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COMPETITIVE HYDRATION AND ASSOCIATION IN HYDROUS MOLTEN SALTS*†

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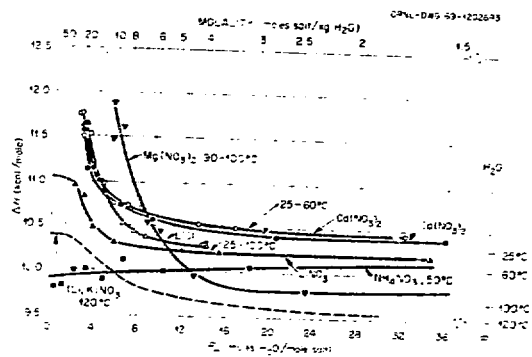
An understanding of very concentrated aqueous electrolyte solutions is essential to the development of a complete interpretation of electrolyte solution behavior from the molten salt to the dilute aqueous solution.

Evidence from thermodynamic data, NMR, and Raman spectra indicates the need for interpretation of hydrous melts in terms of cation-water, cation-anion competition.

In the concentration range below 4-6 moles of water per mole of salt, there is insufficient water to form complete hydration sheaths around the ions.

The solution behavior, no longer controlled by bulk (hydrogen bonded) water properties, is controlled by molten salt properties.

The typical variation of solution properties with water content is presented in the following slide, showing the marked increase of enthalpy of vaporization of water as the water mole ratio content drops below about 4-8.



Enthalpy of Vaporization, ΔH of Water from Concentrated Aqueous Electrolyte Solutions as a Function of the Water Content.

Association equilibria of dilute solute ions in these hydrous melts also provide a useful probe of the effect of changing water content. Electrochemical measurements of these equilibria were carried out with a cell such as that shown on the next slide.

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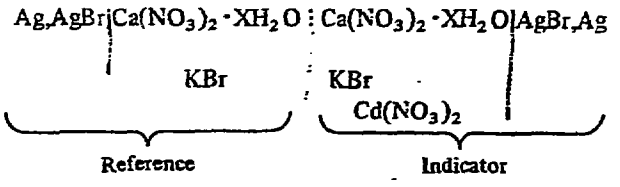
Concentration Cell



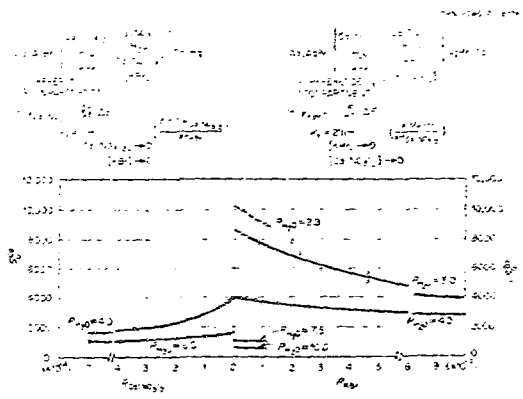
Stoichiometric activity coefficients of bromide are calculated from ΔE, the cumulative emf change on addition of cadmium nitrate to the indicator half cell (relative to the emf before adding cadmium nitrate)

$$\Delta E = -\frac{RT}{2F} \ln \gamma_{CaBr_2} = -\frac{RT}{F} \ln \gamma_{Br}$$

If deviations from Henry's law are due only to association, and the species activity coefficients are constant,

$$\gamma_{Br} = \frac{R_{Br^-}}{R_{KBr}} = \frac{n_{Br^-}/n_{NO_3^-}}{n_{KBr}/n_{NO_3^-}} = \frac{[\text{"free" bromide}]}{[\text{total bromide}]}$$

Mathematical analysis of the activity coefficient data has been described previously, and leads to values of the association equilibrium constants. Some typical results are shown on the next two slides.



Graphical Evaluation of K_1 and K_2 for $CdBr^+$ and $CdBr_2$ at Water Mole Ratios Between 2.8 and 10.0.

