

Supercooled Water

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Apparent First-Order Liquid–Liquid Transition with Pre-transition Density Anomaly, in Water-Rich Ideal Solutions

Zuofeng Zhao and C. Austen Angell*

Abstract: The striking increases in response functions observed during supercooling of pure water have been the source of much interest and controversy. Imminent divergences of compressibility etc. unfortunately cannot be confirmed due to pre-emption by ice crystallization. Crystallization can be repressed by addition of second components, but these usually destroy the anomalies of interest. Here we study systems in which protic ionic liquid second components dissolve ideally in water, and ice formation is avoided without destroying the anomalies. We observe a major heat capacity spike during cooling, which is reversed during heating, and is apparently of first order. It occurs just before the glassy state is reached and is preceded by water-like density anomalies. We propose that it is the much-discussed liquid–liquid transition previously hidden by crystallization. Fast cooling should allow the important fluctuations/structures to be preserved in the glassy state for leisurely investigation.

The apparently diverging response functions (C_p , κ_T , α_p), and relaxation properties of water, that are observed on cooling well below the melting point, have fascinated physical scientists since their discovery some fifty years ago.^[1] Except for the much-studied ST2 pair potential model,^[2] interpretations invoking the existence of a second critical point,^[3] or of a spinodal limit to the stability of normal water,^[4] have been difficult to verify or refute because of the seemingly inevitable intercession of ice crystallization.^[5]

As has long been known, crystallization can be avoided by sufficient addition of hydrophilic second components (salts^[6] or molecules^[7]) to lower the chemical potential of water in the solution. This often results in the formation of aqueous glasses. Unfortunately, it has also resulted in the suppression of the anomalous properties of interest, so the basic problem of decoupling the anomalies from the crystallization has remained unresolved. Typical examples have been aqueous solutions of the water-like molecules hydrazine (N_2H_4) and hydrogen peroxide (H_2O_2) studied in this laboratory^[8] and the aqueous solutions of NaCl studied by Archer and Carter.^[9]

Indeed it had seemed from these studies and others using emulsified solutions^[10] and combining alkali halides with pressure,^[11] that the condition for repression of crystallization was the complete repression of the anomalous fluctuations.

This was presumed due to the breakup of clusters of open tetrahedral topologies from which ice I_h nuclei could form.

However it now appears that the suppression of the “water anomalies” in the presence of glassforming quantities of second components is not inevitable. We have found that some binary solutions of water with salts of large weak-field cations and simple anions, which are themselves glassforming, may show an anomalous excess heat capacity like that of supercooled water—except that crystallization does not at any point terminate the observation and the whole anomaly can be seen. An example of heat capacity behavior then revealed is shown in Figure 1 where it is compared with the behavior of pure water. No crystallization occurs during the cooling of the solution of Figure 1 so the final state is a water-rich ionic glass in which the fluctuations in enthalpy responsible for the peak heat capacity are preserved for leisurely investigation by appropriate methods.

Figure 1 shows, on the same scale, the heat capacity of pure water down to -38°C ,^[12] and the total heat capacity of the special salt solution. The salt combination is ethylammo-

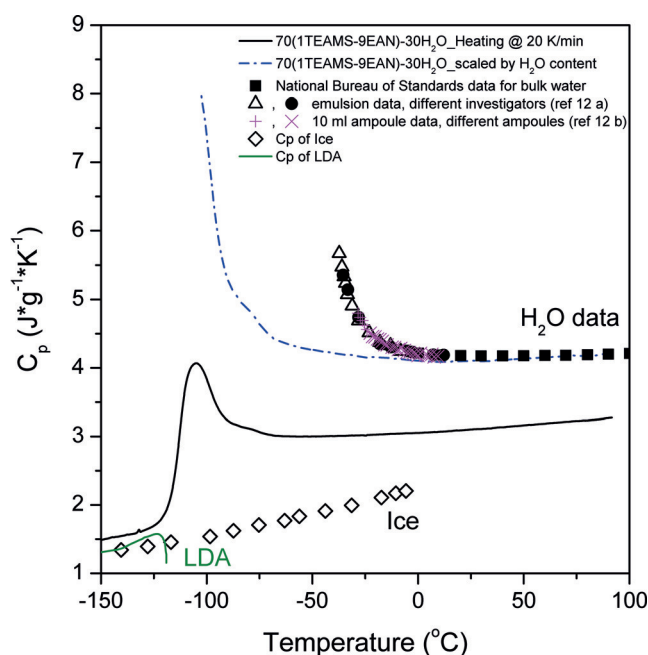


Figure 1. The heat capacity of pure water down to -38°C compared with the heat capacity of the EAN–TEAMS–water solution containing 73.6 mol % water, obtained during a cooling scan at 20 K min^{-1} . If the heat capacity peak in the solution is attributed to the water content and scaled up by its weight percentage the peak height greatly exceeds the heat capacity of pure water at its lowest temperature (see dash-dotted curve: only the ergodic part is shown).

