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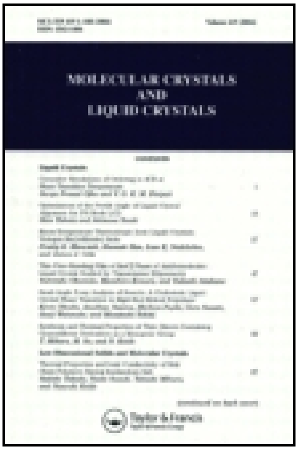

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Effect of Salt on the Density and Expansion Coefficient of the Nematic and Smectic Phases of the Cesium Perfluoro-Octanoate/Water System

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Effect of Salt on the Density and Expansion Coefficient of the Nematic and Smectic Phases of the Cesium Perfluoro-Octanoate/Water System

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The effect of CsCl on the temperature dependence of the density of the nematic and lamellar phases of cesium perfluoro-octanoate (42.57 wt%)/water is reported. When the concentration of salt is increased from 0 to 3.5 wt%, the peak in the expansion coefficient, α, across the nematic-isotopic transition is reduced by 70%. On the other hand, for the same range of excess salt the divergence of α through the nematic-lamellar transition is qualitatively unaffected.

INTRODUCTION

The liquid crystalline phases of the cesium perfluoro-octanoate (CsPFO)/water system have aroused the curiosity of a number of investigators. Two reasons for this interest are: 1) The temperature-concentration phase diagram has many features in common with thermotropic liquid crystals; in particular, homologous series that form isotropic (I)-nematic (N)-(L) lamellar phases.[1] For instance, at about 63 wt% CsPFO, a triple point, (coexisting I, N, L) is observed. Also a possible tricritical point may exist on the N-L transition line at 53 wt% surfactant.[2] 2) Perhaps the greatest interest in this system has been generated by the almost second order character of the I-N transition. This is discussed in a number of recent papers.[2–4]

Another extensively studied system with a similar phase diagram, decylammonium chloride (DACl)/ammonium chloride/water,[5] is available for qualitative comparison. Both DACl and CsPFO are relatively stable compounds, so long term experiments can be made on them.

The nematic phase of both of these systems arises from the average parallel alignment of disc-like micelles formed from the surfactant. The dominant anisotropic interactions inducing alignment are steric, electrostatic and Van der Waals; consequently the stability of the nematic and smectic phases depends on temperature, volume fraction of surfactant, and excess electrolyte concentration.

The above picture of the nematic phase is substantiated by x-ray[6] and conductivity

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measurements on DACl/water[7] and CsPFO/water.[2] In addition, direct observation of micellar structures via freeze fracture transmission electron microscopy[8] support the x-ray studies and also show the micelle sizes (– 100 Å ~ disc diameter, DACl/water) are practically monodisperse.

The detailed structure of the lamellar phase is less certain. Recent results[2] indicate the micelles of CsPFO remain discreet in the lamellar phase; they simply register into layers at the nematic to smectic transition. For DACl, Holmes and Charvolin[6] view the N-L transition as a change in connectedness of the micelles, analogous to a percolation transition. The fusion of the micelles into layers might in part be driven by the increase in translational entropy of the surfactant molecules.

From a theoretical viewpoint, the change of micelle size (or lack of it) at the nematic-smectic transition is in conflict with the ideas of Gelbart and co-workers.[9] They predict a divergence in the average micelle size at the layering transition. In interpreting these results, one must be cautious when comparing equilibrium theory to experiment. It is necessary to separate hysteresis effects,[10] present due to phase separation at first order transitions, from effects due to the slowing down of the dynamics near a continuous transition. The latter being caused by a divergence of certain viscosities as the transition is approached. Likewise, the dynamics of micelle coalesence into layers, and the equilibrium of dislocations must be considered. Thus, the theories are not necessarily incorrect, the experiments simply do not wait long enough for equilibrium to establish.

The present work was motivated by an earlier paper[11] in which excess salt (NH_4Cl) was added to the DACl/water system. The nematic order parameter, Q, was measured by NMR as a function of temperature. It was found that the temperature dependence of Q decreased with added salt. The simplest model to explain this behavior is that the micelles are becoming more like hard particles. If this is the case it should be possible to observe changes in accessible thermodynamic properties.

