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Formation Constants of Silver(I) Chloro Complexes in Fused Lithium Nitrate–Potassium Nitrate Eutectic

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The behavior of silver(I) ions in molten Li–K nitrate eutectic in the presence of excess chloride ions before precipitation is investigated by a potentiometric method. The nonideal behavior of silver(I) ion in the presence of chloride ion is explained in terms of complex ion formation. The existence of these ions and their formation constants are arrived at by a modification of the mathematical treatment suggested by Bjerrum and Leden. The species found are the ion pair, $Ag^+–Cl^-$, and the ion $AgCl_2^-$. The stability constants are, respectively, $1.65 \pm 0.10 \times 10^2$ and $1.20 \pm 0.10 \times 10^3$ on a molarity scale, at 225°.

Introduction

Previous investigations of Ag(I) behavior in fused nitrates in the presence of excess chloride ions before precipitation have been explained on the basis of the "quasi-lattice" theory.[3–5] Briefly, the theory deals with a reciprocal salt mixture and is concerned chiefly with the interactions between the nearest neighbors. Accordingly, the extra-coulombic interaction yields the result for the activity coefficient of the component under consideration. The theory has worked very well in the cases in which it is applicable. One of the restrictions in the basic model, however, is that the sizes of the solvent ions cannot be very different.[5,6] Until such a time that this restriction is removed it would not be very useful to apply the "quasi-lattice" method to studies in $LiNO_3–KNO_3$ eutectic. In this case the ionic sizes are quite different and, in addition, the presence of the small lithium ion might induce considerable polarization of the nitrate ion.

In this contribution we are concerned with a simplified mathematical procedure for determining the formation constants of the species $Ag^+–Cl^-$ and $AgCl_2^-$ in the Li–K nitrate eutectic from potentiometric data. The work also demonstrated the applicability of the glass reference electrode to studies of this type.[7] This has the advantage of eliminating from the experimental cell fritted disks, etc., which these investigators have found very troublesome to work with.

Deduction of the Equations Required for the Calculation of the Formation Constants

Summary of Notations and Symbols

C_m = total concentration of the metal ion
$[M]$ = equilibrium concentration of the metal ion
C_x = total concentration of the complexing ligand
$[X]$ = equilibrium concentration of the free ligand
$MX_1, MX_2, \ldots MX_n$, = intermediate complexes
$[MX_n]$ = concentration of nth complex
$\bar{n}$ = formation function as defined by Bjerrum (see eq. 12)
β_n = formation constant for the nth complex
k = concentration constant formed in consecutive manner
f = availability function as defined by eq. 11

In the derivation of these equations, it is assumed that only mononuclear complexes are formed (see Results section) and it is derived for a general case. For the sake of simplicity the charges on the metal ion M and ligand X are omitted. The formation reaction for the system under consideration may be represented as

$$M + nX = MX_n \qquad (1)$$

For the intermediate complexes, one can write

$$M + X = MX \qquad (2)$$

$$MX + X = MX_2 \qquad (3)$$

and so on. For the nth complex the formation constant in terms of concentrations is given by

$$\beta_n = \frac{[MX_n]}{[M][X]^n} = K_1K_2\ldots K_n = \pi_{i=1}^{i=n} K_i \qquad (4)$$

The total metal ion and ligand concentrations are given, respectively, by the expressions

$$C_m = [M] + \sum_{i=1}^{n} [MX_i] \qquad (5)$$

$$C_x = [X] + \sum_{i=1}^{n} [MX_i] \qquad (6)$$

Equations 4 and 5 may be combined, after rearranging terms, and one obtains

$$\frac{(C_m - [M])}{[M]} = \beta_1[X] + \beta_2[X]^2 \ldots \beta_n[X]^n \qquad (7)$$

For ease of handling, the left-hand side of eq. 7 is defined in terms of [X], thus

$$\phi([X]) = \frac{(C_m - [M])}{[M]} \qquad (8)$$

A plot of $\phi([X])/[X]$ against $[X]$ is prepared and, by extrapolating to zero concentration of $[X]$, the term β_1 may be evaluated according to the procedure of

