

## Microwave dielectric relaxation, thermodynamic and conformational studies of hydrogen bonded binary mixtures of propan-1-ol with methyl benzoate and ethyl benzoate

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The dielectric relaxation studies of propan-1-ol with alkyl benzoates (methyl benzoate and ethyl benzoate) have been carried out, for various mole fractions at different temperatures, using LF impedance analyzer, Plunger method and Abbe's refractometer in radio, microwave and optic frequency regions, respectively. Kirkwood effective correlation factor, corrective Kirkwood correlation factor, Bruggeman parameter, relaxation time and thermo dynamical parameters are calculated using the experimental data. Conformational analysis of the formation of hydrogen bond in the equimolar binary mixture systems of propan-1-ol with alkyl benzoates is supported by experimental and theoretical FT-IR values.

**Keywords:** Corrective Kirkwood correlation factor, Relaxation time, Hydrogen bond, FT-IR

### 1 Introduction

The dielectric relaxation study of solute solvent mixture at microwave frequency gives information about molecular interactions in the system, formation of monomers and multimers. Dielectric relaxation spectroscopy was proved to be a powerful tool for the investigation of H-bond rearrangement dynamics and has been widely applied to study the pure solvents, solvent-solvent mixtures<sup>1,2</sup>. Dielectric investigation of binary polar liquid mixtures consisting of one associative and other non-associative liquids, provides valuable information regarding molecular complex formation in solution. Alcohols are industrially and scientifically important organic compounds and their physical and chemical properties are largely determined by the –OH group. Alcohols are strongly associated in solution because of dipole-dipole interaction and hydrogen bonding. Alkyl benzoates are non-associated in solution, good hydrogen bonding acceptors and important industrial chemicals that are widely used in perfumery and pesticides.

The strength of the molecular association depends on several factors including the molecular structure, temperature, solvent and other factors<sup>3</sup>. The presence of hydrogen bond brings a considerable change in the dielectric properties of liquid mixtures. Therefore, the solution chemistry of these compounds can be

strongly influenced by the aggregation phenomena, which can play a significant role in physical properties like refractive index, dielectric permittivity, density and molar volume. Further, the thermodynamic properties of liquids and liquid mixtures have been used to understand the molecular interactions between the components of the mixture and also for engineering applications concerning heat transfer, mass transfer, fluid flow, activation energy, enthalpy, entropy, etc of the polar molecules<sup>4-9</sup>.

In the course of present study, to get better understanding of the nature of molecular orientation processes, we studied the temperature dependent dielectric relaxation in pure and binary mixtures of propan-1-ol with methyl benzoate and ethyl benzoate at different frequencies. The dielectric data is used to calculate Kirkwood effective correlation factor, corrective Kirkwood correlation factor, Bruggeman parameter, relaxation time and the thermodynamic parameters-Gibb's energy of activation, molar enthalpy and molar entropy<sup>10-14</sup>. Conformational analysis of the formation of hydrogen bond between equimolar mixtures of propan-1-ol with benzoates is studied from FT-IR spectra. The theoretical vibrational frequencies of the pure and equimolar hydrogen bonded systems are obtained from Hamiltonian quantum mechanical calculations using Spartan modeling software.

## 2 Experimental Details

The compounds propan-1-ol (IPN), methyl benzoate (MB) and ethyl benzoate (EB) of AR grade are procured from E. Merck, Germany and are purified by standard methods. The binary mixtures are prepared for different mole fractions i.e., mole fraction ( $X_2$ ) of benzoates (MB and EB) is varied from 0 to 1 in IPN (with a step increment of 0.1). The temperature controller system with a water bath, supplied by M/s Sakti scientific instruments company-India, has been used to maintain the constant temperature within the accuracy limit of  $\pm 1$  K. Densities at different temperatures are measured by using a 10 ml specific gravity bottle and METTLER TOLEDO balance (Model No: AB135-S/FACT) whose accuracy is 0.01mg.

The static permittivity values at the spot frequencies 1 kHz ( $\epsilon_{\text{static}}$ ), 10 kHz, 100 kHz, 1 MHz and 10 MHz for the above systems are measured using HP-LF impedance analyzer (Model No: 4192 A) at different temperatures. The real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the complex dielectric permittivity ( $\epsilon^* = \epsilon' - j\epsilon''$ ) are determined in X-Band (8.60 GHz) using Plunger technique<sup>15</sup> for the above temperatures. The high frequency dielectric permittivity ( $\epsilon_{\infty} = n^2$ ) is obtained from the refractometer measurements using M/s ASCO make Abbe's refractometer with sodium D light as source ( $10^{15}$ Hz) at different temperatures. The error in the estimation of  $\epsilon_{\text{static}}$ ,  $\epsilon'$ ,  $\epsilon_{\infty}$  and density is 1% and the error in the estimation of  $\epsilon''$ ,  $\tau$  is 2%. Dipole moments of the liquids in gaseous state are taken from literature<sup>16</sup>. The FT-IR-spectra of pure and equi molar binary mixture systems were recorded in the 400-4000  $\text{cm}^{-1}$  region on Perkin-Elmer (spectrum bX) series.

