It has been chosen as this value together with $\epsilon = 80$ gives the best fit between calculated and experimentally determined stability constants for outer-sphere complexes[7] of Cr^{3+} and Co^{3+} [8] as well as for the complex OVH_2OSO_4.)

The same seems to hold for the hydrolysis reaction of the vanadyl cation. This reaction according to Rossotti and Rossotti[9] leads to the formation of a binuclear isopolybase

$$2VO^{2+} + 2H_2O \rightleftharpoons (VOOH)_2{}^{2+} + 2H^+ \qquad (6)$$

It is possible to study this reaction with the stopped-flow method.[10]

A rate law is found which formally allows for the bimolecular combination of two vanadyl–monohydroxo cations to the dimer

$$2VOOH^+ \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} (OVOH)_2{}^{2+} \qquad (7)$$

with $k_{12} = 2 \times 10^4\ M^{-1}\ sec^{-1}$ (at $\mu = 0.3\ M$ and at 25°) and $k_{21} = 20\ sec^{-1}$. Then by extrapolation to zero ionic strength we get $k_{12}\ (\mu = 0) = 8 \times 10^3\ M^{-1}\ sec^{-1}$. Applying eq 5 and taking from the formula of Fuoss,[2] $K_0(+1,+1) = 8 \times 10^{-2}\ M^{-1}$ (25°, d = 5 Å). We finally get $k_{23} = 10^5\ sec^{-1}$.

Again from the hydroxyl ion catalyzed path of the complex-forming reactions of the vanadyl ion[8,11] the exchange rate of water in the inner hydration sphere of the vanadyl–monohydroxo cation can be estimated as $k_{H_2O\ exch}(OVOH^+) = 3 \times 10^4\ sec^{-1}$. Since in this case, too, the rate constant for the spontaneous water exchange and k_{23} are of the same order of magnitude, we may conclude that also with the formation of the binuclear complex $(OVOH)_2{}^{2+}$ the rate-determining step is the water exchange in the inner hydration sphere of the monomeric species $OVOH(H_2O)_4{}^+$.

It should be pointed out, however, that into the value of k_{23} enter all possible oversimplifications or mistakes of the Fuoss model. It is possible to apply the Fuoss model to all combinations of interacting species including equally or oppositely charged ions and ion dipoles since in this model only coulombic interaction and the volume of the complex-forming species are considered. However, there always arises the question of the appropriate "contact distance." The "contact distance" of two tightly solvated cations could well be somewhat greater than for solvated cation–anion complexes. Inserting 6 Å instead of 5 Å increases $K_0(2+,2+)$ and decreases $k_{23}(Fe^{3+})$ by a factor of 5 and $K_0(1+,1+)$ and $k_{23}(VO^{2+})$ by a factor of 2, respectively. This gives a better fit of k_{23} and $k_{H_2O\ exch}$ in both cases. However, although the values of K_0 used above may thus be very approximate, it is quite clear that k_{23} and $k_{H_2O\ exch}$ at any rate are of the same order of magnitude.

Obviously the formation also of other binuclear hydroxo complexes and certain inner-sphere redox reactions are expected to proceed *via* the same simple mechanism, which has long been known to operate in a general way with the complex-forming reactions of solvated cations and no special type of mechanism must be postulated for the olation reactions, which lead to binuclear isopolybases. So the suggestion of Eigen and Wilkins[12] can be confirmed although they used in their paper as a proof of their idea the direct comparison of bimolecular (k_{12} for the iron reaction) and monomolecular rate constants ($k_{H_2O\ exch}$ for $FeOH^{2+}$ which was obviously wrong) which can only be compared directly, when K_0 is approximately 1 M^{-1}.

---

(7) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1960, p 380.

(8) H. Strehlow and H. Wendt, *Inorg. Chem.*, **2**, 6 (1963).

(9) F. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

(10) B. Lutz and H. Wendt, to be submitted for publication.

(11) A. Schlund and H. Wendt, *Ber. Bunsenges. Physik. Chem.*, **72**, 652 (1968).

