Dynamic light scattering studies of concentration fluctuations in aqueous t-butyl alcohol solutions

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Dynamic light-scattering measurements using photon correlation spectroscopy have been performed on four different concentrations of t-butyl alcohol in water; 7.25, 13.2, 20.1, and 26.0 mol %. Temperatures ranged from as low as -16 °C in the supercooled regime to as high as 72 °C. Mutual diffusion constants of the concentration fluctuations were extracted from the light-scattering data. Viscosity measurements were also performed on these solutions over these temperature ranges. The correlation length of the concentration fluctuations determined from these measurements increased with increasing temperature, leveled off near room temperature and then showed another increase at lower, especially supercooled temperatures. These behaviors suggested critical demixing or consolute points should exist at both temperatures above the equilibrium boiling and below the freezing points of the mixture. The high temperature critical point is probably due to t-butyl alcohol and water association, whereas the low temperature critical point is most likely due to water–water self-associating. The results are discussed in terms of the unusual critical-phenomena-like properties of supercooled pure water and the possibility that these unusual properties are due to water–water association in the form of clathrate-type structure.

INTRODUCTION

The properties of dilute solutions of tertiary butyl alcohol (tBA) in water have periodically attracted the attention of the literature for some time. Most of these studies have discussed the effects of tBA on the liquid structure of water and hence have been concerned with the structure of water itself. The work of Bale, Shepler, and Sorgen[1] involved x-ray scattering from these solutions and indicated clustering with spatial extent of the order of 20 Å. More recently, Iwasaki and Fujiyama[2] have performed Rayleigh light scattering experiments, the results of which they have interpreted to indicate a system characterized by tBA molecules encaged by several or more hydrogen bonded water molecules.[3,4] Such cages are called clathrates, because of their similarity to stable gas hydrate clathrate inclusion compounds, and have been proposed by various investigators to help explain the properties of liquid water and its solutions. Another somewhat older result, which we have often found interesting, is that addition of tBA to water at low molar concentration produces an effect on the infrared spectra equivalent to an effective cooling of the water.[5] Still other work on these solutions has suggested the presence of phase transitions in these systems,[6] although some of the results have been contended.[7] In general, these studies appear to be motivated by the fact that tBA seems to be best suited to modify or perhaps enhance the structure of liquid water and thus lend insight into the structural properties of this enigmatic substance.

It is tBA's structural properties that make it such an interesting solute for the study of water. It is a mixed solute meaning it has a hydrophillic entity, the hydroxyl group, which promotes the dissolution, and a hydrophobic entity, the t-butyl group. The globular t-butyl group is essentially perfect in size and shape to fit into the spherical cavity of a clathrate cage of water molecules. These cages can be envisioned as involving roughly several water molecules bound together by relatively strain-free hydrogen bonds. Their sta-

bility can be emphasized by the broad variety of stable gas hydrates which possess a definite stoichiometric clathrate structure.[8] Monohydric alcohols bigger than, or without the spherical symmetry of, tBA are not totally miscible with water because they cannot easily fit into the cage, and hence the cage stability is lessened. In fact, tBA is the "last" miscible monohydric alcohol and forms very nonideal solutions with water.

In the past several years interest in the structural properties of water and their relationship to its thermodynamics has been renewed by the discovery that liquid supercooled water displays anomalous critical-phenomena-type properties.[9,10] In recent work from our laboratory,[11,12] we have taken the viewpoint first proposed by Stillinger[13] that clathrate-type structures form in pure water and are responsible for these supercooled anomalies. This viewpoint has also been used by Speedy, Ballance, and Cornish.[14] We have found it useful to use solutes as probes of liquid water's structure either by enhancing or destroying the proposed clathrate-like structures. In this paper we report new measurements which continue this philosophy. This work will describe photon correlation spectroscopy (PCS)[15] measurements on light scattered from aqueous tBA solutions at four different concentrations and a variety of temperatures. PCS allows us to measure mutual diffusion coefficients of the mixture and may be interpreted to give correlation lengths of concentration fluctuations. As discussed below, by using a simple Stokes–Einstein relation, we have determined these correlation lengths and interpreted them in terms of the existence of possible critical points in the extreme supercooled and superheated regions of the solutions. In light of our findings we propose further arguments concerning the nature of the anomalies seen in supercooled water itself.

