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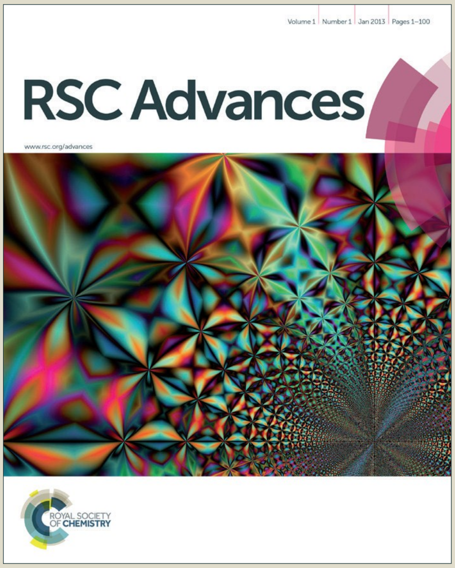

ROYAL SOCIETY OF CHEMISTRY

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ARTICLE TYPE

Disruption of self-molecular association of Pentanol in binary mixtures with Alkylbenzoates: A Dielectric Relaxation Spectroscopy Study

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

The disruption of self-molecular association of pentanol by the presence of alkylbenzoate was studied using dielectric relaxation spectroscopy. The complex permittivity spectra of binary mixtures of pentanol (1-Pentanol, 2-Pentanol, 3-Pentanol) and alkylbenzoate (methylbenzoate, ethylbenzoate, propylbenzoate, butylbenzoate) for the entire composition range was determined in the frequency range of 200 MHz to 20 GHz using vector network analyzer at room temperature. The raw data were fitted to Havriliak-Negami equation to evaluate the various dielectric parameters of static dielectric constant (ε_S), high frequency limiting dielectric constant (ε_α), and relaxation time (τ). The non-linear behaviour of these parameters for the mixtures with pentanol mole fraction represents the hetero-association of polar solvent molecules. The complex of Alkylbenzoate with 2-Pentanol and 3-Pentanol has lesser number of dipoles in the solution than 1-Pentanol and thus, decrease in molar volume of the rotating entity. The relaxation time reflects that the reorientation of –OH group of 1-Pentanol in the binary mixture with alkylbenzoate is more pronounced when compared to 2-Pentanol and 3-Pentanol. The dielectric parameters were used in calculating excess permittivity, excess inverse relaxation time, Kirkwood correlation factor, and Bruggeman factor. These dielectric results were used in interpreting the molecular interaction of the binary mixture with different dipoles in liquid state.

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† Electronic supplementary information (ESI) available: Static dielectric constant, high frequency dielelectric constant, relaxation time, Kirkwood correlation factor, Bruggeman factor, excess parameters for the pure and binary mixtures. See DOI: 10.1039/b000000x/

Cite this: DOI: 10.1039/c0xx00000x

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1. Introduction

Analysis of the dielectric properties is important in the study of the molecular association of polar systems by hydrogen bonds in liquid state.[1] The dielectric relaxation spectroscopy[2] is a powerful tool to study the intramolecular and intermolecular interactions in pure solvents and solvent binary mixtures.[1,3] There have been a number of studies carried out to get insight into the molecular interaction in polar binary mixtures and the nature of the interactions present in binary mixtures is yet to be cleared and the topic of scientific debate.[4,5] In liquid state, a considerable change in dielectric properties takes place upon mixing.[6] In binary mixtures, the molecular interaction caused by hydrogen bonding is complex due to the uncertainty of the involvement of number of molecules and the identification of the particular bond.

Among the polar solvents, alcohols are widely used as solvents and undergo self-molecular association by dipole-dipole interaction and hydrogen bonding through its -OH group. Thus alcohol plays an interesting role in chemistry and biology and has been the topic of several studies to understand the associative property with multiple internal structures which depends on the carbon chain length and the position of -OH group.[7] The disruption of molecular association through -OH group in the case of pure alcohol by different functional groups will provide a better picture of hydrogen bonding behaviour. Benzoic acid esters having the property of dipolar, hydrophobic nature, easily polarizable π electron systems also categorize them to be an important solvent.[6,8,9] Alkylbenzoates do not self-associate but is a good hydrogen bond acceptor and their ability to separate polar compounds from the non-polar, it has been the choice for a variety of applications.[8,10] Dielectric study of binary mixtures of associative alcohol and non-associative alkylbenzoates over the entire composition range will provide information on the molecular complex formation in solution. This interacting pair plays an important role in biological system and drug synthesis.[11] Indeed, this has lead to their extensive use in industries, such as 1-Pentanol is used as a starting compound in pharmaceutical applications and also used in the production of several esters.[12] These solvents, alcohols and esters are a class of the oxygenated volatile organic compounds and are a major part of the atmospheric trace gases, affecting the air quality.[13,14]

In the present work, effect of addition of alkylbenzoates with increasing alkyl chain length [methylbenzoate (MB), ethylbenzoate (EB), propylbenzoate (PB) and butylbenzoate (BB)] on self-association of pentanol [1-Pentanol (1P), 2-Pentanol (2P) and 3-Pentanol (3P)] has been studied at different mole fractions. The study has been carried out with the evaluation of dielectric parameters of excess permittivity, excess inverse relaxation time, Kirkwood correlation factor and Bruggeman factor. These parameters were used in interpreting the molecular interaction of the binary liquid mixture. This study provides information regarding influence of -OH group position in pentanol on the pentanol-alkylbenzoate structure.

