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TEMPERATURE DEPENDENCY OF SOME OF THE THERMODYNAMICAL
PROPERTIES OF AQUEOUS BINARY-MIXTURE SYSTEMS

DISSERTATION

Presented to the Graduate Council of the
University of North Texas in Partial
Fulfillment of the Requirements

For the Degree of

DOCTOR OF PHILOSOPHY

By

Yueming Zheng, B.S, M.S.

Denton, Texas

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The temperature dependence of the refractive index and the density of aqueous binary mixtures of water and ethyl alcohol (C_2H_5OH) were measured by using a modified Michelson interferometer and a narrow glass capillary tube over the temperature range of $278 \leq T \leq 353$ K for solutions of 100, 75, 65, 50, 25, 10 and 0 volume percent ethyl alcohol.

The temperature was cycled over both increasing and decreasing directions to explore hysteresis in the cycling. The data are discussed and compared with the Lorentz-Lorenz (LL) formula. A more accurate formula which fits the experimental data better than the LL relation was derived.

An attempt was made to determine the nature of the solvent-solute interaction through any changes that were found in the refractive index for He-Ne laser light and IR diode signals and to analyze the refractive index and density results to test the accuracy of the available mixing rules in predicting the refractive index values and the density of binary systems.

Conductivity measurements (d. c.) over the temperature range $273 \leq T \leq 363$ K of aqueous solutions of NaCl at various concentrations were made and used to establish transport properties of ions in solution. The dynamical properties of the electrolytes were used to establish the nature of hydrogen bonding in aqueous binary mixture systems. Rate

equations for ion formation and recombination were used to establish the temperature ranges in which hydrogen bonding dominated in forming polymeric species.

From experimental data on the binary mixtures with water, a better understanding of water in its different functions and aggregation is possible. The water molecule itself and its response to the environment are understood when suitable studies are made of the forces in the system. In this work, some qualitative aspects of the interactions and dynamics of the water molecule have been investigated. Classical molecular dynamics simulations were tried to explain some of the thermodynamical properties of the water molecule.

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CHAPTER I

INTRODUCTION

Studies of binary-mixtures of hydrogen-bonded liquids have recently gained considerable interest.¹⁻⁶ Binary aqueous systems also appear to be promising to study to determine the nature of the solute-solvent interaction. Binary-mixtures with water display unique physical, chemical and biological properties which are all due to its high density of hydrogen bonds.

Essential to the model is the assumption that all of the hydrogen bonds in the liquid are intact but that they may be stretched and bent to an extent that varies with temperature and pressure; the existence of "broken hydrogen bonds" in water is not explicitly recognized. The thermodynamic properties of a liquid will depend on the energetics of the bending and stretching of the hydrogen bonds. It will also depend on the intramolecular and intermolecular vibration frequencies, which will be considerably altered by the deformations of the hydrogen bonds.³

Sorensen has examined several aqueous solutions to understand solute-solvent interaction and some thermodynamic properties.⁴⁻⁶ The properties of aqueous solutions show anomalous behavior in the compressibility, viscosity, density, refractive index and the specific heat.⁵⁻⁹ It is further known that these anomalies may be destroyed by application of high pressures or the addition of various solutes which tend to break the hydrogen bonded structure

of the liquid. Thormählen *et al.*⁷ have given results for the dependence of wavelength, temperature and density on the refractive index of water. The density of pure water as a function of temperature is given by Kell.⁸ It seems that complicated empirical equations used to describe the temperature dependence of reactions in water are of limited value, since they cannot shed light on the microscopic details of the processes taking place. If the solvent and the solvation processes undergo changes within short temperature intervals, empirical functions may miss the effect entirely. The author felt that specific solution changes with temperature could best be detected by measuring the reaction rates at narrow intervals (0.5 - 1°C) or continuously change of the temperature in the temperature region chosen for study.

The author chooses to study the refractive index and the density of aqueous water-alcohol systems at different concentrations over the temperature range $278 \leq T \leq 353$ K to understand the solute-solvent interaction, and the conductivity measurement over the temperature range $273 \leq T \leq 363$ K of aqueous solution of NaCl at different concentration to establish the nature of the hydrogen bonding in these aqueous systems.

The refractive index is expected to show an "intrinsic" critical anomaly. The anomalies may be very weak. The relationship between refractive index and density is not straightforward when a high degree of precision is needed. In particular, in the vicinity of the consolute critical point, careful analysis is demanded. Using the simplest formulation of the Lorentz-Lorenz formula (LL) to test the dependence of the refractive index of liquids on the influencing parameters (λ , ρ , T) will not give complete results. The method of data analysis used plays a major role in detecting them. For this reason it is felt that the dependence of the refractive index

of liquid water on these influential parameters should be investigated further.

The author has performed accurate refractive index and density measurements as a function of temperature for a wide range of concentrations of water and ethyl alcohol and used a modified Michelson interferometer as a main technique to get the fringe patterns and to study the refractive index of the aqueous water-alcohol systems at different concentrations over the total temperature range $278 \leq T \leq 353$ K to explore hysteresis in the cycle. Attempts were made to determine the nature of the solvent-solute interaction through any changes that were found in the refractive index as the temperature of each system was cycled.

Data obtained for sodium light (wavelength 5890 and 5896 Å) indicated that the modified LL formula gave a good fit of these data for the refractive index of water.⁹ The equation considers the effect of the density of the liquid ρ . An experiment was set up to explore the refractive index for the He-Ne laser line (wavelength 6328 Å) to make a comparison of the two results. Similar trends in the data were found at the wavelength of the He-Ne laser line, with evidence of hysteresis in the cycle, when the temperature was cycled from low to high and then from high to low values. The range of temperature was divided into two intervals, one for $273 \leq T \leq 322$ K and the other for $322 \leq T \leq 373$ K, to explore the behavior of the aqueous systems and to make comparisons of the data results for each mixture. Several functional forms were tried to fit the data. It was found that linear or quadratic forms were not good fits. Basic equations were derived from theoretical efforts. Test for departure in the data from the theoretically predicted curves were made to establish any systematic variations that lie outside the expected errors in the data.

Microwave data from the investigations of Grant and Shack¹⁰ and Collie *et al.*¹¹ appear to show two characteristic regions for the behavior of the dielectric response of water over the frequency range $3 \leq f \leq 35$ GHz. This temperature and frequency dependence of the dielectric response and refractive index of aqueous systems became the object of this set of experiments.

The investigations of d.c. conductivity measurements of aqueous solutions of NaCl at various concentrations demonstrate that over the range of temperatures $273 \leq T \leq 323$ K the water system maintains a cage like structure which appears to be independent of solute concentration.¹² This is evidenced by the nearly constant slope in the Arrhenius plot of the data over that range. For the higher ranges of temperatures, $323 \leq T \leq 363$ K, the slope of the Arrhenius plot varied more than one order of magnitude for the concentration levels studied. There appear to be discrete levels of structure in the water "cage" formed by the hydrogen bonds which can be characterized as due to polymeric species of water. In the theory section of this work, the equations which were used to determine the range and level of formation of each polymeric species have been expressed.

CHAPTER II

EXPERIMENTAL METHODS

A block diagram of the apparatus used to study the refractive index is shown in figure

1. The basic unit is a modified Michelson interferometer employed to get the fringe patterns and a thermal cell whose volume is 6.5 cm^3 to hold the samples and to vary the temperature of the aqueous samples in a controlled way. In order to facilitate data collection and retrieval, a video camera was trained on a projection screen where the fringe pattern was displayed. In the same field of view, the thermocouple digital display was placed so that a picture of both the fringe pattern and the temperature could be made. The internal clock of the camera was displayed on the screen, as well. Thus, all of the data needed for the experiment could be collected simultaneously. The video speed could then be varied as needed for the final fringe count.

The density was determined by measuring the height of the liquid meniscus in a narrow capillary tube of 2 mm diameter attached to the calibrated cell with a volume of 12.2 cm^3 . Calibration for density is made with pure water in the temperature range of 273 K to 373 K. Tabulated densities above freezing for the water and ethanol solutions were found in the literature, but it was still necessary to supplement these data with our own measurements over the range 277 K to 338 K .

The temperature was measured in a standard way by using an amplified voltage output

from a thermocouple. The thermocouple which senses the voltage for temperature measurement is referenced via a second copper constantan junction immersed in a large ice-water reservoir which maintains the reference temperature over a period in excess of 24 hours to assure stability during the extended measurements. In the present installation, the temperature is read as voltage and converted through software in the computer program as required. The instrument was calibrated to a laboratory standard.

Figure 1. A diagram of the experimental apparatus used to collect refractive index data for binary-mixture system.

Each data run was conducted over a time span of three hours or less. The amount of hysteresis between the curves of increasing and decreasing temperature was found to be time and temperature dependent, so care was taken to conduct each experiment over the same time

interval to remove any time dependent effects. Comparisons could then be made for the dependency of the hysteresis on mixture ratios under the same condition.

The experimental apparatus for the conductivity measurement consists of a standard technique with standard equipment which is shown in figure 2.

Figure 2. Basic apparatus used to measure the d. c. conductivity and temperature of the aqueous solution.

Electrodes separated at fixed distance are immersed in the solution and the conductivity measured across the spacing. The temperature is controlled through a heat exchanging apparatus capable of varying the temperature over the desired range. There are basically two channels for making the measurements, one is required to measure the conductivity and the other to measure the temperature of the cell and solution. These two signals are fed to the computer directly as required.

CHAPTER III

REFRACTIVE INDEX AND DENSITY VARIATIONS IN LIQUID

3.1 Data Analysis

The determination of the refractive index can be made by counting the changes of the interference fringes as the temperature on the cell is changed. The cell thickness changes with temperature and this dependency is incorporated into the change in fringes by expressing the cell dimension as

$$L(T) = L_0(1 + \alpha_{Cu}\Delta T)(1 + \beta \alpha_{Liquid} T), \quad (1)$$

where α is the coefficient of thermal expansion for the metal of which the cell is constructed and for the liquid tested, β is a modified constant and ΔT is the change in temperature. Because the coefficient of thermal expansion for the metal is much smaller than the thermal expansion for the liquid, the change in path length due to metal expansion can be ignored for the range of temperatures studied.

The refractive index is more dependent upon the thermal expansion or the density of the medium through which it is propagating than upon the path length alone. The effective path length is changed by any change in density, so the true path length is a function of the density ρ .

