

# Densities and partial molar volumes of supercooled aqueous solutions

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Density measurements of aqueous solutions of ethanol, *t*-butanol, and hydrazine in the temperature range from 50 °C down to nucleation are presented. From these data, solute partial molar volumes and temperatures of maximum density are determined. The partial molar volumes of the alcohol solutions at low concentration become small below  $-30$  °C, and the characteristic minimum in the partial molar volume vs concentration curve vanishes. The hydrazine solutions display similar behavior except no minimum is observed. It is also found that the temperature of maximum density washes out at finite concentrations and solutions with higher concentration do not seem to nucleate but may be forming glasses. These results are discussed in terms of a liquid clathrate structural model of water which becomes multiply connected to fill all space as the water is supercooled.

## I. INTRODUCTION

In the past few years it has been found that the unique properties of water become even stranger when examined below the freezing point in the liquid's supercooled state. Speedy and Angell<sup>1</sup> first showed that a number of thermodynamic and transport properties could be represented by power-law divergences with temperature as the temperature approached a singularity temperature  $T_s$ . All these properties seemed to be diverging at the same temperature,  $T_s \approx -45$  °C at atmospheric pressure. Since then, a number of experimental and theoretical papers have been presented to help elucidate the nature of supercooled water and the proposed singularity.<sup>2</sup>

Currently it seems that there are three theoretical pictures that have been advanced to explain these phenomena. First is the spinodal picture used by Speedy and Angell<sup>1</sup> and recently expanded upon by Speedy.<sup>3</sup> This picture views  $T_s$  as a spinodal temperature beyond which the liquid is totally unstable to fluctuations. In this picture the spinodal curve,  $T_s$  vs pressure, represents a line of stability limits running continuously from the liquid-solid metastable region to the liquid-gas critical point. The second picture, proposed by Stanley<sup>4</sup> and Stanley and Teixeira,<sup>5</sup> is based on a percolation model of hydrogen-bond connectivity of the water molecules. As the temperature is lowered, the water becomes highly interconnected via hydrogen bonds leading to a large network of hydrogen-bonded water molecules. This theory qualitatively predicts anomalous behavior in supercooled water but no singularity. The third picture, proposed by Stillinger,<sup>6</sup> suggests that clathrate structures, open cagelike structures of several hydrogen-bonded water molecules, form spontaneously as water is cooled. These structures, which are known to form around small hydrophobic solutes, attract each other. This attraction would lead to long range fluctuations which may diverge at  $T_s$ .

The concepts used in these three theoretical pictures are not necessarily mutually exclusive. All rely on

some significant structure probably caused by hydrogen bonding. Several experiments have shown the effect of structure breaking pressure<sup>7</sup> or solutes<sup>8</sup> is to destroy the apparent anomalies. The precise nature of the structure, however, remains an experimental question.

Recently, we have presented viscosity data for supercooled aqueous solutions of hydrazine and ethanol.<sup>9</sup> Our data showed that the viscosity no longer behaved in an anomalous fashion when the structure breaking solute hydrazine was added to the water. This ability to destroy the apparent anomaly in supercooled water corroborated the measurements of Oguni and Angell<sup>8</sup> for the isobaric heat capacity, where hydrazine also destroyed that property's anomalous behavior. Addition of ethanol, on the other hand, seemed to enhance the anomaly in the viscosity. We interpreted our data to suggest that addition of ethanol to water was equivalent to an effective cooling of pure water. Furthermore, since it is known that clathrate type structures form around the ethanol molecule in solution, we inferred that similar clathrate type structures form spontaneously in pure water as the temperature is lowered and that these liquid clathrate structures are responsible for the anomaly at  $T_s$ . Since then, we have learned that Speedy<sup>10</sup> has independently performed measurements of the electrical conductivity of KBr doped water and dilute ethanol solutions. He found that the ethanol enhanced the anomalous divergence of the conductivity, a result similar to our viscosity measurements. He also interpreted his data to indicate clathrate type cages were forming in the solution leading to an enhancement of the anomaly.

These experiments lend support to Stillinger's picture that clathrate type structures form in cooled water and cause the anomalous behavior. They do not, however, eliminate the other theoretical pictures discussed above. The proposed singularity temperature  $T_s$  may still represent a spinodal point with the clathrate being the significant structure. The random gel-like network envisioned in the percolation model could have as its smallest structural units clathrate cages

which while they cannot be periodically repeated to fill space, give supercooled water its characteristic openness.