2. Experimental Section

2.1. Compounds and sample preparation. High-purity alcohols, 1-Pentanol (≥99.0%), 2-Pentanol(98%), 3-Pentanol(98%) and the alkylbenzoates, Methylbenzoate (99%), Ethylbenzoate (≥99.0%), Propylbenzoate (99%), Butylbenzoate (99%) have been purchased from Sigma-Aldrich. All pure compounds were dried over 3Å molecular sieves. The fully miscible binary mixtures of pentanol and alkylbenzoate over the entire composition range were prepared by weight using a digital electronic balance for different mole fraction, X_i for Pentanol ranging from 0 to 1.

2.2. Measurement. The complex permittivity of the pure compounds and the mixtures were recorded at room temperature. The measurements were performed in the frequency range 200 MHz to 20GHz with Agilent E5071C vector network analyzer along with Agilent E85070E dielectric probe kit. The calibration of the instrument setup was performed against air, short circuit and water. The Agilent 85070E dielectric software was used to measure the complex permittivity of the samples.

2.3. Data analysis. The frequency dependent complex permittivity spectra, obtained from the experiment were fitted to Havriliak-Negami (HN) equation[15] by non-linear least-squares fitting based on Levenberg-Marquardt algorithm and is given as follows:

$$\varepsilon^*(\nu)=\varepsilon'-i\varepsilon''=\varepsilon_\alpha+\frac{\Delta\varepsilon}{(1+(i2\pi\nu\tau)^{\alpha})^{\beta}}$$

In this equation, ε^* is the complex permittivity (constant) at frequency ν with real part ε' and imaginary part ε'', ε_α is high frequency dielectric permittivity, the relaxation strength $\Delta\varepsilon=\varepsilon_S-\varepsilon_\alpha$ where ε_S is the static permittivity, τ is the relaxation time, α ($0<\alpha\leq 1$) and β ($0<\beta\leq 1$) are shape parameters representing symmetric and asymmetric shape of the spectrum.

The interaction of polar liquids 1 and 2 in mixture is also indicated by Bruggeman factor[16] f_B with volume fraction φ_2 of alkylbenzoates. f_B is related to static permittivity and the expression of f_B is given by

$$f_B=\frac{(\varepsilon_{sm}-\varepsilon_{s2})}{(\varepsilon_{s1}-\varepsilon_{s2})}\left(\frac{\varepsilon_{s1}}{\varepsilon_{sm}}\right)^{\frac{1}{3}}=1-\varphi_2$$

The plot f_B vs φ_2 is linear for non-interacting solvent mixtures and for interacting solvent mixtures, the plot deviates from linearity. The modified Bruggeman mode[17] is defined as

$$f_B=1-[a-(a-1)\varphi_2]\varphi_2$$

with a having a value of unity for Bruggeman ideal mixtures and deviates from unity for hetero-associative system.

The Kirkwood correlation factor[18], g is related to the dielectric relaxation parameters and useful in obtaining the information of liquid structure, molecular orientation and electric dipole orientation in polar solvents. The g factor for a pure solvent is defined as

$$\frac{4\pi N\mu^2\rho}{9kTM}g = \frac{(\varepsilon_s-\varepsilon_\alpha)(2\varepsilon_s+\varepsilon_\alpha)}{\varepsilon_s(\varepsilon_\alpha+2)^2}$$

where N is the Avogadro's number, μ is the dipole moment, ρ is the density at temperature, T, k is the Boltzmann constant, M is the molecular weight. Values of μ and ρ for the pure solvents are used from literature.[7,19]

For a binary mixture of polar solvent 1 and 2, the effective Kirkwood correlation factor, g^{eff} can be expressed as[20]

$$\frac{4\pi N}{9kT}\left(\frac{\mu_1^2\rho_1}{M_1}X_1+\frac{\mu_2^2\rho_2}{M_2}X_2\right)g^{eff} = \frac{(\varepsilon_{sm}-\varepsilon_{\alpha m})(2\varepsilon_{sm}+\varepsilon_{\alpha m})}{\varepsilon_{sm}(\varepsilon_{\alpha m}+2)^2}$$

The value of g^{eff} changes from g_1(X_1=1) to g_2(X_2=1). $g^{eff} < 1$, indicates the antiparallel orientation of the electric dipoles, $g^{eff} >$ 1 suggests the parallel orientation of the electric dipoles and $g^{eff} =$ 1 indicates no electric dipole correlation. g^{eff} is affected by an amount, g^f in the mixture. The corrective Kirkwood correlation factor, g^f is expressed as

$$\frac{4\pi N}{9kT}\left(\frac{\mu_1^2\rho_1}{M_1}g_1X_1+\frac{\mu_2^2\rho_2}{M_2}g_2X_2\right)g^f = \frac{(\varepsilon_{sm}-\varepsilon_{\alpha m})(2\varepsilon_{sm}+\varepsilon_{\alpha m})}{\varepsilon_{sm}(\varepsilon_{\alpha m}+2)^2}$$

