Comparative dielectric study of mono, di and trihydric alcohols

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Measured values of dielectric permittivity $\varepsilon'$ and dielectric loss $\varepsilon''$ of ethyl alcohol (monohydric alcohol), ethylene glycol (dihydric alcohol) and glycerol (trihydric alcohol) over the whole frequency range of dielectric absorption i.e. -10 MHz to 20 GHz, at 25 °C have been reported. The values of $\varepsilon'$ and $\varepsilon''$ of de-ionized water have also been reported in the same frequency range. The dielectric dispersion behaviour of ethylene glycol obey the Cole-Cole model while for ethyl alcohol and water molecules it can be described by Debye model. In case of glycerol, dielectric dispersion shows the Cole-Davidson type dielectric dispersion. The static dielectric constant $\varepsilon_s$, high frequency limiting dielectric constant $\varepsilon_\infty$, average relaxation time $\tau_\alpha$, dielectric distribution parameter $\alpha$ or $\beta$, free energy of activation $\Delta F$, and Kirkwood correlation factor $g$ have been determined for these hydrogen-bonded liquids. The values of $\varepsilon_s$ and $\tau_\alpha$ are interpreted in terms of number of carbon atoms and the number of hydroxyl groups present in the molecular structure. The effect of viscosity and intermolecular association on the average relaxation time of these molecules has been recognized. Intramolecular group rotations due to breaking and reforming of hydrogen bonds have also been discussed by considering the observed values of $\varepsilon_s - n_0^2$ ($n_0$, square of refractive index) and the corresponding dielectric dispersion models of these liquids containing different number of hydroxyl groups in their molecular structures.

[Keywords: Dielectrics, Ethyl alcohol, Ethylene glycol, Glycerol, Trihydric alcohol]

1 Introduction

Dielectric relaxation of a hydrogen-bonded molecule depends upon the molecular size, shape, intra- and intermolecular interactions and can be used to investigate molecular and intramolecular motions and their relation to molecular structure. These studies can be used to evaluate the barrier height hindering internal rotations, problem of complex formation, dipole-dipole interactions and other short-range intermolecular forces.

Due to hydrogen bonding, alcohols in particular, have been the subject of frequency dependent dielectric measurements in their pure liquid state and also in dilute solution of non-polar solvents since the initial stage of relaxation spectroscopy. Their long relaxation times did allow for informative studies. Technical developments facilitated measurements only over a limited range of relatively low frequencies ($\leq 100$ MHz), while, now-a-days, broad band relaxation spectra are accessible, covering the whole dielectric absorption range. For primary alcohols, the correlated motion of the molecules is responsible for the principal relaxation contribution and their dielectric complex plane plots are often found to be close to the Debye type. It is interesting to compare the dielectric behaviour of monohydric, dihydric and trihydric alcohols studied by using single measurement advance technique for their molecular conformations. Conformational changes originating in monohydric alcohols as a consequence of their interactions with dihydric and trihydric alcohols in binary mixtures have aroused considerable interest. Dielectric relaxation studies of binary mixtures of primary alcohols and polyhydric alcohols, have been undertaken under varying conditions of compositions and temperature, to help in formulating adequate models of liquid relaxation and also in obtaining information about the relaxation processes in hydrogen-bonded mixtures. Many such studies of primary and polyhydric alcohols in aqueous solutions are presently in hand, to gain some insight into the change in homogeneous nature of molecular interactions between the alcohols and water and their dynamics, over whole concentration range of the binary mixtures.

The objective of the present paper is, to report the broad band dielectric data of ethyl alcohol (monohydric alcohol), ethylene glycol (dihydric alcohol) and glycerol (trihydric alcohol), over the
wide frequency range of dielectric absorption which were carried out by using single measurement advance techniques for their comparison and record.

The evaluated dielectric parameters are used to discuss the change in the shape of dielectric dispersion with increase in hydroxyl groups in the molecular structure of primary alcohols to the polyhydric alcohols. Further, the dielectric parameters are also used to explore the molecular dynamic of intermolecular H-bonded species and the hindrance to intramolecular rotations in these alcohols.