EXPERIMENT

Reagent grade tertiary butyl alcohol and triply distilled water were used in preparing our solutions. Some problems

with precipitate particle formation occured in some solutions, so some of the tBA was doubly distilled in a still with 2000 equivalent plates to reduce this problem. This will be discussed further below.

In the light-scattering experiments the samples were contained in a quartz spectrophotometer cell 1.0 cm square by 4.7 cm deep. This cell was positioned at the center of a two-stage metal thermostat device with the temperature monitored by a thermistor connected via a feedback loop to a heater to achieve temperature control. Control was better than ± 0.1 °C. For below ambient temperatures nitrogen gas was bubbled through liquid nitrogen and then this cooled gas was circulated into the thermostated vessel. By adjusting the cooled gas flow rate, the relative ambient could be set at a value which the controled heater could buck against.

The Rayleigh light scattered from the samples was at times quite weak and care had to be taken to insure cleanliness of the quartz cell and removal of dust motes from the liquid sample. The samples were filtered through 0.2 μ nucleopore filters directly into the cell which often had to be rinsed several times before an acceptable sample free of motes could be obtained.

The light source was an argon ion laser operating at 5145 Å focused into the cell by a long focal length lens. Since a wide range of temperatures was studied, the mutual diffusion constant of the solutions changed by more than two orders of magnitude and this made the use of two different scattering angles necessary. As can be seen in Eqs. (1) and (2),

$$\tau_c = (2D_m q^2)^{-1},\qquad(1)$$

$$q = \frac{4\pi n}{\lambda}\sin\theta/2,\qquad(2)$$

the correlation time τ_c of the scattered light is inversely proportional to the mutual diffusion constant D_m. At temperatures above ambient, D_m was large enough to force us to adjust the scattering wave vector q smaller by decreasing the scattering angle θ. In our work we used $\theta = 25.8°$, so that the resulting correlation times were typically 5 μs or longer. Values shorter than this are hard to measure due largely to photomultiplier afterpulsing. At this smaller angle heterodyne detection was used by mixing the scattered light with light elastically scattered from the wall of the cell. In this case the factor of two does not appear in Eq. (1). On the other hand, as the temperature decreased below ambient, D_m became small so that $\theta = 90°$ and homodyne detection could be used which is easier to configure optically. This arrangement also keeps τ_c less than several milliseconds which is desirable because at times building vibrations caused problems for long correlation time runs.

With the above explanation, we summarize by stating that at large temperatures correlation data was obtained at $\theta = 25.8°$ using heterodyne detection. For lower temperatures light was scattered at 90.0° and detected in the homodyne mode. In either case the light was collected by a lens which imaged the scattering volume onto a slit. This light then passed to a FW 130 photomultiplier whose output was amplified and discriminated. These pulses were then correlated by a commercial correlator and the resulting exponential correlation spectra were fit to a two cummulant fit to determine τ_c.

To determine correlation lengths the viscosity of the solutions must also be known. At the beginning of the experiment some of the viscosity measurements were already available from previous work using a Poiseuille flow viscometer held in a thermostated water bath. These measurements were extended for the needs of this work by once again using correlation spectroscopy. This method, which we have described before,[11] is useful in determining the viscosity in the supercooled regime. We doped our solutions with 0.038 μ diameter carboxalated plastic spheres and the correlation time of the light scattered from these spheres, which is quite intense, yields the diffusion constant, via Eqs. (1) and (2). Since for particulate diffusion the Stokes–Einstein relation holds,

$$D = \frac{kT}{6\pi\eta r},\qquad(3)$$

where k is Boltzmann's constant, T is the temperature, η is the solution viscosity, and r is the known particle radius, the viscosity can be determined. Actually, due to some uncertainty in the particle radius specified by the manufacturer, we normalized the viscosity found by light scattering to the flow measurements. This normalization was of the order of a few percent.

Some problems arose in our light scattering correlation measurements from the solutions. The scattering intensity was often quite low and while some spectra could be obtained in 5 min many require accumulation times of 90 min or more. The need for cleanliness regarding dust motes is obvious under these conditions. The lack of scattering intensity also constrained our concentrations between 7–26 mol % tBA and at times limited the temperature ranges. Finally, at lower concentrations, especially in the 7.25 mol % solution, a precipitated formed below room temperature. This precipitated could not be detected by the eye in room light but was visible as a soft glow in the laser beam. Correlation measurements indicated particulate sizes of ~ 1000 Å. The precipitate disappeared upon heating to room temperature. We tried double distilling the tBA and redistilling the water in a quartz still but the precipitate persisted. This problem is very similar to that discussed by Beer and Jolly[7] and is, if other desires were not more pressing, rather interesting. For now we can only speculate that it may be related to some stable solid clathrate of tBA with water perhaps involving a trace help gas to promote stability.

