

The viscosity of supercooled aqueous solutions of ethanol and hydrazine

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We have measured the shear viscosity of solutions of ethanol and hydrazine in water into the supercooled region. Two techniques were used: Poiseuille flow measurements in the range 75°–17.5°C and photon correlation spectroscopy of light scattered from diffusing microspheres suspended in the solutions in the range from 20°C down to nucleation. We have found that addition of hydrazine tends to diminish any anomalous increase in the viscosity of supercooled water, an effect similar to that seen in other types of measurements. Addition to ethanol, on the other hand, enhanced the viscosity. This was interpreted to indicate that the cagelike clathrate structures known to be found in aqueous ethanol solutions are also found in pure water and may be responsible for the anomalous properties of supercooled water which have recently been discussed in the literature.

INTRODUCTION

Experiments on supercooled water have indicated that the unusual properties of water become even more interesting below the equilibrium freezing point.¹ Measurements on such thermodynamic properties as the thermal expansivity,² isothermal compressibility,³ and specific heat at constant pressure^{4,5} may all be interpreted to indicate the possibility of a thermodynamic singularity near the temperature $T_s \approx -45^\circ\text{C}$. It is further known that these anomalies may be destroyed by application of high pressures or addition of various solutes which tend to break the hydrogen bonded structure of liquid water. Oguni and Angell⁵ have shown that addition of structure breaking impurities such as hydrogen peroxide or hydrazine removed the anomalous specific heat leaving only a background part. This separation into critical and background parts has led Angell and co-workers to fit the critical part to a power-law dependence with $(T - T_s)^\chi$ and find a mean field exponent of $\chi \approx 1$ for both the specific heat and compressibility.⁶ These indications of a singularity at T_s are tempered by the fact that data closer than 5° from T_s may be impossible to obtain because of homogeneous nucleation, and recent sound velocity measurements may be interpreted to indicate that no singularity exists.⁷

The unusual properties of water whether supercooled or in the normal range can be attributed to its tetrahedrally coordinated hydrogen bonded character which leads to a rather open, noncompact structure. Stanley and Teixeira⁸ have recently presented arguments which, in a qualitative manner, attempt to explain the anomalous properties of water. The open structure allows for regions of abnormally low density and entropy thus enhancing fluctuations in these quantities. These fluctuations are in turn related to the equilibrium thermodynamic properties. Heat, pressure, and addition of structure breaking impurities break the hydrogen bonds, thus breaking up the open structure and de-enhancing the anomalous properties. In an attempt to experimentally observe this structure of water, Bosio, Teixeira, and Stanley⁹ performed x-ray diffraction measurements. They reported an enhancement of structure with cooling down to -20°C . This enhancement was not observed

with the addition of small quantities of ethanol which they concluded was breaking the structure of the hydrogen bonded network.

Stillinger¹⁰ has suggested that the particular type of structure responsible for water's anomalous supercooled properties is one where relatively strain free hydrogen bonded cages or polyhedra each containing perhaps several water molecules form spontaneously in water. These cages, he further suggested, are the same as those found around nonpolar solutes which lead to the so-called "hydrophobic interaction". The fact that such polyhedra or ringed structures are important for understanding supercooled water has also been proposed by Rice and Sceats.¹¹ We shall discuss further and use some of these ideas later to interpret our data.

In this paper we present measurements of the viscosity of aqueous solutions of ethanol and hydrazine at temperatures from 75°C down into the supercooled region for these solutions. The viscosity, perhaps more so than any other quantity, obeys the power-law behavior over an extended temperature range. Data obtained by Hallett¹² down to -24°C and more recently data obtained by Osipov *et al.*¹³ to -35°C when combined with $T > 0^\circ\text{C}$ data may be fit over the entire available temperature range to a power law with $T_s \approx -45^\circ\text{C}$ and exponent $\chi \approx 1.55$ with no background correction. Here we wish to test the structure breaking abilities of hydrazine, which weakened the specific heat anomaly, and ethanol, which destroyed the structure in x-ray measurements, on the viscosity. Furthermore, viscosity measurements allow for an indirect assessment of the structural properties of a liquid and as such should be interesting in the context of the structural implications in the current work on water as reviewed briefly above.

