



Molecular interaction studies of isopropyl acetate-xylene mixture using dielectric relaxation approach

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Dielectric relaxation parameters of Isopropyl acetate (IPA)-xylene mixtures with different concentrations and temperatures have been measured in the frequency range of 10 MHz to 30 GHz using time domain reflectometry technique. Static dielectric constant, relaxation time, excess permittivity, excess relaxation time, Bruggeman factor, Kirkwood correlation factor and thermodynamic parameters have been determined to understand molecular association between the IPA and xylene molecules. For entire concentrations of IPA-xylene mixture the Kirkwood correlation factor is less than one which shows the antiparallel nature of electric dipole orientation. The experimental values of dielectric constant obtained from time domain reflectometry are in well agreement with theoretical values of dielectric constant obtained by Luzar model. Positive values of enthalpy and entropy indicating that the system is endothermic and less ordered while Gibbs free energy decreases with increase of IPA in xylene.

Keywords: Time domain reflectometry (TDR), Dielectric permittivity, Relaxation time, Kirkwood correlation factor, Thermodynamic parameters

When two liquids (polar and non-polar) mixed with each other, the molecular properties change due to the disturbance caused by the non-polar molecule to the polar organic molecule. The effect of high frequency on molecular properties of the pure liquids as well as on the mixture of the liquid gives important information about solute-solvent interactions and molecular association. It has applications in the field of biological, chemical industries and in many places¹⁻³. This change in properties can be studied by using different spectroscopic techniques; one of them is the time domain reflectometry technique (TDR).

Isopropyl acetate (IPA) is an organic compound ester which is made up from the esterification of acetic acid and isopropanol. It has chemical formula as $C_5H_{10}O_2$. It is colorless, clear liquid with fruity odor. It is a solvent used for cellulose, plastics, oils and fats. It is also used in printing inks and perfumes. It is quite flammable in both its liquid and vapor state⁴. Xylene is one of the frequently used solvents. It is an aromatic compound in the form of colorless and flammable liquid. It is a petroleum product and has applications in printing, lather industries, medical field, widely used in ink, adhesives, paint thinning and varnishes⁵⁻⁶.

Yang⁷ et al. have studied the solubility and thermodynamic parameters of N,N'-Bis (2,2,6,6-tetramethyl-4-piperidiny)-1,6-hexanediamine (HMBTAD) in organic solvents like isopropyl acetate and others. The order of solubility of HMBTAD in pure solvents is isobutyl acetate > isopropyl acetate > propyl acetate > ethyl acetate > methyl acetate > acetone > acetonitrile. They observed that the solubility increases with increase in temperature and with decrease in dielectric constant of solvents. In case of thermodynamic properties of HMBTAD, they concluded that the mixing processes were exothermic and spontaneous because of the negative values of ΔH and ΔG of the mixture. Joseph Nti-Gyabaah⁸ studied solubility of lovastatin in the different acetates including isopropyl acetate. From this case it is found that the solvent studied in the equilibrium solubility, the mole fraction of lovastatin increases with temperature, which indicates the dissolution of lovastatin in these solvents, follows the endothermic process.

In the present paper, the frequency and temperature dependent dielectric relaxation study of IPA - xylene binary mixtures have been carried out using TDR technique in the frequency range from 10 MHz to 30

GHz. This technique is proven to be a powerful technique in the investigation of co-operative and molecular dynamics of H-bonded systems⁹. From the measured complex permittivity spectra, the static dielectric constant (ϵ_0), dielectric relaxation time (τ in ps) was obtained by least square fit method. Excess dielectric permittivity, inverse relaxation time, thermodynamics parameters and Bruggeman factor were also determined to study the intermolecular interaction and dynamics of molecules at molecular level.

Materials and Methods

For present study, IPA was obtained from Thermo Fisher Scientific Pvt. Ltd. Mumbai; India with 98 % of purity and xylene was obtained from Merk Specialties Private Ltd. Mumbai, India with 99.0% and was used without further purification. The mixtures of solutions were prepared for different volume fraction of IPA in xylene.

