ians is found as V(III) within the vanadocytes. It is interesting, however, that even such powerful two-electron reductants as L-ascorbic acid do not readily reduce V(V) to the trivalent state. Indeed, since the exact nature of the reducing species in ascidians remains unclear, ascorbic acid may not be a meaningful model system for the *in vivo* reduction of V(V). On the other hand, it has been observed[19] that, given sufficient time, ascorbic acid will reduce V(IV), apparently to V(II). The residence time of V(V) at the site of reduction in ascidians would have to be sufficiently long for such a slow reduction to occur. Experiments designed to measure the rate of assimilation and loss of V(V) from ascidians will enable the determination of the residence time of the element within the animal. Such experiments are now being conducted in this laboratory.

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Association of Cadmium(II) and Bromide in Anhydrous Molten Mixtures of Calcium Nitrate with Sodium Nitrate or Potassium Nitrate and the Effect of Water[1]

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Association constants of Cd^{2+} with Br^- to form $CdBr^+$ and $CdBr_2$ have been calculated from potentiometrically determined activity coefficients in the solvents molten anhydrous 2:1 KNO_3-$Ca(NO_3)_2$ at 200, 240 and 280° and in 2:1 $NaNO_3$-$Ca(NO_3)_2$ at 260°. From these results, the Cd^{2+}–Br^- pair association constant has been estimated in the hypothetical pure supercooled $Ca(NO_3)_2$ and compared with previously reported association constants in hydrous melts of $Ca(NO_3)_2$. The dependence of the association constant on water activity suggests the possibility that the hydration equilibrium of Cd^{2+} may involve two water molecules.

Introduction

The solution chemistry of aqueous electrolytes shows marked changes when the water content is reduced below 4-8 mol of water per mol of salt.[3,4] In this region of low water content there is insufficient water to provide complete hydration shells around the ions and the continuous dielectric continuum through which the ions are assumed to interact in the primitive model of electrolyte solutions. The behavior of these highly concentrated solutions or *hydrous melts* approaches that of molten salts, and models must take into account the competition among ion–ion, water–water, and ion–water interactions.

We have been studying association equilibria[5,6] and other thermodynamic properties[7] in anhydrous molten salts and in concentrated aqueous electrolytes in order to determine the effect of water on electrolyte interactions. A modified quasi-lattice model was developed to describe competitive hydration and association equilibria of dilute solute ions such as Cd^{2+} and Br^- and was shown to be applicable to the association data in the range between the anhydrous molten salt and about 50 mol % water in $LiNO_3$-KNO_3 as solvent.[8] The model has been applied also to the effect of water on association equilibria of Ag^+,[9] Cd^{2+},[10] or Pb^{2+} [10] with Cl^- or Br^- in molten ammonium nitrate melts.

A meaningful test of the model in hydrous melts requires independent knowledge of the association constants in the absence of water. Although association constants of $CdBr^+$ have been reported in hydrous $Ca(NO_3)_2$ melts, the association constants of $CdBr^+$ in anhydrous calcium nitrate are not known; furthermore, the quasilattice model does not yield physically reasonable association constants on extrapolation from the measured association constants of Cd^{2+}–Br^- in the hydrous solvents $Ca(NO_3)_2$-H_2O or KNO_3-$Ca(NO_3)_2$-H_2O.[5] It is therefore the purpose of this paper to present the results of measurements of association constants in the anhydrous molten salt solvents 2:1 KNO_3-$Ca(NO_3)_2$ and 2:1 $NaNO_3$-$Ca(NO_3)_2$ at several temperatures and to estimate a value in anhydrous $Ca(NO_3)_2$. The results are compared with previous results in the hydrous melts $Ca(NO_3)_2 \cdot 4H_2O$ and $Ca(NO_3)_2 \cdot 6H_2O$ and their mixtures with KNO_3.[5,6b,c] Making use of recent water activity data in these hydrous melts[11] we show that one possible interpretation of the water activity dependence of the ion-pair equilibria is the pairwise rather than stepwise association of water molecules with Cd^{2+} ions in the solvent $Ca(NO_3)_2$. We also present equations for analysis of association equilibria in charge unsymmetric solvent mixtures, *i.e.*, solvents containing different numbers of cations and anions, in terms of the Temkin ion ratios.

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Experimental Section

The association constants of $CdBr^+$ and $CdBr_2$ were calculated from a thermodynamic analysis of the measured stoichiometric activity coefficients of the solute component sodium calcium bromide (or potassium calcium bromide) in the presence of cadmium ion in solutions of these solute components in the anhydrous molten salt solvents sodium nitrate–calcium nitrate and potassium nitrate–calcium nitrate. The activity coefficients were determined from the measured electromotive force of the concentration cell

$$\text{Ag, AgBr}\left|\begin{array}{c}2{:}1\ \text{SNO}_3\text{–Ca(NO}_3)_2\\ \text{(S,Ca)Br}\\ \ \end{array}\right|\begin{array}{c}2{:}1\ \text{SNO}_3\text{–Ca(NO}_3)_2\\ \text{(S,Ca)Br}\\ \text{Cd(NO}_3)_2\end{array}\left|\text{AgBr, Ag}\right.$$