It is reported that for a uniform fluid all of the interparticle distances are assumed to vary as $\rho^{-1/3}$, irrespective of temperature.¹³ So, the effective path length of the liquid over

most of the temperature range is given by

$$L(T) = L_0 [\rho(T)/\rho_0]^{-1/3}, \quad (2)$$

where L_0 is the original length of the sample cell and $[\rho(T)/\rho_0]^{-1/3}$ is the temperature dependent equation for the liquid.

An expression for the temperature dependence on the density of water has been given by Kell.⁸ This expression is:

$$\rho = \frac{999.8676 + 17.801161 T - 0.0079425 T^2 - 52.56328 \times 10^{-6} T^3 + 137.6891 \times 10^{-9} T^4 - 364.4647 \times 10^{-12} T^5}{1 + 17.73544 \times 10^{-3} T} \quad (3)$$

The optical path change due to the index change of a substance is given by

$$2n(T)L(T) - 2n(o)L(o) = \Delta m \lambda, \quad (4)$$

where $n(T)$ is the refractive index at a temperature T and $n(o)$ is the initial index of refraction at temperature T_0 , $L(T)$ is the effective path length through which the light passes at temperature T , Δm is the fringe change due to the refractive index and λ is the wavelength of the light. In principle, a measurement of Δm and knowing $L(T)$ and the wavelength λ , the $n(T)$ can be determined.

Experimental data for each time interval were obtained by counting the fringe change as the temperature of the cell was changed. When the refractive index is determined by counting fringes in a Michelson interferometer, the equation is adapted to the following form

$$\Delta n(T) = [\Delta m \lambda / 2L_0][\rho(T)/\rho_0]^{1/3}, \quad (5)$$

where Δm is the change in fringes, λ is the wavelength, L_0 is the original length and the effective length is given by the equation (3). Combining with equation (4) the formula for the

refractive index is :

$$n(T) = n_0 - [\Delta m \lambda / 2L_0] [\rho(T)/\rho_0]^{1/3} . \quad (6)$$

The refractive index measurements are thus reduced to counting the changes in fringes as the temperature is cycled over the chosen range and incorporating the density change with temperature for the mixtures into the equation.

The microwave data shown in Figure (3) show that water exhibits two characteristic regions of behavior, one which shows a rather strong frequency dependence on the dielectric response and another a higher temperature region which appears to have a small frequency dependency on the dielectric response. It should follow that the refractive index will respond in a similar way for binary water systems.

Figure. 3 A plot of the dielectric response with temperature and frequency dependence for pure water at microwave frequencies. (Reference 10 and 11)

Figure (4) shows the experimental data for the refractive index of pure water for the Na doublet spectral component. The theoretical curve shows a very good fit as shown in A and B of the figure. The greatest departures are found in the lower temperature regions, near 34 °C, of the scale. It is more instructive to show the differences between the data and the theoretical curve, figure (4) the curve labeled C. The differences are small, right hand margin, but there are systematic variations in the data that indicate small oscillations in the refractive index over temperature. The nature of the fluctuations seem to reside in how clusters form due to hydrogen bonding in the mixtures.^{14,15} Similar trends in the data were found at the wavelength of the He-Ne laser line, with the evidence of hysteresis in the cycle, when the temperature was cycled from low to high and then from high to low values. (See figure 5.)

Figure. 4 A plot of the refractive index for pure water and the change in the refractive index relative to modified LL equation (Bold line A) for the Na doublet at 5893.2 Å.

Figure 5. A plot of the refractive index of pure water for He-Ne laser light and its departure from the modified LL equation (Bold line). Curve (A) is the departure for increasing temperature and (B) is the departure for decreasing temperature.

Hydrogen bonding within the pure water provides forces to produce clustering for $273 \leq T \leq 323$ K. Arrhenius plots were used in the work of conductivity measurement of aqueous NaCl solution to obtain a value of 2.7 Kcal/Mole for this bond strength.¹² The addition of solvent to the system produces changes in some properties of the aqueous systems that may be determined through changes in the refractive index. The refractive index of alcohol-water systems changes with changing temperature in a non-symmetrical way. When the temperature is cycled from low to high and then from high to low, the results appear to differ. When the mixture is 50% volume of water and 50% volume of ethyl alcohol, the cycles appear to have similar structure, but not for the other ratios. There appear to be competing forces between

the alcohol and water molecules that do not respond the same for increasing and decreasing of the temperature of the mixtures. It might be interpreted that the ice-like, 4-coordinate H-bond structure of water is broken down to an alcohol-like structure persisting over the whole temperature range studied.

Experiments on the water alcohol mixture were conducted for temperatures of 0 °C to 70 °C to prevent significant evaporation of the alcohol from the mixture for the mixture studies. Under these conditions, the system did not respond the same for increasing to decreasing and then decreasing to increasing values of temperatures. It appears that the hydrogen bond associations do not respond in the same way to temperature change when the bond have been dissociated by temperature above 60 °C. When the water systems were elevated above 323 K, the refractive index curves showed hysteresis over the complete cycle. The presence of the intermolecular alcohol molecules within the bath of water molecules seems to inhibit the hydrogen bond associations after elevation of the temperature above $T=60$ °C.

In figure (6) are shown the data for the refractive index for a spectral line in helium, mercury and sodium that show a very close fit of the refractive index data to a function of the density. The relationship, with no physical meaning ascribed to it, is given by

$$n(T) = \text{Constant} [\rho(T)]^{1/k}, \quad (7)$$

with $k=3.5$ for $\lambda = 5893.2 \text{ \AA}$, $k=3.3$ for $\lambda = 7062.2 \text{ \AA}$ and $4446.6 \text{ \AA}$.

In order to minimize the difference between the data points and values calculated from the LL formula, a similar good fit is derived with the modified LL equation

Figure 6. A plot of the refractive index for three different spectral lines for 4446.6 Å, 5893.2 Å and 7065.2 Å. The lines in the figures represent the fit for the modified LL equation

$$n(T) = \sqrt{\frac{1 + 2A(T) \frac{\rho(T)}{W}}{1 - A(T) \frac{\rho(T)}{W}}} \quad (8)$$

Where A is the mole refractive index, $\rho(T)$ is the temperature dependent density of the liquid and W is the molecular weight of the systems. The density of aqueous ethanol solutions vs temperature was measured. The summary of results is shown in figure 7. The author used the modified LL formula eq(8) as a theoretical formula to calculate the refractive index of a liquid in which the mole refractive index is a function of the temperature. The form of the mole refractive index $A(T)$ was expressed in the form of an exponential as

$$A(T) = A_0 e^{b/(T+273.14)} \quad (9)$$

Where A_0 is chosen for a minimum at $T = 0\text{ }^{\circ}\text{C}$ and b' is a constant dependent upon the wavelength of the radiation and the concentration of the mixture.

Although the data appear to give a good fit to equation (8) when the experimental data and the equation are plotted, assuming the exponential dependence on $A(T)$ given by equation (9), there are systematic departures in the differences between the experimental data and the values predicted by equation (5). The difference depends upon the direction in which the temperature is cycled. In the mixture that is 50% ethyl alcohol and 50% water, the general trends for both increasing and decreasing temperature are the same in structure. This trend was not found in the other mix ratios. The binary system appears to show some non-reversible properties when the temperature is cycled. The experimental data for each mixture are given in figures 8-14.

Figure 7. The density of aqueous ethanol solutions vs temperature. Ethanol concentrations are given in mol%. (Reference 4)

Figure 8. A plot of the experimental refractive index vs. temperature for ethyl alcohol and the change in the refractive index relative to equation (8) for Na doublet line 5893.2Å.

Figure 9. A plot of the experimental data for the refractive index for increasing and decreasing temperature for a mixture of 10 % ethyl alcohol and 90% water and the change in the refractive index relative to the LL formula for the He-Ne laser line 6328 Å.

Figure 10. A plot of the experimental data for the refractive index for increasing and decreasing temperature for a mixture of 25% ethyl alcohol and 75% water and the change in the refractive index relative to the LL formula for the He-Ne 6328 Å laser line.

Figure 11. A plot of the experimental data for the refractive index for increasing and decreasing temperature for a mixture of 50% ethyl alcohol and 50% water and the change in the refractive index relative to the LL formula for the He-Ne 6328 Å laser line.

Figure 12. A plot of the experimental data for the refractive index for increasing and decreasing temperature for a mixture of 60% ethyl alcohol and 40% water and the change in the refractive index relative to the LL formula for the He-Ne 6328 Å laser line.

Figure 13. A plot of the experimental data for the refractive index for increasing and decreasing temperature for a mixture of 75% ethyl alcohol and 25% water and the change in the refractive index relative to the LL formula for the He-Ne 6328 Å laser line.

Figure 14. A plot of the experimental data for the refractive index for increasing and decreasing temperature for pure ethyl alcohol and the departure from the LL formula for the 6328 Å line

The data obtained on electrical conductivity of alcohol-water mixes showed similar hysteresis properties when conductivity is measured over temperature. These results are shown in chapter 4. Arrhenius plots for pure alcohol and pure water showed significant differences over temperature. Introduction of alcohol into the water systems alters the Arrhenius profiles in a systematic way for increasing alcohol concentrations as was also found in the behavior of the refractive index for light in the mix ratios. (See fig 15.)

A series of time dependent experiments was conducted to determine any effect of slow mixing of the two components in the mixture. These results are summarized in table I . There were two effects of interest, one the amount of hysteresis in the two curves for cycling over increasing and then decreasing temperature for short and long time intervals and another, the

Figure 15. A plot of the experimental data for the refractive index vs. temperature for a mixture of ethyl alcohol and water. A-100%, B-75%, C-60%, D-50%, E-25%, F-10% and G - 0 % concentration of ethyl alcohol.

effect of an upper limiting temperature. For the alcohol mixtures, the temperature was not raised above 70 °C as stated above to reduce evaporation of alcohol from the mixtures. The data appeared more repeatable in restricting the upper temperature at this value. This effect on hysteresis may be due in part to partial evaporation of the alcohol from the mixture. Because of this possibility, the mixtures were reexamined for density changes after each experimental cycling. No significant volume change was noticed when the mixtures were kept below the evaporation temperature of alcohol. A series of time dependent experiments were conducted to determine any effect of slow mixing of the two components in the mixture. In fact, hysteresis was found in pure water systems, indicating a fundamental property of water to be responsible for this hysteresis.

