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# The temperature dependency of some of the thermodynamical properties of aqueous binary mixture systems

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**Abstract.** The temperature dependences of the indexes of refraction of aqueous binary mixtures of water and ethyl alcohol ( $C_2H_5OH$ ) were investigated to study hydrogen bonding by using a modified Michelson interferometer. The temperature range  $278 \leq T \leq 353$  K for aqueous solutions of 100, 75, 65, 50, 25, 10 and 0 volume per cent of ethyl alcohol was studied.

Cycling of the temperature in increasing and decreasing directions showed hysteresis in the cycling for periods of 7000 s or less. The data are discussed and compared with the Lorentz–Lorenz (L–L) formula and the mixing rule. A formula was derived with a temperature dependency on the mole index of refraction  $A(T)$  which gives a fit of the experimental data better than that with the simplified L–L relation.

The data for the index of refraction, specific heat and d.c. conductivity were used to obtain a correlation between the hydrogen bond structure and a systematic departure in the data from an assumed mathematical curve for each of these quantities.

## 1. Introduction

Studies of aqueous binary mixtures of hydrogen-bonded liquids are of considerable interest [1, 2] as regards determining the nature of the solute–solvent interaction. Binary mixtures with water display unique physical, chemical and biological properties which seem to be related to the high density of hydrogen bonds in water.

An essential assumption in the model is that all of the hydrogen bonds in the liquid may remain intact and 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 in which hydrogen bonding dominates depend upon the energetics of the bending and stretching modes of the hydrogen bonds. These properties also depend upon the intramolecular and intermolecular vibration frequencies, which can be considerably altered by the deformations of the hydrogen bonds [3].

Sorensen has examined several aqueous solutions in an effort to understand solute–solvent interaction and some thermodynamic properties (see [4–6]). Some properties of aqueous solutions which show anomalous behaviour are 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] published results on the dependence of wavelength, temperature and density on the index of refraction of water. Empirical equations used to describe the temperature dependence of reactions

in water may be 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 not elucidate the effect entirely. The specific solvation changes with temperature can be detected by measuring the reaction rates over narrow intervals (0.1–0.5 °C) or for continuous changes of the temperature in the temperature region chosen for study.

The index of refraction and the density of aqueous water–alcohol systems at different concentrations over the temperature range  $278 \leq T \leq 353$  K were chosen for study in an effort to understand the solute–solvent interaction. Conductivity measurements (d.c.) were made over the temperature range  $273 \leq T \leq 363$  K of aqueous solutions of NaCl at different concentrations, to establish the range of temperature that favoured the formation of hydrogen bonding in these aqueous systems.

The refractive index is expected to show ‘intrinsic’ critical anomalies near 4 °C, the temperature at which the density of water is at its maximum, near 30 °C, the temperature at which the specific heat is at its minimum, near 50 °C, where the bulk modulus has a minimum, and near 75–80 °C, the temperature at which the sound velocity is at its maximum. The anomalies appear to be very weak and difficult to assign. The relationship between the refractive index and density may not be straightforward, and a high degree of precision in measurement is needed. In particular, in the vicinity of the temperatures given above, careful analysis is demanded. Our data indicate that the simplest formulation of the Lorentz–Lorenz (L–L) formula for testing the dependence of the refractive index of liquids on the influencing parameters ( $\lambda$ ,  $\rho$ ,  $T$ ) does not appear to give complete results. The method of data analysis used can play a major role as regards detecting some of the minor departures that seem to reflect changes in microscopic properties of the solutions.

In this work, measurements were made on the index of refraction and density as a function of temperature for a wide range of concentrations of water and ethyl alcohol. A modified Michelson interferometer was used to obtain the fringe patterns and to study the index of refraction of the aqueous water–alcohol systems at different concentrations over the total temperature range  $278 \leq T \leq 353$  K to test for any anomalies in the cycles. Attempts were made to determine the nature of the solvent–solute interaction through any changes that were found in the index of refraction as the temperature of each system was cycled.