reference half-cell indicator half-cell

where S is K or Na. The emf was measured as a function of the cadmium nitrate concentration added incrementally to the indicator (right-hand) half-cell containing a fixed bromide concentration. In the absence of cadmium ion, the Nernst equation was followed for the bromide component dissolved in the melt.[12a] Cadmium ion titrations of bromide were repeated at a series of fixed bromide concentrations. At each fixed bromide concentration the conventional stoichiometric activity coefficient of the solute component (K,Ca)Br was calculated from the equation $F\Delta E = -RT \ln \gamma_{(\mathrm{K,Ca})\mathrm{Br}}$ where ΔE is the emf of the cell with cadmium nitrate in the indicator half-cell relative to the emf before adding cadmium nitrate.[5,12] The cell is the same as described previously.[12a] The asbestos fiber reference half-cell was filled with a melt of the same composition as that in the indicator half-cell in order to minimize the junction potential. Dried nitrogen or helium was bubbled through the melt before and during the run to prevent absorption of moisture, and the solution was stirred continuously to hasten equilibrium. The Pyrex cell was heated in a nichrome wire wound furnace controlled manually to ±0.2°. Reagent grade sodium nitrate, potassium nitrate, and calcium nitrate tetrahydrate were used as starting materials for the solvents. The two former chemicals were oven dried, mixed with appropriate quantities of the tetrahydrate, and melted, and the molten mixture was dehydrated as described previously[13] by bubbling dried helium through the melt overnight. Solid cadmium nitrate tetrahydrate was slowly dehydrated in a vacuum desiccator and weighed into the melt as the anhydrous salt.[14]

Calculations

The principles and methods of the graphical evaluation of association equilibrium constants in molten reciprocal salt systems have been presented and discussed previously[3,5,12,15,16] but primarily for the case of charge-symmetric solvents, *i.e.*, solvents containing equal numbers of cations and anions. The Temkin model[17] of molten salts, supported by structural evidence of short-range order and charge alternation in an ionic melt, considers cations to mix only with other cations and anions to mix only with other anions, without exchange of position between cations and anions. Concentrations of ionic species are expressed in terms of the ratio of the number of species divided by the total number of sites available to species of the same sign. *I.e.*, cations occupy cation lattice positions and anions occupy anion lattice positions. In mixtures of salts of different charge type there are different numbers of cations and anions and hence, differing numbers of sites available to cationic and anionic species.

While the equilibrium constants can be defined and calculated independent of a physical model (such as a quasilattice model), it is desirable, if the results are later to be treated in terms of such a model, to use a concentration scale consistent with that model. With differing numbers of cations and anions, there may be an ambiguity in the choice of concentration units for the equilibrium constants of the associated species when using Temkin ion fractions.[3] Thus, if the equilibria are to be treated in terms of the quasilattice model, it is necessary to assign $CdBr^+$ to either the cation sublattice or the anion sublattice, and these sublattices have differing numbers of sites. While at first sight it might appear obvious that $CdBr^+$ belongs on the cation lattice because of its charge, on reflection it may be noted that the packing must be determined by the large anions rather than by the cations. The assignment of neutral associated species, *e.g.*, $CdBr_2$, to cation or anion sites is similarly ambiguous. One partial solution would be the use of equivalent fractions for the charged species, but the Temkin ion fractions have gained general acceptance in molten salts,[17-19] as pointed out in extensive discussions of mixing statistics by Forland[20] and Blander.[19]

Therefore, in the absence of a complete theoretical resolution of the mixing statistics of charge unsymmetric mixtures, we use the Temkin ion fractions (or, for computational convenience, the ion mole ratios, which are numerically nearly identical for the very dilute solutes ($<10^{-3}$ mole fraction)) and adopt the convention of assigning all Cd-containing species to the cation lattice. Conversion of species concentrations and equilibrium constants to different bases then requires only multiplication by factors such as the ratio of the numbers of solvent cations and solvent anions. Expressions for the Temkin ion fractions of the species and for the equilibrium constants following this convention are given in Table I.

If the deviations from Henry's law are attributed to the formation of associated species, the stoichiometric activity coefficients of the solute components, $\gamma_{\mathrm{Cd(NO_3)_2}}$ and γ_{MBr}, may be equated with the fraction of "free" or unassociated Cd^{2+} or Br^-, following the conventional assumption[15] that the species activity coefficients ($\Gamma_{\mathrm{Cd^{2+}}}$, $\Gamma_{\mathrm{CdBr^+}}$, etc.) are unity for dilute species in solution. [The symbol γ_{MBr} refers to the activity coefficient of the pseudocomponent $K_{0.5}Ca_{0.25}Br$. Although the solute is added as KBr, its mole fraction, $<10^{-3}$, does not significantly alter the ratio of the two solvent cations and the activity "seen" by the electrode, $a_{\mathrm{K_{0.5}Ca_{0.25}Br}} \cong R_{\mathrm{KBr}}\gamma_{\mathrm{K_{0.5}Ca_{0.25}Br}}$.] The thermodynamic basis for the evaluation of association constants from measurements of the stoichiometric activity coefficients has been discussed in detail by Braunstein.[12a] The activity coefficients are related to the association constants through the material balance equations below, in Table II, where, as before, y is the ratio of the numbers of univalent to divalent solvent cations.

As in the case of association equilibria in charge-symmetric solvents, either expansion of the material balance equations into a Taylor's series in the stoichiometric mole ratios or (equivalently) continued iteration of the expressions for the activity coefficients provides power series in the stoichiometric concentrations for the reciprocal activity coefficients or their logarithms. The equations needed to obtain the association constants by graphical extrapolation are tabulated below in Table III for the cases where the measured activity coefficients are those of either ligand or metal ion.

