

AN INVESTIGATION OF SOME PROPERTIES OF SUPERCOOLED
FLUIDS USING PHOTON CORRELATION SPECTROSCOPY

by

BRADFORD LEE HALFPAP

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Manhattan, Kansas

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Approved by:


Major Professor

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Chapter One

INTRODUCTION

The liquid-solid phase transition has long been of interest to scientists and engineers from many disciplines. Its investigation is significant both as an important extension of our basic understanding of the world and, in a more practical sense, as a path to improved material properties and manufacturing techniques^{1,2}. It is generally felt that much useful information concerning this transition can be obtained by the study of supercooled liquids. While most published work, both theoretical^{3,4,5} and experimental^{6,7,8}, in the past two decades concerns water, some investigators have examined other fluids as well^{9,10}.

Studies have led to two viewpoints of the ultimate "driving force" behind the liquid-solid transition and, indeed, phase transitions in general. Langer and others^{11,12,13} suggest that the very high nucleation rates, which occur in fluids at low temperatures, will always place an inherent limit of metastability on the supercooling of liquids. A second point of view, originally taken by Kirkwood and Monroe in 1941⁵, was recently the subject of an intriguing paper by Haus and Meijer⁴. They feel that there is a thermodynamic limit of stability at some temperature below the freezing point. This would be similar to the van der Waals spinodal found in the liquid-gas transition. The model developed by Haus and Meijer upon this basis predicts tell-tale behavior in the thermodynamics properties of highly supercooled liquids. One aim of this research was to search for such behavior in the thermal diffusivity of several materials.

The second goal of this project addressed the unique properties of water. Due to its strong hydrogen bonding, water exhibits unusual behavior near and below its freezing point. An example is the density maximum at 4°C. Two recent works by Stanley³ and Angell⁶ address these unusual properties from a theoretical and an experimental basis. Angell attempted to destroy the anomalous behavior of two thermodynamic properties, specific heat and isothermal compressibility, by the addition of "patch breaking" substances which disrupt the hydrogen bonding in the water. A similar result was searched for by the author in a transport property, viscosity.

The thrust of this research effort relied upon the application of photon correlation spectroscopy, (PCS), to the study of thermal and mass diffusion in supercooled liquids. With an appropriate experimental setup, the relaxation times for these processes fell within the time scales to which PCS can be applied (1 μ s to 1s). The thermal diffusivity information was contained within the Rayleigh component of the light scattered from the density fluctuations within the liquid. The viscosity data can be extracted from the light scattered from polystyrene microspheres diffusing in the sample.

Three general experimental difficulties were encountered and overcome. Because of the scattering angle dependence of the Rayleigh component of the scattered light, only small scattering angles, 1° - 5°, could be used. Optical alignment and the need for extreme cleanliness of the sample cell proved to be nontrivial problems. There was also a collection of difficulties associated with keeping a clear optical path through the sample at subfreezing temperature while keeping good control

of the sample's temperature. Finally, the problem of finding the best supercooling techniques had to be faced.

When these difficulties were overcome, measurements were made on benzene and some of its derivatives in an effort to get thermal diffusivity data near enough to Haus and Meijer's limit of stability to check their predictions. Viscosity data were then taken for water samples with varying concentrations of ethanol, methanol, dioxane, and hydrazine added to disrupt the hydrogen bonding.

Thus, this research is an endeavor to use PCS to gather new data on the thermal and mass diffusion properties of supercooled liquids. These data will be used to improve our understanding of supercooled fluids and the liquid-solid phase transition.

Chapter Two

THEORETICAL MOTIVATIONS

This project was motivated, in large part, by publications in two areas. One was the nucleation vs. thermodynamic limit of metastability views of the liquid-solid phase transition. The second collection of papers was an investigation of the properties of supercooled water. It is my intent that this chapter should give sufficient understanding of the essence of these papers so that the reasons for undertaking this research will be clear.

A number of physicists^{11,12,13} have, in recent years, questioned the existence of a thermodynamic limit of metastability in the liquid-solid phase transition. It has been suggested that nucleation presents not only a practical but an ultimate limit to the degree of supercooling which could be realized. A contrasting point of view provided the motivation for part of this project. Theories have been developed which make specific predictions suitable to experimental verification.

Forty years ago Kirkwood and Monroe⁵ developed a statistical mechanical description of freezing based upon minimum local free energies. Density distributions were calculated using a modified Lennard Jones 6-12 potential assuming only pair interactions. When the resulting function was expanded in reciprocal lattice space as a Fourier series, it was found that at some temperature, T_0 , less than the melting temperature, T_m , all but the first Fourier coefficient vanished. This was interpreted as meaning that the fluid had become unstable to density fluctuations of that wavelength. This was also the lattice spacing of the incipient

crystal. The temperature T_0 would represent a thermodynamic limit of metastability for the liquid.

Among the many papers since 1941 which supported and developed this idea are two which particularly encouraged this work. In 1975 Bosio and Windsor⁷ reported neutron scattering data from highly supercooled gallium. Small gallium droplets were cooled to nearly 150°K without freezing ($T_m = 303^\circ\text{K}$). They found that the structure factor (the frequency distribution of the scattered neutrons) had a Lorentzian line shape with a width that decreased as $T - T_0$ where T_0 was 150°K. The narrowing of the structure factor looks much like Kirkwood's Fourier expansion coefficient behavior as $T \rightarrow T_0$.

In 1976 Haus and Meijer⁴ presented a theory to explain the dynamics of supercooled, metastable fluids. Their work was mostly an extension of earlier work (dating back to Kirkwood) where the intermolecular potential was taken to be a hard sphere plus an attractive tail. Implicit in their model is a Kirkwood type limit of metastability. The importance of this paper was not so much the model itself, which was similar to others, but rather the prediction which was made for the behavior of thermal processes at low temperatures. One would expect diffusion rates to decrease as a fluid is supercooled and becomes more viscid. Haus and Meijer claim that the reverse is true, at least in the neighborhood of the singularity. If this behavior for the thermal diffusivity actually exists, it might extend to temperatures above the nucleation barrier. An attempt to detect such a speeding up of thermal relaxation times is the first part of this experiment.

For several years C. A. Angell and co-workers have been studying

the properties of supercooled water. Two recent papers^{6,14} have suggested that water behaves as a normal fluid except at temperatures near and below the freezing point where anomalous behaviors become dominant. As an example, consider the heat capacity, C_p , of a normal liquid. As it is cooled, C_p decreases in a monotonic fashion. Water, as it nears 0°C , behaves differently. C_p passes through a minimum at $\sim 0^\circ\text{C}$ and increases until it appears to diverge at -45°C . (Data exist only to -30°C .) Similar behavior has been reported by Angell for the isothermal compressibility, K_T .

It has long been known that water readily hydrogen bonds with itself and many other materials. This is one reason for its unusual abilities as a solvent. Very recently Stanley and Teixeira³ published a percolation model for liquid water wherein the hydrogen bonding between the molecules was the dominant feature. The fluid was divided into patches of hydrogen bonded water molecules of various sizes. These patches with their definite structure have a lower density than that of the unbonded water. As the temperature of the water is decreased the number and average size of the patches grows. This model seems to neatly explain such things as the density maximum at 4°C and the behavior of the compressibility. At 4°C the decrease in density due to the growing number of patches just offsets the normal increase in density due to the decreasing thermal energy. The anomalous compressibility is easily understood as the result of the increasing number and size of the patches creates density fluctuations. ($K_T \propto \langle \delta \rho^2 \rangle$)

Both Bosio¹⁹ and Angell⁶ tried to break up the hydrogen bonded

patches with a variety of additives: methanol, ethanol, hydrogen peroxide, and hydrazine. Bosio used concentrations of up to 5.6% ethanol and H_2O or D_2O in his X-ray scattering experiments. They examined the structure factor and found that the anomalous decrease in the width at subfreezing temperatures was reduced by the addition of the ethanol. Angell looked at the heat capacity of supercooled H_2O as a function of the concentration of patch breaking additive. He found that with the addition of 37% hydrogen peroxide the anomalous behavior of the specific heat was suppressed.

The second part of this project was to test this idea of patch breaking on a transport property as opposed to a thermodynamic property. One would expect that, if the formation of large patches of water molecules was inhibited, the increase in the viscosity with decreasing temperature would be less than the increase for untreated water. This is the measurement which I have made.

Chapter Three

EXPERIMENT

The basic experimental tool used in this project was PCS. This section is intended to give the reader a feeling for what PCS is. Mathematical details can be found in appendix one.

Consider a volume of liquid illuminated by a laser beam which has an effective frequency distribution described by a delta function. (Such a frequency distribution implies an infinite wave, perfectly correlated with itself.) Some of the incident light will be scattered, either from 0.109 diameter polystyrene microspheres or from the inherent density fluctuations present within the liquid. If the scattering centers did not move relative to one another, the scattered light would also be monochromatic and perfectly correlated. (One would see a sort of Laue pattern.) However, the temporal behavior of each system is governed by a diffusion equation,

$$\partial T / \partial t = -D_T \nabla^2 T \quad (1a)$$

or

$$\partial \rho / \partial t = -D_m \nabla^2 \rho \quad (1b)$$

In the above equations the thermal diffusivity, D_T , and the mass diffusion constant, D_m , are given by the following expressions:

$$D_T = \lambda / \rho C_p \quad , \quad (2)$$

and

$$D_m = k_B T / (6\pi\eta a) \quad . \quad (3)$$

Here, Λ is the thermal conductivity, T is the absolute temperature, ρ is the density, C_p is the specific heat at constant pressure, k_B is Boltzmann's constant, η is the viscosity, and a is the radius of the diffusing particles. Because of the random nature of this type of motion, the scattered light will no longer be perfectly correlated and its frequency spectrum will spread out from the original delta function. As the particles diffuse more quickly, the width of the frequency spectrum, Γ , increases.

If, as is often the case, the frequency spectrum of the scattered light is a Lorentzian, then the correlation function, its Fourier transform, is an exponential. The decay constant of the correlation function is Γ and $1/\Gamma$ is called the correlation time, τ_c . Γ is related to experimental parameters by,

$$\Gamma = Dq^2 \quad (4)$$

where D is the appropriate diffusion constant and $|\vec{q}|$ is the magnitude of the scattered wave vector,

$$|\vec{q}| = (4\pi n/\lambda) \sin (\theta/2) \quad . \quad (5)$$

Here, λ is the wavelength of the scattered light in vacuo, n is the index of refraction of the liquid, and θ is the scattering angle. Thus, the correlation time is related by Eqs. (4) and (5) to the thermal diffusivity

$$\tau_c = \lambda^2 / [16\pi^2 n^2 D_T \sin^2 (\theta/2)] \quad (6)$$

and by Eqs. (3), (4), and (5) to the viscosity

$$\tau_c = [3n\alpha\lambda^2]/[8\pi k_B T n^2 \sin^2 (\theta/2)] \quad . \quad (7)$$

Because τ_c itself can be found from the Fourier transform of the power spectrum by Eq. (7), we can clearly see that PCS can be used to make viscosity measurements. While this approach does not prove to have the accuracy of flow type measurements⁷, it does have the possibility, due to the very small samples which can be used, to extend, from -20°C to --30°C, the limit for which viscosity data are available for super-cooled water. This possibility has not been realized but no inherently insurmountable problems have been encountered.

B. Setup and Procedure

Figure 1 shows the brass cell holder which was used in the experiment. When assembled, it surrounded the sample volume with ~3/4" of brass on all sides. This large thermal mass was insulated with styro-foam to insure small temperature gradients near the sample. Three windows pierced the insulation and cell holder. They were covered with microscope cover slips and filled with dry nitrogen gas which had passed through a 0.22 μ filter. The nitrogen gas flowed at a low rate, 10-15 cm³/s, through 10' of 1/8" copper tube wrapped around and soldered to the cell holder. As a result, the gas filling the windows was within

Figure One

CELL HOLDER

The spectrometer cell holding the sample fits into piece Q in Fig. 1b. The inside pieces fit together and then slide into the center of the cell holder. Not shown in the drawing are tygon tubes connecting tube L with tubes C and gas jets which wash the outside of each coverslip with dry, warm N₂.

- A = 1 7/8" x 4" Brass rod with 15/16" hole in center
- B = 1/8" Dia copper tube for cooling N₂ gas
- C = 1/8" Dia copper tube. Passes chilled N₂ into windows
- D = Window gas exit holes
- E = Microscope coverslips
- F = 180° Window. 1/4" hole in brass, 3/8" hole in styrofoam
- G = 90° Window. 1/4" hole in brass, 3/8" hole in styrofoam
- H = 0° Window. 1/4" x 1/2" hole in brass, 3/8" x 3/4" hole in styrofoam
- I = Styrofoam insulation 3 3/4" x 3 3/4" x 5"
- J = Hole for thermistor
- K = Entrance to tube B (N₂ warm)
- L = Exit from tube B (N₂ cold)
- M = Steel coupling. From dewar to cell holder. 3/4" x 1 1/2" with 1/2" dia. hole
- N = Made from brass rod. 15/16" x 6"
- O = Connection to heater coils
- P = Part of 90° window
- Q = Spectrometer cell fits into this piece
- R = Heater coils

**THIS BOOK
CONTAINS
NUMEROUS PAGES
WITH DIAGRAMS
THAT ARE CROOKED
COMPARED TO THE
REST OF THE
INFORMATION ON
THE PAGE.**

**THIS IS AS
RECEIVED FROM
CUSTOMER.**

Cell Holder As Seen From Top
Outside Gas Tubes Not Shown

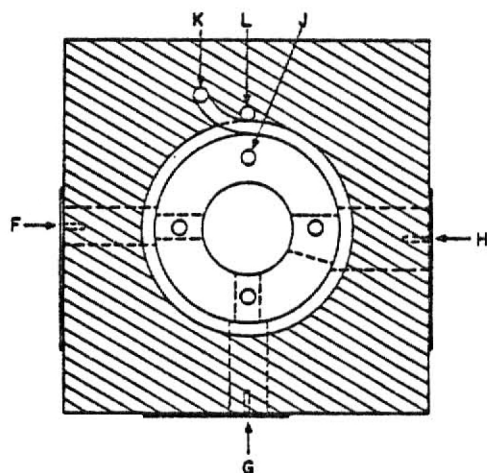


FIGURE 1a

Inside Pieces Of Cell Holder
Two Views Of Each

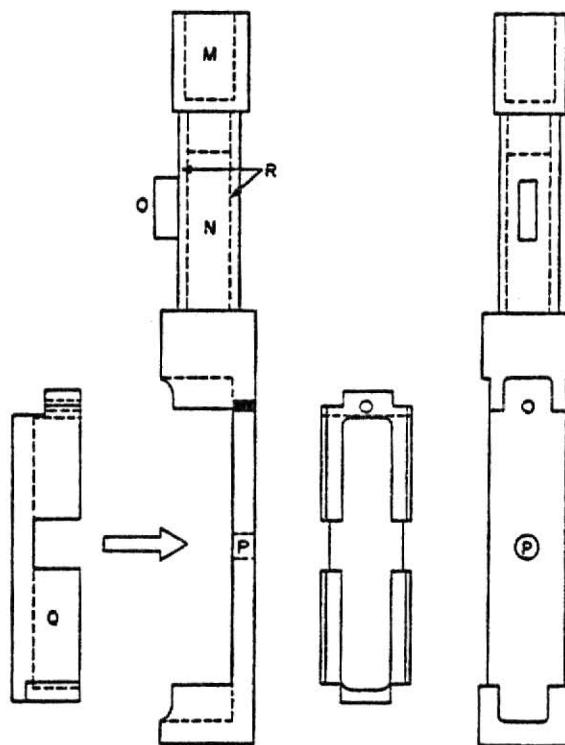


FIGURE 1b

Cell Holder As Seen From 90° Window Side
Outside Gas Tubes Not Shown

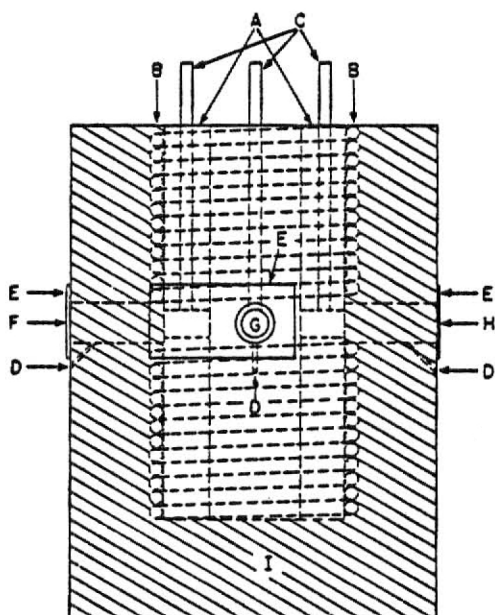


FIGURE 1c

Cell Holder As Seen From 0° Window Side
Outside Gas Tubes Not Shown

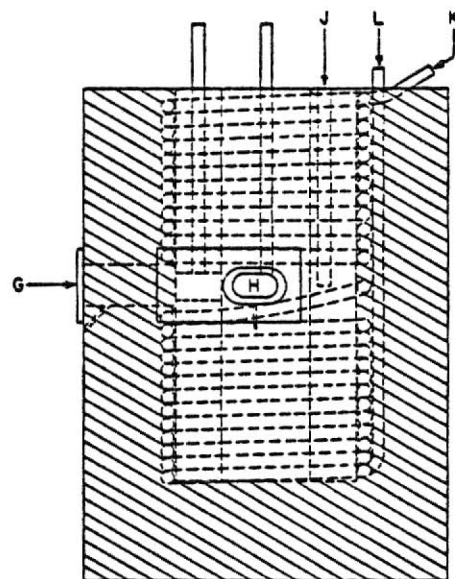


FIGURE 1d

1°C of the cell holder temperature (See Appendix 2.). The outsides of the coverslips were washed by warm dry nitrogen to prevent frosting. A sample volume completely surrounded by materials at a uniform temperature and visible through three clear apertures was then available.

The top of the cell holder extended upward to a cold finger from a liquid nitrogen filled dewar. This extension was wrapped with heater wires and insulation. The heater coils were connected through a differential amplifier/power supply to a D. C. bridge which had as one arm a YSI 44004 precision thermister buried in the cell holder. Temperature measurement and control of $\pm 0.1^\circ\text{C}$ were easily achieved.

A spectrometer cell fit snugly within the sample volume. It was filled with a 50% water - 50% ethylene glycol mixture as a heat transfer path and an index of refraction match. The sample was contained within a 2 cm length of 0.5 mm square capillary tubing, flame sealed at the ends, and glued to a thin steel rod extending downward from the cell's stopper.