Considering the similarities between the CsPFO and DACl systems we conjectured that added salt should have an effect on the temperature dependence of the density, ρ. Consequently, the expansion coefficient, $\alpha = -\partial \ln \rho/\partial T$, should sensitively reflect this dependence.

EXPERIMENTAL

We follow for the most part the procedure outlined in Reference (10). The samples were mixed in Teflon-sealed screw top test tubes. The transition temperatures were checked in bulk by a polarizing microscope using glass capillaries and finally by the densitometer. In Figures 1 and 2 we present photomicrographs of the typical appearance of the N-I and N-L transitions for a sample of composition (CsPFO/CsCl/H_2O) = (41.9/3.0/55.1) wt%. The N-I transition is signaled by the appearance of droplets of the isotropic phase upon entering the two-phase region (T = 43.1°C). Further increase in temperature results in a coalesence of the droplets and the disappearance of the nematic at 43.2°C. The N-L transition is continuous. As the lamellar phase is approached from the nematic side, the divergence of the bend

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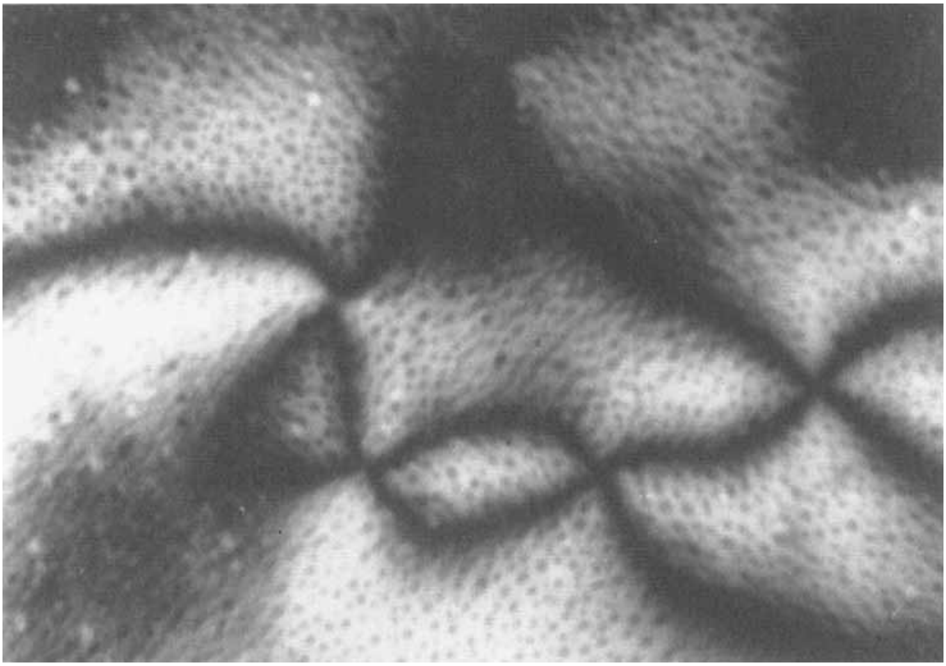

FIGURE 1 Photomicrograph of ($CsPFO/CsCl/H_2O$) = (41.9/3.0/55.1) wt% sample; crossed polars, sample thickness 0.3 mm, T = 43.1°C. Appearance of isotropic droplets upon entering the N-I two phase range.

and twist elastic constants is evident in the change from a schlieren to a fan texture (Figure 2a-b).

Sample compositions and transition temperatures are given in Table I. The calibration error in the absolute density was $\pm 1 \times 10^{-4}$ g/cm^3, while the accuracy of the relative density was $\simeq 10^{-6}$. The temperature dependence of the density in the isotropic phase was fit with the linear form $\rho_i = a_0 - a_1 T$. The values of a_0 and a_1 for each sample are given in Table II.