It is our purpose here to report density measurements of supercooled aqueous solutions. The philosophy of this experiment is that solutes can work as experimental probes of liquid water's structure. Solutes with small hydrophobic groups, such as the smaller monohydric alcohols, should fit into the open vacancies in water's structure as well as stimulate liquid clathrate structure formation. Solutes that hydrogen bond strongly with water, on the other hand, may disrupt water's hydrogen-bonded quasilattice. The temperature of maximum density, TMD, and subsequent expansion of water with further cooling are direct indications of structuring in the liquid and hence should be very interesting to study with solute effects.

## II. EXPERIMENTAL

### A. Method

Aqueous solutions were prepared using freshly boiled, distilled water. Solutes were reagent grade ethanol, *t*-butanol, and hydrazine obtained straight from the bottle without further purification.

To determine the density of our solutions, we measured the meniscus height vs temperature of the solution held in glass capillaries. The glass capillaries were drawn by hand from standard wall, 3 mm i.d. Pyrex glass tubing. The capillaries were found to be quite uniform in diameter with inside diameters ranging from 60 to 90  $\mu$ . They were filled by first flame sealing one end and inserting the other, still open, end into the solution. Heating the closed end expelled air allowing for liquid to be drawn into the capillary after the heat was removed. Once filled the remaining open end was flame sealed, often leaving no air bubble at this second end. The capillaries were usually filled with approximately a 10 cm length of liquid and another 6 to 10 cm length of air above the free meniscus to allow for essentially isobaric expansion. These capillaries were glued to a saw blade shaped metal strip, the points of the blade acted as fiducial marks to which to compare the meniscus level.

Temperature control was achieved by placing the capillaries in a well stirred 30 l ethanol bath equipped with a heater, and two refrigerant probes. One refrigerant probe was mechanical and worked well to

TABLE II. Density ( $\text{g}/\text{cm}^3$ ) of aqueous ethanol solutions (concentrations in mol%).

$T(^{\circ}\text{C})$	1	3.5	5	6.7	8.3	10	15	20
50	0.9832	0.9722	0.9665	0.9608	0.9548	0.9489	0.9316	0.1986
40	0.9874	0.9771	0.9717	0.9662	0.9608	0.9554	0.9388	0.9268
30	0.9908	0.9810	0.9761	0.9712	0.9660	0.9611	0.9458	0.9344
20	0.9935	0.9841	0.9795	0.9749	0.9703	0.9657	0.9520	0.9417
10	0.9949	0.9861	0.9818	0.9777	0.9739	0.9699	0.9579	0.9485
5	0.9952	0.9866	0.9825	0.9784	0.9752	0.9718	...	0.9515
0	0.9952	0.9868	0.9827	0.9795	0.9767	0.9735	0.9634	0.9549
-5	0.9948	0.9866	0.9828	0.9797	0.9774	0.9745	0.9660	0.9581
-10	0.9938	0.9856	0.9824	0.9799	0.9783	0.9757	0.9683	0.9612
-15	0.9922	0.9846	0.9815	0.9796	0.9786	0.9765	0.9709	0.9642
-20	0.9901	0.9827	0.9800	0.9790	0.9786	0.9774	0.9734	0.9675
-25	0.9869	0.9801	0.9781	0.9781	0.9786	0.9778	0.9755	0.9700
-27	...	0.9786	0.9769	0.9778	0.9786	0.9780	...	...
-30	...	0.9763	...	0.9771	0.9788	0.9784	0.9775	0.9730
-32	...	...	...	0.9766	...	0.9790	0.9784	0.9745
-35	...	...	...	...	0.9785	...	...	...
-40	...	...	...	...	...	0.9793	...	0.9785

-35  $^{\circ}\text{C}$ . The other probe used liquid nitrogen forced through copper cooling coils and provided rough control down to -100  $^{\circ}\text{C}$ . The temperature was measured with a thermistor placed near the capillaries that had been calibrated with the melting points of mercury (-39.8  $^{\circ}\text{C}$ ) and water and a high quality mercury thermometer. Over all accuracy of our temperature measurement was better than  $\pm 0.5^{\circ}\text{C}$ .

