Chapter 6

6.A  A Critical experimental study of intermolecular association in monohydroxy alcohols

6.A.1 Introduction

The dielectric behavior of liquids especially monohydroxy alcohols has been the subject of much experimentation and theoretical speculation. The alcohols have attracted a great deal of interest in study of their dielectric dispersion. In some of the first significant work to follow Drude's pioneering measurement, Mizushima (1926) examined the alcohols but great deal of intensive study made by Cole et al. thereby provided major contributions which throw light not only on dielectric absorptions but also on some general aspects of liquid state. It was observed that the main relaxation in alcohols contrary to other liquids can be represented by a single relaxation time i.e. they follow the Debye prediction. It was further realized that the additional relaxation processes exist at frequencies above the main Debye type relaxation and in some cases they can be resolved. Later Litowitz and McDuffie made an interesting observation as regarding their dielectric and mechanical relaxation behavior. They noticed that in monohydroxy liquids, the dielectric relaxation time is larger than the mechanical relaxation time by a factor of a hundred to few thousands. If one defines the dielectric \( T_g \) as the temperature where the dielectric relaxation time is of the order of experimental time scale (200 s) one should observe \( T_g(D) \) to be greater than \( T_g \) for monohydroxy alcohols.

There are three major aspects of dielectric studies of the alcohols. First, the precise representation of the form of the main absorptions; second, the question of the occurrence of subsidiary high frequency processes and third the temperature behavior of the absorptions. Alcohols are reluctant to crystallize; so they can be studied in the liquid
(and supercooled states) over a wide temperature range. Dannhausser\textsuperscript{5,6} and others studied the isomeric octyl-alcohols. Dannhausser made systematic studies on the temperature dependence of the relative permittivity of eight lower alcohols and eight isomeric alcohols and explained the results in terms of the alcohol association into highly polar linear chain \(n\)-mers (\(n = 1, 2, 3, \ldots\)) and ring dimers having small or zero dipole moment. Johari and Goldstein\textsuperscript{12} discussed the importance of mechanical measurements near the glass transition temperature.

Alcohols generally exhibit three relaxation processes at room temperature. Process I shows Debye relaxation and process II shows the non-Debye relaxation. Along with these two processes they show a sub-\(T_g\) relaxation. Though a lot of work has been done on alcohols still it is not clear how these processes terminate as the liquid is supercooled to form the glass. For monoalcohols, the dielectric spectra shows one very striking abnormality, the presence of a strong Debye-like process, which is dominating in the frequency spectra. In fact the presence of a strong Debye like process was in the past often mistakenly attributed to the alpha relaxation. Recently it has been shown by several studies that the process is not structural relaxation and that the true structural relaxation that determines the glass transition is faster and of much lower amplitude than the Debye process. Several suggestions exist for the origin of Debye-like process. Clusters, chains or micelle formation has been put forward as possible structural entities responsible for the Debye process and these structures are thought to be formed due to strong hydrogen bonding between alcohol molecules. The difference between the \(T_{g(D)}\) and \(T_g\) is observed in alcohols which gives a view that the ratio of dielectric to structural relaxation rates comes down as the liquid approaches \(T_g\) as predicted by JG. The dielectric modes responsible for the \(\alpha\)-process are somehow decoupled and are different from structural modes.

Monohydric alcohols provide data which is best represented by a major and one or more subsidiary relaxations. The alcohols studied here are 6-methyl-2-heptanol, 2-ethyl-1-hexanol, 4-methyl-3-heptanol. For alcohols 6-methyl-2-heptanol, 2-ethyl-1-hexanol and 2-butanol, dielectric data has been shown and the results are compared with
the data of shear-mechanical spectroscopy. Both liquids 2-butanol and 2-ethyl-1-hexanol has been studied earlier in refs [6],[14] and refs [15],[19],[24],[25],[26],[36],[37] in detail, respectively.