TABLE I. A summary of the values used in fitting the experimental data to equation (9) for the alcohol and water mixtures. I indicates increasing temperature and D is for decreasing T.

CON (ALCOHOL)	DIR	TIME(S)	A ₀	b(°C ⁻¹)	b' (°K)	SLOPE FOR N
0	I	2,000	3.7	4.3x10 ⁻⁵	2.3	-1.1x10 ⁻⁴
0	D	2,000	3.7	5.3x10 ⁻⁵	3.0	-1.2x10 ⁻⁴
0	I	7,000	3.7	2.8x10 ⁻⁵	2.6	-1.1x10 ⁻⁴
0	D	7,000	3.7	2.9x10 ⁻⁵	2.7	-1.1x10 ⁻⁴
10	I	2,000	3.9	8.9x10 ⁻⁵	9.1	-1.1x10 ⁻⁴
10	D	2,000	3.9	9.9x10 ⁻⁵	10.0	-1.8x10 ⁻⁴
10	I	7,000	3.9	5.3x10 ⁻⁵	5.5	-1.9x10 ⁻⁴
10	D	7,000	4.0	3.3x10 ⁻⁵	3.4	-1.5x10 ⁻⁴
25	I	2,000	4.3	1.4x10 ⁻⁴	14.2	-2.3x10 ⁻⁴
25	D	2,000	4.4	1.1x10 ⁻⁴	11.3	-2.2x10 ⁻⁴
25	I	7,000	4.4	1.0x10 ⁻⁴	10.3	-2.1x10 ⁻⁴
25	D	7,000	4.4	0.9x10 ⁻⁴	9.1	-2.1x10 ⁻⁴
50	I	2,000	5.5	1.8x10 ⁻⁵	18.2	-3.1x10 ⁻⁴
50	D	2,000	5.5	1.6x10 ⁻⁵	16.2	-3.1x10 ⁻⁴
50	I	7,000	5.5	1.6x10 ⁻⁵	16.2	-3.2x10 ⁻⁴
50	D	7,000	5.5	1.5x10 ⁻⁵	15.2	-3.2x10 ⁻⁴
60	I	2,000	6.5	4.3x10 ⁻⁵	4.1	-2.9x10 ⁻⁴
60	D	2,000	6.5	5.0x10 ⁻⁵	4.9	-3.3x10 ⁻⁴
60	I	7,000	6.5	4.1x10 ⁻⁵	4.0	-3.0x10 ⁻⁴
60	D	7,000	6.5	4.9x10 ⁻⁵	4.8	-3.1x10 ⁻⁴
75	I	2,000	7.7	7.0x10 ⁻⁵	7.7	-3.7x10 ⁻⁴
75	D	2,000	7.9	4.0x10 ⁻⁵	4.1	-3.1x10 ⁻⁴
75	I	7,000	8.0	2.3x10 ⁻⁵	2.4	-3.5x10 ⁻⁴
75	D	7,000	7.9	5.3x10 ⁻⁵	5.3	-3.5x10 ⁻⁴
100	I	2,000	12.5	3.4x10 ⁻⁵	3.4	-4.3x10 ⁻⁴
100	D	2,000	12.5	3.0x10 ⁻⁵	3.1	-4.3x10 ⁻⁴
100	I	7,000	12.5	2.9x10 ⁻⁵	3.0	-4.3x10 ⁻⁴
100	D	7,000	12.6	1.9x10 ⁻⁵	2.0	-4.3x10 ⁻⁴

The values of b given in the table I can be assumed to be dependent upon the nature of the intermolecular bonds for aggregation of the water molecules due to hydrogen bonding. When the molecular mix is varied from pure water to 50% alcohol, the value of b increases and decreases systematically for both increasing and decreasing cycles in the temperature. Above 50 % concentration of ethyl alcohol, there is an abrupt drop in the value of b which may be due to the effective cage-like screening of the hydrogen bonds from each other due to the presence of the large concentration of ethyl alcohol to offer shielding of the water molecules. This effect may indicate the complete disruption of cage like structure in the water component of the binary mixture. (See figure 16.)

Figure 16. A plot of b vs. concentration of ethyl alcohol for an aqueous solution. The curves A and C are for 2,000 s cycle time and B and D for 7,000 s cycle time.

The mole refractive index $A(T)$ shows a temperature dependence that is exponential in form. The temperature dependence of A can be explained as due to the change in the effective cross-section of the molecules as they move more or less vigorously in the signal path as the temperature is raised and lowered and as due to disruption of hydrogen bonds in the clusters as the temperature is raised. The process of reassociation of the hydrogen bonds with lowering of the temperature does not recycle over the same statistical path as arises when the bonds are disassociated. This effect is seen in the asymmetrical behavior of the temperature cycles for varying time intervals. The author has incorporated the effect of temperature on A into the calculations for the density and refractive index. This effect of non-symmetrical cycling may also arise in the viscosity change with temperature. Sorensen has shown the viscosity dependence on temperature for binary systems is not that expected for a simple model of mixing two members to produce a resultant viscosity.⁵ The change in viscosity of the solutions should correlate with the change in refractive index of the solutions. The temperature should be cycled in both the forward and reverse directions to test for any asymmetry.

Binary solutions of water and ethanol and water and hydrazine showed larger viscosity than expected by averaging the viscosity of the two members of the mixture.⁷ Sorensen attributed this property to a change in ordering of the system in this mixture to favor a better cage like structure in water. A maximum viscosity enhancement was observed for 17 mole % by Sorensen.⁷ The values of 10 volume % or 3.3 mole % that showed a large hysteresis effect (figure 9) as the temperature was cycled from low to high and then from high to low values. This hysteresis is assumed to be caused by relaxation of the enhanced cage like structure of the

water near this concentration. It is clear that well controlled experiments must be conducted in this region to better understand the structural behavior of the hydrogen bonds that lead to the ordering of the system.

Ojamäe gives the results of a study on the water molecule in solid, liquid and gas surroundings in a dissertation.³² He proposed that the density maximum near 4° C, the fact that liquid water is more dense than ice, the high heat capacity and the high melting points and boiling points of water are due to the strong hydrogen bonding in water and due to the geometry of water molecules. The ability of the water molecule to accept or to donate two hydrogen bonds in a tetrahedral structure makes the formation of a three dimensional network possible. The O...O distance of separation is around 2.84 Å and there are four or slightly more next nearest neighbors, according to Ojamäe. This cage like structure can be broken by an elevation of temperature or by substitution of other molecules than water in the environment. The change in this structuring will manifest itself in a change in the refractive index of the liquid as well as in other physical properties. Our own results show that the process is a dynamical process that is both time and temperature dependent. The author propose further experiments in which the temperature is cycled over increasing and decreasing values for a series of fixed time intervals. The samples will need to recover from the effects of each cycling exercise before they are cycled again. It may not be possible to restore the samples to the unperturbed condition in a time shorter than several hours and new specimen will need to be prepared for each interval of time and temperature to get consistent results..

3.2 General form of the Lorentz-Lorenz equation

The definition of the refractive index of a medium is obtained from Maxwell eqs.

$$\begin{aligned}
 \nabla \cdot \vec{E} &= 0, \\
 \nabla \cdot \vec{B} &= 0, \\
 \nabla \times \vec{E} + \frac{1}{c} \frac{\partial \vec{B}}{\partial t} &= 0, \\
 \nabla \cdot \vec{B} - \frac{\mu \epsilon}{c} \frac{\partial \vec{E}}{\partial t} &= 0,
 \end{aligned} \tag{10}$$

where μ is magnetic permeability which equal to $(1+4\pi\chi)$, χ is the susceptibility, ϵ is the electric permittivity which is equal to $(1+4\pi\eta)$ and η is the electric susceptibility.

From the wave function $U = e^{iKx - i\omega t}$ as a solution to Maxwell equations, the refractive index is defined as

$$n = \frac{c}{v} = \sqrt{\mu\epsilon} \approx \sqrt{\epsilon} . \tag{11}$$

The molecular property α , which is the response of the molecules to an applied field, and the electric susceptibility η , which is a macroscopically defined parameter, provide the experimentally measurable quantities for the properties of the medium. In the general formalism of the molecular orientation theory, the refractive index equation is derived as follows.

With the Einstein notations, the basic expression of the polarization vector $\mathbf{p}$ of a medium along the direction x of the applied optical field $\mathbf{E}$ is written as the electric dipole moment $\mathbf{p}$ for N molecules:

$$\mathbf{p} = \epsilon_0(\epsilon - 1) \mathbf{E} = \epsilon_0(n^2 - 1) \mathbf{E} = N \langle \mathbf{p}_i e_x \rangle. \tag{12}$$

Here ϵ_0 is the dielectric constant of vacuum, N is the number of molecules per unit volume unit, p_i is the component of the induced molecular moment along the major axis and e_x is the cosine of the angle between the x axis and the major axis. The brackets $\langle \rangle$ indicate the statistical average calculated over all molecular orientations.

The molecular moment induced by the local field F is

$$p_i = \alpha_i F_i, \quad (13)$$

where α_i is the principal molecular polarizability along the major axis.

The general expression of the component F_i of F in the spherical cavity model is

$$F_i = E_i - \frac{\bar{n}^2 - 1}{2\bar{n}^2 + 1} E_i + \frac{2(\bar{n}^2 - 1)}{2\bar{n}^2 + 1} \frac{p_i}{3v\epsilon_0}, \quad (14)$$

where v is the volume of the molecular cavity and the bar indicates a mean value in the bulk liquid which surrounds the cavity (See figure 17 sketched below.).

Figure 17. Refractive index n and number of molecules per unit volume N in the bulk liquid and in the local surrounding of the cavity.

The sketch shown in figure (17) is the basis of a spherical model for the liquid. The spherical model is at the origin of the Onsager equation which has been widely applied to the interpretation of the electric permittivity of pure liquids. The good results obtained from the spherical model seem to be due to random molecular movements, which in most cases give a more or less spherical cavity, even when the molecules are not spherical.