## 3 Theory

The molecular interactions between a polar solute and a non-polar solvent can be described by the modified Kirkwood-Frohlich correlation factor. The Kirkwood-Frohlich theory<sup>15</sup> takes into account of the short-range interactions through the introduction of the dimensionless correlation factor  $g$ , which gives information regarding the orientation of the electric dipoles in polar liquids. The Kirkwood correlation factor ( $g$ ) for the pure liquids is given<sup>17</sup> by the expression:

$$\frac{4\pi N_A \mu^2 \rho}{9kTM} g = \frac{(\epsilon - \epsilon_{\infty})(2\epsilon + \epsilon_{\infty})}{\epsilon(\epsilon_{\infty} + 2)^2} \quad \dots(1)$$

where  $N_A$  is the Avogadro's number,  $\mu$  the dipole moment in the gaseous phase,  $\rho$  the density,  $k$  the Boltzmann constant,  $T$  the temperature in kelvin,  $M$  the molecular weight,  $\epsilon$  the dielectric permittivity at static frequency and  $\epsilon_{\infty}$  is the permittivity at optical frequency which is the square of refractive index.

For a mixture of two polar liquids, say 1 and 2 the Eq. (1) could be modified<sup>18</sup> using different assumptions.

(1) Assuming that  $g^{\text{eff}}$  is the effective correlation factor for the mixture, the Kirkwood equation for the mixture can be expressed as:

$$\begin{aligned} \frac{4\pi N_A}{9kT} \left( \frac{\mu_1^2 \rho_1}{M_1} X_1 + \frac{\mu_2^2 \rho_2}{M_2} X_2 \right) \cdot g^{\text{eff}} \\ = \frac{(\epsilon_m - \epsilon_{\infty m})(2\epsilon_m + \epsilon_{\infty m})}{\epsilon_m (\epsilon_{\infty m} + 2)^2} \quad \dots(2) \end{aligned}$$

or

(2) Assuming that the dipole moments of both the liquids are affected by the same amount  $g_f$  the Kirkwood equation for the mixture is modified as:

$$\begin{aligned} \frac{4\pi N_A}{9kT} \left( \frac{\mu_1^2 \rho_1 g_1}{M_1} X_1 + \frac{\mu_2^2 \rho_2 g_2}{M_2} X_2 \right) \cdot g^f \\ = \frac{(\epsilon_m - \epsilon_{\infty m})(2\epsilon_m + \epsilon_{\infty m})}{\epsilon_m (\epsilon_{\infty m} + 2)^2} \quad \dots(3) \end{aligned}$$

where  $X_1$  and  $X_2$  are the mole fractions of liquids 1 and 2 in the mixture respectively and the suffix 1, 2 and  $m$  represents liquid 1, liquid 2 and mixture, respectively.

Here the value of  $g^{\text{eff}}$  in Eq. (2) varies from  $g_1$  to  $g_2$  as the concentration (mole fraction) of liquid 2 increases from 0 to 1 and the value of  $g_f$  in Eq. (3) is unity for pure polar liquids and close to unity if there is no interaction between the liquid mixtures. The deviation of  $g_f$  value from unity indicates the interaction between liquids 1 and 2.

The solute-solvent interaction between the components of a mixture can also be obtained from another dielectric parameter is Bruggeman<sup>19</sup> factor ( $f_B$ ) and it is given by:

$$f_B = \left( \frac{\epsilon_m - \epsilon_2}{\epsilon_1 - \epsilon_2} \right) \left( \frac{\epsilon_1}{\epsilon_m} \right)^{1/3} = (1 - \phi_2) \quad \dots(4)$$

where  $\phi_2$  is the volume fraction of liquid 2 in liquid 1, If there is no interaction between the components in the mixture then the Bruggeman factor ( $f_B$ ) should

vary linearly with volume fraction  $\phi_2$ , but if there is interaction between the components then  $f_B$  varies non-linearly with  $\phi_2$ .

The dielectric data obtained i.e.,  $\epsilon_{\text{static}}$ ,  $\epsilon^* = \epsilon' - j\epsilon''$ ,  $\epsilon_\infty$  and the data from impedance analyzer is used to fit in an Argand diagram to calculate the relaxation time ( $\tau$ ). The distribution of relaxation time is witnessed from Cole-Cole arc plot. Although Cole-Cole equations which signify the distribution of relaxation time, eventually a macroscopic relaxation time (predominant relaxation time) is measured using the equation:

$$\omega\tau = \left(\frac{v}{u}\right)^{\frac{1}{1-\alpha}} \quad \dots(5)$$

where  $\alpha$  (distribution parameter),  $u$  and  $v$  values are determined from their respective Cole-Cole plots.

Eyring<sup>20,21</sup> treated the dipolar rotation on the basis of a chemical rate process. The molecules are assumed to jump from one equilibrium position to another, depending on the following factors:

(a) The number of collisions that it makes with the neighbouring molecules; (b) The entropy  $\Delta S^*$ , which describes the disturbance of the local structure of the medium during orientation; (c) The heat of activation  $\Delta H^*$ , which is equal to the potential barrier separating the successive equilibrium positions.

Using this concept a relation between the microscopic relaxation time and the free energy of activation is given as:

$$\tau = \frac{h}{kT} \exp\left[\frac{\Delta G^*}{RT}\right] = \frac{h}{kT} \exp\left[\frac{\Delta H^* - T\Delta S^*}{RT}\right] \quad \dots(6)$$

where  $h$  is the Planck's constant,  $k$  the Boltzmann constant,  $T$  the temperature in kelvin and  $R$  is the gas constant.

By using Eq. (6), the thermodynamic parameters Gibb's energy of activation  $\Delta G^*$ , molar enthalpy of activation  $\Delta H^*$ , molar entropy of activation  $\Delta S^*$  for various mole fractions and at different temperatures can be determined.

Minimum energy structures of the monomers of propan-1-ol, methyl benzoate, ethyl benzoate and the equi molar hydrogen bonded complexes for the vibrational frequencies are obtained from Semi-empirical Hamiltonian quantum mechanical calculations<sup>22,23</sup> such as Austin Model 1 (AM1), Parameterized Model number 3 (PM3) and Modified Neglect of Differential Overlap (MNDO) converged

geometry optimization procedure using Spartan Modeling software<sup>24</sup>.