In the mixture the reorientation of the constituent solvent molecules cooperatively happens by the hydrogen bonding of –OH group of pentanol and –CO group of alkylbenzoates. The apparent free energy of activation, ΔF_{exp} of the rearrangement of the dipoles is given by the Eyring formula[21]

$$\Delta F_{\exp} = RT\ \ln\left[(kT/h)\ \tau\right]$$

where R is universal gas constant, T is temperature, k is the Boltzmann constant, h is Planck constant and τ is experimentally determined relaxation time. For an ideal mixture of polar liquids in which the individual solvent retains its dynamical structure in the mixture, the theoretically calculated ΔF_{theo} can be expressed as the arithmetic mean of the pure solvent as[22]

$$\Delta F_{theo} = \Delta F_1X_1 + \Delta F_2X_2$$

where ΔF_1 and ΔF_2 are apparent free energy of activation of pure pentanol and alkylbenzoate respectively and X_1 and X_2 are corresponding mole fraction.

The excess parameters,[23] namely excess permittivity, excess inverse relaxation time are useful in obtaining the information regarding the two polar solvent interactions in the mixture. Excess permittivity ε^E, of the binary mixtures is evaluated as

$$\varepsilon^E = (\varepsilon_{sm}-\varepsilon_{\alpha m}) - [(\varepsilon_{s1}-\varepsilon_{\alpha 1})X_1 + (\varepsilon_{s2}-\varepsilon_{\alpha 2})X_2]$$

where, X is the mole fraction. The subscripts m, 1 and 2 signify mixture, pentanol and alkylbenzoate respectively. Excess permittivity ε^E provides molecular interaction information as follows:

(a) If $\varepsilon^E = 0$, the solvents 1 and 2 do not interact. (b) If $\varepsilon^E < 0$, the solvents 1 and 2 interact and the effective dipole moment is decreased. It may lead to the multimer formation in the mixture. (c) If $\varepsilon^E > 0$, the solvents 1 and 2 interact and the effective dipole moment is increased. It may lead to multimer and dimer formation.

The excess inverse relaxation time, $(1/\tau)^E$ of the mixtures represents the average broadening of the dielectric spectra. $(1/\tau)^E$ is calculated using the following equation:

$$(1/\tau)^E = (1/\tau_m) - [(1/\tau_1)X_1 + (1/\tau_2)X_2]$$

Excess inverse relaxation time, $(1/\tau)^E$ provides information on dynamics molecular interaction as follows:

(a) $(1/\tau)^E = 0$ reflects no change in the dynamics of solvents 1 and 2 interaction. (b) If $(1/\tau)^E < 0$, due to the interaction of solvent 1 and 2, the effective dipole rotates slowly. (c) If $(1/\tau)^E >$ 0,the interaction of solvent 1 and 2 results that the effective dipole rotate rapidly.

3. Results and Discusions

The plot of dielectric parameters for butylbenzoate (BB) and 1-Pentanol (1P) binary mixture, as a function of frequency for 1-Pentanol mole fraction, X_1 (from 0 to 1) is shown in Figure 1. In this plot of dielectric loss (ε'') vs frequency, the position of the peak observed shifts towards the lower frequency with increasing the 1-Pentanol mole fraction.

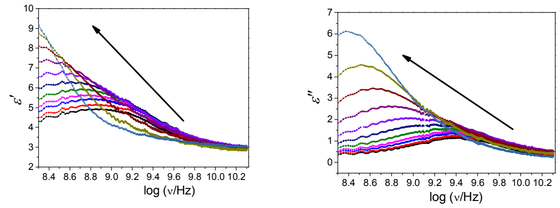

Figure 1. Plot of frequency dependence of the dielectric parameters for butylbenzoate (BB) and 1-Pentanol (1P) mixture at room temperature with increasing 1-Pentanol mole fraction (X_1=0 to X_1=1).

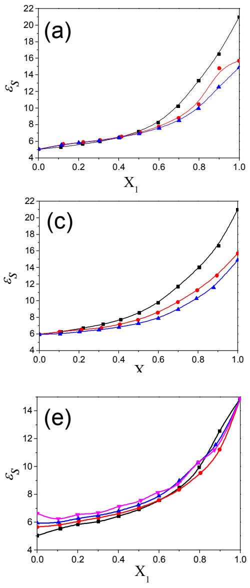

Figure 2. Variation of static permittivity, ε_S for binary mixtures of pentanol and alkylbenzoate with mole fraction of pentanol at room temperature. Butylbenzoate (a), propylbenzoate (b), ethylbenzoate (c) and methylbenzoate (d). ■ 1P, ● 2P, ▲ 3P. Figure (e) is for 3-Pentanol/alkylbenzoate mixture. ■ BB, ● PB, ▲ EB,▼ MB.

