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The Association of Cadmium Ion with Bromide and Iodide Ions in Molten Equimolar $NaNO_3$-KNO_3

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The activity coefficients of alkali bromide at 240 and 300° and of alkali iodide at 240 and 290° in dilute solutions of alkali halide and cadmium nitrate in molten equimolar mixtures of $NaNO_3$ and KNO_3 were determined from measurements of the electromotive force of the concentration cells with silver–solid silver halide electrodes $\mathrm{Ag, AgX(s)|NaX{-}KX, NaNO_3{-}KNO_3||NaNO_3{-}KNO_3, Cd(NO_3)_2, NaX{-}KX|AgX(s), Ag}$. The thermodynamic association constants for the formation of $CdBr^+$ are 1520 and 990 (moles/mole solvent)$^{-1}$ at 240 and 300°, respectively. The association constants for the formation of CdI^+ are 5330 and 3130 (moles/mole solvent)$^{-1}$ respectively. The estimated error of the association constants is 5%. No evidence of polynuclear species was found in either case. The stepwise association constants for the formation of CdI_2 and $CdBr_2$ also were evaluated and the results were compared with the quasi-lattice model.

Introduction

In this paper, an e.m.f. method for the evaluation of metal ion–halide ion association constants is described. It is shown that silver–solid silver halide electrodes are reversible to halide ions in molten alkali nitrates[4] and that the activity coefficients of alkali halides in molten alkali nitrates may be evaluated from measurements of the e.m.f. of the cell

$$\mathrm{Ag, AgX(s)}\left|\begin{matrix}\mathrm{NaNO_3{-}KNO_3}\\ \mathrm{KX}\\ \phantom{[Cd^{2+}]}\end{matrix}\right\|\begin{matrix}\mathrm{NaNO_3{-}KNO_3}\\ \mathrm{KX}\\ [\mathrm{Cd^{2+}}]\end{matrix}\left|\mathrm{AgX(s), Ag}\right. \qquad \mathrm{(I)}$$

where AgX(s) is solid silver bromide or iodide, the halide ions and cadmium ions are present at concentrations below 0.2 mole per cent., and the solvent is a molten equimolar mixture of $NaNO_3$ and KNO_3 at temperatures between 240° and 300°.

Experimental

Reagent grade sodium nitrate, potassium nitrate, silver nitrate, potassium bromide and potassium iodide were used without further purification. Cadmium bromide was recrystallized from water and dried at 110°. Anhydrous cadmium nitrate was prepared from the ground tetrahydrate by dehydration in a vacuum desiccator, raising the temperature gradually from room temperature to 110°. Analysis by ignition to cadmium oxide or by the the Karl Fischer method showed the water content to be below 0.2%.

The cell has been described previously[5] The temperature was measured with a chromel and alumel thermocouple or with a mercury in glass thermometer, both calibrated to ± 0.5 degree against the freezing points of Bi, Cd and Zn. The temperature was maintained constant within 0.5° during a set of measurements by manual control of the electric resistance furnace with a variable transformer, and uniformity of temperature in the melt was ensured by continuous vigorous stirring. The electrodes were silver wires dipping into melts which had been saturated with silver halide by the addition of a weighed amount of silver nitrate (30–60 mg.) and an equivalent quantity of potassium bromide or iodide. Equilibrium was reached more rapidly with the silver halide precipitated *in situ* than with silver–silver halide electrodes prepared in the conventional manner.[4] The stoichiometric concentration of silver nitrate in the reference half cell was less than 10^{-3} mole fraction, and its activity was lowered further by the addition of potassium halide with the precipitation of solid silver halide. The magnitude of the e.m.f. of the concentration cell during a set of measurements was less than 200 mv. The electromotive force was measured to ± 0.1 mv. with a Rubicon Type B potentiometer, a Leeds and Northrup Type K potentiometer or a Gray Instrument Co. "Queen" potentiometer which had been calibrated against the Type K.

