FAR INFRARED AND DIELECTRIC RELAXATION SPECTRA IN SUPERCOOLED WATER AND W. (U) PURDUE UNIV LAFAYETTE IN DEPT OF CHEMISTRY L BOEHM ET AL. AUG 87 TR-11
We report the first measurements of the far IR absorption in supercooled water, the
extend the temperature range of study of the most interesting feature, and H$_2$O bond stretching
mode at $\approx 200 \text{ cm}^{-1}$, to 85$^\circ$C by incorporation of propylene glycol, PC, as solute. Low fre-
cquency dielectric relaxation measurements on a series of glass-forming PG + water solutions
spanning the range 30-100% PG when fitted to the Vogel-Tammann-Fulcher equation suggest this
resonance absorption mode may be the attempt frequency for the relaxation process. Compa-
ison of the strengths of the two dissipation regions in the same (absorptivity units shows
dielectric relaxation as a weak shoulder sliding, with changing temperature, on the edge
of the quasi-resonant absorption band. For most compositions, the dielectric loss
spectrum is only weakly dependent on temperature, but as the composition approaches the edge
of the glass-forming region, the spectral widths become strongly temperature-dependent due,
evidently, to a clustering phenomenon which results finally in an (unexpected) liquid-liquid
phase separation. (Based on measurements performed under an earlier contract No. N7860035 -
article was solicited for R.H. Cole honor issue of J. Mol. Liquids)
FAR INFRARED AND DIELECTRIC RELAXATION SPECTRA IN SUPERCOOLED WATER AND WATER + PROPYLENE GLYCOL SOLUTIONS

L. Boehm, D.L. Smith and C.A. Angell

Prepared for publication in the Journal of Molten Liquids

Purdue University
Department of Chemistry
West Lafayette, IN 47907

August 1987

Prepared for Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217

Division of Sponsored Programs
Purdue Research Foundation
Purdue University
West Lafayette, IN 47907
FAR INFRARED AND DIELECTRIC RELAXATION SPECTRA IN SUPERCOOLED WATER AND WATER + PROPYLENE GLYCOL SOLUTIONS

L. Boehm, D. L. Smith and C. A. Angell

Department of Chemistry, Purdue University West Lafayette, Indiana 47907

SUMMARY

We report the first measurements of far IR absorption in supercooled water, the extend the temperature range of study of the most interesting feature, and H-bond stretching mode at \( \approx 200 \text{cm}^{-1} \), to \(-85^\circ\text{C}\) by incorporation of propylene glycol, PG, as solute. Low frequency dielectric relaxation measurements on a series of glass-forming PG + water solutions spanning the range 30 - 100% PG when fitted to the Vogel-Tammann-Fulcher equation suggest this resonance absorption mode may be the attempt frequency for the relaxation process. Comparison of the strengths of the two dissipation regions in the same (absorptivity \( \alpha \)) units shows dielectric relaxation as a weak shoulder sliding, with changing temperature, on the \( \alpha = k_\text{ff} \) edge of the quasi-resonant absorption band. For most compositions, the dielectric loss spectrum is only weakly dependent on temperature, but as the composition approaches the edge of the glass-forming region, the spectral widths become strongly temperature-dependent due, evidently, to a clustering phenomenon which results finally in an (unexpected) liquid-liquid phase separation.

INTRODUCTION

The process in which energy is dissipated in liquids by the coupling of oscillating electrical fields to the characteristic re-orientation frequencies of polar molecular liquids, has been extensively studied over the frequency range \( 10^{-2} - 10^7 \text{ Hz} \) using a.c. bridge or polarisation current techniques,\(^{(1,2)}\) and less commonly at GHz frequencies using microwave or time domain reflectometry techniques.\(^{(1,3-5)}\) However, it is only rarely\(^{(6-9)}\) that the frequency range of study is extended to the far IR where optical absorption measurements can be used to characterize the relevant processes. This is rather unfortunate because it is in the low frequency IR region that we find the collective molecular librational modes (quasi-lattice librons) which are the "spawning ground" for the re-orientation relaxation process.\(^{(8)}\)

