Study of structuredness and hydrogen bonding in binary solutions using microwave technique

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Dielectric and volumetric information of alcohols with different solvents provide eminent information regarding heteromolecular interactions and hydrogen bonding nature between diverse entities. Ordering of heteromolecules in their pure form as well as in binary mixture is studied thereby obtaining the Kirkwood correlation factor. Luzar model predicts the bonding between the hetero molecules such that the concentration dependent heteromolecular interactions study of isopropyl alcohol with dimethylsulfoxide and water liquid solutions with variations in the physiochemical and volumetric parameters has been revealed. The dielectric permittivity of the binary liquid mixtures have been obtained at 9.685 GHz using X-band microwave technique at room temperature.

Keywords: Static dielectric constant (\(\varepsilon'\)), Dielectric loss (\(\varepsilon''\)), Microwave conductivity, Excess permittivity, Kirkwood correlation factor, Structuredness

Assessment of structural properties using molecular interaction study under the influence of microwave frequency has considerable importance in pharmaceutical and chemical industries to know the physiochemical parameters due to intermolecular interactions executed among the diverse molecules that affects the chemical reactions. The evaluation and spectroscopic analysis of physical and chemical properties were done using time domain1-4 and frequency domain, which has achieved finest results in the analysis of dielectric parameters to signify heteromolecules in the mixture. Frequency domain technique (FDT)5-9 plays a remarkable role in perceptive of molecular assets and intermolecular exchanges through hydrogen bonding in binary liquids9. It is the most convenient method that provides exact static dielectric constant (\(\varepsilon'\)) values, especially of non-polar molecules in microwave region. In present context exposure of microwaves to binary solutions of Isopropyl Alcohol (IPA) with Dimethyalsuloxide (DMSO) and IPA with water causes variations in degree and structural behavior of solute-solvent such that it recognizes the diverse interactions in dielectric properties. The properties such as static dielectric permittivity, dielectric loss, microwave conductivity (\(\sigma\)), penetration depth, loss tangent, excess permittivity, Bruggeman factor, pH and density (\(\rho\)) have been obtained to reveal the effect of structural and intermolecular interactions in the solutions. Thus the structuredness11 or ordering of hetero molecules in its pure form as well as in binary solution is revealed using Kirkwood correlation factor. Luzar model recognizes the hydrogen bonding among the hetero molecules in terms of predicted number of hydrogen bonds, enthalpy, bonding energy and polarizability, respectively.

Isopropyl Alcohol [(CH\(_3\)_2CHOH] is an example of secondary alcohol, non-toxic, colorless, flammable organic compound12. It is widely used as a solvent and for anaesthesia, as a preservative in biological specimen, for etching, in eyeglass cleaning, electrical contacts, in heads of audio and video tapes, DVD and in lenses of optical disc, thermal paste remover for CPUs heat-sinks and other IC packages. It has use as
a major ingredient in gas dryer fuel additives, as a common ingredient in products such as antiseptics, disinfectants, hand sanitizer and detergents etc. Dimethyl sulfoxide \([\text{CH}_3\text{SO}]\) is colorless polar aprotic solvent, water soluble, has garlic-like taste and dissolves in polar, nonpolar compounds and is soluble in a wide range of organic solvents\(^{13-15}\).

S. Guo \textit{et al.} \(^{16}\) recently investigated intermolecular hydrogen bonding of isopropanol–water clusters using DFT calculations. Study concludes that, redshifts of O-H bond tensile peak, indicative of weakened O-H tensile strength and interaction among hydrogen bonds is strengthened with increase in water molecules. T. Sato \textit{et al.} \(^{17}\) studied the dielectric relaxation spectroscopy of 2-propanol–water mixtures with a conclusion that the motion of individual alcohol molecules can be detected due to their relatively large size, they possess a single H-bond with high concentration. Kaatze \textit{et al.} \(^{18}\) investigated dielectric spectrum of DMSO with water as a function of composition and concluded that the static permittivity reflects antiparallel dipole moment ordering. Ritzoulis \(^{19}\) investigated excess properties with negative values and Kirkwood correlation parameters of IPA+DMSO solutions, concluded the negative values of excess permittivity and no dipole interactions for DMSO and that of IPA the values greater than unity suggest antiparallel orientation of molecules.

