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CLATHRATE STRUCTURES AND THE ANOMALIES OF SUPERCOOLED WATER

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ABSTRACT: Many small hydrophobic molecules or molecules with a hydrophobic group form stoichiometric clathrate compounds with water at low temperature. The water in these compounds forms a relatively strain free, hydrogen bonded cage in which resides the hydrophobic entity. It is significant that dilute aqueous solutions of such molecules often show nonideal behavior such as enhanced temperatures of maximum density and specific heats, and binary liquid phase stability. Furthermore it has been shown that the anomalous properties of supercooled water can be enhanced by the addition of small hydrophobic entities. Recent SAXS data on extremely supercooled water showed the correlation length to be nondivergent, which is inconsistent with a critical phenomena type description of water's supercooled anomalies, but can fit with a picture wherein clathrate-like structures are forming. In this paper I will present a broad ensemble of evidence to support the contention that clathrate-like structures of hydrogen bonded water molecules form in liquid water, more so as it is cooled, and that these structures are responsible for the apparent anomalous behavior of supercooled water.

INTRODUCTION

All of us can readily agree that water is a most remarkable substance. It has a number of very rare and even unique properties. It expands upon freezing and the liquid state has a temperature of maximum density, at low temperatures its viscosity decreases with increasing pressure, it has anomalously large melting and boiling points, specific heat and dielectric constant. Its isothermal compressibility is large and has a minimum as a function of temperature. It is the most abundant liquid on the surface of the earth, it shapes our world, and it is the milieu of life.

The beginning of our understanding of these remarkable properties comes from the special nature of the H_2O molecule. Water molecules readily self-associate with hydrogen bonds of energy comparable to the thermal energy. Furthermore, water has a unique balance in that it can both donate and accept two protons to form as many as four hydrogen bonds to any molecule. In addition, these four bonds are arranged in a space filling nearly tetrahedral manner. Thus water has a unique ability to create a network~~s~~ of four-bonded molecules, more so with cooling, that is less dense than an unassociated structure. Herein lies the key to water.

Water became even more remarkable in 1976 when Speedy and Angell [1] showed that liquid water's properties became even more unusual when supercooled.[2] Apparent divergences in the specific heat, compressibility, thermal expansivity and a host of other properties were demonstrated. An outstanding example is the specific heat at constant pressure behavior shown in Fig. 1. Speedy and Angell also showed that all these properties could be described by a power law divergence of the form

$$X \sim (T-T_s)^{-x} \tag{1}$$

for property X with $x > 0$ all with the same $T_s \simeq -45°C$. Given the similarity of Eq.(1) to the behavior of properties near a second order critical point, the implication was that perhaps some sort of critical point exists in liquid water, deep in the supercooled regime at -45°C.

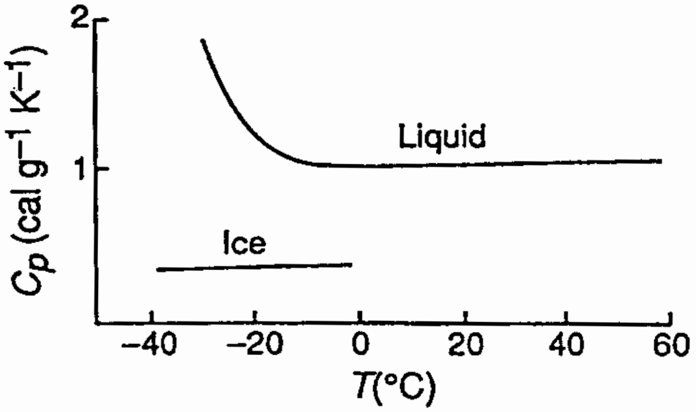

Figure 1. The specific heat of liquid water and ice as a function of temperature.[2]

The problem is that water homogeneously nucleates before -45°C is reached. Most experiments have been limited to ca.-20°C (roughly a heterogeneous limit), -34°C (the homogeneous limit for large samples), or -38° to -40°C (the homogeneous limit for small samples). Thus Eq.(1) is based on an inference of extrapolation. Despite this, the "sameness" of -45°C for so many properties is hard to ignore and significant interpretations have been proposed to use -45°C as a true singular temperature on a line of second order critical points, most likely a spinodal.[1,3]