2 Experimental Details

The permittivity $\varepsilon'$ and dielectric loss $\varepsilon''$ of ethylene glycol and double-distilled de-ionized water in pure liquid state were measured, using an HP 8510C vector network analyzer with the help of an HP8507 B dielectric probe kit, in the frequency range 100 to 20 GHz. The values of $\varepsilon'$ and $\varepsilon''$ of ethyl alcohol were performed using the time domain reflectometry (TDR) in the frequency range 10 MHz to 20 GHz. For glycerol, the values of $\varepsilon'$ and $\varepsilon''$ were measured by the impedance-material analyzer (HP 4291A) in the frequency range 1 MHz-1.8 GHz and by the TDR in the frequency range of 1-25 GHz. Viscosity of these liquids were determined using Ostwal viscometer. The refractive index $n_0$ was measured by Abbe’s refractometer. All these measurements were made at 25°C. Glycerol, ethylene glycol and ethyl alcohol of AR grade were used for their dielectric measurements.

3 Data Analysis

Frequency dependence curves for the dielectric permittivity ($\varepsilon'$) and absorption ($\varepsilon''$) of ethyl alcohol (CH$_3$CH$_2$OH), ethylene glycol (HOCH$_2$CH$_2$OH), glycerol (HOCH$_2$CHOHCHOH$_2$OH), and water (H$_2$O) are plotted in Fig. 1 at 25°C. To evaluate various dielectric parameters, the frequency dependent experimental complex permittivity data were fitted by the non-linear least-squares method to the Havriliak-Negami expression:

$$\varepsilon^*(\omega) = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (j\omega\tau_a)^{\alpha}}$$

with $\varepsilon_s$, $\varepsilon_\infty$, $\tau_a$, $\alpha$, and $\beta$ as fitting parameters. The values of dielectric parameters $\varepsilon_s$, $\varepsilon_\infty$, $\tau_a$, $\alpha$, and $\beta$ obtained from fitting into the Eq. (1) for these molecules are recorded in Table 1. Eq. (1) includes the Cole-Cole ($\beta=1$), Cole-Davidson ($\alpha=0$) and Debye ($\alpha=0$, $\beta=1$) relaxation models. The values of free energy of activation, $\Delta F_a$, have been evaluated by treating dielectric relaxation as rate process, using Eyring’s rate equation. The evaluated values of $\Delta F_a$ are also given in Table 1. The value of $g$ is the product of the Kirkwood correlation factor, $g$ and the square of the molecular dipole moment, $\mu$ have been calculated for these molecules at 25°C using the Kirkwood equation. The $g$ value has been evaluated using the available literature value of molecular dipole moment determined in dilute solutions. These values are given in Table 1.

| Table 1 — Values of viscosity $\eta$, static dielectric constant $\varepsilon_s$, high frequency dielectric constant $\varepsilon_\infty$, square of refractive index $n_0^2$, $\varepsilon_s-n_0^2$, average relaxation time $\tau_a$, distribution parameter $\alpha$ or $\beta$, free energy of activation $\Delta F_a$, dipole moment $\mu$ and Kirkwood correlation factor $g$ of different alcohols and water at 25°C |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\eta$ (m Pas) | $\varepsilon_s$ | $\varepsilon_\infty$ | $n_0^2$ | $\varepsilon_s-n_0^2$ | $\tau_a$ (ps) | $\alpha$ | $\beta$ | $\Delta F_a$ (kcal mol$^{-1}$) | $g$ | $\mu$ (D) | $g$ |
| 964.00 | 42.50 | 4.92 | 2.17 | 2.75 | 1247.00 | 0.00 | 0.64 | 5.28 | 17.07 | 2.55 | 2.60 |
| 16.30 | 41.20 | 4.85 | 2.03 | 2.82 | 92.40 | 0.09 | 1.00 | 3.75 | 13.38 | 2.38 | 2.40 |
| 1.12 | 24.40 | 2.35 | 1.85 | 0.50 | 146.20 | 0.00 | 1.00 | 4.02 | 9.03 | 1.73 | 3.12 |
| 0.89 | 78.80 | 5.60 | 1.77 | 3.83 | 8.30 | 0.00 | 1.00 | 2.33 | 9.82 | 1.82 | 2.96 |
of these molecules at 25 °C are also recorded in Table 1.