The meniscus height relative to the fiducial mark was observed with a stationary, long-working-distance, 2.6 power microscope through a window in the bath. The microscope was equipped with a filar micrometer to measure relative meniscus-to-fiducial mark distances as a function of temperature. Each capillary was cycled in temperature between 20 and 50  $^{\circ}\text{C}$  to ensure reproducibility of the meniscus level measurements. Then the temperature was monotonically lowered, usually in steps of 5  $^{\circ}\text{C}$ , while making meniscus level measurements until the solution either froze or further cooling was difficult.

Densities were obtained by calibrating the data, which involved meniscus-to-fiducial mark distances, to the known densities at 20 and 50  $^{\circ}\text{C}$ . Tabulated densities above freezing for water,<sup>11</sup> ethanol solutions,<sup>11,12</sup> and hydrazine solutions<sup>13</sup> were found in the literature. Some tabulated data for *t*-butanol solutions<sup>14</sup> were also found, but it was still necessary to supplement these data with our own measurements at 20 and 50  $^{\circ}\text{C}$  using a 25 ml pycnometer. Small corrections of the order of a few parts in  $10^4$  due to the thermal expansion of the Pyrex glass capillaries were also included.

From our reproducibility with temperature cycling mentioned above, we estimate the overall accuracy of all our density measurements to be  $3 \times 10^{-4} \text{ g}/\text{cm}^3$ . In Table I we compare our water density values to others offered in the literature.<sup>15,16</sup> Our density values are somewhat larger. The earlier data, however, were not corrected for the expansion of the capillary which would tend to adjust these values to be a few parts in  $10^4$  larger. The data for the three aqueous solutions studied here are given in Tables II, III, and IV.

TABLE I. Density ( $\text{g}/\text{cm}^3$ ) of supercooled water.

$T(^{\circ}\text{C})$	This work	Reference 15	Reference 16
0	0.9998	0.9999	0.9999
-5	0.9994	0.9995	0.9992
-10	0.9984	0.9983	0.9980
-15	0.9965	0.9964	0.9962
-20	0.9939	0.9936	0.9934
-25	0.9901	0.9895	
-30		0.9829	
-34		0.9751	

TABLE III. Density ( $\text{g}/\text{cm}^3$ ) of aqueous *t*-butanol solutions (concentrations in mol %).

$T(^{\circ}\text{C})$	1	2.7	4.8	7.3	11.1	15
50	0.9815	0.9708	0.9580	0.9421	0.9180	0.8982
40	0.9859	0.9759	0.9642	0.9485	0.9258	0.9057
30	0.9895	0.9801	0.9697	0.9549	...	...
20	0.9922	0.9835	0.9746	0.9609	0.9400	0.9200
10	0.9937	0.9857	0.9785	0.9669	...	...
5	0.9941	0.9866	0.9801	0.9696	...	...
0	0.9939	0.9869	0.9813	0.9721	0.9534	0.9336
-5	0.9934	0.9868	0.9824	0.9746	0.9571	0.9370
-10	0.9924	0.9863	0.9831	0.9773	0.9605	0.9405
-15	0.9907	0.9854	0.9832	0.9794	0.9644	...
-20	0.9882	0.9841	0.9834	0.9808	...	...
-25	0.9847	0.9821	0.9830	0.9822	...	...
-27	...	0.9812	0.9828	0.9826	...	...
-30	...	...	0.9827	0.9835	...	...
-32	...	...	0.9827	...	...	...
-35	...	...	...	0.9848	...	...
-40	...	...	...	0.9861	...	...

## B. Results

Figures 1, 2, and 3 give our measured densities as a function of temperature for various concentrations of ethanol, *t*-butanol, and hydrazine, respectively, in aqueous solution. Perhaps the most remarkable characteristic of these plots is the curious intersection or crossover of the density curves near  $-30^{\circ}\text{C}$  for both alcohol solutions. No similar crossover is seen in the hydrazine solutions.