Helium was bubbled through the molten solvent for about an hour before the addition of any solutes. After the precipitated silver halide had coagulated, weighed additions of potassium bromide or iodide were made and the e.m.f. of the cell was measured after each addition. The e.m.f. reached its equilibrium value almost instantaneously and remained constant within ± 0.2 mv. for periods of several hours to several days. On changing the temperature by about ten degrees, the e.m.f. changed but returned to its original value when the original temperature was reestablished, indicating temperature reversibility of the electrodes.

After verification of the Nernst equation for the silver-silver halide electrodes in molten equimolar sodium nitrate–potassium nitrate containing between 10^{-4} and 5×10^{-3} mole fraction of potassium halide, successive weighed amounts of cadmium nitrate or cadmium bromide were added up to a concentration of 3×10^{-3} mole fraction, and the e.m.f. was measured after each addition. When cadmium nitrate or cadmium bromide was added in concentrations up to about 2×10^{-3} mole fraction to melts containing potassium bromide (at similar concentrations) the e.m.f. was stable within ± 0.2 mv. for periods of several hours up to several days. This stability also was observed for e.m.f. measurements with cadmium ion in the presence of iodide ion when the concentration of cadmium nitrate was below about 3×10^{-4} mole fraction. At higher concentrations of cadmium ion in the presence of iodide, the e.m.f. of the cell drifted, and subsequent analysis of the melt showed that a loss of iodide had occurred. The association constants for CdI^+ were evaluated from the results of experiments at concentrations such that the e.m.f. was stable and chemical analysis showed no loss of iodide.

Results

The e.m.f. of the concentration cell (I) is[5]

$$E = \frac{2.303RT}{F} \log \frac{a_{\mathrm{AgNO_3}}}{a'_{\mathrm{AgNO_3}}}$$

where $a_{\mathrm{AgNO_3}}$ is the activity of the component $AgNO_3$ and the prime refers to the reference half cell. If the melt is saturated with silver halide and the activity of the silver halide in the solid phase is constant, the e.m.f. may be written

$$E = -\frac{2.303RT}{F} \log \frac{a_{\mathrm{(Na,K)X}}}{a'_{\mathrm{(Na,K)X}}}$$

The e.m.f. of cell (I) in the absence of cadmium ion, with silver-solid silver bromide electrodes at 240 and 300° and with silver–solid silver iodide electrodes at 240 and 290° in equimolar $NaNO_3$–KNO_3 as solvent and with silver-solid silver iodide

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[3] Operated by the Union Carbide Corporation for the U. S. Atomic Energy Commission.

[4] The reversibility of the Ag–AgCl(s) electrode to chloride ions in a low-melting mixture of alkali nitrates has been demonstrated by M. Bonnemay and R. Pineaux, *Compt. rend.*, **240**, 1774 (1955).

[5] (a) M. Blander, F. F. Blankenship and R. F. Newton, *J. Phys. Chem.*, **63**, 1259 (1959); (b) J. Braunstein and M. Blander, *ibid.*, **64**, 10 (1960); (c) D. G. Hill, J. Braunstein and M. Blander, *ibid.*, **64**, 1038 (1960).

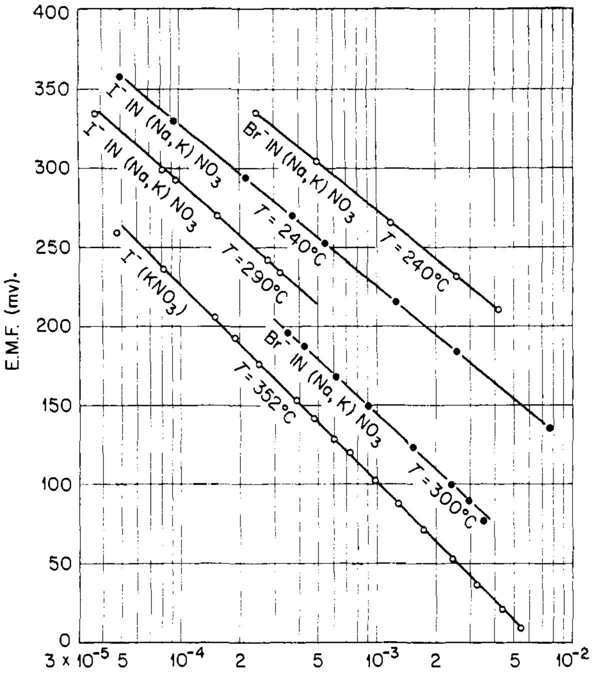

Fig. 1.—E.m.f. of the concentration cell (I) with silver-solid silver halide electrodes. (The e.m.f. scales have been displaced to fit the data on one plot.) The slope of the solid line is 2.303 RT/F.