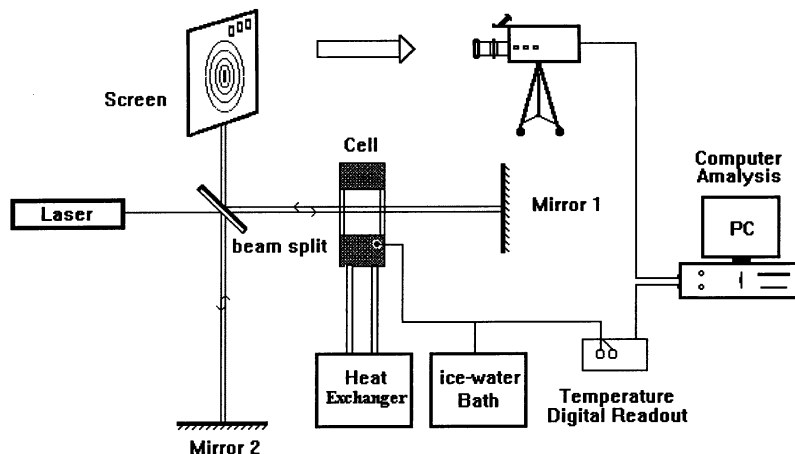
Data available for sodium light (wavelengths 5890 and 5896 Å) showed that the modified L–L formula gives a good fit of these data for the index of refraction of water [9] when the equation takes into consideration the effect of the density of the liquid  $\rho$ . An experiment was set up to explore the index of refraction of water for the He–Ne laser line (wavelength 6328 Å) to compare the two results. Trends in the data similar to those found for the sodium doublet line were found at this wavelength. There was some evidence of hysteresis in the cycle, when the temperature was cycled from low to high and then from high to low values, if the time interval for the cycle was shorter than 7000 s. Results from earlier work [12] indicated that the range of temperature should be divided into two intervals,  $273 \leq T \leq 322$  K and  $322 \leq T \leq 373$  K, to fully explore the behaviour of the aqueous systems.

Several functional forms were chosen to fit the data. Linear and quadratic forms did not give the best fits for all of the data. Tests for departure of the data from predicted curves were made to establish any systematic variations that lie outside the expected errors in the data. Analysis of the experimental uncertainty in the data showed that the condition expected for  $\lambda = 6328$  Å,  $L_0$  (cell length) = 1 cm and an error of one in fringe count would give an optimum error of  $\Delta n < 3 \times 10^{-4}$  in the index of refraction. The systematic departures in the experimental data are  $\Delta n > 9 \times 10^{-4}$ , a factor more than  $3 \times$  the expected

error. This larger value was assumed to be due to systematic changes in the system rather than due to random fluctuations in the data.

The signal from the thermocouple was magnified by an op-amp. The voltage range was 0 to 5.000 V for a temperature range of 0 °C to 100 °C. The digital signal output was stable to better than 1 mV. Thus, the temperature could be measured to better than 0.1 °C, sufficiently accurately for this investigation.

The microwave data from the investigations of Grant and Shack [10] and Collie *et al* [11] were analysed for characteristic regions of behaviour of the dielectric response of water over the frequency range  $3 \leq f \leq 35$  GHz [10, 11]. Two regions of temperature behaviour over the frequency range seem to appear.



**Figure 1.** A diagram of the experimental apparatus used to collect the index of refraction data for binary aqueous mixtures.

Another part of this work was an investigation of the d.c. conductivity of aqueous solutions of NaCl at various concentrations over the range of temperatures  $273 \leq T \leq 363$  K to try to understand better the transport properties of the system. The water system has been assumed to exhibit a cage-like structure [12] which appears to be dependent on the solute concentration over the range of temperature  $273 \leq T \leq 323$  K. This is evident from the nearly constant slope of the Arrhenius plot  $\ln(\text{conductivity})$  versus  $1/T$  of the data over that range. For the lower range of temperatures,  $273 \leq T \leq 323$  K, the slope of the Arrhenius plot varied by more than one order of magnitude for the concentration levels studied, whereas over the upper range of temperature the slope of the Arrhenius plots varied by only 5%. There appear to be characteristic levels of structure in the water ‘cage’ formed by the hydrogen bonds which can be characterized as probably due to polymeric species of water.

## 2. Experimental methods

A block diagram of the apparatus used to study the index of refraction 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<sup>3</sup> 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 obtained. The internal clock of the camera was displayed on the screen, as well, to establish the time interval for cycling. 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<sup>3</sup>. Calibration for density was made with pure water in the temperature range 273 K to 373 K. Highly accurate densities above freezing for the water and ethanol solutions are available in the literature [13, 14], but density measurements over the range of temperature studied were made for each solution for completeness.

The temperature was measured in a standard way by using an amplified voltage output from a calibrated 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 ensure stability during the extended measurements. The temperature is read as voltage to an accuracy better than 1 mV and converted through software in the computer program to a temperature reading.

Data runs were conducted over fixed time spans of time of 2000 and 7000 s, so comparisons could then be made for the dependency of the data on mixture ratios under the same conditions of time.