Figures 1, 2, and 3 also show a decrease in the TMD with increasing concentration of all three substances. Ultimately, the density maximum disappears or washes

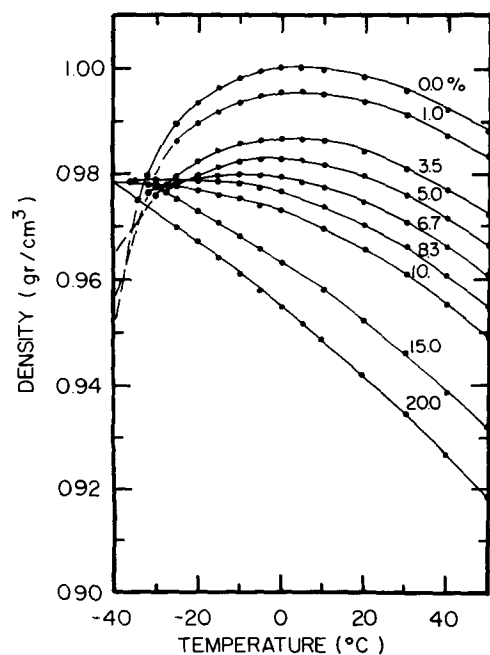


FIG. 1. The density of aqueous ethanol solutions vs temperature. Ethanol concentrations are given in mol %. Dashed lines represent extrapolations of the data to  $-40^{\circ}\text{C}$ .

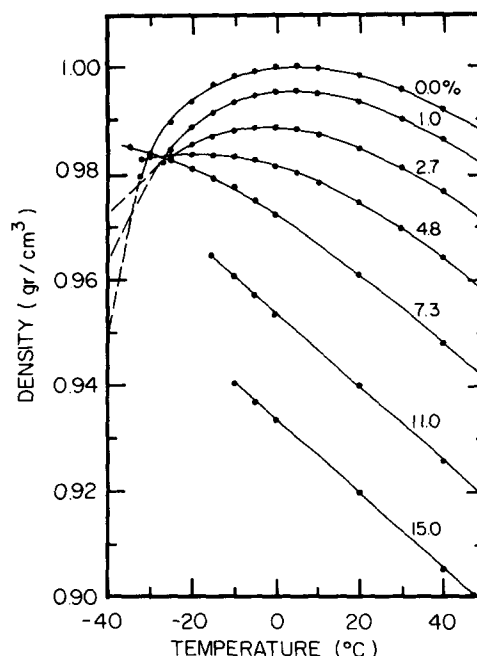


FIG. 2. The density of aqueous *t*-butanol solutions vs temperature. *t*-butanol concentrations are given in mol %. Dashed lines represent extrapolations of the data to  $-40^{\circ}\text{C}$ .

out at a certain concentration, a concentration we shall call the "wash-out" concentration. Figure 4 is a plot of the TMD vs concentration for all three systems. Also included is high precision data from Wada and Umeda<sup>17</sup> at low concentration that shows an initial increase in the TMD with concentration for the alcohol solutions.

A second curious feature of the experiment, not displayed in the figures, concerns the nucleation temperature of the solutions. All of the low concentration solutions were visually seen to nucleate between  $-25$  and  $-35^{\circ}\text{C}$ . Many of the higher concentrations, however,

TABLE IV. Density ( $\text{g}/\text{cm}^3$ ) of aqueous hydrazine solutions (concentrations in mol %).

$T(^{\circ}\text{C})$	1	3.3	5.4	8.9	13
50	0.9894	0.9923	0.9938	0.9968	1.0005
40	0.9933	0.9963	0.9981	1.0016	1.0055
30	0.9966	0.9995	1.0018	1.0060	1.0101
20	0.9991	1.0022	1.0050	1.0095	1.0145
10	1.0007	1.0042	1.0074	1.0126	1.0183
5	1.0013	1.0049	1.0084	...	...
0	1.0014	1.0054	1.0093	1.0149	1.0217
-5	1.0013	1.0056	1.0098	1.0159	1.0239
-10	1.0005	1.0055	1.0103	1.0169	1.0253
-15	0.9994	1.0053	1.0104	1.0178	1.0261
-20	0.9977	1.0044	1.0102	1.0184	1.0273
-25	0.9949	1.0032	1.0097	1.0188	1.0284
-27	...	1.0026	1.0094	...	...
-30	...	1.0013	...	1.0190	1.0294
-32	...	...	...	1.0190	1.0298
-36	...	...	...	1.0188	1.0306
-40	...	...	...	1.0190	1.0311

