

DMF systems anions in the second shell affect the first shell solvent molecules.

There did not appear to be an anion effect on the chemical shift of bound  $\text{CH}_3\text{CN}$  protons. The bound resonance was 35 Hz downfield from free acetonitrile in  $\text{AlCl}_3$  solutions and 33 to 37 Hz in the  $\text{Al}(\text{ClO}_4)_3$  solutions. The position in the perchlorate solutions is a bit surprising in view of the mixed species in the coordination sphere. There also is a published spectrum<sup>6</sup> of  $\text{Al}(\text{ClO}_4)_3$  in  $\text{H}_2\text{O}-\text{CH}_3\text{CN}$  which shows the bound  $\text{CH}_3-$

CN at about 57 Hz downfield from free  $\text{CH}_3\text{CN}$ . It is interesting to note, however, that the bound proton peak for acetonitrile when  $(\text{NH}_3)_2\text{Pt}(\text{ClO}_4)_2$  is the solute is also 35 Hz downfield from bulk  $\text{CH}_3\text{CN}$ .<sup>21</sup>

*Acknowledgment.* The authors wish to acknowledge the valuable assistance of A. E. Florin in obtaining spectra and discussing the results.

(21) J. F. O'Brien, G. E. Glass, and W. L. Reynolds, *Inorg. Chem.*, **7**, 1664 (1968).

## The Importance of the Effect of the Solvent Dielectric Constant on Ion-Pair Formation in Water at High Temperatures and Pressures

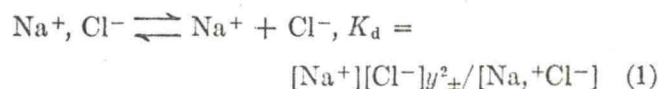
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The contention of Marshall, Quist, and coworkers that ion-pair formation of a number of electrolytes in water at high temperatures and pressures does not depend on changes in the solvent dielectric constant but only on changes in the solvent density and temperature is examined and rejected. Their data are analyzed in terms of the Gilkerson modification of the Fuoss equation for the ion-pair dissociation constant. The data reported by Marshall and coworkers is uniquely suited to experimental separation of the effects of specific ion-solvent and ion-pair-solvent interaction and the effects of changes in solvent dielectric constant. Distances of closest approach are obtained which are somewhat smaller than interionic distances in crystals.

Marshall and coworkers,<sup>2</sup> in reporting a series of studies of the electrical conductances of aqueous electrolytes up to 800° and 4000 bars, have proposed that changes in ion-pair formation in solution at constant temperature are independent of changes in the solvent dielectric constant and depend only on changes in the concentration of a specifically solvating solvent species.<sup>3</sup> This view is quite contrary to that taken by most workers in the field of electrolyte solutions.<sup>4</sup>

The low densities of water (and consequent low values of its dielectric constant) at high temperatures under high pressure result in measurably low values of the ion-pair dissociation constant,  $K_d$ , for the process (for NaCl for instance)



where  $[\text{Na}^+\text{Cl}^-]$  represents the molar concentration of the ion pair,  $\text{Na}^+\text{Cl}^-$ , and  $y_{\pm}$  is the mean ionic activity coefficient calculated using the Debye-Hückel equation. I shall be concerned in this report with the

correlation of the values of  $K_d$  obtained by Marshall and coworkers with the physical properties (dielectric constant, density, and temperature) of the solvents used. I shall not be concerned with the treatment of the conductance data (equivalent conductance, concentration) to yield limiting equivalent conductances and the ion-pair dissociation constant,<sup>5</sup>  $K_d$ . The magnitudes of the changes in the values of  $K_d$  as the solvent system changes can be illustrated by one example;<sup>2b</sup> for NaCl at 400°,  $-\log K_d = 4.43$  at  $d = 0.30$  g/ml, dielectric

(1) This work has been supported in part by a grant from the National Science Foundation, GP-6949.

