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30th October 1992

Details withheld at client's request

I hope that the following collection of thoughts is helpful. I feel that a list of recommendations is now required and that this list should be composed after consultation with you.

Regards

Wayne Davies

**Supercritical Water - A Review, Report and Collection of Thoughts**

**Thoughts on Structure and Solvent Properties**

Ordinary water can be thought of as an extended molecular network. The molecules of H<sub>2</sub>O represent the simplest but not very structural formula for water. As a liquid this material is really a large macromolecule held together by hydrogen bonds i.e. (H<sub>2</sub>O)<sub>n</sub> where n can be a large number (100 or so) which tends to increase as the temperature drops and vice versa. The macromolecules of liquid water is not constant however and the individual H<sub>2</sub>O's which make them up do not remain with the same macromolecule but exchange with their neighbours at high frequency. This is reason for the use of the term "flickering clusters". The dipole moment of water is high owing to the bond angle of the hydrogen-oxygen-hydrogen configuration which is less than 180 degrees. Electrons attracted to the oxygen make it slightly negative leaving the hydrogens slightly positive. This imbalance of charges gives rise to "hydrogen bonding" i.e. the attraction of adjacent oxygens to hydrogens of a different water molecule. The extended network of these hydrogen bonds gives the unique properties of water that we are aware of, i.e. high boiling point, relatively high viscosity, good solvent properties for polar materials etc. Water's ability to dissolve ionic species is more a function of the dissociation of ions and their hydration by water than its hydrogen bonding ability.

As the gas, water molecules are effectively in a monomolecular state. The distances between them are too large to allow hydrogen bonding and their kinetic energy is too great to allow molecular interactions to form larger molecules. The dipole moment is still quite high for the same reasons that it is in liquid water, i.e. the bond angle and the electronegativity of the oxygen compared to the hydrogen.

Supercritical water (SCW) can be viewed from two perspectives. It is either (i) the liquid form of water raised in temperature and pressure to the point where liquid water can no longer exist or (ii) the gaseous form of water which has been compressed such that the molecules are forced into close proximity to each other without liquefying. In either case a new state of matter has been produced. The curious thing about SCW is that the dipole moment is very much reduced compared to the liquid form and is comparable to the values of non-polar solvents, eg benzene, aliphatics, ethers etc. which SCW begins to resemble in terms of its solvent properties. This can be explained by the following tentative model:

Under the extreme temperatures required for SCW to form, liquid water is not allowed so the extended macromolecular "flickering clusters" are unlikely to exist. Similarly the effectively free monomolecular state of gaseous water is not allowed either. What may happen on a molecular scale is that the waters form ring structures which resemble benzene as shown below (Fig.1).

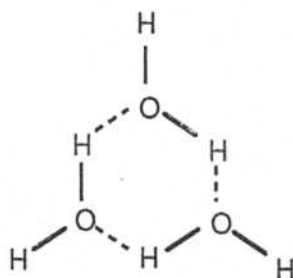


Fig. 1 A Hypothetical Structure for Supercritical Water

These ring structures form an energetically stable configuration with a high level of symmetry, i.e. the dipole moment is low. The hydrogen bonds are effectively forced into existence because the high pressure which keeps the density of SCW high compared to gaseous water. The molecule now resembles benzene in shape and may even have some aromatic quality owing to the potential for delocalising electrons within the ring. This would explain SCW's powerful **non-polar** solvent properties. Removal of one or more hydrogens from the ring would tend to make this structure even more stable by giving one of the oxygens a negative charge with which to attract adjacent hydrogens more strongly. This electron would not remain with just one oxygen however and it too would be delocalised, stabilising the complete ring structure. This may help to explain the function of alkali eg sodium hydroxide which improves the solvency of SCW for coal. In the presence of alkali one of the hydrogens may be removed from the ring. This would leave a type of hydrated "supercritical hydroxide ion" which then may chelate a sodium ion to give a net neutral complex of relatively low polarity. The fig. below offers a molecular model for this hypothesis.

try to discover  
some anticorrosive  
coatings for SS  
eg. Think of anodes  
aluminum para starter.

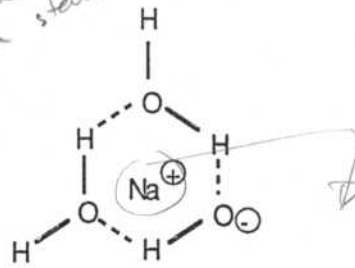


Fig.2 A Hypothetical Supercritical Hydroxide Complex

See box in  
water gas shift  
paper Show at  
see colour only.  
see (F)

Some conclusions from these hypotheses follow. If sodium forms a complex like the above then potassium would form an even better one. Potassium has a lower energy D-shell of electrons which is more accessible to oxygen's electrons. A complex made with potassium would be more stable than a sodium complex. It may have a lower dipole moment and therefore even better solvent properties for hydrophobic materials. *d-shell*