Dielectric relaxation occurs when the molecular motions of a group of molecules - whose individual librational displacements in the thermal bath would usually be reversed by the restoring forces provided by their neighbors - become critically anharmonic (as a manifestation of thermal fluctuations) and proceed to rearrange themselves in some complex cooperative way before settling back into a new low energy local packing for which the collective libration mode falls in the same frequency range as before. The librational frequency of the liquid thus establishes the basic "attempt frequency" for barrier crossing in critical fluctuation.
treatments of dielectric relaxation. The anharmonicity of the mode should therefore be essential to the process of dielectric relaxation, and should be correlated in some way with the characteristic dielectric relaxation frequency. At low temperatures where the molecular packing is tighter and the librational modes less highly excited, the librational motions will be more nearly harmonic and the probability of molecular rearrangements will decrease rapidly. Thus as the librational band sharpens and becomes more intense, the absorption (per unit length) due to the relaxation process will decrease while simultaneously moving to lower frequencies. Conversely, at the high temperature limit (e.g. near the critical point) the librational mode will be greatly broadened, the dielectric relaxation frequency will approach the libration frequency itself, and because of its high probability, energy absorption due to relaxation will approach that due to the quasi-resonant librational motion itself (e.g. see Fig. 3 of ref. 9). The two processes thus become so close in frequency and intensity that finally they are no longer distinguishable. In this extreme, all molecules will be simultaneously involved in both librational and reorientational modes of motion and only a single broad absorption band will be observed.

With a view to supporting this general picture of dynamic processes in polar liquids we report, in the present paper, a combination of low frequency IR absorption studies in the range 50 - 500 cm\(^{-1}\) ([1.5 - 15] x 10\(^{11}\) Hz) and much lower frequency, (0.1 - 10\(^{6}\) Hz) dielectric relaxation studies on both pure components and solutions in the system water + propylene glycol PG. The study covers a wide temperature range 25 to -100\(^\circ\)C, which is made possible by the supercooling ability of this system. The system is of interest on several counts. Firstly, it is the aqueous binary system in which glass-forming ability is achieved with the smallest mole fraction of second component (10 mol\%)\(^{10,11}\). Secondly, and partly because of the first, it is a system of choice for cryobiologists\(^{12,13}\) because of the added advantage that PG is only weakly toxic to living cells. Thirdly (and unexpectedly) it seems to be a system which, in the water-rich composition, region evidently splits into two immiscible liquid phases at low temperature.\(^{11,14}\).

**EXPERIMENTAL**

Solutions were prepared by weighing of triply distilled deionized water and spectroscopic grade propylene glycol (1,2 - propane diol).

Absorption spectra in the range 50 - 500 cm\(^{-1}\) were obtained using a Digilabs FTIR spectrophotometer with a 6.25 \(\mu\)m Mylar beam splitter. The instrument was aligned so that the maximum transmission was 100%. In most cases spectra were taken on each of two separate samples. Samples were held between two 1.0 mm densified polyethylene (DPE) windows in a standard IR sample cell. The latter was attached to the cooling module of an Air
Products Joule Thompson cryostat and mounted into the spectrophotometer sample compartment. To avoid sample distortion the cooling chamber was left unevacuated. This limited the temperature range which could be explored to $T > -90^\circ C$.

For compensation and minimization of reflectance errors, two DPE windows were mounted in the reference beam during all experiments. Baselines for determination of absorption coefficients, were made using an empty cell with two DPE windows in the sample beam. Film thickness of 20-25 $\mu$m were measured by difference micrometry at several points on several samples at room temperature, but are subject to uncertainty due to temperature effects on the window conformation. Since changes in window reflectances with temperature were not compensated, the intensities are rather uncertain and absorption coefficients obtained from these measurements are only considered reliable within a factor of 2, which is adequate for the present purposes.

Each spectrum was obtained by summing a minimum of 128 scans, and applying a smoothing function nine times to the data. Reliability of the procedure was judged from the reproducibility of spectra for duplicate samples.

In the case of pure water, supercooling to -12°C was obtained. Although this was less than hoped for it was sufficient to show considerable refinement of the weak spectral feature at $\approx 180 \text{ cm}^{-1}$ seen in earlier studies, and to permit its comparison with the corresponding feature in ice I.