RESULTS

Overall results for the density vs. temperature of the CsPFO/water system are presented in Figure 3. With no added salt, we estimate the magnitude of the change in relative density for the N-I transition as $\Delta\rho/\rho_i \simeq 1.2 \times 10^{-4}$. The change in the expansion coefficient is displayed in Figure 4 for the N-I transition and Figure 5 for the N-L transition.

For the N-I transition the peak in α decreases by about 70% as w_e increases from 0 to 3.5 wt%. With the same change in salt, the divergence of α at the N-A transition is practically unaffected. Using a sweep rate of 200 mK/6 min., the behavior of the density was reproducible through the N-I transition on heating and cooling. The behavior of the density through the N-L transition was not in general reproducible

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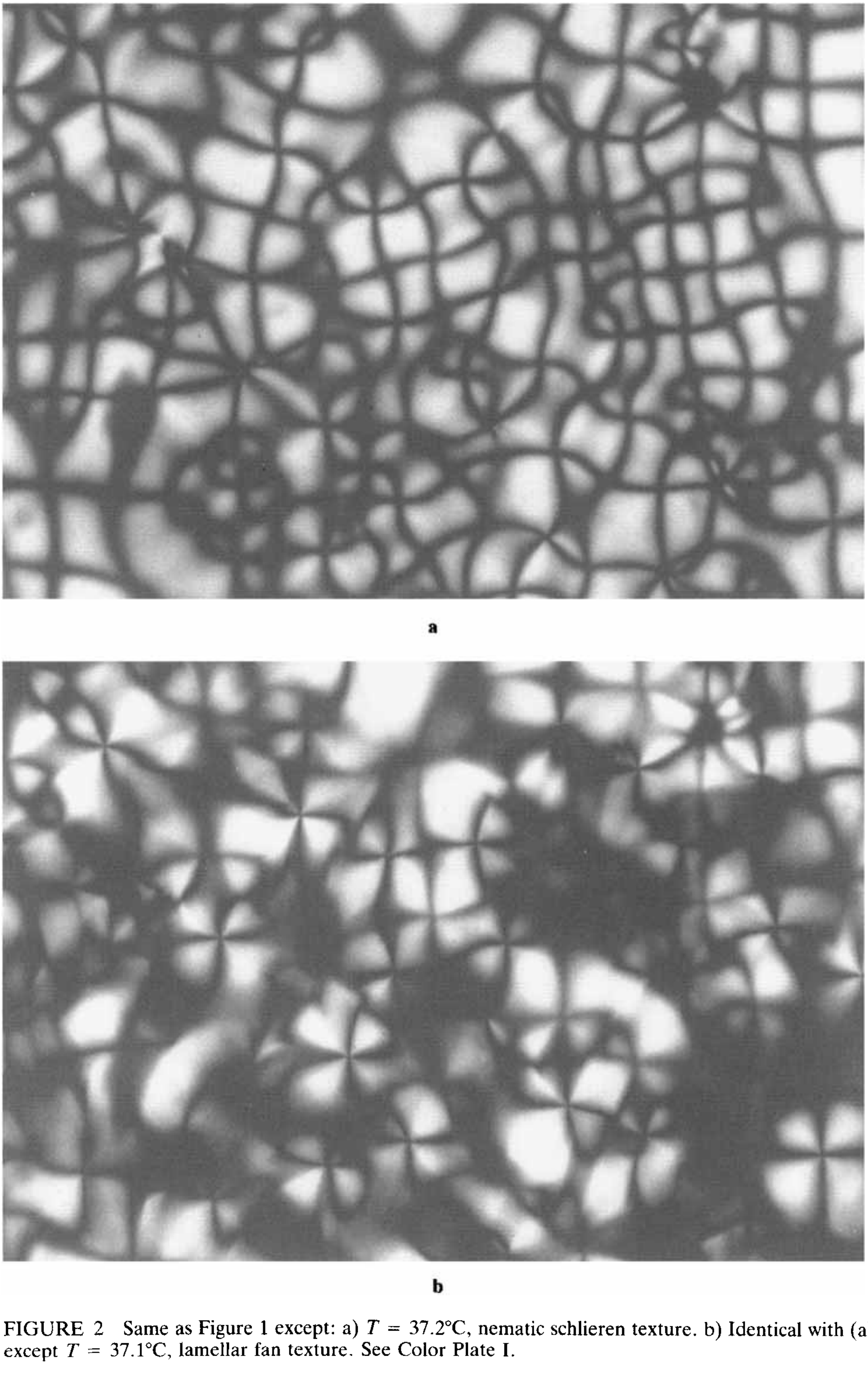

FIGURE 2 Same as Figure 1 except: a) T = 37.2°C, nematic schlieren texture. b) Identical with (a) except T = 37.1°C, lamellar fan texture. See Color Plate I.