EXPERIMENTAL

The viscosities of the solutions were measured in two different ways. In the range 17.5°–75°C standard Poiseuille flow measurements were made. In the range $\sim 23^\circ$ to $\sim -30^\circ\text{C}$, a light-scattering technique which determined the viscosity experienced by microspheres diffusing in small samples of the solutions was used.

This latter arrangement was developed to circumvent some of the problems associated with nucleation of the supercooled liquid. In either case the solutions were made up from reagent grade absolute ethanol or hydrazine (97%) and freshly distilled and boiled water. The two experiments are described below.

The glass flow viscometer was carefully calibrated with pure water against known viscosities.¹⁴ It was immersed in a large, stirred water bath which had a thermostat to give 0.05 °C control. Flow times were measured with a stop watch. Liquid densities necessary to extract the shear viscosity from the kinematic viscosity obtained from the flow measurements were determined by measuring meniscus height displacement with temperature in the neck of 25 ml volumetric flasks which had been calibrated with water. These density measurements when compared with available data for ethanol solutions agreed with the literature¹⁵ to better than 0.1%. The viscosity was determined every 5 °C from 75° to 20 °C inclusive and at 17.5 °C for all solutions. The estimated accuracy of the flow data is better than 1%.

The light-scattering experiment is a bit more elaborate but was deemed necessary to avoid early nucleation of the supercooled solutions. Ideally, experiments would be performed down to the homogeneous nucleation limit, but a review of the literature on the supercooling of water indicates that this limit is difficult if not impossible to achieve especially when the water is contained in glass tubes.¹⁶ The less extreme heterogeneous nucleation process then puts a limit on the degree of supercooling for experiments such as viscosity measurements where the water must be contained in glass tubes. Work we have performed in our laboratory, however, indicated that once the heterogeneous limit is acknowledged, the degree of supercooling is in some cases only a very weak function of the concentration of motes or nucleation sites in the water. This is particularly true for a system of submicron sized polystyrene microspheres suspended in water, where we have been unable to see a concentration dependence of the heterogeneous nucleation temperature. On the other hand, a volume dependence is still seen; the degree of supercooling decreasing approximately linearly with the logarithm of the volume. These facts led us to attempt the experiment, described below, wherein the viscosity is calculated from the diffusion constant of polystyrene microspheres suspended in solution measured using photon correlation spectroscopy (PCS) of light scattered from small samples.

When laser light is scattered from a suspension of diffusing particles the scattered light will have an intensity autocorrelation function which decays with time exponentially to a constant background.¹⁷ The time constant of the decay, the correlation time t_c , is given by

$$t_c = (2Dq^2)^{-1}, \quad (1)$$

where D is the Stokes-Einstein diffusion constant

$$D = \frac{kT}{6\pi\eta r}, \quad (2)$$

and q is the scattering wave vector $q = (4\pi\eta/\lambda) \sin(\theta/2)$. In the above, k is Boltzmann's Constant, T the temperature, η the viscosity, and r the radius of the particles; also n is the liquids' refractive index, λ the wavelength, and θ the scattering angle. Measurement of t_c allows for determination of the viscosity η using Eqs. (1) and (2) given the other variables.

Our samples were prepared by first making a stock solution of 0.109 μm diameter polystyrene latex microspheres, obtained from Dow Chemical Company, in boiled, distilled water to a concentration of 10^{-4} by volume. The solutions were then made by mixing this stock water suspension with either the ethanol or hydrazine. We used only freshly prepared solutions for our viscosity measurements because there is some indication that aqueous hydrazine solutions slowly attack glass.¹⁸ Samples of either solution that were never frozen showed no change in measured viscosity over the two month period of the experiment.

These solutions were loaded into 0.5 mm square capillary tubing using capillary action. A typical length of solution in the tube was 1.5 cm, thus a typical volume was on the order of $2-5 \times 10^{-3} \text{ cm}^3$. For such volumes the heterogeneous nucleation temperature for water is in the -20° to -22°C range. The capillary was flame sealed at each end, being careful to ensure there were no microleaks. The capillary was mounted with epoxy on a small metal rod which hung vertically from the cap of a 1.0 cm square spectrophotometer cell. The cell was filled with an ethylene glycol and water mixture to provide for heat transfer and an index of refraction match. The spectrophotometer cell was then placed into an insulated brass cylinder which was connected to the tail of liquid nitrogen dewar. Cool, dry nitrogen gas which had been equilibrated to the temperature of the brass cell passed over the three exposed windows (0° , 90° , and 180°) of the spectrophotometer cell to alleviate any thermal gradient problems.