4 Results and Discussion

4.1 Dielectric dispersion

Fig. 1 shows the variation of $\varepsilon'$ and $\varepsilon''$ for the alcohols and water with frequency. From these plots, the values of $\varepsilon'$ and $\varepsilon''$ at different frequencies can be read. In these dielectric dispersion plots, only one relaxation peak is observed for the alcohols over wide frequency range. For these molecules, it is found that, the frequency for maximum dielectric loss vary monotonously with increase in number of hydroxyl groups in the molecular structure. The trends of maximum loss frequency for these hydrogen-bonded molecules increases in the order glycerol < ethyl alcohol < ethylene glycol < water. Further, the dielectric dispersion behaviour of ethylene glycol obey the Cole-Cole dispersion while, in case of ethyl alcohol and water, the observed dielectric dispersion behaviour is a simple Debye-type. Dielectric dispersion of glycerol can satisfactorily be represented by Cole-Davidson model. These results confirm that, as the number of hydroxyl group increases in the alcohol molecular structure, the symmetrical shape of the dielectric dispersion about the logarithm of the frequency of maximum loss changes into the asymmetric relaxation curve. The Cole-Cole type dispersion behaviour of ethylene glycol and Cole-Davidson type dispersion behaviour of glycerol confirm that, in these molecules, besides the overall molecular rotation, there is a significant contribution of group rotations to the relaxation processes. The alcohols are highly water-soluble. Earlier studies of these alcohols in water mixtures confirmed that, the shape of the dielectric dispersion curves of alcohol-water mixtures are almost close to the dispersion shape of the individual alcohol which is mixed in water although, there is strong interactions between alcohol and water molecules. Lux & Stockhausen studied the ethyl alcohol-water mixtures, over whole concentration range, at 11 spot frequencies ranging between 5 MHz and 72 GHz, using frequency
domain techniques and interpreted the values in Debye type dispersion. Similarly, the complex permittivity data measured by time domain spectroscopy at frequencies from 0.01 to 10GHz for ethylene glycol-water mixtures were fitted into Cole-Cole type dispersion, while glycerol-water mixture data were interpreted well by Cole-Davidson dispersion.

4.2 Dielectric constant

The dielectric constant of a hydrogen-bonded liquid at constant temperature is mainly dependent on the following factors: the dipole moment, the number of molecules per unit volume and Kirkwood correlation factor. Inter-molecularly hydrogen-bonded substances have high value of static dielectric constant $\varepsilon_s$, while, low values of $\varepsilon_s$ are usually found in intra-molecularly hydrogen-bonded substances. Table 1 shows that, the large value of $\varepsilon_s$ for glycerol and ethylene glycol is due to the intermolecular hydrogen-bonding in pure liquid state although, these molecules have different number of carbon atoms in their molecular structure. Glycerol has three carbon atoms while, in the structure of ethylene glycol, there are two carbon atoms, but, the $\varepsilon_s$ value for both the liquids are nearly equal. In case of homologous series, the value of $\varepsilon_s$ decreases with the increase in number of carbon atoms in the chain of the molecule. Due to presence of one more carbon atom in glycerol in comparison to ethylene glycol, the value of $\varepsilon_s$ for glycerol should be lower than the value of ethylene glycol. Further, in case of ethylene glycol and ethyl alcohol, the $\varepsilon_s$ of ethylene glycol is much higher than the $\varepsilon_s$ value of ethyl alcohol although, both have equal number of carbon atoms in their molecular structure. The comparative $\varepsilon_s$ value of glycerol, ethylene glycol and ethyl alcohol confirms that, the number of hydroxyl groups present in the molecular structure, greatly influences their static dielectric constant. From these $\varepsilon_s$ values of alcohols, it is inferred that, equal number of carbon atoms in molecular structure of different molecules with higher number of hydroxyl groups have high static dielectric constant. Further, the comparative values of $\varepsilon_s$ of ethylene glycol and glycerol confirm that, the lowering in the value of $\varepsilon_s$ by the increase in one carbon atom in the molecular structure is compensated by the addition of one hydroxyl group. The large value of $\varepsilon_s$ of water molecules in comparison to the alcohols is due to the large number of water molecules in per unit volume.