The dielectric spectra of mixtures have been recorded using the time domain dielectric technique¹⁰. This technique used in the frequency range of 10 MHz to 30 GHz on which the present work has been carried out. The Tektronix Model no. DSA 8300 digital serial analyzer sampling mainframe along with the sampling module 80E10B has been used with TDR. A repetitive fast incident rising pulse of 12 ps rise time and reflected back rise pulse of rising time 15 ps was provided through 50 ohm impedance of coaxial line system. Sampling oscilloscope will monitor and records the changes in the step pulse after reflection from end of line. Reflected pulses $R_1(t)$ (without sample) and $R_x(t)$ (with sample) were recorded in the time window of 5 ns and digitized in 2000 points. The Fourier transformation of both these pulses and data analysis was completed to find out the complex permittivity spectra by means of non-linear least square fit method¹⁰⁻¹². Surrounding temperature of sample was maintained with an accuracy of ± 0.1 °C.

Results and Discussion

Complex permittivity spectra

The frequency dependent complex permittivity spectra of IPA-xylene binary mixture at 25 °C and dielectric loss are shown in Fig. 1 (a) and (b), respectively. Increase in frequency decreases the total polarization which affects the dielectric permittivity in mixture¹³. The dielectric permittivity and loss increases as the volume fraction of IPA increases in

xylene. Complex permittivity spectra of IPA-xylene binary mixture were fitted to the Havriliak-Negami equation^{12, 14},

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{[1 + (j\omega\tau)^{1-\alpha}]^\beta} \quad \dots (1)$$

where ϵ_0 is the static dielectric permittivity, ϵ_∞ is the permittivity at high frequency, τ is the relaxation time and α & β are the distribution parameters. β value indicates the uniform distribution of relaxation width, which varies as $0 \leq \beta \leq 1$. The Havriliak-Negami equation involves Cole-Cole ($\beta=1$), Cole-Davidson ($\alpha=0$) and Debye ($\alpha=0$ & $\beta=1$) relaxation models. This system obey Debye relaxation model and is used to fit the data with the value of ϵ_∞ as the square of the refractive index, which is used as fitting parameter in Eqn (1). Static dielectric constant (ϵ_0), relaxation time (τ) and permittivity at high frequency (ϵ_∞) at various temperatures and concentrations are given in the Table 1.

Static dielectric constant and relaxation time

The change in static dielectric permittivity indicates the heteromolecular diverse interactions in IPA-xylene binary mixtures. Increase in volume fraction of IPA in xylene increases the dielectric constant of the mixture and is reported in Table 1. Both static dielectric constant and relaxation time increase with increase in volume fraction of IPA and decrease with temperature for all binary mixtures, as shown in Figs 2 & 3, respectively.

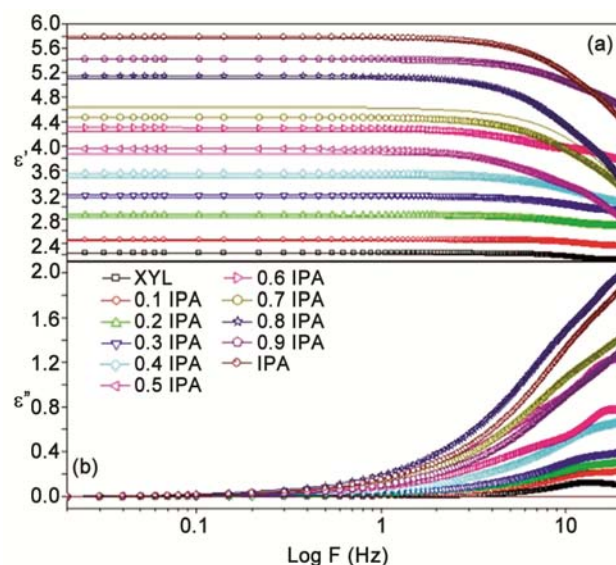


Fig. 1 — Frequency dependent (a) dielectric permittivity (ϵ') and (b) dielectric loss (ϵ'') for IPA-xylene mixtures at 25 °C

Table 1 — Dielectric relaxation parameters for IPA-xylene binary mixtures at different temperatures