[*] Z. Zhao, Prof. C. A. Angell
School of Molecular Sciences, Arizona State University
Tempe, AZ, 85287-1604 (USA)
E-mail: austenangell@gmail.com

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niium nitrate (EAN) and triethylammonium methanesulfonate (TEAMS), in mole ratio 9:1, and the solution contains 70 wt % salt, 30 wt % water. Restated in mol % units, the salt content of the solution is 26.4 mol %, meaning that there are some 3 molecules of water for each pair of oppositely charged ions. Although this is a rather concentrated solution by normal standards it is one in which the water activity coefficient remains at about unity since the freezing point depression remains close to the values predicted by ideal freezing point depression equations for each of the components, ice and EAN, as we show in the Supporting Information (SI). Furthermore, if we convert the heat capacity from $\text{J g}^{-1} \text{K}^{-1}$ to $\text{J g}_{\text{H}_2\text{O}}^{-1} \text{K}^{-1}$, the magnitude of the spike quite overshadows that seen for pure water, which itself is generally considered remarkable.

The heat capacity of this solution was determined using a PerkinElmer DSC7 differential scanning calorimeter, during a *downscan* at 20 K min^{-1} . Since it is a downscan, the increasing heat capacity can have nothing to do with the heat capacity overshoot often seen at the glass transition during *reheating*. That this is not unique to the water + (EAN-TEAMS) system, is seen from the Figure 2 in which similar, and in one case much more pronounced, behavior is seen for a series of solutions of *inorganic* cation salts based on the hydrazinium cation, now paired with trihaloacetate anions and their mixtures to ensure that only ice is formed as a solid phase on reheating. (In the legend TFA is trifluoroacetate, and TCIA is trichloroacetate.) The largest effect is seen for the solution of the single salt hydrazinium trifluoroacetate with 84.4 mol % water. This Figure also shows the behavior of a lower water content solution (60 mol % H_2O), which is that of a normal glassformer.

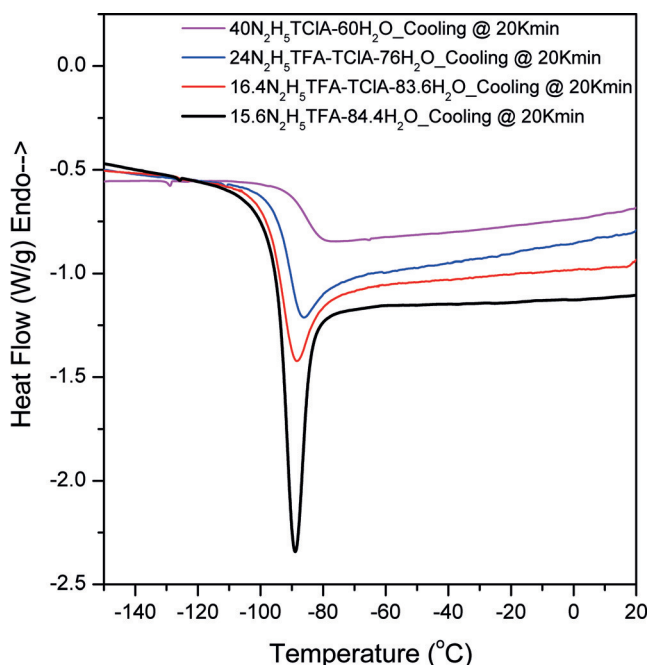


Figure 2. DSC downscans at 20 K min^{-1} of solutions of inorganic salts with large N_2H_5^+ cations and trihaloacetate anions or their mixtures, showing normal glass transition at lower (60 mol %) water content and “spike” anomalies at high water contents.