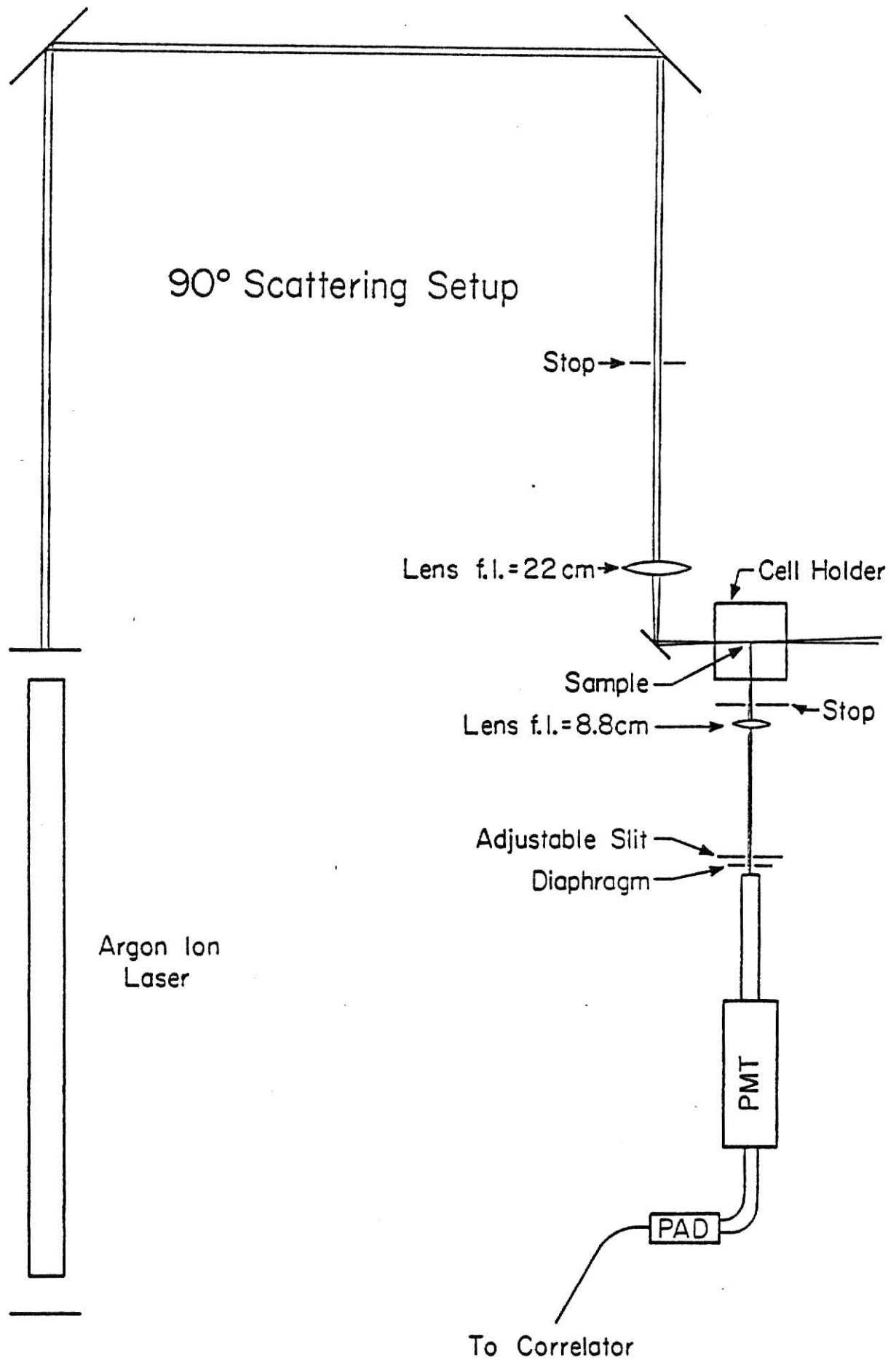
A Coherent Radiation model 52 argon ion laser provided a 50 mW, 457.9 nm beam which was focused through the capillary tube. The light scattered through the 90° window was collected by a lens and focused onto an adjustable slit. See Fig. 2. The slit and the diaphragm just behind it were used to select the portion of the scattering volume which would be seen by the photomultiplier tube, (PMT).

In the second part of the project, the thermal diffusivity measurements, a larger sample was needed due to the small scattering angles required. Because afterpulsing and dead time problems became severe for correlation times of less than 7 or 8 μ sec., scattering angles were restricted to less than 4°. (Measured within the liquid.)

Figure Two

90° SCATTERING SETUP

FIGURE 2



When the laser beam strikes the surface of the cell walls, bright spots are created. It was necessary to look between the spots to see the scattering volume. See Fig. 3. Because the minimum spot size was that of the focused laser beam, (and in practice it was larger) the spectrometer cell itself was used to contain the sample. This allowed sufficient room to see around the spots.

The reason for the enlarged spot size was the presence of micro-scratches and tiny mineral particles left on the surface. The following cleaning and handling procedure resulted in spot sizes small enough to allow interior scattering angles of $\geq 2.7^\circ$. The cleaning consisted of a series of soaks and ultrasonic scrubbing in a mild detergent solution (Joy) followed by 5 to 10 minutes of gentle rinses with warm tap water and distilled water. Soaking in spectrographic grade acetone was followed by rinses with unfiltered and then filtered (0.22μ Millipore filter) sample solution (Benzene, Toluene, Xylene). Finally the cell was filled and then closed with a clean teflon stopper. In the morning, before the general activity in the lab had stirred up the dust, the outside of the cell was given a final cleaning with lens tissue and acetone following the standard procedure for cleaning front surface optical components. This was the only time the cell faces were touched by anything except liquids and gases. Hands were either gloved or washed and degreased with alcohol. Following the final wipe, the cell was quickly loaded into the cell holder where it would remain clean for 3 or 4 days while protected by the filtered nitrogen. It should be emphasized that a cell which was perfectly clean in appearance is quite possibly extremely dirty insofar as this experiment is concerned.

Figure Three

BRIGHT SPOTS ON SPECTROMETER CELL WHEN SCATTERING AT SMALL ANGLES.

The angles are shown larger than was actually the case to improve the clarity of the picture. An image of the spots and scattering volume is actually projected onto the slit by a lens and the slit blocks out the unwanted light. See Fig. 4.

Spectrometer Cell Wall Spots

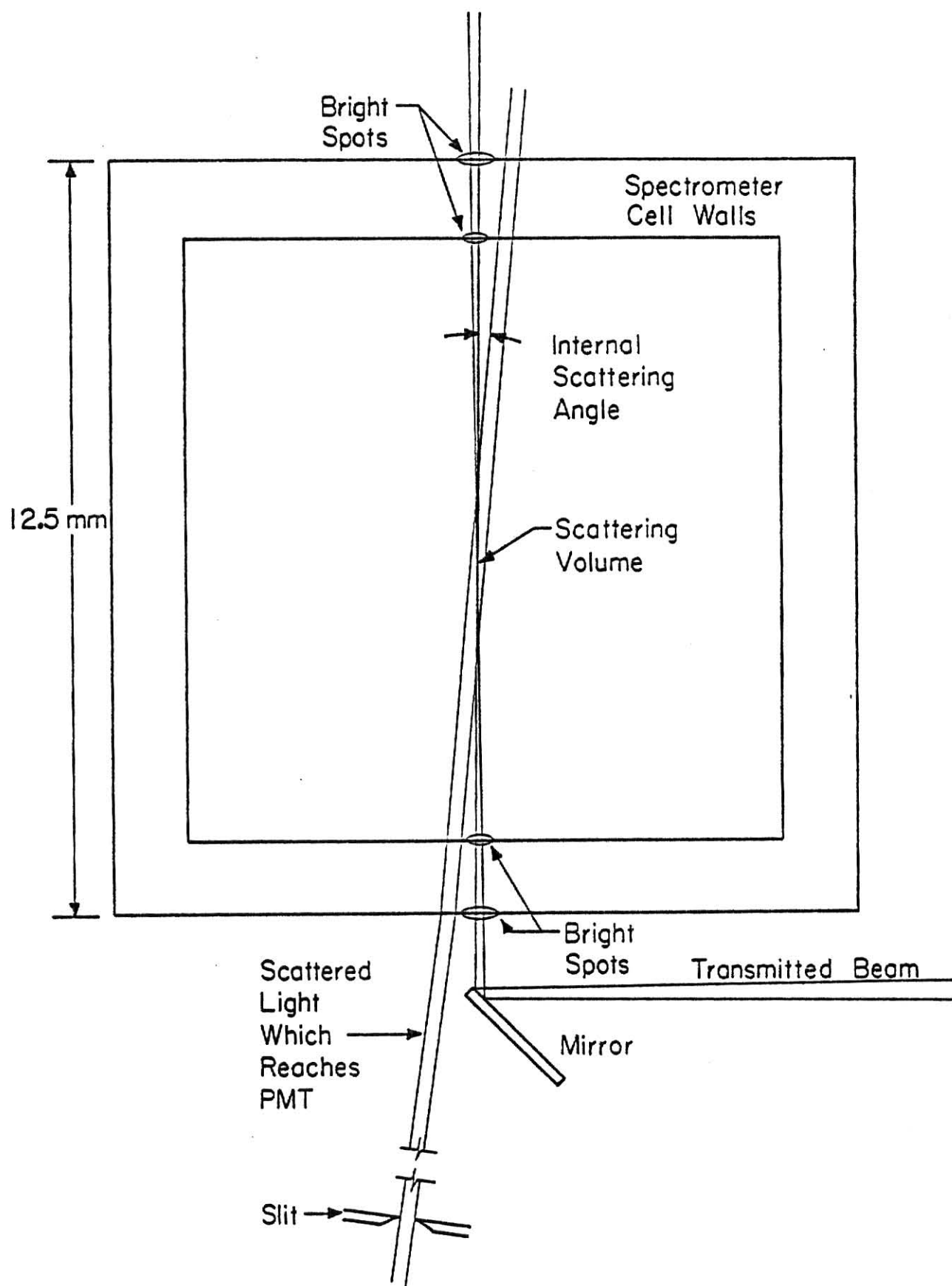


FIGURE 3

The transmitted beam (See Fig. 4.) was deflected by a mirror. Then, as before, the image of the scattering volume was projected onto the slit and only the desired portion of the light was allowed to reach the PMT.

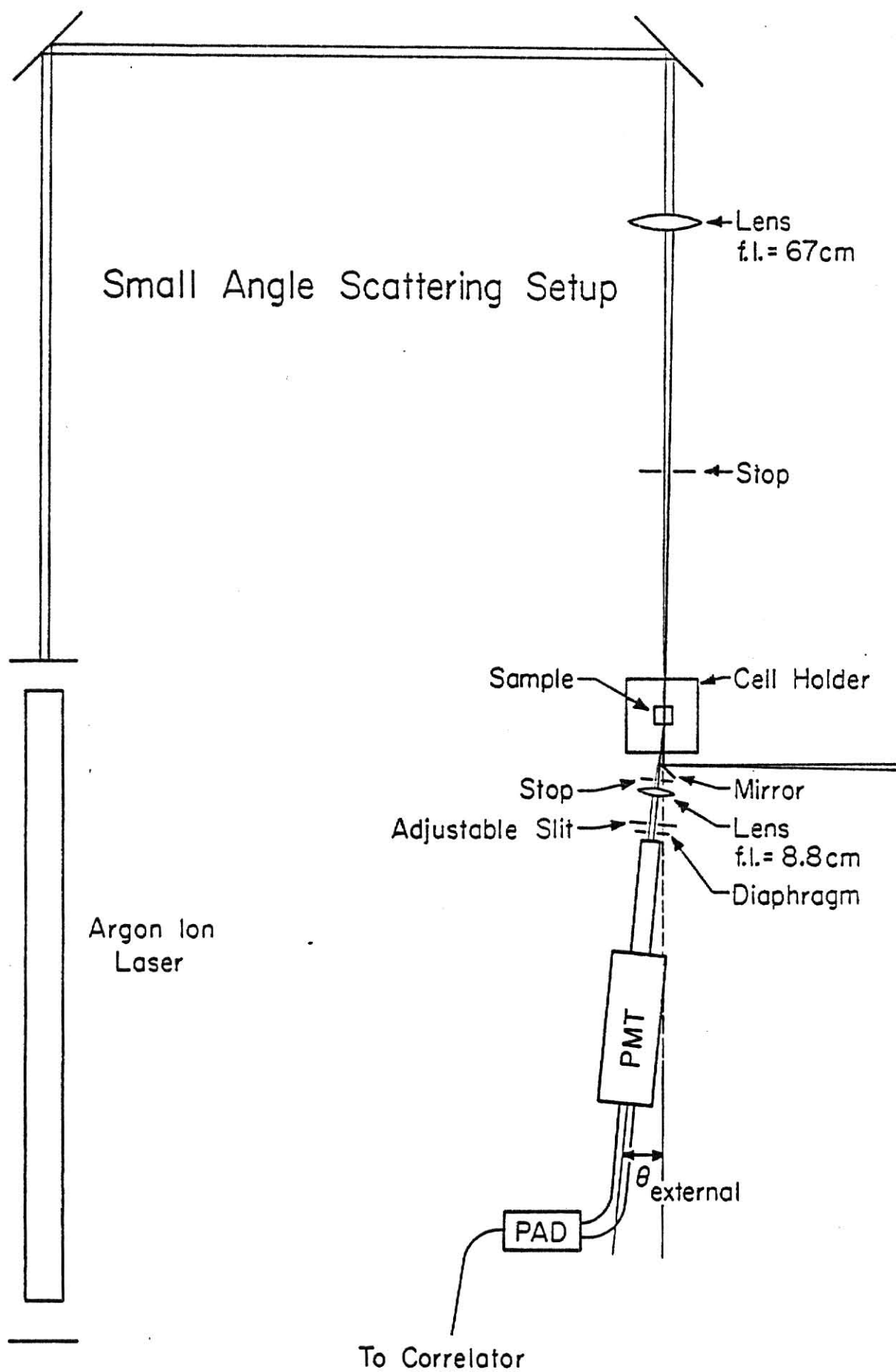
Once the light from either experiment fell upon the photocathode of the ITT FW 130 PMT, an analog signal resulted which was changed into a train of TTL pulses by a Pacific Photometric Instruments model AD-6 amplifier-discriminator. These pulses were used by a Langley-Ford model 1 autocorrelator to compute the correlation function. When sufficient data had collected in the correlator, the correlation function was sent to a PDP 11/34 computer for analysis.

Once the cell was loaded and the beam and slits were adjusted, both experiments proceeded in a similar fashion. The table was floated upon its air shocks, the gas across the coverslips was turned on and neutral density filters were inserted into the beam to reduce the count rate when necessary. Liquid nitrogen was poured into the dewar and 5 - 10 seconds of data were taken each 1 - 2 minutes. The temperature dropped at $\sim 0.5^{\circ}\text{C}$ per minute. Each run continued until the sample froze or a predetermined temperature was reached.

Figure Four

SMALL ANGLE SCATTERING SETUP

FIGURE 4



Chapter Four

ERROR CONSIDERATIONS AND VALIDITY OF DATA

The raw data collected in this project were the scattered-light correlation functions, which were sent to the computer for analysis, and a temperature associated with each. These functions were fit to the form

$$B + A \exp(-t/\tau_c + t^2/b)$$

using a least-squares fitting routine.

There were three parameters which were used to judge the goodness of the fit. A/B , the signal to background ratio, was required to be greater than ~ 0.15 or less than ~ 0.08 . For the region between these limits, the optical mixing on the photocathode changes from the heterodyne to the homodyne mode and prevents the correlation time from being accurately related to the diffusion constant. The cumulant ratio, b/τ_c^2 , is a measure of the nonexponentiality of the fit. If the data were ideal, b would be zero. Reasons for a large cumulant ratio include dirt on or in the sample volume, vibrations from boiling in the dewar, and small movements of the sample cell itself. Experience indicated that a cumulant ratio of less than ~ 0.07 was good while one of less than ~ 0.14 was acceptable. A chi-square test was performed and it was found that $\chi^2 \leq 1.1$ usually indicated reasonably good data.

A visual inspection of the correlation function, displayed on an oscilloscope, was used with the aforementioned restrictions on the fit parameters to select the acceptable correlation functions. This proce-

dure resulted in τ_c values which fluctuated by no more than ~4% at 20°C to ~12% at -25°C.

A platinum resistance thermometer was placed in the scattering volume in a mockup of the sample cell to check the thermistor calibration. See Fig. 1 for the location of the thermistor. Simultaneous readings from each indicated that the thermistor was registering 2.6°C too high. Uncertainty in reading the dials on the D.C. bridges caused corresponding errors in the temperatures and calibration of $\pm 0.1^\circ\text{C}$ and $\pm 0.3^\circ\text{C}$. These errors and the additional error from converting resistance measurements to temperature measurements indicate that a maximum error of $\pm 0.5^\circ\text{C}$ is not unreasonable. Because the error in the calibration would be a systematic error, the precision of the temperature measurement should be good to $\sim \pm 0.2^\circ\text{C}$.

To check the accuracy of the collected data, two comparisons were made with the available published data and one run was repeated using a flow type measuring technique. Figure 5a shows the 100% H_2O data and a combination of data taken from Hallett⁷ and the C.R.C. physics handbook.²⁰ Within the estimated errors, both sets of data agree well. Viscosity vs. concentration of ethanol in water data from this experiment are compared in Fig. 5b to data from a similar measurement as reported by Kay, Cunningham, and Evans.²¹ With the exception of the 30% ethanol point, the agreement is good. The 30% point was rechecked and no change was recorded. I have no explanation for this discrepancy. As was indicated in chapter three, a viscometer can be used to make very accurate measurements of viscosity. One of the stock solutions used in this experiment was placed in a viscometer to check the results

Figure Five

ACCURACY CHECKS ON EXPERIMENTAL RESULTS

- 5a - $\bigcirc$ represent very accurate viscosity data taken with a viscometer by Hallett. $\square$ represent data taken from the C.R.C. Handbook of Chemistry and Physics. $\triangle$ represent my 100% H_2O data.
- 5b - $\triangle$ are data points taken from the literature.²¹ $\bullet$ are my data. As was noted in the text the 30% ethanol point has been rechecked and no explanation is offered for the difference.
- 5c - The 11.5% hydrazine was used in a viscometer to recheck the PCS measurement. $\triangle$ are data from the viscometer and $\bullet$ are data from the PCS measurement.

My data, as shown in Fig. 5a, have been normalized to 1.00 cp at 20°C. If Eq. (7) was used to find η the data would be ~5% smaller than they appear.