6.A.2 Experimental

The samples used here are 6-methyl-3-heptanol (99 % purity, 2-ethyl-1-hexanol (99 % purity, 4-methyl-3-heptanol (> 99% purity) are purchased from Aldrich. Fluorobenzene, neopentyl alcohol, tert-butylox chloride (tBC), tert-butyl alcohol, tert-butyl amine (tBA) are obtained from Spectrochem, India. All the samples have been used as received. Measurements performed on the samples are (i) Differential scanning calorimeter using Perkin Elmer Sapphire DSC with a quench cooling accessory. (ii) Dielectric relaxation measurements using HP4284A precision LCR meter in the frequency range 20 Hz - 10^6 Hz. (iii) Dielectric current measurements in the frequency 10^{-5} - 10^1 using Keithley Model No. 617 programmable electrometer. (iv) FTIR using Varian 3100. More details are given in chapter 2.

6.A.3 Results and Discussion

All the samples are critically examined using DSC before making the dielectric measurements. The T_g values are taken as onset of the step-like change in the DSC trace for a heating rate of 10^0/min. The samples that we have chosen for the present work are 6-methyl-3-heptanol (6M3HOH), 2-ethyl-1-hexanol (2EHOH), 4-methyl-3-heptanol (4M3HOH), 2-butanol (2BOH) which were studied earlier by Dannhausser and Johari11. To get information about the various relaxation processes, the variation of dielectric loss log ε'' for three monohydroxy alcohols viz. 6-methyl-3-heptanol, 2-ethyl-1-hexanol and 4-methyl-3-heptanol at 1 KHz test frequency vs. temperature has been plotted in Figure 6.1. From the figure, it can be seen clearly that there are three relaxation processes, the dominant α- process (α_1) along with shoulder process (α_2) and a sub-T_g process
designated as β-process. Also, the Debye process which is much dominant in 6-methyl-3-heptanol and 2-ethyl-1-hexanol is very much suppressed in the case of 4-methyl-3-heptanol. In all these long chain isomeric octanols, the -OH group is effectively screened due to the presence of the neighboring –CH₃ group. The double logarithm plot of log ε" with frequency is shown in the Figure 6.2 where one can see the spectral curve described as a superposition of two processes which can be resolved by fitting into Debye equation and the higher frequency to the Cole-Davidson equation. The dielectric spectra has been plotted for the temperature range of 165 K to 274 K. The dashed lines shown here represent the Debye fitting and the dotted lines shows the fittings to the Cole-Davidson equation. The relaxation parameters corresponding to the main relaxation α₁ are obtained by fitting the real part of the complex dielectric permittivity to the Cole – Davidson equation which is given by Eq. 1.35 in section B.4 in chapter 1.
The above Eq. 1.35 reduces to Debye form for $\beta_{CD} = 1$. The peak loss frequency $f_m$ is determined with the help of identity

$$f_m = f_0 \tan(\pi / 2(1 + \beta_{CD}))$$  \hspace{1cm} (6.1)

At lower temperature the data can be represented by a Cole-Cole arc function given by

$$\frac{\varepsilon' (f) - \varepsilon_{\infty}}{\varepsilon} = \left[ 1 + i \frac{f}{f_0} \right]^{\alpha_{cc} - 1}$$  \hspace{1cm} (6.2)

where $\alpha_{cc}$ is the symmetric distribution parameter.

(a) 6-methyl-2-heptanol: The dielectric relaxation shows three processes $\alpha_1$, $\alpha_2$ and $\beta$ processes. Figure 6.2 shows the variation of dielectric loss curve of 6-methyl-2-heptanol. The variation of dielectric dispersion and loss spectra as a function of temperature for 6-methyl-2-heptanol can be depicted in Figure 6.3 at various frequencies.

![Figure 6.2 Double logarithm plot of dielectric loss vs log f in supercooled 6-methyl-2-heptanol above $T_g$.](image)
Figure 6.3 Dielectric (a) dispersion and (b) absorption curves as a function of temperature for 6-methyl-2-heptanol at different frequencies.
Figure 6.4 Top shows the Cole-Cole plot and bottom dielectric loss with frequency at 190 K. Dotted line shows the Cole-Davidson fitting for supercooled 6-methyl-2-heptanol above $T_g$. 
The relaxation parameters corresponding to the main $\alpha$-relaxation are obtained by fitting the data in Debye equation described by Eq. 1.48 in section B.6 and Cole-Davidson Eq. 1.35 in section B.4 of chapter 1.

