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Dielectric and conformal studies of 1-propanol and 1-butanol in methanol

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Abstract Hydrogen bonds in small chain alcohol-alcohol binary systems alter the dielectric permittivity of the binary system. With a view to obtain a better understanding of the interactions in such systems, the complex permittivity spectra of mixtures of methanol (ME) with 1propanol (1PR) and 1butanol (1BU) have been measured in the frequency range 10 MHz to 20 GHz using time domain reflectometry at 288 K, 298 K, 308 K and 318 K. The dielectric parameters such as static dielectric constant and relaxation time were obtained using the calibration method based on nonlinear least squares fit method. Using these parameters excess permittivity, excess inverse relaxation time, Kirkwood correlation factor, and thermodynamic parameters were determined. It is observed that the static permittivity decreases with increase in mole fractions of 1PR/1BU in ME whereas the relaxation time increases for both the binary systems. Computational conformational analysis was performed using ab initio Hartree-Fock using Gaussian-03 program. The present studies indicate a difference in the solvation of ME by 1PR/1BU and vice versa. Further, the interaction of ME-1PR is distinctly different at the 0.55 molar concentration of 1PR while the ME-1BU system shows strong interactions in both the methanol and the 1BU rich regions.

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Introduction

Dielectric spectroscopy has been extensively used for a long time to study interactions in hydrogen bonded systems [1–9]. The presence of intermolecular interactions in polar-polar binary systems is mainly due to dipole-dipole interactions or hydrogen bonds. Alcohols are characterized by their ability to participate in intermolecular hydrogen bonding. In the case of small-chain alcohols, each with one –OH group, found in many everyday compounds and products [10–16]. Since they all have the same functional group but differ only in their chain length, the change in dielectric permittivity can be attributed to the intermolecular interactions [17–24]. But dielectric spectroscopic measurements yield macroscopic results although they are sensitive to the intermolecular interactions. In order to ascertain the nature of the interactions it is necessary to obtain the conformation of the alcohol-alcohol systems by other means such as computations [25].

There have been several studies on the dielectric properties of alcohol mixtures using different experimental methodologies, techniques and curve fitting for the excess parameters such as temperature dependence of permittivity [26, 27], study of changes in viscosity and density along with the changes in permittivity [28, 29], time domain reflectometry [30] and dielectric relaxation spectroscopy [31, 32] and non-linear regression model for analysis of dielectric data [33], to name a few. Frequency-dependent dielectric relaxation of polar-polar liquid mixtures system helps in the understanding the dynamics and structure of solvents [34]. The dielectric relaxation measurements on

methanol-water, ethanol-water and 1propanol-water mixtures have been studied using time domain reflectometry [35]. The dielectric relaxation of methanol-1propanol system have been measured up to 10 GHz by time domain reflectometry and discussed in terms of the strength and the associating effect of the hydrogen bond from −37 to + 25 °C [36]. Dielectric properties of methanol with isomers of propanol and butanol were analyzed in terms of the excess parameters over the entire composition range [24]. The dielectric relaxation mechanism of primary alcohols in various solvents, both hydrogen bonding and non hydrogen bonding was studied theoretically using the concept of chemical equilibrium between the hydrogen-bonded multimers and that between the multimers and the solvent [37]. Sengwa et al., have studied the hydrogen bond interactions in methanol + ethanol systems [38] while Smith et al., have studied the dielectric properties of aqueous alcohol solutions[39].

The conformers of alcohols in the pure form and in binary mixtures have been studied extensively [40–42]. The cyclic trimers of methanol clusters were observed using infrared spectroscopy [43]. Infrared and vacuum ultraviolet (IR/VUV) non-resonant photo-dissociation spectroscopy was used to study the clusters of 2-propanol up to pentamers and the results were compared with computations using MP2 and B3LYP calculations [44]. Semi-empirical methods have been successfully applied to systems with hydrogen bonding. [45–48]. Feng et al., have observed the correlation between semi-empirical calculations and calculations using density functional approach and also experiments [49].

The present investigation reports the dielectric relaxation of 1propanol [1PR] and 1-butanol [1BU] in methanol [ME] with 11 different concentrations in the frequency range 10 MHz–20 GHz using TDR. Dielectric parameters, excess dielectric permittivity $(\varepsilon_s)^E$ excess inverse relaxation time $(1/\tau)$, and Kirkwood correlation factor (g^{eff}) were determined. Thermodynamic parameters such as enthalpy of activation (ΔH) of the ME-1PR and ME-1BU systems were determined at 288 K, 298 K, 308 K, and 318 K respectively to know the dynamical structures of the same. Studies of ab initio Hartree-Fock simulations of ME-1PR and ME-1BU systems are also reported.

Methodology

Chemicals

The 1PR, 1BU and ME (Spectroscopic grade, Spectrochem Pvt. Ltd, Mumbai (India) were obtained commercially and used without further purification. The solutions were prepared at room temperature with 11 different volume

percentages of 1PR/1BU in methanol from 0% to 100% in steps of 10%, within 0.001% error limit. The mole fractions are calculated from the volume fraction and density data.