The temperature was measured with a thermistor buried deep into the brass cell near the actual scattering volume. Calibration of the thermistor and the arrangement was achieved by placing a platinum resistance thermometer in a mock-up of the spectrophotometer cell at the scattering volume location. A simulated run was then performed to calibrate the thermistor. Our estimated accuracy was 0.2 °C.

The light-scattering arrangement was rather straightforward. Light of either 5145 or 4579 Å wavelength from an argon ion laser was focused with a 60 cm focal length lens into the spectrophotometer cell and adjusted until it entered the 0.5 mm square capillary at normal incidence. The 90° scattered light was collected with a lens, focused on a slit to eliminate the entrance and exit flares of the beam on the capillary, and detected with a photomultiplier. The pulses from the photomultiplier were sent to a correlator which produced the intensity autocorrelation function which was analyzed to obtain the correlation time t_c in Eq. (1) using an on-line computer.

A typical run was performed by arranging the optics

as described above and then adding the liquid nitrogen to the dewar. The cooling rate was usually a little less than $1^\circ\text{C}/\text{min}$. A suitable spectrum for obtaining t_c and thus η could be obtained in about 10 s causing some spread in the effective temperature. Calibration of the thermistor under actual experimental conditions as discussed above was necessary to include the effects of the cooling rate on the temperature measurement. Spectra were taken periodically from ambient down until the sample either froze or the cooling rate became very slow (usually near -30°C).

Since by Eqs. (1) and (2) the correlation time is directly proportional to the viscosity, the correlation times were fit to a modified Arrhenius or VTF equation of the form

$$t_c \propto \eta = \eta_0 \exp[A/T - T_0] \quad (3)$$

In this way, an effective correlation time at 20°C could be obtained to allow us to calibrate the correlation times relative to the viscosity at 20°C of the solution obtained from our flow measurements described above. This calibration method eliminated small errors due to uncertainties in scattering angle and particle diameter. When, however, these parameters were used, the viscosity obtained from Eqs. (1) and (2) agreed with the calibrated viscosities to about 3%. These data showed more scatter than the flow data, the scatter being about 5% to 6%. The reason for the scatter lies not so much with the light-scattering technique as with the lack of temperature control on the dewar, thus necessitating taking data "on the run" and not allowing for signal averaging.

We compared our viscosity data to other data in the literature when available. Aqueous ethanol flow measurement viscosity at 20°C compared to within 1% with

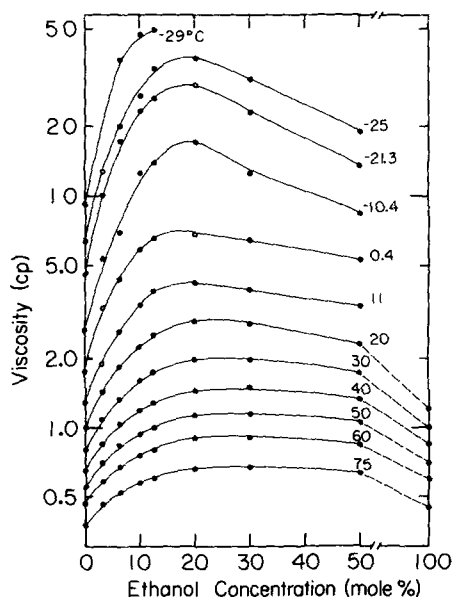


FIG. 1. Ethanol solution viscosity vs concentration for various temperatures. Solid points are data, open points are temperature interpolations from the data. The lines are drawn to aid the eye.