#### 4 Results and Discussion

The permittivity values  $\epsilon_{\text{static}}$  and  $\epsilon_\infty$  for various mole fractions at different temperatures of the binary systems 1PN + MB (System 1) and 1PN + EB (System 2) are determined experimentally and their variation with mole fraction is shown in Figs 1 and 2

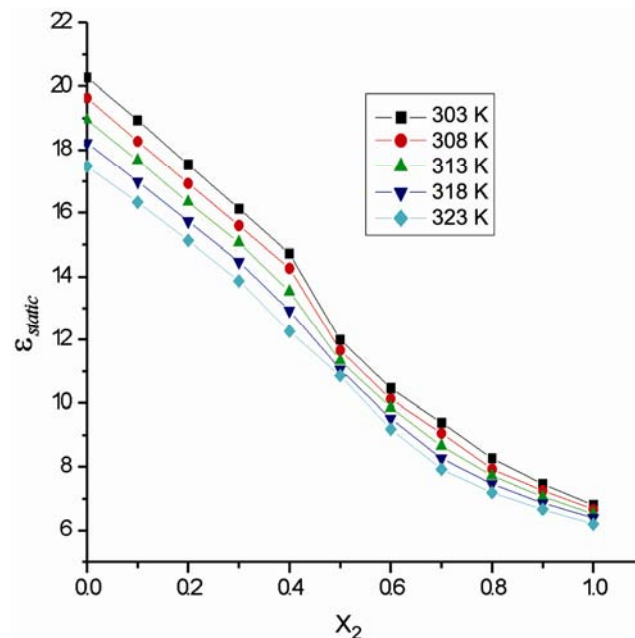


Fig. 1 — Static permittivity ( $\epsilon_{\text{static}}$ ) versus mole fraction ( $X_2$ ) of methyl benzoate in propan-1-ol at different temperatures.

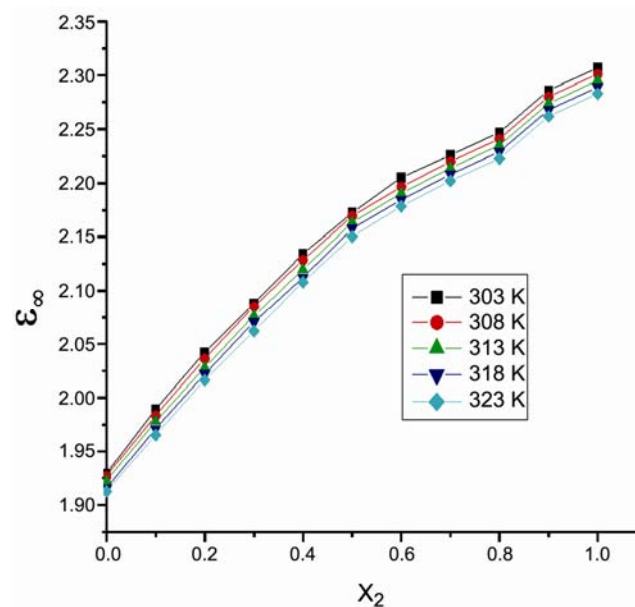


Fig. 2 — High frequency permittivity ( $\epsilon_\infty$ ) versus mole fraction ( $X_2$ ) of methyl benzoate in propan-1-ol at different temperatures

(system 1), 3 and 4 (system 2). From Figs 1-4, it is observed that there is non-linear variation of  $\epsilon_{\text{static}}$  and  $\epsilon_{\infty}$  with mole fractions at all temperatures, which indicates the interaction between the compounds. Similar results were reported by Kroeger<sup>6</sup> for the mixture of alcohols and polar liquids.

The values of  $g^{\text{eff}}$ ,  $g_f$  for system 1 and system 2 at different temperatures are presented in Tables 1 and 2, respectively. The  $g^{\text{eff}}$  values for the pure compounds 1PN and MB are greater than unity at all temperatures, which suggest that molecular dipoles have parallel orientation among themselves. For the pure compound EB, the values of  $g^{\text{eff}}$  are less than unity at all temperatures indicating anti-parallel orientation of the electric dipoles. But for both the mixture systems, the parameter  $g^{\text{eff}}$  exhibits a steadily

decreasing tendency as the concentration of MB or EB goes on increasing in 1PN at all temperatures. This tendency leads to the conclusion that the heterogeneous interaction between the compounds in binary systems, possibly between the –OH group of alcohol and –CH group of benzoates, is in such a way to form multimers with decreasing parallel orientation of electric dipoles<sup>25</sup>. The strength of this heterogeneous interaction is found to depend on the temperature and concentration of the mixture, which shows that temperature and concentration variations impact the structural properties.