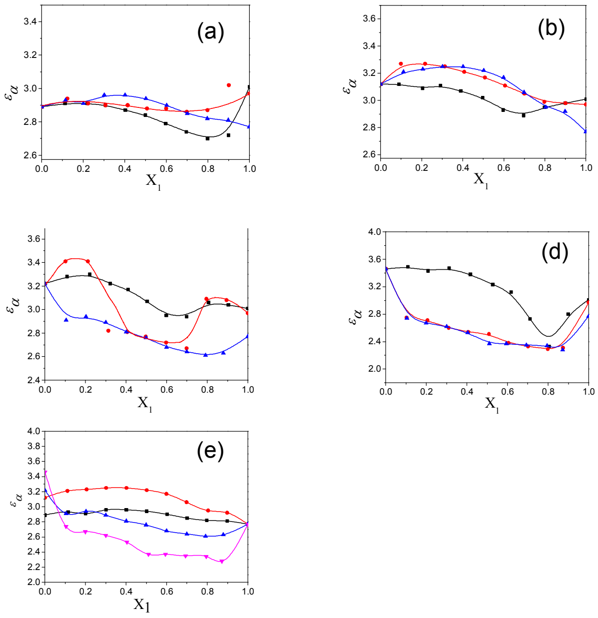

Figure 3. Variation of high frequency permittivity, ε_α for binary mixtures of pentanol and alkylbenzoate with mole fraction of pentanol at room temperature. Butylbenzoate (a), propylbenzoate (b) ethylbenzoate (c) and methylbenzoate (d). ■ 1P, ● 2P, ▲ 3P. Figure (e) is for 3-Pentanol/alkylbenzoate mixture. ■ BB, ● PB, ▲ EB,▼ MB.

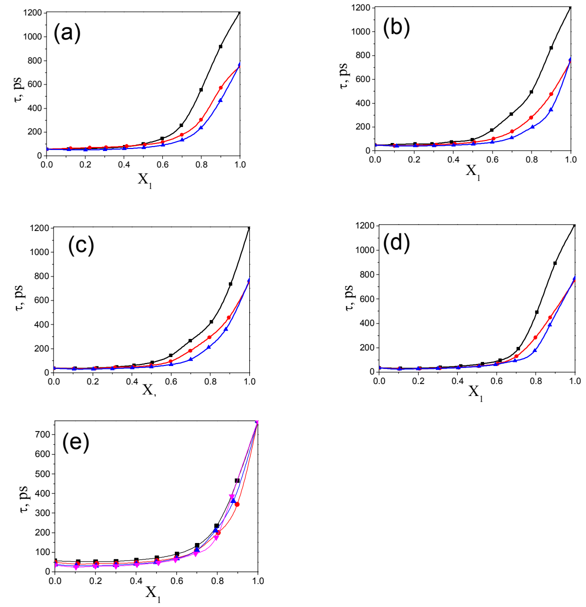

Figure 4. Variation of relaxation time, τ for binary mixtures of pentanol and alkylbenzoate with mole fraction of pentanol at room temperature. Butylbenzoate (a), propylbenzoate (b), ethylbenzoate (c) and methylbenzoate (d). ■ 1P, ● 2P, ▲ 3P. Figure (e) is for 3-Pentanol/alkylbenzoate mixture. ■ BB, ● PB, ▲ EB,▼ MB.