The aim of present article is to investigate heteromolecular interactions and structuredness in homogenous mixtures of IPA+DMSO and IPA+Water such that IPA gets completely mixed in water and DMSO. The effect of high frequency on polarization and structural properties in these solutions was studied using FDT at room temperature such that these molecules possess different values of polarity index (PI).

**Experimental details**

**Materials**

Isopropyl Alcohol and Dimethylsulfoxide were purchased from Thermo Fisher Scientific Pvt. Ltd. Mumbai with 99.00% of purity and distilled water is used without further purification. The probable structural bonding between IPA+DMSO and IPA+Water is shown in Fig. 1.

**Measurements**

Static dielectric parameters were measured at 9.685 GHz frequency by means of frequency domain technique using X-Band microwave bench. Analysis of data with procedure of frequency domain technique using X-Band microwave bench was systematically explicated formerly\(^{5-9}\). The densities of pure liquids and the binary mixtures were measured by using pycnometer, thereby taking doubly distilled water as a reference liquid. \textit{pH} meter used was of Syntronics make and standardized before its experimental use.

**Results and Discussion**

**Static dielectric constant**

Dielectric parameters were obtained using X-band microwave technique. The relative permittivity of binary liquid mixture is obtained using the equation\(^{5-9}\) as,

\[ \varepsilon = \varepsilon' - j\varepsilon'' \]  

where, \(\varepsilon\) is the relative permittivity, \(\varepsilon'\) is the relative real permittivity and \(\varepsilon''\) is relative loss and \(j\) is imaginary number with \(-1\) value. The static dielectric permittivity and loss is calculated by using the equations as\(^{5-9}\),

\[ \varepsilon' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \]  

where, \(\varepsilon'\) is dielectric constant, \(\varepsilon''\) is dielectric loss, \(\lambda_0\) is free space wavelength, \(\lambda_d\) is wavelength in dielectric cell, \(\lambda_g\) is guided wavelength, \(\lambda_c = 2a\) is cut-off wavelength (‘a’ is width of waveguide). To eliminate losses value, \(\frac{d\rho_{\text{mean}}}{dn}\) is used, and is taken from slope of graph plotted between several mean values of \(\rho_n\ versus n\) values\(^{5-9}\).

In IPA+DMSO and IPA+Water binary mixtures, the value of static dielectric constant and dielectric loss goes on decreasing with increasing \(V_{IPA}\), which is an indicative of net change in polarization with transition of elongated molecular aggregation into spherical aggregation structure\(^{20}\), as tabulated in Table 1. These variations of \(V_{IPA}\) cause changes in \(\varepsilon'\) and is the effect of exchanges among unlike molecules which may create structural changes\(^{21-23}\) thereby increasing heterogeneous interactions in solutions.

![Fig. 1 — Probable bonding between (a) IPA+DMSO and (b) IPA+Water.](image-url)
The effect of PI is also seen on the dielectric constant values such that with decrease in polarity index, dielectric constant value of the liquid goes on decreasing that is PI is in the order as Water>DMSO>IPA and $\varepsilon$ is in the order as Water>DMSO>IPA, respectively. Thus the dielectric constant of the systems used for study follows the effect of PI.