Dielectric relaxation spectra were obtained using an all metal cell of design described by Ambrus et al.\textsuperscript{15} and used in a previously reported study of polyalcohols by the present authors.\textsuperscript{16} The frequency range of 8 orders of magnitude was obtained using a combination of a modified Berberian-Cole bridge (0.1 - 500 Hz) and Wayne Kerr B221 and B601 transformer ratio arm bridges (500 - 50 KHz, and 50 KHz - 2 MHz respectively). Since the dielectric relaxation frequency is very sensitive to temperature, temperature control to $\pm 0.1^\circ C$ during the 2-3 hour scan series was necessary. Temperature was measured with a precision of 0.05°C using a copper-constantan thermocouple and a 0.001 mv DVM.

RESULTS

Low frequency IR spectra for water above and below its freezing point are compared with the spectrum of ice and with previous data on water,\textsuperscript{17,18} in Fig. 1. In Fig. 2 we compare the spectrum of pure water with that of propylene glycol at 25°C and with various PG solutions at -12°C. Finally, the effect of temperature on the spectra of the 40% PG solution is demonstrated in Fig. 3. Included in Fig. 3 is a spectrum for the solution 20% PG - 80% H$_2$O for which the lowest temperature of this study was obtained.
DISCUSSION

All the IR spectra have in common a band in the region 150-200 cm\(^{-1}\) which narrows considerably and becomes better defined as temperature is decreased from RT to -12°C for pure water, and to -85°C for PG + H\(_2\)O solutions. The peak frequency of this band does not change significantly with temperature in this range. These observations are consistent with the behavior of a collective oscillation mode, presumably of the same dynamic origin as the
Figure 3. Temperature dependence of the far IR spectra of H$_2$O + propylene glycol solutions.  

*Insert:* Shift with temperature of the absorption minimum, the translational and librational bands, including results from spectra at temperatures intermediate to those shown in the figure.

A mode at 220 cm$^{-1}$ seen in ice (Fig. 1). This mode is believed to be a "hindered translational" mode$^{18-20}$ involving a stretching motion along the hydrogen bond axis. We will see in the following that this band may have special significance in relation to the kinetics of dielectric relaxation in this system.

A more temperature-dependent characteristic of the spectra is the low frequency edge of the broad band at 300-800 cm$^{-1}$ (see Fig. 1(b)) which is of librational origin.$^{19}$ This is shown by the shift to high frequencies of the minimum of the absorption at 300-350 cm$^{-1}$ for
Figure 4(a). Dielectric loss spectra for pure propylene glycol (PG) between -64 and -88°C. Note small but persistent loss at high frequencies for low temperature runs.

Figure 4(b). Dielectric loss spectra for 40 mol % PG aqueous solution between -63 and -97°C. Note small, constant loss at high frequencies for low temperature runs, and broadening at low temperature.

Figure 4(c). Dielectric loss spectra for 30 mol % PG aqueous solution. Note large increase in half width (2.4 decades at -96°C) at low temperatures, but with persistent symmetrical form.
the 40% PG solution as the temperature is decreased. This effect due to band narrowing is the behavior anticipated, in our introductory comments, as the collective librational modes (which occasionally and locally "spill over" to give the relaxation phenomenon) become more sharply defined and less anharmonic with the decrease in thermal energy.

The behavior of the same 40% PG solution in the low frequency (audio and sub-audio) region of the spectrum is very different, see Fig. 4. The strong temperature dependence of the characteristic frequency is the dominant feature of Fig. 4.

To see how the two spectral regions link up, we must reduce the data to a common representation. This is done most effectively by (i) converting the % absorption data in the FIR spectra of Fig. 3 to absorption coefficients $\alpha$ (Neper cm$^{-1}$) using the measured film thickness, $d$, of 20-25 $\mu$m, and the relation

$$\alpha(f) = \frac{-\ln (\%A/100)}{d} \quad (1)$$

and (ii) converting the $\varepsilon''$ (loss/cycle) data to loss/cm and then to optical absorption coefficients using the relation$^{(20)}$

$$\alpha(f) = \frac{2\pi fc''(f)}{cn(f)} \quad (2)$$

where $c$ is the velocity of light, and $n(\omega)$ is the refractive index which is assumed constant at its high frequency value; (in a broad resonance absorption band like the present one, $n(\omega)$ will undergo variations with frequency of some 10-20% which are small compared to other uncertainties in $\alpha$).