(2) (a) A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **70**, 3714 (1966); (b) *ibid.*, **72**, 684 (1968); (c) *ibid.*, **72**, 2100 (1968); (d) *ibid.*, **72**, 1545 (1968); (e) L. A. Dunn and W. L. Marshall, *ibid.*, **73**, 723 (1969).

(3) A. S. Quist and W. L. Marshall, *ibid.*, **72**, 1536 (1968).

(4) (a) M. Szwarc, *Accounts Chem. Res.*, **2**, 87 (1969); (b) D. F. Evans and P. Gardam, *J. Phys. Chem.*, **73**, 158 (1969); (c) J. C. Poirier in "Chemical Physics of Ionic Solutions," B. E. Conway and R. G. Barrades, Ed., John Wiley & Sons, New York, N. Y., 1966, p 9; (d) J. E. Prue, ref 4c, p 163.

(5) Called the conventional ionization constant by Marshall, *et al.*



constant,  $D = 4.9$ , pressure,  $P$ , approximately 220 bars,<sup>6</sup> while  $-\log K_d = 0.97$  at  $d = 0.70$  g/ml, and  $P \approx 1000$  bars.<sup>6</sup>

Marshall and Quist found that, at constant temperature, plots of  $\log K_d$  vs.  $\log C_{H_2O}$  are linear.  $C_{H_2O}$  is the molar concentration of water. They concluded that water should be included explicitly in a "complete equilibrium"



with the equilibrium constant given by

$$K^\circ = a_M a_X / a_{MX} a_{H_2O}^k = K_d / a_{H_2O}^k \quad (3)$$

Marshall and Quist then set the activity of water in the infinitely dilute salt solution to be equal to the molar concentration of water. Their statement regarding the choice of standard state that leads to this is, in one instance,<sup>2b</sup> "...  $a_{H_2O}$  is replaced by the molar concentration of water ( $C_{H_2O}$ ) with a hypothetical standard state of unit molarity at the particular density (or pressure), ...". I submit that this is incorrect if one is concerned with the changes in the activity of the water solvent as the density (pressure) changes. The activity of a substance is defined by the relation

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (4)$$

where  $\mu_i$  is the chemical potential (partial molar free energy) of component  $i$  and  $\mu_i^\circ$  is the chemical potential in some chosen standard state at the temperature  $T$ . If the effects of changes in activity (concentration) of water solvent at different densities on a chemical reaction are to be investigated, the standard state chosen should *not* change with solvent density or pressure. A suitable choice here would be any invariant state of water (constant  $T$  and  $P$ ). Now

$$d\mu_i = \bar{V}_i dP - \bar{S}_i dT \quad (5)$$

where  $\bar{V}_i$  is the partial molar volume of  $i$  and  $\bar{S}_i$  is the partial molar entropy of  $i$ . At constant temperature, this becomes

$$d\mu_i = \bar{V}_i dP$$

and thus

$$d\mu_i^\circ + RT d \ln a_i = \bar{V}_i dP$$

at constant  $T$ . The only variable here is the pressure. I take as a suitable standard state, water at one particular density, say 0.300 g/ml, at the temperature  $T$ . Then  $d\mu_i^\circ = 0$  and

$$d \ln a_i = \bar{V}_i dP / RT$$

or

$$\log a_{H_2O} = (1/2.303RT) \int_{P^\circ}^P \bar{V}_{H_2O} dP \quad (6)$$

where  $P^\circ$  is the pressure corresponding to the density in the standard state at  $T$ , and  $P$  is the pressure corre-