**Microwave Conductivity, Loss tangent and Penetration depth**

The values of Microwave conductivity ($\sigma$), Loss tangent and Penetration depth were obtained using the following relations as $^5$-$^9$,

$$\sigma = \frac{fe''}{1.8 \times 10^{11}} \quad \cdots (4)$$

$$\tan \delta = \frac{\varepsilon'}{\varepsilon''} \quad \cdots (5)$$

$$P_d = \frac{\lambda_o \sqrt{\varepsilon'}}{2\pi \varepsilon'} \quad \cdots (6)$$

where, $\sigma$ is microwave conductivity, $f$ is microwave frequency, $\varepsilon'$ is dielectric constant, $\varepsilon''$ is dielectric loss, $\lambda_o$ is free space wavelength, $P_d$ is penetration depth and $\varepsilon_r$ is relative permittivity.

The microwave conductivity is a function of dielectric loss and in above two solutions, it decreases with increase in $V_{IPA}$ and compared to both the systems the conductivity of pure Water is greater than that of pure DMSO. Ratio of dielectric loss to the permittivity of material is the Loss tangent$^5$, $^26$. For IPA+DMSO, value of loss tangent is least at $V_{IPA} = 0.2$ and it is extreme for pure DMSO. In IPA+Water solutions, the value of loss tangent is maximum at 0.8 $V_{IPA}$ and minimum for pure IPA. The depth, at which power gets reduced to 1/e of its surface value, is nothing but penetration depth $^5$, $^26$. Penetration depth value goes on increasing for both systems with increase in $V_{IPA}$.

**Density and pH**

For present systems, density($\rho$) of the liquid mixtures is obtained using the formula for density as,

$$\rho = \frac{m}{V} \quad \cdots (7)$$

where, $\rho$ is density, $m$ is mass and $V$ is volume of solution.

Density of solutions goes on decreasing with increase in $V_{IPA}$ in both the systems. As IPA having less density than water and DMSO both such that increasing $V_{IPA}$ causes decrease in density of mixture thereby decreasing the values of dielectric constant of mixture in both the systems$^27$, results in dependency of dielectric constant on the density of the mixture. $pH$ is the concentration of hydrogen ions, that is a scale used to measure the nature of molecules such as its acts as base or acid. The $pH$ values of the solutions given in Table 1 shows that for IPA+DMSO solution, the values remain unchanged, that is insignificant and that of for IPA+Water, $pH$ value decreases with increase in $V_{IPA}$ which is indicative of increasing acidic strength in the mixture.

**Excess permittivity**

Interaction among two constituents of liquid mixture is provided in terms of excess permittivity ($\varepsilon'$) and is given as $^28$, $^29$,

$$\varepsilon' = (\varepsilon')_1 - [(\varepsilon')_1 V_1 + (\varepsilon')_2 (1 - V_1)] \quad \cdots (8)$$
where, suffix m, 1 and 2 denote mixture, solute and solvent respectively, $V_1$ is volume fraction of solute.

As shown in Fig. 2, excess permittivity values for IPA+DMSO and IPA+Water binary mixtures are negative thereby indicating strong hydrogen bonded intermolecular interactions among the hetero molecules such that water and DMSO acts here as a structure breaker. Peak negative value for IPA+DMSO is at 0.6 and that of IPA+Water is at 0.2 $V_{IPA}$ respectively. More negative values for IPA+DMSO indicates strong interactions while less negative value for IPA+Water reveals the less strong interaction than that of IPA+DMSO solutions.

**Bruggeman factor**

Information in terms of static permittivity of the mixture constituents is explored using Bruggeman factor, and is given by the relation as

$$f_B = \left[ \frac{(\varepsilon'_m - \varepsilon'_{1})}{(\varepsilon'_2 - \varepsilon'_{1})} \right]^{\frac{1}{3}} = 1 - V_2 ... (9)$$

Bruggeman equation has been modified for binary mixtures as,

$$f_B = \left[ \frac{(\varepsilon'_m - \varepsilon'_{1})}{(\varepsilon'_2 - \varepsilon'_{1})} \right]^{\frac{1}{3}} = 1 - [a - (a-1)V_2]V_2 ... (10)$$

where, $f_B$ is Bruggeman factor, $\varepsilon'_m, \varepsilon'_{1}$ and $\varepsilon'_{2}$ represent static dielectric constant corresponding to mixture, solute and solvent, $V_2$ is volume fraction of solvent. In modified equation, $V_2$ is changed by a factor $[a-(a-1)V_2]$ of the mixture where ‘a’ is the interaction parameter.

