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Study of co-operative dynamics and thermo-dielectric parameters of *n*-butyl acetate-xylene solutions using dielectric spectroscopy

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Temperature and frequency dependent complex permittivity spectra (CPS) of *n*-Butyl Acetate (*n*-BA) with Xylene were measured in the range of 0.1<ν/GHz<50. Dielectric relaxation parameter was measured over a wide range of frequency that confers information regarding the dielectric dispersion, relaxation behavior, molecular dynamics, molecular association, and interfacial polarization. The least squares fit method has been used to obtain dielectric relaxation parameters which are obtained from an analysis of Debye relaxation process and is the time taken by relaxing molecules involved in dynamics, is explicated very well with cooperative domains (CDs) among *n*-BA-*n*-BA and *n*-BA-Xylene,which is being validated with the help of g^{eff} through bonding between them. Molecular relation in hydrogen bonding that causes variations in Kirkwood correlation value from unity is the measure of degree of short-range dipolar ordering.The Luzar model employed for *n*-BA-Xylene mixtures to determine molecular association. Thermodynamic parameters have been obtained to get the information about molecular ordering.

Keywords: Time Domain Reflectometry (TDR), Static dielectric parameters, Co-operative domains (CDs), Kirkwood correlation factor, Luzar model, Thermodynamic parameters, Bruggeman factor

Broadband dielectric relaxation spectroscopy, FTIR, NMR, UV-Vis, X-ray and Raman are very useful spectroscopic techniques, which gives precious information concerning materials' physical and chemical properties. Dielectric relaxation spectroscopy (DRS) is able to monitor co-operative processes at microwave frequency in range of 0.1<ν/GHz<50. This technique is very useful and sensitive to investigate different phenomena in binary liquid mixtures which give information such as strength of molecular relaxation, intermolecular hydrogen bonding, intermolecular rotations, formation of monomers and multimers in polar-non-polar molecules[1-3]. Hydrogen bonding in polar and non-polar molecules plays a vital role in many applications like molecular biology, pharmaceutical industries, and chemical factories[3]. Molecular relaxation study of polar esters with non-polar aromatic hydrocarbons gives significant information regarding molecular association due to internal rotations, temperature variation and bonding between *n*-Butyl Acetate and Xylene molecules.

n-Butyl Acetate [$C_6H_{12}O_2$] is also called as Butyl Ethanoate, is colorless, sweet odoured, flammable liquid at room temperature, used as a flavor in ice-creams, cheese, baked foods, candies[4], *etc*. Xylene [C_8H_{10}] is an aromatic hydrocarbon, colorless, flammable liquid[5,6], used in industries for cleaning steel, in wafers of silicon and widely used in adhesives, varnishes, inks and paints.

Dielectric relaxation behavior of esters like Methyl Acetate (MA), Ethyl Acetate (EA) and Butyl Acetate (*n*-BA) with different alcohols has been studied previously to investigate molecular behavior of O-H group with oxygen atom of ester molecule under different temperatures and concentrations of mixtures. Chaudhari *et al*.[7] investigated dielectric properties of *n*-butyl acetate with methanol, ethanol, 1-propanol binary mixtures and concluded that the parameters show systematic changes in dielectric relaxation parameter. Thenappan *et al*.[8] studied dielectric parameters of esters such as butyl acetate, ethyl acetate, *etc*. with propanoic acid, and revealed that in the studied binary mixture, cyclic and α-multimers were formed. Meenachi *et al*.[9] studied dielectric relaxation parameters of esters with Xylene isomers.

The objective of this work is to investigate and provide more relevant data concerning to dielectric relaxation, Kirkwood correlation factor,

thermodynamicproperties, Bruggeman factor of *n*-BA-Xylene solutions and to know CDs which is explained thereby relating values of theoretical relaxation time (τ_{theo}) with experimentally observed relaxation time (τ_{obs}) and their ratio (τ_{ratio}) at different temperatures and concentrations over a frequency range of 0.1<ν/GHz<50.

Experimental Section

n-Butyl Acetate obtained from Thermo Fisher Scientific Pvt. Ltd. Mumbai, India with 98.0% of purity and Xylene obtained from Merk Specialties Private Ltd. Mumbai, India with 99.0%, are used without further purification. Dielectric relaxation parameters were measured in relaxation frequency range by means of TDR as shown in Fig. 1. Analysis of raw data with procedure of TDR system was systematically explicated formerly[10-12].