The values of dielectric parameters, static dielectric constant (ε_S), high frequency dielectric constant (ε_α), relaxation time (τ) were obtained from fitting the dielectric spectra at room temperature for all pure solvents and mixtures is reported in ESI Table 1†, ESI Table 2† and corresponding figures are shown in Figure 2, Figure 3 and Figure 4. These values of ε_S, ε_α, τ for pure 1-Pentanol and alkylbenzoates are close to the values as reported by Navarro et. al using the same experimental procedure. The static dielectric constant value for pure 2-Pentanol and pure 3-Pentanol are found to be in good agreement with the values evaluated by D'Aprano et. al using bridge method.[24] From ESI Table 2† and Figure 2, it is clear that the static dielectric constant increases for all binary mixture of alkylbenzoate and pentanol with increase in 1-Pentanol (1P), 2-Pentanol (2P) and 3-Pentanol (3P) concentration. A similar increase in the static dielectric constant value of the mixture of 1P, 2P and 3P with water was also observed where all three isomers gave the different static dielectric constant value with same concentration. It is also observed that change in static dielectric constant of the mixture is non-linear with the mole-fraction X_1 of 1-Pentanol, 2-Pentanol and 3-Pentanol when mixed with methylbenzoate (MB), ethylbenzoate (EB), propylbenzoate (PB) and butylbenzoate (BB). The increase in static dielectric constant with increase in a solvent in a binary solvent mixture signifies that spherical molecular aggregates transform to more correlated elongated aggregates resulting in parallel orientation of the dipoles.[5] Though small, there is a difference in static dielectric constant value for the three penanol isomers when mixed with each alkylbenzoate for the same pentanol concentration and this difference is insignificant in the lower pentanol content. The static dielectric constant value for 2-Pentanol and 3-Pentanol are smaller when compared to 1-Pentanol. This may be due to decrease in number of dipoles of the complex formed in the solution and thus, decrease in molar volume of the rotating entity. Upto X_1=0.5, BB shows similar static dielectric constant value with 1P, 2P and 3P whereas it is X_1=0.3 for PB and EB. After this point, the curve rises towards a higher ε_S value with alcohol concentration which is more pronounced in 1-Pentanol when compared to 2-Pentanol and 3-Pentanol. The plot of 3-Pentanol/alkylbenzoate binary mixture is shown in Figure 2e. Like the mixture of 1-Pentanol/alkylbenzoate mixture, a similar trend is observed. From Figure 2e for the mixture of 3-Pentanol/alkylbenzoate, it is noticed that difference in ε_S value among the alkylbenzoates is smaller for same pentanol concentration than observed with methanol[9] and it is lower for the alkylbenzoate with larger alkyl chain length. After X_1=0.6, all alkylbenzoates show similar ε_S value and upto X_1=0.6, the ε_S value follow the order MB>EB>PB>BB. This reflects that with alkylbenzoate having longer alkyl group, the number of complex dipoles decreases and thus decreasing the molar volume of the rotating group. For the plot of ε_α vs X_1 (see Figure 3), non-linearity is observed and indicates interaction between pentanol and alkylbenzoate. A non-linear result of static and high frequency dielectric constant with increasing alcohol concentration for the hetero-association of alcohol with other polar solvents is reported in the literature.[3,5] In the dielectric spectroscopy study of the mixture of alkan-1-ol/alkylbenzoate, it is established that the effect of alcohol concentration on ε_α value is smaller in case of longer chain alcohol.[9] Since the present work deals with long-chained alcohol, namely isomeric pentanols, the same conclusion can be drawn. It is observed that the change in ε_α value (see Figure 3e) is small in case of 3-Pentanol/alkylbenzoate mixture like 1-Pentanol/alkylbenzoate mixture. Figure 3a, 3b, 3c and 3d indicates that the alkylbenzoates behaves differently with the three pentanol isomers 1P, 2P, 3P resulting in different ε_α value for the same pentanol concentration. This change in ε_α is smaller when compared to the mixture of lower alcohol with alkylbenzoates. In Figure 4, dielectric relaxation time (τ) of the mixture of MB, EB, PB and BB with 1-Pentanol, 2-Pentanol and 3-Pentanol are seen to be in increasing order with the pentanol concentration which is due to the hindrance of the rotation of the molecule. The relaxation time of 1-Pentanol/alkylbenzoate mixture is found to be more than 2-Pentanol/alkylbenzoate and 3-Pentanol/alkylbenzoate mixture and this difference increases with increasing pentanol concentration. It indicates that the reorientation of the -OH group of pentanol depends to some extent on the position of -OH group in the pentanol backbone. The reorientation of molecules in the mixture is more for primary alcohol of 1-Pentanol than in secondary alcohol 2-Pentanol and 3-Pentanol when mixed with alkylbenzoates of different alkyl chain length. Difference in relaxation time for mixture between 2-Pentanol and 3-Pentanol is small. Figure 4e shows the effect of 3-Pentanol concentration on the relaxation time of 3-Pentanol/alkylbenzoate mixture. In this figure it is observed that relaxation time, τ follows the order of BB>PB>EB>MB ie. molecular rotation is hindered with increasing alkyl chain length of alkylbenzoates. This observation concurs with the previous study of alkan-1-ol/alkylbenzoate mixture.

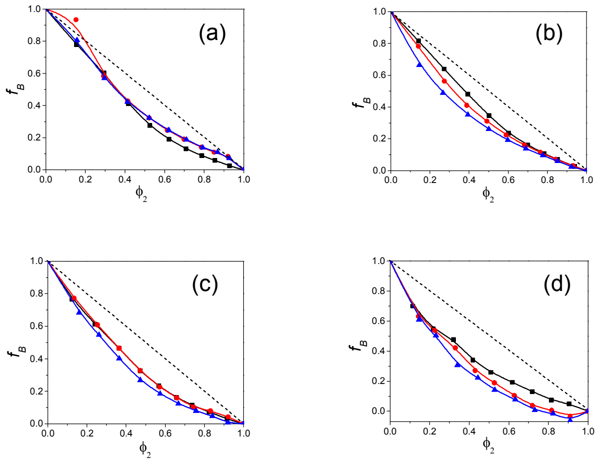

Figure 5. Plot of Bruggeman Factor f_B for binary mixtures of pentanol and alkylbenzoate vs mole fraction of pentanol (X_1) at room temperature. Butylbenzoate (a), propylbenzoate (b), ethylbenzoate (c) and methylbenzoate (d). ■ 1P, ● 2P, ▲ 3P.

The estimated values of Bruggeman factor f_B for all the binary mixtures of polar solvents alkylbenzoates and pentanols are listed in ESI Table 3† and the plot of f_B vs volume fraction φ_2 of alkylbenzoates is shown in Figure 5. These plots are useful in evaluating information the interaction between the pentanol and alkylbenzoate molecules in the mixture. All the plots of f_B reflect the deviation from the linear relationship with φ_2 which is the result from the hydrogen bonding interaction of -OH group of 1P, 2P, 3P with -CO group of BB, PB, EB, MB. A similar nonlinear behavior was also observed for the alcohol when mixed with alkybenzoates.[9] The value of parameter *a* is shown in ESI Table 4†. For Bruggeman ideal mixtures, the parameter *a* equals unity. ESI Table 4† shows that *a* deviates from unity. The values of *a* is greater than 1 and this indicates the presence of significant hetero-association of constituent solvent molecules in all mixtures. It also signifies the increase in effective solvent volume.