From equations 12,13 and 14 one obtain

$$\langle p_i e_x \rangle = N \left\langle \frac{a \alpha_i E_i e_x}{1 - b \alpha_i} \right\rangle, \quad (15)$$

where

$$a = \frac{3\bar{n}^2}{(2\bar{n}^2 + 1)}$$

and

$$b = \frac{2(\bar{n}^2 + 1)}{(2\bar{n}^2 + 1)3v\epsilon_0}.$$

Then, because e_x and $E_i = E e_x$ are the only terms which depend on the molecular orientation , equation (15) becomes

$$\langle p_i e_x \rangle = N \frac{a \alpha_i E_i e_x}{1 - b \alpha_i} \langle (e_x)^2 \rangle. \quad (16)$$

As the orientational averaging gives $\langle (e_x)^2 \rangle = 1/3$ equations (13) and (16) lead to

$$n^2 - 1 = \frac{N}{3\epsilon_0} \frac{a \alpha_i}{1 - b \alpha_i}. \quad (17)$$

In order to obtain a practical equation, one first assume that

$$1 - b \alpha_i \approx 1 - b \bar{\alpha}, \quad (18)$$

where $\bar{\alpha} = (\alpha_1 + \alpha_2 + \alpha_3) / 3$ is the mean molecular polarizability. When take the mean values

of all quantities in (17) and especially $\bar{N} \approx 1/\bar{v}$ that use for the evaluation of $\bar{\alpha}$, get

$$\bar{\alpha} = \frac{3\epsilon_o (\bar{n}^2 - 1)}{N (\bar{n}^2 + 2)}. \quad (19)$$

Finally eqs 17, 18 and 19 give

$$n^2 - 1 = \frac{N}{\epsilon_o} \frac{3\bar{n}^2 (\bar{n}^2 + 2) \bar{\alpha}}{((2\bar{n}^2 + 1)(\bar{n}^2 + 2) - 2(\bar{n}^2 - 1)^2 / \bar{N}\bar{v})}. \quad (20)$$

This is a more general practical formulation of the L-L equation. Two other ways of making the approximations lead to the usual Lorentz-Lorenz and Maxwell equations, which have proved to be unsuitable for our purpose. If it is only assumed that $\bar{N} \approx 1/\bar{v}$, Maxwell's equation is obtained as follow

$$n^2 - 1 = \frac{N (\bar{n}^2 + 2) \bar{\alpha}}{\epsilon_o 3}. \quad (21)$$

Moreover, if $n^2 \approx \epsilon$ one gets the L-L equation

$$\frac{(n^2 - 1)}{(n^2 + 2)} = \frac{N}{3\epsilon_o} \alpha. \quad (22)$$

In both cases the first member N is proportional to the density ρ , considering $\rho = W/V$. If the molar refractivity A is defined by :

$$A = \frac{4\pi}{3\epsilon_o} N\alpha, \quad (23)$$

hence,

$$A = \frac{W}{\rho} \frac{n^2 - 1}{n^2 + 2}. \quad (24)$$

Both n and ρ should exhibit similar critical behavior. The equation may be extended to binary mixtures. By replacing A with A^* , the average molecular polarizability, the equation is

still valid for binary mixture systems. If two liquids of refractivities A_1 and A_2 are mixed and if the number of molecules in a unit volume of V_1 is N_1 and V_2 is N_2 , then the molar refractivity of the mixture will be

$$A^* = \frac{N_1 A_1 + N_2 A_2}{N_1 + N_2} . \quad (25)$$

The author get the modified LL formula as follows:

$$n(T) = \sqrt{\frac{1 + \frac{2A^*(T)\rho^*(T)}{W^*}}{1 - \frac{A^*(T)\rho^*(T)}{W^*}}} , \quad (26)$$

where the form of the mole refractive index A^* is also a function of the temperature and concentration of the mixture.

$$A^*(T) = A_o^* e^{b'/(T+273.14)} , \quad (27)$$

where b' is dependent upon the nature of the intermolecular bonds for aggregation of the water molecules due to hydrogen bonding. $\rho^*(T)$ is the density of the mixture.

CHAPTER IV

DETERMINATION OF HYDROGEN BONDING IN WATER THROUGH CONDUCTIVITY (D. C.) MEASUREMENTS

4.1 Analysis of the experimental data

The d.c. conductivity of aqueous solutions of NaCl was measured. A plot of these data along with the departure of the electrical conductivity from a linear fit are given in figure 18 - 26. The conductivity appears to be linear over temperature until the concentration level is raised above 5% of NaCl by mass. Above this concentration two nearly linear region appear.

Data of departure shown in figures 19, 21 and 23 show asymmetrical properties. Some “memory” of the cycle was encountered in some weak samples with low concentration as they were cycled consecutively. It appears that the water samples had retained some residual property imbedded in them. As the concentration is increased to 49.2 g/l (4.69 % by mass) the memory of the cycles disappear. Sodium ions are assumed to break hydrogen bonds ¹². This means that the NaCl solute tends to break the hydrogen bonded structure of liquid water and removes the structure that may produce the minimum in the specific heat leaving only a background part.

The typical experimental results are shown in figures 26 for various concentrations of NaCl in water. Data show that as the concentration of NaCl is increased, there is a large change of “slope” for the Arrhenius plot in the temperature region above 323 K, but the slope

of this curve in the region $273 < T < 323$ K is essentially constant. It appears that in this region, water has cage like structure, the Na^+ and Cl^- ions do not change the relative behavior of the Arrhenius plot. The linear regions are assumed to correspond to regions in which the relaxation times change. The system may be treated as having several relaxation rates with rate processes controlled by temperature.

A summary of the results for all of the concentrations is given in Table II.

TABLE II. Data for aqueous solutions of NaCl to determine the bond energies of hydrogen bonds. All slopes are minus with units for σ given in $\mu\text{Mho cm}^{-1}$ to obtain each value of E_{HB} . * These values were not included in the averaging as saturation seems to be occurring.

Concentration (% by mass)	Slopes (K)				E_{HB} (Kcal mol ⁻¹)				
	273 ≤ T ≤ 293 K		273 ≤ T ≤ 293 K		273 ≤ T ≤ 293 K		273 ≤ T ≤ 293 K		
NaCl	IN	DEC	IN	DEC	IN	DEC	IN	DEC	AVG
0.000	1234	1198	1646	1782	2.2	2.1	2.9	3.2	2.6
0.008	1363	1173	1516	17.9	2.4	2.1	2.7	3.1	2.6
0.015	1124	1096	1641	1692	2.1	2.0	2.9	3.0	2.5
0.031	1125	1128	1622	1654	2.0	2.0	2.9	3.0	2.5
0.308	1076	1182	1639	1615	1.9	2.1	2.9	2.9	2.5
2.400	1275	1134	1604	1623	2.3	2.0	2.9	2.9	2.5
4.689	1010	991	1478	1487	1.8	1.8	2.6	2.7	2.2
13.043	*407	*349	1661	1661	0.7	0.6	2.7	3.0	1.8
22.481	*121	*101	1510	1510	0.2	0.2	2.7	2.7	1.5
Averages					2.1	2.0	2.8	2.9	2.5

Figure 18. A plot of electrical conductivity vs. temperature for a solution of 3.08 g/l of NaCl dissolved in one liter of pure water with an increasing and decreasing temperature cycle.

Figure 19. A plot of the departure of the electrical conductivity of a NaCl solution with 3.08 g/l concentration of NaCl.

Figure 20. A plot of electrical conductivity vs. temperature for a solution of 24.6 g/l of NaCl dissolved in one liter of pure water with an increasing and decreasing temperature cycle.

Figure 21. A plot of the departure of the electrical conductivity of a NaCl solution with 24.6 g/l concentration of NaCl.

Figure 22. A plot of electrical conductivity vs. temperature for a solution of 49.2 g/l of NaCl dissolved in one liter of pure water with an increasing and decreasing temperature cycle.

Figure 23. A plot of the departure of the electrical conductivity of a NaCl solution with 49.2 g/l concentration of NaCl.

Figure 24. A plot of electrical of conductivity vs. temperature for a solution of 150 g/l of NaCl dissolved in one liter of pure water with an increasing and decreasing temperature cycle.

Figure 25. A plot of electrical conductivity vs. temperature for a solution of 290 g/l of NaCl (saturated solution) dissolved in one liter of pure water with an increasing and decreasing temperature cycle.

Figure 26. A summary of Arrhenius plots of $\text{Ln}(\sigma)$ vs. inverse temperature with different concentration NaCl solutions.,

4.2 Theory

Electrolytic solutions can be difficult to model over temperature in that ionic concentration levels change when the temperature is changed. It is possible to write some relationships for the charges which contribute to transport properties of the system under assumed condition and obtain information about the qualitative behavior of the electrolytes.

The conductivity for a system composed of N charges of mass m , charge q , and with a collision time τ is given by (if assumed only one relaxation time and a single charge unit)

$$\sigma = N q^2 \tau / m. \quad (28)$$

A more general form can be expressed for a medium with ions, charges and masses present as

$$\sigma = \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \dots = \sum_i N_i q_i^2 \tau_i / m_i. \quad (29)$$

If the solution of water and sodium chloride is assumed to have only four ions, Na^+ , Cl^- , H_3O^+ and OH^- , the conductivity equation can be simplified to only four terms.

The number density for ions is given by $L_0 / V_m \approx 6.023 \times 10^{23} / (M_m/\rho)$. Where L_0 is Avogadro's number, V_m is the molar volume, M_m is the molar mass, and ρ is the density. If the systems has many ions, it becomes necessary to express the relative contributions of each ion to the conductivity of the system. Equation (29) can be simplified to a two member system to simplify the transport property of the system if it is assumed that only two ions contribute to the transport property. For pure water, the system can be simplified to a two level one and lends itself to a reasonable solution. By introducing probability for ion formation and recombination, the system can be analyzed by the following scheme.

The addition of "impurity" ions to pure water leads to a model in which the author can assume a "two-level" system for the hydrogen bond formation in water. The assumption of only two states may be valid for the region of temperatures and ion concentrations studied, but should not be assumed to offer a complete model of all processes in the electrolyte formed by dissolving NaCl in water. In this simplified model, the author may chose two states and characterize them as state I and state II. In the presence of an external field, a set of stochastic equations may be written as follows:¹⁶

$$\vec{V}_I(T) = -\gamma_I \vec{V}_I(t) - (1/\tau_I) \vec{V}_I(t) + (1/\tau_{II}) \vec{V}_{II}(t) + \vec{F} + \vec{f}_I(t) \quad (30)$$

and
$$\vec{V}_{II}(T) = -\gamma_{II} \vec{V}_{II}(t) - (1/\tau_{II}) \vec{V}_{II}(t) + (1/\tau_I) \vec{V}_I(t) + \vec{F} + \vec{f}_{II}(t). \quad (31)$$

Where τ_I and τ_{II} are relaxation times for each species, $V_I(t)$ and $V_{II}(t)$, the velocities of each species, F is the force of the applied field, γ the damping term and f the fluctuation term.