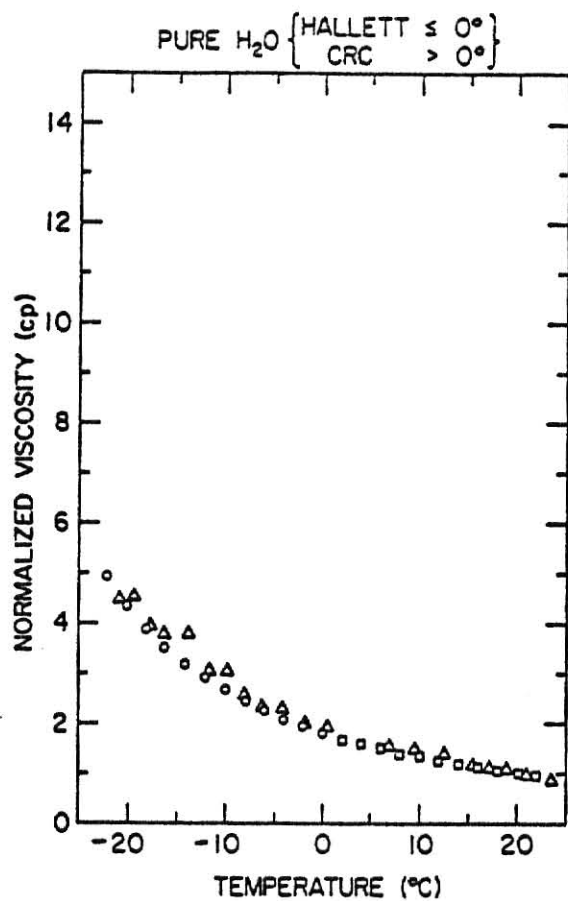


FIGURE 5a

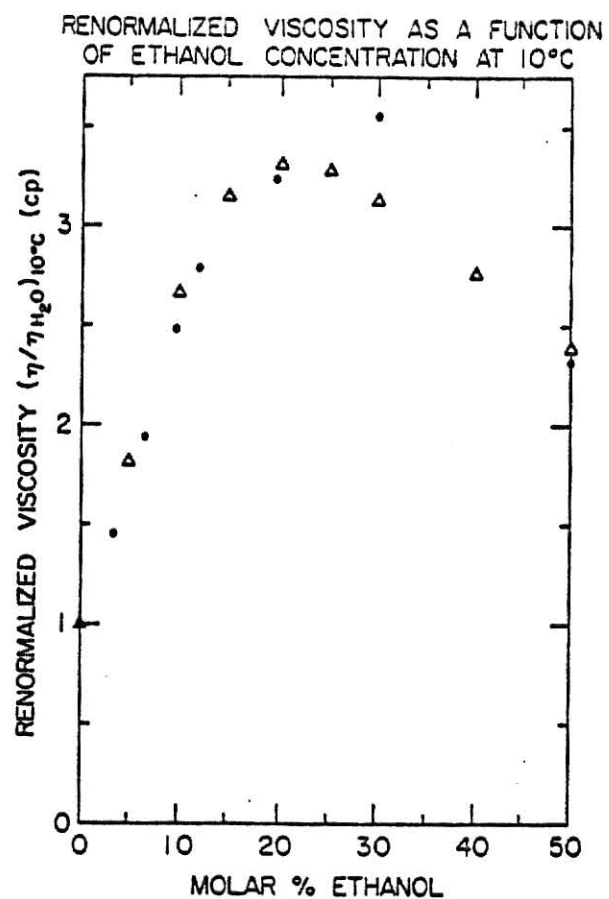


FIGURE 5b

TWO METHODS OF MEASURING VISCOSITY
(11.5 % HYDRAZINE)

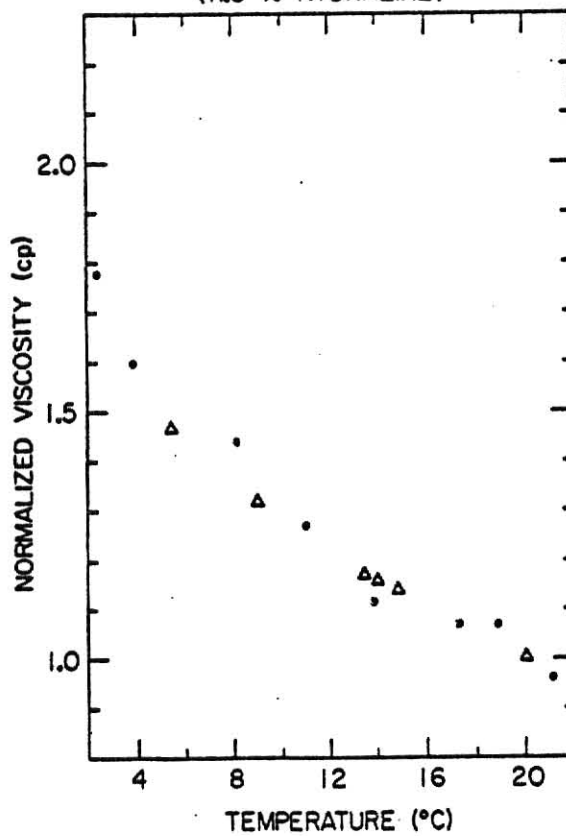


FIGURE 5c

obtained using PCS. Within the stated error limits, the data are the same as can be seen in Fig. 5c. These comparisons give me confidence that my data accurately reflect the true viscosities of the solutions at the corrected temperature.

Chapter Five

DATA ANALYSIS

This chapter will explain the motivations for and methods used in the analysis of the data. The models discussed in chapter two will be used to attempt to explain the behavior of the data and conclusions will be reached, where possible, as to the implications of this experiment for those models. Finally, suggestions for improvements in the experiment will be made.

Throughout this thesis, the project has been divided into two parts. The results of the first part, thermal diffusivity and the search for evidence of a thermodynamic singularity in the liquid-solid phase transition, were rather disappointing. For the case of benzene, if one takes the glass temperature, T_g , as a rough guide for the location of the supposed singularity, then $\sim 90^\circ\text{C}$ of supercooling would be needed to get closer to it. ($T_g \approx 2/3 T_m$, T_m = melting temperature = 278.5°K). If one chose to argue by analogy that, because water seems to have a singularity at $\sim 5^\circ\text{C}$ below its apparent homogeneous nucleation limit of $\sim -40^\circ\text{C}$,¹⁴ benzene might have a similar singularity at $\sim 5^\circ\text{C}$ below its homogeneous nucleation limit of $\sim -65^\circ\text{C}$,²² then $\sim 75^\circ\text{C}$ of supercooling would be expected to get one near any singularity. In either case, the 9°C of supercooling actually achieved was not nearly enough. (It must be pointed out that these are kinetic arguments and not necessarily valid for a prediction involving strictly thermodynamic properties. It is clear, however, that there is no singularity above -65°C . See Fig. 6

Figure Six

TYPICAL BENZENE DATA

The error bars represent the scatter in the data. Each point is the average of from 3 to 10 relaxation times. It appears that the spread in the data does not sufficiently account for the error.

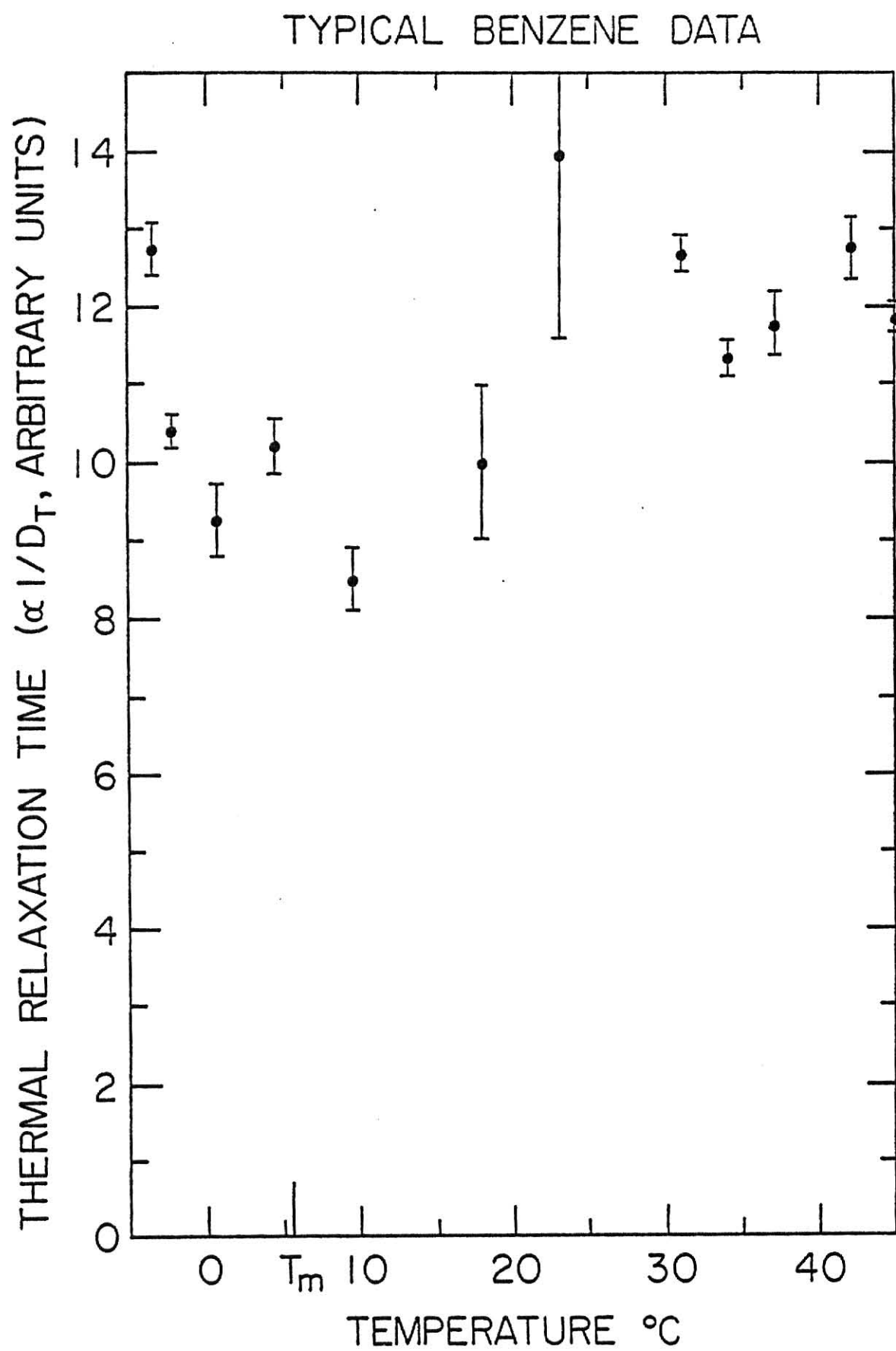


FIGURE 6

for typical data.) Indeed, Haus and Meijer⁴ suggested the condition $(T - T_{\text{singularity}})/T_{\text{singularity}} \leq 0.02$ for placing an upper bound on the temperature for which the thermal relaxation times would show a decrease. For benzene this means that one would need to be within $\sim 4^\circ\text{C}$ of the singularity to see the effect. Similar results were obtained for para-xylene ($T_m = 286.3^\circ\text{K}$). See Fig. 7. Because of the inability to supercool the samples far enough, I feel that, while this was a useful first effort at making this measurement, the only conclusion which can be reached is that there is no evidence of a Haus and Meijer singularity at these temperatures. Certainly the lack of any unusual behavior in Figs. 6 and 7 supports this statement.

For the second measurement, the viscosity of supercooled water solutions and the structure of water, I have discussed how correlation times as a function of corrected temperature were collected. Equation (7) shows that the correlation time, τ_c , is proportional to the viscosity, η . Because the index of refraction, n , is very insensitive to temperature change, (It changes by less than 0.1% over the temperature range used.) the correlation times can be converted to viscosities by normalizing all of the correlation times for the run to the known viscosity at some temperature. Table 1 contains the actual viscosities at 20°C for the solutions used.

The data were normalized in this fashion and were then fit to a modified Arrhenius behavior,

$$\eta = \eta_0 \exp[A/(T - T_0)]$$

Figure Seven

TYPICAL PARA-XYLENE DATA

Each data point shown represents one relaxation time. The reading was taken over a spread of temperatures as indicated by the error bars.

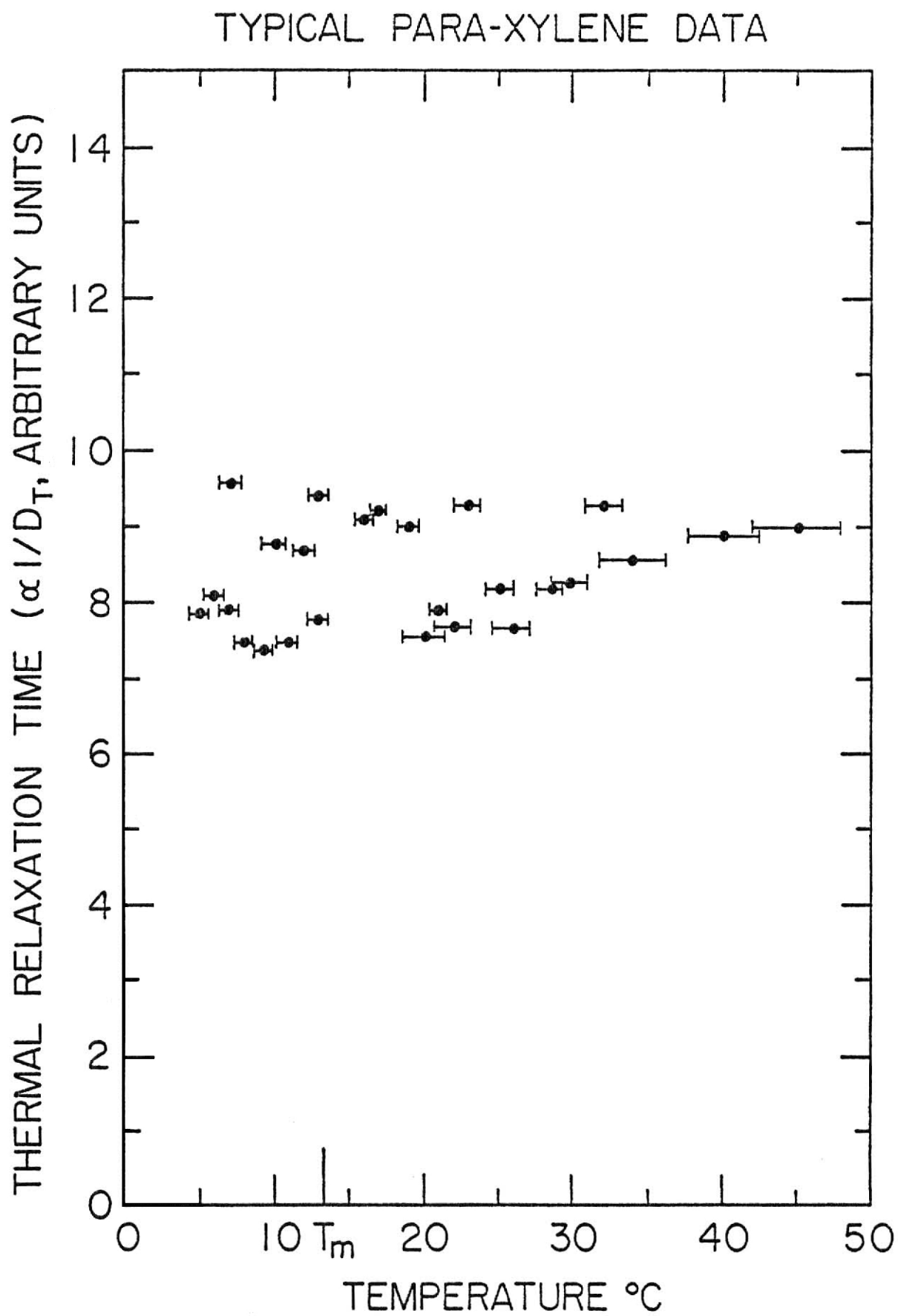


FIGURE 7

Table One

ACTUAL VISCOSITIES OF SOLUTIONS AT 20°C

- a - Found in C.R.C. Handbook of Chemistry and Physics. Ref. 20
- b - Measured with viscometer accurate to within 1%
- c - Measured as in b. Actual viscosity will be proportional to the density of this solution at 20°C. It was assumed to be 1.00 g/cm³.

Actual viscosities of solutions
at 20°C. (η in cp)

Water - Ethanol

a

Molar % Ethanol	η at 20°C
0.0	1.00
3.5	1.42
6.7	1.85
9.8	2.24
12.2	2.47
19.5	2.83
30.0	3.26
50.0	2.21

Water - Hydrazine

b

Molar % Hydrazine	η at 20°C
0.0	1.00
5.0	1.14
11.5	1.32
17.1	1.49
25.0	1.78
36.0	1.93
50.0	1.98

Water - Dioxane

c

Molar % Dioxane	η at 20°C
11.5	1.83

Water - Methanol

a

Molar % Methanol	η at 20°C
3.6	1.20
6.9	1.35
10.0	1.51
12.9	1.62

This is the form normally used to describe the temperature dependence of transport properties for glass forming liquids. A represents a flow activation energy and T_0 is usually a glass transition temperature. The data were actually fit to the form

$$\ln(\eta/\eta_0) = A/(T - T_0)$$

using a least-squares fitting procedure. T_0 was chosen and then η_0 and A were determined by the fit. A chi-square test was run and the T_0 value which produced the minimum χ^2 value was selected. (The average χ^2_{reduced} was about 0.90.) An error was assigned to T_0 using the idea that when χ^2 varied by χ^2_{reduced} , T_0 varied by one standard deviation. Table 2 lists the fit parameters T_0 , η_0 , and A for the solutions used. Some correlation between the concentration of patch-breaking impurity and the fit parameters was searched for, but, as Fig. 8 shows, no such correlation was found.

Because the important behavior is the rate at which the viscosity increases with decreasing temperature, all of the data were normalized to the viscosity of pure water at 20°C (1.00 cp) to facilitate visual comparison of the various graphs. Figures 9 - 14 show all of the data with this normalization. Appendix 3 contains the same information in tabular form. Each plot also includes a reference curve which represents very reliable data for pure water. See Fig. 5a.

The behavior searched for in this part of the project was a decrease in the rate at which the viscosity of the water increased with decreasing temperature. Stanley's³ model proposed that the anomalous properties of water were due to the hydrogen bonded structure of the water molecules.

Table Two

FIT PARAMETERS FOR ETHANOL-WATER
HYDRAZINE-WATER DATA.

The data were fit to the form

$$\eta = \eta_0 \exp[A/(T - T_0)]$$

FIT PARAMETERS FOR WATER - ETHANOL
AND WATER - HYDRAZINE SOLUTIONS.