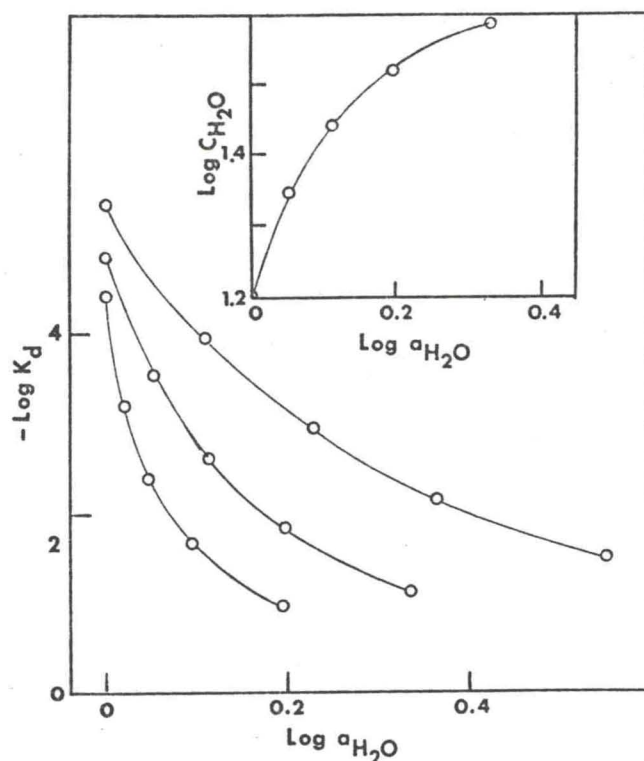


Figure 1. The water concentration,  $C_{H_2O}$ , in the insert, and the ion-pair dissociation constants for NaCl at 400, 500, and 700° as a function of the water activity,  $a_{H_2O}$ . The standard state for the water solvent at all temperatures was taken to be pure water at a pressure producing a density of 0.300 g/ml.

sponding to the density of water whose activity is  $a_{H_2O}$ . Values of  $\log a_{H_2O}$  were calculated from eq 6 at 400, 500, and 700° using available specific volume (or density)-pressure data<sup>7</sup> referenced by Quist and Marshall.<sup>2b</sup> These values at 500° at densities of 0.4, 0.5, 0.6, and 0.7 g/ml are plotted vs.  $\log C_{H_2O}$  in the insert, Figure 1. It can be seen that the activity of water increases at a greater rate with increasing pressure than does the concentration. It might be noted here that the pressure at a density of 0.30 g/ml is 550 bars, while at the highest density here, 0.70 g/ml, the pressure is 2000 bars, at 500°.

I have plotted values of  $\log K_d$  for NaCl vs. these values of  $\log a_{H_2O}$  at the corresponding densities at 400, 500, and 700°, Figure 1, to emphasize the fact that if equation 3 is correct, then the "complete" constant  $K^\circ$  certainly is *not* constant as the density of solvent water changes. Marshall and Quist concluded on the basis of the linearity of isothermal  $\log K_d$  vs.  $\log C_{H_2O}$  plots that the complete equilibrium constant was independent of changes in the solvent dielectric constant. I conclude that the conclusions of Marshall and Quist are

(6) Interpolated from data compiled by A. W. Lawson and A. J. Hughes in "High Pressure Physics and Chemistry," Vol. I, R. S. Bradely, Ed., Academic Press, Inc., New York, N. Y., 1963, p 209.

(7) (a) W. T. Holser and G. C. Kennedy, *Am. J. Sci.*, 257, 71 (1959); (b) S. Maier and E. U. Franck, *Ber. Bunsenges. Phys. Chem.*, 70, 639 (1966).



invalid, being based on an incorrect assumption regarding the relationship of changes in water activity to changes in water concentration due to large pressure changes.