The experimental apparatus for the conductivity measurement consists of a standard technique with standard equipment described by Roberts *et al* [12]. Electrodes separated by a fixed distance were immersed in the solution and the conductivity measured across the spacing. The temperature was 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.

### 3. Data analysis

The determination of the index of refraction can be made by counting the changes of the interference fringes as the temperature in 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

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

where  $\alpha$  is the coefficient of thermal expansion for the metal of which the cell is constructed and for the liquid tested,  $\beta$  is a modified constant and  $\Delta T$  is the change in temperature. Because the coefficient of thermal expansion for the metal is constant, the major thermal expansion to be considered is that for the liquid. The change in path length due to the metal expansion can be ignored for the range of temperatures studied and the changes in volume accounted for in the density variation with temperature.

The index of refraction for the wave is more dependent upon 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  $\rho$ .

For a uniform fluid the interparticle distances are assumed to vary as  $\rho^{-1/3}$ , irrespective of temperature [15]. Thus, 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

$$\begin{aligned} \rho = & [999.8676 + 17.801\,161T - 0.007\,9425T^2 - 52.563\,28 \times 10^{-6}T^3 \\ & + 137.6891 \times 10^{-9}T^4 - 364.4647 \times 10^{-12}T^5]/[1 + 17.735\,44 \times 10^{-3}]. \end{aligned} \quad (3)$$

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

$$2n(T)L(T) - 2n(0)L(0) = \Delta m \lambda \quad (4)$$

where  $n(T)$  is the index of refraction at a temperature  $T$  and  $n(0)$  is the initial index of refraction at a temperature  $T_0$ ,  $L(T)$  is the effective path length through which the light passes at temperature  $T$ ,  $\Delta m$  is the fringe change due to the index of refraction, and  $\lambda$  is the wavelength of the light. In principle, from a measurement of  $\Delta m$  and knowing  $L(T)$  and the wavelength  $\lambda$ , we can determine  $n(T)$ .

Experimental data for each time interval were obtained by counting the fringe change as the temperature of the cell was changed. When the index of refraction 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  $\Delta m$  is the change in fringes,  $\lambda$  is the wavelength,  $L_0$  is the original length and the effective length is given by equation (3). Combining equation (5) with equation (4) the formula for the index of refraction is

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

The index of refraction 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 2 show that water exhibits two characteristic regions of behaviour, one which shows a rather strong frequency dependence on the dielectric response and another, a higher-temperature region, which appears to have only a small frequency dependency on the dielectric response. It is assumed that the index of refraction will respond in a similar way for binary water systems.

Experimental data for the index of refraction of pure water for the Na doublet spectral component are given in the literature [9]. The data show a very good fit to the L-L formula. However, when the differences between the data and the L-L curve are plotted, systematic departures appear in the lower-temperature regions, near 34 °C, and in the higher-temperature region, near 85 °C. The differences are small and show non-random departures of the data that may indicate meaningful fluctuation in the index of refraction over temperature. The departures of the data from an assumed function are more than three times what is expected for random fluctuations. The nature of these fluctuations is assumed to reside in how clusters form due to hydrogen bonding in the mixtures [16, 17].

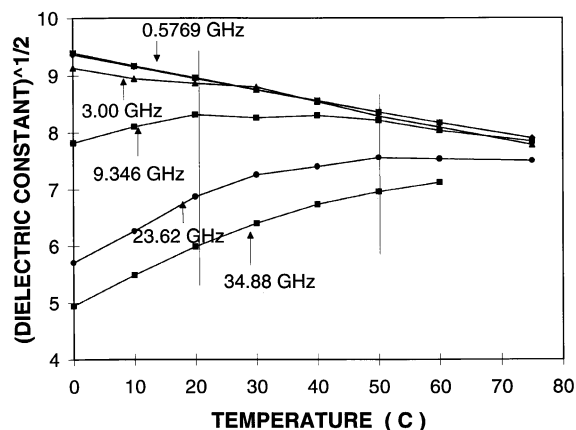


Figure 2. A plot of the dielectric response versus temperature and the frequency dependence of pure water at microwave frequencies (references [10] and [11]).