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TABLE I

Sample Compositions and Transition Temperatures

Sample	($CsPFo/CsCl/H_2O$) wt%	T_{NI}	T_{NA}
1	42.57/0/57.43	30.7	24.7
2	42.04/1.25/56.71	37.1	29.5
3	41.50/2.5/56.00	41.5	34.5
4	41.08/3.5/55.42	44.3	38.8

TABLE II

Coefficients of Linear Fit for Density in Isotropic Phase

Sample	a_0 (gm/cc)	a_1 (10^{-3} gm/cc·°C)
1	1.3343	0.7241
2	1.3495	0.8008
3	1.3611	0.8168
4	1.3692	0.8187

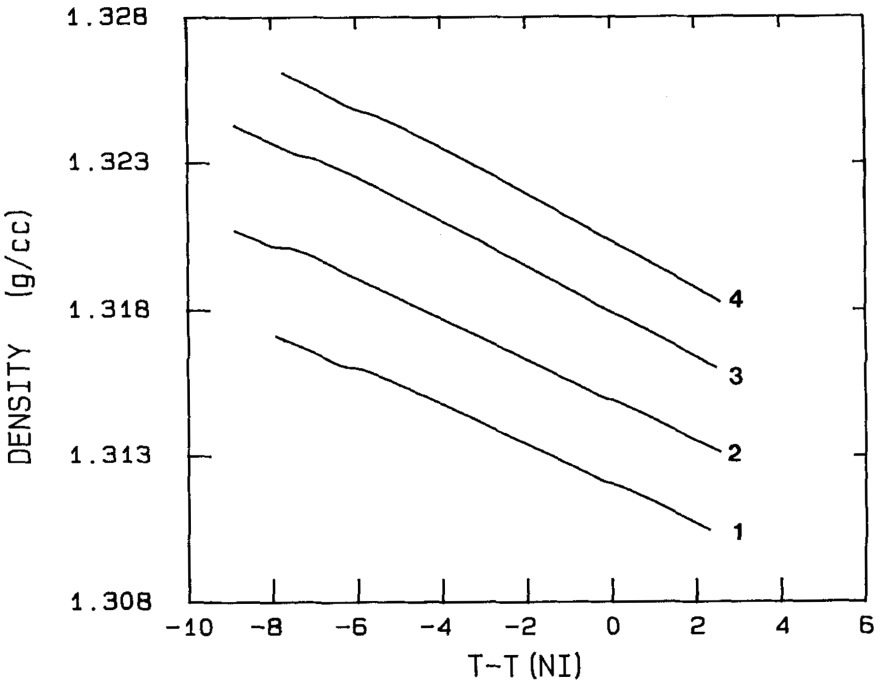

FIGURE 3 Temperature dependence of the density for samples 1–4 of Table II. The curves (1–4) are shifted by the respective amounts, (0, 4.5, 9.2, 12.6) × 10^{-3}, for clarity.