In the case of monohydroxy alcohols, only a single relaxation time (Debye behavior) is found. During the last decades $^{30,34}$, various studies have shown that the low frequency Debye type is decoupled from mechanical relaxation and the non-Debye at higher frequencies reflects the structural alpha relaxation. The relaxation data in our frequency window at a few temperatures above $T_g$ can be well represented as a superposition of three processes – one Debye type and the two depressed Cole-Cole arcs type processes which are designated as $\alpha_\parallel$, $\alpha_\perp$, and $\beta$ processes, respectively. The peak loss frequency ($f_m$) values obtained are plotted in the form of Arrhenius diagrams. The $\alpha$-process follows the critical power law $^{8,28}$ given by Eq. 4.2 in section 4.3 in chapter 4. Alternately, the data can also be described by the Vogel-Fulcher-Tammann equation given by $^{29}$,

$$f_{m,\alpha} = f_{0,\alpha} e^{(-B(T - T_0)/T_0)}$$

(6.3)

where $T_0$ is the limiting glass transition temperature, $f_{0,\alpha}$ and $B$ are constants. Plotted are $T_{g(D)}$ (or dielectric $T_g$, the temperature at which the $f_m$ value is $\sim 10^3$ Hz), the peak loss frequency ($f_{m,\alpha}$) & the dielectric strength of the $\alpha$-process ($\Delta \varepsilon_\alpha$) at specific temperatures.

To establish the relation between the deviations from Arrhenius equation and the Debye behavior of the $\alpha$-relaxation, the dynamic fragility index ($m$)$^{30,31,32}$ given by Eq. 1.13 in section A.8 of chapter 1. The $\beta$-process is found to follow the Arrhenius equation $^{4,5,6}$ for the relaxation frequency ($f_m$) given by Eq. 1.52 in section A.8 of chapter 1.
(b) Comparison of dielectric and mechanical relaxation times

(i) 2-ethyl-1-hexanol: To analyze the time scales associated with the observed processes and their temperature dependences, the loss peak frequencies have determined. A comparative study of various relaxations from the techniques dielectric, mechanical [Jakobsen et al. 30] and specific measurements [Richert et al. 27] have been shown in Figure 6.5. It is clearly seen from the figure that Debye process ($\alpha_1$) is absent in other techniques such as shear mechanical and specific heat spectroscopy. It is only specific to dielectric spectroscopy. The mechanical relaxation data corresponds to the non-Debye relaxation process. Also the $\beta$-process is much more prominent in dielectric. The structural relaxation ($T_r$) corresponds to the non-Debye relaxation.

Figure 6.5 shows the Arrhenius plot for 2-ethyl-1-hexanol showing the data from both dielectric and shear mechanical measurements. It is evident from the figure that shear mechanical data by Jakobsen et al. 30 is coinciding with the non-Debye alpha relaxation. The mechanical alpha and dielectric Debye are separated by approx. one decade of frequency. Complete Arrhenius diagram of 2-ethyl-1-hexanol. The Debye ($\alpha_1$) process is absent in mechanical and specific heat relaxation.
The dielectric spectra for 2-ethyl-1-hexanol is depicted in Figure 6.6 where one can see that the spectra consists of two superimposed processes which can be resolved by fitting into the Cole-Davidson and Cole-Cole fit at $T = 145$. 

Figure 6.6 Double logarithm plot of dielectric loss with frequency for 2-ethyl-1-hexanol at $T = 145$ K and 2-butanol for $T = 122$ K.
(ii) 2-butanol: Dannhausser and Cole\textsuperscript{6,10} studied the dielectric relaxation in isomeric butanols down to fairly low temperatures, but above their glass transitions. The Cole-Cole plot shows the main relaxation region, a single exponential decay of the macroscopic polarization with small departure from this behavior at the high frequency end. The secondary relaxation with a distribution of relaxation times has also been found below $T_g$.