electrodes at 352° in KNO_3 as solvent is plotted in Fig. 1 as a function of the mole ratio, $R_{(\mathrm{Na,\,K})\mathrm{X}}$, of halide ion. The mole ratio (moles of solute per mole of solvent) does not differ significantly, at the concentrations studied, from the ion fraction which was the concentration scale used in previous studies.[5,7] The molal scale which has been used in some investigations of association in molten salts[6] is less convenient for a comparison of association constants in different solvents where some of the differences among the association constants may be correlated with the relative sizes of the solvent and solute ions. The solid lines are the calculated Nernst slopes, $\frac{2.303RT}{F}$. Henry's Law is followed for dilute solutions of bromide or iodide in molten alkali nitrate within ± 0.5 mv. in the range of temperatures and compositions investigated. The experimentally observed temperature reversibility of the e.m.f. indicates that the activity of the silver halide in the solid phase probably is constant, and any solid solutions, if formed, have a negligible effect.

On addition of $Cd(NO_3)_2$ to the right-hand half-cell of (I), the e.m.f. increases and the stoichiometric activity coefficient of the (sodium-potassium) bromide or iodide is given by the equation

$$\log \gamma_{(\mathrm{Na,\,K})\mathrm{X}} = -\frac{F}{2.303RT}\,\Delta E \qquad (1)$$

where the activity coefficient, $\gamma_{(\mathrm{Na,\,K})\mathrm{X}} = \frac{a_{(\mathrm{Na\,K})\mathrm{X}}}{R_{(\mathrm{Na,\,K})\mathrm{X}}}$ is unity at infinite dilution of all solutes. The change of e.m.f. on the addition of $Cd(NO_3)_2$ in the presence of bromide (or iodide) is given in Table I (a and b).

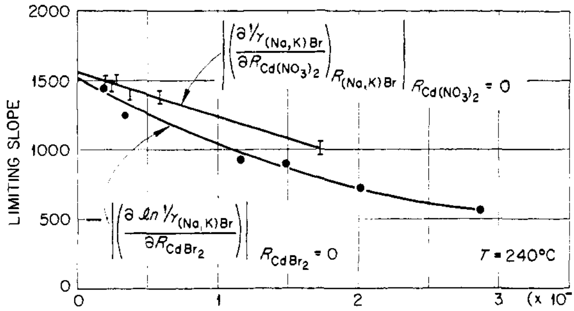

Fig. 2.—Extrapolation of the limiting slopes to infinite dilution of the solutes to evaluate K_1 and K_2.

If association constants for the formation of associated species, CdX^+, CdX_2, Cd_2X^{3+}, etc., are defined as

$$K_1 = \frac{R_{\mathrm{CdX^+}}}{R_{\mathrm{Cd^{2+}}} + R_{\mathrm{X^-}}} \qquad (2)$$

$$K_2 = \frac{R_{\mathrm{CdX_2}}}{R_{\mathrm{Cd^{2+}}} + R_{\mathrm{2X^-}}} \qquad (3)$$

$$K_{12} = \frac{R_{\mathrm{Cd_2X^{3+}}}}{R^2_{\mathrm{CdX^+}} + R_{\mathrm{Cd^{2+}}}} \qquad (4)$$

etc., in which the R are mole ratios of the species indicated, the stoichiometric activity coefficient of (sodium, potassium) halide may be written as the Maclaurin expansion[7]

