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Solvent Effect on Association in Molten Nitrates. Cadmium(II) and Bromide in Equimolar Lithium Nitrate–Sodium Nitrate[1]

BY JERRY BRAUNSTEIN AND A. S. MINANO

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The association constant of cadmium(II) with bromide has been reported from potentiometric measurements in the molten salt solvents sodium nitrate,[2] potassium nitrate,[2] and equimolar potassium nitrate–sodium nitrate,[3] and in mixtures of lithium nitrate with potassium nitrate.[4] Measurements have not been possible in lithium nitrate because of the instability and apparent irreversibility of the emf in cells with silver or silver–silver halide electrodes in the solvent lithium nitrate. However, the Helmholtz free energy of association, calculated from the association constants with an equation of the quasi-lattice model of molten salt solutions, $K = Z[\exp(-\Delta A/RT) - 1]$,[5] has been found to vary linearly with the composition of the solvent in mixed solvents.[4,6] Hence, an estimate of the Helmholtz free energy of association in lithium nitrate may be obtained by extrapolation of the results obtained in solvent mixtures containing lithium nitrate.

In this note we report measurements of the association constant of cadmium ion with bromide ion in molten equimolar lithium nitrate–sodium nitrate at 240°. The Helmholtz free energy of association, ΔA_1, is calculated from the association constant, and ΔA_1 in lithium nitrate is obtained by graphical extrapolation and by a least-squares fit of the values of ΔA_1 in sodium nitrate, potassium nitrate, and the mixtures of lithium nitrate with sodium nitrate or potassium nitrate. The estimate is in agreement with the one obtained previously from mixtures of lithium nitrate with potassium nitrate and is discussed in terms of the apparent "radius" of the nitrate ion in molten alkali nitrates.

The association constant for the formation of $CdBr^+$ in $LiNO_3$–$NaNO_3$ was calculated from measurements of the electromotive force of concentration cells with silver–silver bromide electrodes by methods which have been described previously.[3,4] The electromotive force data are available from the ADI Auxiliary Publications Project.[7] Representative plots of the function $(1/\gamma_{Br} - 1)$, calculated from the electromotive force measurements, are shown in the lower half of Figure 1 at various bromide concentrations. γ_{Br} is the stoichiometric activity coefficient of the solute (Li,Na)Br in the presence of cadmium nitrate.[3,4] The concentrations are expressed as the mole ratios $R_{Cd} = n_{Cd(NO_3)_2}/n_{(Li,Na)NO_3}$ and $R_{Br} = n_{(Li,Na)Br}/n_{(Li,Na)NO_3}$, where the n values are the numbers of moles of the components. The upper half of Figure 1 is a plot of the limiting slopes, $\lim_{R_{Cd}\to 0} (\partial(1/\gamma_{Br})/\partial R_{Cd})_{R_{Br}}$ *vs.* R_{Br}, the concentration of bromide. The extrapolated value of this slope is the thermodynamic association constant for the association of cadmium(II) with bromide ion and was found to be $K_1 = 2700 \pm 200$ (moles of nitrate/mole). The Helmholtz free energy of association is $-\Delta A_1 = 6.23$ kcal/mole, calculated from the equation $K_1 = Z\,[\exp(-\Delta A/RT) - 1]$ with the value of the quasi-lattice coordination number $Z = 6$.

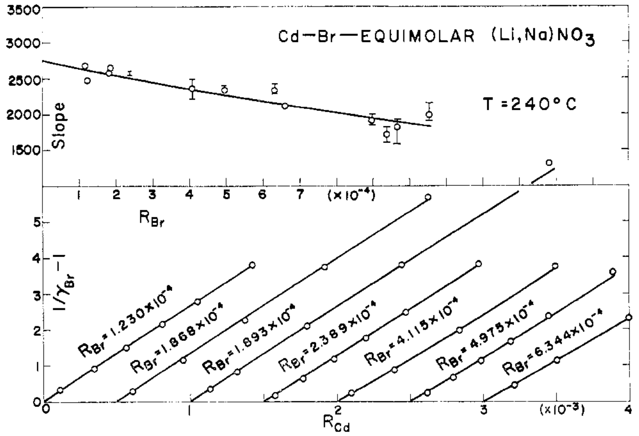

Figure 1.—Lower: $(1/\gamma_{Br}) - 1$ *vs.* the mole ratio of $Cd(NO_3)_2$ at various fixed mole ratios of (Li,Na)Br in equimolar $LiNO_3$–$NaNO_3$ at 240°. Upper: Extrapolation of the limiting slopes, $[(\partial \ln (1/\gamma_{Br})/\partial R_{Cd(NO_3)_2})]_{R_{Cd(NO_3)_2}=0}$, to infinite dilution of (Li,Na)Br to obtain the association constant.