Two points worth noting are (1) because of the charge asymmetry of the solvent melt, the expressions for obtaining association constants from the anionic ligand activity coefficients

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Table I. Association Equilibria and Corresponding Association Constants[a]

$$\mathrm{Cd^{2+} + Br^- = CdBr^+} \qquad \mathrm{CdBr^+ + Br^- = CdBr_2} \qquad \mathrm{CdBr^+ + Cd^{2+} = Cd_2Br^{3+}}$$

$$K_1 = \frac{R_{\mathrm{CdBr^+}}}{R_{\mathrm{Cd^{2+}}}R_{\mathrm{Br^-}}} \qquad K_2 = \frac{R_{\mathrm{CdBr_2}}}{R_{\mathrm{CdBr^+}}R_{\mathrm{Br^-}}} \qquad K_{12} = \frac{R_{\mathrm{Cd_2Br^{3+}}}}{R_{\mathrm{CdBr^+}}R_{\mathrm{Cd^{2+}}}}$$

$$R_{\mathrm{Cd^{2+}}} = \frac{n_{\mathrm{Cd^{2+}}}}{n_{\mathrm{Ca(NO_3)_2}} + n_{\mathrm{KNO_3}}} \qquad R_{\mathrm{CdBr^+}} = \frac{n_{\mathrm{CdBr^+}}}{n_{\mathrm{Ca(NO_3)_2}} + n_{\mathrm{KNO_3}}} \qquad R_{\mathrm{CdBr_2}} = \frac{n_{\mathrm{CdBr_2}}}{n_{\mathrm{Ca(NO_3)_2}} + n_{\mathrm{KNO_3}}}$$

$$R_{\mathrm{Cd_2Br^{3+}}} = \frac{n_{\mathrm{Cd_2Br^{3+}}}}{n_{\mathrm{Ca(NO_3)_2}} + n_{\mathrm{KNO_3}}} \qquad R_{\mathrm{Br^-}} = \frac{n_{\mathrm{Br^-}}}{2n_{\mathrm{Ca(NO_3)_2}} + n_{\mathrm{KNO_3}}} \qquad \frac{n_{\mathrm{KNO_3}}}{n_{\mathrm{Ca(NO_3)_2}}} = y^b$$

[a] The mole ratio, R, is defined in terms of n, the number of moles of species and the numbers of moles of solvent cations or anions. [b] The ratio of numbers of univalent to divalent solvent cations.

Table II. Material Balance Equations and Activity Coefficients

$$R_{\mathrm{Cd(NO_3)_2}} = \frac{n_{\mathrm{Cd(NO_3)_2}}}{n_{\mathrm{Ca(NO_3)_2}} + n_{\mathrm{KNO_3}}} = R_{\mathrm{Cd^{2+}}} + R_{\mathrm{CdBr^+}} + R_{\mathrm{CdBr_2}} + R_{\mathrm{Cd_2Br^{3+}}} + \ldots$$

$$R_{\mathrm{KBr}} = \frac{n_{\mathrm{KBr}}}{2n_{\mathrm{Ca(NO_3)_2}} + n_{\mathrm{KNO_3}}} = R_{\mathrm{Br^-}} + \left(\frac{1+y}{2+y}\right)R_{\mathrm{CdBr^+}} + \left(\frac{1+y}{2+y}\right)2R_{\mathrm{CdBr}} + \left(\frac{1+y}{2+y}\right)R_{\mathrm{Cd_2Br^{3+}}} + \ldots$$

$$R_{\mathrm{Cd(NO_3)_2}}\gamma_{\mathrm{Cd(NO_3)_2}} = a_{\mathrm{Cd(NO_3)_2}} = R_{\mathrm{Cd^{2+}}}$$

$$R_{\mathrm{KBr}}\gamma_{\mathrm{MBr}} = a_{\mathrm{MBr}} = R_{\mathrm{Br^-}}$$

$$\frac{1}{\gamma_{\mathrm{Cd(NO_3)_2}}} = \frac{R_{\mathrm{Cd(NO_3)_2}}}{R_{\mathrm{Cd^{2+}}}} = 1 + K_1R_{\mathrm{KBr}}\gamma_{\mathrm{MBr}} + K_1K_2R_{\mathrm{KBr}}^2\gamma_{\mathrm{MBr}}^2 + 2K_1K_{12}R_{\mathrm{KBr}}R_{\mathrm{Cd(NO_3)_2}} \times \gamma_{\mathrm{MBr}}\gamma_{\mathrm{Cd(NO_3)_2}} + \ldots$$

$$\frac{1}{\gamma_{\mathrm{MBr}}} = \frac{R_{\mathrm{KBr}}}{R_{\mathrm{Br^-}}} = 1 + \left(\frac{1+y}{2+y}\right)K_1R_{\mathrm{Cd(NO_3)_2}}\gamma_{\mathrm{Cd(NO_3)_2}} + 2\left(\frac{1+y}{2+y}\right)K_1K_2R_{\mathrm{Cd(NO_3)_2}}R_{\mathrm{KBr}}\gamma_{\mathrm{Cd(NO_3)_2}}\gamma_{\mathrm{MBr}} + \left(\frac{1+y}{2+y}\right)K_1K_{12}R_{\mathrm{Cd(NO_3)_2}}^2\gamma_{\mathrm{Cd(NO_3)_2}}^2 + \ldots$$

$$y = \frac{\text{moles of univalent salt}}{\text{moles of divalent salt}} \qquad \mathrm{MBr = K_{y/(2+y)}Ca_{1/(2+y)}Br}$$