V_{IPA}	ϵ_0	τ (ps)	ϵ_∞	ϵ_0	τ (ps)	ϵ_∞
0.0	2.23 (6)*	2.75 (6)	2.0	2.40 (1)	3.58 (1)	2.0
0.1	2.44 (1)	2.88 (3)	2.0	2.75 (1)	3.80 (5)	2.0
0.2	2.81 (2)	3.43 (5)	2.0	3.14 (2)	3.93 (5)	2.0
0.3	3.15 (2)	3.74 (4)	2.0	3.63 (2)	4.03 (4)	2.0
0.4	3.46 (4)	4.21 (4)	2.0	3.87 (3)	4.32 (4)	2.0
0.5	3.81 (7)	6.15 (4)	2.0	4.09 (5)	6.22 (8)	2.0
0.6	4.23 (4)	6.20 (8)	2.0	4.67 (5)	6.27 (8)	2.0
0.7	4.43 (4)	6.38 (2)	2.0	5.04 (2)	6.53 (1)	2.0
0.8	5.05 (6)	6.34 (2)	2.0	5.41 (4)	6.47 (2)	2.0
0.9	5.42 (4)	6.18 (4)	2.0	5.90 (4)	6.34 (3)	2.0
1.0	5.76 (3)	6.04 (1)	2.0	6.57 (3)	6.24 (1)	2.0
		15 °C		10 °C		
0.0	2.81 (3)	4.20 (2)	2.0	3.50 (1)	4.33 (5)	2.0
0.1	3.21 (1)	4.28 (4)	2.0	3.83 (1)	4.37 (5)	2.0
0.2	3.63 (2)	4.35 (5)	2.0	4.03 (2)	4.46 (5)	2.0
0.3	4.03 (2)	4.47 (4)	2.0	4.79 (3)	4.57 (5)	2.0
0.4	4.45 (3)	6.57 (3)	2.0	5.27 (3)	4.69 (4)	2.0
0.5	4.73 (1)	6.44 (5)	2.0	5.47 (7)	6.72 (6)	2.0
0.6	5.19 (4)	6.54 (8)	2.0	5.93 (5)	6.77 (9)	2.0
0.7	5.74 (2)	6.70 (1)	2.0	6.37 (3)	6.87 (2)	2.0
0.8	6.03 (7)	6.63 (2)	2.0	6.63 (4)	6.71 (3)	2.0
0.9	6.41 (3)	6.45 (2)	2.0	7.13 (5)	6.64 (2)	2.0
1.0	6.76 (3)	6.42 (2)	2.0	7.22 (4)	6.54 (2)	2.0

*Numbers in the bracket denotes uncertainties in least significant digit obtained by least square fit method eg. 2.23 (6) means 2.23 ± 0.06

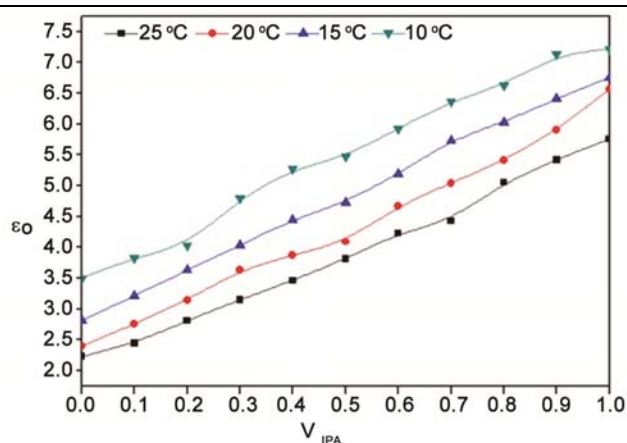


Fig. 2 — Static dielectric constant with volume fraction of IPA in xylene

Relative variation in values of dielectric constant with concentration may be due to interactions between unlike molecules, which may produce structural changes in binary mixture. The molecular relaxation depends upon the temperature, chain length, viscosity, molecular size and concentration of polar or non-polar liquid etc.¹⁵.

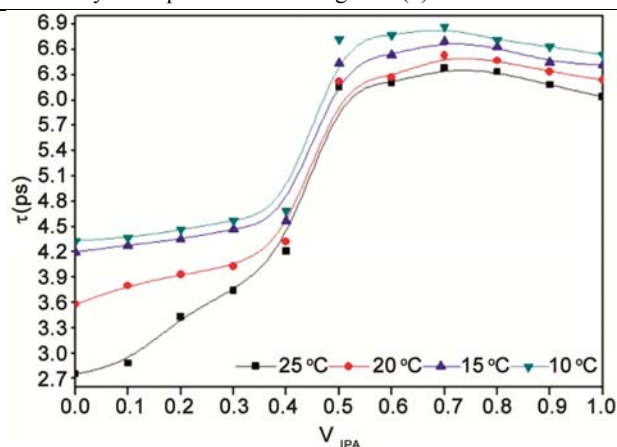


Fig. 3 — Relaxation time with volume fraction of IPA in xylene

The plot for values of relaxation time versus volume fraction of IPA (as shown in Fig. 3) shows non-linear nature of the curve. The sudden increase in relaxation time at 0.5 volume fraction of IPA is observed may be due to the increase in molecular size which results in to the slow rotation of molecules at this particular volume fraction¹⁶⁻¹⁷. The bonding between hetero-molecular entities through weak

intermolecular forces experiences larger barrier i.e. large value of τ , while entities bonded through stronger bonds with stronger force provides smaller barrier i.e., small value of τ ¹⁸.