The association constant and Helmholtz free energy of $CdBr^+$ in equimolar $LiNO_3$–$NaNO_3$ are compared in Table I with previously reported results in the solvents sodium nitrate,[2] potassium nitrate,[2] and equimolar sodium nitrate–potassium nitrate,[2,3] and in mixtures of lithium nitrate and potassium nitrate.[4] The Helmholtz free energies are plotted, as the circles in Figure 2, as functions of the composition of the mixed solvents. The equations of the three lines were obtained by simultaneously fitting the ΔA values for all of the solvents by the method of least squares, assuming a linear dependence on composition and assigning equal weight to each of the points. The least-squares values and standard deviations of $-\Delta A$ in KNO_3, $NaNO_3$, and $LiNO_3$

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[1] Supported by the USAEC under Contract No. AT(30-1)-2873.

[2] H. Braunstein, J. Braunstein, and D. Inman, submitted.

[3] J. Braunstein and R. M. Lindgren, *J. Am. Chem. Soc.*, **84**, 1534 (1962).

[4] J. Braunstein and A. S. Minano, *Inorg. Chem.*, **3**, 218 (1964).

[5] (a) D. G. Hill, J. Braunstein, and M. Blander, *J. Phys. Chem.*, **64**, 1038 (1960); (b) M. Blander, *J. Chem. Phys.*, **34**, 342 (1961); (c) J. Braunstein, M. Blander, and R. M. Lindgren, *J. Am. Chem. Soc.*, **84**, 1529 (1962).

[6] D. G. Hill and M. Blander, *J. Phys. Chem.*, **65**, 1866 (1961).

[7] The data have been deposited as Document No. 8750 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

TABLE I

ASSOCIATION CONSTANTS, K_1 (MOLES/MOLE OF SOLVENT)$^{-1}$, OF $CdBr^+$ AND SPECIFIC HELMHOLTZ FREE ENERGIES OF ASSOCIATION, $-\Delta A$ (KCAL/MOLE), IN MIXTURES OF $LiNO_3$, $NaNO_3$, AND KNO_3; $Z = 6$

Solvent, mole %					
KNO_3	$NaNO_3$	$LiNO_3$	T, °C	K_1	$-\Delta A$
100	0	0	358	650	5.88[a]
0	100	0	331	625	5.58[a]
0	0	100	...	....	6.87[b]
50	50	0	240	1520	5.67[c]
50	50	0	258	$1500\begin{cases}+0\\-100\end{cases}$	$5.83\begin{cases}+0^a\\-0.07\end{cases}$
50	50	0	300	990	5.83[c]
0	50	50	240	2700	6.23[d]
74	0	26	240	2300	6.06[e]
60	0	40	240	2650	6.20[e]
50	0	50	240	3200	6.38[e]
35	0	65	240	3600	6.58[e]
20	0	80	240	4200	6.67[e]
50	0	50	171	8000	6.33[e]

[a] See ref 2. [b] Least-squares value; see also ref 4. [c] See ref 3. [d] This work. [e] See ref 4.

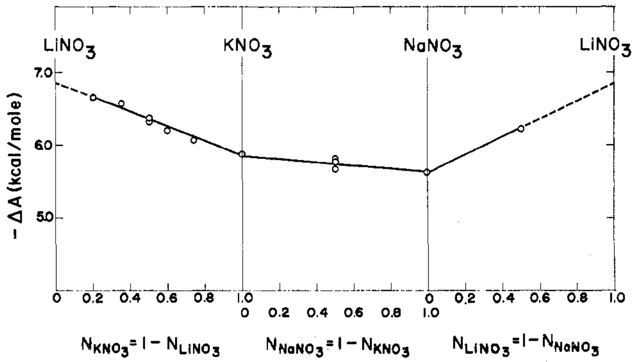

Figure 2.—Variation of the specific Helmholtz free energy of formation of $CdBr^+$ in mixtures of $LiNO_3$, KNO_3, and $NaNO_3$. The points are calculated from the measured association constants, and the lines were determined by a least-squares fit of the points.

are 5.85 ± 0.04, 5.61 ± 0.04, and 6.87 ± 0.05 kcal/mole. These results agree, within ±0.03, with the values which are accessible by direct measurement and with the value of ΔA in $LiNO_3$ estimated previously from results in mixtures only of $LiNO_3$ and KNO_3.