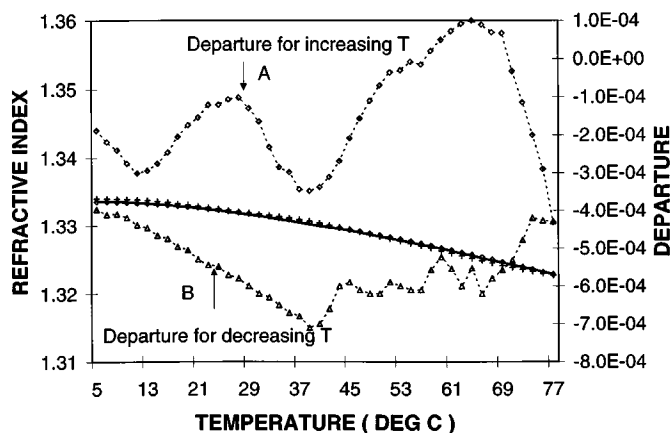


Figure 3. A plot of the refractive index of pure water for He-Ne laser light and its departure from the modified L-L equation (bold line). Curve A is the departure for increasing temperature and curve B is the departure for decreasing temperature.

Similar trends in the data were found at the wavelength of the He-Ne laser line, with more surprising results: the evidence of hysteresis in the cycle, when the temperature was cycled from low to high and then from high to low values for total time intervals shorter than 7000 s. (See figure 3.)

Arrhenius plots were used in previous conductivity measurement work on pure water and aqueous NaCl solutions to obtain a value of  $2.7 \text{ kcal mol}^{-1}$  for the hydrogen bonding within pure water [12]. There was evidence that showed hydrogen bonding and clustering for  $273 \leq T \leq 323 \text{ K}$  that was different from that for  $323 \leq T \leq 373 \text{ K}$ . This experiment was devised to test for changes in properties of the aqueous systems that may be determined through changes in the index of refraction to compare the two results.

Experiments on the water-alcohol mixture were conducted for temperatures of  $0 \text{ }^\circ\text{C}$  to  $70 \text{ }^\circ\text{C}$ . The temperature was cycled from lower to higher and then from higher to lower temperatures. Under these conditions, the system did not respond in the same way for

increasing to decreasing and then decreasing to increasing values of temperatures, except in the 50% alcohol and 50% water mixtures, for time intervals shorter than 7000 s. When the water systems were elevated above 323 K, the index of refraction curves showed hysteresis over the complete cycle for 7000 s or less. The presence of the intermolecular alcohol molecules within the bath of water molecules seems to inhibit the hydrogen bond associations for elevation of the temperature above  $T = 60\text{ }^\circ\text{C}$ .

The indexes of refraction for a spectral line in helium (7065.2 Å), mercury vapour (4446.6 Å) and the sodium doublet (5893.2 Å) show a very close fit of the index of refraction data to a function of the density. The relationship that gives a good fit, with no physical meaning ascribed to it, is given by

$$n(T) = \text{constant} \times [\rho(T)]^{1/k} \tag{7}$$

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

The difference between the data points and values calculated from the L-L formula are improved by the modified L-L equation

$$n(T) = [1 + 2A(T)\rho(T)/W]/[1 - A(T)\rho(T)/W]^{0.5} \tag{8}$$

where  $A$  is the mole index of refraction,  $\rho(T)$  is the temperature-dependent density of the liquid and  $W$  is the molecular weight of the systems. The form of the mole index of refraction  $A(T)$  is expressed in the form of an exponential as

$$A(T) = A_0 e^{b'/(T+273.14)} \tag{9}$$

$A_0$  is chosen to give 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.

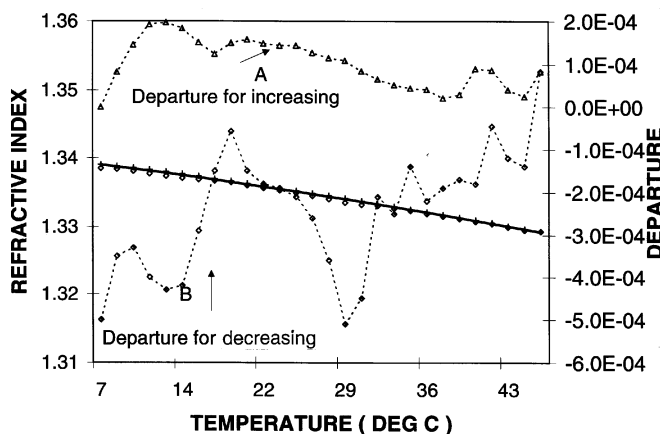
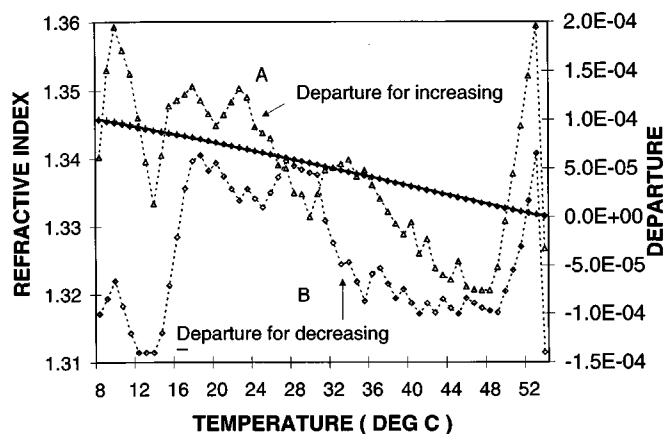