Excess permittivity

The interactions between the binary liquids of IPA-xylene binary mixture and its relative information can be obtained by excess properties¹⁹ associated with permittivity and inverse relaxation time. Excess permittivity gives information regarding interaction between the constituents of binary mixture using the following equation as¹⁶,

$$\epsilon_0^E = (\epsilon_0)_m - [(\epsilon_0)_{IPA} V_{IPA} + (\epsilon_0)_X(1 - V_{IPA})] \dots (2)$$

where, the subscripts m, X and IPA represent mixture, xylene, IPA, respectively and V_{IPA} represent the volume fraction of IPA. The entity $\epsilon_0^E < 0$ indicates mixture constituent molecules interface in such a way that the total number of effective dipoles contributed in the mixture gets decreased and $\epsilon_0^E > 0$ shows that the number of dipoles contributed in the mixture gets increased²².

The negative values of excess permittivity for IPA-xylene binary mixture shows strong intermolecular interactions²⁰⁻²¹ at 25 °C and 20 °C, respectively, while for 15 °C and 10 °C, positive values shows weak intermolecular interactions. This indicates that the molecules in binary mixture form multimers through hydrogen bonding, so that in complete process the total effective dipole moment gets decreased (for 25 °C and 20 °C) and increased (for 15 °C & 10 °C)²². It is also observed that the variation in excess dielectric permittivity ϵ_0^E is more negative at 0.3 volume fraction of IPA in Xylene at 25 °C and more positive at 0.6 volume fraction of IPA in xylene at 10 °C as shown in Fig. 4.

Excess relaxation time

The structural variations in the liquid binary mixture constituents can be studied by using excess inverse relaxation time and is determined using the equation as¹⁶,

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_{IPA} V_{IPA} + \left(\frac{1}{\tau}\right)_X (1 - V_{IPA})\right] \dots (3)$$

where, suffix m, X and IPA represents mixture, xylene and IPA, respectively, $(1/\tau)^E$ is the excess

inverse relaxation time, which indicates an usual broadness of dielectric spectra. Spectral line broadening in resonant spectroscopy gives the concept of inverse relaxation time²³.

For IPA-xylene binary mixture, values of excess relaxation time is negative for all concentrations and temperatures indicating slower rotation of dipoles, as interaction in the binary mixture forms hydrogen bonded structures i.e. polymeric structure²⁴. Variation in excess relaxation time $(1/\tau)^E$ with volume fraction of IPA at all temperatures is shown in Fig. 5. It is also observed that the change in excess relaxation time is more negative at 0.5 volume fraction of IPA in xylene at all temperatures.

Bruggeman factor

Bruggeman provides the information regarding the static permittivity of the binary mixture using the formula as²⁵,