The complex permittivity spectra were studied using time domain reflectometry [50, 51] method. A Hewlett Packard HP 54750 sampling oscilloscope with HP 54754A TDR plug-in module was used. A fast rising step voltage pulse having rise time 40 ps was allowed to interact with the system under study. The details of the experimental setup are as previously reported [52]. All measurements were carried out under open load conditions. The change in the shape of the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In the experiment, a time window of 5 ns is set. The reflected pulses without sample $R_1(t)$, and with sample $R_x(t)$, were digitized in 1024 points in the memory of the oscilloscope and transferred to a PC through a 1.44 MB floppy diskette drive. The temperature controller system with water bath and a thermostat has been used to maintain constant temperature within the accuracy limit of ±1 K. The sample cell is surrounded by a heat insulating container through which water of constant temperature using a temperature controller system is circulated.

Data analysis

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency from 10 MHz to 20 GHZ using Fourier transformation [53–55] as

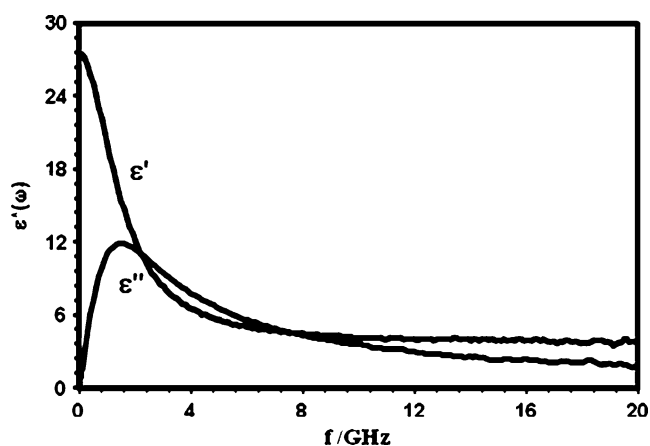$$\rho^*(\omega) = (c/j\omega d).[p(\omega/q(\omega)], \quad (1)$$

where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $[R_1(t)-R_x(t)]$ and $[R_1(t) + R_x(t)]$ respectively, c is speed of light, ω is angular frequency, d is effective pin length and $j = \sqrt{-1}$, $R_1(t)$ and $Rx(t)$ are reflected pulse without sample and with sample.

The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by using calibration method. A sample $\varepsilon^*(\omega)$ is shown in Fig. 1 for the mixture of 50% of 1-PR + 50% of ME at 298 K.

The experimental values of ε^* are fitted with the Debye expression [56]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau} \quad (2)$$

with ε_s, ε_∞ and τ as fitting parameters. In Eq. 2, ε_s is the static dielectric constant, ε_∞ is the high frequency dielectric constant, ω is the angular frequency and τ is the relaxation time of the system. A nonlinear least-squares fit method [57] was used to determine the values of these parameters.

Fig. 1 The complex permittivity spectra $\varepsilon^*(\omega)$ for the mixture of 50% of methanol +50% of 1-propanol at 298 K

Computational details

The present work involves the conformational analysis based on the Hartree-Fock formalism, involving the Born-Oppenheimer approximation. Only the electronic wave function and not the complete wave function of electrons and nuclei is considered. The multi electron Schrödinger wave equation is given by [58]

$$\left[-\frac{1}{2} \sum_i \nabla_i^2 - \sum_{A,i} \frac{Z_A}{r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} + \sum_{i>j} \frac{1}{r_{ij}} \right] \Psi(r;R)$$
$$= E\Psi(r;R) \tag{3}$$

where the symbols have the usual meanings. The capital suffixes denote the nuclei and the lower case suffixes refer to the electrons. E(R) gives the potential energy surface, from which the equilibrium geometry and other physical parameters such as vibrational frequencies can be determined. $\Psi(r;R)$, the electronic wave function, contains information pertinent to the molecular polarizabilities, the dipole moment and higher multipole moments of the system. Here the relativistic effects are not considered.

Conformational analysis was performed using self consistent field (SCF)-Hartree-Fock (HF) formalism using Gaussian-03 software [59]. Optimization of the conformations was done at the semi-empirical MNDO level and the hydrogen bond distance and energy were determined using the 6–31G and 6–31G (d,p) basis set level.

Solvation effects were studied using two methods. The first involves considering the individual solvent molecule and its interaction with the solute. The second involves the calculation of the conformations using Onsager's solvation model which is a continuum solvation model, i.e., the solvent is treated as a continuous medium.

The self consistent reaction field (SCRF) model considers the solvent as a continuous medium of dielectric permittivity ε with the solute placed inside a cavity of appropriate shape of the solvent. The solvation energy is the sum of energies required for the creation of the cavity, the dispersion interactions between the solute and solvent molecules and the polarization effects caused by the solute molecule in the cavity. The charge distribution of the solute molecule can be considered either as a dipole or as a multipole expansion [58].

Onsager's solvation model uses a spherical cavity for the solvent and approximates the solute to be a dipole. The reaction field as calculated in Gaussian-03 is given by Eq. 4

$$R = [(2\mu(\varepsilon - 1)/V(2\varepsilon + 1)], \tag{4}$$

where V is the volume of the solvent molecule, μ the dipole moment of the solute and ε the permittivity of the solvent. The cavity size V strongly effects the calculations. In the present study V was determined using an in-built calculation in Gaussian-03 where V is defined as the volume inside a contour of 0.001 electrons/bohr^3 density. The molecular volume thus determined is accurate to two significant figures [59].