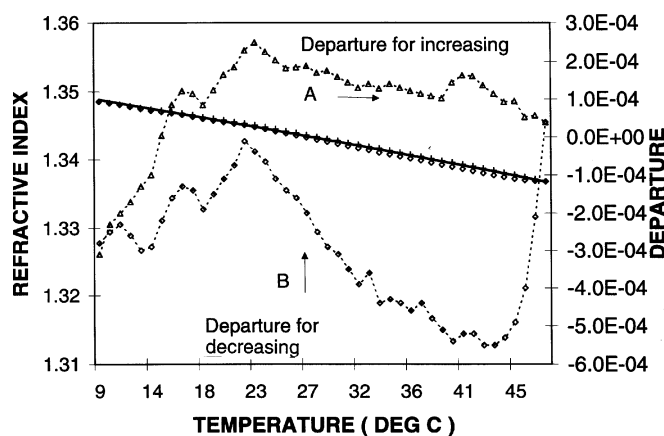
Figure 4. A plot of the experimental data for the index of refraction for decreasing and increasing temperature for a mixture of 25% ethyl alcohol and 75% water and the change in the index of refraction relative to the modified L-L equation for the 6328 Å line of the He-Ne laser light.

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 (8). There are systematic departures in the differences between the experimental data and the values predicted by equation (5). (See figures 4, 5 and 6.) In the mixture that is 50% ethyl alcohol and 50% water (figure 5), the general trends for both increasing and decreasing temperature are approximately the same in structure. This trend was not found in the other mix ratios.





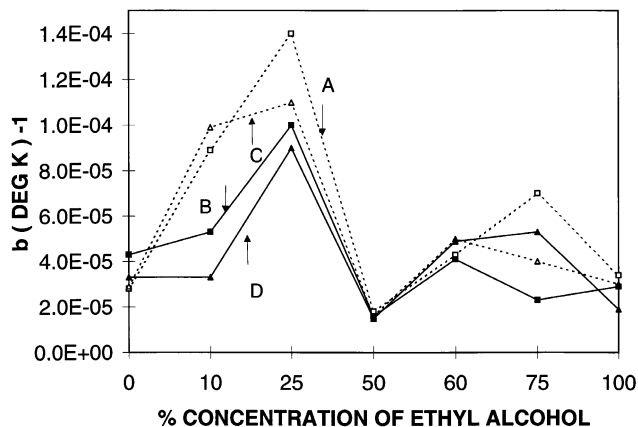
**Figure 5.** A plot of the experimental data for the index of refraction for decreasing and increasing temperature for a mixture of 50% ethyl alcohol and 50% water, and the change in the index of refraction relative to the modified L-L equation for the 6328 Å line of the He-Ne laser light.



**Figure 6.** A plot of the experimental data for the index of refraction for decreasing and increasing temperature for a mixture of 60% ethyl alcohol and 40% water and the change in the index of refraction relative to the modified L-L equation for the 6328 Å line of the He-Ne laser light.

The data obtained on the electrical conductivity of alcohol-water mixes showed similar hysteresis properties when conductivity was measured over temperature and the time intervals were shorter than 7000 s. Arrhenius plots for pure alcohol and pure water showed significant differences as the temperature was varied. 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 behaviour of the index of refraction for light with changes of the mix ratios.

When the molecular mix is varied from pure water to 50% alcohol, the value of  $b'$  in equation (9) increases and decreases systematically for both increasing and decreasing cycles of the temperature. Above 50% concentration of ethyl alcohol, there is an abrupt drop in the value of  $b'$  (see figure 7) 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



**Figure 7.** A plot of  $b$  versus the concentration of ethyl alcohol for aqueous solutions. A and C are for time intervals of 2000 s and B and D are for time intervals of 7000 s for the complete cycle. The temperature was cycled from low to high and then from high to low values.

ethyl alcohol which offers shielding of the water molecules.