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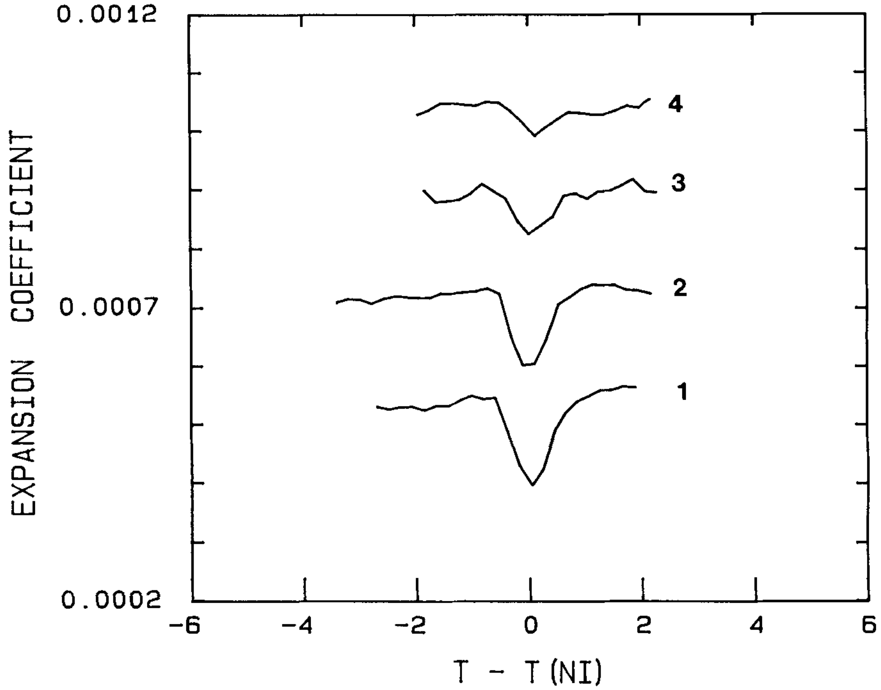

FIGURE 4 Temperature dependence of the expansion coefficient through the isotropic-nematic transition of samples 1–4 of Table II. The curves are shifted by the respective amounts, (0, 1.8, 3.0, 4.3) × 10^{-4}, for clarity.

on heating and cooling due to the above mentioned hysteresis effects. However, the data for different runs were reproducible provided one compared heating and cooling curves separately. If the amount of added salt exceeded 3.5 wt%, none of the data were reproducible on heating and cooling. In this case the sample became inhomogeneous due to gravitational effects.

DISCUSSION

N-I Transition

Addition of salt reduces the temperature dependence of the density in the transition region. This is most easily seen by observing the expansion coefficient, α. At least two effects can lead to the above decrease in the peak of α.

First we consider the chain packing. It is reasonable to assume the area per head group (σ) in a micelle decreases with increasing excess electrolyte. This is due to the increased electrostatic screening of the charged headgroups. As σ decreases the chains pack more closely and thus approach an optimum density. Assuming the change in overall density across the N-I transition is, for the greatest part, due to a change in the surfactant density,[10] then solutions with added salt should show a smaller change in overall density through the transition since the surfactant is

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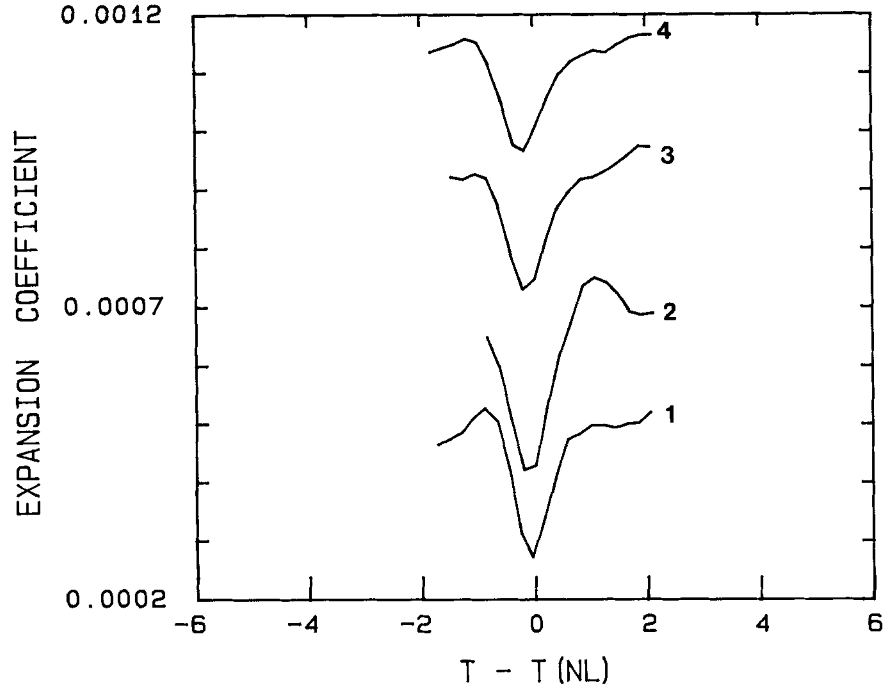

