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 CH_3CN protons. The bound resonance was 35 Hz downfield from free acetonitrile in $AlCl_3$ solutions and 33 to 37 Hz in the $Al(ClO_4)_3$ 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[6] of $Al(ClO_4)_3$ in $H_2O–CH_3CN$ which shows the bound CH_3-CN at about 57 Hz downfield from free CH_3CN. It is interesting to note, however, that the bound proton peak for acetonitrile when $(NH_3)_2Pt(ClO_4)_2$ is the solute is also 35 Hz downfield from bulk CH_3CN.[21]

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,[2] 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.[3] This view is quite contrary to that taken by most workers in the field of electrolyte solutions.[4]

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)

$$Na^+, Cl^- \rightleftharpoons Na^+ + Cl^-, K_d =$$

$$[Na^+][Cl^-]y^2_{\pm}/[Na,^+Cl^-] \quad (1)$$
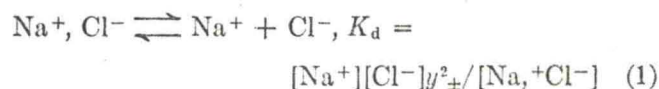
where $[Na,^+Cl^-]$ represents the molar concentration of the ion pair, $Na,^+Cl^-$, and $y_{\pm}$ is the mean ionic activity coefficient calculated using the Debye–Hückel equation. I shall be concerned in this report with the correlation of the values of K_d obtained by Marshall and coworkers with the 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,[5] K_d. The magnitudes of the changes in the values of K_d as the solvent system changes can be illustrated by one example;[2b] for NaCl at 400°, $-\log K_d = 4.43$ at $d = 0.30$ g/ml, dielectric

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(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.*