The value of interaction parameter ‘a’ for IPA+DMSO systems is found to be 0.44, which suggests increased effective dipoles with strong intermolecular interactions and for IPA+Water, it is 1.43, with decreased dipoles with weak intermolecular interactions thereby suggesting decrease in effective volume fraction of IPA in Water and intermolecular interactions are less strong than IPA+DMSO as compared in both solutions at room temperature, as shown in Fig. 3.

**Kirkwood correlation factor**

Orientation of dipoles, which measures the extent of association and correlation between the hetero molecules, thereby ensuring the hindrance in the rotation is explained by Kirkwood. Effective Kirkwood correlation factor $g^{eff}$ is calculated from modified Kirkwood equation as

$$g^{eff} = \frac{(\varepsilon'_m - \varepsilon'_{om}) (2\varepsilon'_m + \varepsilon'_{om})}{\varepsilon'_m (\varepsilon'_{om} + 2)^2} = \frac{4N}{9\pi} \left[ \mu_1^2 \rho_1 V_1 + \mu_2^2 \rho_2 (1 - V_1) \right] \times g^{eff} ... (11)$$

where, $g^{eff}$, $\varepsilon'_m, \varepsilon'_{om}, \mu_1, \mu_2, \rho_1, \rho_2, M_1, M_2, N, K, T$ has their usual meanings and $V_1$ is volume fraction of solute.

Dipole-dipole orientations in the solution of diverse molecules are effectively understood by using Kirkwood correlation factor ($g^{eff}$). $g^{eff}$ for IPA, DMSO and Water at room temperature is found to be 2.647, 1.199 and 2.875 respectively. For IPA+DMSO and IPA+Water solutions, $g^{eff}> 1$ at room temperature indicates the strong interactions with antiparallel orientation of electric dipoles among hetero molecules.

The value of $g^{eff}$ increases with increase in $V_{IPA}$ in IPA+DMSO solutions thereby indicating strong interaction while in IPA+Water solutions, the value of $g^{eff}$ decreases with increase in $V_{IPA}$ such that it confirms weak interactions in IPA+Water than that of...
IPA+DMSO solutions if the two systems are compared together\textsuperscript{38}. The structuredness\textsuperscript{11} or the ordering of molecules is studied from the Kirkwood correlation factor very well. In IPA+DMSO, the pure IPA and Water show structured nature while DMSO show unstructuredness or non-ordering of the molecules. The comparative study confirms the values of static dielectric constant and Kirkwood correlation factor, which are included in the Table 2 with orderedness of molecules. With increase in $V_{\text{IPA}}$, the structuredness of IPA molecule goes on increasing in case of IPA+DMSO while in case of IPA+Water, both are structured and ordering nature of Water is more than that of IPA, goes on decreasing.

$g_1$ and $g_2$ are the average correlation factors derived from a single value of $\varepsilon'$ such that for separate class $i = 1$ and 2 and these values are obtained by using Luzar model with succeeding equations as\textsuperscript{42-43},

$$g_1 = 1 + Z_{11} \cos \Phi_{11} + Z_{12} \cos \Phi_{12} \left( \frac{\mu_2}{\mu_1} \right)$$ ... (12)

$$g_2 = 1 + Z_{21} \cos \Phi_{21} \left( \frac{\mu_1}{\mu_2} \right)$$ ... (13)

where, $Z_{11} = 2 <n_{11}^{\text{HB}}>$, $Z_{12} = 2 <n_{12}^{\text{HB}}>$ and $Z_{21} = 2 <n_{21}^{\text{HB}}>(1-Vx)/Vx$ are average number of hydrogen bonds with solute-solute and solute-solvent pairs respectively. $\Phi_{11}$, $\Phi_{12}$ and $\Phi_{21}$ show angles between neighboring dipoles of unlike molecules.

