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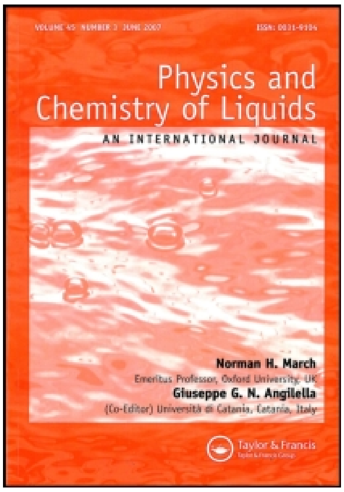

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Letter

Does Solvent Structure Underlie Osmotic Mechanisms?

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Intermolecular interactions in liquids are proposed to give rise to dynamic structures which are propagated as a wave through the medium. In the pure solvent the wavelength of this motion, which determines the size of the oscillating clusters, is set by the thermodynamic conditions. However, the presence of solutes shortens the wavelength thus decreasing cluster size. At the solvent-solution boundary the differently sized clusters interact to bring about equilibrium. This picture provides us with a simple interpretation of osmotic effects.

The thermodynamic interpretation of colligative properties is the dilution of solvent by solute. However, on viewing this interpretation in terms applicable at the molecular level, several weaknesses become apparent. Firstly, rigorous derivation yields functions which depend on mole fraction, which in turn means that colligative phenomena arise because of solute displacement of solvent, molecule for molecule, without regard to size. On the other hand, experiment shows that colligative properties vary rather with volume, or mass, concentration as readily seen in the case of large solutes. Another difficulty, especially serious for those workers interested in molecular mechanism, is the absence of intermolecular interactions required by the thermodynamic interpretation. However, it is simply not possible today to present models without taking into account solvent-solvent and solvent-solute interactions, unless one dismisses a whole area of recent research in the fields of physical, colloid, interface and biological chemistry, which clearly establishes the importance of these forces. Another factor is the increasing emphasis given to other explanations of colligative properties, as exemplified by Hammel's recent series of papers[1,2]. Alternative ideas are beginning to receive serious attention precisely because they contain notions of mechanism which unavoidably confront workers in the colloid and biological fields.

In the model described here, in contrast to the view of classical thermodynamics, colligative properties are presented as being the direct outcome of structuring within the liquid. Intermolecular interactions are assumed here to involve much more than in the usual picture where a molecule interacting with its surroundings is described by a potential energy well. The interactions are co-operative and as a result impose definite kinetics on local structural changes, because neighbouring molecules influence each other as they move to fit into and break away from transient aggregates. Thus clusters do not flicker on and off at random, but regions of order and disorder are propagated with definite size and velocity through the bulk liquid medium, just like continuous polymerization and depolymerization reactions[3]. For an idealized picture we take the illustration from the well-known text of Eisenberg and Kauzmann[4] on water structure. It is based on an idea of Frank and Wen[5], and depicts the to-and-fro flickering of a cluster as a sinusoidal function of time. Using the arguments above, it is an easy step to interpret the illustration as three neighbouring regions in the liquid, then we have a wave function in distance as well and coherent wave motion results. The motion is all-pervading and in the pure solvent travels unhindered in three dimensions setting up stationary structural oscillations. In this way we picture the medium subdivided into equally sized regions, each contained within the cube having an edge of one wavelength representing the basic oscillating entity, the wave unit with

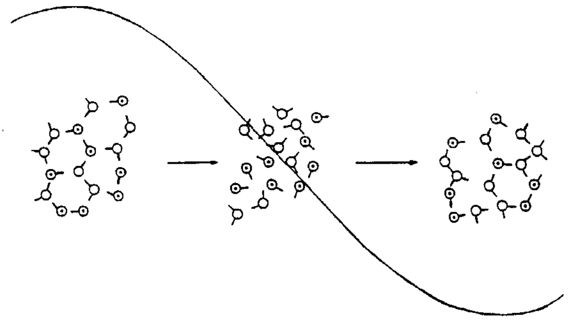

Figure 1 Illustration of the flickering cluster within the structure of liquid water taken from Eisenberg and Kauzmann[4]. The arrows indicate time intervals, but if taken to be distance as well then definite wave motion emerges, in which the cluster can be imagined to be either travelling or stationary.

volume u_0. At the corners of the cubes neighbouring units meet forming the nodes where no structural movement takes place. The number of nodal positions equals the number of units.

The introduction of solute particles into the medium sets restrictions on the movement of the solvent molecules. Those molecules in the first hydration layer closest to the solutes can no longer rotate as freely as before. Their motion must become subject to new constraints, whatever the nature of the solute-solvent interaction. This means an extra node will locate itself at the position of each solute. This idea should not be taken as a peculiarity of the model of liquid structure presented here. On the contrary, a localized obstacle to the movement of any vibrating system will in general produce a node. As a consequence, there will be an increase in the concentration of wave units, because their volume is smaller owing to the shortened wavelength and so the concentration of solutes or number of extra nodes reads

$$z = \frac{1}{u} - \frac{1}{u_0} \tag{1}$$

In the usual situation where osmosis occurs, solvent and solution are separated by a semipermeable membrane. Since the solvent can move through this membrane it can be considered as a single continuous medium pervading both phases. This means in turn that the structure wave can pass unhindered from one phase to the other transferring structural energy as it does so. We must, therefore, look at this boundary for the conditions which determine equilibrium and ask, how does raising the pressure, P, on the solution ensure smooth passage of the wave resulting in no further changes?

To see this question in more familiar terms we use the gas analogy, in which two perfect gases, separated by a membrane they can cross, set up imaginary osmotic equilibrium. One of them, equivalent to the solution, has a higher concentration of molecules, equivalent to the smaller sized wave units, and so is at the higher pressure. These molecules must also have lower speed to ensure that an equal number reaches the membrane from each side in a given time so there is no net transfer of material. Then they must also have higher mass to keep the kinetic energy per molecule, or temperature of the two gases, equal. This situation is equivalent to an equilibrium because the transfer of molecules from each side produces no change, i.e. there is exchange of molecule for molecule each carrying the same energy. But on transfer, the molecules must take on the properties, mass and velocity, of the other gas, and although real molecules cannot do this, a wave can. There are numerous examples of physical processes where a wave changes its character at a boundary while the system remains in equilibrium[6]. Returning now to the liquid case, we have exchange of wave unit for wave unit across the boundary, and to ensure no net transfer of energy we need

$$Pu = P_0 u_0 \tag{2}$$

which states that each unit contains the same amount of structural energy. In fact, we expect this result if in the analogy the volume of a wave unit is taken to be the volume occupied by one molecule of gas, because it simply expresses Boyle's Law, which must hold in the case of the gases. It therefore leads to the conclusion that the units of the structure wave behave like the molecules of a perfect gas and so obey the gas equation

$$P_0 u_0 = kT \tag{3}$$

where k and T are Boltzmann's constant and temperature. Now, Eq. (2) can be rewritten using Eqs (1) and (3) to give the osmotic pressure

$$P - P_0 = zP_0 u_0 \tag{4}$$

or

$$\prod = zkT \tag{5}$$

When van't Hoff proposed this expression, its form implied that the solute molecules, whose presence is indicated by their concentration z, must be the analogs of gas molecules; and hence the bombardment theory. In the model here however, z arises from the smaller size of the wave units in the solution compared to the solvent. This implies that it is the structure wave itself, and not the solutes, which governs the molecular motions underlying osmosis. In the following note this concept is extended to give a simple explanation of the other colligative properties.

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