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[1] Part of the work submitted by H. T. Tien to Temple University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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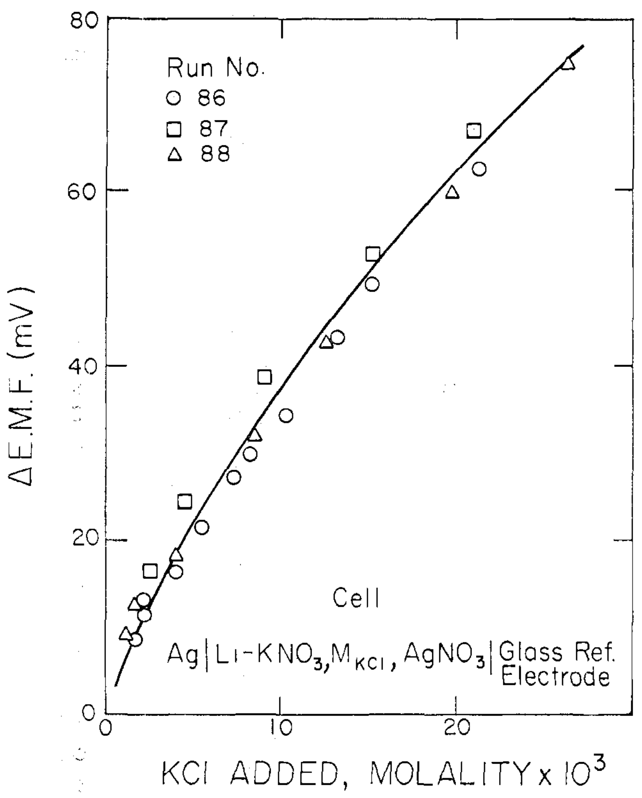

Fig. 1.—Variation of cell potential with concentration of KCl.

Leden.[8] This graphical limit is shown by the equation

$$\lim_{[X]\to 0} \frac{\phi([X])}{[X]} = \beta_1 \qquad (9)$$

in a similar manner, the term β_2 may be evaluated. Thus

$$\psi([X]) = \frac{\phi([X])/[X] - \beta_1}{[X]} \qquad (10)$$

$$\lim_{[X]\to 0} \psi([X]) = \beta_2 \qquad (11)$$

The extension of these procedures to obtain β_n is self-evident. In order to evaluate the function $\phi([X])$, however, experimental data of [M] at the concentration of [X] must be available. Since [M] is the measured quantity in the present study, the problem remaining to be solved is that of the calculation of [X]. Instead of using the method of successive approximation proposed by Leden,[8] which is lengthy and tedious, the method of Bjerrum[9] is utilized. The advantage of Bjerrum's method lies in fact that it allows judicious smoothing of the data. In addition, the numerical calculation has an immediate physical meaning in that the number of complexes formed is readily apparent. Bjerrum defines a useful quantity, $\bar{n}$, which is the so-called formation function, by the equation

$$\bar{n} = \frac{(C_x - [X])}{C_m} \qquad (12)$$

The physical significance of $\bar{n}$ is seen to be the average coordination number of the metal ion. Substituting the terms of C_m and C_x in eq. 12 by the terms in eq. 5 and 6, respectively, eq. 12 becomes

$$\bar{n} \doteq \frac{\sum_{i=1}^{n} i\beta_i[X]^i[M]}{[M] + \sum_{i=1}^{n} \beta_i[X]^i[M]} \qquad (13)$$

In order to evaluate $\bar{n}$ from the experimentally determined quantity, a term f is introduced, where f is given by the equation

$$f = \frac{[M]}{C_m} \qquad (14)$$

This quantity f measures the fraction available for further complex formation. Hence, it is termed the "availability function." It will be shown later that the logarithm of f is directly proportional to the experimentally measured e.m.f. of the cell. Combining eq. 5 and 14, one has

$$f = \frac{[M]}{[M] + \sum_{i=1}^{n} \beta_1[X]^i[M]} \qquad (15)$$

Differentiating eq. 15 with respect to [X] and simplifying, expression 16 is obtained.

$$\frac{\partial f}{\partial [X]} = -\frac{\sum_{i=1}^{n} i\beta_i[X]^{i-1}}{(1 + \sum_{i=1}^{n} \beta_i[X]^i)^2} \qquad (16)$$

Transforming and rearranging eq. 16 in conjunction with eq. 13, one has

$$\partial \ln f = -\bar{n}\, \partial \ln [X] \qquad (17)$$

It will be shown in the following section that the e.m.f. of the cell in the present study is directly proportional to the quantity on the left-hand side of eq. 17, thus

$$\partial E = +\bar{n}\left(\frac{RT}{nF}\right) \partial \ln [X] \qquad (18)$$

Here, R, T, F, and $\bar{n}$ have the usual significance. The value of $\bar{n}$ may be obtained *via* graphical differentiation by plotting $\partial E/\partial \ln X$ *vs.* [X]. The point on the curve at a given value of [X] defines $\bar{n}$. Once $\bar{n}$ values are known, eq. 12 may be used to compute [X]. The stepwise formation constants may then be evaluated graphically as indicated in eq. 8 to 11.