In Figure 3, the 84.4 mol % H_2O case of Figure 2 is selected for detailed comparison with the behavior of pure supercooled water. It is seen that the cooling behavior, now shown as solution heat capacity, is reversible with small hysteresis (dashed curve). Ice crystals form during further heating above the “spike”, with an enthalpy release almost twice that of the “spike” anomaly. These ice crystals then re-dissolve, terminating at temperatures lying on an equilibrium ice liquidus line (see SI) which is found to almost coincide with the ideal melting point depression line calculated using the heat of fusion of ice according to the equation,^[13]

$$\Delta T_m = -(R T_m^2 / \Delta H_m) 2 X_{\text{salt}} \quad (1)$$

where $\Delta T_m = (T_m - T_1)$, T_m and ΔH_m are the melting point and heat of fusion of ice I_h , respectively, T_1 is the liquidus temperature, X_{salt} is the mole fraction of salt, and the approximation $T_m \cdot T_1 \approx T_m^2$ has been introduced. The factor 2 represents the number of moles of new particles added to the solution, per mole of salt. The small deviations from ideality when observed, are positive, implying a weak tendency of water molecules to cluster.

The sharply rising heat capacity spike of Figure 3 cannot even be approximated by a power law, as in the case of the pure water phenomenon,^[14] because the best fit to a power law yields a divergence temperature that, rather than lying well below the peak temperature as in the case of mW water,^[16] lies above it (see SI). The sharp spike is thus largely of first order character.

To interpret these observations we turn to the studies of Koop et al.^[17] (see also Zobrist et al.^[18]) who showed that both the melting points on the ice saturation line, and the homogeneous nucleation temperature of solutions of high pressure water and a wide variety of binary solutions, are determined by the water activity alone—which they^[17] account for by showing (by a variety of structural techniques) that the water structure is invariant at constant water activity. This quantification of the old idea that the effect of pressure on water structure is the same as the effect of solute additions, allows us to relate the observations of Figures 2 and 3, at least approximately, to observations that would be made in pure water at high pressures, if crystallization of ice did not occur. We do this as follows.

If the main effect of adding a second component that mixes almost ideally with water, is to make nucleation of ice more difficult, then careful choice of composition should allow access to whatever process might lie below the temperature of homogeneous nucleation temperature of ice, that is, in the “no-man’s land” of the pure water case. Based on comparison of melting points of pure water under pressure with liquidus temperatures in the binary systems, Ref. [17] and [18] suggest an equivalence of the solutions of Figure 3 and pure water in the pressure range of 150–200 MPa. The lower limit is supported by the volumetric data of Figure 3, lower panel (to be discussed below).

But the analysis of laboratory compressibility data on pure water,^[19] supported by the excellent data matching by the athermal two-state model of Holten and Anisimov,^[20] suggests that, at 160 MPa pressure and between the homoge-