Water - Ethanol

Molar % Ethanol	$\eta_o \times 10^{-5} p$	A (°K)	T _o (°K)
0.0	0.15	2420	18 ± 10
3.6	6.07	860	133 ± 11
6.7	42.2	431	179 ± 3
9.8	5.78	882	145 ± 10
12.0	2.61	1110	131 ± 10
19.5	1.23	1370	116 ± 15
30.0	4.87	1080	127 ± 10
50.0	0.06	3070	1 ± 20

Water - Hydrazine

Molar % Hydrazine	$\eta_o \times 10^{-5} p$	A (°K)	T _o (°K)
0.0	0.15	2420	18 ± 10
5.0	14.0	721	129 ± 10
11.5	19.7	664	135 ± 15
17.1	0.26	2520	2 ± 20
25.0	1.08	1910	35 ± 20
36.0	0.92	1920	42 ± 20
50.0	16.6	807	124 ± 15

Figure Eight

FIT PARAMETERS AS A FUNCTION OF CONCENTRATION OF IMPURITY

8a - T_0 as a function of concentration of impurity. Δ represent ethanol data and $\square$ represent hydrazine data. The sizes of the error bars are based upon the variation of χ^2 for each fit.
(See text.)

8b - n_0 as a function of concentration of impurity. Δ are ethanol data points. $\square$ are hydrazine data points.

8c - A as a function of concentration of impurity. Δ represent ethanol data and $\square$ represent hydrazine data.

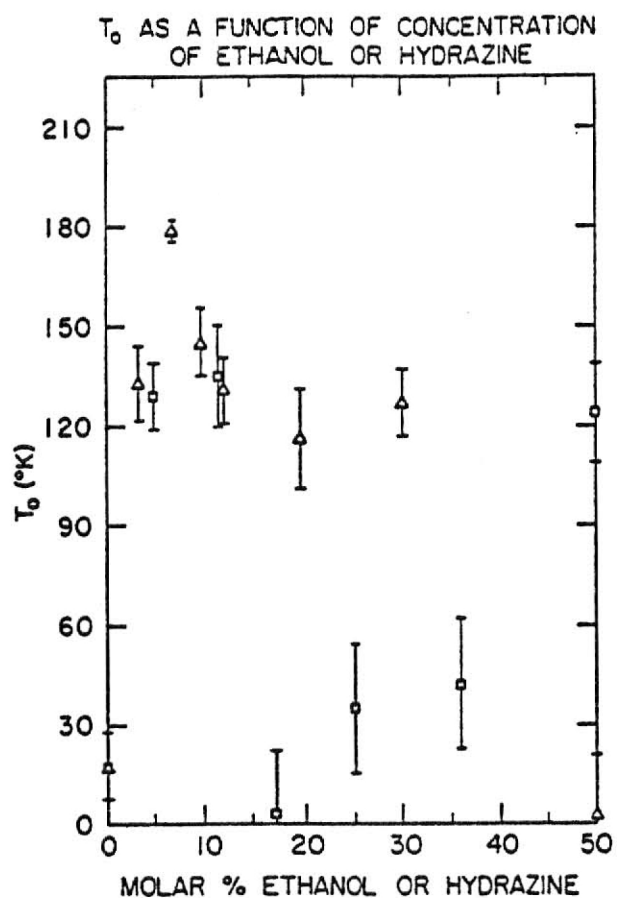


FIGURE 8a

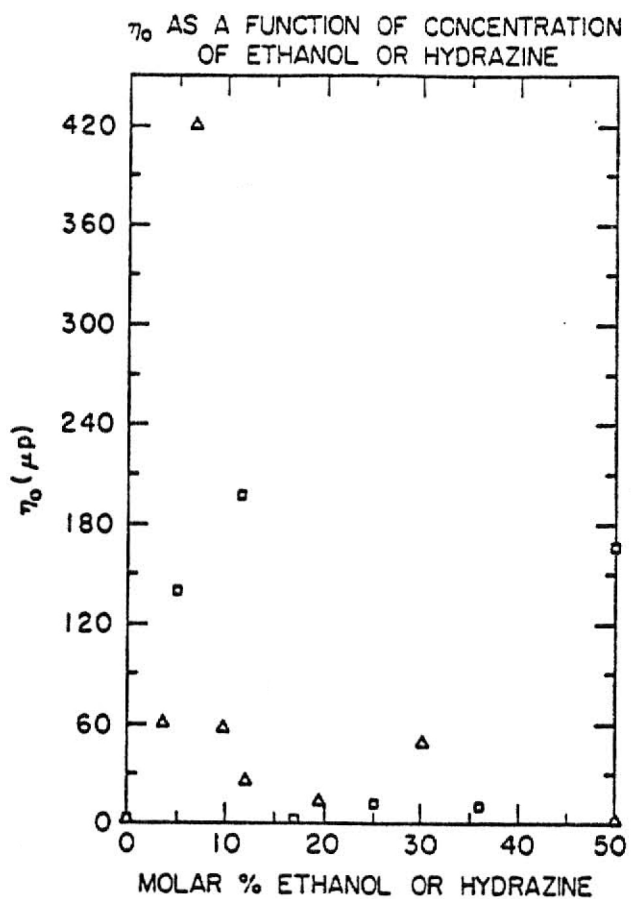


FIGURE 8b

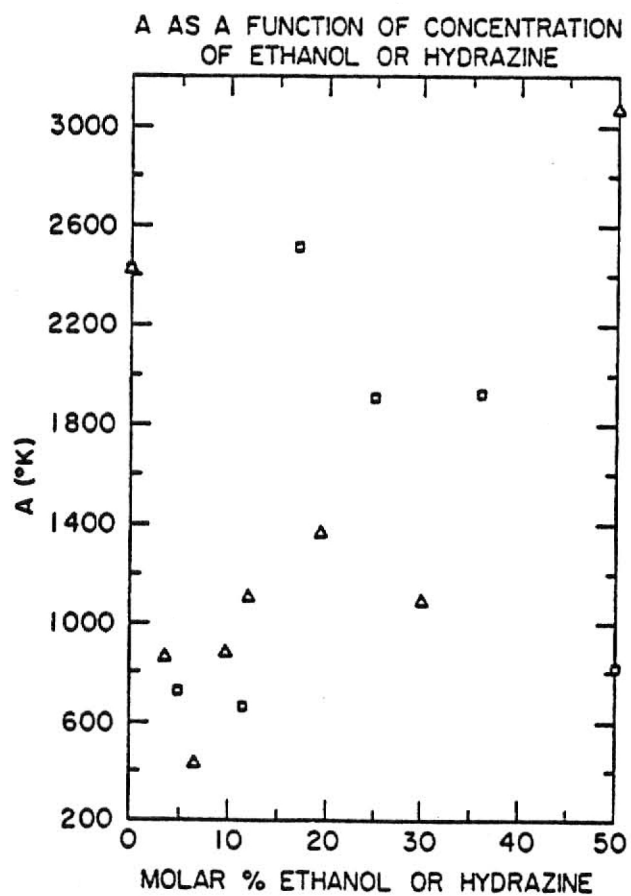


FIGURE 8c

Figure Nine

NORMALIZED VISCOSITY DATA FOR ETHANOL-WATER SOLUTIONS.

The solid line represents reliable viscosity data for pure water. It is included as a reference line. All data were normalized to 1.00 cp at 20°C.

9a - 0% ethanol

9b - 3.6% ethanol

9c - 6.7% ethanol

9d - 9.8% ethanol

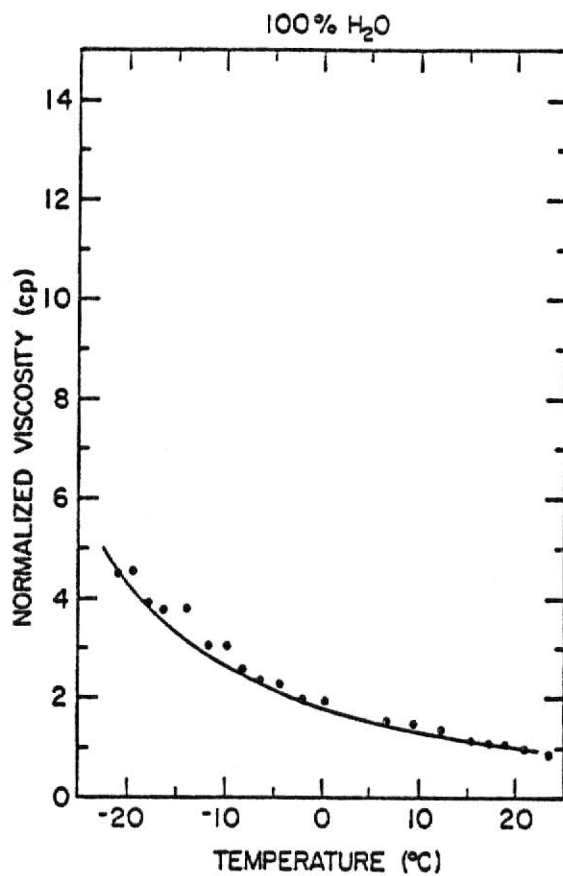


FIGURE 9a

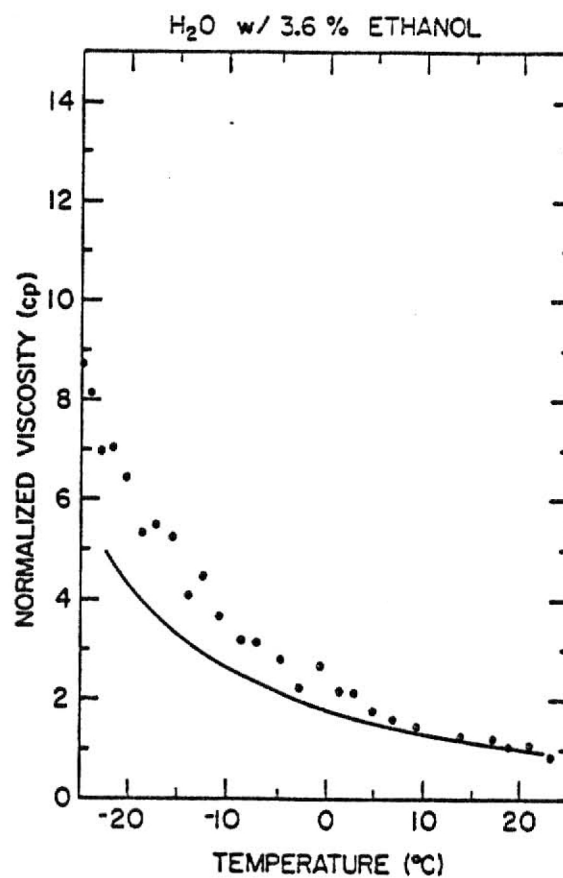


FIGURE 9b

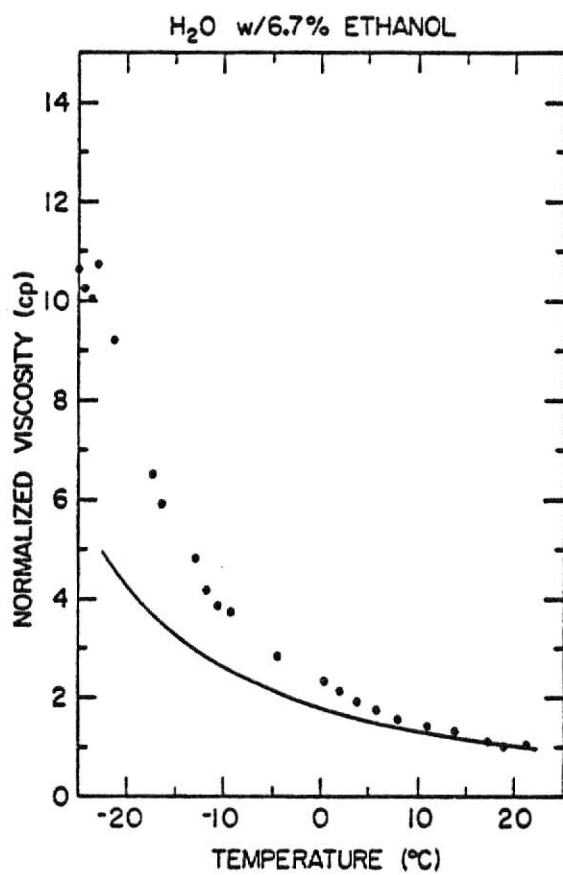


FIGURE 9c

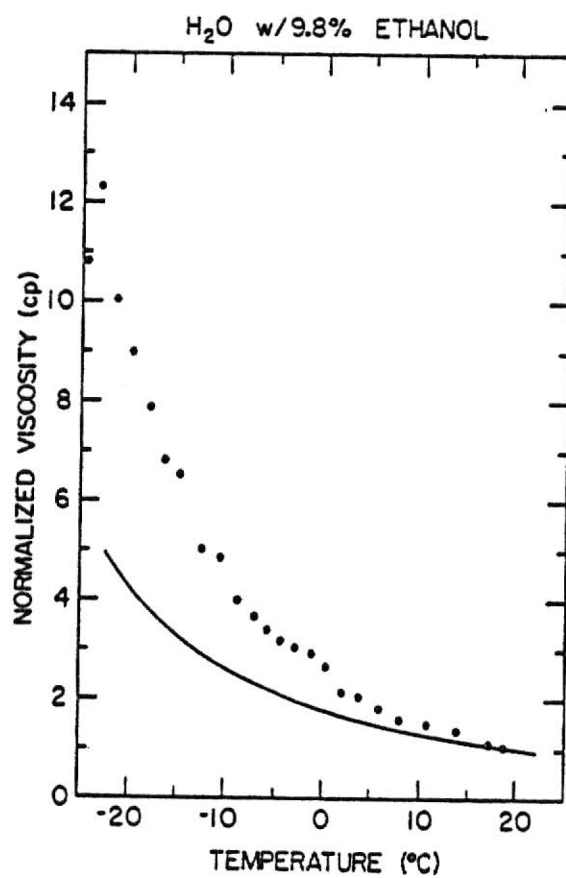


FIGURE 9d

Figure Ten

NORMALIZED VISCOSITY DATA FOR ETHANOL-WATER SOLUTIONS.

The solid line represents reliable viscosity data for pure water. It is included as a reference line. All data were normalized to 1.00 cp at 20°C.

10a - 12% ethanol

10b - 19.5% ethanol

10c - 30% ethanol

10d - 50% ethanol

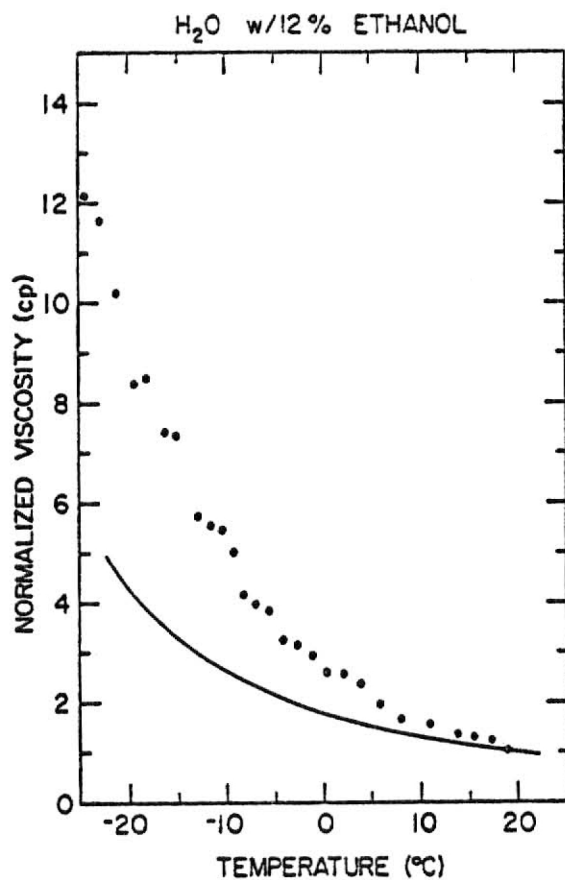


FIGURE 10a

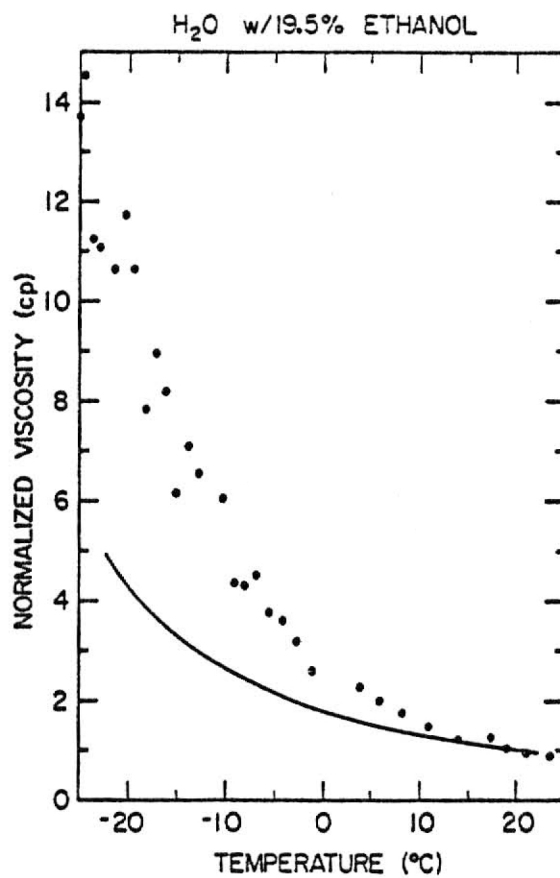


FIGURE 10b

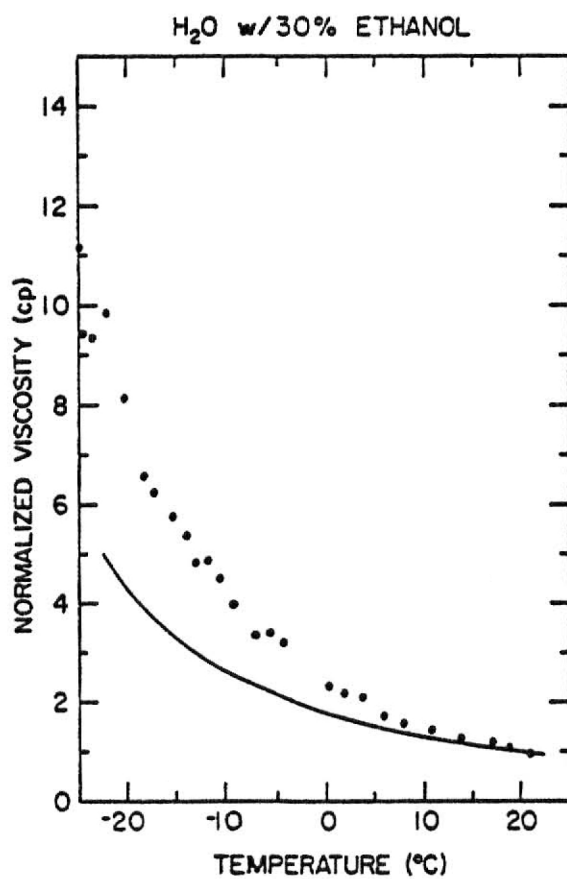


FIGURE 10c

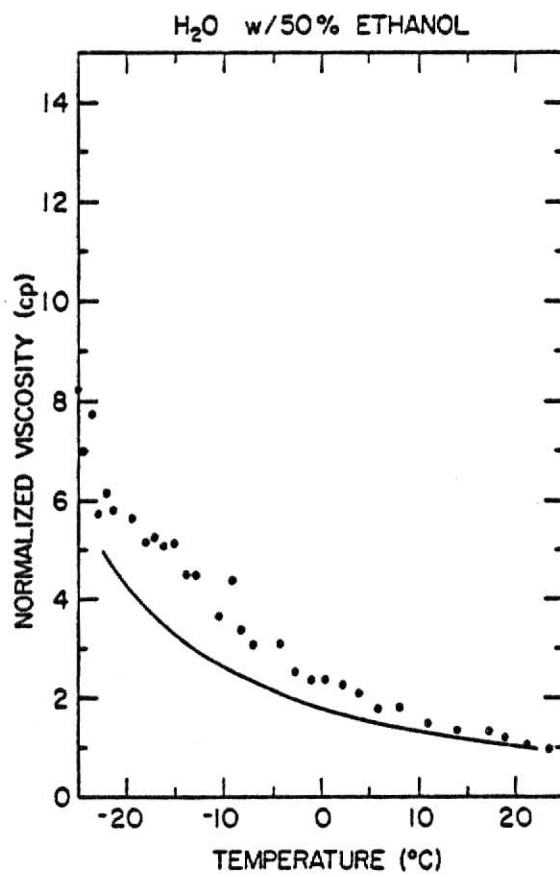


FIGURE 10d

Figure Eleven

NORMALIZED VISCOSITY DATA FOR HYDRAZINE-WATER SOLUTIONS.