The process of reassociation of the hydrogen bonds with the lowering of the temperature may not recycle over the same statistical path as arises when the bonds are disassociated. This effect may explain the asymmetrical behaviour of the temperature cycles for varying time intervals. The non-symmetrical cycling may also arise in the viscosity change with temperature. Sorensen has shown that the dependence of the viscosity on temperature for binary systems is not that expected for a simple model of mixing two members to produce a resultant viscosity [6]. The change in viscosity of the solutions will affect the speed of the wave through the medium and can correlate with the change in index of refraction of the solutions.

Sorensen has found that binary solutions of water and ethanol and water and hydrazine showed larger viscosity than expected from averaging the viscosity of the two members of the mixture [6]. He attributed this property to a change in ordering of the system in this mixture to favour a better cage-like structure in water. A maximum viscosity enhancement was observed for 17 mol% by Sorensen (see [5]). For our solution of 10 vol% or 3.3 mol% a large hysteresis effect was observed.

Ojamäe summarized the results of a study on the water molecule in solid, gas and liquid surroundings in a dissertation [31]. He proposes 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. 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. Ojamäe proposed that the the O–O distance of separation is around 2.84 Å and that there may be four or slightly more next-nearest neighbours. This cage-like structure may be broken by a high temperature or by the presence of molecules other than those of water in the environment.

#### 4. Some basic properties of pure water

Water has been studied by almost all available techniques [18–26]. In spite of the large 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 the mixture and the 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 proposed by Röntgen [30] in 1892. The continuous model originated from the x-ray structure of water given by Bernal and Fowler [37], 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 were 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 probably with broken H bonds which increase in number with rising temperature. By considering from the anomalies in the physical parameters of liquid water [27], including the specific heat, viscosity, compressibility, index of refraction, and density, the two-states model may be supported.

Data for pure water show that the specific heat 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]

$$C_p(T) = 4.1855\{0.996185 + 0.0002874[(T + 100)/100]^{5.26} + 0.01116 \times 10^{-0.0367}\} \quad (10)$$

and

$$dC_p/dT = 6.317 \times 10^{-5}[(T + 100)/100]^{4.26} + 0.003872 \times 10^{-0.0367}. \quad (11)$$

The microwave data shown in figure 3 show that water exhibits some characteristic behaviour over frequency—one type for  $273 \leq T \leq 323$  K and another for  $323 \leq T \leq 373$  K. The higher-temperature region appears to have little frequency dependency on the dielectric response. The index of refraction may respond 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 the temperature and density. The viscosity is often represented by the free-volume equation [16]

$$\eta = \eta'_0 \exp[-\Delta\epsilon'_\eta/(T + C)] \quad (12)$$

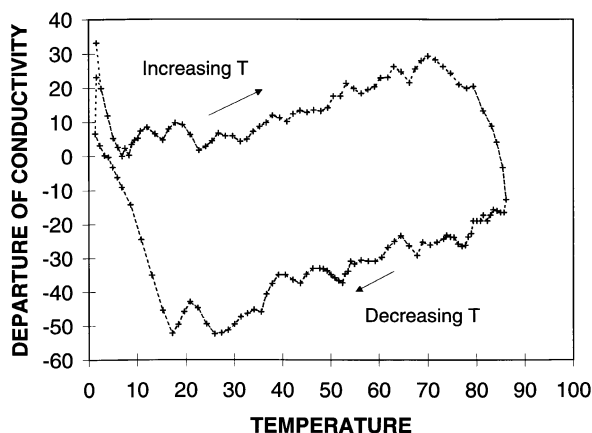
and  $T = -C$  is the glass transition temperature. The constants for this equation are  $A = -1.64779$ ,  $B = 262.37$ , and  $C = -133.98$  K, thus estimating the glass transition temperature of water as  $-133$  K. The departure of the data from the free-volume equation shows some structure near the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

Data available for the index of refraction for sodium light (wavelengths 5890 and 5896 Å) and He–Ne laser light indicate a systematic departure from the modified L–L formula fit that has features near 35 °C. The L–L equation takes into consideration the effect of the density of the liquid  $\rho$ , so any departure should appear in other physical properties of the system that depend upon density. Characteristic properties appear in the density differences when Kell's equation, equation (3), is assumed and departures from that equation are considered, in the temperature range 0–100 °C. These departures are near 17, 35 and 82 °C. The experiment made to explore this effect for the He–Ne laser line (wavelength 6328 Å) verified what the data of others had shown. One effect that does not have an explanation is that of hysteresis in the cycle, when the temperature is cycled from low to high and then from high to low values in time intervals shorter than 7000 s.