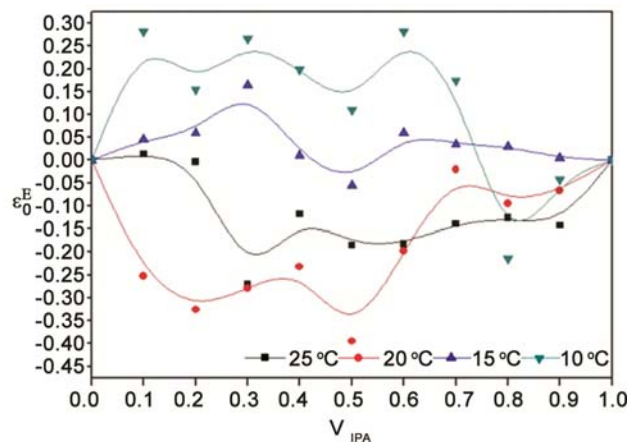


Fig. 4 — Plot of excess permittivity with volume fraction of IPA in xylene

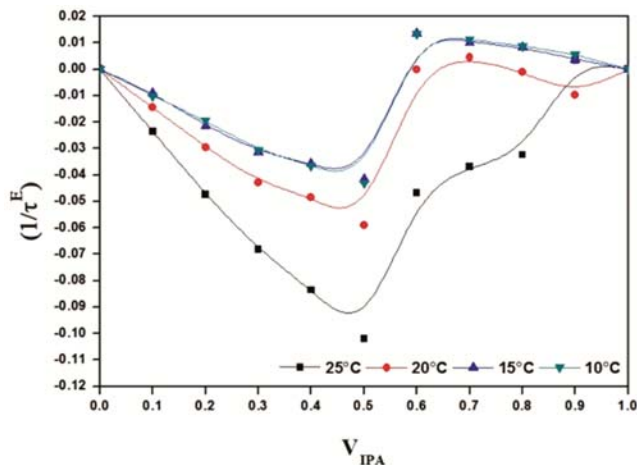


Fig. 5 — Plot of excess relaxation with volume fraction of IPA in xylene

$$f_B = \left[\frac{(\epsilon_{om} - \epsilon_{oX})}{(\epsilon_{oIPA} - \epsilon_{oX})} \right] \left[\frac{\epsilon_{oIPA}}{\epsilon_{om}} \right]^{\frac{1}{3}} = 1 - V_{IPA} \quad \dots (4)$$

where, f_B is the Bruggeman factor, ϵ_{om} , ϵ_{oIPA} and ϵ_{oX} are the static dielectric constants corresponding to the mixture, xylene and IPA, respectively. V_{IPA} is the volume fraction of IPA. From this equation, a graph is plotted between f_B versus V_{IPA} . The Bruggeman equation has been modified for binary liquid mixtures²⁵ as follows.

$$f_B = \left[\frac{(\epsilon_{om} - \epsilon_{oX})}{(\epsilon_{oIPA} - \epsilon_{oX})} \right] \left[\frac{\epsilon_{oIPA}}{\epsilon_{om}} \right]^{\frac{1}{3}} = 1 - [a - (a - 1)V_{IPA}]V_{IPA} \quad \dots (5)$$

In Eqn 5, volume fraction (V_{IPA}) is changed by a factor $[a - (a - 1)V_{IPA}]$ of the mixture and 'a' is the interaction parameter. If value of 'a' is one, in that case it indicates the perfect mixture and has no molecular interaction between solute & solvent. Determination of strength of the intermolecular interaction between solute & solvent molecules of the binary mixture is nothing but change in the value of 'a'.

The Experimental and theoretical Bruggeman factor with volume fraction of IPA in xylene has been evaluated and shown in Fig. 6. It is clear that the Bruggeman factor (f_B) is quite linear to the volume fraction of IPA at 25 °C and 20 °C only, as predicted by Bruggeman²⁶. For 15 °C and 10 °C the values of Bruggeman factor deviates from its ideal expected values. These deviations are less than one which indicates the increased dipoles. The value of 'a' is

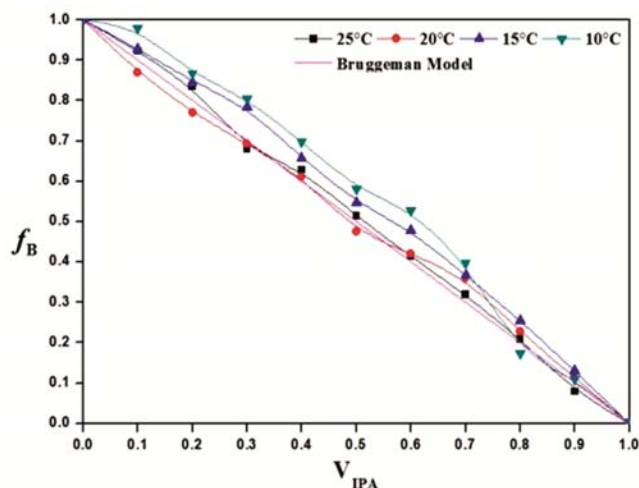


Fig. 6 — Variation of Bruggeman factor with volume fraction of IPA in xylene

determined by least squares fit method and is found to be 0.93 at 25 °C.

Kirkwood correlation factor

Electric dipole-dipole orientation in the liquid can be evaluated by using Kirkwood correlation factor. For pure liquids, the Kirkwood-Frohlich equation is given as²⁷,

$$\frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} = g\mu^2 \frac{4\pi N\rho}{9kTM} \quad \dots (6)$$

where, ϵ_0 is the static dielectric constant, ϵ_∞ is permittivity, g is Kirkwood correlation factor, μ is dipole moment, ρ is the density, k is Boltzmann's constant, M is the molecular weight, N is Avogadro's number and T is temperature.