$$\frac{1}{\gamma_{(\mathrm{Na,\,K})\mathrm{X}}} = 1 + K_1R_{\mathrm{Cd(NO_3)_2}} + K_1K_{12}R^2_{\mathrm{Cd(NO_3)_2}} + (2K_1K_2 - K_1^2)R_{\mathrm{Cd(NO_3)_2}}R_{(\mathrm{Na,\,K})\mathrm{X}} + \ldots \qquad (5)$$

in the range of concentrations in which the associated species follow Henry's Law. Large-scale plots of $1/\gamma_{(\mathrm{Na,K})\mathrm{X}}$ *versus* the mole ratio of $Cd(NO_3)_2$ were made and the slopes at $R_{\mathrm{Cd(NO_3)_2}} = 0$ were estimated for each fixed stoichiometric mole ratio of (Na,K)X. The first association constants were evaluated graphically as the limiting slopes[7]

$$K_1 = \lim_{\substack{R_{\mathrm{Cd(NO_3)_2}} \to 0 \\ R_{(\mathrm{Na,K})\mathrm{X}} \to 0}} \left(\frac{\partial^{1/\gamma}{}_{(\mathrm{Na.K})\mathrm{X}}}{\partial R_{\mathrm{Cd(NO_3)_2}}}\right)_{R_{(\mathrm{Na,K})\mathrm{X}}} \qquad (6)$$

The limiting slopes were obtained by extrapolation to $R_{(\mathrm{Na,K})\mathrm{X}} = 0$ as shown in the upper curve in Fig. 2 for the bromide at 240°. The intercept is K_1 and the limiting slope of this plot leads to values of K_2 by means of the relation

$$\lim_{\substack{R_{\mathrm{Cd(NO)_{32}}} \to 0 \\ R_{(\mathrm{Na,K})\mathrm{X}} \to 0}} \left(\frac{\partial^2{}_{1/\gamma(\mathrm{Na.K})\mathrm{X}}}{\partial \mathrm{R}_{(\mathrm{Na,K})\mathrm{X}}\partial \mathrm{R}_{\mathrm{Cd(NO_3)_2}}}\right) = K_1\,(2K_2 - K_1) \qquad (7)$$

The function $1/\gamma$ rather than ln γ[7] was used in this evolution because it was found to give more nearly linear plots because of the relative values of K_1, K_2 and K_{12} in this system. Values of K_1 and K_2 obtained by this method for bromide ion at 240° and for iodide ion at 240 and 290° are listed in Table II. It may be seen from the coefficient of the quadratic term in $R_{\mathrm{(Cd,NO_3)_2}}$ in (5) that the association

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(6) (a) E. R. Van Artsdalen, *J. Phys. Chem.*, **60**, 172 (1956); (b) F. R. Duke and M. L. Iverson, *ibid.*, **62**, 417 (1958); (c) J. H. Christie and R. A. Osteryoung, *J. Am. Chem. Soc.*, **82**, 1841 (1960).

(7) J. Braunstein, M. Blander and R. M. Lindgren, *ibid.*, **84**, 1529 (1962).

TABLE I

(a) E.M.F. CHANGE IN VOLTS OF THE CELL (I) ON ADDITION OF $Cd(NO_3)_2$. ($X = Br^-$)

$T = 240°$

$R_{\text{(Na,K)Br}}$					
2.002×10^{-4}		2.514×10^{-4}		2.556×10^{-4}	
$R_{\text{Cd(NO}_3)_2} \times 10^3$	Δe.m.f.	$R_{\text{Cd(NO}_4)_2} \times 10^3$	Δe.m.f.	$R_{\text{Cd(NO}_3)_2} \times 10^3$	Δe.m.f.
0.0453	0.0033	0.0522	0.0042	0.0543	0.0043
.1091	.0067	.1459	.0090	.1503	.0092
.2207	.0119	.3422	.0175	.3346	.0170
.4282	.0213	.7082	.0295	.7982	.0318
.8505	.0341	1.1628	.0407	1.4049	.0462
1.3090	.0454	1.4733	.0472		

