

GENERAL INTRODUCTION

It has long been recognised that water belongs to the class of "anomalous" liquids in that many of its properties differ essentially from those of 'normal' liquids of simpler structures. The deviations from regularity indicate some kind of association of water molecules. Probably, the earliest suggestion that liquid water might contain some "solid particles" was made in 1884¹, followed in 1891 by Vernon², who postulated the existence of some aggregation of water molecules in order to account for the phenomenon of maximum density at 4°C. A year later, Röntgen³ suggested that the water molecules bound together in liquid state might be regarded as "ice molecules", and offered qualitative explanations of several of the apparently anomalous properties of water. The latter have fascinated the Physicist and the Chemist as well, for a very long time as to the possible structural arrangements that may be responsible for imparting very unusual properties to water. The importance of such understanding lies in the realisation that one of the most fundamental problems in the realm of aqueous solutions concerns with the effects the unique structure of water exerts on various processes that take place in these solutions. Concepts like "structure-making" and "structure-breaking" solutes appear almost in every discussion of the physicochemical properties of aqueous solutions. In fact, a more general concept would be the "structural changes in the solvent", induced by any process, not necessarily the dissolution process, which occur in aqueous solution. The latter holds a particular

prominence in biochemistry, where it is recognised that understanding of the "structural changes in the solvent" may be crucial to the study of the role of water in biological systems.

That a clear knowledge about the solvent structure is a pre-requisite for a thorough understanding of the properties of the solutions is exemplified in many a cases where anomalies as well as the deviations from the expected trends of experimental results can not be suitably accounted for owing to an unjustified ignorance of the effects of the medium. Thus, for instance, the concept that the relative acidities of alcohols in aqueous solutions are governed by the electron-repelling effects of the alkyl groups (independent of the medium) is merely a popular textbook justification in that a reversal of such acidities is observed in the gas-phase⁴. Furthermore, the yet unresolved anomalous observations such as those on viscosity - composition maxima, and negative relative partial molar volumes, exhibited by the hydroxy organic compounds⁵ in aqueous solutions, present cases where a solution has to be sought possibly in terms of the changes, brought about by the solutes, in the structure of water.

It is rather interesting to note in this context that there is as yet no satisfactory and undisputed agreement among workers in the field regarding the structure of water, the most widely used and studied liquid of importance, despite an exhaustive amount of investigations (of diverse kinds) conducted so far on the elucidation of properties of water and aqueous solutions. Controversy reigns as to the choice between the continuum and mixture model theories for water structure⁶.

For various reasons it may be a useful proposition to study such structures in terms of the modifications brought forth by the dissolution of solutes, which manifest themselves in various properties of aqueous solutions. In particular, solutes of different types (exhibiting different hydration behaviours) may be chosen, and their properties referred back to a unique structural model for water as present in these aqueous solutions. A convenient tool in such elucidation of the nature of solute-solvent interactions involves the studies of transport properties of solutions such as relaxation of the dielectric polarisation and of spin through lattice, conductance, viscosity and self-diffusion. In the present thesis, diffusion and viscosity behaviour of aqueous solutions of a number of solutes, namely organic electrolytes and a number of (mixed) largely hydrophobic non-electrolytes have been followed, and the results have been interpreted (at a qualitative level) in the light of the solute-solvent interactions, on the basis of the "flickering cluster"^{7,8} model for water structure. In addition, an attempt has been made to extend the principle of additivity of the viscosity B coefficient to mixtures, and further invoke such extended additivity to work out the conformation of large molecules. The hypothesis is tested with a polymer of natural origin, i.e., humic acid, a fraction of soil organic matter, as well as such smaller molecules as "synthetic humic acids".

Regarding the transport of solutes by diffusion, the most convincing method for understanding the relationship between the diffusion coefficients of substances, and the structural changes caused by them in aqueous solutions, seems to be the determination

of self-diffusion coefficient of water in the presence of dissolved solutes. The latter were not, however, determined for certain experimental limitations. Instead, the mutual diffusion coefficients of the present (largely hydrophobic) solutes have been measured in aqueous solution, using the Stokes type of diaphragm diffusion cell⁹, followed by the concentration analysis by the conductometric titrations and the spectrophotometric determinations. Such mutual diffusion coefficient data are, by themselves, of interest in view of a general non-availability of the diffusion data in the literature, and in particular, those for the present solutes. Furthermore, the consideration that these diffusion coefficient data may be of importance in establishing correlations between diffusion and other processes in solution that characterise the complex transport phenomena (especially in biological and industrial processes), emphasises that it will not be out of context to present the mutual diffusion coefficients of the given solutes, and briefly discuss them in the present thesis.

Some of the data presented in the thesis have already been published, while some others have been communicated for publication. The reprints of the published papers (including those accepted for publication) are enclosed at the end.

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