

SUMMARY

The present thesis deals with the elucidation of the "local" modifications of the structure of water (the solvent) in the neighbourhood of solute molecules that are largely hydrophobic in nature. For the purpose, transport studies, such as those manifest in the viscosity B coefficient as well as the diffusion of these solutes, have been conducted, and the data interpreted in terms of the solute-solvent interaction on the basis of the "flickering cluster" model for water structure. A larger emphasis in course of such investigations has been put on the viscosity studies.

The solutes chosen have been the organic electrolytes such as alkyl carboxylates and the organic non-electrolytes such as phenols and benzyl alcohol. The viscosity B coefficients have been determined at a number of temperatures in the range of 30°C to 40°C. The temperature coefficient of B, i.e., dB/dT has also been ascertained. The B values of these organic compounds are generally large, and in a homologous series, the numerical values of B increase with the size of the solute molecule. Introduction of a hydroxyl group into the solute molecule results in a sharp reduction in B, while the hydrophobic methyl/methylene group causes a rise in B. Aromatic compounds generally have smaller values of B than saturated aliphatic compounds with the same number of carbon atoms.

Depending upon the relative strengths of "structure-making" and "structure-breaking" influences that result from the net content, as well as the relative proximities of hydrophobic and hydrophilic groups in the molecule, the B values have been different, and the trends analysed in the light of the theory of "hydrophobic hydration". In addition, in some cases, intramolecular hydrogen bonding, "aromaticity"- its full retention or partial loss - and partial overlapping of the spheres of influence of successive groups in a molecule are invoked to explain the relative efficiencies of the various characteristic (and/or substituent) groups, in question, towards "local" structure enforcement or disruption in water; the latter is reflected in the overall B coefficients.

The B values and their temperature coefficients, dB/dT , have been correlated with the thermodynamic parameters such as partial molal volumes, partial molar heat capacities, entropies of transfer from water to heavy water, heat and entropy of transport etc., which are also taken as measures of solute-solvent interactions. Furthermore, the semi-quantitative model of Agar and Sanyal (1978), regarding the correlation between entropy of transport of alcohols and the corresponding entropies of hydration, has been found to hold good in the case of the present alkyl carboxylates as well (with some approximations though), in that a similar correlation, involving the B values of the carboxylates, has been worked out.

As an associated work, the principle of additivity of the viscosity B coefficient has been tested for the mixtures of weak acids and their salts, and the degree of dissociation (α) of

acetic acid and propionic acid have thus been calculated, and compared with the α obtained from direct pH measurements. The concept of such "extended" additivity has subsequently been applied to more heterogeneous a system, such as soil organic matter, where attempts have been made to determine the state of conformation of large polymers such as humic acid and fulvic acid (components of soil organic matter) in aqueous medium. To interpret the experimental data, a semi-quantitative model has been developed to have an idea about the shape (nature and extent of coiling) of such macromolecules of natural origin.

Lastly, the mutual diffusion coefficients of the present solutes have been determined at 30°C by adopting the Stokes diaphragm diffusion technique, and the data interpreted in terms of the classical hydrodynamic treatments.