The variation of dielectric loss for 2-BOH is shown in Figure 6.7. The spectral dependence of dielectric loss with frequency is described in Figure 6.6 at a temperature of 122 K. The complete Arrhenius diagram showing the comparison of all the relaxation processes from dielectric and mechanical relaxation methods is shown in Figure 6.8. As it is seen, 2-butanol shows three relaxation processes namely $\alpha_1$, $\alpha_2$, and $\beta$-process. The shear mechanical data is obtained from Jakobsen et al. Figure shows that the Debye process in dielectric is absent in shear mechanical measurements and the non-Debye relaxation of dielectric measurement agrees well with the data of mechanical relaxation.

![Figure 6.7 Dielectric loss curves as a function of temperature for 2-butanol.](image-url)
Figure 6.8 Complete Arrhenius diagram of 2-butanol [Murthy et al.\textsuperscript{14}, Jakobsen et al.\textsuperscript{30}] showing the dielectric and shear mechanical data.

Two monohydroxy alcohols (2-ethyl-1-hexanol and 2-butanol) were investigated by dielectric spectroscopy and the results are compared with the shear mechanical data of Jakobsen et al. in the temperature range down to $T_g$ glass transition temperature. In the dielectric spectrum Debye type process is prominent as is generally observed for monohydroxy alcohols. As viewed from the shear mechanical perspective the liquid behaves as a generic glass former. Besides a clear non-Debye relaxation, and a minor JG relaxation, a P-relaxation process is observed. The dielectric and mechanical alpha relaxation are separated by roughly one decade in frequency as generally observed. These observations support the existing\textsuperscript{16-25} idea that the minor non-Debye peak observed by dielectric spectroscopy is the true structural alpha relaxation.
6.B Intermolecular association in 4-methyl-3-heptanol and some of its binary mixtures

B.1 Introduction

Glass forming monohydroxy alcohols exhibit not only the structural relaxation but also a slower Debye type single exponential relaxation process which already freezes in the liquid phase. Smyth and coworkers advocated the existence of these processes to the H-bonded network and the reorientation of the free molecules. Here the alcohol matrix is studied by mixing it with other hydrogen-bonded and non-hydrogen bonded molecules. One way to study alcohol is to add a small quantity of dipolar solute. These dipolar molecules are expected to reorient along with the free alcohol molecules and this may lead to enhancement of process II. Murthy and Tyagi\textsuperscript{20} succeeded in studying 2-ethyl-1-hexanol with non-polar methylcyclohexane and polar 1-bromobutane has succeeded and explained the existence of process II due to the reorientation of the free alcohol molecules. We have chosen 4-methyl-3-heptanol which is found to be exceptionally interesting as process I was found to decrease in its importance on lowering the temperature (because of the preference of the ring formation as opposed to the chain formation in the case of 2E1H) and was found to be absent at a few degrees above $T_g$. We present here the dielectric and calorimetric study of 4-methyl-3-heptanol with other hydrogen bonded and non-hydrogen bonded systems which would help to study the process II.

The variation of dielectric loss $\varepsilon''$ of 4-methyl-3-heptanol with various solutes as non-hydrogen bonded symmetric molecules fluorobenzene (FB) and tert-butyl
chloride and with hydrogen bonded tBOH, tBA and NPA at test frequency of 1 KHz with
temperature.

4-methyl-3-heptanol is a good glass former and the rigid molecular solutes FB and tBC are not good glass formers on their own. The double logarithmic plot of $\varepsilon''$ with frequency at different temperatures is shown in Figure 6.9. FB and tBC are studied earlier in OTP matrix where these molecules show the secondary relaxation $\beta$-process which can be identified with $\beta_{SG}$-relaxation along with the dominant alpha process. The secondary process exhibited by the solute below $T_g$ is possibly due to small angle rotation of the solute molecules in the cages formed predominantly by the solvent glass matrix\textsuperscript{32}. These molecules enhance the non-Debye relaxation in 4M3HOH.