Experimental

(A) **Chemicals and Apparatus.**—The materials and apparatus were the same as described previously.[10–12]

(B) **Potentiometric Measurements.**—The measurements were made in the form of a potentiometric titration in which Ag was measured with a silver electrode as a function of the chloride concentration. The total silver concentration was kept constant within each run. The cell used is represented by

$$\text{Ag} \left| \begin{array}{c} \text{AgNO}_3 + x\text{KCl} \\ \text{Li–K nitrate melt} \end{array} \right| \text{glass ref. electrode}$$

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TABLE I

COMPUTATION OF STEPWISE FORMATION CONSTANTS[a]

E.m.f., mv.	$-\log C_{KCl}$	Δe.m.f.	$\Delta \log C_{KCl}$	$\bar{n}$	$\bar{n} \times (C_{Ag} \times 10^5)$	$[Ag] \times 10^4$, M	$[Cl] \times 10^2$, M	$\phi([X])/[X]$	$\frac{(\phi([X])/[X]) - \beta_1}{[X]}$
24.0	2.69								
		3	0.30	0.101	0.76	2.86	0.40	6.35	1.75
27.0	2.39							(1.75)[b]	
		8	0.35	0.230	1.73	2.37	0.90	3.40	1.00
35.0	2.04							(1.77)	
		1.5	0.05	0.333	2.50	2.29	1.00	3.18	1.00
36.5	1.99							(1.78)	
		15	0.30	0.504	3.79	1.62	2.00	2.27	1.20
51.5	1.69							(1.92)	
		14	0.18	0.804	6.05	1.165	3.00	2.12	1.23
65.5	1.51							(2.05)	
		13	0.13	1.052	7.91	0.861	4.00	2.16	1.20
78.5	1.38								
		11.5	0.09	1.201	9.03	0.659	5.01	2.26	1.16
90.0	1.29								
		10.5	0.08	1.284	9.66	0.516	6.02	2.40	1.20
100.5	1.21								

[a] Data derived from the smoothed curve based on three runs (see Fig. 1). [b] Figures in parentheses are extrapolated values.

From the Nernst equation, the e.m.f. of the cell is given by

$$E_1 = E' - \frac{RT}{nF} \ln C_{Ag} \tag{19}$$

in the absence of added ligand (*i.e.*, $C_{Cl} = 0$), and by

$$E_2 = E' - \frac{RT}{nF} \ln [Ag^+] \tag{20}$$

in the presence of added ligand. E' is a constant for a given cell under consideration. The calculations presented in Table I are therefore based on the equation

$$\Delta E = E_2 - E_1 = -\frac{RT}{nF} \ln \frac{[Ag^+]}{C_{Ag}} = -\frac{RT}{F} \ln f \tag{21}$$

Hence, ΔE is the potential difference of the following hypothetical cell, which has the same total silver ion concentration in the two half cells.

$$\text{Ag} \left| \begin{array}{l} \text{AgNO}_3\text{, KCl} \\ \text{Li–K nitrate} \\ \text{melt} \end{array} \right| \begin{array}{l} \text{AgNO}_3 \\ \text{Li–K nitrate} \\ \text{melt} \end{array} \left| \text{Ag} \right. \tag{22}$$

Results

The results of the measurements for three runs at 225.0° with C_{Ag} at 7.117×10^{-4}, 7.521×10^{-4}, and 1.116×10^{-3} M, respectively, are shown graphically in Fig. 1. The smoothness of the data at low chloride concentrations supports the assumption made above that only mononuclear complexes are formed to an appreciable extent at the particular silver ion concentrations used in this investigation. If species such as Ag_2Cl^+ were formed in significant amounts a greater scatter of data would occur in the region of low chloride ion concentration.

Assuming that the change of e.m.f. of the cell as a function of added chloride is due to complex ion formation, the stepwise formation constants are calculated using the procedure given earlier. The results of these calculations are given in Table I. The extrapolated formation constants β_1 and β_2 for the postulated species $Ag^+–Cl^-$ and $AgCl_2^-$ are, respectively, $1.65 \pm 0.10 \times 10^2$ and $1.20 \pm 0.10 \times 10^3$ on a molarity scale.

Thus this method of analysis indicates that two, rather stable, species are formed in this solvent. It should be pointed out that these species have been called complex ions for convenience only. The use of this term is not meant to convey anything concerning the nature of the bonding present.