



## Solvent Cluster Size and Colligative Properties

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## Letter

### Solvent Cluster Size and Colligative Properties

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It is proposed that the occurrence of colligative phenomena is a result of structured aggregates of solvent molecules which exist within the liquid medium. In a solution these formations are smaller than in the pure solvent. Using simple kinetic arguments it is shown how this difference in cluster size shifts the equilibria which establish vapour pressure, as well as the boiling and freezing points.

In a foregoing note it was proposed that local structuring in liquids can take on well-defined concerted, as opposed to random, fluctuations<sup>1</sup>. According to this idea, regions of more or less structure do not flicker on and off unpredictably but travel as a wave form through the medium. In a uniform homogeneous liquid all molecules can move equally freely and so are able to rotate to fit into or break away from a passing region of structure. In such a medium without restraints the wave travels unhindered in three dimensions and can set up stationary fluctuating clusters. So we envisage the basic wave unit to be contained within the cube of volume,  $u_0$ , determined by the wavelength. It was found that the size of these units responds to pressure,  $P_0$ , and temperature,  $T$ , as though they were molecules of an ideal gas

$$P_0 u_0 = kT \quad (1)$$

The introduction of solute particles into this medium sets restrictions on the movement of the solvent molecules. Those molecules in contact with the solute, i.e. in the first hydration layer, can no longer rotate as freely as before. This means an extra node in the vibration of the solvent will locate itself at the position of each solute. As a consequence the

wavelength will be shortened and the wave units in the solution no longer follow the Gas Law

$$P_0 u < kT \quad (2)$$

In the case of a gas the smaller volume,  $u$ , would correspond to a compression and thus increased pressure. In the situation where osmosis can occur, it was argued that the osmotic pressure behaves analogously to such an increased pressure and the units in the solution, now in equilibrium with those in the solvent, again obey the Gas Law

$$Pu = P_0 u_0 = kT \quad (3)$$

In developing this model, the concept of exchange of wave units between the two phases was used to determine the equilibrium state. These units were depicted as independent entities able to behave in some respects like molecules. Thus, although at any instant they are formed out of an interconnected cluster of molecules, they can also be viewed as individual packages of defined size.

When the solvent is in equilibrium with its own vapour as a closed two-component system, the pressure becomes the vapour pressure for temperature  $T$ . The cause of the drop in pressure due to the presence of solute molecules is usually attributed to the corresponding fall in the mole fraction of solvent molecules. However, as pointed out previously<sup>1</sup>, it is difficult to visualize how a given number of solutes displaces, or directly affects, an equal number of individual solvent molecules. The concept of wave units introduces the idea that vaporization of the unit as an entity, rather than the escape of single molecules, determines the amount of solvent in the vapour. Under the assumption that the presence of the solutes affects only the size of the vaporizing unit, i.e.  $u_0$  is reduced to  $u$ , correspondingly fewer molecules enter the gas phase and the pressure falls by the factor  $u/u_0$ , which is in inverse proportion to the volume concentration of the solutes. This shows that the changed value of the vapour pressure is determined by simple spacial considerations within the liquid and not by the displacement of individual solvent molecules by individual solute molecules.

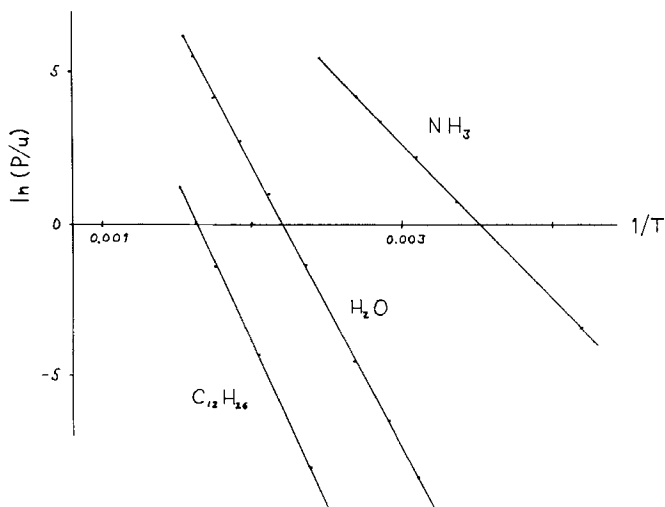
At equilibrium we have the kinetic requirement of equal rates of evaporation and condensation. As the latter is directly proportional to the vapour pressure, the arguments above lead us to the relationship

$$P = ru \quad (4)$$

where  $r$  is the ratio of the rate constants and so represents an equilibrium constant. This can be tested in the case of the pure solvents, since the volume,  $u$ , can be calculated from the vapour pressure using

Eq. (1). In this way the temperature dependence of  $r$  can be checked. I have plotted the function  $\ln(P/u)$  against  $1/T$  for over 30 liquids up to their critical points, covering a wide range of polarity, temperature and pressure. The plots are linear in every case as shown for the three representative examples in the Figure.

The explanations for the elevation of boiling point and depression of freezing point are usually argued via the reduced vapour pressure using inspection of the phase diagram<sup>2</sup>. Here again, the concept of the wave unit as the entity involved in the process of evaporation or crystallization, as opposed to single molecules, provides a very simple explanation. These properties are observed when comparing two systems, solvent and solution, at the same imposed external pressure, usually one atmosphere. Both are brought to the equilibrium temperature for the solvent, i.e., its boiling point in the liquid-vapour case or its freezing point in the liquid-solid case. Then, following the kinetic argument leading to Eq. (4), we expect boiling to stop while condensation proceeds, or crystallization to stop while melting proceeds, in the solutions. In each case the shift in equilibrium is simply caused by the smaller size of the wave unit in the solutions. These arguments further illustrate how it may well be the existence of intermolecular interactions



**Figure 1** Log Plot of ratio  $P/u$  in  $\text{atm}/(\text{nm})^3$  against reciprocal temperature for *n*-dodecane, water and ammonia. The upper end of each line represents the critical point. These 3 lines cover the temperature range from  $-34$  to  $386^\circ\text{C}$  and pressure range from  $0.0060$  (triple point of water which lies on the line at  $1/T = 0.00366$ ) to  $218$  atm. Data from CRC Handbook of Chemistry and Physics, 55th Ed., pp. D158-D189.

producing structured formations within the solvent, rather than their absence, that is directly responsible for colligative behaviour.

### References

1. J. G. Watterson, *Phys. Chem. Liquids*, preceding article.
2. S. Glasstone, "Text Book of Physical Chemistry" (MacMillan & Co., 2nd Ed., London, 1960) pp. 642-644.