The results of the great amount of work by Marshall, *et al.*, are uniquely suited to a separation of specific ion-solvent interaction effects from the effects of changes in solvent dielectric constant; the latter I shall show is by no means unimportant. The effect of varying the dielectric constant of the solvent at constant temperature on ion-pair dissociation has been studied in most instances by either varying the composition of a polar-nonpolar solvent mixture<sup>8</sup> over a wide range or by determining  $K_d$  in a series of similar solvents of varying dielectric constants.<sup>9</sup> In either case, the ion-pair dissociation constants have been considered in terms of the equation<sup>10</sup>

$$K_d = (3000/4\pi Na^3) \exp(-E_s/RT) \times \exp(-e^2/akDT) \quad (7)$$

where  $N$  is Avogadro's number,  $a$  is the distance of closest approach of the anion and cation in the ion pair,  $E_s$  is the molar internal energy of specific solvation of the free ions less that of the ion pair,  $e$  is the electronic charge, and  $k$  is Boltzmann's constant. The transformation from the free-volume formulation<sup>10b</sup> of the ion-pair dissociation process to the hard sphere in a continuum approach<sup>11</sup> to which is grafted<sup>10b,12</sup> a specific solvation term was not rigorous. One correction that should be made in eq 2 is the replacement of  $E_s$  by the change in molar free energy of specific solvation,  $\Delta G_s = \Delta H_s - T\Delta S_s$ .

$$K_d = (3000/4\pi Na^3) \exp[-\Delta H_s/RT + \Delta S_s/R - e^2/akDT] \quad (8)$$

Clearly, if one varies the solvent composition as in either of the approaches outlined above, not only does the dielectric constant change, but also does the value of  $\Delta G_s$  change. These changes in the difference in free energy of solvation,  $\Delta G_s$ , will in general lead to curvature in the usual plots of  $\log K_d$  vs.  $1/D$ , or to physically unreal values of the distance of closest approach,  $a$ .

Experimental separation of the three terms in the exponential of eq 8 is almost impossible without some simplifying assumptions. Two different approaches, and the assumptions necessary, are set out as follows: (a) study a set of systems in which it is known or assumed that  $\Delta G_s$  (or  $\Delta G_s/T$ ) and the distance of closest approach,  $a$ , are constant, but in which the product  $DT$  varies; or (b) study a set of systems in which  $a$  and  $\Delta S_s$  are known or may be assumed to be constant and in which the product  $DT$  is held constant while  $T$  varies. I believe the data of Marshall and coworkers satisfy the criteria for approach (b). Examination of Marshall and Quist's compilation<sup>13</sup> of the dielectric constants of water as a function of density shows that the  $DT$

Table I:  $DT$  Product for Water

$T, ^\circ\text{C}$	Density, g/ml				
	0.3	0.4	0.5	0.6	0.7
400	3300	4780	6520	8560	10,800
500	3320	4710	6420	8360	10,400
600	3400	4710	6380	8200	10,200
700	3400	4770	6330	8080	10,100
800	3440	4840	6340	8050	10,000

product, at constant density, remains almost constant from 400 to 800°, Table I.

Examination of eq 8 shows that, if the parameters  $\Delta H_s$ ,  $\Delta S_s$ , and  $a$  are independent of the temperature at constant density, then the only variables remaining that determine  $K_d$  are the temperature  $T$  in the first term of the exponential and the product  $DT$  in the third term of the exponential factor. Further, if this last, the  $DT$  product, is almost constant as the temperature changes from 400 to 800°, the only remaining variable is the temperature in the first exponential term. Under the conditions of constant density then

$$\log K_d = [\log (3000/4\pi Na^3) + \Delta S_s/2.30R - e^2/2.30akDT] - \Delta H_s/2.30RT \quad (9)$$

The term in brackets on the right-hand side is a constant. A plot of  $\log K_d$  vs.  $1/T$  should then yield values of  $\Delta H_s$  from the slope. Using Marshall and Quist's data we can obtain values of  $\Delta H_s$  for each electrolyte at each water density. The plots are in general linear, as Marshall has already pointed out.<sup>2b</sup> The slopes of these plots do change with density, however. As an example, for the NaCl system, I obtained the values of the slopes (in units of deg K) of  $\log K$  vs.  $1/T$  at 0.3 g/ml, 2300; at 0.4 g/ml, 1660; at 0.5 g/ml, 1200; at 0.6 g/ml, 1120; and at 0.7 g/ml, 1180. The value of the solvation energy difference *does* depend on the solvent density in these systems.