Equations (30) and (31) can be solved to give a mean velocity

$$\langle \vec{V} \rangle_{stationary} = \sigma \vec{F}, \quad (32)$$

where σ is the resultant conductivity and is given by the two terms

$$\tau_{II} \sigma_{II} / (\tau_{II} + \tau_I) \text{ and } \tau_I \sigma_I / (\tau_{II} + \tau_I), \quad (33)$$

with the terms σ_I and σ_{II} given by the relations

$$\sigma_I = (\gamma_{II} + 2/\tau_{II}) / (\gamma_I \gamma_{II} + \gamma_I/\tau_{II} + \gamma_{II}/\tau_I) \quad (34)$$

and

$$\sigma_{II} = (\gamma_I + 2/\tau_I) / (\gamma_I \gamma_{II} + \gamma_{II}/\tau_I + \gamma_I/\tau_{II}). \quad (35)$$

If the damping terms γ_I and γ_{II} are large, any fluctuations in the hydrogen bonds will dominate. The relations $1/\gamma_I$ and $1/\gamma_{II} \ll \tau_{(Hydrogen \text{ bond fluctuation})}$ are expressed as τ_I and τ_{II} respectively. Equation (34) and (35) simplify to

$$\sigma_I = 1/\gamma_I \text{ and } \sigma_{II} = 1/\gamma_{II}. \quad (36)$$

Bertolini et al.¹⁷ give a probability relationship as follows

$$P_B/(1-P_B) \approx \tau_I/\tau_{II}, \quad (37)$$

where P_B is the probability that a hydrogen bond is randomly intact. The following relationship also holds that

$$P_B/(1-P_B) = (1/A) \exp[E_{HB}/RT], \quad (38)$$

where E_{HB} is the energy barrier that must be overcome to break some hydrogen bonds. Upon combining these last two equations the author get

$$\tau_I/\tau_{II} = (1/A)\exp[E_{HB}/RT]. \quad (39)$$

Finally, the resultant conductivity of the system may be written, subject to some restrictions, in the form

$$\sigma_R = \sigma_{II}/(1+\tau_I/\tau_{II}) + \sigma_I/(1+\tau_{II}/\tau_I). \quad (40)$$

Analysis of the data can now be done in terms of the "constants" A and E_{HB} . The results for the system assumed to have two relaxation times are given in Table II, along with the values of each constant used in deriving the results. Combining the results given above leads to the equation:

$$\frac{\sigma_R}{\sigma_I} = \left(\frac{\sigma_{II}}{\sigma_I}\right) \left[1 + \frac{1}{A} e^{\frac{E_{HB}}{RT}}\right]^{-1} + \left[1 + A e^{\frac{-E_{HB}}{RT}}\right]^{-1}. \quad (41)$$

Equation (41) can be used to fit the data by varying A and E_{HB} as required to minimize differences. A was chosen to be 28 as suggested by Grigolini *et al*¹⁷. A value of $E_{HB} = 2.4$ Kcal mol⁻¹ gives a slope for the pure water data of 1204 K. The data given in Table II reflect the results for E_{HB} . In the limiting case for an ultrapure sample of water the value of σ_{II}/σ_I may be used to determine a value for A .

4.3 Data Acquisition Design for d. c. Conductivity and Temperature measurement

The data acquisition use the ML16A/D board. The computer C++ program will perform interrupt driven acquisitions on three channels which are time, temperature and d. c. conductivity. The real-time measurement results of these parameter will display on the screen in graphic mode. Figure 27 show the data acquisition design. C++ program are shown in appendix IV.

Figure 27. Data Acquisition Program Design Diagram

CHAPTER V

BASIC PROPERTIES OF PURE WATER

5.1 Some thermodynamical properties of water

Water has been studied by almost all available techniques. In spite of the enormous number of studies of water and reactions in water during the last century, water at its molecular level is still far from being satisfactorily understood.^{27,28,29} Two main views referred to as *mixture* and *continuous* water models have dominated the discussion in the latter half of the century. The *mixture* model, which is composed of a bulky, ice-like structure and a dense, broken-ice structure was already proposed by Röntgen³⁰ in 1892. The *continuous* model originated from the x-ray structure of water by Bernal and Fowler³¹, who showed that the average, dynamic structure of cold liquid water has a tetrahedral configuration. The changes of the radial distribution curves of water with rising temperature was due to distortion rather than breaking of H-bonds in the tetrahedral network of water. Water can be treated as a mixture of two components, one with intact H-bonds dominating at low temperature, and a second component most likely with broken H-bonds which increase in amount with rising temperature. Considered from the anomalies of the physical parameters of liquid water,²⁸ including the specific heat, viscosity, thermal conductivity, bulk modulus, compressibility, refractive index, density etc. , the two-states model may be supported. They should be some relations between any anomalies in water properties as a function of due to temperature change.

Figure 28 present data that show the specific heat of the pure water is a function of the temperature and it has a minimum value near 35 °C. The equation that shows the relationship between specific heat and temperature is given by:²⁸

$$C_p(T) = 4.1855 \{ 0.996185 + 0.0002874[(T + 100)/100]^{5.26} + 0.01116 \times 10^{-0.036T} \} \quad (42)$$

Figure 28. Specific heat of pure water and its departure from a parabolic fit.²⁸

Figure 29. A plot of the experimental data⁸ for the density of pure water and its departure from the Kell equation (43).

When using a parabolic fit over the two region from 0 °C ~ 35 °C and 35 °C ~ 100 °C is made , the departure from this fit has two bumps near 17 °C and 32 °C. This departure is shown in figure (28) as the non-smooth curve.

The density of pure water is a function of temperature as given by Kell⁸. The data are shown in figure (29). The equation derived by Kell is given as:

$$\rho = \frac{999.8676 + 17.801161T - 0.0079425T^2 - 52.56328 \times 10^{-6} T^3 + 137.6891 \times 10^{-9} T^4 - 364.4647 \times 10^{-12} T^5}{1 + 17.73544 \times 10^{-3} T} \quad (43)$$

In figure (29) can be seen a plot of the data using Kell's equation and the departure of the experimental data from it. Kell claims this equation holds for T=-50 °C to 150 °C.

The microwave data shown in figure (3) show that water exhibits some characteristic behavior over frequency, one for $273 \leq T \leq 343$ K and the other for $343 \leq T \leq 373$ K. The higher temperature region appears to have only a small frequency dependency on the dielectric response. It should follow that the refractive index responds in a similar way for binary water systems.

The equations for the viscosity and thermal conductivity can yield the transport properties of pure water as functions of temperature and density. The viscosity is often represented by the *free-volume* equation²⁸

$$\eta = \eta_0' \exp [- \Delta \epsilon_{\eta}' / (T + C)] \quad (44)$$

and $T = -C$ is the glass transition temperature. The constants for this equation are $A = -1.64779$, $B = 262.37$, and $C = -133.98$ °K, thus estimating the glass transition temperature of water as 133 °K . The data departure from the *free-volume* equation shows some transition structure around the minimum specific heat temperature 35 °C. (See figure 30.)

The equation for thermal conductivity for a two state systems is:

$$\frac{\sigma_R}{\sigma_I} = \left(\frac{\sigma_{II}}{\sigma_I} \right) \left[1 + \frac{1}{A} e^{\frac{E_{HB}}{RT}} \right]^{-1} + \left[1 + A e^{\frac{-E_{HB}}{RT}} \right]^{-1}, \quad (45)$$

Figure 30. A plot of the viscosity data⁸ of pure water and change in the viscosity relative to the *free-volume* equation (44).

Figure 31. A plot of electrical conductivity of pure water with increasing and decreasing temperature.

where A was chosen to be 28 as suggested by Grigolini *et al*¹⁷. A value of $E_{HB} = 2.4 \text{ Kcal-mol}^{-1}$ is the slope found for the pure water for a plot of $\ln(\sigma)$ vs. $1/T$. I and II indicate the conductivities of the two states. The d. c. conductivity of pure water data shown in figure (31) clearly show some asymmetrical properties. Some “memory “ of each cycle was encountered as each sample was cycled consecutively. This effect can be seen in figure (31).

Data obtained for sodium light shown in figure (4) (wavelength 5890 and 5896 Å) indicated that the departure from the modified LL formula fit corresponds to the similar properties of the specific heat departure (figure 28). The LL equation considers the effect of the density of the liquid ρ , so the departure should correspond to the same properties of the density, which show some structured properties in the temperature range 0-100 °C. See figure (29). There are departures near 17, 35 and 85 °C. These anomolous departures became the object of this study. An experiment was set up to explore this effect for the He-Ne laser line (wavelength 6328Å) to make a comparison of the two results (Figure 5). Similar trends in the data were found at the wavelength of the He-Ne laser line, with evidence of hysteresis in the cycle, when the temperature was cycled from low to high and then from high to low values.

Most of the data investigated for water in the temperature range of 0-50 °C such as specific heat, density, viscosity, microwave dielectric response, refractive index etc. seem to support the hypothesis that some kind of higher order transitions take place, tentatively assumed to be caused by transitions among 5- to 4- to 3- to 2-coordinately, H-bonded assemblies of water of slightly different enthalpies and entropies. Studies of the refractive index in aqueous solutions measured at every half degree support the hypothesis that the H-bond

structure of water possesses inherent instabilities in the temperature interval 0-50 °C.

The refractive index and absorption coefficient for liquid water is a function of frequency and can be expressed in the complex form as:

$$n = \text{Re} \sqrt{\epsilon(\omega)}$$

and
$$\alpha = 2 \text{Im} \sqrt{\epsilon(\omega)} \frac{\omega}{c} . \quad (46)$$

Figure 32. Refractive index and absorption coefficient for water vs. frequency.³³

Figure (32) shows the refractive index (top) and the absorption coefficient (bottom) for liquid water. The visible region of the frequency spectrum is indicated by the vertical dashed lines. At very low frequencies near the microwave region, $n(\omega) \sim 9$, a value which arises from the partial orientation of the permanent dipole moments of the water molecules. Above 10^{10} Hz the curve falls relatively smoothly to the structure in the infrared. In the visible region, $n(\omega) \sim 1.34$ with little variation. Then, in the ultraviolet region there is more structure. Above 6×10^{15} Hz there are no data on the real part of the refractive index.

