

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° (their complete dissociation constant), a value of n , and ΔE_v° (related to the change of K° with temperature). The present approach requires values of ΔH_s at each solvent density and a constant a , and one value of K_d at some temperature.

Ion-Pairing Parameters. Values of ΔH_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 ^a | 29.8 ^a |
| 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 ^c |

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

as the sums of crystallographic ionic radii, $r_+ + r_-$. ΔH_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 ΔH_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.¹³ I believe then that the observed trend in ΔH_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;¹⁴ 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 understand¹⁵ 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.