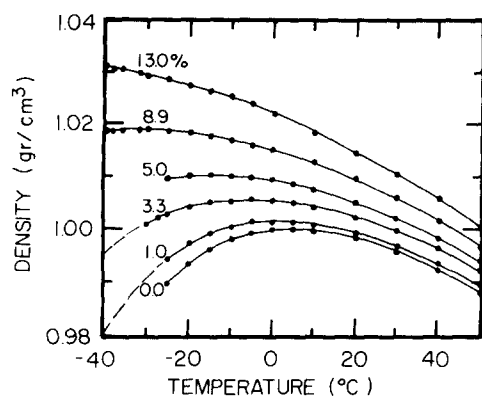


FIG. 3. The density of aqueous hydrazine solutions vs temperature. Hydrazine concentrations are given in mol%. Dashed lines represent extrapolations of the data to  $-40^{\circ}\text{C}$ .

were never seen to nucleate even down to  $-80^{\circ}\text{C}$ , but rather always appeared clear and homogeneous. One might assume that these solutions supercooled to a glass. Interestingly, the concentration dividing the nucleating from the nonnucleation region for all three solutions corresponded to the wash-out concentration defined above.

### III. DISCUSSION

As mentioned in the Introduction, our intent was to use solutes as probes of liquid water's structure. The TMD of water is a direct indication of an open structure developing in water as the temperature is lowered. Examination of Figs. 1 and 2 shows that as the less dense alcohol is added to water for any temperature above  $-30^{\circ}\text{C}$  the solution becomes less dense. If we make reasonable extrapolations of our data below  $-30^{\circ}\text{C}$ , however, the solution would seem to become denser as

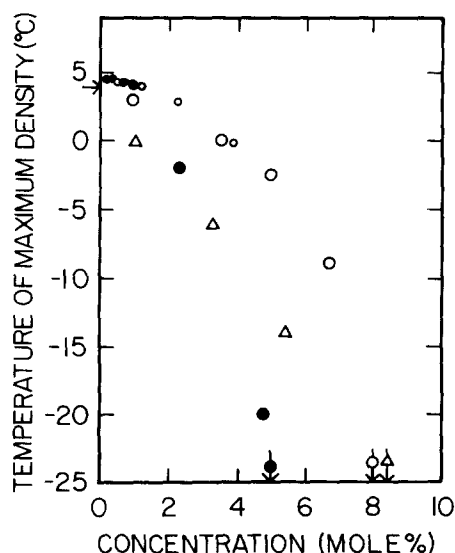


FIG. 4. Temperature of maximum density for aqueous solutions of:  $\circ$  ethanol,  $\bullet$  *t*-butanol,  $\blacktriangle$  hydrazine. Small symbols represent data from Ref. 17. Arrows represent estimated wash-out concentrations.

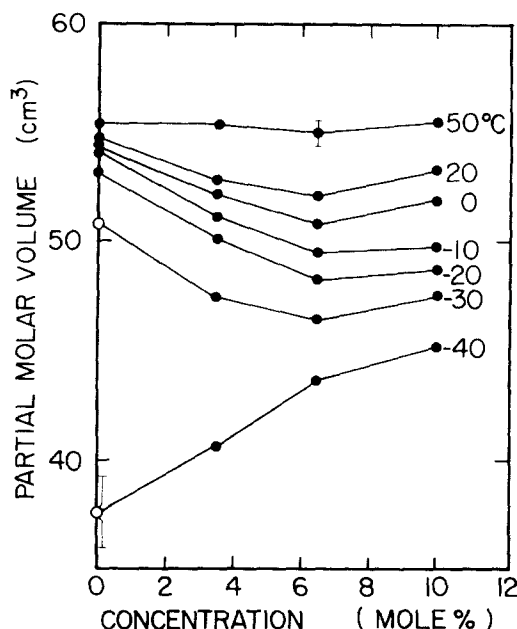


FIG. 5. Partial molar volume of ethanol in aqueous solution vs concentration for various temperatures. Solid circles represent partial molar volumes calculated directly from the data, open circles represent partial molar volumes calculated from extrapolated data shown in Fig. 1. Representative error estimates are shown.

the alcohol is added, implying that the alcohol is filling the voids in the open water structure.

To quantify this we have calculated the solute partial molar volume  $\bar{V}_2$  from our density data. Our data are spaced rather widely for accurate calculation of the molar volume, but the values we do obtain can still be used to indicate the trends of molar volume with concentration and temperature. Comparisons of our molar volumes with available literature<sup>18</sup> are quite satisfactory. The molar volumes are plotted in Figs. 5, 6, and 7 as function of concentration.