Solvation model has been used to study the following systems (a) ME solvated by 1PR (b) ME solvated by 1BU (c) 1PR solvated by ME and (d) 1BU solvated by ME. These correspond to the extremes of concentrations of the ME-1PR and ME-1BU systems, where the 1:1 conformational analysis cannot be used to interpret the experimental results. The 1:1 ab initio calculation is ideally suited best for 50–50 concentration.

The present calculations have been done using the Hartree-Fock formalism using the 6–31G and 6–31G(d,p) basis levels. The basic conformations for 1-butanol were the TTg and the TGg structures that were previously proposed [60]. Similar conformations were taken up for 1-propanol.

Results

Table 1 gives the values of static dielectric constant and density for pure liquids along with literature values. ε_s values for the pure liquids differ slightly than the literature values due to the fluctuation in the temperatures within ±1 K. The determined values of ε_s and τ for mixtures of different concentrations of 1PR and 1BU in ME at different temperatures are tabulated in Tables 2, 3.

The information about the interaction of solute and solvent may be obtained from excess properties [61] such as excess permittivity and excess inverse relaxation times in

Table 1 Comparison of static permittivity for pure liquids and density used with literature values at 298 K

Liquid	ε_s		τ[ps]		Density [gcm^{-3}]
	This work	literature	This work	literature	literature
Methanol	32.64	32.63[a]	51.37	51.98 [b]	0.7914[a]
1-propanol	20.18	20.10[b]	274.60	274.06 [a]	0.8035 [a]
1-butanol	17.21	17.30[b]	433.60	434.16 [b]	0.8098 [a]

[a] [70]
[b] [71]

the mixture. The excess permittivity $(\varepsilon_s)^E$ were calculated using the relation

$$(\varepsilon_s)^E = (\varepsilon_s)_m - \left[(\varepsilon_s)_A X_A + (\varepsilon_s)_B X_B\right] \tag{5}$$

where x is volume fraction and suffices m, A and B represent the mixture, ME (solvent) and 1-PR, 1-BU (solute) in the mixtures respectively.

The excess static dielectric constant provides qualitative information about interactions [62] in the mixture as stated below.

a) $(\varepsilon_s)^E=0$ indicates that the solute and solvent do not interact and do not change their individual structural properties in the presence of other liquid.

b) $(\varepsilon_s)^E<0$ Indicates that the solute and solvent interact in such a way that total no. of dipoles decreases in the mixture, and hence there is decrease in net effective dipole polarization.

c) $(\varepsilon_s)^E>0$ Indicates that the solute and solvent interact in such a way that effective dipole polarization increases. This may be due to breaking of multimer structure into monomer structure due to the presence of other molecules.

The reorientational thermodynamic parameters, based on a bistable model, were determined using the Eyring rate equation [63], the relaxation time τ is

$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta H - T\Delta S}{RT}\right), \tag{6}$$

Table 2 Dielectric relaxation parameters for 1-PR + ME mixtures at different temperatures

Vol. fra. of 1-PR	288K	298K	308K	318K
ε_s for 1-PR ± ME				
0.0000	34.48	32.64	31.31	30.44
0.1703	34.43	31.89	30.20	28.71
0.3160	32.61	29.96	29.03	27.80
0.4419	31.43	28.77	27.11	26.19
0.5519	28.84	26.80	25.91	25.05
0.6489	29.01	27.43	26.71	25.93
0.7349	27.58	25.76	25.05	24.37
0.8117	25.86	24.48	23.89	22.87
0.8808	24.35	23.83	22.90	21.63
0.9433	23.20	22.48	21.96	20.88
1.0000	21.71	20.18	19.60	18.72
τ (ps) for 1-PR ± ME				
0.0000	58.03	51.37	43.80	42.04
0.1703	67.66	60.75	55.53	50.83
0.3160	83.37	72.58	58.47	54.46
0.4419	93.49	88.64	70.58	64.15
0.5519	102.74	92.70	80.78	72.30
0.6489	128.66	106.9	94.41	85.43
0.7349	144.20	123.41	106.1	95.84
0.8117	174.85	150.21	124.44	106.21
0.8808	212.37	181.10	143.72	130.44
0.9433	256.08	210.93	178.00	152.93
1.0000	314.70	274.60	207.32	176.45

Table 3 Dielectric relaxation parameters for 1-BU + ME mixture at different temperatures