(12) M. Eigen and R. G. Wilkins in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.

CONTRIBUTION FROM THE REACTOR CHEMISTRY DIVISION,
OAK RIDGE NATIONAL LABORATORY,
OAK RIDGE, TENNESSEE 37830,
AND THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MAINE, ORONO, MAINE 04473

Association of Cd^{2+} and Br^- in the Solvent $KNO_3 + Ca(NO_3)_2 + H_2O$[1a]

BY JERRY BRAUNSTEIN[1b] AND HELEN BRAUNSTEIN[1c]

Received December 16, 1968

The solution chemistry of electrolytes at concentrations intermediate between anhydrous fused salts and "ordinary" aqueous electrolytes has received little attention, in spite of its importance in the development of theories of electrolyte solutions.[2] The temperature dependence and water concentration dependence of equilibrium constants for the association

$$Cd^{2+} + Br^- \rightleftharpoons CdBr^+ \qquad (1)$$

in the solvent $\{$equimolar $(Li,K)NO_3\} + H_2O$ containing up to 50 mol % water have supported a quasilattice model of competing association and hydration equilibria.[3]

The present work is part of an extension of these studies to other solvent systems. Studies of transport properties[4,5] and volumetric properties[6] in $Ca(NO_3)_2 \cdot 4H_2O$ and in its mixtures with KNO_3 have suggested that these hydrate melts may be considered as analogs of molten salts, consisting of nitrate ions and hydrated cations. In this note we describe measurements of the

---

(1) (a) Research sponsored by the U. S. Atomic Energy Commission under contracts with the Union Carbide Corp. and with the University of Maine. (b) Oak Ridge National Laboratory. (c) National Science Foundation Cooperative Fellow at the University of Maine, 1964–1966.

(2) J. Braunstein, *Inorg. Chim. Acta Rev.*, **2**, 19 (1968).

(3) (a) J. Braunstein, *J. Phys. Chem.*, **71**, 3402 (1967); (b) P. C. Lammers and J. Braunstein, *ibid.*, **71**, 2636 (1967).

(4) C. T. Moynihan, *ibid.*, **70**, 3399 (1966).

(5) J. Braunstein, L. Orr, A. R. Alvarez-Funes, and H. Braunstein, *J. Electroanal. Chem.*, **15**, 337 (1967).

(6) J. Braunstein, L. Orr, and W. MacDonald, *J. Chem. Eng. Data*, **12**, 415 (1967).

association equilibrium 1 in the solvent KNO_3 + $Ca(NO_3)_2$ + H_2O at 50° which provide partial support for this view. At this low temperature, it was not possible to reduce the water content sufficiently to provide a valid test of the quasilattice model of competing equilibria.[3a]

Experimental Section

The emf of the cell

$$\underbrace{\mathrm{Ag, AgBr}|\underset{[\mathrm{KBr}]}{\mathrm{KNO_3 + Ca(NO_3)_2 + H_2O}}\;||}_{\text{reference half-cell}}\ \underbrace{\underset{\substack{[\mathrm{Cd(NO_3)_2}]\\ [\mathrm{KBr}]}}{\mathrm{KNO_3 + Ca(NO_3)_2 + H_2O}}|\mathrm{Cd(Hg)}}_{\text{indicator half-cell}} \quad \text{(I)}$$

was measured at 50°. The solvent compositions were $Ca(NO_3)_2 + 6H_2O$, $Ca(NO_3)_2 + 0.5KNO_3 + 6H_2O$, $Ca(NO_3)_2 + 0.5KNO_3 + 4H_2O$, and $Ca(NO_3)_2 + KNO_3 + 4H_2O$. They were prepared from AR grade KNO_3, $Ca(NO_3)_2 \cdot 4H_2O$, and (where required) distilled water. Silver–silver bromide reference half-cells[3b,7] and cadmium amalgam indicator electrodes[8] were prepared as described previously. A diagram of the cell is shown in Figure 1.