Table III. Equations in the Stoichiometric Mole Ratios and Analysis for Evaluating the Thermodynamic Association Constants[a]

Part a

$$\frac{1}{\gamma_{\mathrm{MBr}}} = 1 + \left(\frac{1+y}{2+y}\right)K_1R_{\mathrm{Cd}} - \left(\frac{1+y}{2+y}\right)K_1^2R_{\mathrm{Cd}}R_{\mathrm{Br}} + 2\left(\frac{1+y}{2+y}\right)K_1K_2R_{\mathrm{Cd}}R_{\mathrm{Br}} + \left(\frac{1+y}{2+y}\right)K_1K_{12}R_{\mathrm{Cd}}^2 + \ldots$$

$$\left(\frac{\partial\left(\dfrac{1}{\gamma_{\mathrm{MBr}}} - 1\right)}{\partial R_{\mathrm{Cd}}}\right)_{R_{\mathrm{Br}}} = \left(\frac{1+y}{2+y}\right)K_1 + \left(\frac{1+y}{2+y}\right)K_1[2K_2 - K_1]R_{\mathrm{Br}} + 2\left(\frac{1+y}{2+y}\right)K_1K_{12}R_{\mathrm{Cd}} + \text{higher terms in } R_{\mathrm{Br}} \text{ and } R_{\mathrm{Cd}}$$

$$S_0^{\mathrm{Br}} = \lim_{R_{\mathrm{Cd}}\to 0} \frac{\partial\left(\dfrac{1}{\gamma_{\mathrm{MBr}}} - 1\right)}{\partial R_{\mathrm{Cd}}} = \left(\frac{1+y}{2+y}\right)K_1 + \left(\frac{1+y}{2+y}\right) \times K_1[2K_2 - K_1]R_{\mathrm{Br}} + \text{higher terms in } R_{\mathrm{Br}}$$

$$S_{0,0}^{\mathrm{Br}} = \lim_{R_{\mathrm{Br}}\to 0} S_0^{\mathrm{Br}} = \left(\frac{1+y}{2+y}\right)K_1$$

$$\lim_{R_{\mathrm{Br}}\to 0} \frac{\partial S_0^{\mathrm{Br}}}{\partial R_{\mathrm{Br}}} = \left(\frac{1+y}{2+y}\right)K_1[2K_2 - K_1]$$

$$y = \frac{n_{\mathrm{KNO_3}}}{n_{\mathrm{Ca(NO_3)_2}}} \qquad \mathrm{MBr = K_{y/(2+y)}Ca_{1/(2+y)}Br}$$

Part b

$$\frac{1}{\gamma_{\mathrm{Cd(NO_3)_2}}} = 1 + K_1R_{\mathrm{Br}} - \left(\frac{1+y}{2+y}\right)K_1^2R_{\mathrm{Br}}R_{\mathrm{Cd}} + 2K_1K_{12}R_{\mathrm{Br}}R_{\mathrm{Cd}} + K_1K_2R_{\mathrm{Br}}^2 + \ldots$$

$$\left(\frac{\partial\left(\dfrac{1}{\gamma_{\mathrm{Cd}}} - 1\right)}{\partial R_{\mathrm{Br}}}\right)_{R_{\mathrm{Cd}}} = K_1 - K_1\left[\left(\frac{1+y}{2+y}\right)K_1 - 2K_{12}\right]R_{\mathrm{Cd}} + 2K_1K_2R_{\mathrm{Br}} + \text{higher terms in } R_{\mathrm{Br}} \text{ and } R_{\mathrm{Cd}}$$

$$S_0^{\mathrm{Cd}} = \lim_{R_{\mathrm{Br}}\to 0} \frac{\partial\left(\dfrac{1}{\gamma_{\mathrm{Cd}}} - 1\right)}{\partial R_{\mathrm{Br}}} = K_1 + K_1\left[2K_{12} - \left(\frac{1+y}{2+y}\right)K_1\right]R_{\mathrm{Cd}} + \text{higher terms in } R_{\mathrm{Cd}}$$

$$S_{0,0}^{\mathrm{Cd}} = \lim_{R_{\mathrm{Cd}}\to 0} S_0^{\mathrm{Cd}} = K_1$$

$$\lim_{R_{\mathrm{Cd}}\to 0} \frac{\partial S_0^{\mathrm{Cd}}}{\partial R_{\mathrm{Cd}}} = K_1\left[2K_{12} - \left(\frac{1+y}{2+y}\right)K_1\right]$$

$$y = \frac{n_{\mathrm{KNO_3}}}{n_{\mathrm{Ca(NO_3)_2}}}$$

[a] Subscripts Cd and Br refer to the components $\mathrm{Cd(NO_3)_2}$ and KBr.

