions are made: (i) $\varepsilon_{M\cdot\cdot A}=\varepsilon_M+\varepsilon_A$, and (ii) $\varepsilon_{M\cdot A}=\varepsilon_{M\cdot A(CT)}+\varepsilon_M$. The symbol c denotes the analytical concentration of each species, and $\varepsilon_{M\cdot A(CT)}$ is the molar extinction coefficient of the iodide-to-complex charge transfer absorption in the contact ion-pair. Assumption (i) is equivalent to defining the separated ion-pair as the class of ion-pairs that were not spectrophotometrically distinguished from the bulk of ions in the experiment. According to assumption (ii), iodide-to-complex charge transfer absorption occurs in the contact ion-pair in place of iodide-to-solvent charge transfer absorption, whereas the absorption due to transitions in the metal complex remains unaffected.

The values for $\varDelta D$ were obtained by comparing the absorbance at each wave number of a solution containing the complex and iodide ions with those of two solutions containing each ion separately. Figure 1 shows three series of results obtained with different concentrations of the complex ion, but with the same iodide concentration. An isosbestic point exists at $\nu=40.7\pm0.1$ kK and $\varDelta D=0$. Here, $\varepsilon_{M\cdot A(CT)}$ is equal to ε_A, which was measured to be 1600± 150. This observation implies that the above-mentioned assumptions are a good approximation.

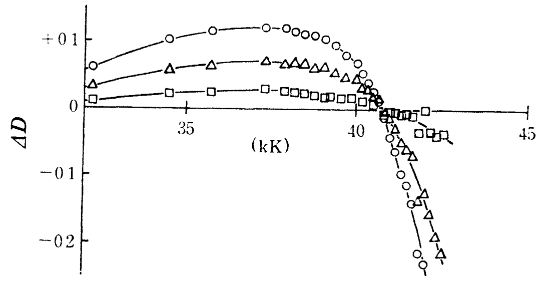

Fig. 1. $\varDelta D$ for $[Co(NH_3)_6]$ $(ClO_4)_3$-KI-$NaClO_4$ solutions of ionic strength of 0.062. $c_A=0.002$M; $c_M=0.002$M(□), 0.006M(△) and 0.010M(○)

Assuming different values of [M·A] and using the observed ε_A values, we calculated $\varepsilon_{M\cdot A(CT)}$ for each wave number and drew hypothetical absorption curves. Only certain values of [M·A] within a narrow range gave absorption curves of a reasonable shape. Thus, we obtained 2300±300 for the $\varepsilon_{M\cdot A(CT)}$ value at 37.3 kK, where the charge transfer band has its maximum, and 1150± 150 at 32.3 kK, where measurements were made for the determination of the ion-association constants, as will be described below.

We define the *partial ion-association constants* for the separated and contact ion-pairs as well as the *total ion-association constant* as follows:

$$K_{sep} = \frac{[M\cdot\cdot A]}{[M][A]}, \quad K_{cont} = \frac{[M\cdot A]}{[M][A]}$$

$$K = K_{sep}+K_{cont} = \frac{[M\cdot\cdot A]+[M\cdot A]}{[M][A]} = \frac{x}{(c_M-x)(c_A-x)}$$

where x is the total molar concentration of ion-pairs. Combining these equations with Eq. (1), one has:

$$\frac{c_M c_A}{\varDelta D} = \frac{K(c_M+c_A-x)}{K_{cont}(\varepsilon_{M\cdot A(CT)}-\varepsilon_A)} + \frac{1}{K_{cont}(\varepsilon_{M\cdot A(CT)}-\varepsilon_A)}$$

Plots of the observable quantity on the left-hand side *vs.* c_M+c_A-x (where x is a small correction to be considered in successive approximations) will give the total ion-association constant, K, as (slope)/(intercept). Actually, from spectrophotometric measurements at 32.3 kK on aqueous $[Co(NH_3)_6]$ I_3-KI systems of a constant ionic strength of 0.06, we obtained 9.0±0.6 for K and 2.41×10^{-4} for the intercept, $1/\{K_{cont}\ (\varepsilon_{M\cdot A(CT)}-\varepsilon_A)\}$. The latter, in combination with the $\varepsilon_{M\cdot A(CT)}$ value given above, leads to the values of the partial ion-association constants: 3.6±0.5 for K_{cont} and, accordingly, 5.4±0.8 for K_{sep}.

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