Because of the enormous range of $\alpha$ and frequency covered in this combined presentation it is necessary to use log-log plots in the display. This is done in Fig. 5 for the case 60% H$_2$O + 40% PG solution for which the largest temperature range was studied. Arrows indicate the peak frequencies from Fig. 4(c), and also calculated values at higher temperatures obtained from the fit of the low temperature relaxation times to the VTF equation discussed below.

Figure 5 shows that a smooth connection between the two data sets from the two very different frequency ranges is possible. In this representation, the dielectric loss peak appears as a weak and highly temperature-dependent shoulder on the resonance absorption band at 180 cm$^{-1}$. While this band at is not obviously a part of the libration-reorientation complex related to dielectric relaxation in the introduction, its possible relevance will be seen in our analysis of dielectric relaxation times in this system given below. The loss peak could, however, also be regarded as a shoulder on the broad higher frequency librational band at 750 cm$^{-1}$.$^{(19)}$
Figure 5. Dielectric loss and far IR absorption data for PG + H₂O solutions plotted as absorption coefficients, α, showing connection between resonant absorption and relaxation regimes via a regime $\alpha = kf^\gamma$ where $\gamma = 1.0$. Insert: Temperature dependence of $\%A$ ($\%$ of incident beam absorbed by 20 $\mu$ film of 40% PG solution) vs frequency.

Figure 5 is essentially a collection of density of states diagrams for this solution at different thermal excitation levels and the observed dependence properly emphasizes the dominance of quasi-harmonic modes at all but the highest temperatures. The diagram does not contain direct information on the different system configurational or potential energy states assumed by the system at different temperatures although it seems that the frequency of the reorientational absorption shoulder reflects this density of configurational states at each temperature, see below.

The connecting link of slope 1.0 between the two regions of study implies that the dielectric loss $\epsilon''$ (loss per cycle) of Fig. 2, does not fall to zero at high frequencies as simple relaxation theory suggests it should. Instead it approaches a constant frequency-independent value as indicated in Fig. 4. This phenomenon, which requires the presence of a density of energy dissipating mechanisms which is linear with frequency, seems to be rather general in relaxing amorphous systems. Indeed, Jonscher(22) has presented evidence that this behavior
occurs in any type of system in which a dielectric loss can be observed, and has proposed a simple "hopping dipole charge cloud relaxation" model to explain its origin.

One of the most interesting aspects of the dielectric relaxation phenomenon in these solutions is the way in which the relaxation frequency $f_{\text{max}}$ changes with temperature, particularly as we approach pure water in composition. An Arrhenius temperature dependence is clearly inappropriate not only because it fails to linearize the data but also because the pre-exponential frequency factor at best fit, e.g. $10^{32}$ Hz for the composition of 40% PG, bears no relation whatever to any feature of the vibrational frequency spectrum. Indeed, if one assumes the basic attempt frequency is that of the librational band, then the above pre-exponential term would require a positive entropy of activation of 10 e.u. corresponding to a transition state with a configurational degeneracy $10^{17}$ greater than that of the ground state ($\Delta S = kA n W$). Fortunately the problem is avoided by use of the simple modification of the Arrhenius expression known variously as the Vogel equation, the Fulcher equation, or the Vogel-Tammann-Fulcher equation (since it was Tammann who first related it clearly to the glass transition phenomenon). This has the form

$$f_{\text{max}} = f_0 \exp \left[ -B(T-T_0) \right]$$

where $f_0$, $B$ and $T_0$ are constants, and was first exploited for dielectric relaxation by Davidson and Cole.\(^{(23)}\) This form linearizes the data and restores a reasonable value to the pre-exponential term.