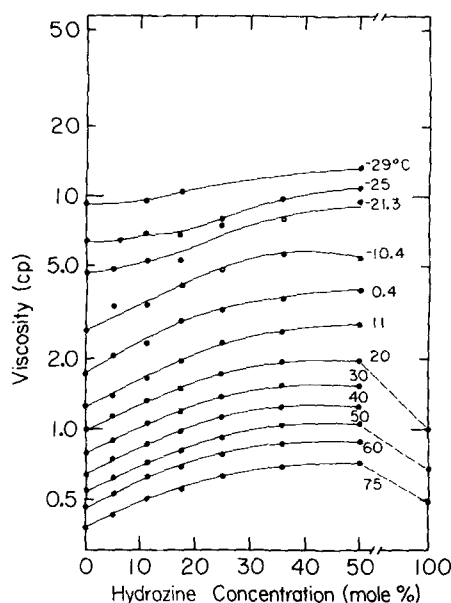


FIG. 2. Hydrazine solution viscosity vs concentration for various temperatures. Solid points are data, open points are temperature interpolations from the data. The lines are drawn to aid the eye.

data available¹⁴ except at a mole concentration of 50%, where our value was 6% too large. This value was remeasured and confirmed; we can not explain the discrepancy. Graphical comparison of ethanol solution viscosities given by Kay *et al.*¹⁹ versus concentration at $T = 10$ and 25°C was quite good. Pure water viscosity to -21°C obtained from our light-scattering measurement was compared to Hallet's¹² data and found to be about 6% larger at the lowest temperatures. Since this is about the scatter in the light scattering data, we do not consider the deviation significant. Finally, flow measurements for the 11.5% hydrazine solution were made down to 4°C and they compared well to those obtained from the light-scattering method.

DISCUSSION

Figures 1 and 2 display the results of our viscosity measurements using either technique for ethanol and hydrazine, respectively. These figures represent about half the data, the rest were not plotted so as not to overburden the graphs. Both figures show an enhancement of the viscosity over pure water with increasing concentration, the maximum enhancement occurring at 20–25 mol% for ethanol and 40–50 mol% for hydrazine. These data suggest that both substances have either promoted the structure of water or changed it in such a way that the liquid is now in some way more connected or has larger subunits than before.

Such a conclusion is not unreasonable for either hydrazine or ethanol. Hydrazine readily forms hydrogen bonds with water and has a hydrate $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$.¹⁸ The bulkier hydrated hydrazine molecules could possibly give rise to a larger viscosity than either pure component, a behavior seen in Fig. 2. Ethanol is known to form clathrate structures with water.^{20,21} In the clath-

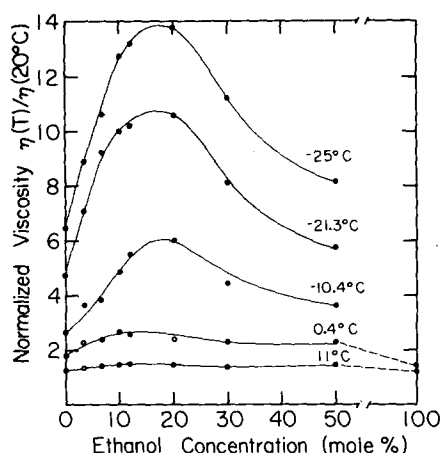


FIG. 3. Ethanol solution viscosities normalized to their viscosity at the same concentration at 20 °C.

rate structure, water molecules cluster around the ethanol molecule forming a cage which screens the hydrophobic ethyl group from the rest of the liquid. The cage itself is held together by hydrogen bonds between the water molecules. Water forms clathrates with many small hydrophobic molecules and two basic structural types are known Type I and Type II. A stable Type II clathrate of ethanol has been found to exist at -73°C with formula $\text{C}_2\text{H}_5\text{OH} \cdot 17\text{H}_2\text{O}$. A stable Type I hydrate, represented by $\text{C}_2\text{H}_5\text{OH} \cdot 5\frac{3}{4}\text{H}_2\text{O}$, has not been found, although there is evidence to suggest it exists in solution. Our viscosity data strongly suggest that this Type I ethanol hydrate is present and the larger structural units of the clathrate lead to a larger viscosity.