RESULTS

In Fig. 1 are displayed the mutual diffusion constants D_m of the concentration fluctuations determined from correlation times of the scattered light using Eqs. (1) and (2) vs temperature for four concentrations of tBA in water: 7.25, 13.2, 20.1, and 26.0 mol %. The darkened data points indicate data obtained at 25.8° scattering angle in the heterodyne mode while the open points correspond to 90°, homodyne data. As can be seen the data are smooth at the junction of these two data sets indicating good consistency in our experiment.

Figure 2 contains the viscosity of the four solutions as a function of temperature. No attempt has been made here to
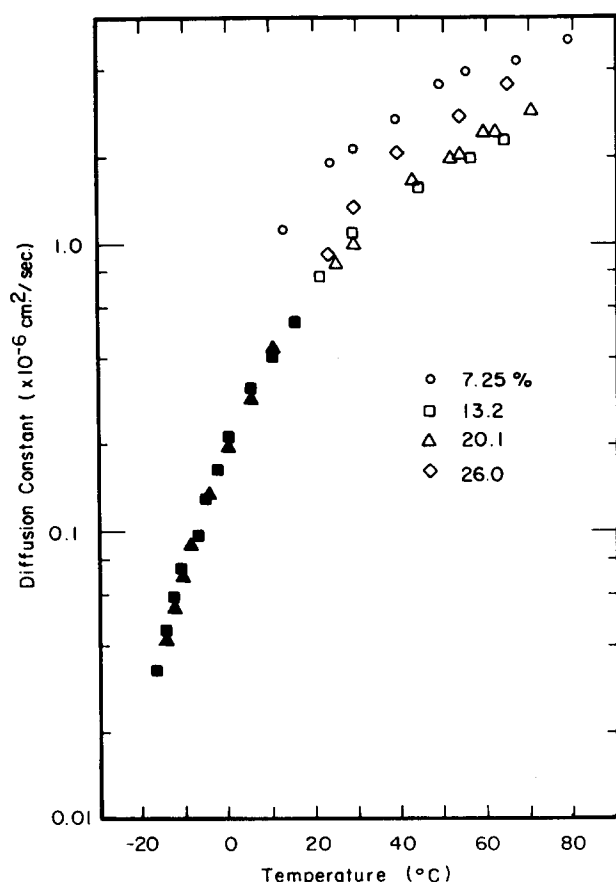
FIG. 1. Mutual diffusion constant vs temperature for four solutions of tBA in water. Closed figures represent data obtained in the heterodyne mode at $\theta = 25.8$ °C, open figures represent values obtained in the homodyne mode at $\theta = 90°$ using Eqs. (1) and (2).
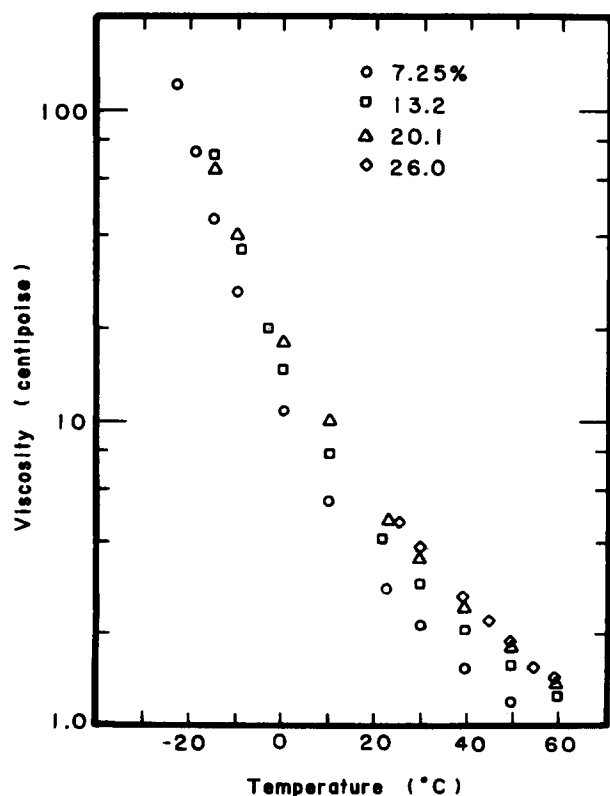
distinguish between flow data and correlation spectroscopy data although all the supercooled data (roughly below 0 °C for these solutions[16]) were obtained with the light scattering technique.