Kirkwood correlation factor g^{eff} of unlike molecules in binary mixture is calculated from the modified Kirkwood equation²⁸,

$$\frac{(\epsilon_{om} - \epsilon_{\infty om})(2\epsilon_{om} + \epsilon_{\infty om})}{\epsilon_{om}(\epsilon_{\infty om} + 2)^2} = \frac{4\pi N}{9kT} \left[\frac{\mu_{IPA}^2 \rho_{IPA}}{M_{IPA}} V_{IPA} + \frac{\mu_X^2 \rho_X}{M_X} (1 - V_{IPA}) \right] \times g^{\text{eff}} \quad \dots (7)$$

where, g^{eff} is the effective Kirkwood correlation factor, μ_{IPA} is the dipole moment of IPA, μ_X is the dipole moment of xylene, N is Avogadro's number, ρ_{IPA} , ρ_X are the densities of IPA & xylene, respectively, ϵ_{om} is static dielectric constant of mixture at high frequency, k is Boltzmann's constant, M_{IPA} is the molecular weight of IPA and M_X is the molecular weight of xylene, T is the temperature, V_{IPA} is volume fraction of xylene. Values of effective Kirkwood correlation factor ' g^{eff} ' for Xylene at 25 °C is found to be 0.31 and that of for IPA is 0.94, is greater than the value of xylene. It is seen that for entire mixture the g^{eff} value is < 1 at 25 °C, which indicates the antiparallel orientation of electric dipoles with weak dipole interaction²⁹. It is much complex to split the average correlation factors g_1 and g_2 from a single value of the static dielectric constant.

The Kirkwood-Frohlich theory can be applied to the binary mixture containing two different molecules and cross relationship terms must be taken into concern for separation of g_1 and g_2 ³⁰. Luzar model is used to understand the role of hydrogen bonding in dipole-dipole correlation. Kirkwood correlation factors for separate class $i = 1$ and 2 are modified. The correlation factors g_1 and g_2 are obtained by using the following equations³¹,

$$g_1 = 1 + Z_{11} \cos \Phi_{11} + Z_{12} \cos \Phi_{12} \left(\frac{\mu_2}{\mu_1} \right) \quad \dots (8)$$

$$g_2 = 1 + Z_{21} \cos \Phi_{21} \left(\frac{\mu_1}{\mu_2} \right) \quad \dots (9)$$

where, $Z_{11} = 2 \langle n_{HB}^{11} \rangle$, $Z_{12} = 2 \langle n_{HB}^{12} \rangle$ and $Z_{21} = 2 \langle n_{HB}^{21} \rangle$ ($1 - V_X$) / V_X are the average number of hydrogen bonds with IPA-IPA and IPA-xylene pairs, respectively. V_X and V_{IPA} are the volume fraction of xylene and IPA, respectively. Φ_{11} and Φ_{12} are the angles between the neighboring dipoles of IPA and xylene molecules. The values of g^{eff} , g_1 and g_2 for different concentration are tabulated in Table 2.

It is clear from the Table 2, the values of g_1 and g_2 and g^{eff} increases with increasing V_{IPA} in the same manner, whereas from Fig. 7, the value of n_{HB}^{11} increases and n_{HB}^{12} decreases with increasing the volume fraction of IPA³⁰⁻³².

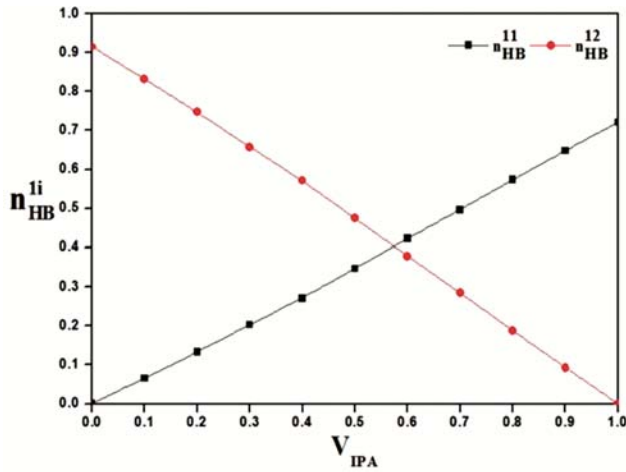


Fig. 7 — Plots of the average number of hydrogen bonds per unit volume against volume fraction of IPA in xylene