(as reported in this paper from emf measurements with bromide electrodes) and from cationic activity coefficients no longer are symmetrical and (2) asymmetry of the solute (*e.g.*, $\mathrm{Cd(NO_3)_2}$ rather than $\mathrm{AgNO_3}$) does not affect the expressions for the association constants when the Temkin ion fractions (or ion mole ratios) are used, although they obviously would be if equivalent fractions, *e.g.*

$$R'_{\mathrm{Cd(NO_3)_2}} = \frac{2n_{\mathrm{Cd(NO_3)_2}}}{2n_{\mathrm{Ca(NO_3)_2}} + n_{\mathrm{KNO_3}}}$$

were used. As discussed previously,[16] the activity coefficients are expressed in terms of the known stoichiometric concentrations of solutes, rather than estimated or evaluated species concentrations, without restricting the number or types of associations considered. Evaluation of the association constants is accomplished, without the need to truncate the series, by successive graphical differentiation and extrapolation.[5,6c,14] Uncertainties in the evaluation are usually no more than 5-10% for association constants derived from emf measurements of electrochemical cells.

Results

Stoichiometric activity coefficients of the solute components (K,Ca)Br at 200, 240, and 280° and (Na,Ca)Br at 260°

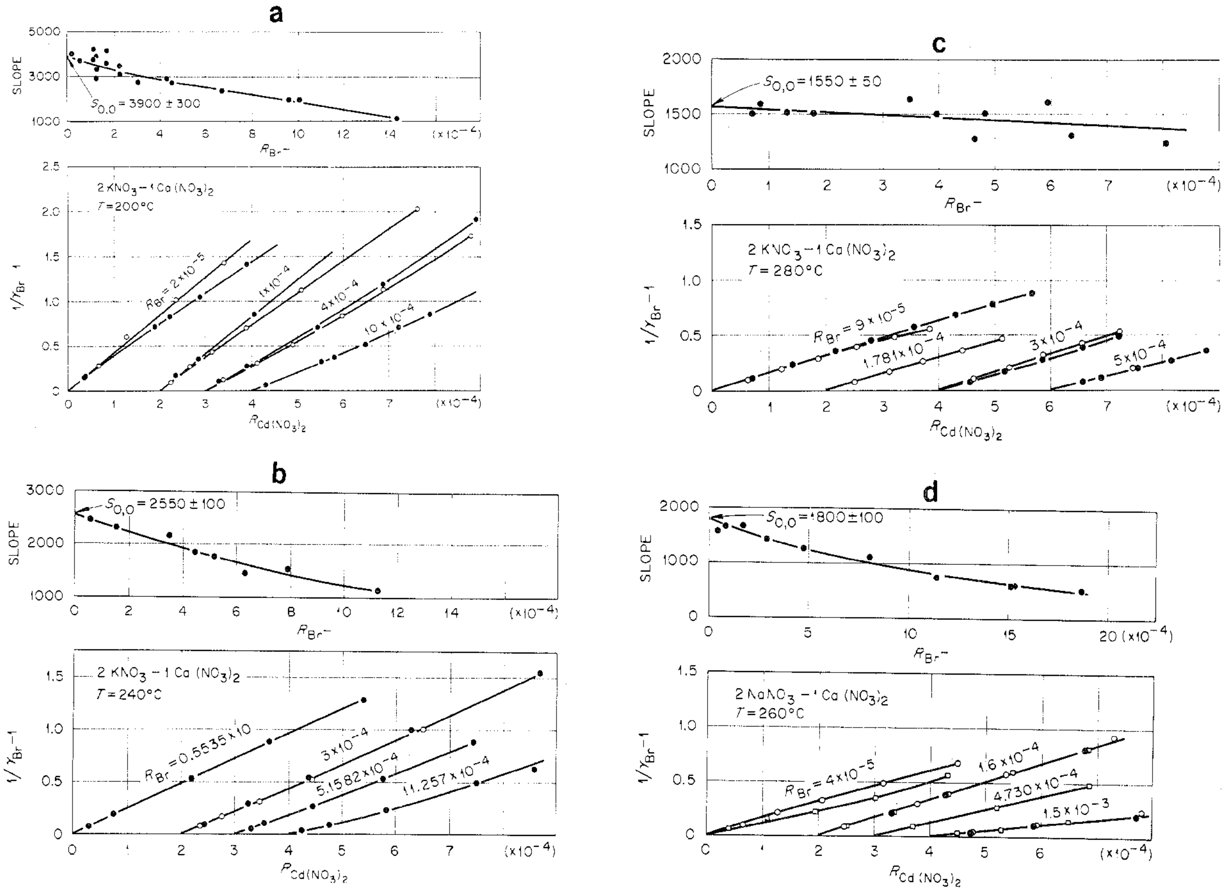

Figure 1. Reciprocal activity coefficients of bromide as a function of cadmium ion and bromide ion stoichiometric concentrations and their extrapolation to obtain the association constants for $CdBr^+$ and $CdBr_2$: (a) 2:1 KNO_3-$Ca(NO_3)_2$, 200°; (b) 2:1 KNO_3-$Ca(NO_3)_2$, 240°; (c) 2:1 KNO_3-$Ca(NO_3)_2$, 280°; (d) 2:1 $NaNO_3$-$Ca(NO_3)_2$, 260°.