The solid line represents reliable viscosity data for pure water. It is included as a reference line. All data were normalized to 1.00 cp at 20°C.

11a - 0% hydrazine

11b - 5% hydrazine

11c - 11.5% hydrazine

11d - 17.1% hydrazine

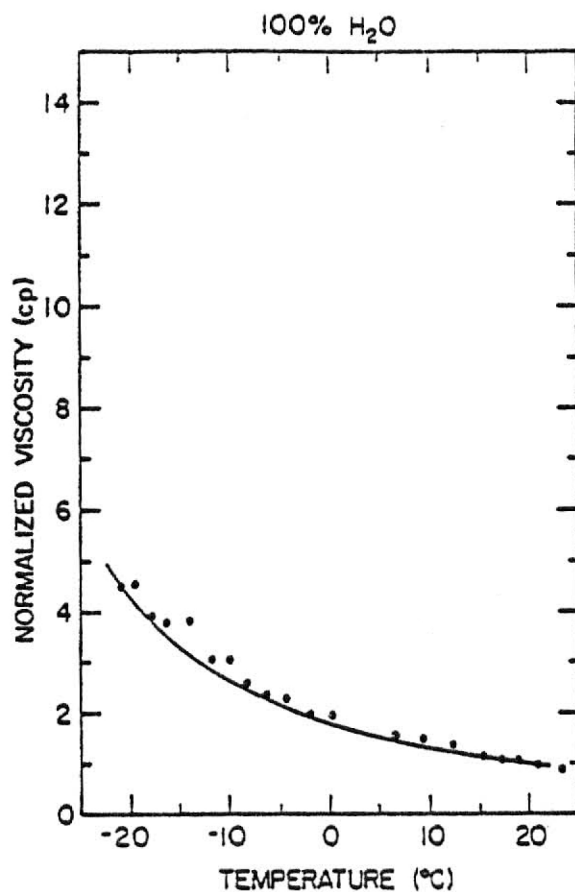


FIGURE 11a

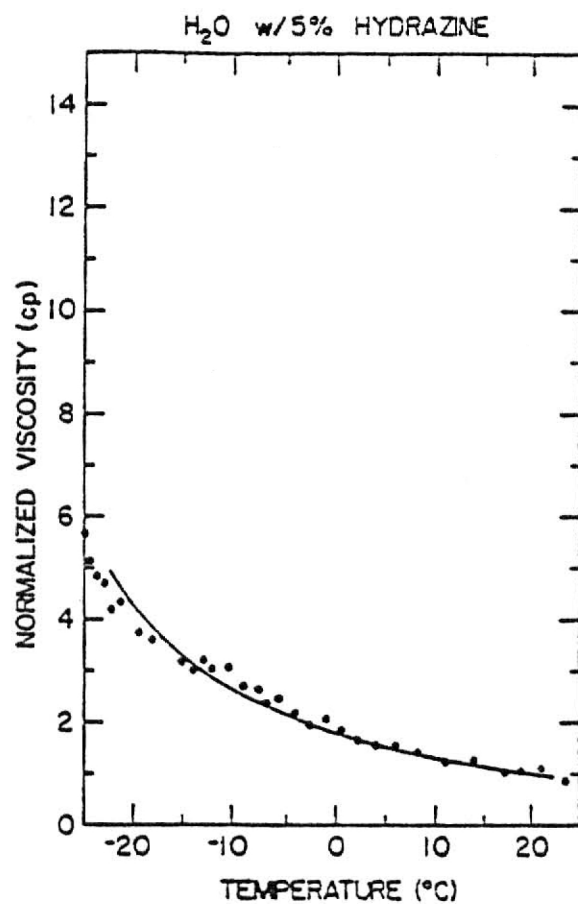


FIGURE 11b

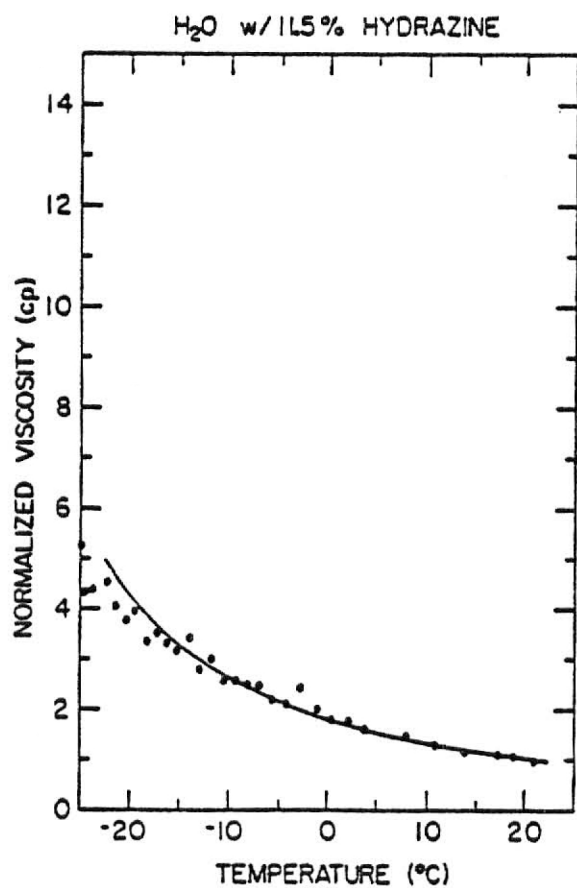


FIGURE 11c

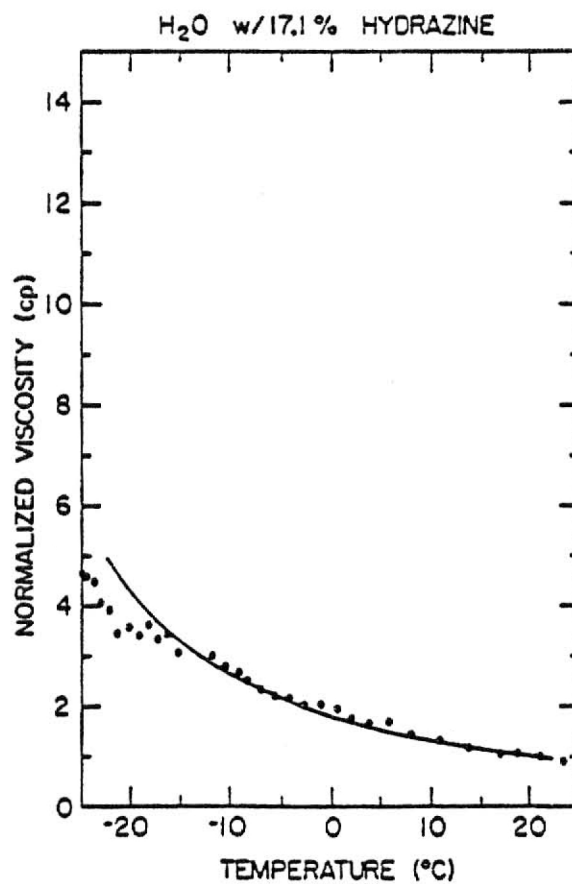


FIGURE 11d

Figure Twelve

NORMALIZED VISCOSITY DATA FOR HYDRAZINE-WATER SOLUTIONS.

The solid line represents reliable viscosity data for pure water. It is included as a reference line. All data were normalized to 1.00 cp at 20°C.

12a - 25% hydrazine

12b - 36% hydrazine

12c - 50% hydrazine

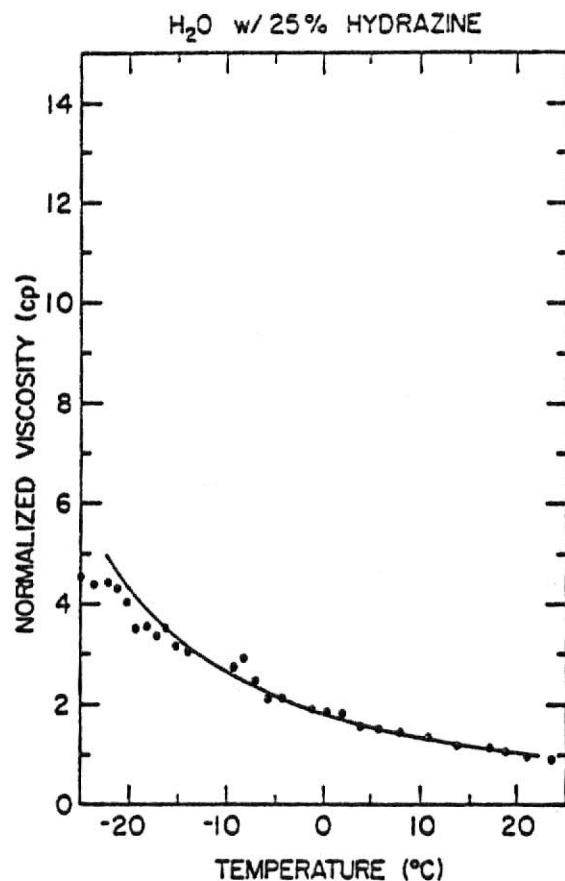


FIGURE 12a

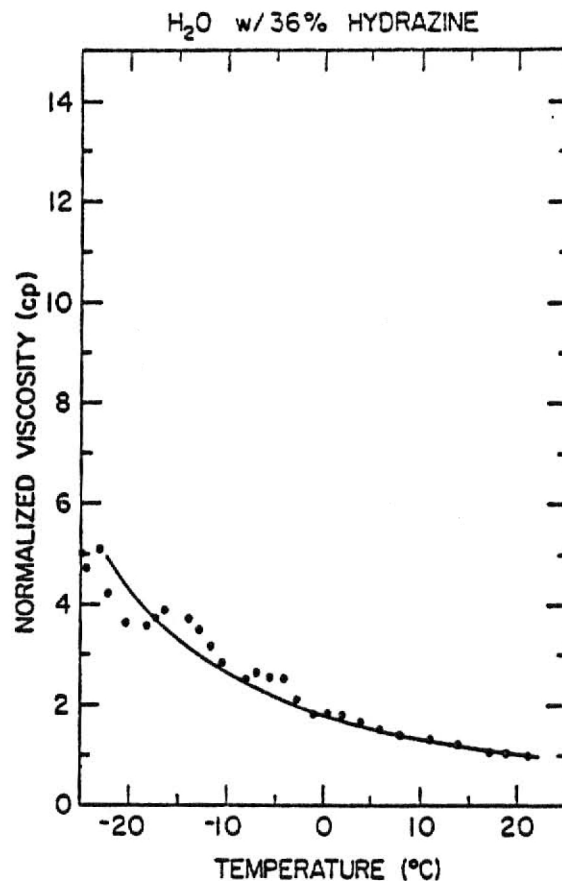


FIGURE 12b

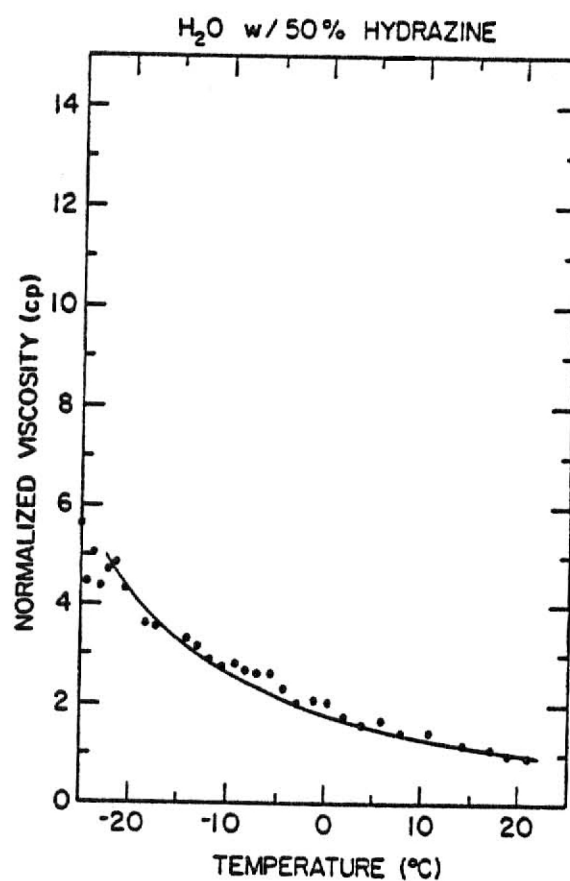


FIGURE 12c

Figure Thirteen

NORMALIZED VISCOSITY DATA FOR METHANOL-WATER SOLUTIONS.

The solid line represents reliable viscosity data for pure water. It is included as a reference line. All data were normalized to 1.00 cp at 20°C.

13a - 3.6% methanol

13b - 6.9% methanol

13c - 10% methanol

13d - 12.9% methanol

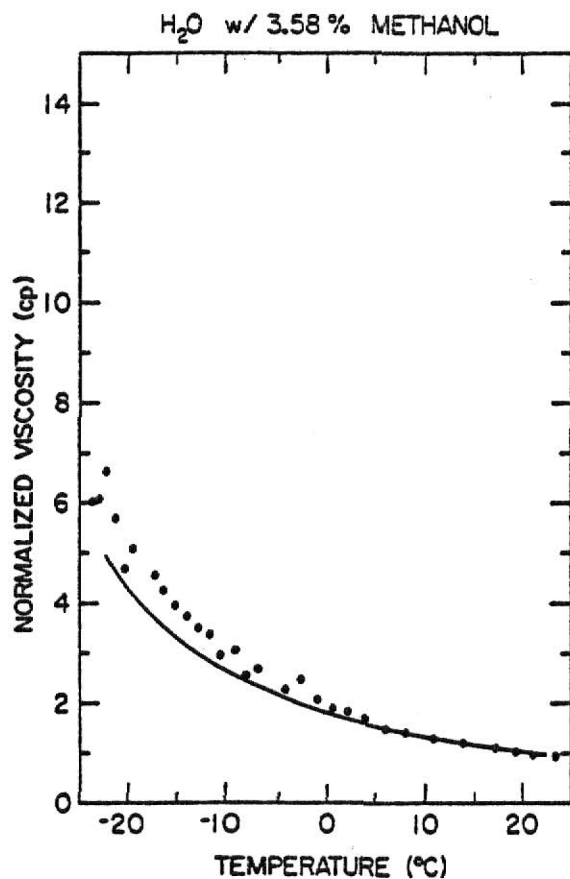


FIGURE 13a

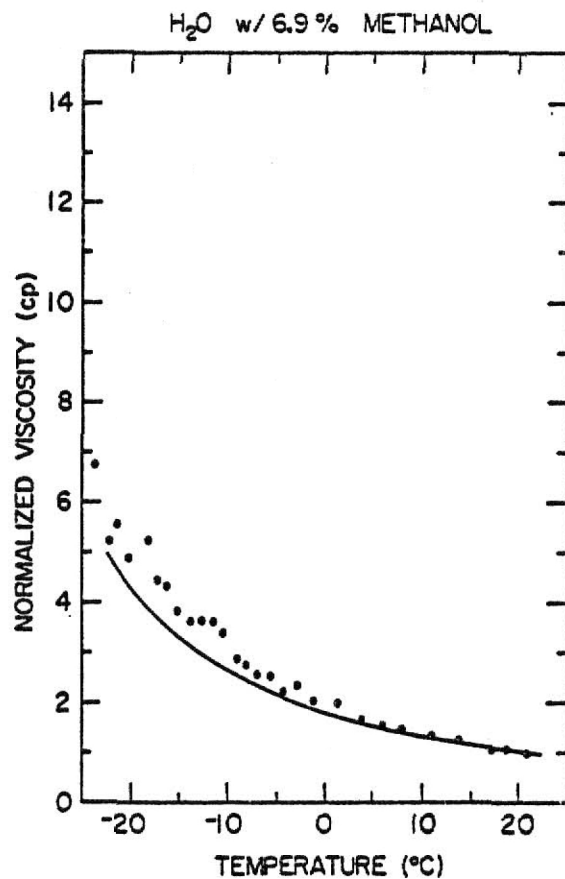


FIGURE 13b

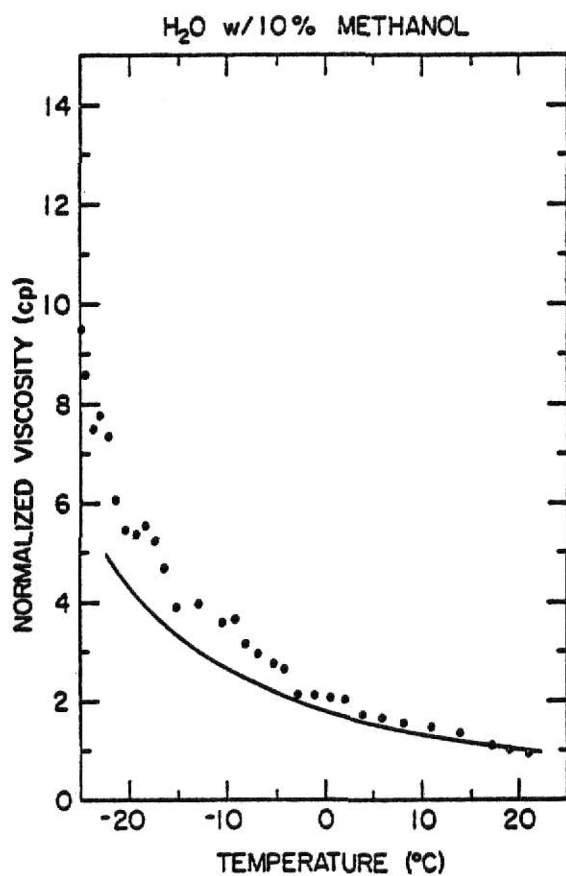


FIGURE 13c

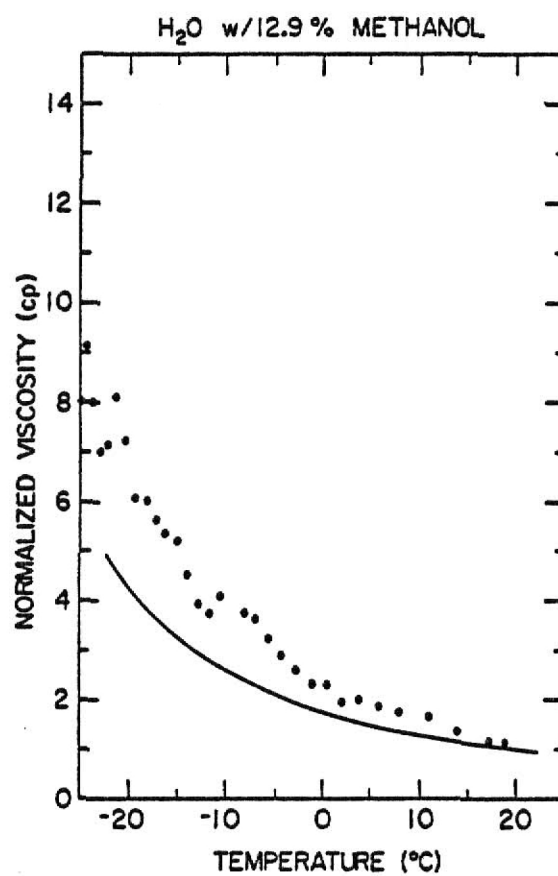


FIGURE 13d

Figure Fourteen

NORMALIZED VISCOSITY FOR AN 11.6% DIOXANE-WATER SOLUTION.