Most of the data investigated for water in the temperature range 0–50 °C, such as the specific heat, density, viscosity, microwave dielectric response, and index of refraction, seem

to support the hypothesis that some kinds of higher-order transition are taking place. We have tentatively assumed these to be caused by transitions among 5-, 4-, 3- and 2-coordinate, H-bonded assemblies of water with slightly different enthalpies and entropies. Our studies of the index of refraction in aqueous solutions measured at only half-degree intervals support the hypothesis that the H-bond structure of water possesses inherent instabilities in the temperature interval 0–50 °C.

The index of refraction of water is characterized approximately as follows. At very low frequencies near the microwave region,  $n(w) \approx 9$ , a value which arises from the partial orientation of the permanent dipole moments of the water molecules. Above  $10^{10}$  Hz the response falls relatively smoothly to the structure in the infrared. In the visible region,  $n(w) \approx 1.34$  with little variation. Then, in the ultraviolet region there is more structure. Above  $6 \times 10^{15}$  Hz there are no data on the real part of the index of refraction [32].



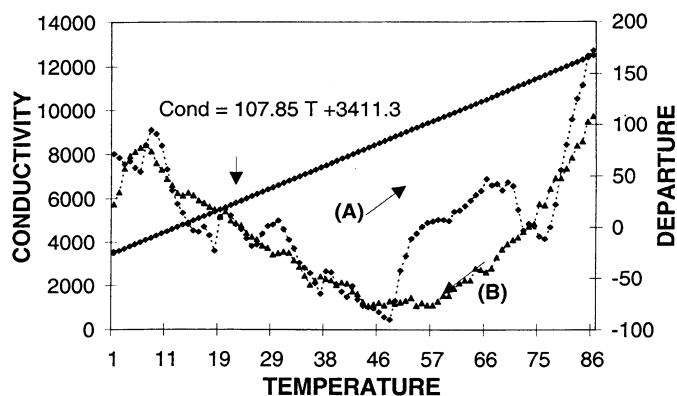
**Figure 8.** A plot of the departure of the d.c. conductivity from a linear fit of the d.c. conductivity versus temperature for a solution of  $3.08 \text{ g l}^{-1}$  of NaCl dissolved in one litre of pure water for temperature cycling. The arrows indicate the order of cycling of the temperature.

The index of refraction of media has been investigated by using several techniques [18–20]: the prism, double-slit Rayleigh refractometer, Fabry–Perot interferometer, Michelson interferometer, differential interferometric and two-wavelength interferometric techniques. We chose the Michelson interferometer technique as the one best suited for studying the index of refraction of aqueous water–alcohol systems.

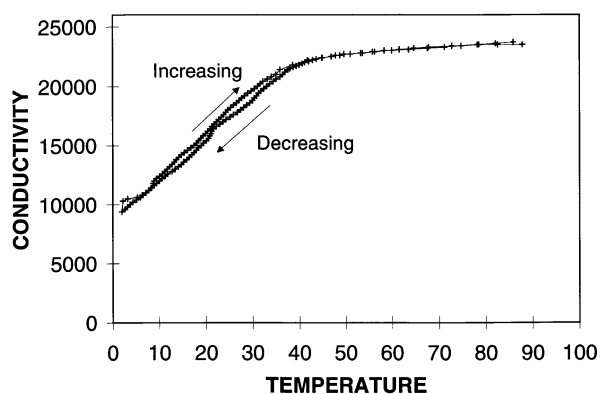
### 5. Determination of hydrogen bonding with conductivity

The d.c. conductivities of aqueous solutions of NaCl and aqueous systems of ethyl alcohol were measured. The curves for conductivity versus temperature are assumed to be linear. The departures of the electrical conductivities from a linear plot are given in figure 8. The data show asymmetrical properties with temperature cycling. Some ‘memory’ of the cycle seems to persist for samples with low concentration as they were cycled consecutively for time intervals shorter than 2000 s. It appears that the water samples retain some residual property embedded in them by the heat energy. As the concentration is increased to  $24.6 \text{ g l}^{-1}$  the memory of the cycles disappears; see figure 9. Sodium ions are assumed to disrupt the hydrogen bonds [12].

Data show that as the concentration of NaCl is increased, there is a large change of



**Figure 9.** A plot of the d.c. conductivity versus temperature and the departure (A and B) of the d.c. conductivity from a linear fit of the d.c. conductivity versus temperature for a solution of  $24.6 \text{ g l}^{-1}$  of NaCl dissolved in one litre of pure water for temperature cycling. The arrows indicate the direction of cycling of the temperature.