The corrective Kirkwood correlation factor ( $g_f$ ) is a dielectric parameter, which can give information regarding the interaction between the compounds in the mixture. For an ideal non-interacting mixture,  $g_f$  must be unity and the magnitude of deviation of  $g_f$  from unity indicates the strength of interaction

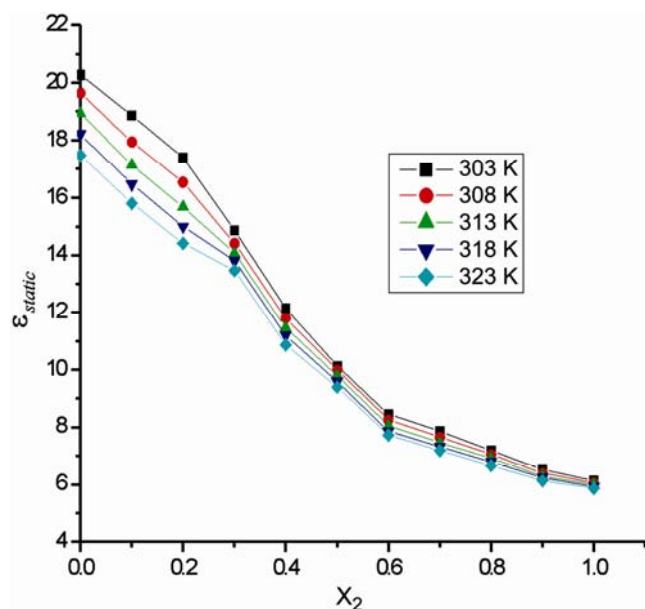


Fig. 3 — Static permittivity ( $\epsilon_{\text{static}}$ ) versus mole fraction ( $X_2$ ) of ethyl benzoate in propan-1-ol at different temperatures

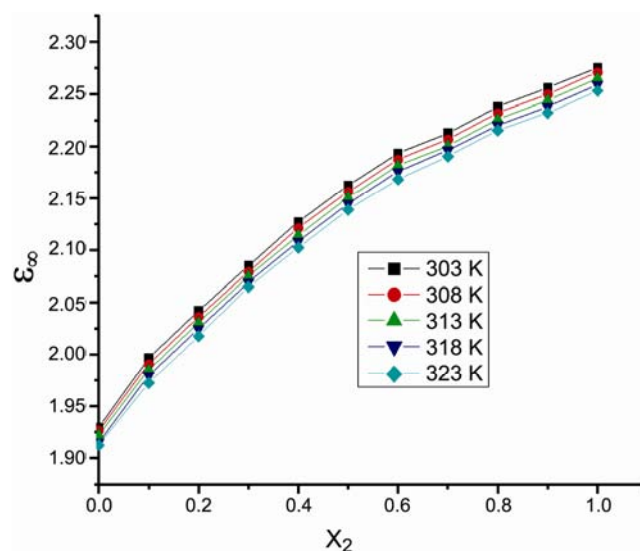


Fig. 4 — High frequency permittivity ( $\epsilon_{\infty}$ ) versus mole fraction ( $X_2$ ) of ethyl benzoate in propan-1-ol at different temperatures

Table 1 — Values of  $g^{\text{eff}}$  and  $g_f$  with mole fraction ( $X_2$ ) of methyl benzoate in propan-1-ol at different temperatures

$X_2$	$T=303\text{ K}$		$T=308\text{ K}$		$T=313\text{ K}$		$T=318\text{ K}$		$T=323\text{ K}$	
	$g^{\text{eff}}$	$g_f$	$g^{\text{eff}}$	$g_f$	$g^{\text{eff}}$	$g_f$	$g^{\text{eff}}$	$g_f$	$g^{\text{eff}}$	$g_f$
0	3.3959	1.0000	3.3592	1.0000	3.3020	1.0000	3.2547	1.0000	3.1857	1.0000
0.1	3.1342	0.9752	3.0909	0.9721	3.0556	0.9772	3.0068	0.9755	2.9489	0.9775
0.2	2.8799	0.9532	2.8423	0.9505	2.8049	0.9535	2.7600	0.9516	2.7087	0.9543
0.3	2.6373	0.9354	2.6011	0.9322	2.5696	0.9357	2.5179	0.9296	2.4645	0.9295
0.4	2.3938	0.9187	2.3672	0.9174	2.2908	0.9018	2.2332	0.8910	2.1529	0.8774
0.5	1.9170	0.8054	1.8191	0.7716	1.8823	0.8102	1.8763	0.8183	1.8829	0.8388
0.6	1.6551	0.7729	1.6355	0.7707	1.6237	0.7757	1.5970	0.7727	1.5671	0.7743
0.7	1.4833	0.7857	1.4551	0.7770	1.4110	0.7630	1.3634	0.7461	1.3260	0.7408
0.8	1.2903	0.7969	1.2555	0.7810	1.2455	0.7830	1.2196	0.7751	1.1913	0.7729
0.9	1.1423	0.8569	1.1297	0.8521	1.1155	0.8482	1.0995	0.8437	1.0819	0.8471
1	1.0280	1.0000	1.0253	1.0000	1.0217	1.0000	1.0154	1.0000	0.9959	1.0000

Table 2 — Values of  $g^{\text{eff}}$  and  $g_f$  with mole fraction ( $X_2$ ) of ethyl benzoate in propan-1-ol at different temperatures

$X_2$	$T=303\text{ K}$		$T=308\text{ K}$		$T=313\text{ K}$		$T=318\text{ K}$		$T=323\text{ K}$	
	$g^{\text{eff}}$	$g_f$	$g^{\text{eff}}$	$g_f$	$g^{\text{eff}}$	$g_f$	$g^{\text{eff}}$	$g_f$	$g^{\text{eff}}$	$g_f$
0	3.3959	1.0000	3.3592	1.0000	3.3020	1.0000	3.2547	1.0000	3.1857	1.0000
0.1	3.1196	0.9706	3.0275	0.9521	2.9534	0.9444	2.8997	0.9404	2.8416	0.9409
0.2	2.8733	0.9513	2.7858	0.9317	2.6919	0.9148	2.6306	0.9063	2.5776	0.9059
0.3	2.4378	0.8658	2.4115	0.8648	2.4054	0.8758	2.4128	0.8900	2.4022	0.9033
0.4	1.9595	0.7541	1.9451	0.7554	1.9298	0.7603	1.9245	0.7675	1.9031	0.7729
0.5	1.6116	0.6810	1.6256	0.6924	1.6258	0.7018	1.6253	0.7093	1.6226	0.7201
0.6	1.3178	0.6217	1.3107	0.6226	1.3021	0.6258	1.2924	0.6272	1.2962	0.6385
0.7	1.2292	0.6624	1.2185	0.6601	1.2065	0.6598	1.2062	0.6648	1.2056	0.6727
0.8	1.1180	0.7107	1.1174	0.7124	1.1158	0.7158	1.1133	0.7178	1.1087	0.7210
0.9	1.0055	0.7919	1.0010	0.7877	1.0029	0.7902	1.0119	0.7977	1.0126	0.8006
1	0.9432	1.0000	0.9503	1.0000	0.9578	1.0000	0.9649	1.0000	0.9715	1.0000