The calculated Kirkwood correlation parameter g_i for pure solvents and g^{eff} for the binary mixtures for all mole fractions of pentanol are included in ESI Table 5† and ESI Table 6† respectively. The g_i parameter for the pure solvents is in good agreement with the literature values.[9] This parameter is important for the information of dipole orientation and the structure of the hetero-association. ESI Table 5† shows that the Kirkwood correlation parameter is less than unity for all pure alkylbenzoates (MB, EB, PB and BB) which indicates the anti-parallel orientation of the electric dipoles in alkylbenzoates. Pure solvents 1-Pentanol, 2-Pentanol and 3-Pentanol have g_i value greater than unity and thus the molecular dipoles have parallel orientation. In Figure 6, it is observed that g^{eff} for the binary mixture is concentration dependent and it increases with the addition of 1-Pentanol, 2-Pentanol and 3-Pentanol. The present work indicates that g^{eff} increases with isomeric pentanol concentration and has been postulated in a similar system,[24] that the increase shows presence of anti-parallel configuration of dipoles. This increase in g^{eff} with pentanol content suggests the reorientation of neighboring polar molecules in a mixture with the parallel alignment of the electric dipoles. In a mixture -OH group of pentanol acts as a proton donor and participates in hydrogen bonding with the polar –CO group of alkylbenzoates. The hetero-associative interaction possibly is due to the hydrogen bonding between -OH group of pentanol and -CO group of alkylbenzoates to form the multimers occurs in such a way to increase the effective dipole moment in the mixture.[25] g^{eff} value is higher for PB and BB when mixed with 1-Pentanol than with 2-Pentanol and 3-Pentanol. But with decrease in alkyl chain length for MB and EB there is less difference in g^{eff} value in the binary mixture with all three pentanols. Binary mixture of PB and BB with 2-Pentanol or 3-Pentanol shows less difference in g^{eff} value.

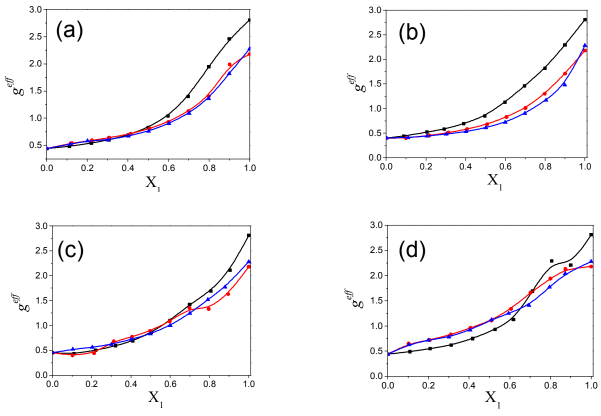

Figure 6. Plot of Kirkwood Effective Correlation factor g^{eff} for binary mixtures of pentanol and alkylbenzoate vs mole fraction of pentanol (X_1) at room temperature. Butylbenzoate (a), propylbenzoate (b), ethylbenzoate (c) and methylbenzoate (d). ■ 1P, ● 2P, ▲ 3P.

The Kirkwood corrective correlation factor g^f value, which deviates from unity for all the binary mixtures of the polar solvents are reported in ESI Table 6† and corresponding plots are shown in Figure 7. The deviation from unity is the significance of the interaction of the constituent solvent molecules in the mixture. The g^f value for pure solvents is unity and it is close to unity for the binary mixtures with lower concentration of pentanol or alkylbenzoate, is the indication of absence or weak heteromolecular interaction respectively.[3] All pentanol/alkylbenzoates show g^f value that deviates from unity for the whole composition range and the presence of re-alignment of dipoles of the neighboring polar molecules. g^f value of MB is close to unity in the case of 2-Pentanol and 3-Pentanol. This deviation is also less for EB with 2-Pentanol and 3-Pentanol. The apparent activation energy values of experimentally determined, ΔF_{exp} and theoretically calculated, ΔF_{theo} are recorded in ESI Table 6†. From this table, it is observed that the observed free energy deviates from the theoretically calculated free energy of ideal solution. This is reflected by the difference, $\Delta F_{diff} = \Delta F_{theo} - \Delta F_{exp}$ for all binary mixtures in the entire composition range. This deviation from ideal behaviour can be interpreted as the co-operativity of pentanol and alkylbenzoate molecules by hydrogen bonding. The difference, ΔF_{diff} value exhibits a parabolic nature with increasing mole fraction of pentanol. The maximum region is co-operativity region between pentanol and alkylbenzoate molecule and is in the composition range of X_1=0.4 to 0.6. Indeed, the maximum co-operativity region implies hydrogen bonding. This is further supported by the non-linear dependency of relaxation time of the mixture with pentanol composition. In this region the concentration of the co-operative domain of the pentanol-alkylbenzoate complex is maximum.

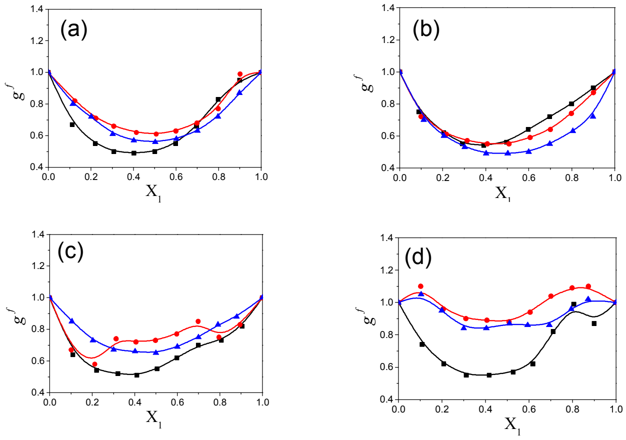

Figure 7. Plot of Kirkwood Corrective Correlation factor g^f for binary mixtures of pentanol and alkylbenzoate vs mole fraction of pentanol (X_1) at room temperature. Butylbenzoate (a), propylbenzoate (b), ethylbenzoate (c) and methylbenzoate (d). ■ 1P, ● 2P, ▲ 3P.