Vol. fra. of 1-BU	288K	298K	308K	318K
ε_s for 1-BU ± ME				
0	34.48	32.64	31.31	30.44
0.1	31.62	30.37	29.58	28.43
0.2	29.62	28.86	28.19	26.34
0.3	27.64	26.54	25.13	24.39
0.4	24.99	24.02	23.04	21.91
0.5	22.98	22.55	22.23	21.44
0.6	21.74	21.24	20.41	19.8
0.7	20.14	19.68	19.33	18.65
0.8	18.85	18.34	17.68	17.05
0.9	18.04	17.52	16.83	16.3
1	18.03	17.21	15.32	14.31
τ (ps) for 1-BU ± ME				
0	58.03	51.37	43.80	42.04
0.1	65.81	59.84	47.84	48.03
0.2	70.01	65.92	62.67	56.92
0.3	86.31	75.46	71.15	61.02
0.4	109.07	100.75	94.30	78.30
0.5	148.29	129.15	115.09	98.83
0.6	179.16	162.15	140.10	125.13
0.7	222.66	196.63	170.98	150.78
0.8	287.89	252.96	212.64	177.38
0.9	364.11	305.24	245.09	219.68
1	472.81	433.60	368.57	315.09

where R is the gas constant, T is the absolute temperature, k is the Boltzmann constant, h is Planck's constant, τ is experimentally determined value of relaxation time and ΔH, ΔS are the enthalpy of activation and the entropy of activation. The bistable model considers only two possible orientations of the molecule's dipole; parallel and anti-parallel to the direction of the applied field. The calculated values of ΔH and ΔS for 1-PR + ME and 1-BU + ME systems at different temperatures are presented in Tables 4, 5.

Since the Eyring model is essentially a borrowed model, not much significance can be attributed to the absolute values of ΔH, ΔS etc.; only the sign and the relative magnitude are noteworthy. A detailed account of analysis of reorientational thermodynamic parameters with respect to the conformations has been discussed previously [64].

The information regarding the correlation of electric dipoles in polar liquids can be obtained from Kirkwood correlation factor (g) [65]

$$g = \frac{9kTM}{\mu^2 \cdot N\rho} \cdot \frac{(\varepsilon_s - \varepsilon_\infty) \cdot (2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s \cdot (\varepsilon_\infty + 2)^2} \cdot \varepsilon_o, \tag{7}$$

where μ is the dipole moment in gas phase, ρ is the density, M is the molecular weight, k is the Boltzmann constant, N is the Avogadro's number and ε_o is the permittivity of free space. The dipole moment values (in the gas phase) used [66] were 1.70, 1.68 and 1.66 for methanol,1-propanol and1-butanol respectively. Modified forms of this equation have been used to study the orientation of electric dipoles in binary mixtures [67, 68]. Such equation is used as follows:

$$g^{eff} = \frac{9kT}{N} \cdot \frac{(\varepsilon_s - \varepsilon_\infty) \cdot (2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s \cdot (\varepsilon_\infty + 2)^2} \cdot \varepsilon_o$$
$$\cdot \left(\frac{M_A}{\mu_A^2 \cdot \rho_A \cdot x_A} + \frac{M_B}{\mu_B^2 \cdot \rho_B \cdot x_B} \right), \tag{8}$$

Table 4 Enthalpy of activation (ΔH in kJ mol^{-1}) for mixture of 1-PR + ME and at different temperatures

Vol.fra.of 1-PR	288K	298K	308K	318K
0	6.134	6.051	5.968	6.217
0.1	4.745	4.662	4.579	4.828
0.2	8.921	8.838	8.755	9.005
0.3	7.832	7.748	7.665	7.915
0.4	6.587	6.504	6.421	6.670
0.5	7.859	7.776	7.693	7.942
0.6	8.026	7.942	7.859	8.109
0.7	10.332	10.249	10.165	10.415
0.8	10.439	10.356	10.273	10.522
0.9	10.604	10.521	10.438	10.687
1	12.856	12.773	12.690	12.939

Table 5 Enthalpy of activation (ΔH in kJ mol^{-1}) for 1-BU + ME mixture at different temperatures

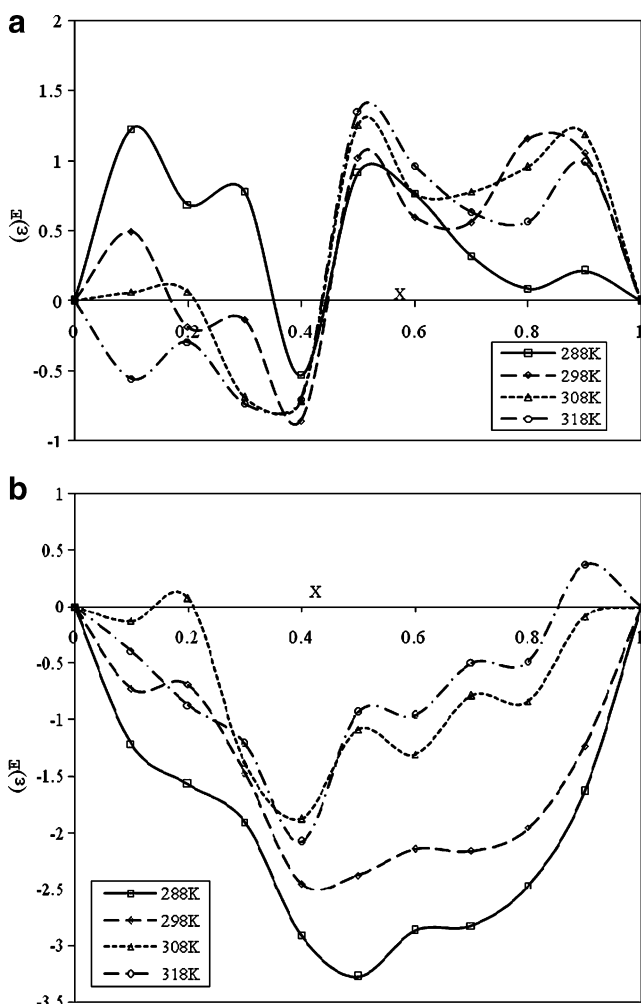| Vol.fra.of 1-BU	288K	298K	308K	318K
0	6.2173	6.1341	6.0510	5.9678
0.1	6.5466	6.4635	6.3804	6.2972
0.2	2.6978	2.6147	2.5315	2.4484
0.3	5.9601	5.8770	5.7938	5.7107
0.4	5.6226	5.5395	5.4563	5.3732
0.5	7.7392	7.6561	7.5729	7.4898
0.6	6.9047	6.8216	6.7385	6.6553
0.7	7.5677	7.4846	7.4014	7.3183
0.8	9.9564	9.8732	9.7901	9.7069
0.9	10.8438	10.7607	10.6775	10.5944
1	8.0713	7.9881	7.9050	7.8218