Table 2 — Kirkwood correlation factors g^{eff} , g_1 , and g_2 for IPA-xylene binary mixtures at 25 °C

V_{IPA}	g^{eff}	g_1	g_2
0.0	0.31	--	1.00
0.1	0.57	1.09	1.17
0.2	0.77	1.13	1.36
0.3	0.82	1.17	1.54
0.4	0.83	1.21	1.73
0.5	0.85	1.26	1.91
0.6	0.89	1.30	2.09
0.7	0.85	1.34	2.28
0.8	0.93	1.39	2.44
0.9	0.94	1.43	2.60
1.0	0.94	1.48	--

Average number of hydrogen bonds (n_{HB}^{11}) and (n_{HB}^{12}) per xylene molecule for 1i pairs ($i=1$ or 2) has been calculated by the following equation³³,

$$n_{HB}^{11} = n_{HB}^{11} n_{1i} \omega^{11} / n_1 \quad \dots (10)$$

where $\omega^{11} = 1/[1 + \alpha^{11} \exp(\beta E^{11})]$ is the possibility of creation of bond between IPA and xylene. n_1 is the number density of IPA molecules, $\beta = 1/kT$ and α^{11} are the statistical volume ratios of two sub-volumes of the phase space related to the non hydrogen-bonded and hydrogen bonded pairs. These hydrogen bonded pairs have two energy levels, E^{11} and E^{12} , for 11 and 12 pair created bonds, respectively. Values of (n_{HB}^{11}) and (n_{HB}^{12}) depend on the number of densities of the hydrogen-bonded pairs between IPA and xylene (n_{12}) and between IPA molecules ($n_{11} = 2n_1 - n_{12}$), respectively. These are calculated, during the formation of IPA-IPA (11 pair) and IPA-xylene (12 pair)²⁸.

Luzar model provides good qualitative values of dielectric permittivity of IPA-Xylene binary mixtures. Feasible molecular parameters of theoretical static dielectric permittivity are in good agreement with experimental data and are reported in Table 3 and as shown in Fig. 8.

Thermodynamic parameters

The temperature dependent dielectric relaxation time of IPA-xylene binary mixture is described in terms of chemical rate theory by using Arrhenius plot, which is inversely proportional to changes in temperature³³⁻³⁶ and is shown in Fig. 9. The thermodynamic parameters are evaluated by using Eyring equation as³⁷,

$$\tau = \left(\frac{h}{kT} \right) \exp \left(\frac{\Delta H}{RT} \right) \exp \left(\frac{-\Delta S}{R} \right) \quad \dots (11)$$

Table 3 — Molecular parameters used in computation of Static Dielectric Constant (ϵ_0) at 25 °C

Molecular Parameters	Values
Effective Dipole Moment ^a of IPA	1.88
Effective Dipole Moment ^a of Xylene	0.34
Polarizability ^b of IPA	4.3
Polarizability ^b of Xylene	13
Binding energy ^c of IPA- IPA	-7
Binding energy ^c of IPA -Xylene	-9
Enthalpy ^c of IPA- IPA	30
Enthalpy ^c of IPA-Xylene	45
No. of Hydrogen Bonds	2

^aUnit : Debye; ^bUnit : A⁰³; ^cUnit: kJ/mol

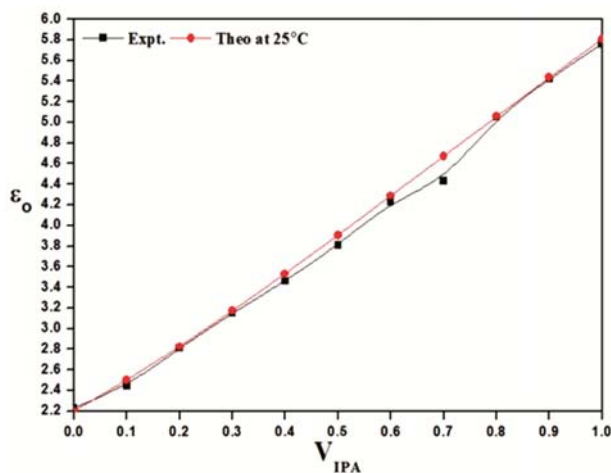


Fig. 8 — Comparison of experimental and theoretical values of ϵ_0 versus volume fraction of IPA in xylene