$R_{\text{(Na,K)Br}}$					
3.914×10^{-4}		5.925×10^{-4}		1.732×10^{-3}	
$R_{\text{Cd(NO}_4)_2} \times 10^3$	Δe.m.f.	$R_{\text{Cd(NO}_3)_2} \times 10^3$	Δe.m.f.	$R_{\text{Cd(NO}_3)_2} \times 10^3$	Δe.f.m.
0.1349	0.0080	0.0926	0.0059	0.1045	0.0037
.2415	.0129	.1854	.0098	.5192	.0178
.4678	.0222	.4762	.0219	.6980	.0232
.9400	.0372	1.0771	.0395	1.0404	.0330
1.4795	.0498	1.4936	.0494	1.5961	.0468

(b) E.M.F. CHANGE IN VOLTS OF THE CELL (I) ON ADDITION OF $Cd(NO_3)_2$. ($X = I^-$)

$T = 240°$

$R_{\text{(Na,K)I}}$					
0.53×10^{-4}		1.39×10^{-4}		2.10×10^{-4}	
$R_{\text{Cd(NO}_3)_2} \times 10^4$	Δe.m.f.	$R_{\text{Cd(NO}_3)_2} \times 10^4$	Δe.m.f.10^4	$R_{\text{Cd(NO}_3)_2} \times$	Δe.m.f.
0.25	0.0055	0.06	0.0012	0.24	0.0034
.67	.0126	.27	.0052	1.01	.0134
.99	.0176	.52	.0092	1.31	.0171
.153	.0248	.83	.0137	2.02	.0249
2.40	.0346				

$R_{\text{(Na,K)I}}$			
2.84×10^{-4}		3.54×10^{-4}	
$R_{\text{Cd(NO}_3)_2} \times 10^4$	Δe.m.f.	$R_{\text{Cd(NO}_3)_2} \times 10^4$	Δe.m.f.
0.25	0.0035	0.20	0.0025
1.01	.0125	0.80	.0098
1.45	.0190	1.44	.0168
		2.39	.0270
		3.76	.0387

$T = 290°$

$R_{\text{(Na,K)I}}$			
2.55×10^{-4}		3.24×10^{-4}	
$R_{\text{Cd(NO}_3)_2} \times 10^4$	Δe.m.f.	$R_{\text{Cd(NO}_3)_2} \times 10^4$	Δe.m.f.
0.33	0.0038	0.19	0.0010
0.63	.0085	0.64	.0100
1.08	.0145	1.08	.0180
1.86	.0240	1.56	.0242
2.70	.0323	2.25	.0350

$R_{\text{(Na,KI)}}$			
3.49×10^{-4}		6.78×10^{-4}	
$R_{\text{Cd(NO}_3)_2} \times 10^4$	Δe.m.f.	$R_{\text{Cd(NO}_3)_2} \times 10^4$	Δe.m.f.
0.17	0.0020	0.17	0.0019
.45	.0065	0.88	.0101
.88	.0127	1.27	.0140
1.39	.0185		
1.77	.0228		

(c) E.M.F. CHANGE IN VOLTS OF THE CELL (I) ON ADDITION OF $CdBr_2$. ($X = Br^-$)

$T = 240°$

$R_{\text{(Na,K)Br}}$							
2.013×10^{-4}		3.438×10^{-4}		1.163×10^{-4}		1.493×10^{-4}	
$R_{\text{CdBr}_2} \times 10^3$	−Δe.m.f.	$R_{\text{CdBr}_2} \times 10^3$	−Δe.m.f.	$R_{\text{CdBr}_2} \times 10^3$	$R_{\text{CdBr}_2} \times 10^3$	$R_{\text{CdBr}_2} \times 10^3$	−Δe.m.f.
0.0551	0.0142	0.1066	0.0149	0.2033	0.0050	0.0473	0.0003
.1174	.0260	.2710	.0302	.4228	.0095	.1152	.0017
.1210	.0382	.4506	.0393	.6948	.0131	.2550	.0038
.4692	.0570	.6810	.0481	1.1252	.0173	.4655	.0055
.7831	.0692	1.0910	.0574	1.4722	.0195	.6461	.0073
1.2818	.0803	1.4445	.0629	1.9759	.0220	.9164	.0100
1.5741	.0852					1.3918	.0131
2.0052	.0899					1.6969	.0150