Results and Discussion

Experimentally obtained CPS is fitted using non-linear least square fit method to Havriliak-Negami[13] equation,

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{[1+(j\omega\tau)^{1-\alpha}]^\beta} \quad \ldots(1)$$

where, ε_o is the static dielectric permittivity, ε_∞ is high frequency permittivity, τ is relaxation time and α, β are parameters of distribution. Debye (α = 0 & β=1) relaxation model[14] is used for present system to fit the raw data.

A frequency dependent CPS for *n*-BA-Xylene mixture at 25° C is shown in Fig. 2. In CPS, ε' increases with increase in concentration indicates increase polarization effect in the mixture with concentration of *n*-BA.Value of ε' decreases with frequency indicates the decrease in molecular orientation with increase in frequency[15]. Value of ε_∞ is the square of refractive index and is used to fit raw data.

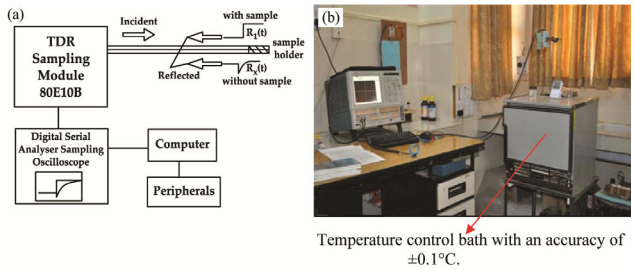

Fig. 1 — (a) Block Diagram (b) Experimental setup of TDR with temperature controller bath.

Values of ε_o and τ increase with increase in $V_{n\text{-BA}}$ thereby indicating increase in electric dipoles density within the mixture. $\varepsilon_o$value changes owing to interactions between dissimilar molecules, which may create structural variations and also indicates change in molecular aggregation from spherical to linear with increase in $V_{n\text{-BA}}$[16]. Effect of temperature on dielectric constant is also observed for *n*-BA-Xylene mixtures, which suggests increase in orientation polarization with decreasing temperature[16]. As $\varepsilon_\infty$is the square of refractive index at highest frequency and should be greater than unity unless approaching resonance absorption with a very narrow absorption. So there is possibility of occurrence of this resonance for the 0.3 *n*-BA in present system.

The variations in ε_o and τ with $V_{n\text{-BA}}$at different temperatures is shown in Fig. 3 (a) and (b) respectively. The dielectric relaxation properties are listed in Table 1. It can be seen from Table 1 that the values of τ increases with $V_{n\text{-BA}}$ such that at 0.3 volume fraction, the value of τ suddenly increases, which may be due to increase in molecular size[17,18] such that hetero-molecular entities with higher value of τ are due to weak intermolecular attachment and smaller value of τ is caused due to strong bonding affection between them[19] and dependent on viscosity, temperature and molecule chain length[20].

Theoretical relaxation time for *n*-BA-Xylene binary solutions is assessed by the relation as[21],

$$\tau_{theor} = \tau_{Xyl} V_{Xyl} + \tau_{n-BA}\,(1 - V_{Xyl}) \quad \ldots(2)$$

where, τ_{Xyl} ,$\tau_{n\text{-BA}}$ are the relaxation time of Xylene and *n*-BA, V_{Xyl} and $V_{n\text{-BA}}$ is volume fraction of Xylene, *n*-BA respectively.

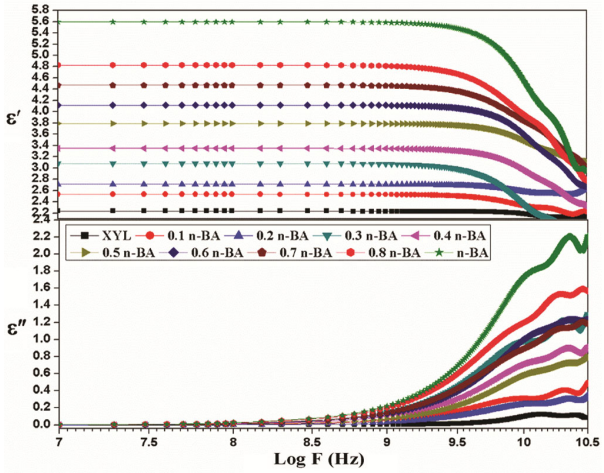

Fig. 2 — Frequency dependent dielectric permittivity (ε') and loss (ε") for *n*-BA-Xylene mixtures at 25° C.