The refractive index of a medium has been investigated by using several techniques¹⁹⁻²⁴, prism, double slit Rayleigh refractometer, Fabry-Perot interferometer, Michelson Interferometer, differential interferometric-technique and 2-wavelength interferometric-technique. The reason the author chooses the Michelson interferometer as one technique to study the refractive index of aqueous water - alcohol systems is that it is the most accurate technique to measure the refractive index. The error is given by

$$\Delta n = \frac{\lambda}{2L_o} = \frac{632.8^{nm}}{2 \times 1^{cm}} \approx 0.00004, \quad (47)$$

where L_o is the length of sample holder. It is hard to see the structure of liquid if the author do not take difference from the theoretical predictions. The refractive index departure data show some anomalies below the temperature of 50 °C. They correspond to the specific heat and density behaviors in some temperature region. The relationship between specific heat and density are derived in appendix eq (II-4).

5.2 Water Structure

From the refractive index data at microwave frequencies on the water molecules the author knows that the water system responds differently to the applied microwave field as the surrounding molecules are perturbed by changing the temperature while probing at a given microwave frequency, because the bonding structures are altered by temperature. In addition to the temperature dependence of the structure of water, the application of different frequency microwave fields should enable the range of relaxation times for the water systems to be determined. The different effective slope of the refractive index vs. temperature data as the driving frequency is changed from 3 to 35 GHz shows a transition frequency around 17 GHz⁵¹. Note that the data at 9 GHz (figure 3) shows both positive and negative trends in the dielectric response with a transition temperature of 300 K. From the d. c. conductivity for the liquid water can obtain a better understanding of the fundamental nature of the hydrogen bonds in water systems and polyphasal clustering in systems.

The isolated H₂O molecule is shaped like a wide-open V, figure (33), with the oxygen nucleus at the central bend and hydrogen nuclei forming “arms” of length 0.96 Å. the HOH angle is 104.5°. These dimensions can vary slightly as the molecule vibrates and interacts with neighbors in a crystal or the liquid, but the overall shape is retained.

The dominant effect in water molecule interactions is the formation of hydrogen bonds. When two water molecules form a hydrogen bond, one (the hydrogen donor) points one of its OH groups toward the back side of the oxygen atom of the second (the hydrogen acceptor). This arrangement is illustrated in Figure 33. The oxygen-oxygen lengths of these bonds

normally lie in the range 2.7-3.0 Å, so that the donated hydrogen resides only about one third of the way between oxygens and so still “belongs” to the donor.

Figure 33 Schematics for three dimeric forms of the water molecule according to Cannon.³⁴ (I) linear, (II) cyclic and (III) bifurcated form.

The maximum hydrogen bond strength is achieved when the molecules are arranged as show in figure 33(I). This strength is about 6.0 Kcal / mole of bonds, and exceeds the thermal energy KT by a factor of 10 at room temperature. The existence of these relatively strong hydrogen bonds between water molecules explains the relatively high melting and boiling temperatures for water, compared to other substances of comparable molecular weight (e. g. Ne, CH_4 , NH_3).

Figure 34 Theoretically predicted equilibrium structures of the water trimer, tetramer, and pentamer³⁶, which have been confirmed by far-infrared VRT spectroscopy experiments. The dashed lines represent hydrogen bonds.⁴⁰

Theory and experiment are in fairly good agreement for the structure of the water dimer, determined spectroscopically in 1977 by Dyke³⁵. A number of recent high-level ab initio calculations³⁶ have predicted the structures of larger water clusters in figure 34. All of the calculations predict that a quasi-planar cyclic form with each monomer acting as both a single donor and single acceptor, and with the free hydrogen oriented above and below the ring, constitutes the lowest energy structure for the trimer, tetramer, and pentamer. For the heptamer and larger clusters, a tendency toward three-dimensional (3D) structures is predicted,

with the nature of the hexamer structure being ambiguous.³⁷ In this evolution of structure with cluster size, the critical feature is the competition between maximizing the number of hydrogen bonds and minimizing the geometrical strain. The highest level ab initio calculations³⁸ predict a 3D cage structure to be the most stable for the hexamer, although at least three other structures lie within 0.3 kcal/mol and vibrational-averaging effects are likely to change their ordering. The predicted ring forms of the trimer, pentamer, and heptamer have no symmetry elements and are therefore chiral.

The recent far-infrared laser vibration-rotation tunneling (VRT) studies support the theoretical predictions.³⁹

CHAPTER VI

SUMMARY AND CONCLUSIONS

In figure 3 the microwave data indicate a frequency dependence of the refractive index for $T < 60^{\circ}\text{C}$. The limiting temperature appears to be about $T = 80^{\circ}\text{C}$, the temperature at which the velocity of sound in water is a maximum. The refractive index for visible spectral components (figures 4-6) in each water sample were examined for any systematic departures in the data relative to the theoretical curve. The data show features in the departure that are not random as is expected for a collection of data points.

Figures 8 through 13 show changes in the data departures for 10%, 25%, 50%, 60%, 75% and 100% ethyl alcohol aqueous systems that show asymmetry in the temperature except for a 50% mixture. The patterns are essentially the same structure for this mixture ratio for both increasing and decreasing temperature. These trends could not be detected without analyzing the differences. In figure 15 are shown data from all of the aqueous mixtures studied. The curves for both increasing and decreasing temperature nearly overlap.

From the differences in the refractive index in departure from the LL equation for various concentrations of ethyl alcohol in water, obvious structure is shown in pure water with large data departures near 13°C , 37°C and 75°C . Data for 10 % and 25% also show some structure and data for 50% are essentially featureless. Some minor patterns arise in the data at other mixtures. For 60% and 75% concentrations of ethyl alcohol, some water features

reappear. When the samples are made 100% ethyl alcohol, some peaks appear around 17°C and 50°C. Data presented by Sorensen⁶ for Raman spectral of methyl alcohol (0.1 mol% to 10 mol%) and water mixtures show some fluctuations of the Raman line intensities with changing temperature. Those data were not as definitive as can be seen in increments of less than 1°C in the temperature. The temperature intervals appear to be too broad, about 5°C or more. The fluctuations observed by us may be due to the OH oscillators in the solutions. A more careful study of the Raman spectra with 1°C or less interval of temperature change may resolve this.

Figures 18 to 26 show results of d. c. conductivity measurements for various concentrations of NaCl in water. There appears to be a difference in the response of the d. c. conductivity for increasing and decreasing temperatures as the temperature is cycled. When the NaCl concentration is 49.2 g/l, the path for departure from a linear plot traces nearly the same path (See figure 23) for increasing and decreasing temperatures. As the aqueous solutions are increased to 150g/l and 290g/l concentration of NaCl, there emerge two regions of response, one for $0 \leq T \leq 50^\circ\text{C}$ and $50 \leq T \leq 100^\circ\text{C}$.

The data on d. c. conductivity in figure 26 show a change in the slope near 50°C. Since conductivity depends upon the mobility of charge carriers in the solution, the data indicate a change in the nature of the mobility above and below 50°C. Since the refractive index is also dependent upon the mobility of the system through which the wave is propagating, the refractive index may show a transition region as well.

A summary of the Arrhenius plots of the data for a range of solutions of NaCl and water is given in figure 26. When all of the data are reviewed, there appear to be temperatures

of 17°C, 37°C, 50°C and 80°C where systematic departures in the data from assumed plots of thermodynamic properties occur. This generally holds true for the pure water systems as well as the aqueous systems with ethyl alcohol and NaCl in them. Since OH is in all of these systems studied, it seems reasonable to conclude that the OH oscillators play a major role in the systematic departures in the data at these temperatures,

Figure 28 specific heat data shows three temperatures at which the data depart systematically from a parabolic fit at 17°C, 35°C and 85°C. The structure near 17°C, 35°C and 85°C is also seen in figure 5 for the refractive index data near 13°C, 37°C and near 80°C. Two regions of structure in the data agree with the minimum in the specific heat near 30°C and a maximum in the sound velocity near 80°C. Figure 29 shows structure in the density departure from the Kell equation near 17°C, 37°C and 85°C. As well, figure 30 shows large departures in the viscosity near 37°C.

Specific heat has a minimum near 37°C, the bulk modulus has a minimum near 50°C and the velocity of sound has a maximum near 80°C. These temperatures are assumed to correlate with bond structure changes in the molecular systems. The somewhat persistent pattern near 17°C does not correlate with a known thermodynamic property, but it seems to correspond to the “kinks” in the data around 17-23 °C, which are predicted by Malmberg and Maryott⁴⁹. It is possible that “kinks” exist in the temperature-dependent functions of the physical properties of water and aqueous solutions. Discontinuities in these functions might indicate the existence of “higher-order phase transitions”.

The fact that the Arrhenius plots of the d. c. conductivity for various aqueous solutions over temperature show several regions of linear behavior in $\ln(\sigma)$ vs. temperature indicates many relaxation times for some of the systems. The mechanisms which drive the response are not identified at this time. There appear to be discrete levels of structure in the water "cages" formed by the hydrogen bonds which can be characterized as due to polymeric species of water. It is not clear that all of the structural property is attributed to hydrogen bonding in that the hydroxyl OH^- bond may play a role in the structuring.

The Na^+ ion seems to break hydrogen bonds so the structure of the cages should be concentration dependent for this ion. However, it is not clear that there is a preferential bond that the Na^+ ion attacks. This effect is demonstrated by the change in number of linear regions (hence, differing relaxation times) as the NaCl concentration is varied systematically. The sodium may be attaching itself to the OH^- ion in solution in a temporary bond. Other perturbed ions of various masses and charges are being studied to characterize the transport properties of the ions in solution.

In that, the refractive index at microwave frequencies shows a pronounced dependency upon wavelengths, a series of experiments is being conducted over the range of 3 to 35 GHz. to establish further the nature of that dependency by using a resonant microwave cavity spectrometer⁵¹. Experiments on the infrared refractive index of water are also in progress to determine the temperature dependency of the refractive index and to attempt to further characterize the memory effects in the water systems⁵⁰.