$R_{\text{(Na,K)Br}}$					
2.018×10^{-4}		2.880×10^{-4}		2.874×10^{-3}	
$R_{\text{CdBr}_2} \times 10^3$	−Δe.m.f.	$R_{\text{CdBr}_2} \times 10^3$	−Δe.m.f.	$R_{\text{CdBr}_2} \times 10^3$	−Δe.m.f.
0.0496	0.0003	0.0685	0.0003	0.1210	0.0000
.1519	.0010	.1170	.0006	.1994	.0000
.3704	.0033	.2574	.0008	.4775	.0002
.7524	.0053	.6839	.0014	1.0967	.0009
1.5001	.0083	.9981	.0015		
		1.4706	.0016		

constant for the formation of the binuclear species Cd_2Br^{3+} is given by the limiting curvature of $1/\gamma_{(Na,K)X}$ at zero concentration of (Na,K)X. Plots of $1/\gamma_{(Na,K)X}$ at the lowest concentrations of (Na,K)X were linear in the concentration of $Cd(NO_3)_2$ up to concentrations at which more than half of the halide was associated ($1/\gamma_{(Na,K)X} > 2$), indicating (within the experimental error) the absence of the binuclear species. (It may be noted that if the activity of the cation rather than of the ligand had been measured, as in previous work,[7] the limiting curvature of a plot of $1/\gamma_{Cd(NO_3)_2}$ would have been proportional to the formation constant of CdX_2, K_2, rather than to the binuclear association constant K_{12}.) Attempts to calculate the binuclear association constants, K_{12}, by plotting the difference function

$$\left(\frac{1}{\gamma_{(Na,K)X}} - R_{Cd(NO_3)_2}\left[\left(\frac{\partial^{1/\gamma_{(Na,K)X}}}{\partial R_{Cd(NO_3)_2}}\right)_{R_{(Na,K)X}} \Bigg| \begin{matrix} R_{Cd(NO_3)_2} \\ = 0 \end{matrix}\right]\right)$$

against the square of the mole ratio of $Cd(NO_3)_2$ and extrapolating the slope of this function to zero halide concentration led to a scatter of about ± 100 about zero for K_{12}. The dependence of the limiting slopes on the concentration of (Na,K)Br emphasizes the necessity of extrapolation to infinite dilution of cadmium ion as well as of halide ion in the evaluation of the association constants.

TABLE II

SUCCESSIVE ASSOCIATION CONSTANTS[a] AND HELMHOLTZ FREE ENERGIES OF FORMATION[b] OF CADMIUM ION–HALIDE ION ASSOCIATIONS

Temp., °C.	Bromide				Iodide			
	K_1	$-\Delta A_1$	K_2	$-\Delta A_2$	K_1	$-\Delta A_1$	K_2	$-\Delta A_2$
240	1520	5.67	680	5.73	5330	6.94	2200	6.94
290					3130	7.03	1300	7.03
300	990	5.83	450	5.93				

[a] (moles/mole $(Na,K)NO_3)^{-1}$. The estimated uncertainties are ± 5% for K_1 and ± 10% for K_2. The association constants on the molality scale are 0.0933 multiplied by the above values. [b] Kcal/mole. The estimated uncertainties are ± 0.06 for ΔA_1 and ± 0.10 for ΔA_2.

In order to determine the usefulness of the e.m.f. method for the evaluation of association constants of cations whose anhydrous nitrates could not be prepared, the association constants of Cd^{2+} and Br^- were also evaluated at 240 and 300° from measurements of the e.m.f. of the cell (I) after the addition of $CdBr_2$ instead of $Cd(NO_3)_2$ to the right-hand half-cell. These data are given in Table Ic. The stoichiometric activity coefficients may be calculated from the equation

$$\log \gamma_{(Na,K)Br} = -\frac{F}{2.303RT}\Delta E - \log \frac{R_{(Na,K)Br} + 2R_{CdBr_2}}{R_{(Na,K)Br}} \tag{8}$$