**Figure 10.** A plot of the d.c. conductivity versus temperature for a solution of  $290 \text{ g l}^{-1}$  of NaCl dissolved in one litre of pure water for temperature cycling. The arrows indicate the direction of cycling of the temperature.

'slope' for the Arrhenius plot in the temperature region below 323 K with a transition of the slope near 45–50 °C. See figure 10. It appears that in the low-temperature region water has different transport properties, which the  $\text{Na}^+$  and  $\text{Cl}^-$  ions change more than they do for the higher-temperature range, above 323 K. The linear regions are assumed to correspond to regions in which the relaxation processes are different. The system may be treated as having several relaxation rates with rate processes controlled by temperature.

## 6. Summary and conclusions

Uncertainties in the measurements of temperature and the index of refraction do not seem to account for the systematic differences between the measured values and the values calculated using acceptable models. From these differences, temperatures have been identified that appear to correlate with basic changes in the aqueous systems studied. The characteristic

behaviour is assumed to correlate with changes in the coordination numbers for water molecules and the environment. The nature of the molecular correlation seemingly should be independent of the direction in which the temperature is cycled over the samples. If we assume that the breaking and bending of hydrogen bonds in cycling from a lower to a higher temperature is achieved when the energy  $kT$  is high enough to overcome a barrier, the re-establishment of this barrier when the temperature is cycled in the decreasing direction may require a finite time for reassociation of the molecules. This reassembling of the ensemble of water molecules to the original statistical distributions may take enough time to be measurable—hence, the hysteresis effect observed. We are developing a set of experiments to try to establish a time dependency of the amount of hysteresis observed for the systems cycled in a time of less than 7000 s.

In figure 2 the microwave data indicate a frequency dependence of the index of refraction for  $T < 60$  °C. The limiting temperature appears to be about  $T = 80$  °C, the temperature at which the velocity of sound in water is a maximum [33].

The index of refraction for visible spectral components in each water sample show features in the departure that are not as random as is expected for a collection of data points. The features in these curves were assumed to be indicative of changes in composition of the aqueous systems as the temperature is cycled.

Data for 10%, 25%, 75% and 100% ethyl alcohol aqueous systems show asymmetry in the temperature cycles for 2000 s or less as shown by plotting differences in the data points and the values predicted by the L–L equation. In the 50% mixtures of alcohol and water, the patterns are essentially the same for both increasing and decreasing temperature. See figure 5. These trends could not be detected without analysing the differences.

When differences between the data points and the L–L equation are obtained through plots of differences versus temperature for the pure water samples, obvious structure is seen with large data departures near 13 °C, 37 °C and 75 °C. When the samples are made of 100% ethyl alcohol, some peaks appear at around 17 °C and 50 °C. Data presented by Sorensen [34] for Raman spectra of methyl alcohol (0.1 mol% to 10 mol%) and water mixtures show some fluctuations of the Raman line intensities with changing temperature. The fluctuations observed by us may be due to the OH oscillators in the system. Some of the fluctuations may be attributed to tetrameric and pentameric species forming in the water systems [35, 36].

The data in figure 7 indicate that  $b'$  changes as the alcohol concentration is changed. This dependency may be due to a change in structure of the water and alcohol molecules as the solvent–solute ratio is changed. This effect seems to show up in several physical properties of aqueous systems.

When the specific heat is fitted to a quadratic function and differences between this curve and the experimental data are determined, there is structure near 17 °C, 35 °C and 85 °C. If a plot is made of the difference between the index of refraction and the L–L equation for the He–Ne laser line, structure is found near 13 °C, 37 °C and 80 °C. Two of these regions of structure in the data departure agree with the minimum in the specific heat near 30 °C and a maximum in the sound velocity near 80 °C. In addition, the density data show departures from the Kell equation near 17 °C, 37 °C and 85 °C. If the data for viscosity are analysed by obtaining differences between the viscosity equation and the data points for viscosity, a systematic departure is found in the viscosity near 37 °C.

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 of the data from assumed plots of thermodynamic properties occur. Since OH is in all of the systems studied, it seems reasonable to conclude that the OH oscillators play a major role in the systematic departures of the data at these

temperatures.

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 13–17 °C does not correlate with a known thermodynamic property.

Work is being conducted on D<sub>2</sub>O systems to study any isotopic effects and to obtain data to determine whether the effects observed in H<sub>2</sub>O persist in the D<sub>2</sub>O systems.

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