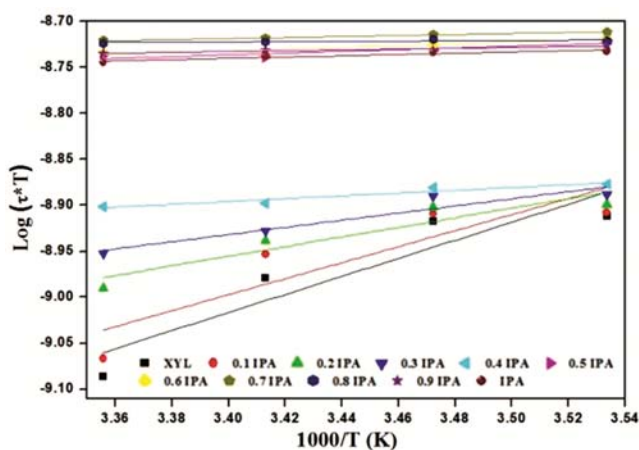


Fig. 9 — Plot of $(\text{Log } \tau * T)$ versus $1000 / T$ for IPA-xylene binary mixture

where, ΔS is the entropy of activation, ΔH is the enthalpy of activation energy in kJ/mole, τ is the relaxation time in ps, T is the temperature in Kelvin, k is the Boltzmann's constant and h is Plank's constant.

Gibb's free energy (ΔG) is related to enthalpy of activation (ΔH) and the entropy of activation (ΔS) by following relation,

$$\Delta G = \Delta H - T \times \Delta S \quad \dots (12)$$

IPA-xylene binary mixture gives positive values of enthalpy (ΔH) which indicates endothermic reaction³⁸ i.e. heat is absorbed in the molecular process of dipole reorientation. From Table 4, it is clear that, IPA requires $1.323 \text{ kJ mol}^{-1}$ and for xylene $18.806 \text{ kJ mol}^{-1}$ energy of activation to reorient the dipoles. Entropy (ΔS) of a system provides information regarding orderliness of molecules in mixture. If entropy is

Table 4 — Enthalpy, Entropy and Gibb's free energy of activation for IPA-xylene binary mixture

V_{IPA}	Enthalpy ΔH (kJ mol^{-1})	Entropy ΔS ($\text{J mol}^{-1}\text{K}^{-1}$)	Gibb's Free Energy (ΔG) (kJ mol^{-1})
0.0	18.806	0.268	18.728
0.1	16.668	0.261	16.592
0.2	9.999	0.237	9.930
0.3	7.443	0.228	7.376
0.4	2.915	0.212	2.854
0.5	1.816	0.205	1.756
0.6	1.887	0.205	1.827
0.7	1.059	0.202	1.000
0.8	0.310	0.200	0.252
0.9	0.836	0.202	0.778
1.0	1.323	0.203	1.263

positive, it indicates that the activated system becomes less ordered than normal and if entropy is negative, it indicates the activated system becomes more ordered than the normal one^{28, 38}. Entropy values of IPA and xylene found to be positive for all mixtures indicating that the system is less ordered. Gibbs free energy of activation decides the stable condition of a system³⁹. Increases in volume fraction of IPA, decreases the interaction in the mixture such that the value of free energy of activation decreases with increase in concentration of IPA. IPA has $1.263 \text{ kJ mol}^{-1}$ Gibb's free energy of activation.

Conclusions

Complex permittivity frequency spectra of IPA-xylene binary mixture is studied using time domain dielectric reflectometry technique in the frequency range 10 MHz to 30 GHz. As the volume concentration of IPA increases in xylene, static dielectric constant increases and the relaxation time increases suddenly at 0.5 concentrations and then it is decreases in IPA rich region. The excess permittivity and excess relaxation time values are reported for all temperatures and concentrations. This indicates the slower rotations of dipoles because there is a formation of polymeric structure in the mixture. The modified Bruggeman factor for IPA-xylene binary mixture is less than one for all temperatures studied here. For entire concentrations of IPA-xylene mixture the Kirkwood correlation factor is less than one which shows the antiparallel nature of electric dipole orientation. Theoretical & experimental static dielectric permittivity values are well in accordance with Luzar Model. Positive values of enthalpy and entropy indicating that the system is endothermic and

less ordered while Gibbs free energy decreases with increase in IPA in xylene.

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