Table 3 — Values of Bruggeman parameter ( $f_B$ ) with volume fraction ( $\phi_2$ ) of methyl benzoate and ethyl benzoate in propan-1-ol at different temperatures

$\phi_2$	$T=303\text{ K}$		$T=308\text{ K}$		$T=313\text{ K}$		$T=318\text{ K}$		$T=323\text{ K}$	
	1PN+MB	1PN+EB	1PN+MB	1PN+EB	1PN+MB	1PN+EB	1PN+MB	1PN+EB	1PN+MB	1PN+EB
0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.1	0.9486	0.9545	0.9368	0.9400	0.9427	0.9315	0.9459	0.9341	0.9461	0.9302
0.2	0.8876	0.9020	0.8884	0.8830	0.8878	0.8725	0.8875	0.8706	0.8909	0.8660
0.3	0.8299	0.8470	0.8242	0.8280	0.8244	0.8077	0.8214	0.8011	0.8240	0.7978
0.4	0.7546	0.7428	0.7519	0.7342	0.7546	0.7257	0.7369	0.7303	0.7428	0.7395
0.5	0.6733	0.5979	0.6707	0.5953	0.6530	0.5978	0.6445	0.6123	0.6359	0.6202
0.6	0.5029	0.4393	0.5055	0.4419	0.4996	0.4361	0.5029	0.4505	0.5140	0.4478
0.7	0.3522	0.2827	0.3548	0.2794	0.3607	0.2801	0.3404	0.2853	0.3522	0.2804
0.8	0.2447	0.1765	0.2303	0.1693	0.2158	0.1647	0.2040	0.1660	0.1929	0.1654
0.9	0.1116	0.0867	0.0998	0.0828	0.0972	0.0826	0.0887	0.0789	0.0854	0.0808
1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

between the compounds i.e., greater the deviation from unity larger the strength of interaction<sup>26</sup>. In the present case, for both the systems at low concentrations of benzoate in 1PN, the values of  $g_f$  are closer to unity indicating weaker inter molecular interactions between the compounds, but as the concentration of MB and EB increases in 1PN  $g_f$  values deviate more from unity indicating the increment in the strength of hetero interaction between the compounds. The values of  $g_f$  are found to depend more on concentration than temperature as reported by Krishnan S *et al*<sup>27</sup>. Further, it is observed that  $g_f$  values deviate more from unity, in system 2 than in system 1, at all temperatures indicating stronger hetero interaction in case of system 2.

The other dielectric parameter, which gives information about the interaction between the components in the mixture, is Bruggeman parameter ( $f_B$ ). The values of  $f_B$ , for both the systems, are found to vary non-linearly with volume fraction  $\phi_2$  at all temperatures are provided in Table 3. This phenomenon indicates that there is an interaction

taking place between the components of the binary systems<sup>28</sup>.

The relaxation times ( $\tau$ ) of pure 1PN are higher and is due to the formation of intra molecular hydrogen bonding between one alcohol molecule and another (R-O-H...OH-R), which leads to the formation of self associated groups<sup>21</sup>. The increase in the number of self associated groups causes to absorb more electromagnetic energy. Due to this, molecules relax very slowly leading to higher relaxation times<sup>29</sup>. But the relaxation times of pure MB and EB are very low<sup>30</sup> compared to pure 1PN. The relaxation times of pure EB are greater than that of pure MB due to the increase in molecular size and effective radius of the rotating unit<sup>31</sup>. The relaxation times are found to decrease as the concentration of MB and EB increases in 1PN at all temperatures as shown in Figs 5 and 6, respectively.

At high concentrations of alcohol in the mixture, there are a large number of 1PN molecules surrounding the benzoate molecules and these associative alcohol molecules are forming hydrogen

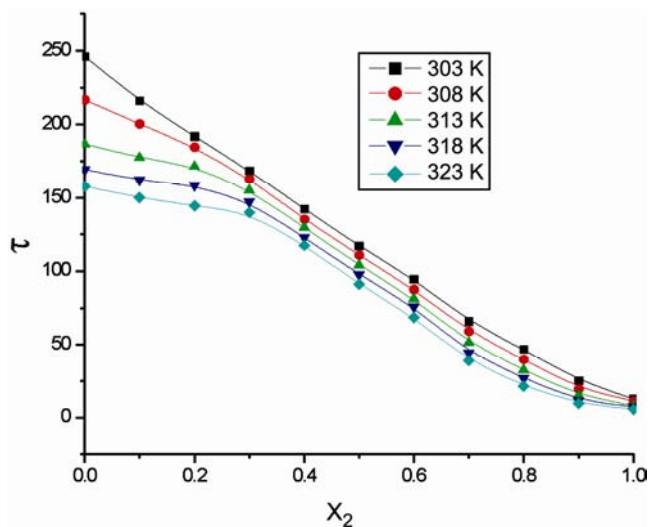


Fig. 5 — Relaxation time ( $\tau$ ) with mole fraction ( $X_2$ ) of methyl benzoate in propan-1-ol at different temperatures