in which ΔE is the change in the electromotive force on addition of $CdBr_2$ to a solution in which the initial concentration of (sodium–potassium) bromide is $R_{(Na,K)Br}$. (The second term on the right-hand side corresponds to the change of the e.m.f. which would be caused by the addition of bromide ion if there were no deviations from ideality in the presence of cadmium ions.) The association constants were obtained by graphical extrapolations analogous to the extrapolations described above with the use of equations derived by the substitution of $R_{(Na,K)Br\,(initial)} + 2R_{CdBr_2}$ for $R_{(Na,K)Br}$ and of R_{CdBr_2} for $R_{Cd(NO_3)_2}$ in (5) (*i.e.* redefining the solute components) and taking the logarithm of (5). The association constants are given by the relations

$$K_1 = \lim_{\substack{R_{CdBr_2} \to 0 \\ R_{(Na,K)Br} \to 0}} \left(\frac{\partial \ln 1/\gamma_{(Na,K)Br}}{\partial R_{CdBr_2}}\right) \tag{9}$$

$$\lim_{\substack{R_{CdBr_2} \to 0 \\ R_{(Na,K)Br} \to 0}} \left(\frac{\partial^2 \ln 1/\gamma_{(Na,K)Br}}{\partial R_{(Na,K)Br}\partial R_{CdBr_2}}\right) = K_1(2K_2 - K_1) \tag{10}$$

The function $1/\gamma_{(Na,K)Br}$ could have been used here as well as in the calculations described previously (and was used to check the consistency of the calculations.) Since the logarithmic function, $\ln 1/\gamma_{(Na,K)Br}$, was more nearly linear in the case of $CdBr_2$ additions than in the case of $Cd(NO_3)_2$ additions, it was used here to illustrate the lack of dependence of the results on the method of calculation if reliable data are available at sufficiently low concentrations. The extrapolation for the results at 240° is shown as the lower curve of Fig. 2. The values of K_1 and K_2 at 240° obtained by this method agreed with the values obtained from the experiments with additions of $Cd(NO_3)_2$ within the estimated uncertainties of 5% in K_1 and 10% in K_2. The results are summarized in Table II.

Discussion

The thermodynamic association constants of cadmium ion and bromide ion reported in this paper are about four times as high as values obtained by recalculation of the data of Duke and Iverson.[6b,7] The results of Duke and Iverson showed a positive temperature coefficient for the association constant and no difference between the constants for the formation of $CdBr^+$ and $CdCl^+$. Our studies of the association of silver ion with chloride, bromide or iodide ion in potassium nitrate and in sodium nitrate[5,8] and unpublished work on the association of cadmium ion with chloride ion or bromide ion in $LiNO_3$–KNO_3 indicate a value of about four for the ratio of the formation constants of the bromide complexes to the formation constants of the chloride complexes and also show negative temperature coefficients.[8a] Christie and Osteryoung[6c] also report a greater degree of association for the bromide than for the chloride complexes, although they were unable to obtain accurate association constants of the bromide because of experimental difficulties. Although third and higher association constants could in principle be evaluated by the extension of equation 5 to higher terms, their significance would be questionable because of the magnification of errors in the computation and the need for precise data at higher concentrations where the liquid

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(8) A. R. Alvarez-Funes, J. Braunstein and M. Blander, *J. Am. Chem. Soc.*, **84**, 1538 (1962).

(8a) NOTE ADDED IN PROOF.—Duke and Garfinkel recently reported formation constants for $CdBr^+$ in $NaNO_3$–KNO_3 eutectic (F. R. Duke and H. M. Garfinkel, *J. Phys. Chem.*, **65**, 1627 (1961)). Their results appear to be about twenty-five per cent. lower than ours. A direct comparison was not possible since their solvent composition was slightly different from ours and they did not report the bromide concentrations at which their measurements were carried out. The strong dependence on the bromide concentration of the *apparent* association constant is indicated in Fig. 2 of this paper.

junction potential of the cell might not be negligible[5b] and where the increased solubility of silver halides in excess halide would necessitate a knowledge of the association constants of AgX and X^-.