We wish not only to infer structural change information from our data but also want to explore the effects of solutes on the apparent power-law divergence of water's viscosity. Comparison of Figs. 1 and 2 shows that the viscosity increases at a much larger rate with decreasing temperature for the ethanol solutions than for the hydrazine solutions. Closer inspection of the figures paying attention to the pure water (concentration equal zero axis) viscosity increase with decreasing temperature, shows that the anomalous increase in water's viscosity seems to be enhanced, i.e., the viscosity increases faster with decreasing temperature in the ethanol solutions. The viscosity increase in the hydrazine solutions, on the other hand, is slower with decreasing temperature than for pure water. Thus, the hydrazine has de-enhanced the anomaly. To make the enhancement clearer, we plot in Fig. 3 the viscosity for ethanol solutions normalized by the viscosity of the solution at 20 °C. The largest relative increase is for concentrations of 15–20 mol %. This concentration corresponds well with the Type I clathrate $\text{C}_2\text{H}_5\text{OH} \cdot 5\frac{3}{4}\text{H}_2\text{O}$, which is 17 mol % ethanol.

We may now attempt to interpret some of our results. As discussed in the introduction, the origin of the anomalous properties of supercooled water most likely lies in the open, hydrogen bonded structure of the liquid. Breaking this structure with either pressure or foreign molecules destroys the apparent singularity. From

specific heat measurements hydrazine is known to be such a structure breaking molecule. Our data indicate that hydrazine also destroyed the viscosity anomaly corroborating the specific heat data implication that hydrazine is a structure breaker. The fact that addition of hydrazine to water did increase the viscosity means that whereas the old structure was destroyed a new structure was created, probably involving hydrazine–water hydrogen bonding. Hydrazine is perhaps most properly called a “structure modifier”.

Addition of ethanol to water not only increased the viscosity but increased the rate at which the viscosity increased with lowering temperature. This suggests that ethanol enhanced the open structure of water responsible for the singularity, not alter it as did hydrazine. This suggestion is quite reasonable in light of Stillinger's conjectures mentioned briefly above.¹⁰ Stillinger proposed that the open structure of water manifests itself in “strain free polyhedra” of water molecules which are similar, if not identical, to the cagelike clathrate structures formed around molecules like ethanol with small hydrophobic units. Ethanol is known to form clathrates and thus should promote formation of the structure responsible for the singularity, if indeed the singularity is due to these clathrate cages or polyhedra.

As far as the viscosity is concerned, it seems to us immaterial whether the formation of polyhedron structures is stimulated by a lowering of the temperature or an addition of a solute like ethanol. In one case, the structures are hollow; in the other case, the cavity is filled with an ethanol molecule, but the result is the same; a bulky convex cage leading to an enhanced viscosity. Since the stoichiometric formula of Type I ethanol hydrate is $\text{C}_2\text{H}_5\text{OH} \cdot 5\frac{3}{4}\text{H}_2\text{O}$, we expect for concentrations up to 15 to 20 mol % that very few free ethanol molecules will be found, most of them bound away inside their cages having no other affect than to promote cage formation. Thus, it is not unreasonable for us to suggest that the addition of a solute molecule like ethanol is equivalent to lowering the temperature of pure water, the more ethanol added the larger the effective cooling.

We have used our data to test whether the addition of ethanol is equivalent to lowering the temperature of pure water for the viscosity. To do so, we determined the viscosity of an ethanol solution at 75 °C the largest temperature used; for example, $\eta(75^{\circ}\text{C}) = 0.46$ cp for the 3.6% solution. We then found at what temperature pure water has this same viscosity, in our example this is at $T = 61^{\circ}\text{C}$. We then shifted the temperatures for the ethanol solution so that the viscosity of the solution at 75 °C matched the viscosity of the pure water. In our example this would be a -14°C shift. The data were then plotted on the same graph, the solution data all shifted to lower effective temperatures. The data will match at the normalization point of course, but if they continue to match for a significant temperature range thereafter, we may conclude that addition of ethanol is at least somewhat equivalent to a lowering of the temperature of pure water by an amount equal to