We have fit both sets of data with a modified Arrhenius or Vogel–Tamann–Fulcher[17] (VTF) equation of the form

$$X = X_0 e^{A/(T - T_0)},\qquad(3)$$

where X represents either the viscosity or the mutual diffusion constant determined using Eq. (1). The fitting parameters are X_0, A, and T_0, the most physical being T_0 which can be related to the glass transition temperature when the fit is applied to the viscosity. The fits to both D_m and η were quite good and Table I gives the resulting fitting parameters. The viscosity T_0's are all greater than that for pure water indicating that addition of tBA raises the glass temperature relative to that of water. Surprisingly, the diffusive T_0's are at higher temperatures than the viscosity T_0's. This suggests that the diffusive nature of the two components is slowing down quicker than the fluidity of the mixture. These fit parameters must be viewed with some caution, however, due to the different temperature spans of the data.

Our primary purpose here is to determine the correlation length ξ of the concentration fluctuations in these mixtures. Near a consolute point of a binary mixture, which is known to be a critical point or second-order phase transition, the mutual diffusion constant is given by[18]

$$D_m = \frac{kT}{6\pi\eta\xi}.\qquad(4)$$

This is, of course, the Stokes–Einstein diffusion constant for particles of radius ξ. Equation (4) holds as long as ξ is not too large so that $\xi < 1/q$. This reciprocal of the scattering wave vector in our experiments is roughly 60 Å, and as will be seen below, this inequality holds. Far from a critical point Eq. (4) will still roughly hold even as ξ approaches molecular dimensions. For instance, Czworniak, Anderson, and Pecora[19] have studied mixtures of simple liquids with correlation spectroscopy and application of Eq. (4) to their results yields reasonable molecular radii when the hydrodynamic slip factor 4π is used instead of the stick factor of 6π. In what follows we will use our diffusion and viscosity data to determine the concentration correlation lengths using Eq. (4) with the factor 6π as prescribed by the dynamic theory of critical phenomena.

Figure 3 presents the correlation length ξ as a function of temperature for the four concentrations studied. Data points were determined from Eq. (4) using the experimental values of D_m and the viscosity given by the fit of the VTF equation [Eq. (3)] to the viscosity data. The error estimate is roughly ± 0.7 Å. This estimate was derived from the scatter of τ_c over several correlation spectra at a given temperature and the estimated error in η. The lines drawn through the points are ξ calculated from both VTF fits to both D_m on η and therefore represent smoothed data. Notice that the magnitude of the correlation length varies from 4 to 10 Å, which when compared to the molecular radius of tBA of 3 Å, indicates considerable association of the tBA and water molecules. Use of the factor 4π in Eq. (4) would make ξ 50%

FIG. 2. Viscosity vs temperature for four solutions of tBA in water.

TABLE I. Viscosity and mutual diffusion constant fit parameters to the modified Arrhenius equation, Eq. (3).

tBA concentration (mol %)	Viscosity			Diffusion		
	$n_0(\times 10^{-2}$ cp)	A (K)	T (K)	$D_0(\times 10^{-5}$ cm^2/s)	A (K)	T (K)
7.25	4.45	407	199	1.35	-109	242
13.2	6.45	384	203	2.00	-259	216
20.1	2.60	604	181	3.20	-319	210
26.0	1.38	766	167	0.99	-74	266

larger, again supporting the conclusion of considerable association.

Two characteristic behaviors are seen in the data. First, the correlation length increases with temperature above room temperature. Second, this behavior levels off with decreasing temperature and appears to reverse this trend. The correlation length definitely increases with decreasing temperature in the supercooled regions of the 13.2 and 20.1 mol % solutions just before nucleation and may be present near ambient in the 26.0 mol % solution. These two behaviors can be explained in terms of two different processes occurring in the solution.