where g^{eff} is the Kirkwood correlation factor for binary mixture g^{eff} varies between g_A and g_B.

Discussion

The variation in static dielectric constant (ε_s) and relaxation time (τ) with mole fraction of 1PR and 1BU in ME at different temperatures are shown in Tables 2, 3. In an ideal mixture of polar liquids, if the molecules are non-interacting, a linear variation in dielectric constant and relaxation time with concentration is expected. But data in Tables 2, 3 show nonlinear variation in static dielectric constant and relaxation time with change in mole fraction of 1PR and 1BU in methanol. This suggests the intermolecular association is taking place in 1PR-ME and 1BU-ME binary systems.

It has been observed that the values of static dielectric constant decreases with increase in concentration of 1PR/1BU in ME and with increase in temperature. The relaxation time, for 1PR-ME and 1BU-ME systems increases with increase in concentration of 1PR and 1BU in ME. The relaxation time decreases with increase in temperature.

The excess property related to permittivity and relaxation time provides valuable information regarding interaction between the polar – polar liquid mixtures. The excess dielectric constant (ε_s)^E of mixtures was calculated using Eq. 3 and it's variation with mole fraction of 1PR and 1BU in ME at 288 K, 298 K, 308 K and 318 K is shown in Fig. 2. From Fig. 2a it is observed that (ε_s)^E is negative at 0.55 mole fraction of 1PR at all temperatures and positive for the rest of the mole fraction of 1PR in the liquid mixtures. From Fig. 2b it can be seen that (ε_s)^E is negative for all concentrations and temperatures for 1BU in the mixture, but at 0.36 and 0.95 mole fraction of 1BU it is
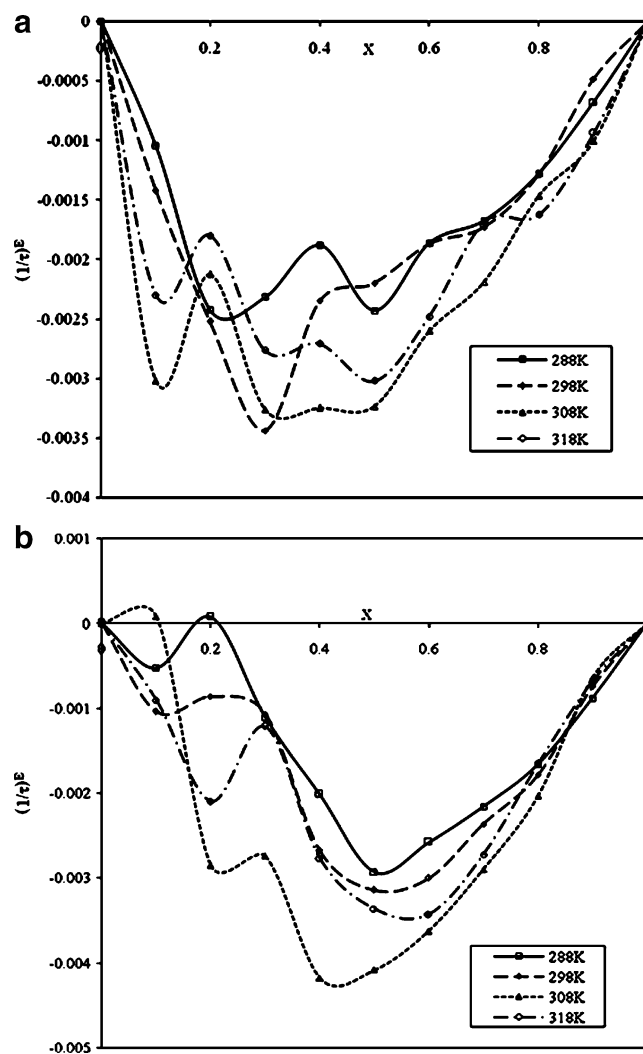
Fig. 2 Excess permittivity versus mole fraction for (a) 1-propanol-methanol, (b) 1-butanol-methanol binary mixtures

Fig. 3 Excess inverse relaxation time versus mole fraction for (a) 1- propanol- methanol, (b) 1-butanol-methanol binary mixtures

positive. Negative $(\varepsilon_s)^E$ indicates that molecules of the mixtures may form multimer structures via hydrogen bonding in such a way that the effective dipole gets reduced.