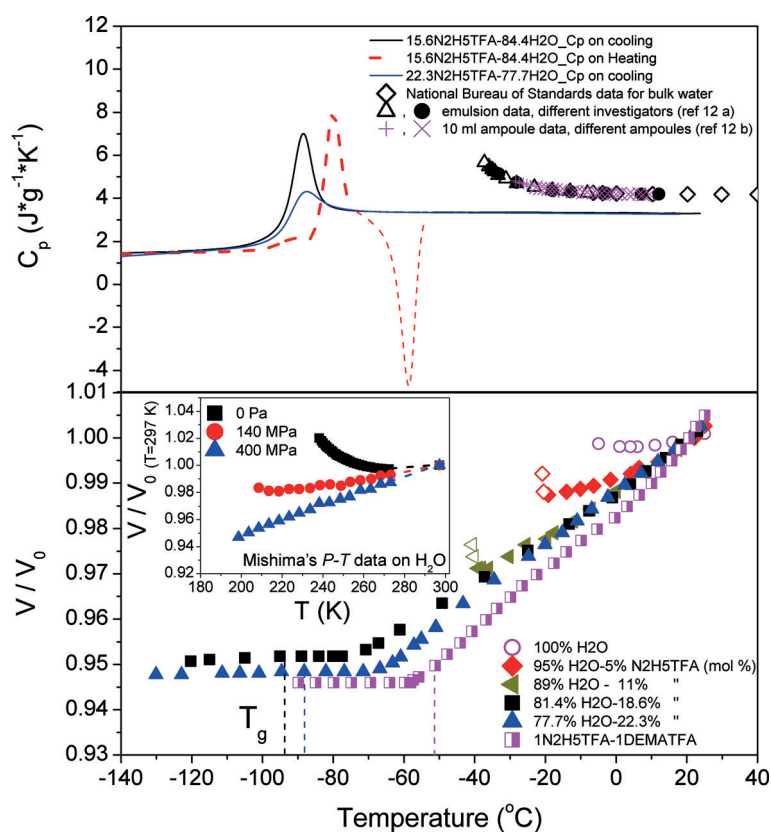


Figure 3. Upper panel: The C_p “spike” anomaly in two hydrazinium trifluoroacetate solutions during cooling, and also during subsequent heating for the more striking case. Comparison is made with the much-studied power law-diverging heat capacity of supercooled pure water. Lower panel: The volumes, relative to those at 25 °C, of 1) solutions of water + hydrazinium trifluoroacetate with water contents 100 to 77.7 mol % water. Onset of ice crystallization at high water contents shown by vertical jumps. Note, at lower water contents, the arrest of the solution volume well above the temperature of the heat capacity anomaly, and 2) an anhydrous binary ionic solution [DEMA⁺][TFA⁻]_{0.5} [N₂H₅⁺][TFA⁻]_{0.5}, with a simple glass transition arrest of volume. Vertical dashed lines indicate the values of the onset heating T_g for solutions of same color symbols. Inset: Behavior of the volume of supercooled water (from Ref. [15]) scaled to have common values at 297 K. Figure shows that the volume minimum disappears at about 140–160 MPa.

neous nucleation temperature of pure high density liquid (HDL) water at -75°C and the spinodal limit to HDL at -87°C , there should exist a liquid–liquid (L–L) transition from the high density liquid (HDL) to the low density liquid (LDL). The enthalpy change in this transition would then replace the diverging heat capacity seen in pure water as it approaches the spinodal limit to the HDL liquid itself.^[5,21,22]

If we are indeed observing water-like behavior in absence of crystallization then some other predictions can be made. For instance, the phenomenon of interest should be preceded by a density anomaly. Furthermore, since we are apparently simulating the behavior at high pressure, the density anomaly should not be an actual density extremum but a density arrest like that seen at about 160 MPa in the studies of Mishima.^[15] Remarkably, this is also found to be the case. Figure 3, lower panel, shows the relative volume observations on the solutions (including that with the C_p spike) made by a simple bulb-capillary volume measurement (see SI), and compares them with the recent data on pure water (in

emulsion form) by Mishima^[15] shown in the insert to Figure 3, lower panel.

Unlike the L–L transition observed in the recent study of Murata and Tanaka^[23] (in glycerol–water solutions of 82–86 mole % water), the present phenomenon shows no sign of ice crystal formation in the small DSC samples, until after the reverse process (heating at the same rate 20 K min^{-1}) has produced an endothermic spike of essentially the same area (enthalpy). Only at the conclusion of the latter process, does ice I_h crystallization, an exothermic process, swing the trace in the opposite direction, (see Figure 3, upper panel, light dashed curve), producing a heat release nearly twice that absorbed in the prior L–L transition.

While the combination of observations described above makes it seem very plausible that we have observed the solution equivalent of the putative HDL–LDL transition in water that was previously hidden by ice nucleation, our observation does not make a forceful argument for the occurrence of such a transition in water itself at the (ambient) pressure of our measurement. This is because, as implied by the observations of Koop et al.,^[17] and as argued by Biddle et al.,^[24] the presence of a solute effectively shifts any critical point that pure water might have, to lower (and negative) pressures. We can only say that we have made the existence of a liquid–liquid transition in water at the high pressure of 140–160 MPa, seem considerably more plausible than it was before. This, however, is an important step forward as it provides support for the recent direct observations of Winkel et al.^[25] for a liquid-to-liquid transition shortly above the glass transition temperature in initially pressure-amorphized water, and offers the possibility of follow-up liquid state studies of the phenomenon, both electron-microscopic and 2D vibrational spectroscopic (Sander Woutersen, private communication), to name just two. It is hoped that such observations will become available in the near future.

The existence of first order transitions between liquid states of different structures, has been controversial since they were first identified,^[26] mainly because they tend to occur in domains of temperature where the liquid is metastable with respect to crystallization. Under these circumstances, the transition itself makes its own observation problematical by serving as an Ostwald step to the nucleation of the stable state. The present case, where the transition not only occurs, but can be completely reversed before any crystallization takes over, is significant, as it serves as a laboratory connection to those model systems^[27] where it can occur in the stable liquid state.

Experimental Section

The synthesis of EAN and TEAMS protic ionic liquids has been described often and will not be repeated here. The hydrazinium

haloacetates were likewise simply obtained by weighing and cautious mixing of the anhydrous molecular components.

Calorimetric studies were performed using a PerkinElmer DSC-7 scanning calorimeter, at 20 K min⁻¹ unless otherwise stated.

Volumetric data were obtained using a simple home-made long (scale) stem bulb densitometer with camera recording. Temperature during cooling was monitored by a fine teflon-sheathed thermocouples located inside and outside the bulb. Provision for uniform temperature was by an aluminium metal sheath (for details see SI).

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