The solid line represents reliable viscosity data for pure water. It is included as a reference line. All data were normalized to 1.00 cp at 20°C.

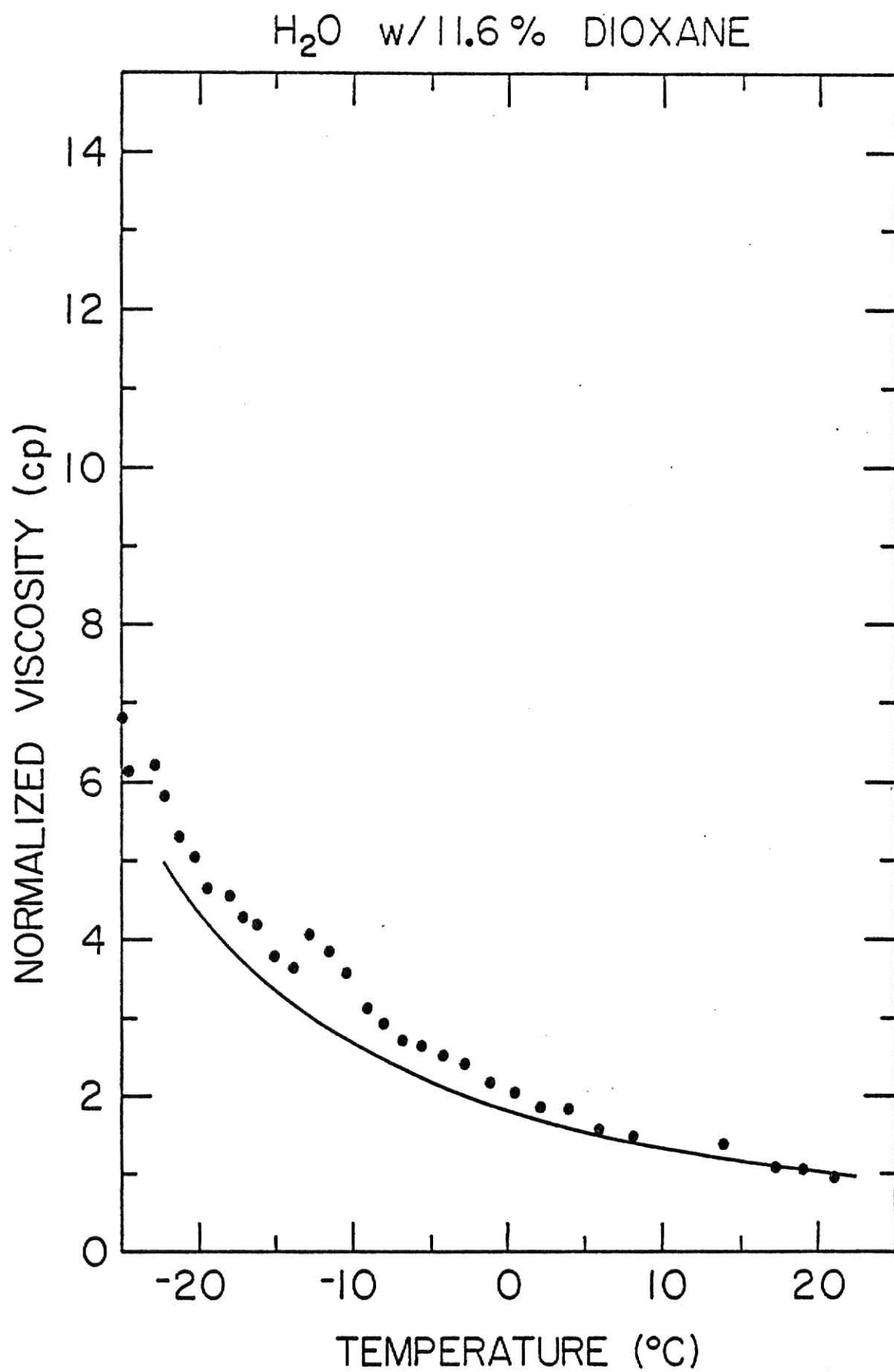


FIGURE 14

This structure manifested itself in the form of patches of hydrogen bonded water molecules. The impurities were added to break up, or at least partially break up, the formation of these patches. The impurities accomplish this by substituting themselves for water molecules. When a water molecule hydrogen bonds, it has two sites for accepting protons and two protons ready to donate to bonds. Water has a 1:1 acceptor-donor ratio. The impurities have neither the same acceptor-donor ratio nor the same site geometry. Thus, when a water molecule is replaced by an impurity, the neat tetrahedral structure of the water patches is disrupted. It was thought that this overall reduction in intermolecular interactions would diminish the rate of viscosity increase. This should be the case because as the temperature decreases below 0°C the water patches form more quickly and grow larger. The impurity would then be more effective as the temperature decreased and the rate of viscosity increase would be reduced. This is just the sort of behavior observed by Angell⁸ and Speedy¹⁴ for the compressibility and specific heat.

A glance at the ethanol-water data shows that something else must be happening. The rate at which the viscosity increases is strongly enhanced by the addition of the ethanol. The same is true for the methanol and dioxane to a lesser degree. The hydrazine, however, appears to have had the anticipated effect, albeit a small one. To more clearly show what is happening to the viscosity and the rate at which it is increasing, Fig. 15 shows normalized viscosity and its temperature derivative $dn/dT|_{T_{\text{constant}}}$ as functions of concentration of impurity. The dn/dT plots were created by using the least-squares fits to the data described earlier. Only ethanol and hydrazine are shown because they illustrate the two effects that were seen.

Figure Fifteen

VARIATION OF THE NORMALIZED VISCOSITY AND THE
RATE OF CHANGE OF VISCOSITY WITH TEMPERATURE
AS THE CONCENTRATION OF IMPURITY CHANGES.

The η vs. concentration plots are taken from the fits to the data in Figs. 9 - 12. The lines are eye guides through the isotherms. The $d\eta/dT|_{T_{\text{constant}}}$ graphs are made from the derivatives of the fits to the non-normalized data. They represent the actual rate of change of viscosity w.r.t. temperature. Again the eye guides are isotherms.

15a - η vs. concentration of ethanol

15b - $d\eta/dT|_{T_{\text{constant}}}$ vs. concentration of ethanol

15c - η vs. concentration of hydrazine

15d - $d\eta/dT|_{T_{\text{constant}}}$ vs. concentration of hydrazine

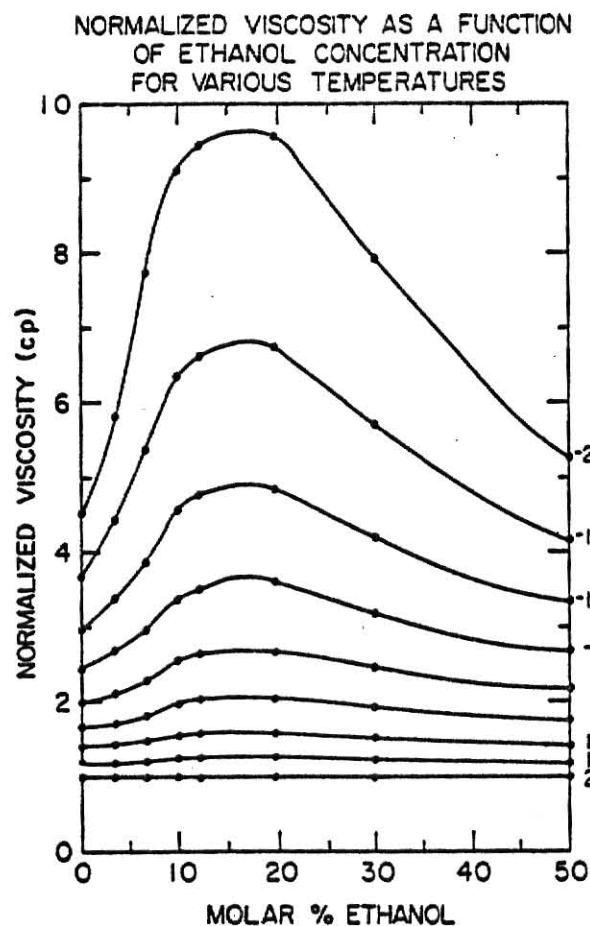


FIGURE 15a

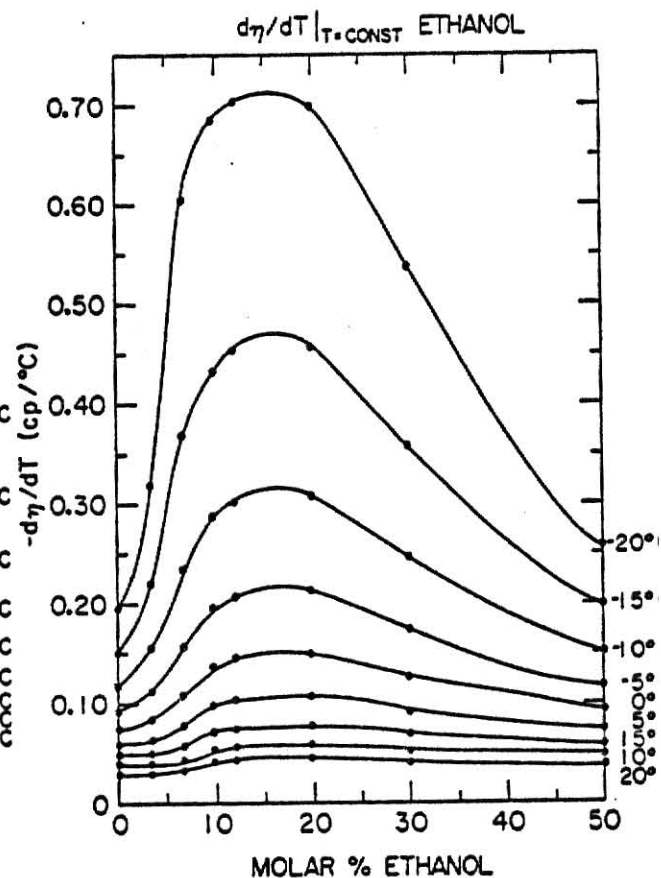


FIGURE 15b

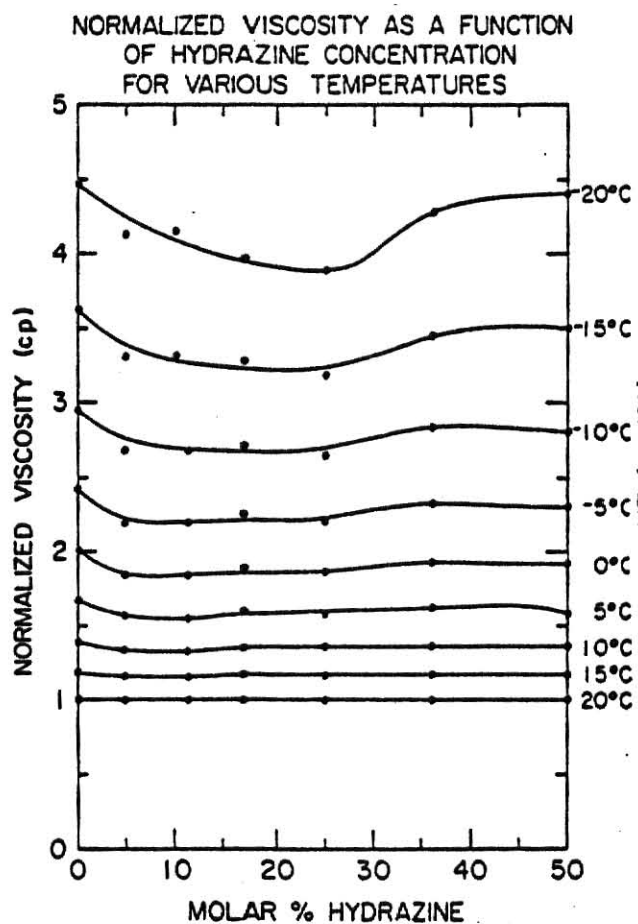


FIGURE 15c

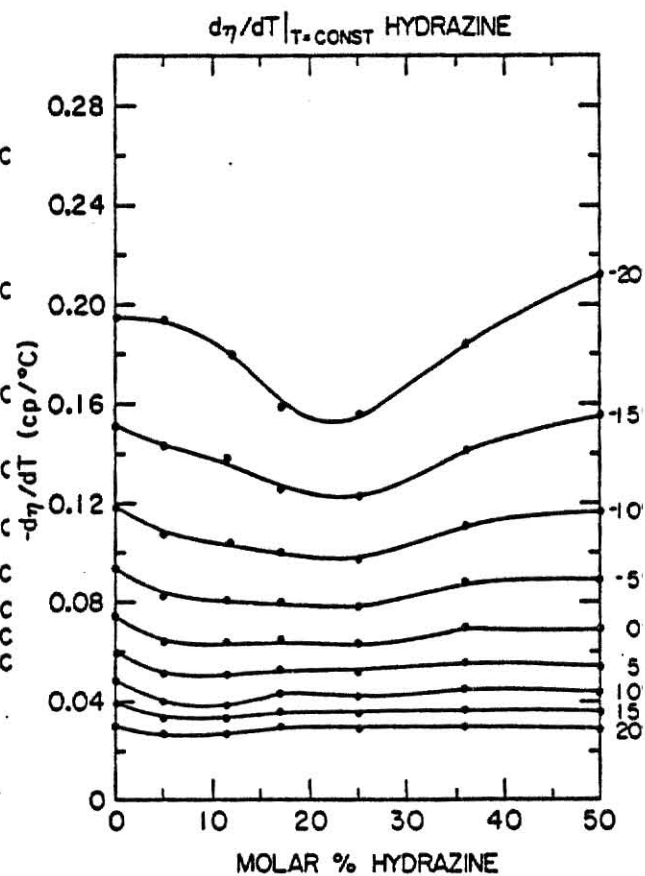


FIGURE 15d

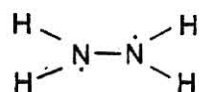
The addition of ethanol was shown by Bosio et al.¹⁹ to break up the structure of water. They measured the density fluctuations in water (recall $\langle \delta \rho \rangle^2 \propto$ compressibility) and found that the anomalous increase normally observed was reduced when ethanol was added. I found a dramatic increase in the viscosity for the same system. I believe that this apparent contradiction can be resolved with the following explanation.

Following the arguments of Stanley and Teixeira,³ remember that the compressibility, κ_T , is proportional to the square of the density fluctuations. When the water patches form, they create a local decrease in the density thus increasing κ_T . The addition of ethanol will, to some extent, decrease the number and size of these patches and thereby reduce κ_T . Other work^{21,23} indicates that the major effect of adding ethanol to water is to form a completely new structure. This new formation is called a clathrate and consists of an ethanol molecule surrounded by a "cage" of as many as 136 water molecules. The result is not a reduction but a change in structure. According to information provided by Davidson,²³ the mean number of water molecules which will be found in a clathrate structure surrounding an impurity like ethanol is 5.75. A solution of 14.8 molar percent ethanol might be expected to have all or nearly all of both species participating in the formation of clathrate structures. Figures 15a and 15b show a maximum in the rate of viscosity increase near 15% ethanol. This fits the above picture well.

Davidson²³ also provides a mean radius for the clathrate structure from which a density of $.994 \text{ g/cm}^3$ can be calculated. This is so near to the global density of the water that it explains why Bosio et al. saw a decrease in κ_T . Essentially, by accident, the new clathrate

structure does not produce density fluctuations within the solution, thus, Bosio sees a decrease in κ_T as ethanol is added.

The hydrazine data, Figs. 15c and 15d, also fit into this picture easily. Hydrazine looks much like a pair of water molecules.



The differences are the slightly changed geometry and the 2:1 instead of 1:1 acceptor-donor ratio. Because there is no alkane or similar type group in the molecule, no clathrate structure forms. Thus, we expect and do find that hydrazine breaks up the water patches and the rate of increase of viscosity is reduced. This is strong corroborating evidence for the results of Oguni and Angell⁶ (specific heat).

There seems to be a broad minimum in Figs. 15c and 15d where the addition of small amounts of hydrazine have little effect on the system. Near 25 molar percent hydrazine the viscosity begins to rise once again. I speculate that this may be due to the rise of a secondary hydrazine-hydrazine structure.