This means that there is association of 1PR-ME and 1BU-ME hydrogen bonding with the formation of multimer. Positive $(\varepsilon_s)^E$ indicates that molecules of the mixtures may form monomers or dimers structures in such a way that the number of effective dipoles increases. A comparative study of plots of the two systems gives some qualitative idea about the strength of the interaction in the mixtures. The deviation in $(\varepsilon_s)^E$ from zero is the highest in the 1PR-ME mixture and least in 1BU-ME mixture. The excess inverse relaxation time of 1PR and 1BU in ME system at 288 K, 298 K, 308 K and 318 K is shown in Fig. 3.

This suggests that there is a stronger interaction in the mixture of 1PR-ME in comparison to 1BU-ME. This is

confirmed from the simulation results where the hydrogen bond energy for the 1PR-ME system is more than that of the 1BU-ME system as seen from Table 4.
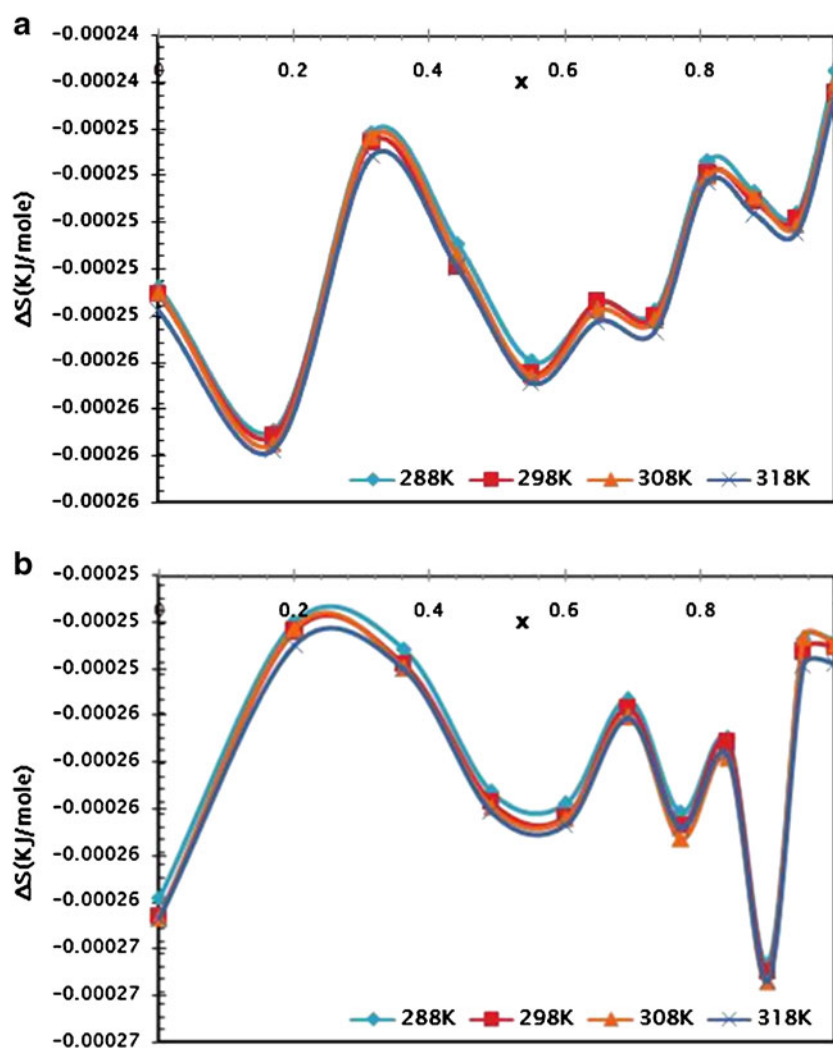
To know the dynamics of the 1PR and 1BU in ME mixtures enthalpy of activation ΔH has been calculated by using Eq. 5. The estimated value of energy parameters are given in Tables 5, 6. From Tables 5, 6, it is seen that the enthalpy of activation, ΔH, has low value in methanol rich region. This indicates that less energy is required to achieve group dipole reorientation in this region. Entropy of reactivation for both the systems is shown in Fig. 4. In the case of the former, the maximum entropy is for a concentration of 0.175 1 PR and for the later at 0.35 1BU. In both cases the maximum entropy region is the region of excess methanol. Maximum entropy implies a freedom in the reorientation of the molecules. These results imply that methanol is better solvated by 1PR and 1BU than it solvates the other two. This is also reflected in the

Table 6 Entropy of reactivation (ΔS in kJ mol^{-1}) for 1-BU + ME mixture at different temperatures