The present data lack the precision to determine the three parameters of Eq (3) without large uncertainties in all parameters. However, if we fix one parameter we find systematic variations of the others which are of interest. For instance the simplest possible assignment would be $T_0 = \text{const} = 122$ K, the value for PG itself.\(^{(16)}\) This is, in fact, a reasonable value since $T_g$ is only weakly dependent on composition (see Fig. 6 insert), and decreases in $B$, which will cause decreases in $T_g$ at constant $T_0$, are expected because of the relative fragility of water. The choice $T_0 = 122$ K constant yields $f_0 = 5.3 \pm 1 \times 10^{12}$ Hz (170 $\pm$ 40 cm$^{-1}$) and gives $B$ values which decrease with decreasing PG as seen from the slopes in Fig. 7. As a check on the plausibility of this set of parameters, we use them to predict the temperature of the glass transition on the basis that $T_\alpha = \tau$ (enthalpy relaxation) $\approx 100 \sim 200$ sec.\(^{(22)}\) The latter corresponds to a value $f_{\text{max}} \approx 10^{13}$ Hz. The temperatures for $f_{\text{max}} \approx 10^{13}$ Hz are indicated on the Fig. 6 axis and are plotted together with the experimental values in the insert. The agreement is seen to be quite good.

The above parameterisation reduces the $f_{\text{max}}$ data for PG and the four solutions to a simple pattern, see Fig. 6. We note that the intercepts at $(T-T_\alpha)^{-1} = 0$ cluster around the value $4.5 \times 10^{12}$ Hz (150 cm$^{-1}$) which is smaller than the librational frequency of 750 cm$^{-1}$ by a
factor of 5, but the same as the frequency of the quasi-lattice H-bond stretching mode of Figs. 1-3. In fact the weak composition variation of the best fit \( f_0 \) when we choose \( T_0 \) constant is the same as that of the far IR band, (though this is surely fortuitous given the sensitivity of \( f_0 \) to the other parameters). This raises the possibility that the prerequisite for librational modes becoming critically anharmonic and thus permitting rearrangements could be a critical stretching of the H-bonded quasi-lattice.

![Graph showing Vogel-Tammann-Fulcher equation representation of the dielectric relaxation time](image)

Figure 6. Vogel-Tammann-Fulcher equation representation of the dielectric relaxation time obtained for the choice \( T_0 = 122 \) K for all solutions. Insert: Comparison of \( T (f_{\text{max}} = 10^{-3} \text{ Hz}) \) with experimental \( T_g \) values obtained by DSC at 10 deg min.

The present data can be used to perform a qualitative test of the Adam-Gibbs interpretation of the temperature dependence of the relaxation time in viscous liquids. According to these authors, the relaxation time for any type of perturbation on a viscous liquid increases as the density of accessible configurational states decreases. The latter is to be viewed as the number of minima in the \( 3n - 1 \) dimensional potential energy surface for the \( n \) particle system which lie at potential energies accessible at the temperature at which the relaxation occurs. It scales with the excess entropy of the liquid over that of the corresponding crystalline solid, a quantity designated \( S_c \), which enters the Adam-Gibbs equation as a factor modifying the
normal Arrhenius equation, as follows:

\[ \tau_D = A_\tau \exp \left( \frac{K}{TS_c} \right) \]  

(4)

where \( K \) is a constant. \( S_c \) can be estimated using heat capacity and entropy of fusion data in the case of a pure substance, and tends to vanish at \( T_o \) for a number of polyalcohols.\(^{(16)}\).

To obtain Eq. (3) from the Adam-Gibbs equation as an exact relation, the excess heat capacity of the liquid over that of the corresponding crystal or amorphous solid must be assumed to have the form

\[ \Delta C_p = D/T \]

(5)

where \( D \) is a constant, so that

\[ S_c = \int_{T_o}^{T} \frac{\Delta C_p}{T} \, dT = \int_{T_o}^{T} \frac{D}{T^2} \, dT \]

(6)

This leads to the VTF equation (Eq. 3) with the parameter \( B \) identified as

\[ B = KT_o/D = K/\Delta C_p(T_o) \]

(7)