APPENDIX

I. A Computer Simulation Model of NaCl Association in Polarizable Water

A general scheme for the reaction of two solutes may be written as

in which RX is the product of a reaction between the ions R^+ and X^- . The intermediate states $R^+ | X^-$ and $R^+ \parallel X^-$ represent a contact ion pair (CIP) and a solvent-separated ion pair (SSIP), respectively. Here the polarizable water model (labeled RPOL water) is used.

A polarizable interaction model (RPOL water model) developed by Dang⁴¹ has three interaction sites and the same rigid tetrahedral geometry as the simple point charge (SPC) models. There are fixed charges and point polarizabilities attached to each atomic site, along with a Lennard-Jones (LJ) interaction centered on the oxygen. Each ion in the aqueous solution simulations is represented similarly by a fixed charge plus point polarizability and a LJ term. The ion and water parameters used in the present study are summarized in Table III. Ion-water and ion-ion cross terms are defined using the usual sum rules. The water parameters are taken from

Table III NaCl aqueous solution parameters for simulation⁴⁸

Model	Atom Type	σ (Å)	ϵ (kcal/mol)	q (e)	α (Å)
SPC/E ⁴²	O	3.166	0.1554	-0.8476	...
	H	...	...	0.4238	...
RPOL	O	3.196	0.1600	-0.7300	0.528
	H	...	...	0.3650	0.170
	Na ⁺	2.350	0.1300	1.0000	0.240
	Cl ⁻	4.450 ^b	0.1000	-1.0000	3.250

Dang ⁴¹ while the procedure for choosing the ion parameters is described below.

The bulk water properties of the RPOL and SPC/E models have been calculated by D.E Smith and L. X. Dang etc ⁴³ from simulations of 216 water molecules in a cubic simulation box at a constant density of 0.997 g cm⁻³. See Table IV.

Table IV Ion-water structural properties. ⁴¹

	RPOL	SPC/E	Experiment
R(Na ⁺ - O), Å	2.33	2.33	2.38, 2.4 ^a
R(Na ⁺ - H), Å	3.00	2.98	...
Na ⁺ - O coordination No.	5.6	5.8	4, 6 ^a
R(Cl ⁻ - O), Å	3.20	3.20	3.1 ± 0.1 ^b
R(Cl ⁻ - H), Å	2.22	2.22	2.28 ± 0.03 ^b
Cl ⁻ - H coordination No.	6.5	6.9	6.4 ± 0.3 ^b

- a. G. W. Neilson and J. E. Enderby, *Annu. Rep. Prog. Chem., Sect. C* 76, 185 (1979)
b. D. H. Powell, G. W. Neilson, and J. E. Enderby, *J. Phys. : Condens. Matter* 5, 5723 (1993)

The total potential energy for the aqueous system is

$$U_{\text{total}} = U_{\text{pair}} + U_{\text{pol}}, \quad (\text{I-2})$$

where the pair-additive part of the potential is a sum of LJ and Coulomb interactions

$$U_{\text{pair}} = \sum_i \sum_j \left\{ 4\epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \right\}, \quad (\text{I-3})$$

The polarization energy is given by

$$U_{\text{pol}} = -\frac{1}{2} \sum_i \mu_i \cdot E_i^0, \quad (\text{I-4})$$

where μ_i is the induced dipole moment on atom site I and E_i^0 is the electric field at site I due to

the fixed charges in the system. The dipole moments are determined at each step in the simulation by iteratively solving the equations

$$\mu_i = \alpha_i E_i \quad (\text{I-5})$$

$$\text{and} \quad E_i = E_i^o + \sum_{i \neq j} \mu_j \cdot T_{ij}^o, \quad (\text{I-6})$$

where α_i is the atomic polarizability and T_{ij} is the dipole tensor.

The study of solvent-averaged forces or potentials of mean force (PMF) has made a significant contribution to the understanding of chemical dynamics in solutions. A knowledge of the PMF allows one to examine in detail the effect of solvent on the solute-solute or ion-ion interactions, and to determine various thermodynamic properties. Because of the fundamental importance of the Na^+ and Cl^- ions in the chemistry and physics of ionic solutions, a number of theoretical and computer simulation of PMF of the Na^+ and Cl^- pair have been undertaken using different potential models.^{44,45} These studies indicate two minima in the PMF. Berkowitz *et al*⁴⁴ report 3.3 and 2.0 kcal/mol. It is of interest to examine the dependence of the water models on the thermodynamic quantities of ionic solutions.

The PMFs of the Na^+ and Cl^- pair using simple point charge (SPC and SPC/E) water models has been used widely in many studies of water and aqueous solution.^{46,47} The PMF was determined using thermodynamic perturbation theory and the molecular dynamics technique. The system studied consists of a sodium ion and a chloride ion immersed in a periodic box of 603 water molecules with box lengths of 31 Å, 24 Å and 24 Å in the x, y and z directions, respectively.⁴⁸ The calculated PMFs display two minima corresponding to contact and solvent-separated ion pairs which are presented in figure 35.

Figure 35. The NaCl potential of mean force in RPOL water (filled circles) and SPC/E water (open Squares). The primitive model predictions are shown for continuum solvents with static dielectric constants corresponding to RPOL(dashed line) water.⁴⁸

II. Thermodynamic Properties

Classical thermodynamics is based on laws of bulk matter, such as the conservation of energy, laws which are independent of the structure of matter. In this appendix some useful equation and properties of molecules are derived. From the macroscopic viewpoint, the Gibbs energy G may be chosen as the primary thermodynamic function. The following relationship are obtained:

Volume	$V = (\partial G / \partial P)_T$	
Entropy	$S = -(\partial G / \partial T)_P$	(II-1)
Enthalpy	$H = G + TS$	
Internal energy	$U = H - PV.$	

For further differentiation

$$\begin{aligned}
 \text{Isopiestic (isobaric) thermal expansivity} \quad \alpha_p &= [\partial(\ln V)/\partial T]_p \\
 \text{Isothermal compressibility} \quad \chi_T &= -[\partial(\ln V)/\partial P]_T \\
 \text{Isopiestic specific heat} \quad C_p &= (\partial H/\partial T)_p \\
 \text{Isochoric specific heat} \quad C_v &= (\partial U/\partial T)_v
 \end{aligned} \tag{II-2}$$

The microscopic approach to thermodynamic properties starting from molecular properties and applying either statistical mechanics or computational methods does not yet reproduce experimental values for liquid water very closely. A thermodynamic description of a substance involves a thermal quantity, such as the enthalpy, as well as the volume. The relationship between C_p and C_v involve only the isothermal compressibility and the isobaric thermal expansion, that has only volume properties:

$$C_p = C_v + T \frac{(\partial V / \partial T)_p^2}{(\partial V / \partial P)_T} \tag{II-3}$$

And the relationship between C_p , density ρ and internal energy U is :

$$C_{p,C_c} = \left(\frac{\partial U}{\partial T} \right)_p + P \frac{\rho}{V} \frac{\partial V}{\partial T} \tag{II-4}$$

It is reported that in dense fluids, that the LL formula also relates the refractive index n to the mass density ρ ²⁵. The density is related to the specific heat $C_{p,Cc}$ at constant pressure p and concentration c , which exhibits an anomaly near the critical point. The relation ρ - $C_{p,Cc}$ can be expressed as ²⁵ (C_c is the critical concentration.)

$$C_{p,Cc} = (T_c \rho^2) (dp/dT) (dT_c/dp)^{-1} \tag{II-5}$$

The specific heat diverges according to²⁶

$$C_{p,Cc} = A t^{-\alpha} + B , \quad (\text{II-6})$$

where $t = (T_c - T)/T_c$ is the reduced temperature, T_c is the critical temperature. The constant B is the sum of critical and noncritical background terms and $\alpha = 0.1$ is a universal critical exponent. Equation (I-5) predicts that there is a critical contribution to the density of the $t^{1-\alpha}$ type.

III. Dielectric Constant and Electric Conductivity

Models for the Molecular Polarizability

The polarization of a collection of atoms or molecules can arise in two ways: (a) the applied field distorts the charge distributions and so produces an induced dipole moment in each molecule; (b) the applied field tends to line up the initially randomly oriented permanent dipole moments of the molecules.

To estimate the induced moments, a simple model of harmonically bound charges (electrons and ions) is considered. Each charge e is bound under the action of a restoring force

$$\mathbf{F} = -m\omega_o^2 \mathbf{x} , \quad (\text{III-1})$$

where m is the mass of the charge, and ω_o the frequency of oscillation about equilibrium. Under the action of an electric field $\mathbf{E}$ the charge is displaced from its equilibrium by an amount $\mathbf{X}$ given by

$$m\omega_o^2 \mathbf{x} = e \mathbf{E} . \quad (\text{III-2})$$

Consequently the induced dipole moment is

$$p_{mol} = eX = \frac{e^2}{m\omega_o^2} E . \quad (\text{III-3})$$

This means that the polarizability is $e^2 / m\omega_o^2$. If there are a set of charges e_i masses m_i and oscillation frequencies ω_i in each molecule, then the molecular polarizability is

$$\gamma_{mol} = \sum_j \frac{e_j^2}{m_j \omega_j^2} . \quad (\text{III-4})$$

The equation of motion for an electron of charge $-e$ bound by a harmonic force (III-1) and acted on by an electric field $E(x, t)$ is given by

$$m \left[\ddot{x} - \gamma \dot{x} + \omega_o^2 x \right] = -eE(x, t) , \quad (\text{III-5})$$

where γ measures the damping force and any magnetic force effects are neglected. Make the approximation that the amplitude of oscillation is small enough that the electric field can be evaluated at the average position of the electron. If the field varies harmonically in time with frequency ω as $e^{i\omega t}$, the dipole moment contributed by one electron is

$$p = -eX = \frac{e^2}{m \omega_o^2 - \omega^2 - i\omega\gamma} E . \quad (\text{III-6})$$

If suppose that there are N molecules per unit volume with Z electrons per molecule, and that, instead of a single binding frequency for all, there are f_i electrons per molecule with binding frequency ω_i and damping constant γ_i , then the dielectric constant, $\epsilon = 1 + 4\pi\eta_e$, is given by

$$\epsilon_{(\omega)} = 1 + \frac{4\pi N e^2}{m} \sum \frac{f_i}{\omega_i^2 - \omega^2 - i\omega\gamma_i} , \quad (\text{III-7})$$

where the oscillator strengths f_i satisfy the sum rule,

$$\sum_i f_i = Z. \quad (\text{III-8})$$

With suitable quantum-mechanical definitions of f_i , γ_i , ω_i , (III-7) is an accurate description of the atomic contribution to the dielectric constant.