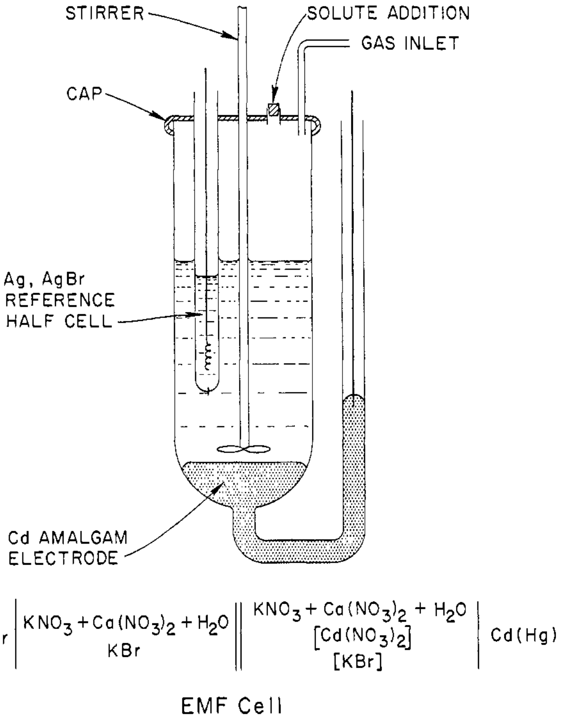

Figure 1.—Pyrex cell for emf measurements with amalgam electrodes in hydrate melts.

In all measurements, the solvent composition was the same in both half-cells of (I) to minimize the liquid junction potential. In order to prevent loss of water at 50°, a stream of nitrogen, equilibrated with a reservoir of solvent of the same composition and temperature as that in the cell, was passed over the solution in the cell. Additions of reagent grade KBr and $Cd(NO_3)_2$ to the right-hand half-cell of (I) were made with a micrometer syringe containing solutions of known concentrations. It has been demonstrated that the small amounts of additional water have no effect on the emf of the cell.[3b,7,8] The cell was suspended in a water bath thermostated at 50 ± 0.02°. Vigorous mechanical stirring of the solution just above the surface of the cadmium amalgam provided rapid equilibration.

The emf of the cell first was measured at several concentrations of cadmium nitrate with no potassium bromide in the indicator half-cell in order to verify adherence to the Nernst equation in the concentration of cadmium nitrate. The emf then was measured after successive additions of KBr.

Polarographic measurements were made at the lowest concentrations of cadmium. We have shown[7] that association constants obtained from the shift of half-wave potential on addition of ligand are consistent with the values obtained from emf measurements.

Results and Calculations

The change of emf of cell I and the shift of the half-wave potential of Cd^{2+} were measured as a function of the mole ratio of KBr

$$R_{KBr} = n_{KBr}/(n_{KNO_3} + 2n_{Ca(NO_3)_2})$$

at several mole ratios of $Cd(NO_3)_2$

$$R_{Cd(NO_3)_2} = n_{Cd(NO_3)_2}/(n_{KNO_3} + n_{Ca(NO_3)_2})$$

in each solvent mixture. The denominators in the expressions for the mole ratios of KBr and $Cd(NO_3)_2$ are the numbers of moles of solvent anions ($n_{NO_3^-}$) and of solvent cations ($n_{K^+} + n_{Ca^{2+}}$) so that R_{KBr} and $R_{Cd(NO_3)_2}$ are the ion ratio analogs of the Temkin ion fractions in charge-unsymmetric molten salt mixtures.[2]