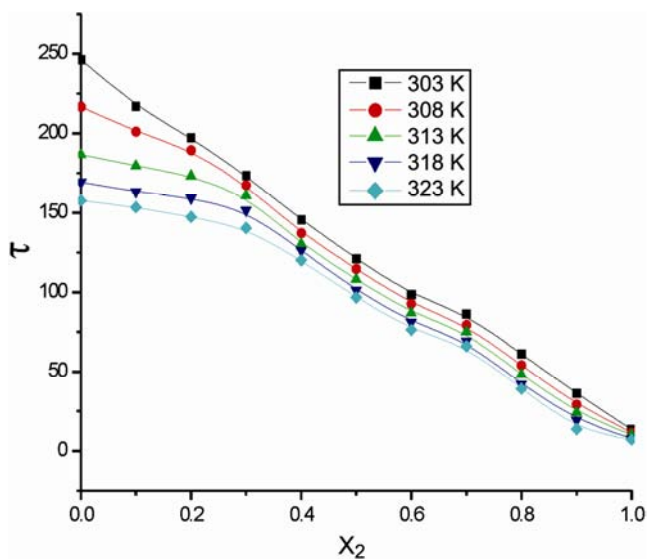


Fig. 6 — Relaxation time ( $\tau$ ) with mole fraction ( $X_2$ ) of ethyl benzoate in propan-1-ol at different temperatures

bond with the benzoate molecules. Thus, dipole-dipole interaction occurs in such a way that the effective dipole moment gets increased and linear  $\alpha$ -multimers are formed<sup>25</sup>. At low concentration of 1PN in the mixtures, there are only a small number of alcohol molecules to enable dipole-dipole interaction through hydrogen bonding with the non-associative benzoate molecules. As a result, weak intermolecular interaction occurs. The relaxation time increases with increasing alkyl chain length of benzoate indicating that the degree of cooperation for reorientation of the molecules increases with increasing length and the bulk of cluster increases. So the formation of

Table 4 — Values of Gibb's energy of activation ( $\Delta G^*$  kJmol<sup>-1</sup>) with mole fraction ( $X_2$ ) of methyl benzoate in propan-1-ol at different temperatures

$X_2$	$T=303$ K	$T=308$ K	$T=313$ K	$T=318$ K	$T=323$ K
1	11.0641	11.0082	10.3672	10.2441	9.7951
0.9	12.7608	12.3673	11.9480	11.4615	11.1952
0.8	14.3207	14.1983	13.9348	13.6921	13.3563
0.7	15.1947	15.2022	15.1321	15.0305	14.9666
0.6	16.0958	16.2085	16.3204	16.4405	16.4704
0.5	16.6344	16.8105	16.9644	17.1052	17.2338
0.4	17.1237	17.3214	17.5316	17.7112	17.9150
0.3	17.5488	17.7932	18.0009	18.0995	18.3793
0.2	17.8780	18.1146	18.2609	18.3846	18.4680
0.1	18.1773	18.3266	18.3494	18.4469	18.5701
0	18.5052	18.5257	18.4807	18.5583	18.7019

Table 5 — Values of Gibb's energy of activation ( $\Delta G^*$  kJmol<sup>-1</sup>) with mole fraction ( $X_2$ ) of ethyl benzoate in propan-1-ol at different temperatures

$X_2$	$T=303$ K	$T=308$ K	$T=313$ K	$T=318$ K	$T=323$ K
1	11.1793	11.0785	10.9292	10.4735	10.3912
0.9	13.6785	13.4024	13.1587	12.8465	12.1559
0.8	15.0020	14.9790	14.9605	14.8848	14.9660
0.7	15.8633	15.9573	16.1156	16.2059	16.3728
0.6	16.2006	16.3529	16.4926	16.6188	16.7550
0.5	16.7213	16.8965	17.0628	17.2058	17.3912
0.4	17.1792	17.3562	17.5420	17.7836	17.9723
0.3	17.6226	17.8670	18.0947	18.2664	18.3912
0.2	17.9470	18.1815	18.2855	18.3987	18.5213
0.1	18.1895	18.3358	18.3784	18.4660	18.6307
0	18.5052	18.5257	18.4807	18.5583	18.7019

hydrogen bonding between hydroxyl group ( $-\text{OH}$ ) of 1PN and  $-\text{CH}$  group of benzoates restricts the free internal rotation of the molecules.

The values of thermodynamic parameter, Gibb's energy of activation ( $\Delta G^*$ ) exhibited positive deviations, increased with decreased concentrations of benzoates (MB and EB) in propan-1-ol at different temperatures are presented in Tables 4 and 5, respectively. The increasing positive values of  $\Delta G^*$  suggest the existence of molecular associations between unlike molecules in the mixture<sup>32</sup>. In the present study,  $\Delta G^*$  values of system 2 are greater than that of system 1 indicating the strength of bond formation in system 2 is high compared to system 1.

The molar enthalpy of activation ( $\Delta H^*$ ) and molar entropy of activation ( $\Delta S^*$ ) for various mole fractions of benzoates (MB and EB) in propan-1-ol are also calculated and are given in Table 6. The positive value of  $\Delta H^*$  gives the amount of heat liberated in the process of dielectric reorientation<sup>14,34</sup>. The molar enthalpy values for both the systems (1 and 2) are

positive indicating the bond formation. The negative values of  $\Delta S^*$ , in both the systems, indicate that the activated complexes have lower entropy than the reactants, since entropy is a measure of disorder or chaos of the reaction. This is the situation encountered with most bimolecular reactions because the two molecules initially in random situation must come together with the resulting loss of entropy<sup>33</sup>. These values also indicate that there are fewer configurations possible in the activated state and for these configurations the molecules are ordered to higher extent than in the normal state<sup>34</sup>.