Low Frequency Behavior, Electric Conductivity

In the limit $\omega \rightarrow 0$ there is a qualitative difference in the response of the medium depending on whether the lowest resonant frequency is zero or nonzero. Then at $\omega=0$ the molecular polarizability is given by (III-4), corresponds to the limit $\omega = 0$ in (III-7).

If some fraction f_o of the electrons per molecule are “free” in the sense of having $\omega_o = 0$, the dielectric constant is singular at $\omega = 0$. If the contribution of the free electrons is exhibited separately, (III-7) becomes

$$\epsilon(\omega) = \epsilon_o + i \frac{4\pi N e^2 f_o}{m\omega(\gamma_o - i\omega)}, \quad (\text{III-9})$$

where ϵ_o is the contribution of all the other dipoles. From the Maxwell-Ampere equation

$$\nabla \times H = \frac{4\pi}{c} J + \frac{1}{c} \frac{\partial D}{\partial t} \quad (\text{III-10})$$

and Ohm's law, $J = \sigma E$ with harmonic time dependence, have

$$\nabla \times H = -i \frac{\omega}{c} (\epsilon_o + i \frac{4\pi\sigma}{\omega}) E. \quad (\text{III-11})$$

Comparison of (III-9) and (III-11) yields an expression for the electric conductivity

$$\sigma = \frac{f_o N e^2}{m(\gamma_o - i\omega)}. \quad (\text{III-12})$$

High-Frequency Limit, Plasma Frequency

At frequencies far above the highest resonant frequency the dielectric constant takes on the simple form

$$\epsilon(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2}, \quad (\text{III-13})$$

where
$$\omega_p^2 = \frac{4\pi NZe^2}{m}.$$

The frequency ω_p , which depends only on the total number NZ of electrons per unit volume, is called the plasma frequency of the medium.

IV. Data Acquisition Program

```

/*****

```

C++ Program for d. c. Conductivity Data Acquisition

This is a demonstration program to be used with the ML16 A/D board. The program will perform interrupt driven acquisitions on three channels and display the results.

```

*****/

```

```

/* List of all Head files, Pre-compiled headers*/

```

```

#include    <dos.h>
#include    <time.h>                // for getting time
#include    <stdlib.h>
#include    <stdio.h>
#include    <graphics.h>
#include    <fstream.h>             // for input output file, data etc.
#include    <constrea.h>
#include    <string.h>              // for string manipulated
#include    ml16drv.h

```

```

/*Declar the global parameter passing to the driver and data buffer*/

```

```

int    index, status, task, param[8], d[8];
int    DelayConst, SecT, count;
float  m[3000], s[3000], m1[3000], n2[3000], m2, s2;
const  int  chanel1 = 3, chanel2 = 0, chanel3 = 5;
const  float tadj = 0.5;
const  int  flagt = 1, flaga1 = 8, flagx = 0;
const  int  distance=60 , sen=2;

```

```

/*Function prototypes*/

```

```

void  calldriver();                //Checks driver
void  ml16drv (int, int, int );    //Checks for an error code
void  menua10();                   //Test operation

```

```

void  initial0();           //Initial the data array
void  initial1();
void  initial2();
void  DataAqLoop();
void  graphics (float, float,int );    //Plot the data on the screen
int   GetTimeSec();           //Get the current time in second
void  TempControl();          //Thermal control
void  AutoTempControl();      //Automatic temperature control
void  LowTemp();
void  equilT();
void  VoltToTemp();           //Transfer voltage to temperature
void  manaul0();              //Test operation
void  reads0(int,int );
void  reads1(int,int);
void  finalstage ();
void  Request();
void  HeatupTemp();

void main()
{
    char * FileName;
    clrscr();                // clear screen
    initial1();              //Initial the digital output array
    gotoxy ( 10, 1);
    cout <<"===== "<<endl;
    cout << "   Welcome to use the Data Acquisition System   "    <<endl;
    cout << "===== "<<endl;
    cout << "If you what quit the Data Acquisition type QUIT.  "    <<endl;
    cout << "Enter the recorded data file name : "                <<endl;
    cin >> FileName;          //Input data file name

```

```

if ( strcmp ( FileName, "quit" ) == 0)
exit (0);
clrscr();
initial2();          //Initial the data acquisition address
calldriver();
//Setup and initial the machine
mmanual0();          // Test operation
initial0();          // Initial all the data array d[8]
cout << "Enter the time delay constant: "<<endl;
cin >> DelayConst;
DataAqLoop();
}
/* Data acquisition loop for the whole experiments.*/
void DataAqLoop(int DelayConst)
{
clrscr();
count =1;
SecT = GetTimeSec();    // Start time in second
cout << SecT;
int plot;
Request();
delay (1000*DelayConst); //delay DelayConst second time
do{ count++;
reads0(count,plot );
reads1(count,plot);
gotoxy( 1, 1);
cout << count << " " << s[count]<< " " << m[count]<<endl;
} while ( getch() !='q');
if (count >3000)

```

```

        finalstage ();
        else
            Request();
    }
/* plot the data graphic for temperature reading*/
void reads0(int count, int ptot)
{
    int dist;
    task = 1;
    param[1] = chanel1;
    param[2] = 1;
    calldriver();
    SecT=GetTimeSec();           //Read the current time by second
    s[count] = SecT;
    m1[count] = ptot;
    m2 = m1[count];
    s2 = s[count];
    dist = distance + 30;        // distance for shift graphics
    graphics(s2, m2,dist);
}
/* Plot the data for Voltage*/
void reads1(int count, int ptot)
{
    int dist;
    task = 1;
    param[1] = chanel2;
    param[2] = 1;
    calldriver();
    n2[count] = ptot;
    SecT = GetTimeSec();

```

```

    s [count] = SecT;
    m2 = n2[count];
    s2 = s [count];
    dist = distance + 50;
    graphics(s2,m2, dist);
}

/*Initial the data array  and the data buffer*/
void  initial0()
{
    count = 0;
    for (int i = 1; i <= 3000 ; i++)
    {
        m1[i] = 0;      // voltage for temperature
        n2[i] = 0;      // voltage for conductivity
        m [i] = 0;      // voltage for temperature2
        s[i]   = 0;      // time in second for time record;
    }
}

void  initial1 ()          //Initial the data buffer
{
    int d[10];
    for ( int i=0; i<10; i++)
        d[i]=0;
}

void  initial2()           //Initial the DAC card
{
    task = 0;              // Setup driver
    param[1] = &H300;      // Set Base Address to 300 hex
    param[2] = 0;          // differential mode inputs, 1 would be S/E
    param[3] = 1;          // bipolar mode, 0 would be unipolar
    param[4] = 4;          // IRQ line jumped on board
}

```

```

/* store the data to file*/
void finalstag(char * Filename)
{
    char * file2, *request;
    clrscr();
    gotoxy ( 1, 1);
    cout<< "Recording the data to the file, wait .....";
    file2 = strcat (Filename, ".dat");
    ofstream OutDataFile;
    OutDataFile.open ( file2, ios::app);
    cout << *file2 ;
    for (int i = 1; i<= count; i++)
        OutDataFile << s[i]<<' '<< m1[i]<<' '<< n2[i]<<endl;
    //count2 ++;
    //AutoTempControl();
    task = 4;
    initial0();
    cout << "Thank you for using data acquisition system"<<endl;
    cout << "Do you want to continue experiment? Yes or exit";
    Request();
}

void Request()
{
    char *request;
    cout << "Enter any key for processing data acquisition "<<endl;
    cout << "'quit' to quit recording, 'Exit' to exit system"<<endl;
    cin.getline(request, 80, '\n');
    if ( strcmp ( request, "quit" ) == 0)
        finalstage();
    else if ( strcmp (request, "exit") == 0)

```



```

        exit (0);
    else    {
        count =0;
        DataAqLoop();
    }
}

/*      Final stage for asking request
void DoneRecord()
    { char *input;
    clrscr();
    cout << "Do you want to continue data acquisition? "<<endl;
    cin.getline(input, 80, '\n');
    if ( strcmp ( input, "yes") == 0 )
        DataAqLoop();
    else if (strcmp (input, "no")==0)
        exit(0);
    }

*/

/*Plot the data on the screen*/
void graphics(float s2, float m2, int dist)
{
    int driver, mode;
    driver = DETECT;                // set to best graphics mode
    initgraph(&driver, &mode, "f:\\dos\\programm\\borlandc\\bgi");
    //initgraph(&driver, &mode, "e:\\prog\\borlandc\\bgi");
    float x2;
    int scr = 1200;
    if (( s2 - int(s2 / scr) * scr) == 0.0 ) // if s2 is integer
        clrscr();

```

```

else
x2 = s2 - int(s2 / scr) * scr;
lineto (x2 / 4, m2 / 1.5 + dist);
gotoxy(30,22);
cout <<"Press any key to return main menu if you want quit graphics";
getch();                // wait for key press
closegraph();           // close graphics system
}
/* Get the current time in second*/
int GetTimeSec()
{
    time_t t, t0;
    t0= time(NULL);
    t=t0%86400;    //convert 24 hrs to second
    return t;
}
void calldriver(int sen )
{
    int ptot;
    ptot = 0;
    for(int i = 1 ; i<= sen; i++)
    {
        ml16drv(task, param[1], status);
        if ( task == 2)
            param[3] = param[1];
        ptot = ptot + param[3];
    }
    ptot = ptot / sen;
    if ( status > 0 )    // an error has occurred
    {cout << "A status error code of"<< status<< " was detected.";
    cout << endl;

```

```

        cout << "Program terminated." <<endl;
    }
}

/*Test operation manually*/
void manual0()
{
    task = 4;
    for (int i = 0; i<= 7; i++)
        d[i] = 0;
    TempControl();
    clrscr();
    cout << "Please key the order using the first Letter " <<endl;
    cout << "H for heat up temperature" <<endl;
    cout << "L for cool down temperature" <<endl;
    cout << "E for equil temperature" <<endl;
    cout << "Q to exit" <<endl;
    char a;
    cout << "enter the request, H,L,E or Q"<<endl;
    //a = getch();
    switch(getch())
    {
        case 'H':    HeatupTemp(); break;
        case 'L':    LowTemp();    break;
        case 'E':    equilT();     break;
        case 'Q':    exit(1);
    }
}

```

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