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ASSOCIATION CONSTANTS IN $Ca(NO_3)_2$-H_2O AT 50°C

$Cd^{2+} + Br^- \rightleftharpoons CdBr^+ : K_1 \quad CdBr^+ + Br^- \rightleftharpoons CdBr_2 : K_2$

R_{H_2O} $\left(\frac{\text{moles water}}{\text{mole } Ca(NO_3)_2}\right)$	K_1 $\left(\frac{\text{moles anion}}{\text{mole}}\right)$	K_2 $\left(\frac{\text{moles anion}}{\text{mole}}\right)$	K_2/K_1
0.0	7.1×10^5*	–	(0.4)
2.8	10200	4550	0.44
3.0	8600	3720	0.43
4.0	3900	1550	0.40
6.0	1550	–	–
7.5	1030	(306)	(0.3)
10.0	600	(133)	(0.2)

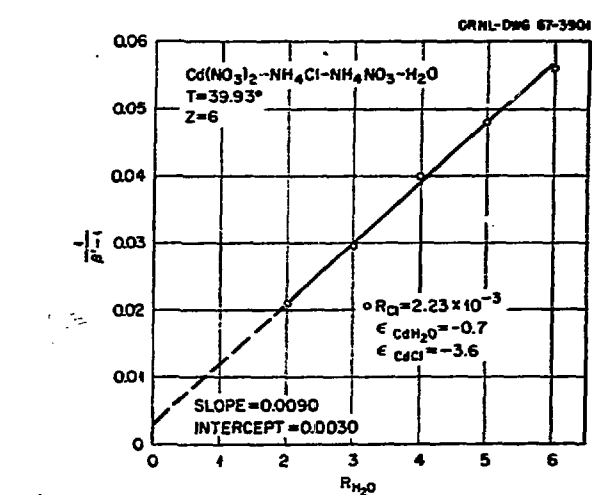
*By extrapolation.

It may be noted that ratios of K_2 to K_1 for the water contents at which sufficient data were taken to obtain precise values of K_2 as well as K_1 are about 0.4, very close to the ratio observed for consecutive association equilibria in anhydrous molten salts, and to the statistically expected value for the case of nearly equal energies of addition of successive ligands. The statistical ratio

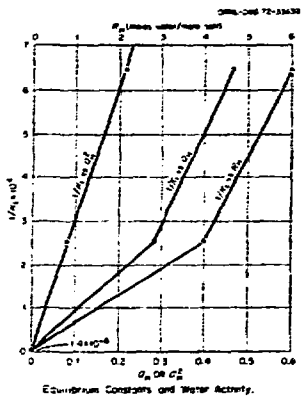
$$(K_2/K_1)_{\text{statistical}} = \frac{1/2\ Z\ (Z-1)/Z}{Z} = \frac{Z-1}{2Z}$$

has the values 4/10 and 5/12 for assumed values 5 or 6 for Z, the coordination number.

Previously, a quasi-lattice model of competing hydration and association equilibria had been shown to apply at very low water contents, in the Henry's Law range, as seen in the next slide.



The model sis not apply for solutions outside the Henry's Law range as seen in the next slide.



However, the linearity of 1/K, in the square of the water activity, suggests that the general features of competitive equilibria may be followed, in accord with the mass action assumptions on the following slide.

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The assumptions of the competitive hydration-association model are:

1. Ions in a very concentrated aqueous solution behave like those of a molten salt, but with water associated with the ions. Concentrations are Temkin ion fractions.
2. Anions and water compete to associate with solute cations in accord with their concentrations and relative interaction energies.
3. Dilute "free" and associated species follow Henry's Law in solution.
4. One hydrated solute species is dominant in the very concentrated solution range.

The reciprocal association constant is linear in the nth power of the water activity over the entire concentration range investigated in NH_4NO_3-H_2O and (Li,K)NO_3-H_2O mixtures and is linear to 7.5 moles of water per mole of salt in the $Ca(NO_3)_2$-H_2O solvent. At a water mole ratio of 10.0(5.5 molal), the model deviates from the data. This is not unexpected considering the simplifications of the model, in particular, the assumption that only one hydrated species is dominant over the entire concentration range.