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Figure 6.9 Variation of dielectric loss with temperature at frequency of 1 KHz.
6.B.2 Results and discussion

(a) 4-methyl-3-heptanol with fluorobenzene: The temperature variation of dielectric constant ($\varepsilon'$) and loss $\varepsilon''$ curves for the mixture 4M3HOH with FB for 10% weight fraction is shown in Figure 6.13 (a) & (b). A close inspection of the data can be described by a superposition of symmetrically broadened high frequency peak and with an asymmetrically broadened low frequency peak. However the data above $T_g$ can be fitted to the Debye form ($\beta_{CD} = 1$). It also shows the sub-$T_g$ process which can be considered as Johari-Goldstein process below $T_g$ which shows an activation energy of 12 KJ/mol. The DSC scans of the mixtures show one observable $T_g$ and no definitely observable heterogeneity due to liquid-liquid separation has been noticed. The $T_g$ of the mixture is found to follow the equation $^{33,34}$,

$$T_g = T_{g1}(1-x) + T_{g2}x + k_x(1-x) \quad (6.4)$$

where $T_{g1}$ and $T_{g2}$ are the glass transition temperatures of component 1 (4M3HOH) and component 2 respectively and $x$ is the weight fraction of the component 2. The validity of Eq. 6.8 confirms that the mixtures are more or less homogeneous.

![Figure 6.10 Double logarithm plot of pure 4M3HOH with frequency at different temperatures.](image)
Figure 6.11 The double logarithm plot of binary system 4M3HOH-FB with frequency at different temperatures.

Figure 6.12 The double logarithm plot of binary system 4M3HOH-tBC with frequency at different temperatures
Figure 6.13 Dielectric behavior of binary system 4M3HOH-FB, with \( x_w = 0.10 \)
Figure 6.14. Dielectric behavior of binary system 4M3HOH-tBC, with $x_w = 0.10$. 
(b). 4-methyl-3-heptanol and tert-butyl chloride

The frequency dependence of the complex dielectric constant of the 10% by weight mixture of 4-methyl-3-heptanol with can be clearly tert-butyl chloride is shown in Figure 6.14 (a) and (b). Three relaxation processes can be seen in the Figure. The primary process at low frequency, the Debye at higher frequency above $T_g$ and the secondary process below $T_g$. The temperature dependence of the spectral shape of primary process can be seen in Figure 6.12 where two loss peaks are clearly evident. The fitting of the spectral shape has been done using the Debye and Cole-Davidson equation. The secondary process below $T_g$ can be considered as JG-process. The fitting of $\beta$-process shows the Arrhenius behavior. The peak loss frequency against the temperature for the relaxation due to the molecular motions in the mixture can be plotted as shown in Figure 6.16.

(e) 4-methyl-3-heptanol with hydrogen-bonded liquids

The isomeric octanol has been studied with the hydrogen bonded liquids as neopentyl alcohol, tertiary butyl alcohol and tert-butyl amine with concentration, $x_w = 0.10$. These solutes have the ability to form the complexes with the solvent as well as self association and these molecules penetrate the ring structure of 4M3HOH and hence the Debye process is enhanced in these binary systems. The variation of dielectric loss with frequency for 4M3HOH - NPA, $x_w = 0.10$ is depicted in Figure 6.15. The dielectric behaviour can be seen in Figure 6.9 and the complete Arrhenius curve is shown in Figure 6.17. It is interesting to see that the $f_m$ values corresponding to processes I and II for the binary systems of alcohols studied here, if plotted against temperature segregate into two bands, one for process I and the other for process II as shown in Figure 6.16. Although some amount of uncertainty is expected in the resolved values of process II even though these values form a band different from process I. It is also clear that process II ($\alpha_{II}$) reflects the structural relaxation whose freezing causes the glass transition event at $T_g$. 