If now at constant temperature, for each density of water solvent, we form the sum  $(\log K_d + \Delta H_s/2.30RT)$  this, according to eq 8, should be related to  $DT$  as follows,

$$(\log K_d + \Delta H_s/2.30RT) = [\log (3000/4\pi Na^3) + \Delta S_s/2.30RT] - (e^2/2.30ak)(1/DT) \quad (10)$$

Values of the left-hand side of eq 10 have been calculated for NaCl at 500° and were plotted vs.  $1/DT$ .

(8) The classical studies of this sort were those of C. A. Kraus and R. M. Fuoss, *J. Amer. Chem. Soc.*, **55**, 21 (1933).

(9) References 4b and 4d are examples of this approach.

(10) (a) H. Sadek and R. M. Fuoss, *J. Amer. Chem. Soc.*, **81**, 4511 (1959); (b) W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956).

(11) R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958).

(12) W. R. Gilkerson and R. E. Stamm, *ibid.*, **82**, 5295 (1960).

(13) A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **69**, 3165 (1965).



The graph was quite linear and encouraged a more thorough investigation.

I have proceeded to treat the data for NaCl,<sup>2b</sup> NaBr,<sup>2c</sup> NaI,<sup>2e</sup> and HBr,<sup>2d</sup> using eq 8 in the following manner; for each salt, initial values of  $\Delta H_s$  were obtained at each density for plots of  $\log K_d$  vs.  $1/T$  (eq 9). These values of  $\Delta H_s$  were used to form, at constant temperature, the sums  $(\log K_d + \Delta H_s/2.30RT)$ , which were then plotted vs.  $1/DT$  (eq 10). Recalling that the  $DT$  products showed some variation with temperature, Table I, the slopes from the plots vs.  $1/DT$ , being initial values of  $(e^2/2.30ak)$ , were used to correct for the variation of  $DT$  at constant density, eq 9. The sums  $(\log K_d + e^2/2.30akDT)$  were formed at each density and plotted vs.  $1/T$ . This gave new and improved values of  $\Delta H_s$  for each solvent density. These values of  $\Delta H_s$  were used again to form the sums, at constant temperature,  $(\log K_d + \Delta H_s/2.30RT)$ , which were again plotted vs.  $1/DT$ , eq 10. These revised plots are shown in Figure 2. The linearity of these plots of  $\log K_d$ , corrected for specific (ion, ion-pair)-solvent interaction, in terms of the variable  $1/DT$  furnish strong evidence that the data of Marshall, *et al.*, are in agreement with previous ideas concerning the influence of both solvent dielectric constant<sup>11</sup> and the influence of specific ion-solvent interaction,<sup>10b</sup> rather than requiring complete revision of our notions concerning the relative importance of these two factors.

Repetition of the calculational procedure beyond the point described in the paragraph above was not attempted for the following reasons; Marshall and Quist<sup>2b</sup> point out that the values of  $K_d$  ( $10^{-4}$  to  $10^{-5}$ ) at low densities are uncertain due to difficulties in extrapolating to infinite dilution, while I believe the values of  $K_d$  ( $10^{-1}$  to  $10^{-2}$ ) at high densities are uncertain since it is well known that the value calculated from a set of data when such a small fraction of the salt is ion paired depends on the particular form of the conductance equation used. The values of the dielectric constant of water at high temperatures and pressures<sup>13</sup> were obtained by extrapolation of experimental data at lower to higher temperatures. There is some uncertainty then in these resulting values of the dielectric constant of water. These are the same reasons I use here to argue that more sophisticated data-handling techniques such as least-squares procedures are of doubtful applicability in this case.