Table IV. Association Constants and Specific Helmholtz Free Energies of Association for $Cd^{2+} + Br^- \rightleftharpoons CdBr^+, K_1$; $CdBr^+ + Br^- \rightleftharpoons CdBr_2, K_2$

Amt of solvent								
$Ca(NO_3)_2$ mol/mol of salt	KNO_3 mol/mol of salt	H_2O mol/mol of $Ca(NO_3)_2$	Temp, °C	K_1, mol of anion/mol	K_2, mol of anion/mol	K_2/K_1	$-\Delta A_1$, kcal/mol	$-\Delta A_2$, kcal/mol
0.33	0.67	0	200	5200	2065	0.40	6.36	6.31
0.33	0.67	0	240	3400	1367	0.40	6.46	6.43
0.33	0.67	0	280	2067	917	0.44	6.42	6.49
0.33	0.67 ($NaNO_3$)	0	260	2400	867	0.36	6.35	6.20
1.0	0	6	50	1550[b]				
0.67	0.33	6	50	1460[b]				
1.0	0	4	50	3900[c]	1500[c]	0.38		
0.67	0.33	4	50	3880[b]				
0.50	0.50	4	50	4250[b]				
1.0	0	0	50	7.1×10^5 [a]			7.5[a]	

[a] By extrapolation. [b] Reference 5. [c] Reference 6b.

in the solvents 2:1 KNO_3-$Ca(NO_3)_2$ and 2:1 $NaNO_3$-$Ca(NO_3)_2$ are shown in Figure 1, along with graphical extrapolations to the association constants for $CdBr^+$ and $CdBr_2$. The association constants are listed in Table IV along with values reported previously[5,6b,c] in several hydrous melts. The specific Helmholtz free energy of association or relative bond free energy is tabulated also for association in the anhydrous melts, as calculated from the association constants with equations of the quasilattice model.[3,18] A maximum variation of 0.1 kcal/mol is evident in the values of ΔA_1 for the KNO_3-$Ca(NO_3)_2$ mixtures in column 8, but there appears to be no trend with temperature and the values are considered constant within the uncertainty of the measurements. The smaller magnitude of ΔA in $NaNO_3$-$Ca(NO_3)_2$ relative to KNO_3-$Ca(NO_3)_2$ mixtures is not unexpected and is in the same direction as in the pure alkali nitrates, −5.88 in KNO_3 and −5.58 in $NaNO_3$.[21] The ratio of the second to first association constant, K_2/K_1, in column 7 reflects the near equality of ΔA_1 and ΔA_2. For cations with a coordination number Z, the statistically expected ratio[18] is $(Z - 1)/2Z$, *i.e.*, 0.40 or 0.42 for $Z = 5$ or 6. Values near this are found also in the hydrous melts.[22] The low value, 0.36, of the ratio in the $NaNO_3$-$Ca(NO_3)_2$ mixture is within the 10% uncertainty in K_2 and is not considered significantly low.

An estimate of ΔA_{CdBr} in pure supercooled $Ca(NO_3)_2$ was obtained by extrapolation of the results in the mixtures and pure KNO_3 and $NaNO_3$. The specific Helmholtz free ener-

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gies, $\Delta A_{\text{Cd-Br}}$, in mixed solvents have been found[21] to be very nearly temperature independent and linear in the solvent composition for most of the reciprocal nitrate systems studied. Bombi[23] has recently questioned the linearity of ΔA in solvent composition on the basis of mixing statistics of the quasilattice model and has derived an expression, nonlinear in the composition dependence of the free energies but approximately linear in the reciprocal association constants.[24] Bombi's analysis of the variation of association constants with solvent composition should eventually provide a more rigorous basis for extrapolation, but there remain some difficulties at present with his approach.

Three points are noteworthy in connection with the Bombi equation. First, an attempt to estimate the association constant in pure $Ca(NO_3)_2$ with Bombi's equation resulted in different, negative (and therefore unrealistic) association constants by extrapolation from both the potassium nitrate–calcium nitrate and sodium nitrate–calcium nitrate mixtures. Second, a fit of the Bombi expression to Cd–Br association constants in pure $NaNO_3$ and equimolar $LiNO_3$-$NaNO_3$[21] should extrapolate to the same value in pure $LiNO_3$ as Bombi's extrapolation of the data in $LiNO_3$-KNO_3 mixtures,[23] *i.e.*, −7.4 kcal/mol. The result, however, is −8.5 kcal/mol, a value 1.1 kcal/mol more negative. Last, linear extrapolation of ΔA for the Cd–Br association in $LiNO_3$-KNO_3 mixtures yields −5.90 kcal/mol in pure KNO_3 which is closer to the experimental value of −5.88 kcal/mol[14] than the Bombi extrapolation of −5.82 kcal/mol.

Although there is no theoretical basis for a linear relationship in the composition dependence of the free energies and, as correctly stated by Bombi, the mixing statistics cannot be expected to be the same in a quaternary as in a ternary mixture, there appears to be ample empirical evidence[21,25] for linearity which suggests the possibility that additional factors such as variation of coordination number may have a canceling effect. [ΔA for the Ag–I association in $NaNO_3$-KNO_3 appears to be nonlinear in the composition (Figure 4 in ref 25) but the neglected data point at −9.13 kcal/mol in pure KNO_3[26] definitely improves the linearity.]

Therefore, in view of the empirically observed linear dependence of ΔA on composition and the fact that the Bombi extrapolation leads to physically unreasonable estimates and large uncertainties, we continue to employ the linear expression for ΔA

$$\Delta A_{\text{mixture}} = X_{\text{SNO}_3}\Delta A_{\text{SNO}_3} + X_{\text{Ca(NO}_3)_2}\Delta A_{\text{Ca(NO}_3)_2}$$

where the X's are mole fractions and S is K or Na. The estimated ΔA_{CdBr} and association constant, K_1, in hypothetical pure supercooled calcium nitrate are given in the bottom row of Table IV.