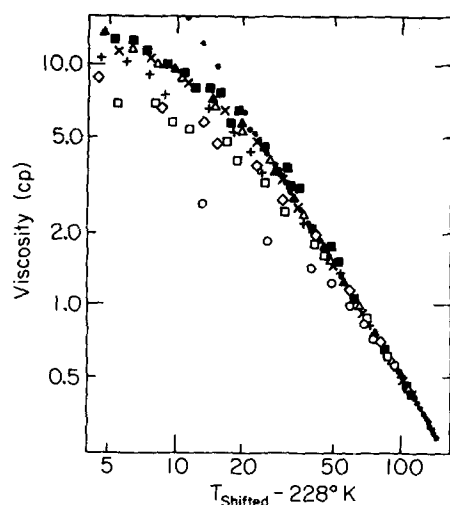


FIG. 4. Ethanol solution viscosity vs the difference in their shifted temperature from the singularity temperature $T_s = -45^\circ\text{C} = 228\text{ K}$. Symbols, concentration and temperature shift are: \bullet 0% (pure water), no shift; \blacksquare 3.6%, -14°C ; \triangle 6.7%, -22°C ; \times 10%, -27.5°C ; \blacktriangle 12.2%, -30°C ; $+$ 20%, -35°C ; \diamond 30%, -36.5°C ; \square 50%, -33°C ; \circ 100%, -14°C .

the temperature shift.

Such plots are given in Figs. 4 and 5, where the logarithm of the viscosity is plotted against the logarithm of the temperature difference from the singularity at $T_s = 228\text{ K} = -45^\circ\text{C}$. The temperature shifts are given in the figure captions. The water data follow a straight line indicating a power-law divergence with exponent (slope) of 1.55. The ethanol solution data in Fig. 4 are seen to match quite well with the water data for a significant range of temperature, roughly 60°C , for concentrations $\leq 20\text{ mol } \%$. This is the behavior expected from the argument above if ethanol addition is equivalent to temperature lowering. Certainly, it would

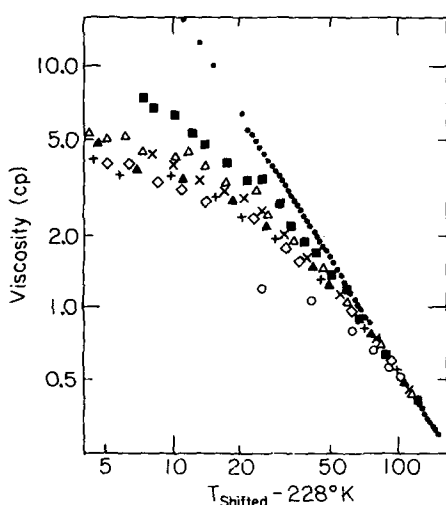


FIG. 5. Hydrazine solution viscosity vs the difference in their shifted temperature from the singularity temperature $T_s = -45^\circ\text{C} = 228\text{ K}$. Symbols, concentration and temperature shift are: \bullet 0% (pure H_2O), no shift; \blacksquare 5%, -10°C ; \triangle 11.5%, -19.5°C ; \times 17%, -26°C ; \blacktriangle 25%, -32.5°C ; $+$ 36%, -38°C ; \diamond 50%, -39°C ; \circ 100%, -19.5°C .

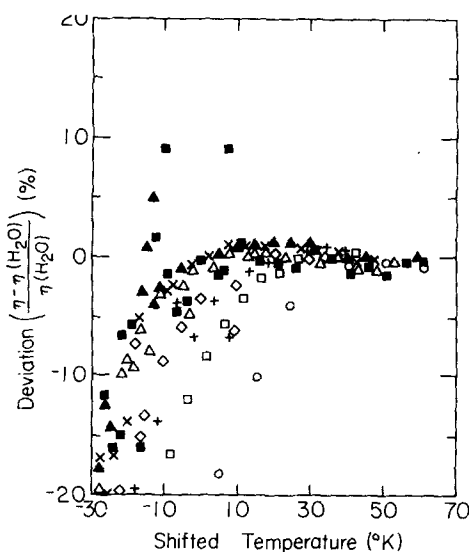


FIG. 6. Deviation plot of the ethanol solution viscosities from the pure water viscosity vs the ethanol solution shifted temperature. Symbol, concentration and temperature shift are: \bullet 0% (pure water), no shift; \blacksquare 3.6%, -14°C ; \triangle 6.7%, -22°C ; \times 10%, -27.5°C ; \blacktriangle 12.2%, -30°C ; $+$ 20%, -35°C ; \diamond 30%, -36.5°C ; \square 50%, -33°C ; \circ 100%, -14°C .

be interesting if all that occurred was a similar power-law dependence in the ethanol solutions with a new and higher, by the amount of the temperature shift, singularity temperature. What we feel is remarkable is that the ethanol solution behavior, once scaled in temperature difference from the singularity, is identified with the pure water behavior for a rather large temperature range. The hydrazine solution data, shown in Fig. 5 does not behave in this manner indicating that the ethanol data behavior is not coincidental and that hydrazine has the ability to destroy the anomaly.