*Comparison of the Two Approaches.* The experimental limitations listed above should be kept in mind in the following discussion. Note that the plots of eq 10, Figure 2, for the several electrolytes, fall on the same straight lines at the two temperatures, 500 and 700°, with the exception of several sets of data at lowest densities. The approach to ion-pair dissociation outlined in this paper allows, at one temperature, for changes in differences in energies of solvation as the water density changes. The entropy differences had to be assumed

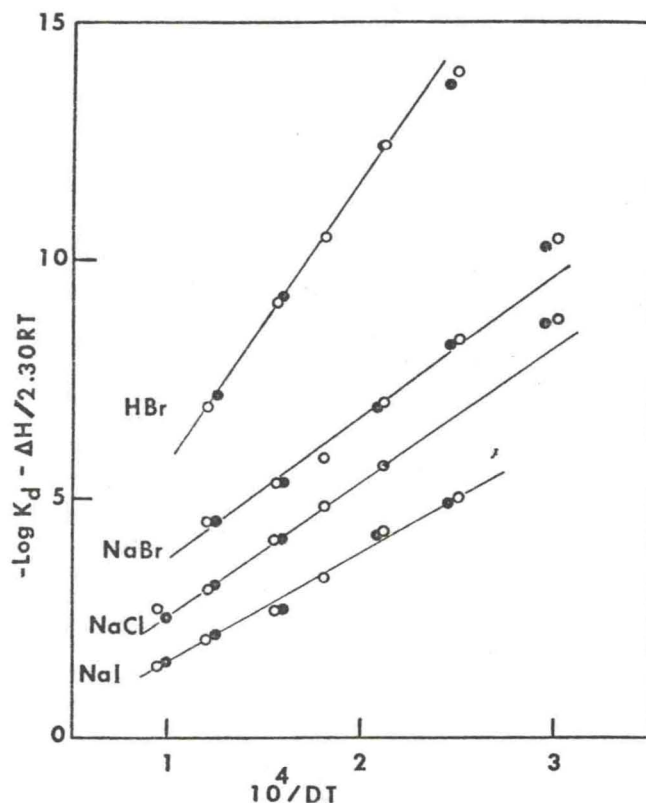


Figure 2. The logarithms of the ion-pair dissociation constants, corrected for specific ion-solvent and ion pair-solvent interaction, for HBr, NaBr, NaCl, and NaI at 500° (open circles) and at 700° (closed circles) vs. the reciprocal of the product of the dielectric constant and the temperature,  $1/DT$ .

to be constant. This approach also allows for the change in electrical free energy as the solvent dielectric changes. To be more specific, the free energy change, upon ion-pair dissociation, is assumed to contain three terms, an energy term ( $\Delta H_s$ ) which is independent of temperature and solvent dielectric constant, an energy term ( $W_{s1}$ ) which is inversely proportional to the solvent dielectric constant, and an entropy term ( $T\Delta S$ ) which includes all other factors, is not dependent on the solvent dielectric constant, and of which the factor  $\Delta S$  itself is temperature independent. These are all simplifications of an admittedly complex process. It is difficult to imagine the process broken into discrete steps, the free energy changes for which would correspond to those outlined above.

Marshall and Quist, in their treatment of these data, allowed only for changes in the free energy of solvation through changes in the water concentration as the density changed. This approach has been shown above to be incorrect in principle. One of the most interesting aspects, to this author, of these data of Marshall and Quist is that they provide a vivid illustration of an experimental technique by means of which the contribution to  $K_d$  of changes in dielectric constant may be separated from the contribution to  $K_d$  of changes due to specific solvation effects.



I cannot claim that the present treatment compared to that of Marshall and Quist reduces the number of parameters necessary to describe the data for a particular salt in water at high pressures and temperatures. Marshall and Quist need a value of  $K^\circ$  (their complete dissociation constant), a value of  $n$ , and  $\Delta E_v^\circ$  (related to the change of  $K^\circ$  with temperature). The present approach requires values of  $\Delta H_s$  at each solvent density and a constant  $a$ , and one value of  $K_d$  at some temperature.