Since \( \Delta C_p \) at any temperature should be relatively large for a liquid with relatively large \( \Delta C_p(T_o) \), a test of consistency of the data with the Adam-Gibbs theory would be that the reduced excess heat capacity of the liquid at some fixed temperature \( T \) should vary inversely with the slope \( B \) of the Fig. 6 plots when reduced by the appropriate \( T_o \) value. We designate the reduced excess heat capacity as \( \Delta C_{p,r} \) and define it as \( (C_p(p) - C_p(s)) / C_p(s) = \Delta C_{p,r} \) (where \( C_p(s) \) is a solid-like contribution, to be obtained from glass or crystal values using Copp’s rule). For the present case \( T_o = \text{const} \), and the product \( B\Delta C_{p,r} \) should therefore be constant to the extent that \( K \) of Eq. 4 remains constant. Heat capacity data for propylene glycol-water solutions 298 K are available\(^{(27)}\) and, although 298 K is rather distant from the temperature range of our dielectric measurements, the predicted correlation is borne out insofar as the product \( B\Delta C_{p,r} \) varies only slowly with composition in comparison with its components, as shown in Fig. 7.

Finally, we consider briefly the dielectric behavior of the water-rich solutions seen in Fig. 4. The loss spectra for pure PG and for solutions of composition 60% and 80% PG are very narrow and in some cases almost Lorentzian in shape (e.g. for PG at -64°C the FWHH is 1.26 decades, vs. 1.12 decades for a Lorentzian. The latter is the narrowest possible relaxation spectrum, and corresponds to exponential decay in the time domain). Nearly exponential relaxation seems to be common phenomenology for alcohols and diols though the reason is not well understood. By contrast, the 40% and particularly the 30% solutions show a
Figure 7. Strong and opposite composition dependences of the parameter B of Eq. 3 and $\Delta C_{p,r}$, the reduced excess specific heat of the liquid solution oven glass, $\Delta C_{p,r}$ compared with the weak variation of the product $B \Delta C_{p,r}$. This compensation is predicted by Adam-Gibbs equation (Eq. 4).

remarkable low temperature broadening of the loss curves although the $T/T_g$ range explored is no greater than for the other solutions. The broadening is not associated with a rapid increase in the apparent activation energy for relaxation, as is sometimes seen. Furthermore the broadened spectra are not of the usual unsymmetrical Cole-Davidson form or Kohlrausch-Williams-Watts form but rather are almost symmetrical as if formed from overlap of symmetrical peaks of comparable intensity.

The abruptness with which this broadening occurs implies some divergent phenomenon is imminent, and it now seems clear that these solutions can undergo a critical, or spinodal, de-mixing to water-rich and PG-rich fractions. MacFarlane has examined heating scans through the glass transition obtained by differential scanning calorimetry of PG-$H_2O$ solution in the range 10 - 30% PG and has shown that they imply the presence of two different glass transitions that separate in temperature increasingly as the composition tends toward pure water. This inference has now been confirmed by Vassoule et al through the observation of an evolution in time of the amorphous diffraction ring in a quenched sample of the $\sim 13\%$ PG solution (40% w/w). The ring present in the quenched sample split into two separate diffuse rings over a three hour period at $T_g$ (163 K). Presumably there will be other instances of this type of low temperature de-mixing to be identified and exploited in structural diagnoses.
CONCLUDING REMARKS

We believe the physics involved in Fig. 5, which has been discussed earlier without adequate documentation,\(^{(33)}\) should be rather general amongst relaxing molecular systems: comparable data available for the highly polar case of propylene carbonate will be published elsewhere.\(^{(34)}\) However, the sudden broadening of the loss curves at low temperatures in water-rich solutions is particular to the present system. Follow-up studies using techniques such as light-scattering, which are sensitive to long range fluctuations in the dielectric constant, could be of much interest as an approach to investigating the dynamics of the unmixing process, as well as to defining the domain of immiscibility.

ACKNOWLEDGEMENTS

The authors are indebted to the Office of Naval Research for support of this research under Contract No. N78C0035.

REFERENCES

10. R. K. Kadiyala, unpublished work, extending range of study using emulsions.


34. C.A. Angell, L. Boehm, M. Oguni and D. L. Smith, to be published.
END
9-87
DTIC