DISCUSSION

The increase of the correlation length ξ is an indication of an approaching critical point or region.[18] Our data indi-
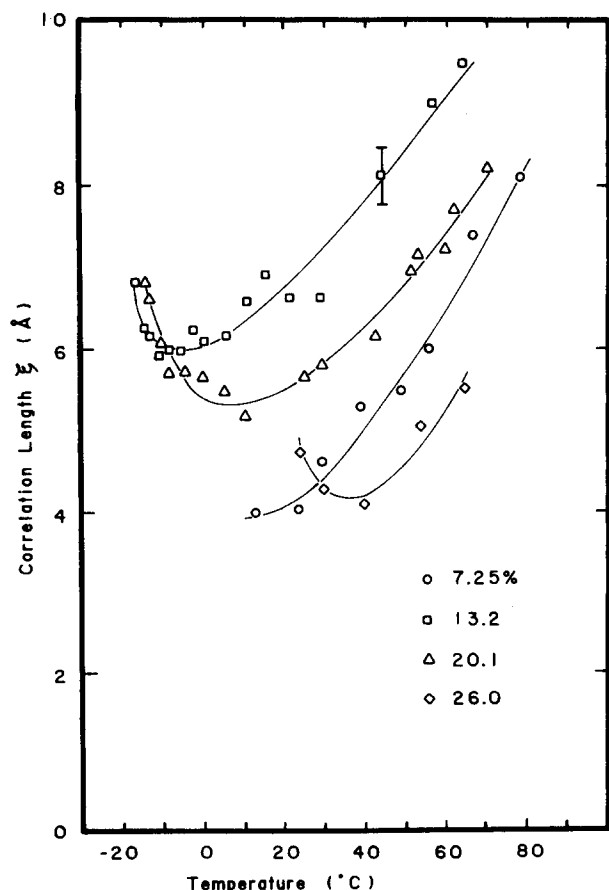

FIG. 3. Correlation length of concentration fluctuations vs temperature for four solutions of tBA in water. A typical error bar is shown. Lines represent correlation lengths calculated using the fits to both the mutual diffusion constant and viscosity; fit parameters given in Table I.

cates that a critical point may lie at high temperatures above the equilibrium boiling points of the mixtures at atmospheric pressure. Since ξ measures the concentration correlation length, this critical point would be a demixing of phases at a lower critical solution temperature, LCST.

This conclusion is reasonable in terms of the thermodynamics of aqueous tBA solutions which have a positive deviation from ideality. The closeness of these solutions to separation is also illustrated by the fact that the higher alcohols, C_5 and greater, are only partially soluble with water, and of the C_4 or butyl alcohols, only tBA is completely miscible. Franks[20] has also discussed the possibility that tBA–water solutions would demix at high temperature citing the increasing x-ray scattering with temperatures seen by Bale et al.,[1] which indicates an increase in ξ, and the fact that tetrahydrofuran and water solutions, while miscible at all equilibrium temperatures, phase separate just above the boiling point.[21]

Lüdemann[22] has found that the tBA–water system does phase separate at higher temperatures if the solution contains finite concentrations of the salt KCl. A closed immiscibility loop was observed which disappeared before the KCl concentration became zero. Thus, the implication is that tBA–water solutions do *not* have a LCST at any temperature, but can be induced to have one when further thermodynamic degrees of freedom are present, such as addition of a salt. The increasing correlation lengths we observed may then be interpreted as caused by the approach to a LCST with increasing T that is not actually on the salt concentration equal zero plane of the phase diagram. One might speculate that ξ would continue to increase with T until the system passed by the immiscibility dome in the finite salt concentration region and then decrease as the distance from the dome increased with yet higher T.

In a like manner, the increase of ξ with decreasing T in the supercooled solutions also indicates the approach to another critical point. Again, since ξ measures concentration fluctuations, this critical point would be due to an immiscibility transformation. Figure 4 presents a possible phase diagram for the tBA–water–salt system which illustrates these ideas graphically. Our experiments have been performed with a salt concentration of zero and could be represented as short vertical lines on the water–tBA plane.