FIGURE 5 Temperature dependence of the expansion coefficient through the nematic-lamellar transition of samples 1–4 of Table II. The curves are shifted by the respective amounts, (0, 1.8, 4.0, 5.8) × 10^{-4}, for clarity.

nearing the optimum density. The micelles might be viewed as becoming stiffer, i.e., approaching the limit of hard core particles as far as the short range interactions are concerned. That is, in addition to the increased screening of the intermicellar electrostatic interaction, the micelles show an increased resistance to deformations of their shape due to the tighter packing of the chains.

The fluorine chains are considerably more hydrophobic than the alkyl chains.[12] Since the headgroups are smaller relative to the fluorine chains, excess salt may affect the chain packing and hence the density to a greater degree than for alkyl chains. (There is some indication that increasing salt increases the chain order in the DACl/water system.)[11]

Second, it is known that added salt accentuates the first order nature of the N-I transition. We can qualitatively show how this affects the expansion coefficient by writing $\alpha = \alpha_0 + \Delta\alpha$, where α_0 is the background and

$$\Delta\alpha \simeq b(\Delta T)^{-\nu},$$

represents the diverging part. Here b is taken to be independent of temperature and salt and $\Delta T = T - T^*$. For the discontinuous N-I transition ΔT is never zero; it reaches its smallest value at the N-I transition temperature, T_{NI}, there $\Delta T = T_{NI} - T^*$. (T^* is the extrapolated supercooling temperature.)[1] For a weight ratio of CsPFO/H_2O of 1.5, Rosenblatt and Zolty[13] find $\Delta T = 0.033°C$, with no added salt; with 3.5 wt% salt, $\Delta T = 0.133°C$. Using the mean field value of $\nu = \frac{1}{2}$, and assuming the increase in ΔT is similar for our weight ratio ($\simeq 1.35$) for the given change in excess salt, we find $\Delta\alpha$ decreases by about one-half. The remaining discrepancy might be accounted for by relaxing the assumption that b is independent of salt. The value of b is a complicated function of material parameters,[14] all of which may be influenced to some degree by added salt, either directly or through mechanisms similar to the first point discussed above.

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N-L Transition

We find that excess salt (up to 3.5 wt%) gives no qualitative change in the peak of α through the nematic-lamellar transition. The added salt has little effect on the continuous nature of the transition, thus the divergence of α (or the specific heat) is preserved.

Finally, our results may be compared to previous experiments. Using the Clapeyron-Clausius equation, the relative volume change at the transition is

$$\Delta V/V_i = (L/T_{NI}V_i)(dT_{NI}/dP).$$

Where L is the latent heat, P is the pressure (= 1 atm) as V_i is the molar volume of CsPFO. From Fisch et al.[15] we find $dT_{NI}/dP \simeq 5.0 \times 10^{-9}$ K/Pa. From Imaizumi and Garland[16] we obtain $L \simeq 0.24\ J/g = 131\ J/\text{mole}$. Estimating V_i as 240 cm^3/mole, it is found $\Delta V/V_i \simeq 0.9 \times 10^{-5}$. This is an order of magnitude smaller than the volume change we observe. A more serious discrepancy lies in the sign of ΔV. Reference (15) yields $\Delta V > 0$ whereas we find $\Delta V < 0$. This point is crucial when one tries to understand, on a microscopic scale, the interplay between chain packing and water structure. In this respect, we must stress that our results for the N-I transition are reproducible on heating and cooling to within the accuracy of the relative density ($\sim 10^{-6}$). Considering the errors involved in the various experiments, the differences in purity, and possible water loss; the comparison is not entirely unsatisfactory. However, it is clear that future experiments must pay careful attention to these sources of errors.

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