We study these anomalous and perhaps singular behaviors of supercooled water for their own sake and because they are a window to water in general. That is, if we study water in the supercooled regime where it shows its uniqueness so well, then what we learn there will aid us in a description of water at all temperatures. In our work we have tried to understand what self-associating structure forms in water, especially when supercooled. The picture we have developed is one in which the structure in liquid water is similar to the gas clathrate hydrates. [4,5] These compounds involve cages of water molecules formed with planar pentagonal and hexagonal sides, examples of which are shown in Fig. 2. The oxygen atoms lie at the verticies of these polygons and the sides are hydrogen bonds. The compounds are typically stable at low temperatures, and despite the vast variety of compounds that can be encaged, the variety of cage structures is small and they are simply related to each other. Indeed, the clathrate cages seem to have an existence separate from the guest molecules with which they interact only weakly. As far as liquid water is concerned, one could view clathrate-like structures as an alternative to the more traditional picture of ice-like structures in liquid water, and the idea is not new.[6] A well connected argument that clathrate-like structures exist in water, more so when cooled, has not, however, been presented. It is the purpose of this paper to fill that void. Our emphasis will be with supercooled water and we will argue that these structures are the cause of the anomalies.

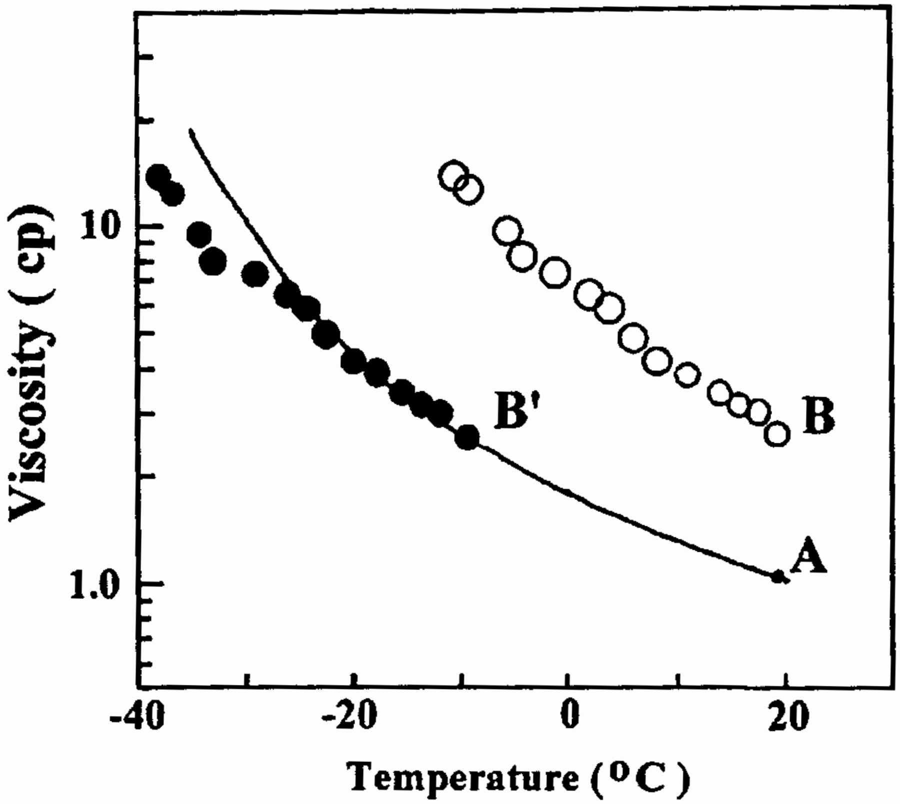

Figure 4. The viscosities of water (solid line) and a 12 mole% ethanol solution (open circles) as a function of temperature. Closed circles are the ethanol data shifted to lower temperature by 29°C.

Connection with the supercooled anomalies comes with the temperature dependence of the ethanol solution viscosities which tell a remarkable story in Fig. 4. Compare the temperature dependence of the viscosity of pure water to a 12 mole% ethanol solution. After the enhancement due to ethanol addition, the temperature dependence of the solution and the pure water is the same. That is if the solution η vs. T curve is shifted to lower temperatures by 29°C, i.e., point B is shifted to point B′ in Fig. 4, the two curves overlap. Our interpretation above was that ethanol addition causes clathrate cage formation which increases the viscosity. That explains the displacement from point A to point B in Fig. 4. The shift from B to B' shows that once ethanol stimulates clathrate cage formation, the viscosity and its temperature dependence are the same as in pure water at a set of temperatures uniformly shifted colder from the solution. Thus we conclude pure water at B′ has the same clathrate-like structure as the solution at B. The cages that formed upon addition of ethanol to move from A to B also formed in pure water on going from A to B′ upon cooling. Hydrazine addition can also cause an increase in the viscosity but yields a completely different temperature dependence. In summary the large increase in water's viscosity upon cooling in the supercooled regime is due to the formation of clathrate-like cages in the liquid.