The variation of excess dielectric parameters, namely excess static permittivity, ε^E and excess inverse relaxation time, $(1/\tau)^E$ with pentanol mole fraction X_1 at room temperature for all binary mixtures are shown in Figure 8 and Figure 9 respectively. These two parameters are important which may be evident for the formation of multimers due to polar-polar intermolecular interaction in the mixture. These excess parameters are relative to the ideal solution and can be used to interpret the deviation of the binary mixture from ideality. The trend in behaviour for the three parameters is similar to the three pentanols with MB, EB, PB and BB. From Figure 8, it is noticed that the value of ε^E is negative for whole composition range in case of all pentanols with alkylbenzoates mixtures. It indicates that the alignment of the two dipoles through hydrogen bonding of -OH group of the pentanol with –CO group of alkylbenzoate occurs in such a way that the effective dipole of the mixture is decreased. For all binary mixtures, ε^E value is more negative for 1-Pentanol in comparison to 2-Pentanol and 3-Pentanol. It reflects that there is strong intermolecular interaction of the esters with 1-Pentanol when compared to the other two pentanol isomers. This indicates that the primary alcohols have greater ability to break the alkylbenzoate structure in comparison to the secondary alcohols. The minima for the mixture of the three isomeric pentanols with alkylbenzoate have been found in the range of X_1=0.6-0.7. There is no order found in the negative value of ε^E for 3-

Pentanol/alkylbenzoate mixture as shown for methanol/alkylbenzoates[9]. The difference within the alkylbenzoates is small.

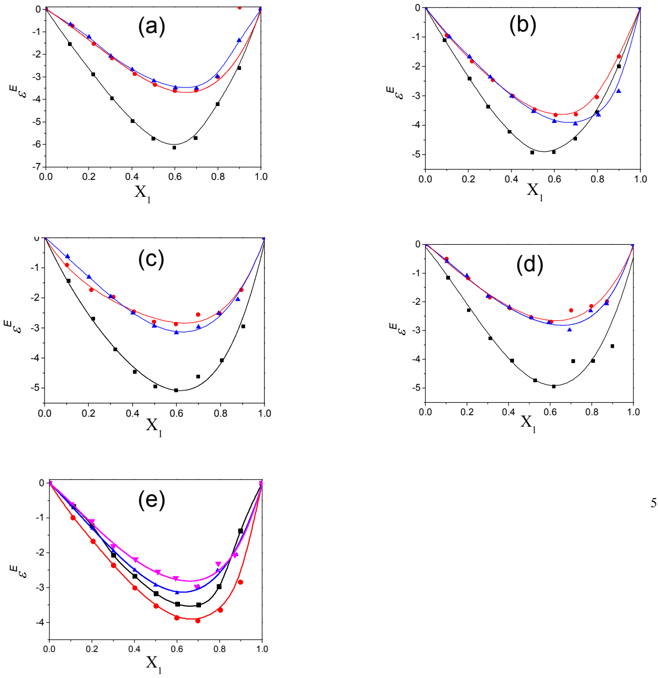

Figure 8. Variation of excess permittivity, ε^E for binary mixtures of pentanol and alkylbenzoate with mole fraction of pentanol at room temperature. Butylbenzoate (a), propylbenzoate (b), ethylbenzoate (c) and methylbenzoate (d). ■ 1P, ● 2P, ▲ 3P. Figure (e) is for 3-Pentanol/alkylbenzoate mixture. ■ BB, ● PB, ▲ EB,▼ MB.

The variation of $(1/\tau)^E$ with an increasing mole fraction of pentanol, X_1 is shown in Figure 9. From this graph, it is clear that in the ester rich region, the values of $(1/\tau)^E$ is positive and in the pentanol rich region the values become negative. The positive $(1/\tau)^E$ value was also noted for alkan-1-ol/alkylbenzoate mixture in the alkylbenzoate rich region and became negative in alcohol rich region.[9] In the ester rich region, where the pentanol content is low the effective dipole rotates faster in the field created as a result of the intermolecular interaction. With increasing pentanol content, the binary mixture of pentanol and alkylbenzoates start showing negative values of $(1/\tau)^E$ and this indicates a slower rotation of the effective dipole in the field created as a result of heteromolecular interaction through hydrogen bonding of –OH group of pentanol with –CO of alkylbenzoate. The zero-crossing position of $(1/\tau)^E$ occurs at different mole fractions for the three pentanol isomers in all binary mixtures. For this position, there is a consistent increase in mole fraction as one traverses from 1-Pentanol to 3-Pentanol in all binary mixture. In the case of 3-Pentanol with BB, PB, EB, MB binary mixture, it displays a large positive $(1/\tau)^E$ value when compared to 1-Pentanol and 2-Pentanol. From Figure 9e, it is observed that the order of positive $(1/\tau)^E$ value is MB>EB>PB>BB with 3-pentanol. In this study, zero-crossing position of $(1/\tau)^E$ for 1-Pentanol/MB mixture is found to be different from Navarro et. al.[9]

