Association of Silver Ion and Chloride Ion in Molten Lithium Nitrate–Potassium Nitrate

Sir:

In a recent paper,[1] Tien and Harrington reported formation constants of silver(I) chloro complexes in fused lithium nitrate–potassium nitrate eutectic at 225° which appeared to be inconsistent with measurements made in this laboratory of similar systems but at 391°.[2] They subsequently reported an error in their original calculations which, when corrected,[3] led to better agreement with the results from this laboratory.

We report here the results of additional measurements[4] at 240° in 70–30 mole % potassium nitrate–lithium nitrate which confirm the corrected results of Tien and Harrington and our previous results. The data were obtained potentiometrically and analyzed graphically by methods described previously.[5] The association constant for the formation of AgCl was found to be $K_1 = 860 \pm 40$ moles of solvent (nitrate)/mole, corresponding to a specific Helmholtz free energy of association[6] $\Delta A = -5.1$ kcal./mole with an assumed coordination number $Z = 6$. The corrected result reported by Harrington and Tien was $\beta_1 = 96 \pm 11$ kg./mole or $K_1 = 1090 \pm 130$ moles of solvent/mole, corresponding also to $\Delta A = -5.1$ kcal./mole. In our experiments, the solubility of silver chloride was found to be too low to permit reliable measurement of K_2 (the association constant for the formation of $AgCl_2^-$); *i.e.*, it was not possible to prepare solutions with high chloride concentrations and also with silver concentrations high enough to yield a satisfactory Nernst slope for the silver electrode. This is reflected in the large uncertainty reported by Harrington and Tien for β_2.

Tien and Harrington assert[1] that "smoothness of the data at low chloride concentrations" demonstrates the absence of binuclear complexes. As a matter of fact, their eq. 6 and 7[1] combined with our eq. 6 and 9[5] lead to the expression

$$\frac{C_m - [M]}{[M]} = \beta_1 C_x + \beta_2 C_x^2 - \beta_1^2 C_m C_x + \ldots$$

in the absence of polynuclear species; hence, combining with their eq. 21,[1] the limiting slope of Fig. 1 will be $(\beta_1 - \beta_1^2 C_m)$ in the absence of polynuclear species. On the other hand, a limiting slope independent of the metal ion concentration corresponds to a value of the binuclear association constant $\beta_{12} = {}^1/_2\beta_1^2$, as demonstrated by eq. 9 and 16 of ref. 5. The concentration dependence of the limiting slopes of our data indicated that β_{12} was not zero, although scatter prevented a reliable calculation. The function $(C_m - [M])/[M]$ is, in the notation of ref. 5, $(1/\gamma_{AgNO_3} - 1$. The magnitudes of the association constants in this system, however, are such that the function $\log 1/\gamma_{AgNO_3}$ (which is proportional to Δ(e.m.f.)) leads to a more linear and hence a more reliable extrapolation, with equal statistical weight for all points.

The use of molarity units in fused salt systems makes comparisons between different solvents difficult (particularly in the absence of complete density–temperature data) unless the association constants are to be analyzed in terms of a Debye–Hückel-type theory. To correlate the association constants in different solvents in terms of ionic radii and charges, ionic mole fractions or mole ratios should be used.

Finally, as Tien and Harrington state, the quasi-lattice model cannot be expected to apply to systems in which the sizes of the ions are quite different; however, the perhaps fortuitous near-constancy of ΔA over appreciable ranges of temperature for several solutes in mixtures of $LiNO_3$ and KNO_3,[7] and even in mixtures of $Ca(NO_3)_2$ with KNO_3 (results to be published shortly), indicate that the equations are useful, in the absence of additional information, for the extrapolation of association constants, at least over small ranges of temperature.

Acknowledgment.—The authors wish to acknowledge support of this work by the U. S. Atomic Energy Commission under Contract At(30-1)-2873.

---

[1] H. T. Tien and G. W. Harrington, *Inorg. Chem.*, **3**, 215 (1964).

[2] C. Thomas and J. Braunstein, *J. Phys. Chem.*, **68**, 957 (1964). (This note was in press but not yet published at the time ref. 1 appeared.)

[3] G. W. Harrington and H. T. Tien, *Inorg. Chem.*, **3**, 1333 (1964).

[4] The data have been deposited as Document No. 7995 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[5] J. Braunstein, M. Blander, and R. M. Lindgren, *J. Am. Chem. Soc.*, **84**, 1529 (1962).

[6] (a) M. Blander and J. Braunstein, *Ann. N. Y. Acad. Sci.*, **79**, 838 (1960); (b) M. Blander, *J. Chem. Phys.*, **34**, 432 (1961).

[7] J. Braunstein and A. S. Minano, *Inorg. Chem.*, **3**, 218 (1964).

DEPARTMENT OF CHEMISTRY J. BRAUNSTEIN
UNIVERSITY OF MAINE H. BRAUNSTEIN
ORONO, MAINE A. S. MINANO

RECEIVED MAY 28, 1964

"Five-Coordinated Intermediates" in the Substitution Reactions of Acidopentaamminecobalt(III) Complexes

Sir:

Recently, Haim and Taube[1] have postulated that substitution reactions of ions $Co(NH_3)_5Y^{2+}$ go by a dissociation mechanism in which the five-coordinated intermediate $Co(NH_3)_5{}^{3+}$ lasts long enough to discriminate between possible nucleophiles.

$$Co(NH_3)_5Y^{2+} \xrightarrow{k_d} Co(NH_3)_5{}^{3+} + Y^- \qquad (1)$$

$$Co(NH_3)_5{}^{3+} + X^- \xrightarrow{k_x} Co(NH_3)_5X^{2+} \qquad (2)$$

$$Co(NH_3)_5{}^{3+} + H_2O \underset{k_{ex}}{\overset{k_w}{\rightleftharpoons}} Co(NH_3)_5H_2O^{3+} \qquad (3)$$

From a study of aquation–anation equilibria and from separate competition experiments, ratios of rate constants, k_x/k_w, have been reported for several anions.[1]

[1] A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).