Since the Nernst equation is obeyed by $Cd(NO_3)_2$ in the solutions without bromide, the activity coefficient of $Cd(NO_3)_2$ may be taken as unity at the concentrations investigated (up to about 10^{-2} mole fraction). The change of cell emf on addition of bromide to the right-hand half-cell is related to the stoichiometric activity coefficient of $Cd(NO_3)_2$ in the presence of bromide as[3b,7,8]

$$\ln \gamma_{Cd(NO_3)_2} = \frac{2F}{RT}\Delta E$$

At each solvent composition, the equilibrium constant ($K_1 = K_{CdBr^+}$) for the association reaction (eq 1) in that solvent is[3b,7,8]

$$K_{CdBr^+} = K_1 = \frac{R_{CdBr^+}}{R_{Cd^{2+}}R_{Br^-}} = -\lim_{\substack{R_{KBr}\to 0\\ R_{Cd(NO_3)_2}\to 0}} \left(\frac{\partial \ln \gamma_{Cd(NO_3)_2}}{\partial R_{KBr}}\right)_{R_{Cd(NO_3)_2}} \qquad (2)$$

Graphical extrapolation of eq 2 to the association constants is shown in Figure 2. The association constants are in Table I, with solvent compositions indicated by the molar ratios of water to calcium ion and of potassium to calcium ion. The last two columns indicate the molar ratios of water to total solvent cations (K^+ and Ca^{2+}) and of water to nitrate ion. The over-all uncertainties in the evaluation of K_{CdBr^+} are 5–10%. The potentiometric and polarographic data have been deposited with ASIS-NAPS.[9]

---

[7] J. Braunstein, A. R. Alvarez-Funes, and H. Braunstein, *J. Phys. Chem.*, **70**, 2734 (1966).

[8] J. M. C. Hess, J. Braunstein, and H. Braunstein, *J. Inorg. Nucl. Chem.*, **26**, 811 (1964).

[9] For detailed polarographic and potentiometric data, order Document No. NAPS-00449 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. Remit $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

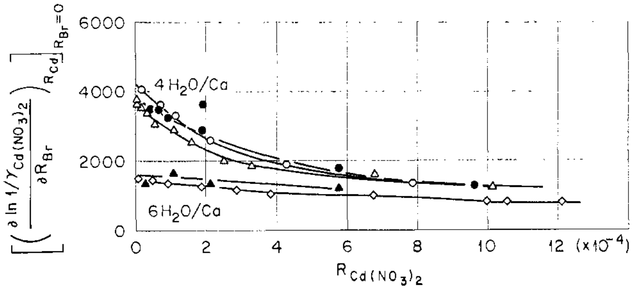

Figure 2.—Evaluation of thermodynamic association constants (at 50°) for $CdBr^+$ in the solvents $KNO_3 + Ca(NO_3)_2 + H_2O$ by graphical extrapolation to infinite dilution of both Cd^{2+} and Br^- of the slopes $[\partial \ln (1/\gamma_{Cd(NO_3)_2})/\partial R_{KBr}]_{R_{Cd(NO_3)_2}}$: △, $Ca(NO_3)_2 \cdot 4H_2O$; ●, $Ca(NO_3)_2 \cdot 4H_2O + 0.5KNO_3$; ○, $Ca(NO_3)_2 \cdot 4H_2O + 1KNO_3$; ▲, $Ca(NO_3)_2 \cdot 6H_2O$; ◇, $Ca(NO_3)_2 \cdot 6H_2O + 0.5KNO_3$.

Table I

Association Constants in the Mixtures $Ca(NO_3)_2 + KNO_3 + H_2O$ at 50° for $Cd^{2+} + Br^- = CdBr^+$ (K_{CdBr^+})

K_{CdBr^+}	Mol of H_2O/mol of Ca^{2+}	Mol of K^+/mol of Ca^{2+}	Mol of H_2O/mol of cation	Mol of H_2O/mol of nitrate
1550	6	0	6	3
1460	6	0.5	4	2.4
3900[a]	4	0	4	2
3880	4	0.5	2.67	1.6
4250	4	1	2	1.33

[a] Reference 7.