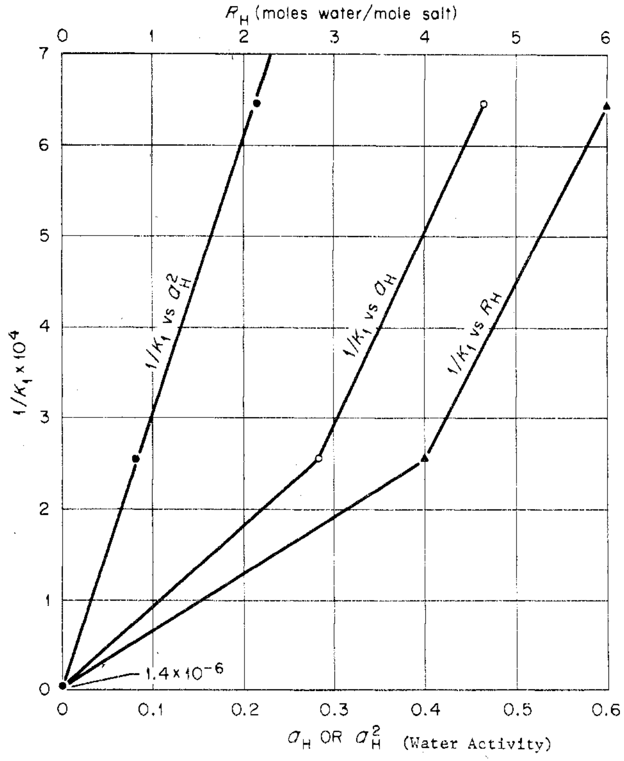

Figure 2. Reciprocal equilibrium constants for the association $Cd^{2+} + Br^- \rightleftarrows CdBr^+$ (K_1) in hydrous melts of $Ca(NO_3)_2$: ●, $1/K_1$ *vs.* $a_H{}^2$; ○, $1/K_1$ *vs.* a_H; ▲, $1/K_1$ *vs.* R_{H_2O}.

Discussion

The new data on association equilibria in the anhydrous melt make possible a partial test of the equations of the aqueous quasilattice model.[8] In spite of the small number of compositions of hydrous melts studied,[5,6b,c] the rightmost curve in Figure 2, a plot of the reciprocal association constant *vs.* the mole ratio of water, can be seen not to be fitted with constant bond energies by the equation of the quasilattice model

$$\frac{Z}{K} \approx e^{\epsilon_c/kT} + e^{(\epsilon_c - \epsilon_h)/kT}R_H$$

$$= \frac{Z}{K_{10} + Z} + \frac{K_H + Z}{K_{10} + Z}R_H$$

where Z is the quasilattice coordination number, ϵ_c and ϵ_h are the respective cation–ligand and cation–water relative bond energies, and R_H is the mole ratio of water (moles of water per mol of salt). The lack of fit is not surprising in view of the fact that the assumptions of the model can only be valid in the limit of very low water contents,[8] while the water mole ratios here are 4 and 6 (80 and 86% water, respectively). Although molten hydrated salts behave in some respects like salts of a large (hydrated) cation,[27,28] there is increasing evidence from thermodynamic data[4] and nmr[29] and Raman spectra[30] for cation–water, cation–anion competition in these melts. Hence, while these melts are beyond the range of validity of the simple quasilattice model, it nevertheless appears worthwhile to consider the implications of applying the qualitative features of competitive hydration and association equilibria of the solute to the data currently available.

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[23] G. G. Bombi and G. A. Sacchetto, *J. Electroanal. Chem.*, 34, 319 (1972).

[24] Application of the quasilattice expression $K = Z(\beta - 1)$, where $\beta = e^{-\Delta A/RT}$, to Bombi's eq 11 in ref 23 yields

$$\frac{1}{K_M + Z} = X_B\frac{1}{K_B + Z} + (1 - X_B)\frac{1}{K_C + Z}$$

which becomes

$$\frac{1}{K_M} \cong X_B\frac{1}{K_B} + (1 - X_B)\frac{1}{K_C}$$

when $K \gg Z$, where Z is generally taken as 5 or 6. This may be compared with the Flood equation $\Delta A_M = X_B\Delta A_B + (1 - X_B)\Delta A_C$.

[25] Y. T. Hsu, R. B. Escue, and T. H. Tidwell, Jr., *J. Electroanal. Chem.*, 15, 245 (1967).

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[30] D. E. Irish and A. R. Davis, *Can. J. Chem.*, 46, 943 (1968); D. E. Irish, A. R. Davis, and R. A. Plane, *J. Chem. Phys.*, 50, 2262 (1969); M. Peleg, *J. Phys. Chem.*, 76, 1019 (1972).