From the differences of the values of the specific Helmholtz free energies of association in Table I, we find the solvent effect: $\Delta A_{Na} - \Delta A_K = 0.29$ kcal/mole (destabilization of $CdBr^+$ in $NaNO_3$ relative to KNO_3) and $\Delta A_{Li} - \Delta A_K = -0.99$ kcal/mole (stabilization in $LiNO_3$ relative to KNO_3). These differences may be compared with the differences of the coulombic energy of exchange of nearest neighbor ions (*i.e.*, the "reciprocal coulomb effect")[4,8,9] in the association reactions

$$CdNO_3^+ + KBr = CdBr^+ + KNO_3 \qquad \Delta U_K$$

$$Cd(NO_3)^+ + LiBr = CdBr^+ + LiNO_3 \qquad \Delta U_{Li}$$

$$Cd(NO_3)^+ + NaBr = CdBr^+ + NaNO_3 \qquad \Delta U_{Na}$$

The differences are more nearly consistent with a smaller "effective radius" of nitrate ion than the value 2.19 A assumed previously.[4] Kapustinskii[10] has suggested the value 1.89 A for the "thermochemical" radius of nitrate ion. We have reported[4,11] that the solvent effect (stabilization in $LiNO_3$ and destabilization in $NaNO_3$) indicates a smaller "effective radius" of nitrate ion in lithium nitrate than in the other alkali nitrates. Meschel and Kleppa later reported that their thermochemical data indicate a nitrate ion "effective radius" of 1.93 A in typical fused nitrates and 1.85 A in lithium nitrate.[12] In the present work, the solvent effect would be in agreement with the calculated reciprocal coulomb effect with a nitrate ion radius or "distance of closest approach" of 1.98 A in sodium nitrate and potassium nitrate and 1.94 A in lithium nitrate. Such correlations may be useful in predicting solvent effects on association equilibria but must be recognized as empirical since the change of coulombic energy due to ions other than nearest neighbors, as well as the effects of polarization and dispersion, are not considered in the simple calculations of the reciprocal coulomb effect.

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(9) J. Braunstein and J. D. Brill, *J. Phys. Chem.*, **70**, 1261 (1966).

(10) A. F. Kapustinskii, *Quart. Rev.* (London), **10**, 283 (1956)

(11) The following corrections to ref 4, which do not alter the conclusions, should be noted. The second term in the bracket on the right of eq 1 should read $1/(r_B + r_X)$, without a prime. The subscripts $LiNO_3$ and KNO_3 in the equation for $-\Delta A_{CdBr^+}$ under the graph in Figure 3 are reversed. The numerical values calculated for β, α, and Δ in the last paragraph should read −0.20, −0.068, and −0.028 (instead of −0.16, −0.053, and −0.018), respectively, and the decrease in the distance of closest approach which would reverse the sign of the calculated $\Delta(\Delta U)$ should read 0.10 instead of 0.08.

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Alcoholysis of $(CF_3P)_n$ Rings. A Volatile Open-Chain Tetraphosphine[1]

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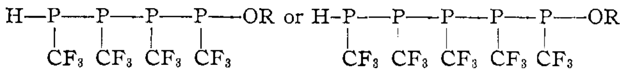
Alcohols cleave a P–P bond in $(CF_3P)_4$ or $(CF_3P)_5$,[2] evidently forming first a full-length open chain



$$H{-}\underset{CF_3}{P}{-}\underset{CF_3}{P}{-}\underset{CF_3}{P}{-}\underset{CF_3}{P}{-}OR \text{ or } H{-}\underset{CF_3}{P}{-}\underset{CF_3}{P}{-}\underset{CF_3}{P}{-}\underset{CF_3}{P}{-}\underset{CF_3}{P}{-}OR$$

The relatively electronegative F_3CPOR end group could be expected to attract basic invasion (by O of ROH) more effectively than other P atoms in the chain, and indeed scarcely less effectively than P in the original rings. In fact, a secondary alcoholysis begins long before the first step is complete and gives higher yields of $CF_3P(OR)_2$ and the open-chain polyphosphine $H_2(CF_3P)_{n-1}$ than random P–P cleavage could account for. Thus, we have a relatively convenient and efficient method of making the triphosphine $H_2(CF_3P)_3$;[2] and by

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(1) This research was supported by the United States Air Force under subcontracts of Prime Contracts AF 33(616)-5435 and 7810, monitored by the Materials Laboratory, Wright-Patterson Air Force Base, Ohio. The work with $(CF_3P)_4$ was done by A. B. B. in 1958; that with $(CF_3P)_5$, by L. K. P. in 1961.

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