Discussion

The principal observation, from Table I and Figure 2, is that, within the experimental error of 5–10%, the association constants appear to depend primarily on the ratio of water to calcium ion (4 or 6) and are virtually independent of the ratio of water to nitrate ion or of the ratio of potassium ion to calcium ion. We have reported similar behavior for partial molar volumes[6] and solute diffusion coefficients.[5] The partial molar volume, at 100°, of $Ca(NO_3)_2 \cdot 4H_2O$ in mixtures with up to 60 mol % potassium nitrate is constant and equal to the molar volume of pure $Ca(NO_3)_2 \cdot 4H_2O$.[6] The polarographic diffusion coefficient of cadmium ion in these mixtures also is independent of the concentration of added potassium nitrate.[5] Pmr studies have shown that, at temperatures up to 100°, the addition of KNO_3 to $Ca(NO_3)_2 \cdot 2H_2O$ does not affect the chemical shift.[10] It therefore may seem reasonable to consider these mixtures to be constituted of K^+, NO_3^-, and $Ca(H_2O)_6^{2+}$ or $Ca(H_2O)_4^{2+}$, *i.e.*, as analogs of molten salts of weak-field cations.[11]

Raman and infrared spectral studies of concentrated aqueous calcium nitrate solutions, however, have been interpreted in terms of the formation of contact ion pairs $CaNO_3^+$.[12] This is not necessarily inconsistent with the thermodynamic and nmr results for the melts with a water to calcium ion ratio of 4:1, since the water molecules could all be bound to the divalent ions and still leave sites in the coordination sphere of the calcium ions for Ca^{2+}–NO_3^- contacts. It is more difficult to reconcile Ca^{2+}–NO_3^- contacts with hexahydrated calcium ions in the melts with higher water contents. Extension of structural as well as thermodynamic studies through this concentration region are needed to elucidate the ion–ion and ion–water interactions in the hydrate melts.

It is clear that when the water content of these mixtures is reduced below that required to form complete hydration shells about the cations, the behavior must approach that of molten salts, with competition between water and anions for sites adjacent to the cations.[3a]

---

[10] C. T. Moynihan and A. Fratiello, *J. Am. Chem. Soc.*, **89**, 5546 (1967).

[11] C. A. Angell, *J. Electrochem. Soc.*, **112**, 1224 (1965).

[12] R. Hester and R. A. Plane, *J. Chem. Phys.*, **40**, 411 (1964); D. E. Irish, private communication.

Contribution from the Department of Chemistry,
San Diego State College, San Diego, California 92115

Thermal Reaction of Silane with Hydrogen Chloride

By R. A. Gorse, Jacqueline DuVigneaud, and M. A. Ring

Received January 7, 1969

Silane and hydrogen chloride react at 100° in the presence of aluminum chloride to produce the chlorosilanes, while no reaction occurs in the absence of a catalyst even at 200°.[1] Purnell and Walsh[2] have demonstrated that the pyrolysis of silane over a silicon mirror is homogeneous at 375°. Further, their results were most consistent with the mechanism

$$SiH_4 \longrightarrow SiH_2 + H_2 \qquad (1)$$

$$SiH_2 + SiH_4 \longrightarrow Si_2H_6 \qquad (2)$$

We have examined the reactions of silane–hydrogen chloride mixtures at 362°. The reaction was very surface dependent. In an uncoated Pyrex reaction vessel, the major products were the three chlorosilanes with little disilane being formed. With silane-d_4 and hydrogen chloride, the products were chlorosilane-d_3, dichlorosilane-d_2, and disilane-d_6. When the reaction vessel was coated with a silicon mirror, the over-all reaction was slower and the disilane to chlorosilanes ratio greatly was increased. These results demonstrate the following points: (1) the thermal reaction between silane and hydrogen chloride is catalyzed by Pyrex to form the chlorosilanes; (2) this catalyzed reaction does not involve silene insertion into hydrogen chloride; (3) if silene is formed during the silane pyrolysis, the insertion of silene into silane is much faster than the insertion into hydrogen chloride.

Experimental Section

Silane was prepared by the lithium aluminum hydride reduction of silicon tetrachloride and treated with water to remove hydro-

---

[1] A. Stock and C. Semieski, *Ber.*, **52**, 695 (1919).

[2] J. H. Purnell and R. Walsh, *Proc. Roy. Soc.* (London), **A293**, 543 (1966).