To interpret these graphs we recall the results of earlier workers such as Glew<sup>19</sup> and Franks<sup>20</sup> on aqueous solution properties. Apolar solutes or mixed solutes with apolar parts such as the monohydric alcohols stimulate the formation of clathrate-type structures in water. These structures are similar to the stable solid clathrates or gas hydrates<sup>21</sup> except that in the liquid they are not rigid and their stoichiometry is less well defined. Dissolution of an apolar or mixed solute is accomplished either by filling clathrate-like voids already present in the water or forming additional structures, which is energetically favorable because of the enhanced water-water hydrogen bonding. These experimental inferences are supported by molecular dynamics calculations<sup>8,22</sup> which have shown the presence of short-lived polyhedra of water molecules similar to the clathrate structure. These polyhedra may be clustered around a solute molecule or may form spontaneously in pure water. Thus the liquid clathrate picture of water is one of clathrate-like polyhedra of hydrogen-bonded water molecules with voids similar to

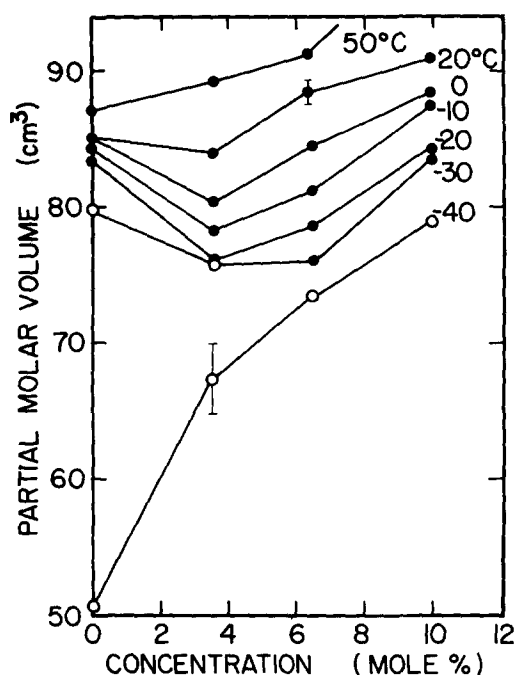


FIG. 6. Partial molar volume of *t*-butanol in aqueous solution vs concentration for various temperatures. Solid circles represent partial molar volumes calculated directly from the data, open circles represent partial molar volumes calculated from extrapolated data shown in Fig. 2. Representative error estimates are shown.

those seen in solid clathrates. The polyhedra responsible for these voids are short lived and randomly distributed but recall their stable clathrate cousins in size and stoichiometry.

Figures 5 and 6, for ethanol and *t*-butanol, show the usual room temperature behavior for solutes. The partial molar volumes at infinite dilution are less than the pure solute molar volume indicating void filling by the solute molecules. This effect increases on cooling indicating more voids. Also characteristic of such solutes is the initial decrease to a minimum of the partial molar volume with concentration. This has been interpreted as a stabilization of the water structure. Franks<sup>20</sup> related this decrease to the increase in the TMD for these solutions. Thus, the solution is becoming more "waterlike" which might mean more clathrate structures are formed.

We interpret this initial decrease of  $\bar{V}_2$  vs the concentration  $x_2$  to indicate that more voids are created than filled upon addition of the solute, since subsequent addition, leads to smaller partial molar volumes, which implies more voids. This is not unreasonable because Glew *et al.*<sup>23</sup> have interpreted the increased argon solubility in dilute ethanol solutions<sup>24</sup> over pure water as due to the formation of more voids than are filled by the ethanol molecules. Also, it is known that many gases which do not form stable clathrates can with the aid of a "help gas" form a stable double hydrate.<sup>21</sup> The help gas stimulates voids that the first gas can fill.

Figures 5 and 6 also show that the minimum in  $\bar{V}_2$  vs  $x_2$  occurs at a smaller concentration for *t*-butanol than

ethanol. This may be due to the fact that the *t*-butanol molecules are bigger and hence use up the water molecules more quickly than the ethanol molecules during clathrate formation. A similar size dependence has been seen in other solution properties.<sup>20</sup> Such a size dependence is not seen in the stable solid clathrates which is an indication of the lack of an exact stoichiometry in the liquid clathrate structure.