When we published our results, there was plenty of other evidence available in the literature to support the idea that clathrate-like structures form in water, more so as it is cooled. To further implicate these structures for a role in the supercooled anomalies was easy. The temperature of maximum density (TMD), perhaps water's most "water-like" property, increases upon addition of simple alcohols.[8,9] This increase is critically dependent on the shape of the hydrophobic entity. For example, the globular molecule tert-butyl alcohol (tBA) can increase the TMD by 0.2°C whereas the isomeric n-butyl alcohol only decreases the TMD.[8] The rationalization of this observation is that the globular tBA molecule fits very well into the essentially spherical clathrate cages and hence can act as a template to stimulate their formation, whereas the n-butyl group does not, and hence does not induce the structure responsible for the TMD--clathrate cages. It is important to remark that the interstitial cavities of ice I_h would not hold the tBA molecule, hence it is wrong to invoke the formation of ice-like structures as water is cooled. In fact, tBA is the best enhancer of the TMD and it is also the molecule that best fits a clathrate cage [8,10], being spherical and neither too big nor too small.

Other evidence shows the solubilities of gases increase with decreasing temperatures and the most soluble gases are roughly spherical and have van der Waals radii of 4-5Å, just right for fitting into cages.[10,11] The implication is obvious. The enhancement of the specific heat with dilute addition of alcohols to water is suggestive of the anomalously increasing specific heat in supercooled pure water.[12] Computer simulations have shown evidence for clathrate structures.[13-15] Stillinger argued strongly for "relatively strain free polyhedra of water molecules" similar to the cages formed in stoichiometric clathrates as the possible source for the supercooled anomalies [13], and this was the inspiration for our interpretation. Geiger et al. [15], also found evidence for clathrate-like cages in their simulations of supercooled water at constant density. One wonders what would be seen with a realistic density change.

More direct evidence for clathrate-like structures in supercooled water has come from recent small angle x-ray scattering experiments.[16] These data yielded a correlation length ξ that was essentially constant at ~ 3.8Å down to -34°C. This remarkable result implies that a critical phenomena interpretation of the anomalies may not be viable because ξ should increase with decreasing T. On the other hand the data could readily be interpreted as indicating clathrate-like structures in water of constant radius of gyration of 5Å but with increasing number density with decreasing temperature. Ice-like fluctuations did not work well because their larger mass density required a larger number density to the point where individual clusters would overlap with each other.

An advantageous concept to pursue for the study of supercooled water is that solutes with hydrophobic entities can: 1) act as passive probes of water's structure particularly when supercooled and containing the purported clathrate structures, and 2) enhance the anomalous behavior or promote analogous behavior in temperature regimes above the nucleation limits. We have followed both lines of investigation.

The use of the solute as a probe concept was made with volumetric measurements on aqueous ethanol, tBA and hydrazine solutions.[17] Results for tBA are shown in Fig. 5. Recall that the density of tBA is $0.8 g/cm^3$ at 20°C. One can see that addition of the less dense tBA to water at room temperature decreases the overall density of the solution in a manner consistent with a simple linear combination of the two densities. Note, however, the remarkable behavior near -30°C where addition of the less dense tBA actually <u>increases</u> the density. The implication is that holes exist in supercooled water into which the tBA molecules can fit without significant disruption of the liquid structure. Water is a sponge for the alcohol and the pores in the sponge are clathrate cages.

A quantitative analysis of these data shows the partial molar volume of the alcohols in dilute solution decreases with decreasing temperature until at -40°C, by a short extrapolation, they are roughly 55% of their bulk value. Hydrazine also shows a declining partial molar volume with declining temperature but becomes a large <u>negative</u> value at -40°C. This negative value implies not hole filling, but a wholesale destruction of the volumetrically inflated liquid water structure.