This indication of a critical point in a supercooled aqueous solution may have interesting implications concerning supercooled water. We note, however, that Bosio et al.[23] have seen density fluctuations with $\xi \lesssim 8$ Å in supercooled water using x-ray scattering but these fluctuations were destroyed upon addition of small amounts of ethanol. Since
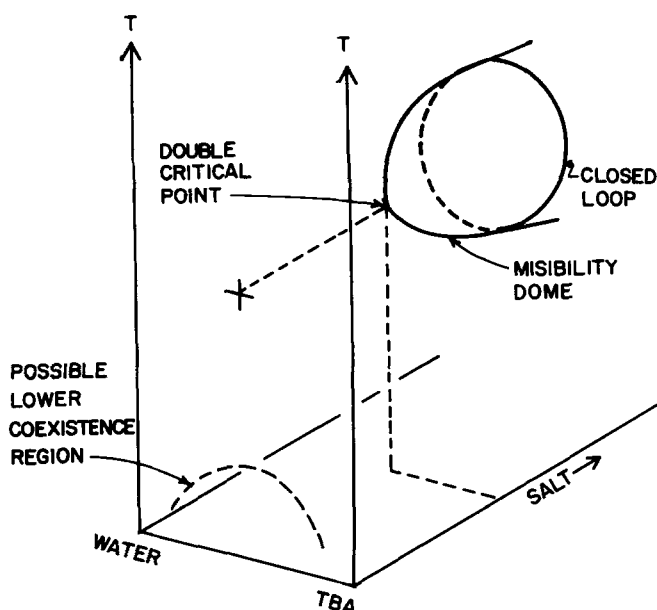
FIG. 4. Possible phase diagram for a system *t*-butyl alcohol–water and a salt. Our data have indicated a critical region associated with a possible lower coexistence region in the supercooled, salt-free state. The upper "miscibility dome" has been indicated by Lüdemann's data (Ref. 22) and its effect in the salt-free plane has also been detected in our measurements.

there are similarities in the thermodynamics of ethanol and tBA solutions, these results are perplexing when compared to ours. The solution concentrations were, however, different; Bosio *et al.* used concentrations of 5.8 mol % or less. Perhaps a transformation from density to concentration fluctuations may be involved with increasing alcohol concentration.

To understand the behavior of these solutions from a molecular point of view, we rely on the work of Wheeler and Andersen,[24] and Walker, Vause, and Goldstein[25] concerning closed loop coexistence curves. The general picture presented by these workers is that the uppermost critical demixing or consolute point is due to the struggle between the tendency of like molecules to segregate to themselves due to energy reasons and the entropy of mixing which promotes dissolution. As the temperature is lowered, the entropy term in the free energy eventually loses the struggle and a miscibility gap appears. The immiscibility region may become reentrant, i.e., miscibility reappears, if directional bonds between unlike molecules can form. These directional bonds are not favorable in entropy terms and thus do not become important until lower temperatures are achieved. The system may experience yet another miscibility gap at even lower temperatures below the reentrant phase if directional bonds between like molecules is more favorable than between unlike molecules. Such behavior is actually observed in a variety of aqueous systems, the hydrogen bond being the source of directional bonding.

In light of the above, our indication with increasing ξ and T of a LCST above the boiling point of our mixture is most reasonably ascribed to directional bonding between *unlike* molecules, in this case hydrogen bonding between water and tBA. Whether clathrate-type structures form as well

seems to be unimportant to the onset of the LCST. Of course Ludemann's data indicate that the LCST does not exist on the ionic salt free plane of the phase diagram, but must be "salted out" with KCl. Goldstein and Walker[25] have discussed how the addition of a salt serves to shield the hydrogen bonding sites of each molecule and thus inhibit the reentrance of the phases. Thus Lüdemann's data supports the view that the LCST is due to water–tBA hydrogen bonding.

We may conclude that the increase in the correlation length ξ with increasing temperature T which we observed in aqueous solutions of tBA is due to a LCST at a temperature above the boiling temperature. While this LCST can never in fact be reached on the salt free plane of the tBA–water phase diagram, its presence still causes the observed effect on ξ. The structural source of this LCST is the onset of favorable tBA–water hydrogen bonds.

This leaves us to conclude that the increase of ξ with lowering T in the supercooled mixtures, which indicates yet another critical point, must be ascribed to favorable directional bonding between *like* molecules. This is most probably water–water hydrogen bonding since tBA self-association is rather weak. The water self-association is consistent with the suggested presence of clathrate-type structures in water and aqueous solutions. Increasing ξ indicates that the average size of the clathrate structures is increasing with decreasing T.

It is interesting to compare these conclusions to the system of 2-butanol and water.[26] While at atmospheric pressure this system displays a continuous miscibility gap with an upper critical solution temperature and with some pinching in at intermediate temperatures, higher pressures cause reentrance of the phases, with a phase diagram displaying a closed loop and then another upper consolute point at lower temperatures. The upper loop can be made to disappear above 845 atm similar to the upper loop dependence with KCl concentration observed by Lüdemann in aqueous tBA. In fact the phase diagram of 2-butanol and water is very similar to that we propose for tBA and water in Fig. 4 if one replaces the salt axis with a pressure axis and includes a definite lower coexistence region. This analogous behavior for an isomer of tBA makes our conclusions regarding the presence of critical points at extreme high and low temperatures more reasonable. tBA's higher solubility at lower temperatures can be related to its more globular shape allowing it to fit into the clathrate cages of the liquid water.