New results that can be obtained from these data concern behavior of the partial molar volume in the sub-zero temperature region. Since our density data are limited to  $T > -30^\circ\text{C}$  for low concentrations, we have in some cases extrapolated the data by eye to  $T = -40^\circ\text{C}$  in order to calculate  $\bar{V}_2$  at this temperature. These extrapolated values are indicated by the open circles in Figs. 5, 6, and 7. The extrapolated values cannot be considered as highly accurate, but they are accurate enough to indicate the general behavior in the partial molar volume at these temperatures.

The partial molar volumes of ethanol and *t*-butanol at infinite dilution decrease slowly with temperatures until about  $-30^\circ\text{C}$  when the decrease accelerates. At  $T = -40^\circ\text{C}$  the partial molar volumes are only 55% to 60% of the pure solute values. This, we believe, is a dramatic indication that the water is quickly developing a very open network in which the alcohol molecules easily fit with very little increase in volume.

The second important feature at  $T = -40^\circ\text{C}$  is that the minimum in  $\bar{V}_2$  vs  $x_2$  has vanished. This may be interpreted to mean that, contrary to the higher temperature behavior, addition of the alcohol no longer promotes further void or clathrate formation. This is

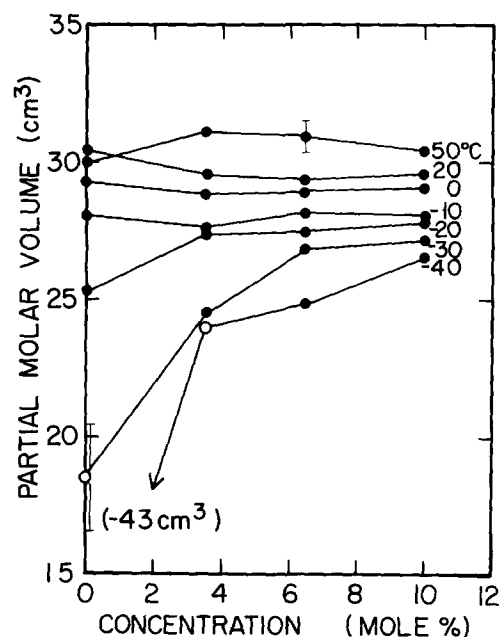


FIG. 7. Partial molar volume of hydrazine in aqueous solution vs concentration for various temperatures. Solid circles represent partial molar volumes calculated directly from the data, open circles represent partial molar volumes calculated from extrapolated data shown in Fig. 3. Representative error estimates are shown.

not surprising since the apparent vanishing of  $\bar{V}_2$  with decreasing temperature at zero concentration indicates that the water is approaching a state which is totally saturated with regard to void formation. Solutes can not promote more void or clathrate structures because nearly all the water molecules are already participating in such structure at  $-40^\circ\text{C}$ . The general nature of this behavior as well as the drastic decrease in  $\bar{V}_2(x_2=0)$  are both a consequence of the crossover near  $-30^\circ\text{C}$  in the density vs temperature plots, Figs. 1 and 2, and it is important to note, are not dependent upon the details of our extrapolation to  $-40^\circ\text{C}$ .

We may now reconsider our viscosity data for supercooled ethanol solutions.<sup>9</sup> We found for dilute solutions that addition of ethanol was equivalent to reducing the temperature because both caused clathrate structure formation. The equivalence worked well for describing the viscosity down to temperatures to within roughly  $20^\circ\text{C}$  of the singular temperature  $T_s = -45^\circ\text{C}$ . After this, the equivalence seemed to relax and the power-law behavior waned. We can now interpret this to indicate that the clathrate building ability of the ethanol is no longer as effective as at higher temperatures which qualitatively corroborates our interpretation of the partial molar volume behavior above.

Figure 7 shows the behavior of the hydrazine solution partial molar volume. Pure hydrazine's molar volume is  $31.6\text{ cm}^3$  at  $20^\circ\text{C}$  only slightly larger than the solution partial molar volume. This is in contrast to both alcohol solutions. Also in contrast is the lack of any concentration dependence of the partial molar volume. The partial molar volume at infinite dilution does, however, become much smaller with temperature similar to the alcohol solutions and even appears to become negative at  $-40^\circ\text{C}$ .