Considering only the cations to form hydrated species, the competitive equilibria may be written

$$Cd^{2+} + nH_2O \rightleftarrows Cd(H_2O)_n^{2+} \quad K_H$$

$$Cd^{2+} + Br^- \rightleftarrows CdBr^+ \quad K_{10}$$

The latter equilibrium constant is derived from the association of the solutes in the anhydrous molten salt solvent. The measured equilibrium constant in the hydrous melt may thus be written

$$\frac{1}{K_1} = \frac{([Cd^{2+}] + [Cd(H_2O)_n^{2+}])[Br^-]}{[CdBr^+]}$$

$$= \frac{1}{K_{10}} + \frac{K_H}{K_{10}} a_{H_2O}{}^n$$

The analogy between this equation and that of the quasilattice model is apparent and not surprising, since the latter also corresponds to the mass action principle, applied to bonds on the quasilattice. The left-hand curve in Figure 2 shows a plot of the reciprocal equilibrium constants *vs.* the square of the activity of water. The water activities were obtained from our previously reported isopiestic measurements[4,11] and from earlier measurements by Ewing.[31] The slope of this plot gives the ratio of the equilibrium constants for hydration and association, leading to the value for the hydration equilibrium constant, $K_H = 2 \times 10^3$.

One possible interpretation of this calculation, although there are insufficient data as yet to be conclusive, is that hydration of cadmium may proceed *via* addition of two water molecules, *i.e.*, that water-water interactions in the coordination spheres of the ions may play a significant role in the buildup of the hydration shells as water is added to an anhydrous molten salt. It would imply also strong entropy effects since the bulk of the water is associated with the calcium nitrate solvent, although the cadmium-water interaction is stronger than the calcium water interaction on the basis, *e.g.*, of the water activities.[11] Cooperative addition of two water molecules may not be unreasonable, although additional data are needed to test the possibility. Formation of water dimers in organic solvents has been reported on the basis of both thermodynamic and nmr results.[32]

The tacit assumption of only cation hydration needs to be reexamined for hydrous melts. As water is added to a molten salt, water dipoles probably orient themselves between a cation and an anion, the negative end adjacent to a cation and the positive end adjacent to an anion. With filled hydration shells, the structure may be determined largely by the orientation of water dipoles toward the cations, but even with appreciable differences between cation-water and anion-water interactions, entropic effects must produce significant contributions from anion-water interactions. Additional measurements at higher and lower water contents are in progress to test this interpretation of the competitive association and hydration equilibria.

Registry No. $CdBr^+$, 15691-37-9; $CdBr_2$, 7789-42-6; cadmium, 7440-43-9.

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[31] W. W. Ewing and W. R. Guyer, *J. Amer. Chem. Soc.*, **60**, 2707 (1938).

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Infrared and Raman Spectra of Acetonitrile-Antimony Pentafluoride

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Infrared and Raman spectral data are reported for three isotopic variants of solid $SbF_5 \cdot NCCH_3$, and Raman polarization data are presented for acetonitrile and SO_2 solutions. The data are in full accord with a molecular adduct of local C_{4v} symmetry for the SbF_5N moiety. Furthermore, selection rules for the local symmetry approximation are identical with those based on the permutation group, E_{24}, which represents the situation of free methyl group rotation. Bands characteristic of coordinated SbF_5 are discussed.

Introduction

Although a variety of different complexes having the general formula $SbF_5 \cdot L$ ($\sim C_{4v}$) exist,[1] there are no detailed assignments available for the SbF_5 moiety in such species. Vibrational data on SbF_5 complexes are of general interest because of the extensive use of antimony pentafluoride as a strong Lewis acid[2] and is of specific interest to us in our vibrational study of the unusual sulfur dioxide adduct $SbF_5 \cdot SO_2$.[3]

The adduct with acetonitrile was chosen for several reasons. First, this complex is easily prepared[1c] and is quite stable (in the absence of moisture) at room temperature. Second, the vibrational spectra of acetonitrile[4] and also of its 1:1 adducts with the boron trihalides[5] are well known, there being available in the literature complete vibrational analyses. Finally, and most important, acetonitrile has only one fundamental

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[1] For example: (a) SbF_5OH^-: J. E. Griffiths and G. E. Walrafen, *Inorg. Chem.*, **11**, 427 (1972); W. A. Mazeika and H. M. Neumann, *ibid.*, **5**, 309 (1966); (b) $SbF_5 \cdot PF_3$: R. D. W. Kemmitt, V. M. McRae, R. D. Peacock, and I. L. Wilson, *J. Inorg. Nucl. Chem.*, **31**, 3674 (1969); (c) $SbF_5 \cdot NCCH_3$, $SbF_5 \cdot py$, $SbF_5 \cdot$dioxane: L. Kolditz and W. Rehak, *Z. Anorg. Allg. Chem.*, **342**, 32 (1966).

[2] For example: (a) J. Bacon and R. J. Gillespie, *J. Amer. Chem. Soc.*, **93**, 6914 (1971); (b) G. A. Olah, J. R. DeMember, R. H. Schlosberg, and Y. Halpern, *ibid.*, **94**, 156 (1972).

[3] D. M. Byler and D. F. Shriver, unpublished data.

[4] (a) Gas phase: F. W. Parker, A. H. Nielson, and W. H. Fletcher, *J. Mol. Spectrosc.*, **1**, 107 (1957); W. H. Fletcher and C. S. Shoup, *ibid.*, **10**, 300 (1963); (b) liquid phase: B. Swanson and D. F. Shriver, unpublished infrared spectra; D. M. Byler and D. F. Shriver, unpublished Raman spectra.

[5] (a) B. Swanson and D. F. Shriver, *Inorg. Chem.*, **9**, 1406 (1970); (b) D. F. Shriver and B. Swanson, *ibid.*, **10**, 1354 (1971).