Vol.fra.of 1-PR	288K	298K	308K	318K
0	−0.000257	−0.000257	−0.000257	−0.000258
0.1	−0.000263	−0.000263	−0.000263	−0.000264
0.2	−0.000025	−0.000251	−0.000025	−0.000251
0.3	−0.000255	−0.000256	−0.000255	−0.000256
0.4	−0.000026	−0.000026	−0.000261	−0.000261
0.5	−0.000257	−0.000257	−0.000258	−0.000258
0.6	−0.000258	−0.000258	−0.000258	−0.000259
0.7	−0.000251	−0.000252	−0.000252	−0.000252
0.8	−0.000253	−0.000253	−0.000253	−0.000254
0.9	−0.000254	−0.000254	−0.000254	−0.000254
1	−0.000248	−0.000248	−0.000248	−0.000249

computational data as seen in Table 7. In the case of methanol solvated by 1PR/1BU there is a small change in the dipole moment and the total energy of the system in comparison to the solvation of 1PR/1BU by methanol.

While in the ME-1PR entropy of reactivation goes through multiple local minima between 0.3 and 0.8 1PR, it is between 0.5 and 0.85 of 1BU for ME-1BU as seen from Table 8. In the case of the former, the lowest entropy

Fig. 4 Kirkwood correlation factor g^{eff} versus mole fraction for (**a**) 1-propanol-methanol, (**b**) 1-butanol-methanol binary systems

Table 7 Results of ab initio calculations

System	HB distance	Energy		HB energy Kcal/mol	Dipole moment	6–31G (d,p)
Methanol		−114.9862948	−115.0446452		2.3707	1.9250
1 Propanol		−193.0321597	−193.1281128		2.0100	1.6423
1 Butanol		−232.0503204	−232.1655637		2.0419	1.6594
Methanol + 1 Propanol	3.409 A	−308.0110391	−308.1838588	4.6532377	2.1437	2.6343
Methanol + 1 Butanol	3.464 A	−347.0312314	−347.2208247	3.37838834	4.0463	3.0772

of reactivation is at 0.3 1PR, it is at both 0.15 and 0.95 1BU for the later. Lowering of entropy means that the system is being driven into a "frozen state", where the intermolecular interactions are such that the reorientational dynamics is frozen. In ME-1PR system the ΔS values indicate that for intermediate compositions, where neither of the components is in very much excess, the intermolecular interactions are strong enough for the reorientation to be frozen. While in the ME-1BU system, such strong interactions are seen for concentrations where one of the components is more dominant.

The computational results of the dipole moment for the two systems are useful to understand the nature of interactions in them. Solvation of methanol by PR/BU is indicative of the PR/BU rich regions while solvation of ME by PR/BU is indicative of the methanol rich region. The 1:1 conformation study corresponds to the 50–50 or the mid-concentration region Fig. 5. The three monomers have nearly the same dipole moments in the gas phase owing to the presence of the same functional group. However, on solvation, the change in the dipole moments in the two binary systems is different. In the case of 1PR-ME system the dipole momen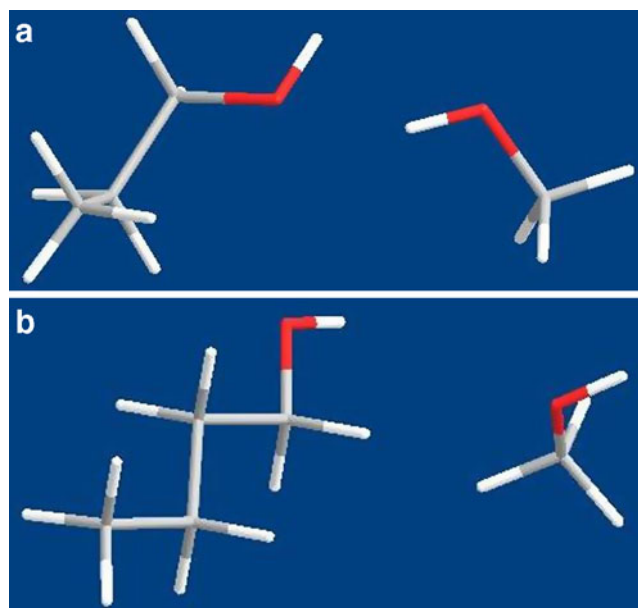ts for the methanol rich and the 1PR rich regions are nearly the same, and close to the gas phase value, indicating that the molecules of either alcohol exist mostly as monomers, as reflected by the excess permittivity value being positive for most concentrations.

In the 1BU-ME system the 1BU rich region reflects the dipole moment of a single molecule of methanol while the methanol rich region, with a large dipole moment (of ~2.12D) indicates the presence of multimers of 1BU. This is also reflected in the excess permittivity values being negative.