4.3 Dielectric relaxation

The large value of average dielectric relaxation time $\tau_\alpha$ for monohydric, dihydric and trihydric alcohols, in their pure liquid state, is attributed to the reorientation of H-bonded homo-molecular polymeric clusters. Due to presence of hydroxyl groups in the molecular structure of these molecules, intermolecular associated clusters formed with (O-H···O) linkage. For the interpretation of the relaxation time $\tau_c$ of these molecules the rotational tumbling of long-lived clusters on the one hand, and the internal fluctuation or association-dissociation dynamics on the other hand, may be considered. The comparative values of $\tau_c$ (Table 1) of these alcohols suggest that, the length of polymeric clusters formed in pure liquid state vary with the number of hydroxyl groups present in the alcohols molecular structure. This is confirmed by the evaluated values of Kirkwood correlation factor, $g$ of ethylene glycol and ethyl alcohol. Further, the $g$ value of these molecules greater than unity confirmed that, the alcohol molecules in pure liquid state tend to direct themselves with parallel dipole moment. The observed high value of relaxation time for glycerol (τ _c = 1247 ps) in comparison to the relaxation time of ethylene glycol (τ _c = 92.4 ps) and ethyl alcohol (τ _c = 146.2 ps) is due to the combined effect of bigger size of the glycerol molecules and also the high value of its viscosity (η =964 m pas). The high value of viscosity produces large steric hindrance to the molecular reorientation. If only, the effect of viscosity is considered for higher value of $\tau_c$ for glycerol then, the $\tau_c$ value for ethylene glycol must be higher than the $\tau_c$ value of ethyl alcohol. But, the observed higher $\tau_c$ value of ethyl alcohol in comparison to ethylene glycol suggests that, the length of the reorienting cluster and its flexibility contributed significantly, to the relaxation processes. Further, the strength of intermolecular hydrogen-bonding also affects the molecular dynamics. Besides the high value of viscosity, low $\tau_c$ value of ethylene glycol in comparison to ethyl alcohol confirms that, the strength of intermolecular hydrogen-bonding as confirmed by observed $g$ value and the length of reorienting polymers cluster in ethyl alcohol molecules is much higher than the
ethylene glycol. Earlier\textsuperscript{1}, it was confirmed that, the \(\tau_c\) value of a homologous series of mono or trihydric alcohols increases with the increase in viscosity but, it is not true on going from mono- to di-, and di- to trihydric alcohols, which implies that, the probably different motional processes are involved in dielectric relaxation and viscous flow. The difference in relaxation processes of monohydric, dihydric and trihydric alcohols are due to presence of hydrogen group/s in the molecular structure. In case of ethylene glycol, it is confirmed earlier\textsuperscript{4} that, in addition to intermolecular association, the end hydroxyl groups also form intra-molecular hydrogen bonds in dynamic equilibrium. The formation of intra-molecular hydrogen bonding in glycerol molecules is also expected due to presence of various sites available for H-bonding. Further, the glycerol molecule promotes a set of transient cross-links between neighbouring molecules, through intermolecular H-bonding. In such a case, relevant transient structures such as, branched associated species and/or chains are formed. It seems that, the cross-linked structures of glycerol molecules also contributed significantly, in the relaxation process together with their high viscosity and molecular size. Further, low value of \(\tau_c\) of ethylene glycol in comparison to the ethyl alcohol shows that, the probability of breaking and reforming of intermolecular hydrogen bonds in ethylene glycol molecular cluster is faster due to which, the hindrance to molecular reorientation decreases and hence, the \(\tau_c\) of ethylene glycol decreases.