Figure 6 displays the deviation of the shifted ethanol solution viscosity from that of pure water. The data match to within a few percent for some 80°C for the 3.6 mol % solution $\sim 60^\circ\text{C}$ for 6.7, 10, and 12 mol % and $\sim 20^\circ\text{C}$ for higher concentrations including, it is interesting to note, pure ethanol. The cutoff for matching lying in the 12–20 mol % range compares well with the estimate made above of above 15–20 mol % for the concentration of greatest viscosity increase with decreasing temperature and the concentration of a Type I clathrate $(5.75)^{-1} \approx 17\text{ mol } \%$. The deviation from matching for $T - T_s \leq 20^\circ\text{C}$ may be due to the inability of the more massive ethanol clathrates to form extended clusters as the empty polyhedra in pure water may do.

CONCLUSION

The viscosities of water solutions of ethanol and hydrazine were found to be larger than would be expected from an average of the pure component viscosities, implying that both solutes enhanced the structure relative to that of pure water. Our data also showed that the rate of increase of the viscosity with decreasing temperature was lower for hydrazine solutions than for pure water which suggested that any anomalous char-

acter in pure water's viscosity had been attenuated in a manner similar to that seen in specific heat measurements.

The rate of change of viscosity with temperature was greatly increased in ethanol solutions. To explain this, we used Stillinger's ideas that the anomalous supercooled properties and the hydrophobic interaction have the same source, namely, interaction of polyhedron cage structures in water. These structures arise spontaneously in pure water at low temperatures or are stimulated by nonpolar solutes or solutes with nonpolar groups such as ethanol. Ethanol is known to cause the formation of polyhedron structures called clathrates with an average of 5.75 water molecules per ethanol molecule. This concentration, about 17 mol%, corresponds well with the observed maximum viscosity enhancement. This led us to propose that, since both temperature reduction and addition of a solute like ethanol increase the concentration of these cage-like structures, one should be able to obtain lower effective temperatures by addition of ethanol. This proposal was tested in Fig. 4, and was seen to be reasonable.

Our physical picture is one where the viscosity increases with increasing concentration of these cage-like polyhedra. Whether the structures arise from the addition of ethanol or appear spontaneously, more so at low temperatures is immaterial because only the outer surfaces of the cages see each other. The ethanol molecule, below ~20 mol%, is bound inside the cage and so does not effect the viscosity except to cause formation of the cage. Bosio *et al.*⁸ saw structural enhancement in supercooled water and heavy water but did not see the enhancement in dilute solutions of ethanol. The open cages which spontaneously form in cold water would be less dense than the mean water density and hence would scatter x rays. Addition of ethanol would tend to fill these cages, not destroy them. The filled cages would be denser, probably closer to the mean density. Because of this smoothed density, the x rays might not detect the structure.

Finally, what might we speculate concerning other properties of aqueous ethanol solutions? Certainly, if addition of ethanol were a means of creating lower effective temperatures and thus greater degrees of effective supercooling, experiments on ethanol solutions would be quite interesting. Using Stanley and Teixeira's qualitative arguments the filled cages of such solutions would, unlike the empty cages of pure supercooled water, promote only small fluctuations in density and thus no anomalous behavior in the compressibility. On the other hand, the cage structure does have a large degree of order and so a small entropy whether it is empty or filled with a foreign molecule. Thus, we might argue that the same large fluctuations in entropy occur in both supercooled pure water and ethanol solutions, or other clathrate forming solutions, may exhibit anomalous behavior of both the specific heat at constant pressure, which is dependent on the mean square of the

entropy fluctuations, and the thermal expansivity, which is related to the cross correlation of entropy and density fluctuations, similar to that seen in supercooled water. In fact, Wada and Umeda²² have seen an elevation in the temperature of maximum density with addition of small quantities of ethanol and other simple alcohols to water. These alcohols are the only known substances to have this ability and they are all considered clathrate formers. Further experiments with clathrate formers in aqueous solution on both the thermal expansivity and the specific heat should be most helpful in elucidating the nature of the singularity in supercooled water.

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