Observing the FT-IR spectra for the equi molar mixture of 1PN+MB (system 1), there is a shift of  $163\text{ cm}^{-1}$  wave number in the position of  $-\text{OH}$  and  $11\text{ cm}^{-1}$  wave number in the position of  $-\text{CH}$  for the mixture compared with the pure spectrums of 1PN and MB, respectively. Similarly, the FT-IR spectra for the equimolar mixture of 1PN+EB (system 2), there is a shift of  $199\text{ cm}^{-1}$  wave number in the position of  $-\text{OH}$  and  $12\text{ cm}^{-1}$  wave number in the position of  $-\text{CH}$  for the mixture compared with the pure spectrums of 1PN and EB, respectively. These shifts

are caused by the strong interaction between the high electro-negative charge of oxygen in 1PN and hydrogen of the benzoates (MB and EB). Thus, the IR analysis convinces intermolecular hydrogen bonding of the equi molar binary mixtures (system 1 and system 2) effectively with proportionate variations in stretching frequencies of  $-\text{OH}$  and  $-\text{CH}$  compared to their respective pure systems<sup>35</sup>.

The comparison of experimental and theoretical FT-IR values are provided in Table 7 and the obtained theoretical values are in good agreement with the experimental values<sup>38</sup>. The Optimized geometrical structures for the formation of hydrogen bonding in 1PN + MB and 1PN + EB, which are obtained from Hamiltonian quantum mechanical calculations using Spartan Modeling software are shown in Figs 7 and 8, respectively.

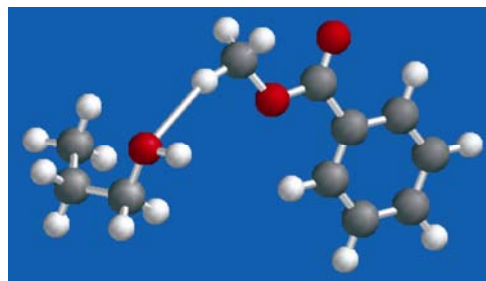


Fig. 7 — Optimized converged geometrical structure of hydrogen bonded propan-1-ol and methyl benzoate. (red: oxygen, black: carbon, white: hydrogen)

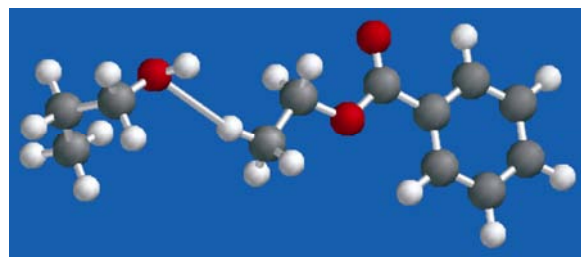


Fig. 8 — Optimized converged geometrical structure of hydrogen bonded propan-1-ol and ethyl benzoate. (red: oxygen, black: carbon, white: hydrogen)

Table 6 — Values of molar enthalpy ( $\Delta H^*$ ) and molar entropy ( $\Delta S^*$ ) for various mole fractions ( $X_2$ ) methyl benzoate and ethyl benzoate in propan-1-ol

$X_2$	$\Delta H^*$ (kJmol <sup>-1</sup> )		$\Delta S^*$ (kJmol <sup>-1</sup> K <sup>-1</sup> )	
	1PN+MB	1PN+EB	1PN+MB	1PN+EB
1	30.453	23.903	0.0636	0.0417
0.9	29.603	22.438	0.0535	0.0228
0.8	28.482	15.675	0.0464	0.0022
0.7	18.620	08.041	0.0111	-0.0257
0.6	09.945	07.716	-0.0203	-0.0280
0.5	07.427	06.601	-0.0304	-0.0334
0.4	05.069	04.896	-0.0398	-0.0405
0.3	04.964	05.740	-0.0416	-0.0393
0.2	08.881	10.000	-0.0298	-0.0264
0.1	12.452	11.834	-0.0189	-0.0210
0	15.671	15.671	-0.0092	-0.0092

Table 7 — Experimental and theoretical FT-IR analysis for the pure and binary mixtures of 1PN, MB and EB

Compound	Band	Experimental		Theoretical					
		$\nu$ (cm <sup>-1</sup> )	$\Delta\nu$ (cm <sup>-1</sup> )	AM1		PM3		MNDO	
				$\nu$ (cm <sup>-1</sup> )	$\Delta\nu$ (cm <sup>-1</sup> )	$\nu$ (cm <sup>-1</sup> )	$\Delta\nu$ (cm <sup>-1</sup> )	$\nu$ (cm <sup>-1</sup> )	$\Delta\nu$ (cm <sup>-1</sup> )
1PN	OH	3346	—	3493	—	3879	—	4006	—
MB	CH	2952	—	2983	—	3141	—	3234	—
EB	CH	2984	—	3071	—	3185	—	3276	—
1PN+MB	OH-CH	3509	163-OH	3597	104-OH	3985	106-OH	4203	197-OH
		2963	11-CH	2997	14-CH	3174	33-CH	3250	16-CH
1PN+EB	OH-CH	3545	199-OH	3654	161-OH	3818	61-OH	4132	126-OH
		2972	12-CH	3061	10-CH	3122	63-CH	3293	17-CH

## 5 Conclusions

The dielectric parameters Kirkwood effective correlation factor, corrective Kirkwood correlation factor, Bruggeman parameter, relaxation time and thermodynamic parameters Gibb's energy of activation, molar enthalpy of activation and molar entropy of activation are computed for the pure and binary mixture systems of propan-1-ol with methyl benzoate and ethyl benzoate at different temperatures for various mole fractions. The formation of hydrogen bond between the mixture systems is identified by studying the variations in the parameters determined. The existence of hydrogen bond between –OH group of propan-1-ol with –CH group of methyl benzoate and ethyl benzoate is confirmed through FT-IR spectra. The FT-IR values are determined theoretically using quantum mechanical calculations and are in good agreement with the experimental values.