Table 1 shows that, the values of dipole moment, \(\mu\) and Kirkwood correlation factor, \(g\) for ethyl alcohol and water molecules are nearly equal but, the \(\tau_c\) for ethyl alcohol molecules is very large in comparison to water molecules, however, both the systems obey the Debye dispersion model. From \(\tau_c\) values of ethyl alcohol and water, it is inferred that, the strength of intermolecular correlation in ethyl alcohol is much stronger than the water molecules. Further, it also seems that, the homogeneous cluster of ethyl alcohol has large number of molecules in comparison to the water cluster. For water, earlier dielectric relaxation studies\textsuperscript{25,26} confirmed that, six water molecules constitute a cluster by intermolecular H-bonding. The value of relaxation time \(\tau_c=8.3\) ps for water is assigned to the reorientation of the water cluster of six molecules. But, in case of ethyl alcohol, there is the reorientation of long chain polymeric cluster and hence, its \(\tau_c\) value is high in comparison to the \(\tau_c\) value of water.

The observed value of distribution parameter \((\alpha\) and \(\beta)\) for ethylene glycol and glycerol shows that, there is a significant contribution of group rotation to the relaxation processes in these molecules. The intramolecular rotation in ethylene glycol and ethyl alcohol molecules is also supported by the notable difference between the value of high frequency dielectric constant \(\varepsilon_{\infty}\) and the square of refractive index \(n_0^2\), i.e. \(\varepsilon_{\infty}-n_0^2\) (Table 1). In these molecules, there is intramolecular rotation of \(-\text{OH}\) groups about the C-O bonds in dynamic equilibrium due to breaking and reforming of hydrogen bonds in the intermolecular polymeric structure. In case of ethyl alcohol, this motion may be introduced for the associated phase which can be interpreted as switch process of the \(-\text{OH}\) dipole from one hydrogen bond direction to another. Earlier workers\textsuperscript{27-30} also considered the cooperative switch-over mechanism in the homogeneous intermolecular H-bonded species of ethyl alcohol molecules for the interpretation of the evaluated dielectric parameters in the binary mixtures of ethyl alcohol with polar molecules. For the switch-over mechanism in monohydric alcohols, it is possible that on breaking a hydrogen bond, not only one dipole switches to another position but that, all (or orientationally correlated) dipoles of a cluster (a chain-like associated structure) are cooperatively reoriented. For water, the significant value of \(\varepsilon_{\infty}-n_0^2\) is corresponding to the second Debye dispersion in high frequency region which is recently confirmed by advance THz reflection spectroscopy\textsuperscript{31,32}. Localized motions within the network of H-bonded water molecules cause the high frequency relaxation process of double-Debye model of water.

The observed value of free energy of activation \(\Delta F_T\) for these alcohols are in agreement with the activation energy required for the breakage of the hydrogen bond. Due to breaking of hydrogen bonds, there is reorientation of the H-bonded homomolecular clusters. This reorienting cluster form new hydrogen bond with other clusters, in dynamic equilibrium, due to which there is change of clusters size of these alcohols. During breaking of H-bond, there is also the orientation of \(-\text{OH}\) dipole about its C-O bonds.
5 Conclusion

From the comparative dielectric studies of monohydric, dihydric and trihydric alcohols, it is inferred that, the static dielectric constant of the alcohol increases with increase in number of hydroxyl groups, but also decreases with increase in carbon atoms in the molecular structure. Different homologous series of alcohols are associates to form multimers due to intermolecular hydrogen bond with parallel dipole moment as confirmed by Kirkwood correlation factor. The comparative relaxation studies also confirmed that, the relaxation time of alcohols is influenced by the viscosity, number of hydroxyl groups present in the molecular structure, and the strength of intermolecular hydrogen-bonding. Further, different types of mechanisms are responsible for reorientational motion in these H-bonded molecules due to presence of different number of sites available for H-bonding.

The high value of relaxation time for monohydric alcohol in comparison to the dihydric alcohol confirmed that, the intermolecular association masks the effect of viscosity. Further, it seems that, the length of the reorientating intermolecular polymeric cluster decreases with increase in number of hydroxyl groups in these alcohols.

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