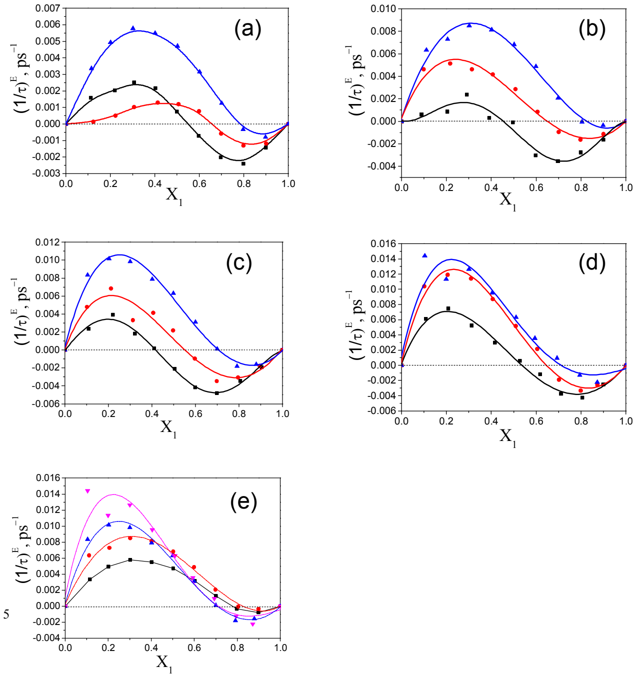

Figure 9. Variation of excess inverse relaxation time, $(1/\tau)^E$, ps^{-1} for binary mixtures of pentanol and alkylbenzoate with mole fraction of pentanol at room temperature. Butylbenzoate (a), propylbenzoate (b), ethylbenzoate (c) and methylbenzoate (d). ■ 1P, ● 2P, ▲ 3P. Figure (e) is for 3-Pentanol/alkylbenzoate mixture. ■ BB, ● PB, ▲ EB,▼ MB.

4. Conclusion

The structural behaviour of binary mixture of 1-Pentanol/alkylbenzoate, 2-Pentanol/alkylbenzoate and 3-Pentanol/alkylbenzoate has been studied using dielectric relaxation spectroscopy. The dielectric parameters of static dielectric constant, dielectric constant at high frequency limit, relaxation time, Bruggeman factor, Kirkwood correlation factor and the excess permittivity parameters of excess static permittivity, excess inverse relaxation time have been evaluated at room temperature for the binary mixed solvents at various mole fractions. The formation and strength of the complexes formed in the mixture due to heteromolecular polar-polar interaction through hydrogen bonding has been described with change in parameters with the concentration of the constituent solvents. The non-linear behaviour of static dielectric constant, high frequency dielectric constant, relaxation time with pentanol mole fraction for all the studied binary mixtures signifies the presence of intermolecular interaction. In pentanol rich region the effective dipole of the binary mixtures rotates slowly and in the ester rich region this rotation is faster. The number of dipoles of the complex of secondary alcohols/alkylbenzoates formed in the solution is smaller than for primary alcohol and thus, there is a decrease in molar volume of the rotating entity. 1-Pentanol is found to have greater ability to interrupt formation of alkylbenzoate aggregrates in comparison to its isomeric counterparts.

ACKNOWLEDGEMENT

All authors are grateful to IIT Patna for providing research facilities. S.B. is thankful to IIT Patna for financial support. A. V. and A. C. gratefully acknowledge the Department of Science and Technology (Inspire) for financial assistance. The authors are also thankful to Department of Physics, IIT Patna for their cooperation in usage of vector network analyzer.

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Graphical abstract

Disruption of self-molecular association of Pentanol in binary mixtures with Alkylbenzoates: A Dielectric Relaxation Spectroscopy Study

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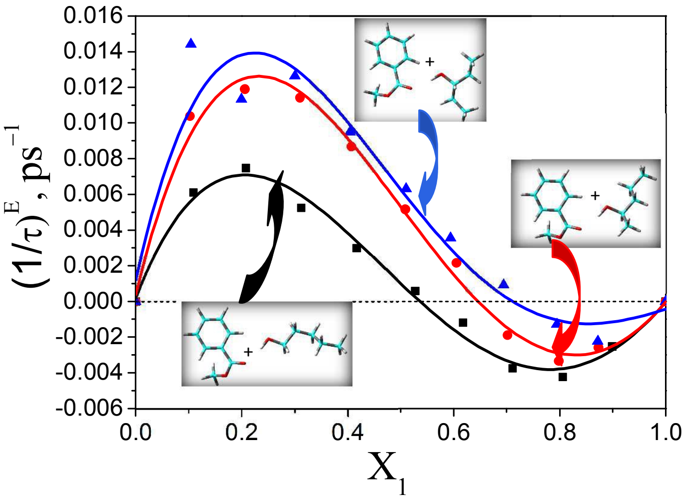
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x



Dielectric relaxation study of binary mixtures of associative pentanol isomers and non-associative alkylbenzoates at different mole fractions. The effective dipole rotates faster and thus shows positive excess inverse relaxation time, $(1/\tau)^E$ in the alkylbenzoate rich region and become negative due to slower rotation of the effective dipole in the pentanol rich region.

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