*Ion-Pairing Parameters.* Values of  $\Delta H_s$  and distances of closest approach,  $a$ , appear in Table II, as well

Table II: Ion Pairing Parameters in Water at High  $P$  and  $T$

density, g/ml	$-\Delta H_s$ , kcal/mol			
	NaCl	NaBr	NaI	HBr
0.3	13.9	17.7	8.5 <sup>a</sup>	29.8 <sup>a</sup>
0.4	7.6	9.5	7.9	26.6
0.5	5.6	7.0	5.2	19.8
0.6	4.6	6.5	6.0	16.3
0.7	4.4	7.1	6.2	...
$a$ , $10^{-8}$ cm	2.57	2.47	3.16	1.15
$(r_+ + r_-)^b$	2.81	2.97	3.22	1.43 <sup>c</sup>

<sup>a</sup> At a density of 0.35 g/ml. <sup>b</sup> Interionic distance in the crystals from N. K. Adam, "Physical Chemistry," Clarendon Press, Oxford, 1952, p 197. <sup>c</sup> HBr bond distance, gas phase.

as the sums of crystallographic ionic radii,  $r_+ + r_-$ .  $\Delta H_s$  is exothermic for the ion-pair dissociation process, in accord with the view that this process is attended by a net increase in the numbers of water molecules specifically solvating the ions. Note that  $\Delta H_s$  tends to become more negative as the solvent density decreases. The water molecules being specifically bound to the ions in this process are being removed from bulk water and transferred to the immediate neighborhood of the free ions. The removal of water molecules from bulk water must be attended by the rupture of hydrogen bonds. At lower water densities, it is expected that the fraction of water molecules in an H-bonded condition would be less than at higher densities.<sup>13</sup> I believe then that the observed trend in  $\Delta H_s$  with water density is a reflection

of the smaller energies required to remove water molecules from bulk water as the density decreases.

The distances of closest approach,  $a$ , are much smaller than values for the alkali metal halides usually obtained from slopes of isothermal  $\log K$  vs.  $1/D$  plots in water-dioxane mixtures;<sup>14</sup> the  $a$  value for NaCl at high dioxane content is found to be 6.9 Å in this system. The  $a$  values found in the present treatment, Table II, are even slightly smaller than the sums of the crystallographic radii. I shall not argue that these small  $a$ -values are real; the electrostatic model is primitive, attractive forces other than simple charge-charge interaction are involved, in addition to repulsive forces of a form which can only be guessed. The macroscopic dielectric constant  $D$  factor is only a crude representation of the real reduction in charge-charge interaction due to polarization of the solvent molecules by the intense electric fields surrounding the ions. It must be admitted that until the contribution of specific ion-solvent interaction to the ion-pairing process can be separated experimentally and understood theoretically most distances of closest approach contain this variable (polarization of the solvent molecules by the ions) as a hidden parameter. The ion pairs formed at 25° in water-dioxane mixtures may well be solvent-separated while those formed at high temperatures and low densities in water fluid are contact ion pairs. Both species may be present to an appreciable extent in both systems. An effort to experimentally determine the separate influences of specific ion solvent interaction and charge-charge interaction in the water-dioxane system would be profitable in this connection. I understand<sup>15</sup> that high-temperature-high-pressure conductance measurements are being carried out on alkali metal salts in water-dioxane mixtures. It is strongly urged that measurements of the dielectric constants of the solvent systems be carried out to as high a precision as possible. Analysis of the results of these experiments using the approach suggested here would then throw further light on the problem of the distance of closest approach.

(14) R. M. Fuoss and K. L. Hsia, *Proc. Natl. Acad. Sci. U. S.*, **57**, 1550 (1967); **58**, 1818 (1967).

(15) Private communication from W. L. Marshall.