In the mid concentration region, as seen from Table 7, both ME-1PR/1BU systems show an increase in the net dipole moment; the values being ~2.63D and ~3.07D respectively. These results, taken along with the excess permittivity results, indicate the formation of multimers of ME-1PR/BU systems. Multimers of methanol -1propanol seem to be favorable only at this equimolar concentration.
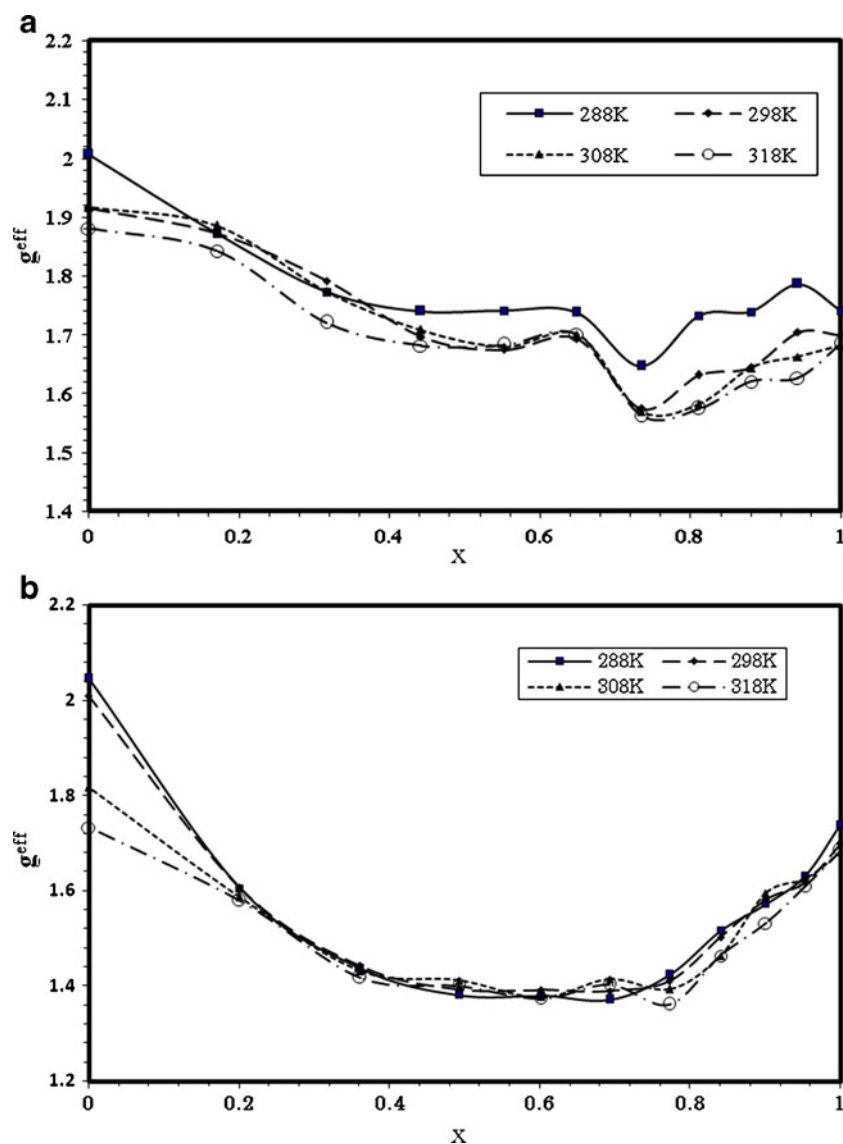
Table 8 Results of ab initio Onsager solvation model at 6–31G ab initio level

System	Energy	Dipole moment		
Methanol solvated by 1 propanol	−114.9840067	2.5936	−115.0355596	1.8797
Methanol solvated by 1 butanol	−114.9819647	2.4344	−115.0353912	1.8616
1 Propanol solvated by methanol	−193.0216381	1.9910	−193.1160212	1.8852
1 Butanol solvated by methanol	−232.0357392	2.0946	−232.1496803	2.1278

Fig. 5 Entropy of reactivation (ΔS in kJ mol^{-1}) for mixture of 1-PR,1-BU + ME at different temperatures

Fig. 6 Molecular interactions between 1:1 systems of ME-1PR and ME-1BU

The Kirkwood correlation factor g^{eff} calculated using Eq. 7 and is shown in Fig. 6 for different temperatures. From Fig. 6 it can be seen that, the values of $g^{eff} > 1$. For a given alcohol mixture, g^{eff} decreases with temperature, indicating that the increasing Brownian motion breaks the molecular association [69]. This is also seen in the results of the relaxation time which decreases with an increase in temperature signifying an increased random motion.

Conclusions

The temperature dependent dielectric relaxation parameters, excess parameters, Kirkwood correlation factor, thermodynamic parameters and results of ab initio calculations have been reported for 1-propanol-methanol and 1-butanol- methanol binary mixtures. The results show that the interaction between ME-1PR is different from that of ME-1BU.

While ME-1PR system shows a distinct interaction between the two species near the equi-molar concentration (0.55 mole fraction of 1PR), ME-1BU system shows stronger interactions in the ME and the 1BU rich regions, as seen from the thermodynamic data. Solvation of ME by 1PR/1BU is more favorable than the solvation of 1PR/1BU by ME. The values of dipole moments from ab initio calculations indicate the presence of ME and 1PR in predominantly small clusters (monomers, dimers etc). The solvation of 1BU by ME indicates the formation of clusters of larger size leading to a distinct change in the dipole moment from the gas phase value. Increasing the temperature leads to a decrease in the value of g^{eff}

demonstrating the breaking of molecular association with increasing Brownian motion.

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