To use a solute as an enhancer of the anomaly we performed dynamic light scattering (DLS) experiments to determine the correlation length of fluctuations, ξ. Given the critical-phenomena-like divergence seen in supercooled water, it is reasonable to argue that at or near -45° some

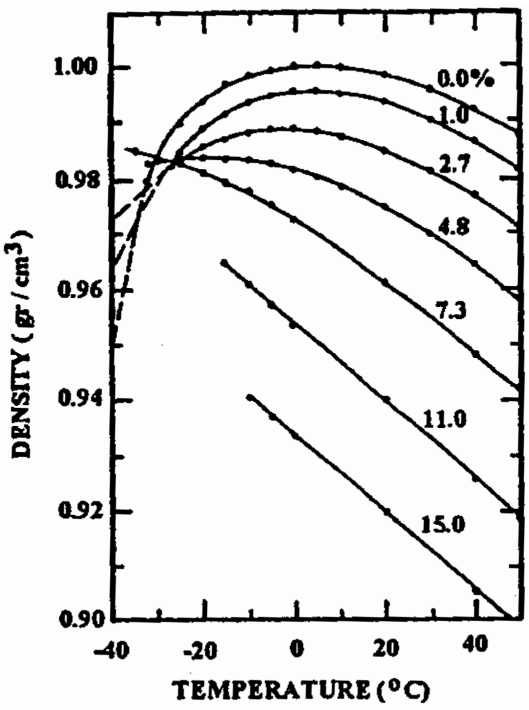

Figure 5. The density of aqueous t-butyl alcohol solutions versus temperature. Alcohol concentrations are given in mole%. Dashed lines are extrapolations of the data.

sort of critical point exists. If so, the correlation length should diverge there. At the time we did our work there was small angle x-ray scattering evidence for increasing ξ with decreasing temperature in pure water, but nucleation intervened when ξ was only 8Å.[18] Would addition of tBA show an enhanced ξ and singular temperature dependence?

We performed DLS on tBA/H_2O solutions.[19] (Water is a very weak Rayleigh scatterer so it could not be studied directly with this technique.) We found ξ had a minimum as a function of temperature. Unpublished data of Ludemann indicated a lower critical solution temperature (LCST) in tBA/KCl/H_2O solutions near 120°C, depending on KCl concentration. If this was zero, there was no LCST; the system was miscible everywhere. We concluded that our increasing ξ with increasing temperature was caused by the LCST in the KCl solutions even though there was no KCl in ours. We used the term "virtual critical point" to describe a critical point not on the particular plane of the phase diagram, in our case the [KCl]=0 plane, but which affects the thermodynamics in that plane nonetheless.

The enhancement in ξ below the minimum was not large but, combined with what we learned above, lead us to propose a lower dome of phase separation, topped by an upper critical solution temperature (UCST). This might be either deep in the supercooled regime or off in another dimension of the phase diagram, i.e., a virtual critical point.

Subsequent work showed the idea of virtual critical points to be true. For instance H_2O and 3-methyl pyridine (3MP) are miscible yet mild critical opalescence occurs near 76°C and 8 mole% 3MP. DLS shows ξ goes through a significant maximum here.[20] Addition of D_2O leads to phase segregation and a closed loop two phase region centered at 76°C. Thus one could claim a virtual critical point exists for the H_2O/3MP system and it can be made real by addition of D_2O. We found that addition of sec-butyl alcohol (sBA) caused tBA/H_2O systems to phase separate in a fascinating series of curves, schematically represented in Fig. 6.[21,22] The lowest UCST (T_{c3} in Fig. 6) extrapolates with $[sBA] \rightarrow 0$ to -30°C and [tBA]=16 mole%. Its presence vindicates, we believe, our analysis above.

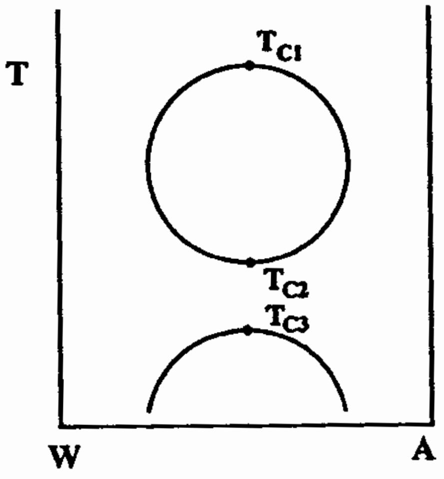

Figure 6. Schematic of a phase diagram of an alcohol (A) water (W) system (e.g., tBA plus sBA in water). Three critical points are indicated.