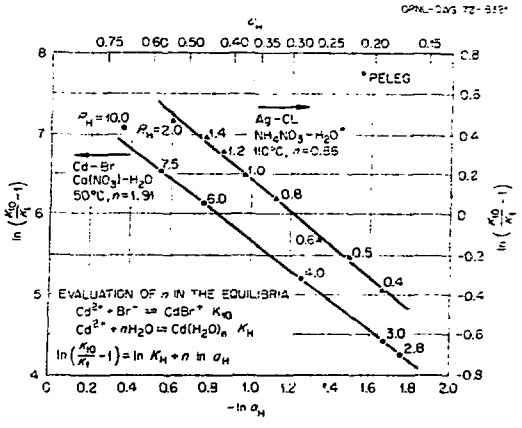
$$Cd^{2+} + Br^- \rightleftharpoons CdBr^+ \quad , \quad K_{10} = \frac{[CdBr^+]}{[Cd^{2+}]\,[Br^-]}$$

$$Cd^{2+} + nH_2O \rightleftharpoons Cd(H_2O)_n^{2+} \quad , \quad K_H = \frac{[Cd(H_2O)_n]}{[Cd^{2+}]\,a_H^n}$$

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

$$\frac{1}{K_1} = \frac{1}{K_{10}} + \frac{K_H}{K_{10}}\,a_H^n$$

The next 2 slides presents values of hydration equilibrium constants and free energies in the hydrous melts studied to date.



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HYDRATION EQUILIBRIUM CONSTANTS

$M + n\,H_2O \rightleftharpoons M(H_2O)_n$; K_H

Ion Pair	Solvent Electrolyte	Temperature °C	Range of Water Content $R_H = \frac{\text{moles water}}{\text{moles electrolyte}}$	K_H	n	$\frac{-RT \ln K_H}{n}$ Kcal/mole H_2O
Cd Br	$Ca(NO_3)_2$	50	2.9–7.5	2000	1.9	−2.5
Cd Br	$(Li,K)NO_3$	119	0.26–1.26	19	1.0	−2.3
Cd Cl	NH_4NO_3	40	2.0–6.0	(31)	(3.3)	(−0.65)
Ag Cl	NH_4NO_3	110	0.4–2.0	2.86	0.56	−0.93

The relation between the quasi-lattice hydration interaction free energy and the mass action relative free energy of hydration are shown on the next slide.

ORNL DWG. 73-5662

Ratio of the hydration equilibrium constants based on the quasi-lattice model and on the mass action model:

$$\frac{e^{-\Delta A_H/RT}}{e^{-\Delta G^0_H/RT}} \cong \frac{K^{Q.L.}_H/Z}{K^{M.A.}_H} = \frac{a^n_{H_2O}}{R_{H_2O}} \left(\xrightarrow[(n\to 1)]{} k\right)$$

Henry's law constant: $k = (a_{H_2O}/R_{H_2O})_{R=0}$

a_{H_2O} = water activity.
R = water mole ratio.
n = number of water molecules associated with solute cations.
Z = quasi-lattice coordination number.

When $n \cong 1$ and also water is in the Henry's Law region, as for $CdBr^+$ in $(Li, K)NO_3$-H_2O, the models are not distinguishable.

The last 2 slides summarize the way in which the competitive hydration-association model in hydrous melts applies to our experimental results:

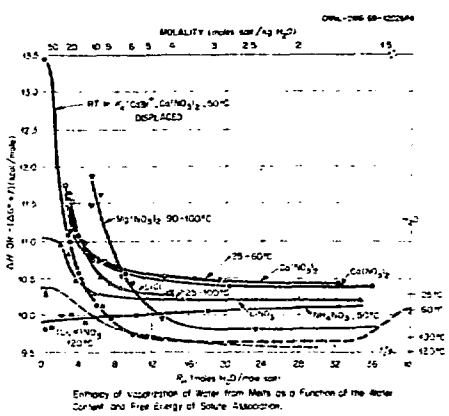
ORNL DWG. 73-5664

COMPETITIVE HYDRATION-ASSOCIATION EQUILIBRIA IN HYDROUS MELTS

WATER AND ANIONIC LIGANDS COMPETE FOR COORDINATION SITES ABOUT SOLUTE IONS.

CATION HYDRATION PREDOMINATES OVER, BUT DOES NOT EXCLUDE, ANION HYDRATION.

FORMATION OF HYDRATION SHELLS MAY INVOLVE COOPERATIVE ADDITION OF WATER MOLECULES.



Entropy of vaporization of water from melts as a function of the water content and free energy of solute association.