We must remember that hydrazine readily hydrogen bonds with water. Our data indicate neither a TMD nor a minimum in  $\bar{V}_2(x_2)$ . Furthermore, it has been found that hydrazine destroys the anomalous behavior of the specific heat<sup>8</sup> and viscosity<sup>9</sup> in supercooled solutions. Because of this, hydrazine is called a structure breaker. We may conclude then that the drastic decrease in the partial molar volume for  $T < -30^\circ\text{C}$  seen in Fig. 7 is not due, as in the alcohol solutions, to the interstitial filling of clathrate voids with hydrazine molecules; but rather, graphically demonstrates the wholesale destruction of the large volume, open network structure of the water at these temperatures.

Before concluding this section, we would also like to comment on the "washing out" of the TMD. First note that the wash-out concentrations are approximately 8 and 5 mol% for the ethanol and *t*-butanol, respectively. Thus, once again, a size dependence is seen, the ratio of wash-out concentrations being roughly equal to ratio of molecular weights. We also mentioned above that solutions with the wash-out concentration or higher often did not nucleate but seemed to form glasses. We have argued above that the alcohol molecules are filling voids in the water, more ethanol molecules are needed than *t*-butanol molecules because the ethanol molecules are smaller. One might further argue that this void filling

is fairly complete at the wash-out concentration; concentrations that qualitatively correspond to the minima in the  $\bar{V}_2(x_2)$  curves. The wash-out concentration may represent a concentration where the clathrate structure is, to some degree, stabilized by the alcohol molecules relative to icelike fluctuations. A preponderance of clathrate structures might tend to eliminate icelike fluctuations and thus retard nucleation to the stable ice phase and enhance the probability of glass formation. We will investigate these glass forming abilities further in future work.

#### IV. CONCLUSIONS

We have presented density data for three aqueous solutions supercooled down to their nucleation temperatures. The data for the alcohol solutions showed an interesting crossover behavior at roughly  $-30^\circ\text{C}$ . Solute partial molar volumes  $\bar{V}_2$  derived from these data showed: (1)  $\bar{V}_2(x_2=0)$  decreased very rapidly below  $-30^\circ\text{C}$ , and (2) the minimum in the  $\bar{V}_2(x_2)$  curve disappeared below  $-30^\circ\text{C}$ . These results, which are a consequence of the crossover, were interpreted to imply that water develops a very open structure as it is supercooled with voids similar to those found in clathrate structures. The disappearance of the  $\bar{V}_2(x_2)$  minimum indicated that essentially all the water molecules are participating in this open structure formation below  $-30^\circ\text{C}$ .

The data also indicated that the TMD disappeared or washed out at approximately 8 and 5 mol% for the ethanol and *t*-butanol solutions, respectively. These wash-out concentrations corresponded well to the concentration minima in  $\bar{V}_2(x_2)$  for these solutions, and since their ratio was equal to the ratio of the molecular weights of the alcohols, this result was interpreted as a solute size dependence. Furthermore, solutions with concentrations greater than the wash-out concentrations in all three systems appeared not to nucleate and may be forming glasses.

It is interesting to speculate, in light of the results above, on the ultimate state of water at the singularity temperature  $T_s$  near  $-45^\circ\text{C}$ . Would  $\bar{V}_2(x_2=0) \rightarrow 0$  at  $T_s$  for all small apolar and mixed solutes? Such a result may be speculatively inferred from the behavior of  $\bar{V}_2(x_2=0)$  as the temperature decreases. It would certainly be consistent with the picture implied by our results where an amorphous lattice work of clathrate cages involving every water molecule is forming in supercooled water. Such a picture is a direct implication of results (1) and (2) above, as well as being a natural extension of the room temperature liquid clathrate picture. Spectroscopic evidence<sup>25</sup> indicating increased water-water hydrogen bonding as the temperature decreased is also favorable to this model. This picture has elements of both the Stanley-Teixeira percolation model and the Stillinger clathrate model discussed above, but does not eliminate, because our data cannot eliminate, the Speedy-Angell spinodal concept.

In future work we shall use either smaller capillaries or emulsion techniques to study the density of clathrate forming aqueous solutions at lower temperatures. Such

measurements will allow us to vindicate our extrapolations to low temperature. We will also explore the effect of solutes on glass formation near the TMD wash-out concentration.

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