Chapter Six

CONCLUSIONS AND SUGGESTIONS FOR IMPROVEMENTS

In summary, viscosity data have been collected to test the applicability of Stanley's model of hydrogen bonded water patches to a transport property. Patch breaking compounds, which had been shown by other researchers to disrupt the structure of water insofar as some thermodynamic properties are concerned, were added. Secondary structure, which varied from impurity to impurity, was found to arise. In some cases this secondary structure caused the viscosity to increase more quickly than the primary structure of water patches had. For the case of hydrazine, the primary structure was to some extent disrupted and the viscosity decreased until the hydrazine concentration reached ~25%. At this point the viscosity increased until it had reached that of pure water at a concentration of 50% hydrazine. It is speculated that the viscosity increase may be due to hydrazine-hydrazine interactions.

Several changes could be made in this experiment which would increase the range and accuracy of the data. A recent paper²⁴ contained an idea for a small angle scattering cell which would allow very small scattering volumes to be used without running into the window spot problem. A prototype has been made and seems to be most promising. The adoption of this new cell could be a large step toward getting the data needed to check Haus and Meijer's prediction.

The viscosity measurement could be improved by reducing the size of the capillary tube used to hold the sample from 0.5 mm square to 0.05 mm square. In principle there is no reason that the smaller tubes could

not be used. If this could be accomplished the sample volume could be reduced by a factor of 10^3 . This might allow the collection of viscosity data for pure water to $\sim -30^\circ\text{C}$. No one has yet been able to collect this data. Finally, a new support for the dewar should be designed as the current support is vibration prone. This would probably improve the precision of the data.

Appendix One

The purpose of this appendix is to provide the mathematical detail which was left out of the first section of chapter three. What follows is a synthesis of several publications related to PCS^{15,16,17,18}.

A plane electric wave, $\vec{E}_I(t)$ (i.e. a well correlated monochromatic laser beam), illuminates a volume of liquid containing N particles.

$\vec{E}_I(t)$ is defined by

$$\vec{E}_I(t) = \vec{E}_0 \exp [i(\vec{k}_0 \cdot \vec{r} - \omega_0 t)] \quad , \quad (1)$$

where $|\vec{E}_0|$ is the electric intensity, $\vec{k}_0$ is the incident wave vector, $\vec{r}$ is a position vector, and ω_0 is the frequency of the wave. Each particle in the volume will scatter some of the incident wave in the direction of a detector. See Fig. 16. The scattered wave from the j th particle will have this form

$$\vec{E}_j(t) = \vec{E}'_0 \exp [i(\phi_j(t) - \omega_0 t)] \quad (2)$$

where $|\vec{E}'_0|$ is a particle independent scattering amplitude

$$|\vec{E}'_0| = |\vec{E}_0| [\exp (i\vec{k}_s \cdot \vec{R})/|\vec{R}|] (\omega_0/c)^2 (\alpha - \alpha_0) V \sin \phi. \quad (3)$$

In this expression $\vec{k}_s$ is the scattered wave vector, $\vec{R}$ is the position vector of the detector, α and α_0 are the dipole polarizabilities of the particle and the fluid, V is the volume of the particle, and ϕ is angle between the initial polarization vector and $\vec{k}_s$. ϕ_j in Eq. (2) is a position dependent phase factor,

Figure Sixteen

SCATTERING GEOMETRY¹⁸

Scattering Geometry

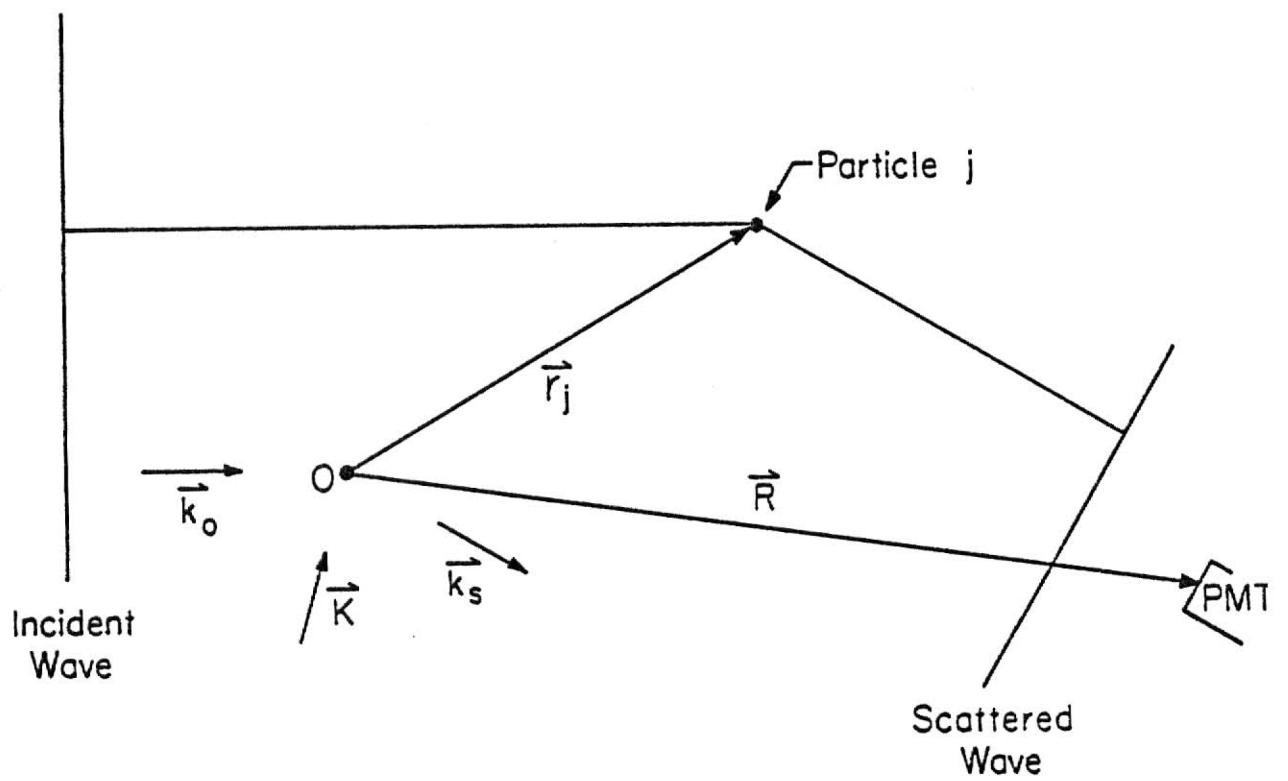


FIGURE 16

$$\phi_j = (\vec{k}_0 - \vec{k}_s) \cdot \vec{r}_j(t) \quad (4)$$

The detector sees the superposition of the waves scattered from all the particles and produces an output proportional to the square of the resulting field.

$$I(t) = \beta \left| \sum_{j=1}^N \vec{E}_j(t) \right|^2 \quad (5)$$

This intensity function will be a rapidly varying noise signal. By definition the correlation function of a signal $I(t)$ is

$$\langle I(t) I(t + \tau) \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_t^{t+T} dt' I(t') I(t' + \tau) \quad (6)$$

If $I(t)$ is a stationary property, t can be set equal to any convenient value. Using Eqs. 2 and 5 the correlation function can then be written in terms of ensemble averages on the electric field.

$$\begin{aligned} \langle I(t) I(t + \tau) \rangle &= \beta^2 |E_0|^4 \langle \sum_j \sum_k \sum_l \sum_m \exp \{i[\phi_j(t) - \phi_l(t)]\} \\ &\quad \exp \{i[\phi_k(t + \tau) - \phi_m(t + \tau)]\} \rangle \end{aligned} \quad (7)$$

Because the positions of the particles are independent of one another, any term with one index which is different from the other three will contain a factor like $\langle \exp [i\phi_j(t)] \rangle$. Because $\phi_j(t)$ is a random variable, this must be zero. This leaves three groups of terms: N^2 terms with $j = l$ and $k = m$, $N^2 - N$ terms with $j = m$, $l = k$, and $j \neq l$, and terms with $j = k$, $l = m$, and $j \neq l$. The third group will yield zero when averaged over starting phases. The first group results in N^2

ones. Because each particle is equivalent to the others, the following expression is the correlation function where $N^2 - N \approx N^2$ for large N .

$$\begin{aligned} \langle I(t) I(t + \tau) \rangle &= N^2 |\vec{E}_0|^4 \beta^2 (1 + \langle \exp \{i[\phi_1(t) - \phi_1(t + \tau)]\} \\ &\quad \exp \{-i[\phi_2(t) - \phi_2(t + \tau)]\} \rangle) \end{aligned} \quad (8)$$

Again because the particles are equivalent and independent, this expression can be condensed.

$$\langle I(t) I(t + \tau) \rangle = N^2 \beta^2 |\vec{E}_0|^4 (1 + |\langle \exp \{-i[\phi(t) - \phi(t + \tau)]\} \rangle|^2) \quad (9)$$

The argument of the exponent can be written in a more interesting form.

$$\begin{aligned} \phi(t) - \phi(t + \tau) &= (\vec{k}_0 - \vec{k}_s) \cdot \vec{r}(t) - (\vec{k}_0 - \vec{k}_s) \cdot \vec{r}(t + \tau) \\ &= -\vec{K} \cdot \Delta\vec{r} \end{aligned} \quad (10)$$

Here $\vec{K} = \vec{k}_0 - \vec{k}_s$ and $\Delta\vec{r} = \vec{r}(t + \tau) - \vec{r}(t)$. The correlation function written this way

$$\langle I(t) I(t + \tau) \rangle = N^2 \beta^2 |\vec{E}_0|^2 (1 + |\langle \exp(i\vec{K} \cdot \Delta\vec{r}) \rangle|^2) \quad (11)$$

is much easier to understand. The ensemble average

$$\langle \exp(i\vec{K} \cdot \Delta\vec{r}) \rangle = \iiint d^3\Delta\vec{r} P(\Delta\vec{r}, \tau | 0, 0) \exp(i\vec{K} \cdot \Delta\vec{r})$$

can be evaluated directly using the well known probability density, $P(\Delta\vec{r}, \tau | 0, 0)$, for a particle executing three dimensional random walk motion from point 0 to $\Delta\vec{r}$ in time τ .

$$\iiint d^3\vec{\Delta r} \{(4\pi D\tau)^{-\frac{3}{2}} \exp(-\Delta r^2/4D\tau)\} \exp(i\vec{K} \cdot \vec{\Delta r}) = \exp(-DK^2\tau) \quad (12)$$

D is the appropriate diffusion constant for the particles. In the case of spheres which are large compared to the molecules of the fluid

$$D = k_B T / 6\pi\eta a. \quad (13)$$

This is the same relation stated in chapter three for the mass diffusion constant. The final expression for the correlation function is this.

$$\langle I(t) I(t + \tau) \rangle = N^2 \beta^2 |\vec{E}_0|^4 [1 + \exp(-2DK^2\tau)] \quad (14)$$

In the case of Rayleigh scattering, (scattering from density fluctuations in the fluid), a slightly different development is used but the end result is the same.

Several times the statement has been made that the spectral density or structure factor and the correlation functions are Fourier transform pairs. This is a result of the Wiener-Khinchine theorem. A brief justification of this theorem follows.

Consider a random noise signal $A(t)$, which is assumed to be stationary. A Fourier transform of $A(t)$ will yield its frequency spectrum.

$$B(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt A(t) e^{-i\omega t} \quad (15)$$

$$A(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega B(\omega) e^{i\omega t} \quad (16)$$

If $A(t)$ is real, Eq. (15) requires that $B(\omega) = B^*(-\omega)$. When this fact is combined with the result of Parseval's theorem.

$$\int_{-\infty}^{\infty} dt A^2(t) = \int_{-\infty}^{\infty} d\omega |B(\omega)|^2, \quad (17)$$

the time average of $A^2(t)$ can be written in this form,

$$\begin{aligned} \langle A^2 \rangle &= \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-\infty}^{\infty} dt A^2(t) \\ &= \int_0^{\infty} d\omega C(\omega) \end{aligned} \quad (18)$$

where

$$C(\omega) = \lim_{T \rightarrow \infty} \frac{2}{T} |B(\omega)|^2 \quad (19)$$

is called the spectral density or structure factor.

The autocorrelation function for $A(t)$ would be defined as

$$\langle A(t) A(t + \tau) \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-\infty}^{\infty} dt A(t) A(t + \tau) \quad (20)$$

This expression can be related to the spectral density using Eqs. 15 - 19.

$$\begin{aligned} \langle A(t) A(t + \tau) \rangle &= \lim_{T \rightarrow \infty} \int_{-\infty}^{\infty} d\omega B(\omega) e^{i\omega t} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega B(\omega) e^{i\omega(t + \tau)} \\ &= \lim_{T \rightarrow \infty} \frac{1}{T} e^{i\omega\tau} \int_{-\infty}^{\infty} dt A^2(t) \\ &= \int_0^{\infty} d\omega C(\omega) e^{i\omega\tau} \end{aligned} \quad (21)$$

Thus, the spectral density and the correlation function are Fourier transform pairs.

Appendix Two

The purpose of this appendix is to show that the gas filling the windows is at nearly the same temperature as the cell holder itself. I begin by assuming Newton's law of convective cooling, a constant wall temperature in the tube and laminar flow. The last assumption is justified by the low Reynolds number which is calculated later on.

Given:

$$l = \text{length of tube} = 300 \text{ cm}$$

$$D = \text{diameter of tube} = .191 \text{ cm}$$

$$\bar{\eta} = \text{average } N_2 \text{ viscosity} = 156 \text{ } \mu\text{p}$$

$$C_p = \text{specific heat of } N_2 = 1.04 \cdot 10^7 \text{ erg/g}^\circ\text{K}$$

$$\rho = \text{density of } N_2 = 1.25 \cdot 10^{-3} \text{ g/cm}^3$$

$$\bar{k} = \text{average thermal conductivity of } N_2 = 2.22 \text{ erg/cm s}^\circ\text{K}$$

$$\bar{v} = \text{average gas velocity} \leq 60 \text{ cm/s}$$

$$h = \text{convective heat transfer coefficient}$$

Assume:

$$q = hA (T_w - T_f) \quad \text{Newton's law of cooling} \quad (1)$$

where q = heat transfer rate

A = cross sectional area

T_w = wall temperature

T_f = fluid temperature

See Fig. 17.

Define:

$$T_f \equiv T(x) \equiv T$$

Figure Seventeen

HEAT FLOW FROM N_2 TO COPPER TUBE.

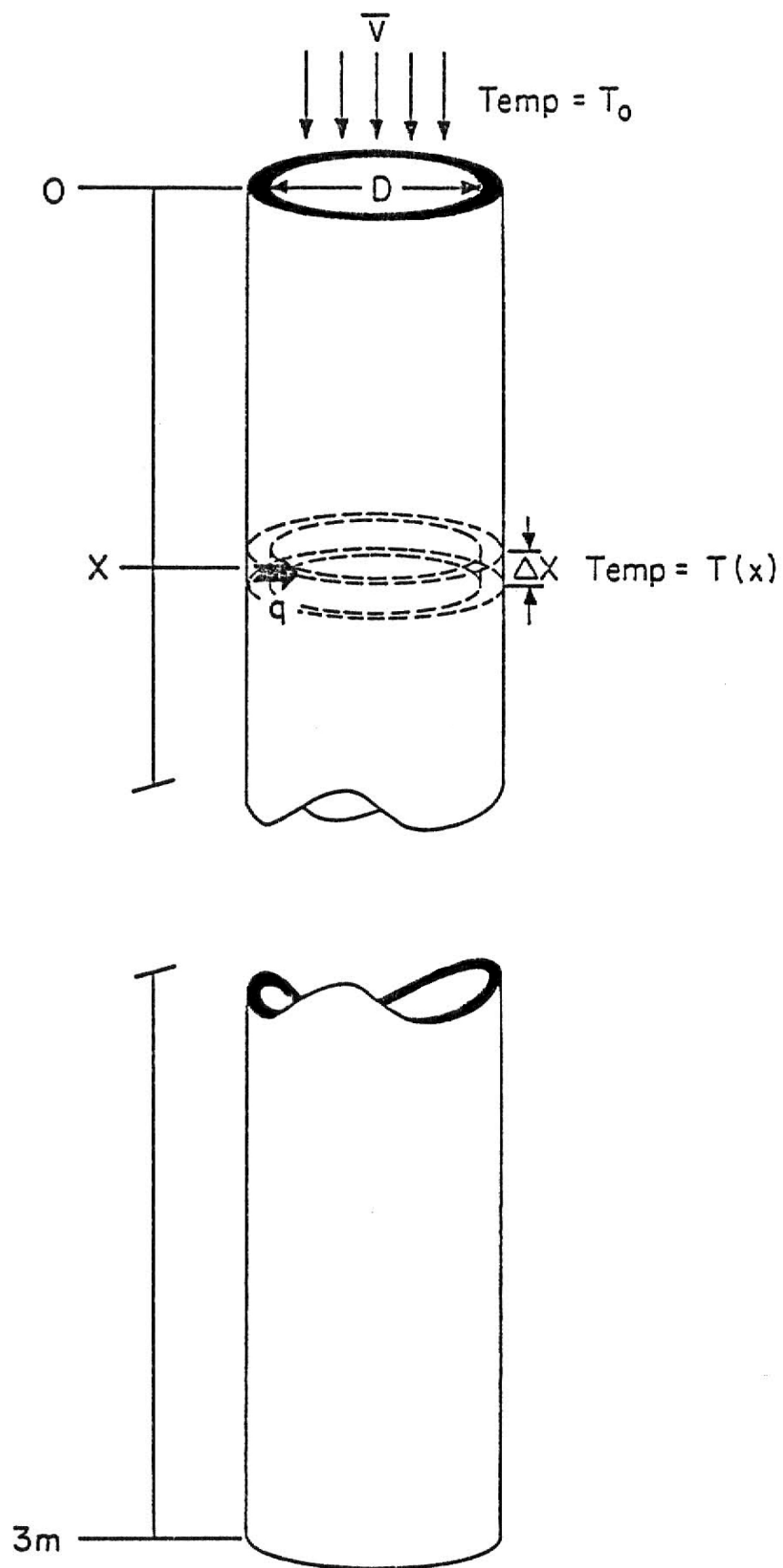


FIGURE 17

$$x_n \equiv n \cdot \Delta x$$

$\Delta t \Delta q_n \equiv$ heat transferred to gas in time Δt while passing Δx about x_n .

$\Delta V =$ volume of gas in Δx

$C \equiv$ heat capacity of gas in ΔV

One should be able to see that the following relations are true.

$$\Delta V = (\pi D^2/4) \Delta x \quad (2)$$

$$C = \Delta V \rho C_p \quad (3)$$

$$\Delta t = \Delta x / \bar{v} \quad (4)$$

Equation (1) can be rewritten as:

$$\Delta q_n = h(\pi D \Delta x) (T_w - T(x_n)). \quad (5)$$

In each Δx the gas volume will gain (lose) an amount of heat $\Delta t \Delta q_n$.