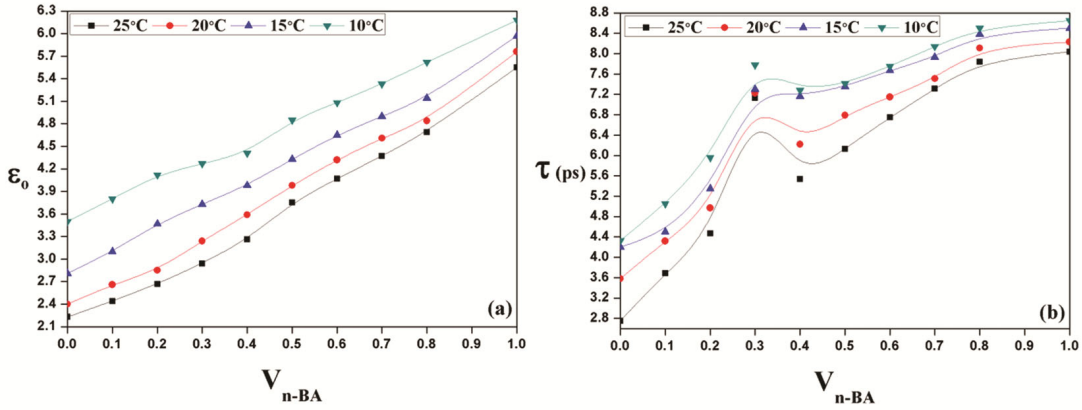

Fig. 3 — (a) Static dielectric constant (ε_o) and (b)Relaxation time (τ) *vs*. $V_{n\text{-BA}}$.

Table 1 — Dielectric relaxation parameters for *n*-BA-Xylene binary solutions at different temperatures.

$V_{n\text{-BA}}$	ε_o	τ (ps)	ε_∞	ε_o	τ (ps)	ε_∞
	25° C			20° C		
0.0	2.23 (6)*	2.75 (6)	1.74 (1)	2.40 (1)	3.58 (1)	2.02 (2)
0.1	2.44 (4)	3.69 (9)	1.23 (5)	2.66 (4)	4.32 (9)	1.93 (3)
0.2	2.67 (2)	4.47 (9)	1.93 (3)	2.85 (3)	4.97 (9)	1.99 (3)
0.3	2.94 (7)	7.13 (1)	0.59 (6)	3.24 (1)	7.22 (6)	0.83 (5)
0.4	3.26 (8)	5.54 (7)	0.92 (8)	3.59 (8)	6.22 (7)	1.10 (7)
0.5	3.75 (4)	6.13 (6)	2.13 (3)	3.98 (5)	6.79 (6)	2.14 (4)
0.6	4.07 (6)	6.75 (3)	1.53 (3)	4.32 (4)	7.15 (4)	2.09 (3)
0.7	4.37 (7)	7.31 (6)	1.93 (5)	4.61 (7)	7.51 (6)	2.10 (6)
0.8	4.69 (9)	7.84 (7)	1.57 (7)	4.84 (1)	8.11 (5)	1.08 (6)
1.0	5.55 (9)	8.04 (5)	1.35 (6)	5.76 (7)	8.23 (4)	2.03 (4)
	15° C				10° C	
0.0	2.81 (3)	4.20 (2)	2.57 (4)	3.50 (1)	4.33 (5)	2.75 (2)
0.1	3.10 (3)	4.50 (2)	2.04 (4)	3.80 (3)	5.05 (9)	2.98 (3)
0.2	3.47 (4)	5.35 (8)	2.34(4)	4.12 (3)	5.96 (7)	2.99 (2)
0.3	3.73 (7)	7.30 (6)	1.81 (4)	4.27 (3)	7.78 (6)	2.90 (2)
0.4	3.98 (7)	7.16 (6)	1.21 (6)	4.41 (6)	7.28 (5)	1.91 (5)
0.5	4.33 (4)	7.35 (5)	2.27 (3)	4.85 (2)	7.41 (5)	3.45 (2)
0.6	4.65 (3)	7.67 (3)	2.44 (2)	5.08 (1)	7.75 (2)	3.45 (2)
0.7	4.90 (6)	7.93 (5)	2.26 (4)	5.33 (7)	8.14 (6)	2.59 (5)
0.8	5.14 (1)	8.38 (5)	1.18 (6)	5.62 (1)	8.50 (6)	2.18 (7)
1.0	5.97 (7)	8.50 (4)	2.20 (4)	6.18 (7)	8.65 (4)	2.63 (4)