We now discuss the implication of the observations above for the properties of supercooled water. Stillinger[13] first suggested that the anomalous properties of supercooled water were a result of clathrate-like structures forming as water is cooled. The clathrate model for liquid water structure, however, predates recent interest in supercooled water and was primarily promulgated by Glew.[3,27] These structures are similar to stable gas hydrate clathrates in that they are polyhedral associations of several water molecules bond together by hydrogen bonds. Cavities are formed in these clathrate cages and may be filled by small hydrophobic solutes.

Halfpap and Sorensen[11] found that addition of ethanol to water enhanced the anomalous behavior of the viscosity

and argued that this enhancement was due to promotion of clathrate structures by the ethanol equivalent to lowering the temperature. The implication was that clathrates are in some way responsible for the anomaly. In further work, one of us[12] has shown that the molar volume of both ethanol and tBA in supercooled water became quite small as the temperature was decreased. This again implied extensive structuring with voids that may be filled by these solutes. It was also found that, contrary to the room temperature behavior of alcohols to stimulate more clathrate structures in water as evinced by the minimum in the alcohol partial molar volume at small but finite concentrations,[4,28] alcohols no longer stimulated clathrate formation in water at temperatures below roughly $- 30\,°C$.

Our results above can be understood in terms of a critical demixing point below the nucleation temperatures of the low concentration solutions. Whether this critical point actually resides on the phase diagram or is some sort of "virtual" critical point which must be, for instance, salted out as in the case of the high temperature LCST, is immaterial for our purposes. The important point is that long-range ordering was developing in these solutions as the temperature was lowered primarily because of the formation of water–water hydrogen bonds. That the resulting water associations were "clathrate-like," in terms of the meaning implied by the brief review above, is most reasonable. Certainly, our data for the partial molar volume of tBA in these solutions supports this conclusion. Thus we may rephrase to say that the onset of long-range order in these supercooled solutions is a result of the formation of clathrate-like structures.

What happens in pure water? At room temperatures addition of tBA no doubt stimulates clathrate structuring. We have found evidence, however, to indicate that this structure promotion ceases below $- 30\,°C$.[12] Thus, we might argue that at these low temperatures the correlation length ξ would continue to increase regardless of the presence of the tBA. This is supported by the x-ray data of Bosio et al.[23] In our work addition of tBA stimulated clathrate formation and thus has brought the region of increasing ξ barely into the observable, and for low concentration metastable region. But without a structure promoting solute like tBA, this clathrate structuring leading to long-range order would still occur because it is due to water–water hydrogen bonding. The structure of this long-range order would be clathrate like. Onset of long-range order is a primary ingredient to understanding the critical-phenomena-type divergence seen in supercooled water.

CONCLUSION

Our photon correlation light scattering measurements on aqueous solutions of tBA have yielded concentration fluctuation correlation lengths ξ which indicate molecular associations in these solutions. The correlation length was found to increase both with increasing temperature above room temperature and decreasing temperature particularly in the supercooled region. The high temperature behavior was ascribed as due to the presence of a lower critical solution temperature at yet higher temperatures. While Lüdemann's data indicated that such LCST does not exist unless

finite salt concentrations (KCl) were added, its proximity to the high temperature salt concentration zero region of the phase diagram must still be felt. Interpretation of this LCST in terms of modern theories suggested it was due to tBA–water hydrogen bonding and the formation of clathrate structures was probably not important in causing fluctuations of increasing ξ.

The low temperature increase in ξ was ascribed to the presence of another critical point at the top of a low temperature miscibility gap. Again, interpretation of this in terms of modern theories suggested that this critical point was due to water–water hydrogen bonding which most probably resulted in clathrate-type structure formation.

Finally, we argued that this supercooled critical point due to water clathrate formation probably occurs in pure water as well since the structure promotion effects of the tBA disappear below $- 30\,°C$. Such a critical point which is a result of clathrate formation leading to long-range order can then be used to explain the anomalous properties of supercooled water.

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