This will change its temperature by ΔT_n .

$$\Delta T_n = \Delta t \Delta q_n / C \quad (6)$$

An equation can be written for the temperature of the gas at any point.

$$T(x_1) = T_o + \sum_{n=0}^1 \Delta T_n \quad (7)$$

Combining Eqs. 2 - 7 produces this expression for $T(x_1)$

$$T(x_1) = T_o + (4h/DvC_p\rho) \sum_{n=0}^1 \Delta x (T_w - T(x_n)) \quad (8)$$

Clearly, this can be transformed into an integral equation

$$T(x) = T_o + (4h/DvC_{p\rho}) \int_0^x dx' (T_w - T(x')) \quad (9)$$

which can be differentiated with respect to x to produce this result.

$$dT/dx = (4h/DvC_{p\rho}) (T_w - T) \quad (10)$$

$$dT/(T - T_w) = (-4h/DvC_{p\rho}) dx$$

$$\ln (T - T_w) = (-4hx/DvC_{p\rho}) + \ln B$$

$$T = T_w + B \exp [-4hx/DvC_{p\rho}]$$

$$@ x = 0 \quad T = T_o$$

$$T = T_w + (T_o - T_w) \exp [-4hx/DvC_{p\rho}] \quad (11)$$

The problem is to estimate h . The following modified Dittus-Boelter relation is supposed to be good for gases up to 2000°F.

$$h = (2\bar{k}/D) (Re)^{.8} \quad (12)$$

In Eq. 12 Re is the well known Reynolds number.

$$Re \equiv Dv\rho/\eta \quad (13)$$

For this system $Re \approx 90$ which also insures that the flow is laminar. (Transition to turbulent flow occurs at $Re \approx 2300$.) Combining Eqs. 11, 12, and 13 yields the final expression for the gas temperature.

$$T = T_w + (T_o - T_w) \exp (-8\bar{k}x\eta^{.8}/C_p D^{1.2}(\bar{v}_p)^{.2}) \quad (14)$$

The result is

$$T_{\text{outlet}} \approx T_w + (T_o - T_w) (1/1000)$$

or if the cell holder temperature was -80°C , $|T_{\text{gas}} - T_{\text{cell holder}}| \approx .1^{\circ}\text{C}$.

Admittedly, this model is somewhat crude but I have confidence that it is easily good to an order of magnitude.

Appendix Three

This appendix contains the viscosity data, expressed in cp, for all of the solutions used. They are normalized to 1.00 cp at 20°C. To recover the actual viscosities, multiply by the appropriate factor as found in Table 2.

ILLEGIBLE DOCUMENT

**THE FOLLOWING
DOCUMENT(S) IS OF
POOR LEGIBILITY IN
THE ORIGINAL**

**THIS IS THE BEST
COPY AVAILABLE**

HALLETT'S H2O DATA

100% H2O

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
0.0	1.79
-1.0	1.86
-2.0	1.93
-3.0	2.01
-4.0	2.08
-5.0	2.16
-6.0	2.25
-7.0	2.35
-8.0	2.45
-9.0	2.55
-10.0	2.66
-11.0	2.78
-12.0	2.90
-13.0	3.03
-14.0	3.17
-15.0	3.34
-16.0	3.50
-17.0	3.67
-18.0	3.87
-19.0	4.07
-20.0	4.33
-21.0	4.60
-22.0	4.91
-23.0	5.20

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
23.5	0.85
21.1	0.96
18.9	1.04
17.3	1.08
15.5	1.14
12.4	1.35
9.6	1.44
6.9	1.52
0.4	1.93
-1.8	1.97
-4.3	2.26
-6.3	2.32
-8.1	2.57
-9.8	3.05
-11.6	3.05
-13.8	3.79
-16.3	3.74
-17.6	3.90
-19.4	4.53
-20.8	4.47

3.55% ETHANOL

H2O w/ 6.7% ETHANOL

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
23.3	0.62
21.1	0.80
18.9	0.78
17.3	0.87
13.9	0.93
9.6	1.05
6.9	1.16
4.9	1.20
2.9	1.56
1.4	1.57
-0.6	1.96
-2.7	1.62
-4.9	2.04
-6.9	2.30
-8.6	2.34
-10.6	2.67
-12.3	3.25
-13.9	2.95
-15.6	3.83
-17.3	4.02
-18.6	3.90
-20.3	4.69
-21.6	5.12
-22.9	5.08
-23.9	5.92
-24.9	6.37
-25.8	6.56

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
21.1	1.02
18.9	1.00
17.3	1.09
13.9	1.31
11.0	1.41
8.1	1.54
5.9	1.76
3.9	1.90
2.1	2.13
0.4	2.35
-4.3	2.83
-9.1	3.72
-10.4	3.84
-11.6	4.17
-12.8	4.82
-16.3	5.92
-17.1	6.51
-21.3	9.21
-22.9	10.72
-23.6	10.02
-24.4	10.27
-25.0	10.57
-25.6	10.97
-26.1	12.05
-26.8	14.44
-27.3	16.29
-28.5	18.57
-29.0	20.74
-30.8	20.85

H2C W/ 9.8% ETHANOL

H2C W/ 12% ETHANOL

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
--	---

18.9	1.04
17.3	1.12
13.9	1.37
11.0	1.49
8.1	1.60
5.9	1.82
3.9	2.05
2.1	2.17
0.4	2.69
-1.1	2.92
-2.7	3.05
-4.3	3.18
-5.6	3.41
-6.9	3.79
-8.6	4.02
-10.4	4.89
-12.3	5.04
-14.6	6.53
-16.3	6.84
-17.6	7.91
-19.4	8.99
-21.3	10.06
-22.9	12.34
-24.4	10.83
-25.6	13.80
-26.8	18.29
-27.9	15.93
-29.0	21.65
-30.1	22.22
-31.3	24.80
-32.4	23.45

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
--	---

18.9	1.05
17.3	1.22
15.5	1.28
13.9	1.34
11.0	1.54
8.1	1.65
5.9	1.96
3.9	2.35
2.1	2.57
0.4	2.60
-1.1	2.95
-2.7	3.15
-4.3	3.26
-5.6	3.84
-6.9	3.99
-8.1	4.16
-9.1	5.02
-10.4	5.47
-11.6	5.58
-12.8	5.74
-15.1	7.34
-16.3	7.42
-18.1	8.51
-19.4	8.39
-21.3	10.21
-22.9	11.67
-24.4	12.16
-25.6	15.81
-26.8	18.60
-27.9	20.06
-29.0	20.67
-30.1	23.23

H2O W/ 19.5% ETHANOL

H2O W/ 30% ETHANOL

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
--	---

23.5	0.89
21.1	0.92
18.9	1.04
17.3	1.24
13.9	1.23
11.0	1.47
8.1	1.73
5.9	1.99
3.9	2.26
-1.1	2.60
-2.7	3.19
-4.3	3.59
-5.6	3.75
-6.9	4.50
-8.1	4.31
-9.1	4.36
-10.4	6.08
-12.8	6.56
-13.8	7.09
-15.1	6.19
-16.3	8.20
-17.1	8.96
-18.1	7.83
-19.4	10.65
-20.3	11.72
-21.3	10.65
-22.9	11.08
-23.6	11.26
-24.4	14.54
-25.0	13.80
-25.6	16.41
-26.1	13.55
-27.3	15.79

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
--	---

21.1	0.92
18.9	1.05
17.3	1.15
13.9	1.25
11.0	1.40
8.1	1.56
5.9	1.71
3.9	2.07
2.1	2.17
0.4	2.29
-4.3	3.20
-5.6	3.40
-6.9	3.36
-8.1	3.56
-9.1	3.96
-10.4	4.47
-11.6	4.88
-12.8	4.81
-13.8	5.37
-15.1	5.77
-17.1	6.23
-18.1	6.53
-21.3	8.13
-22.1	9.84
-23.6	9.38
-24.4	9.45
-25.0	11.17
-26.1	11.61
-26.8	14.14
-27.3	13.34
-27.9	14.37

H2O W/ 50% ETHANOL

H2O W/ 5% HYDRAZINE

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
23.5	0.96
21.1	1.01
18.9	1.18
17.3	1.29
13.9	1.33
11.0	1.47
8.1	1.80
5.9	1.78
3.9	2.08
2.1	2.26
0.4	2.33
-1.1	2.34
-2.7	2.52
-4.3	3.08
-6.9	3.04
-8.1	3.37
-9.1	4.38
-10.4	3.65
-12.8	4.50
-13.8	4.50
-15.1	5.11
-16.3	5.08
-17.1	5.26
-18.1	5.15
-19.4	5.62
-21.3	5.81
-22.1	6.18
-22.9	5.75
-23.6	7.73
-24.4	7.00
-25.0	8.21
-25.6	7.76
-26.1	8.68
-26.8	9.00
-27.3	8.07

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
26.2	0.86
23.8	1.06
21.6	1.05
20.0	1.00
16.5	1.24
13.6	1.24
10.7	1.39
8.5	1.53
6.5	1.57
4.7	1.66
3.0	1.85
1.5	2.05
-0.1	1.92
-1.7	2.17
-3.0	2.46
-4.3	2.37
-5.5	2.62
-6.5	2.72
-7.8	3.05
-9.0	3.04
-10.1	3.21
-11.2	3.01
-12.5	3.20
-15.5	3.62
-16.8	3.76
-18.7	4.34
-19.5	4.20
-20.3	4.71
-21.0	4.85
-21.8	5.14
-22.4	5.71
-23.0	5.79
-23.5	5.72
-24.1	6.04
-24.7	6.75
-25.3	6.45

H2O W/ 11.5% HYDRAZINE

H2O W/ 17.1% HYDRAZINE

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
--	---

21.1	0.94
18.9	1.07
17.3	1.07
13.9	1.12
11.0	1.27
8.1	1.44
3.9	1.60
2.1	1.74
0.4	1.78
-1.1	2.00
-2.7	2.42
-4.3	2.11
-5.6	2.18
-6.9	2.45
-8.1	2.47
-9.1	2.55
-10.4	2.57
-11.6	2.99
-12.8	2.78
-13.8	3.40
-15.1	3.16
-16.3	3.31
-17.1	3.51
-18.1	3.34
-19.4	3.93
-20.3	3.79
-21.3	4.02
-22.1	4.51
-23.6	4.38
-24.4	4.31
-25.0	5.24
-25.6	5.57
-26.1	5.01
-26.8	5.96
-27.3	6.43
-27.9	6.61
-28.5	5.91
-29.0	6.53
-29.6	7.89
-30.1	7.85
-31.3	8.17
-31.8	8.55

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
--	---

23.5	0.88
21.1	0.98
17.3	1.02
18.9	1.07
13.9	1.16
11.0	1.31
8.1	1.44
5.9	1.68
3.9	1.62
2.1	1.73
0.4	1.94
-1.1	2.01
-2.7	2.00
-4.3	2.14
-5.6	2.20
-6.9	2.31
-8.1	2.48
-9.1	2.63
-10.4	2.79
-11.6	2.99
-15.1	3.06
-16.3	3.46
-17.1	3.34
-18.1	3.62
-19.1	3.41
-20.3	3.60
-21.3	3.47
-22.1	3.91
-22.9	4.06
-23.6	4.46
-24.4	4.59
-25.0	4.64
-25.6	4.59
-26.1	5.70
-26.8	4.87
-27.3	5.43
-27.9	6.02
-28.5	6.94
-29.0	6.94

H2O W/ 25% HYDRAZINE

H2O W/ 36% HYDRAZINE

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
23.5	0.89
21.1	0.95
18.9	1.08
17.3	1.13
13.9	1.17
11.0	1.35
8.1	1.47
5.9	1.50
3.9	1.58
2.1	1.63
0.4	1.84
-1.1	1.92
-4.3	2.13
-5.6	2.12
-6.9	2.47
-8.1	2.94
-9.1	2.79
-13.8	3.06
-15.1	3.16
-16.3	3.55
-17.1	3.38
-18.1	3.56
-19.1	3.53
-20.3	4.05
-21.3	4.32
-22.1	4.43
-23.6	4.40
-25.0	4.55
-25.6	5.18
-26.1	5.18
-27.3	5.37

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
21.1	1.00
18.9	1.05
17.3	1.06
13.9	1.23
11.0	1.34
8.1	1.41
5.9	1.56
3.9	1.69
2.1	1.82
0.4	1.87
-1.1	1.83
-2.7	2.13
-4.3	2.55
-5.6	2.54
-6.9	2.68
-8.1	2.54
-10.4	2.86
-11.6	3.18
-12.8	3.51
-13.8	3.72
-16.3	3.92
-17.1	3.75
-18.1	3.61
-20.3	3.64
-22.1	4.24
-22.9	5.10
-24.4	4.72
-25.0	5.03
-26.1	6.08
-26.8	6.46
-27.3	6.04
-27.9	6.39

H2O W/ 50% HYDRAZINE

H2O W/ 3.58% METHANOL

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
21.1	0.94
18.9	0.99
17.3	1.11
13.9	1.20
11.0	1.44
8.1	1.43
5.9	1.69
3.9	1.59
2.1	1.75
0.4	2.04
-1.1	2.08
-2.7	2.01
-4.3	2.31
-5.6	2.61
-6.9	2.61
-8.1	2.69
-9.1	2.82
-10.4	2.75
-11.6	2.91
-12.8	3.17
-13.8	3.32
-17.1	3.56
-18.1	3.63
-20.3	4.34
-21.3	4.85
-22.1	4.70
-22.9	4.37
-23.6	5.02
-24.4	4.45
-25.0	5.57
-25.6	5.65
-26.1	5.57
-26.8	5.73
-27.3	6.08
-27.9	7.00
-29.0	6.76
-29.6	7.68
-30.1	8.91
-30.8	9.19
-31.3	9.59
-31.8	8.59
-32.8	9.59

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
23.5	0.95
21.1	0.96
18.9	1.01
17.3	1.10
13.9	1.22
11.0	1.28
8.1	1.41
5.9	1.49
3.9	1.70
2.1	1.83
0.4	1.90
-1.1	2.08
-2.7	2.47
-4.3	2.28
-6.9	2.72
-8.1	2.58
-9.1	3.08
-10.4	2.95
-11.6	3.38
-12.8	3.49
-13.8	3.73
-15.1	3.97
-16.3	4.27
-17.1	4.56
-19.4	5.10
-20.3	4.70
-21.3	5.72
-22.1	6.58
-22.9	6.09
-23.6	6.03
-25.0	7.83
-25.6	7.76
-26.1	8.09

H2O w/ 6.9% METHANOL

H2O w/ 10% METHANOL

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
21.1	0.97
18.9	1.04
17.3	1.06
13.9	1.24
11.0	1.33
8.1	1.45
5.9	1.55
3.9	1.67
1.4	1.98
-1.1	2.06
-2.7	2.35
-4.3	2.23
-5.6	2.53
-6.9	2.57
-8.1	2.79
-9.1	2.91
-10.4	3.40
-11.6	3.64
-12.8	3.66
-15.1	3.83
-13.8	3.64
-16.3	4.36
-17.1	4.46
-18.1	5.26
-20.3	4.91
-21.3	5.57
-22.1	5.23
-23.6	6.78

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
21.1	0.92
18.9	1.00
17.3	1.11
13.9	1.33
11.0	1.46
8.1	1.53
5.9	1.67
3.9	1.72
2.1	2.02
0.4	2.06
-1.1	2.11
-2.7	2.12
-4.3	2.66
-5.6	2.73
-6.9	2.98
-8.1	3.14
-9.1	3.69
-10.4	3.60
-12.8	3.94
-15.1	3.91
-16.3	4.69
-17.1	5.22
-18.1	5.55
-19.4	5.38
-20.3	5.47
-21.3	6.08
-22.1	7.37
-22.9	7.79
-23.6	7.50
-24.4	8.64
-25.0	9.50
-25.6	8.56
-26.1	8.97
-26.8	9.22

H2C W/ 12.9% METHANOL

H2C W/ 11.6% DIOXANE

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
18.9	1.12
17.3	1.15
13.9	1.35
11.0	1.56
8.1	1.75
5.9	1.87
3.9	1.99
2.1	1.96
0.4	2.32
-1.1	2.31
-2.7	2.61
-4.3	2.89
-5.6	3.25
-6.9	3.62
-8.1	3.76
-10.4	4.07
-11.6	3.72
-12.8	3.93
-13.8	4.52
-15.1	5.21
-16.3	5.38
-17.1	5.64
-18.1	6.04
-19.4	6.10
-20.3	7.25
-21.3	8.15
-22.1	7.13
-22.9	7.01
-23.6	7.99
-24.4	9.17
-25.0	8.02
-25.6	9.94
-26.1	10.55
-26.8	10.87
-27.3	10.43
-27.9	11.88
-28.5	11.53
-29.0	14.30
-29.6	12.34
-30.1	14.41
-30.8	15.80
-31.3	16.37

CORRECTED TEMPERATURE IN DEGREES CENTIGRADE	VISCOSITY NORMALIZED TO 1.00 AT 20 DEGREES
21.1	0.95
18.9	1.05
17.3	1.08
13.9	1.35
8.1	1.49
5.9	1.58
3.9	1.83
2.1	1.86
0.4	2.03
-1.1	2.17
-2.7	2.43
-4.3	2.52
-5.6	2.66
-6.9	2.72
-8.1	2.94
-9.1	3.12
-10.4	3.59
-11.6	3.83
-12.8	4.06
-13.8	3.62
-15.1	3.79
-16.3	4.19
-17.1	4.30
-18.1	4.57
-19.4	4.67
-20.3	5.03
-21.3	5.30
-22.1	5.84
-22.9	6.24
-24.4	6.14
-25.0	6.81
-26.1	8.06
-26.8	7.22
-27.9	8.16

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AN INVESTIGATION OF SOME PROPERTIES OF SUPERCOOLED
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by

BRADFORD LEE HALFPAP

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Department of Physics

KANSAS STATE UNIVERSITY
Manhattan, Kansas

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ABSTRACT

This thesis presents the results of an investigation of the behavior at supercooled temperatures of, (1) thermal relaxation times in benzene and para-xylene and, (2) the viscosity, η , in solutions of water and various additives. The investigation was undertaken in an effort to find experimental verification of predictions made in the literature concerning the liquid-solid phase transition. Samples of benzene and para-xylene were supercooled to a modest degree and the linewidth of the Rayleigh scattered light was measured. The resulting information about the thermal relaxation times indicated no anomalous behavior for the temperatures reached. Solutions of water and ethanol, methanol, hydrazine, and para-dioxane were doped with 0.109μ polystyrene microspheres, sealed in 0.5 mm square capillary tube, and supercooled. The laser light scattered from the spheres allowed a determination of the viscosity. Based upon reports in the literature of the behavior of the specific heat and the isothermal compressibility in similar systems, all four additives were expected to decrease $dn/dT|_{T_{\text{constant}}}$. Only hydrazine was found to do so. The other three increased $dn/dT|_{T_{\text{constant}}}$. These results were interpreted as being caused by the formation of various intermolecular structures in these solutions.