Experimental Section

Materials. Dimethyl sulfoxide was dried over CaH_2 and distilled at 2 mm. Tetra-*n*-butylammonium hydroxide, 10% aqueous (Eastman), was titrated with HCl and found to have the composition $(n\text{-}C_4H_9)NOH \cdot 130.9H_2O$. Tetra-*n*-butylammonium tetra-*n*-butylboride (Alfa Inorganics), mp 99–103°, was recrystallized from isopropyl ether, mp 111–112° (lit.[9d] mp 110.6–112.0°).

Heats of Solution. The calorimeter and the procedure employed have been described previously.[8c]

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On the Possibility of Like-Charged Ion Pairing in Solution

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Abstract: Previous experimental work provides evidence for strong cation–cation interactions in water. Using a kinetic approach it has been shown that for large ions there is a reasonable probability of forming stable cation pairs despite the repulsive potential. The lifetime of such dimers is comparable to the lifetime of usual ion pairs.

In recent years much attention has been given to the study of tetraalkylammonium salts in water and other solvents. Atkinson has stated that the $R_4N^+X^-$ salts exhibit some of the most complex electrolyte behavior seen to date.[1] There is no doubt that, in water, much of the observed behavior is due to ion–solvent interactions.[2] Nevertheless, a multitude of experimental findings indicate that strong cation–cation interactions occur. The techniques used in these investigations include emf measurements,[3] ultrasonic absorption studies,[1] nmr studies,[4,5] and measurements of volume changes upon mixing.[6] The possibility of cation pairing has been considered in a few cases.[1,5,7,8] While the concept of a stable cation pair is somewhat difficult to accept without invoking some type of attractive forces between the cations, no such forces are necessary. The simple sphere in a continuum model can qualitatively predict that such species might exist.

We must define ion pairs as any pair of ions which are in contact, without regard for the duration of such contact, and without intervening solvent molecules. This definition is the one adopted by Fuoss for the calculation of association constants between ions of unlike charge.[9] The equilibrium constant for association can be calculated by taking the ratio of the rate constant for the formation of ion pairs (which we will take to be the rate at which ions collide) to the rate constant for the dissociation. If the interionic forces are purely electrostatic, it is reasonable to assume that the rate constant for the formation of the pair is equal to the diffusion-controlled rate constant, k_D, calculated by Debye[10]

$$k_D = C(D_A + D_B)\frac{afN}{1000} \qquad (1)$$

with D_A, D_B the diffusion coefficients of species A and B, respectively, a the ion size parameter, N Avogadro's number, and C a constant equal to 4π for distinct species A and B, equal to 2π for a dimerization.[11]

The factor f is given by

$$f = \left[a\int_a^\infty e^{u/kT}\frac{dr}{r^2}\right]^{-1} \qquad (2)$$

where u is the potential energy of interaction between the ions. u is taken to be the coulombic potential

$$u = \frac{Z_A Z_B e_0^2}{rDkT} \qquad (3)$$

with Z_A, Z_B, the charges of the ions with their algebraic signs, e_0 the charge on the electron, r the distance between ions, and D the dielectric constant; other symbols have their usual significance.

Using this value for u, f becomes

$$f = \frac{Z_A Z_B e_0^2}{DkT}\left[\exp\left(\frac{Z_A Z_B e_0^2}{aDkT}\right) - 1\right]^{-1} \qquad (4)$$

Combining eq 4 with eq 1 yields the Debye equation for ionic combination reactions. This equation has been tested for both like-charged[12,13] and unlike-charged[14] ion combination reactions and found to give reasonable approximations to the experimental rate constants.

The rate constant for the reverse reaction, k_{-D}, can be calculated by means of the treatment derived by Eigen.[15] Using the same approximations as for the forward rate constant gives

$$k_{-D} = \frac{3Z_A Z_B e_0^2}{DkTa^3}(D_A + D_B)\left[1 - \exp\left(\frac{-u(a)}{kT}\right)\right]^{-1} \qquad (5)$$

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where $u(a)$ is the coulombic potential evaluated at $r = a$ and where the Z values again have their algebraic sign.

By taking the ratio of k_D to k_{-D} the association constant can be calculated

$$K_A = \frac{k_D}{k_{-D}} = \frac{CNa^3}{3000}\exp\left(\frac{-u(a)}{kT}\right) \tag{6}$$

For unlike-charged ions, $-u(a)/kT$ is equal to the Bjerrum parameter, b, and $C = 4\pi$. The equation is then identical with that derived by Fuoss[9] for the same physical situation. For like-charged ions, the equation becomes

$$K_A = \frac{2\pi Na^3}{3000}\exp\left(\frac{-u(a)}{kT}\right) \tag{7}$$

Using eq 7 we can now estimate the association constant for like-charged ion pairs. The expression contains two terms, the preexponential and the exponential term, each of which is a function of the ion size parameter a. The exponential term asymptotically approaches unity as a increases while the preexponential term increases with the third power of a. The product of these two terms therefore approximately increases with the third power of a in the range of ionic sizes where the exponential is a slowly changing function of a.

Substituting values of D, k, T, etc., for water at 25° into eq 7 gives a value of K_A equal to unity for a equal to about 11.5 Å. This means that a cation of radius greater than 5.75 Å could dimerize in water with a resultant decrease in the free energy. Examination of crystal radii of tetraalkylammonium ions[16] indicates that the tetra-*n*-heptylammonium ion is sufficiently large to fulfill this requirement. For the tetrabutylammonium ion ($r = 5.00$ Å), the calculated K_A for cation association is of the order of 0.6. This indicates that there would be a moderately large degree of cation pairing in concentrated solutions of tetrabutylammonium salts. For the smallest tetralkylammonium salt, the tetramethyl, the calculated value of $K_A = 0.15$ while the largest common monatomic ion, iodide ion, gives an anion dimerization constant of $K_A = 0.02$. Hence the tetraalkylammonium ions are considerably different from the common univalent ions with respect to the ability to dimerize.

One might expect that such complexes would be too short lived to be true chemical species. The lifetime of such a complex can be estimated by means of eq 5. The value of k_{-D} calculated is 4×10^9 sec^{-1} for the dissociation of the tetrabutylammonium dimer in water. This is quite comparable to the value of k_{-D} calculated for the dissociation of Bu_4NI in acetone[14] ($k_{-D} = 2 \times 10^9$ sec^{-1}).

There is of course the possibility of additional "attractive" forces. Diamond[17] has proposed that the solvent structure enhances ion pairing when both ions are large. Such an effect could increase the importance of the like-charged ion association when there is a great difference between the size of the cation and the anion.

In order to investigate the importance of solvent structure on like-charged ion pairing, some of the experimental techniques previously used for aqueous systems might be applied to a mixture of water with *N*-alkylamides. Such solutions have dielectric constants greater than that of water.[18] The structure of the pure solvents, however, would be destroyed in the mixtures and hence the influence of solvent order should be more plainly evident.

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