Average number of hydrogen bonds formed as $n_{1i}^{\text{HB}}$ and $n_{2i}^{\text{HB}}$ per solute molecule for $1i$ pairs ($i = 1$ or 2), have been obtained using the relation\textsuperscript{42-43},

$$n_{1i}^{\text{HB}} = \frac{n_{1i}^{\text{HB}} \omega_{1i} / n_1}{g_{11}^i}$$ ... (14)

where, $\omega_{1i} = 1/[1 + \alpha_{1i} \exp(\beta E_{1i})]$ represents probability of forming the bonds between solute and solvent molecule. $n_i$ is density of solute molecule, $\beta = 1/kT$, and $\alpha_{1i}$ are statistical volume ratios of hydrogen-bonded and non-hydrogen-bonded pairs related to two sub-volumes of phase space. Energy levels for 11 and 12 pairs are $E_{11}$ and $E_{12}$. Density value causes variation in $n_{11}^{\text{HB}}$ and $n_{12}^{\text{HB}}$ of solute, solvent and solute-solute pair of molecules, respectively\textsuperscript{44}.

For two different binary solutions of IPA+DMSO and IPA+Water, values of $g_1$ and $g_2$ increases with increase in $V_{\text{IPA}}$, as represented in Fig. 4 (a) and (b). Increase in $V_{\text{IPA}}$ causes decrease in bonding amongst IPA+DMSO and IPA+Water molecules such that $n_{11}^{\text{HB}}$ value increases with decrease in $n_{12}^{\text{HB}}$, as shown in Fig. 5 (a) and (b), respectively\textsuperscript{44-45}. In IPA+DMSO system, $\varepsilon'$ values obtained theoretically in comparison with experimental values found good as shown in Fig. 6 (a) and that of IPA+Water solutions, the values are nearly equal such that theoretical and experimental values are in better agreement as shown in Fig. 6 (b). The theoretical $\varepsilon'$ values were obtained using feasible molecular

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<td>15.45 Str.</td>
<td>19.13 Str.</td>
<td>3.9 Polarity Index \textsuperscript{39-40}</td>
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<td>DMSO</td>
<td>$\varepsilon'$</td>
<td>47.84 Unstr.</td>
<td>47.00 Unstr.</td>
<td>7.2 Polarity Index \textsuperscript{39-40}</td>
</tr>
<tr>
<td>Water</td>
<td>$\varepsilon'$</td>
<td>78.78 Str.</td>
<td>78.36 Str.</td>
<td>10.2 Polarity Index \textsuperscript{39-40}</td>
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Fig. 4 — Variation of correlation factor ($g_1$ and $g_2$) vs. $V_{\text{IPA}}$ for (a) IPA+DMSO and (b) IPA+Water solutions at room temperature.
parameters, as tabulated in Table 3 for IPA+DMSO and IPA+Water solutions, respectively.

**Conclusions**

Static dielectric permittivity values of both systems were determined using frequency domain technique at 9.685 GHz. The variation in concentration of IPA causes decrease in dielectric constant thereby confirming the variations in structural properties and heteromolecular behavior such that presence of strong intermolecular forces cause change in structural arrangement, physical as well as intermolecular interactions, which follows the effect of density, polarity index on dielectric properties of IPA+DMSO and IPA+Water solutions. Kirkwood correlation factor and Bruggeman factor confirms antiparallel orientation, increased effective dipoles with strong intermolecular interactions. The structuredness of
increasing $V_{IPA}$ indicate increasing acidic strength of formation of hydrogen bonding. For IPA + Water, increasing $V_{IPA}$ indicate increasing acidic strength with decrease in $p\text{H}$ value.

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References