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## References

- 1 Ediger M D, Angell C A & Nagel S R, *J Chem Phys*, 100 (1996) 13200.
- 2 Nath G, Sahu S and Paikaray R, *Indian J. Phys.* 83 (2009) 429
- 3 Gupta K K, Bnashal A K, Singh P J & Sharma K S, *Indian J Pure & Appl Phys*, 41 (2003) 57.
- 4 Rowlinson J S & Swinton F L, *Liquids and Liquid Mixtures*, (Butterworth, London), 3<sup>rd</sup> Edn, 1982.
- 5 Liakath Ali Khan F, Sivagurunathan P, Raja Mohamed Kamil S & Mehrotra S C, *Indian J Pure & Appl Phys*, 44 (2007) 754.
- 6 Kroeger M K, *J Mol Liq*, 36 (1987) 101.
- 7 Sengwa R J, Vinita Khatri & Sonu Sankhla, *J Sol Chem*, 38 (2009) 763.
- 8 Jacobo Troncoso, Claudio Cerdeiriña A, Yolanda Sanmamed A, Luís Romani, & Luís Paulo N Rebelo., *J Chem Eng Data*, 51(5) (2006) 1856.
- 9 George A J, *An introduction to hydrogen bonding* (Oxford University Press, London), 1997.
- 10 Parthipan G, Arivazhagan G & Thenappan T, *Philosophical Magazine Letters*, 88 (2008) 125.
- 11 Bruggeman D A G, *Ann Phys (Leipzig)*, 5 (1935) 636.
- 12 Cole K S & Cole R H, *J Chem Phys*, 9 (1941) 341.
- 13 Chaudhari A & Mehrotra S C, *Mol Phys*, 100 (2002) 3907.
- 14 Dharmalingam K, Ramachandran K, Sivagurunathan P, Prabhakar under B, Khirade P W & Mehrotra S C, *Chem Pap*, 61(4) (2007) 300.
- 15 Nora E Hill, Vaughan E, Price A H & Davies M, *Dielectric Properties and Molecular Behavior* (Northland Reinhold Company, London) 1968.
- 16 DR Lide, *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton) 78<sup>th</sup> Edn, 1971.
- 17 Kirkwood J G, *J Chem Phys*, 7 (1939) 911.
- 18 Puranic S M, Kumbharkhane A C & Mehrotra S C, *J Mol Liq*, 50 (1991) 143.
- 19 Kaatze U, *Z Phys Chem*, 153 (1987) 141.
- 20 Eyring H, Cernuschi F, *J Chem Phys*, 7 (1939) 547.
- 21 Kauzmann W, *Rev Mod Phys*, 14 (1942) 12.
- 22 Chitra M, Subramanyam B & Murthy V R K, *Indian J Pure & Appl Phys*, 39 (2001)461.
- 23 Sundaraganesan N, Dominic Joshua B, Rajamoorthy M & Gangadhar C H, *Indian J Pure & Appl Phys*, 45 (2007) 969.
- 24 *Spartan version 5.1.1*. (Wave function Inc, CA: USA) 1999.
- 25 Thenappan T, Prabakar Devaraj A, *J Mol Liq*, 123 (2006) 72.
- 26 Ajay Chaudhari, Antia Das, Garigipati Raju, Harish Chaudhari, Prakash Khirade, Navinkumar Narain, Suresh Mehrotra, *Proc Natl Sci Counc Roc (a)*, 25 (2001) 205.
- 27 Balamurugan D, Kumar S, Krishnan S, *J Mol Liq*, 122 (2005) 11.
- 28 Sivagurunathan P, Dharmalingam K, Ramachandran K, Prabhakar Undre B, Khirade P W & Mehrotra S C, *J Mol Liq*, 133 (2007) 139.
- 29 Vyas A D, Rana V A, Bhatnagar S P & Vashisth V M, *Indian J Pure & Appl Phys*, 46 (2008) 521.
- 30 Rajala G E & Crossley J, *Candadian J Chem*, 50 (1972) 99.
- 31 Chitra M, Subramanyam B & Murthy V R K, *Mol Phys*, 99 (2001) 1569.
- 32 Patil S P, Chaudari A S, Lokhande M P, Landle M K & Mehrotra S C, *J Chem Eng Data*, 44 (1999) 875.
- 33 Pal A & Kumar S, *J Mol Liq*, 109 (2004) 23.
- 34 Sharma V, Thakur N, Sharma D R, Rangra V S & Negi N S, *Indian J Pure & Appl Phys*, 46 (2008) 212.
- 35 Bansal R K, *Organic Reaction Mechanisms*, (Tata McGraw-Hill, New Delhi) 1998.
- 36 Singh A, Misra R, Shukla J P, Saxena M C, *J Mol Liq*, 23 (1983) 29.
- 37 Silverstein R M, Bassler G C & Morrill T C, *Spectroscopic Identification of Organic Compounds* (John Wiley & sons, Singapore) 5<sup>th</sup> Edn, 1991.
- 38 Singh H J & Srivastava P, *Indian J Pure & Appl Phys*, 47 (2009) 557.