Figure 6 tells a delightful story that I believe holds a key to water's supercooled behavior. The story describes the reasons for the three critical solution temperatures in terms of the battle between mechanical energy and entropy.[23,24] In the free energy the coefficient of entropy is the temperature thus the entropy wins at high temperatures and all things mix. This explains the region above T_{c1} in Fig. 6. As T is lowered, however, the alcohol (a term now used generically) and water energetic dislike becomes more important than the entropy and the two unmix at T_{c1}. Further decrease in T continues to lessen the influence of entropy so that energetically favorable directional bonds (entropically disfavorable, hydrogen bonds) may form between the alcohol and the water, and the two remix at T_{c2}. With yet a further T decrease, energetically more favorable directional water-water bonds (again, hydrogen bonds) may form. These bring yet more order, hence less entropy to the system, but the temperature is low now so that despite this entropy loss and the loss on unmixing energy wins and the system unmixes again at T_{c3}. Thus we see this lowest critical point is caused by water-water self association. We ask, how important is the alcohol for this critical point?

We now gather our empirical evidence together. Addition of simple alcohols to water enhances the supercooled anomalies. The structures created by alcohol addition are clathrate-like. Alcohol-water systems can phase separate with a critical point and at low temperatures this is due to water-water self association. Alcohol promotes this self association. Does this self association occur if no alcohol is present? The data reviewed above tell us yes. And in the absence of alcohol, in pure water, does the self association occur strongly enough to still create a T_{c3} critical point?

We believe the implication of the data reviewed above is that the answer to this last question is yes. That is, at low enough temperature supercooled water would phase separate from itself into low density and high density phases. The low density phase would be strongly self associated and have many clathrate-like cages. The density would probably lie between the density of an empty-cage, stoichiometric solid clathrate, 0.8 g/cm^3, and ice I_h, 0.92 g/cm^3. The high density phase would contain water molecules with very few linear hydrogen bonds.

In the current state of affairs these ideas are not as radical as when I first envisioned them. Poole et al. [25], have studied simulated water and proposed a first-order phase transition line terminated by a critical point lies between the high and low density phases of amorphous ice deep in the supercooled regime at high pressure. Hence the concept of coexistence between some sort of low and high density phases of water has support from simulations. Whether these phases are liquid or solid and the possible existence of clathrate-like structures should be studied further in the simulations.

DISCUSSION

And now, given all we have reviewed above, we come back to the original question, why the anomalies of supercooled water? Certainly the existence of clathrate-like cages, more so as water is cooled, is well established from numerous points of view. There is also a strong propensity for water to self associate at low temperatures to the point where water might even phase separate into associated and nonassociated phases. Is this phase transition and associated critical point the source of the anomalies? Although this proposition is very tantalizing, I think not because the correlation length measured by SAXS in supercooled water does not change with temperature.[16] This need not negate the idea of a low density, high density critical point, rather it implies that this critical point is still far away from pure water at -34°C, and perhaps even virtual.

If we remember what clathrate cages can do, there is no need to invoke a critical point. Recall the enhancement of the TMD in alcohol solutions and then one may qualitatively explain water's negative expansivity with the formation of low density clathrate cages. Recall also the enhanced specific heat for clathrate cage forming alcohol solutions to infer a similar source for the specific heat anomaly in pure water. The anomalous compressibility can be ascribed to the open structure which is readily destroyed by pressure. This explains the decoupling of the compressibility and ξ since the compressibility is due to cage formation whereas ξ is related to some yet very distant critical point. Also, addition of a hydrophobic unit, say with an alcohol, should not ~~necessary~~ increase the compressibility because these entities fill the cage and make ✓ necessarily them more durable against pressure.

The critical point picture is attractive because of the special temperature, -45°C, at which most of water's properties seem to be diverging. This is an extrapolation, of course, so we can never be certain if divergences really exist there, but the "sameness" of -45° for so many properties is remarkable. The clathrate picture can qualitatively account for the "sameness" because all the anomalies have the same source--clathrates. But it cannot account for a divergence at -45°C unless some sort of critical point is included. We have proposed what the critical point might be, T_{c3} in Fig. 6, but the experimentally nondivergence ξ holds us away from that interpretation. For now we conclude that clathrate-like cage formation in supercooled water is the cause for the anomalous behavior of water's properties, but the existence of a true divergence at -45°C and a possible low density, high density critical point in the supercooled regime remain unresolved.

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