The specific Helmholtz free energies of formation ΔA of CdX^+ and CdX_2 (where X is bromide or iodide) were evaluated using the equations of the quasi-lattice model[9,10] (asymmetric approximation) with the coördination number $Z = 6$. Since the equations of the model were derived for ions of the same charge, they might not be expected to apply to a mixture of singly charged and multiply charged ions. It is seen from the values of ΔA in Table II that the variation with temperature although very small is somewhat larger than in the case of singly charged ions.[11] The decrease of ΔA with increasing temperature is in the same direction as was observed for the association of silver ions with sulfate ions in molten KNO_3.[12] The "specific entropy of association"[9] $\left(-\left(\frac{\partial \Delta A}{\partial T}\right)\right)$ may be characteristic of a change in the internal degrees of freedom of the ions involved in the association, although the effect in this case is almost within the experimental uncertainty. The relatively small variation of ΔA with temperature indicates that the quasi-lattice model may be useful for predicting the temperature coefficients of the association constants of singly charged ions with multiply charged ions as well as with other singly charged ions.

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[9] M. Blander, *J. Chem. Phys.*, **34**, 342 (1961).

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Thermodynamic Association Constants of Silver Ions with Bromide or Iodide Ions in Molten Potassium Nitrate and their Comparison with the Quasi-lattice Theory

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Electromotive force measurements in dilute solutions of Ag^+ and Br^- in molten KNO_3 at 403, 438, 452, 474 and 500° and Ag^+ and I^- in molten KNO_3 at 402° were used to evaluate the association constants K_1, K_2 and K_{12} for the formation of AgX, AgX_2^- and Ag_2X^+, respectively, where X = Br or I. The comparison of the values of K_i in the bromide containing system with the theoretical calculations based on the quasi-lattice model demonstrated that the temperature coefficients of the K_i are correctly predicted by the theory for any reasonable choice of the coördination number using values of the "specific bond free energies" ΔA_i, which are independent of temperature. For $Z = 5$ average values of ΔA_1, ΔA_2 and ΔA_{12} are 7.14, 7.0 and 6.7 kcal./mole, respectively. The values of the "specific bond free energies" for the formation of the ion pairs Ag^+–Cl^-, Ag^+–Br^- and Ag^+–I^- in KNO_3 for $Z = 5$ are 5.8_8, 7.1_4 and 9.3_8 kcal./mole, respectively, and are consistent with the relative but not absolute values of the predictions of Flood, Førland and Grjotheim.

Introduction

Measurements of the activity coefficients of $AgNO_3$ in molten KNO_3 in dilute solutions of Ag^+ and Br^- ions at five temperatures ranging from 403 to 500° and of Ag^+ and I^- at 402° are described in this paper. In previous papers the comparison with calculations based on the quasi-lattice model[4-6] of similar measurements in dilute solutions of Ag^+ and Cl^- in pure KNO_3,[7,8] pure $NaNO$[9] and in equimolar $NaNO_3$–KNO_3[10] mixtures demonstrated that the temperature coefficient of the association constant K_1 for the formation of the ion pair Ag^+–Cl^- is correctly predicted by the expression derived from the theoretical calculations

$$K_1 = Z\,(\exp\,(-\Delta A_1/RT) - 1) \qquad (1)$$

where Z is a coördination number and ΔA_1 is the "specific bond free energy" and was constant.[11] ΔA_1 was about 1 kcal. more negative in the solvent KNO_3 than in $NaNO_3$ and the value of ΔA_1 in the equimolar $NaNO_3$–KNO_3 mixture appeared to be the average of the values of ΔA_1 in the pure nitrates.

The purpose of this paper is to demonstrate that equation 1 gives a correct prediction of the temperature coefficient of K_1 in the bromide containing system. We shall show further that the generalized calculations[6] based on the quasi-lattice model, within experimental error, lead to a correct prediction of the temperature coefficients for the as-

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[11] In systems in which the change of the entropy of the internal degrees of freedom of the ions involved in the association process is small $d\Delta A_i/dT \cong 0$ and $\Delta A_i \cong \Delta E_i$.