141
Figure 6.15 The double logarithm plot of binary system 4M3HOH-NPA with frequency.

Figure 6.16 Complete Arrhenius diagram for 4M3HOH with various solutes.
6.B.3 Kirkwood Correlation factor

The Kirkwood correlation factor for pure liquids is \(^{1,20}\),

\[
g = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} \cdot \frac{9KTM}{4\pi N\mu^2 \rho} \tag{6.5}
\]

where \(\mu\) is dipole moment of the molecule in vacuum, \(\rho\) the density at temperature \(T\), \(M\) the molecular weight, \(K\) the Boltzmann constant, \(N\) the Avogadro's number. Here \(\varepsilon_0\) is the equilibrium dielectric constant, density \(\rho(T) = \rho_0 - \alpha T\) (with \(\alpha\) approximated as \(8.4 \times 10^{-4} \text{ gm/(cm}^3\text{K)}\)).

The Kirkwood Correlation factor has been calculated using the following relation:

\[
g = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} \cdot \frac{9KT}{4\pi N \left( \frac{\mu_A^2 \rho_A}{M_A} \Phi_A + \frac{\mu_B^2 \rho_B}{M_B} \Phi_B \right)} \tag{6.6}
\]

where \(g\) is the effective Kirkwood correlation factor for binary mixture, \(\Phi_A\) and \(\Phi_B\) are the volume fractions of the liquids A and B respectively.

The calculated value of \(g\) factor has been plotted in Figure 6.17. In long chain isomeric octanols (2EHOH, 6M2HOH, 4M3HOH) the \(-\text{OH}\) group is so effectively screened due to the presence of the neighboring \(-\text{CH}_3\) group that association is restricted to small weakly polar multimers preferably ring dimers, the value of \(g\) for pure liquids being less than unity. Association into highly open chain \(n\)-mers of highly polar cyclic tetramers is not possible due to steric effects. These results agree with the Dannhauser and Crossley. For parallel alignment of the dipoles, \(g > 1\) and for antiparellel alignment \(g < 1\). In alcohols the parallel alignment occurs when the molecules are hydrogen bonded in a linear chain and antiparellel alignment occurs when the molecules are H-bonded in the form of ring\(^{16}\).
We suggest that the extraordinarily small correlation factor of these compounds is due to intermolecular association into small rings whereas in carboxylic acid dimers, the molecular dipoles largely cancel each other. In 4M3HOH which has a $g$ value closer to 1 on the high temperature side has almost a near zero value on the low temperature side which may be attributed to the increasing tendency for ring formation as $T_g$ is approached.

6.4.4 IR Results

The IR studies on these solutions is shown in Figure 6.18 and Figure 6.19. These studies reveal that there is no detectable change in the hydrogen bonding as can be seen
Figure 6.18 IR results of 4M3HOH with NPA at different concentrations.

Figure 6.19 IR spectra for 4M3HOH with tBC, tBOH, tBA and PG.
in the IR spectral band in the wavelength region 3000 – 3500 Å. We are unable to see any changes in this wavelength region within the solution in our experimental set-up. Further studies at low temperature will solve the problem.

6.C Conclusion

(a) The monohydroxy alcohols were investigated by conventional dielectric spectroscopy and compared with the shear-mechanical spectroscopy in the temperature range down to glass transition temperature. In the dielectric spectrum a low frequency Debye type process is dominant and the high frequency non-Debye process actually corresponds to the structural relaxation shown by mechanical spectroscopy. These results show that non-Debye peak shows the actual structural relaxation and the origin of the Debye type relaxation is due to –OH group flipping as advocated by Murthy et al. (1996). The dielectric modes of process I are absent in the other techniques, which indicates that it is specific to the dielectric relaxation.

(b) FB and tBC which cannot interact via hydrogen bonding shows a clear sub-T_g process due to the solute (β_s) which may be identified with the β_{HG}- process. In all other cases the sub-T_g losses are of comparable magnitude to that of pure 4-methyl-3-heptanol. The relaxation process I which is Debye in nature is due to the flipping of –OH group in the residual linear chains of the alcohol molecules. Addition of H-bonded liquids like tBOH, tBA increases the Debye process of 4M3HOOH due to breaking of the ring formation of 4M3HOH resulting in preference for linear chain formation. This can be seen as increase in the parameter 'g' on addition of these H-bond breaking liquids.

6.D References