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

Molecular size difference in *n*-BA and Xylene confirms presence of self-associated heterogeneous structure due to greater value of g^{eff} than that of xylene such that intermolecular interactions between them gives rise to a dynamics with molecular reorientation, revealing CDs[21].

CD size changes with variation in interactions, such that stronger interactions create large CD[22,23]. The τ_{ratio} is maximum at $V_{n\text{-BA}}$ = 0.3 and minimum at $V_{n\text{-BA}}$= 0.1 suggesting that the population of $CD_{n\text{-BA-XYL}}$ is maximum at these concentrations such that $CD_{n\text{-BA-XYL}}$ size is more heterogeneous due to coexistence of $CD_{n\text{-BA}}$, $CD_{n\text{-BA-XYL}}$ and CD_{XYL} in definite proportions as shown in Fig. 4(b). The equation (2) is applied in case of steric hindrances in a homogeneous mixture, deviations from the above equation implies molecular association is retained to some extent during the relaxation, *e.g.* as a super molecule. Also from Fig. 4(a), the strong deviation from equation (2) is observed at 0.3 $V_{n\text{-BA}}$ implying that the assumption of a sequence of independent relaxations does not hold for this composition.

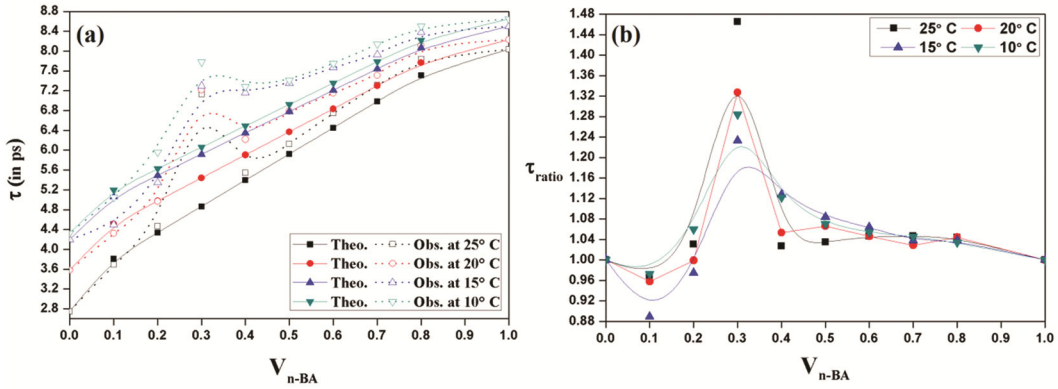

Fig. 4 — (a) τ_{obs} and τ_{theo} (b) τ_{ratio}*vs.* $V_{n\text{-BA}}$ at different temperatures.

Usual information regarding orientation of electric dipoles in pure liquids and molecular interactions between two unlike polar-non-polar molecules is described by effective Kirkwood correlation factor 'g^{eff} and is obtained by using modified Kirkwood equation[24,25]. As tabulated in Table 2, using Luzar model[26] the average correlation factors g_1 and g_2 were obtained from a single value of static dielectric constant such that, for separate class i = 1 and 2, using the following equations as[27,28],

$$g_1 = 1 + Z_{11}\cos\Phi_{11} + Z_{12}\cos\Phi_{12}\left(\frac{\mu_2}{\mu_1}\right) \quad \ldots(3)$$

$$g_2 = 1 + Z_{21}\cos\Phi_{21}\left(\frac{\mu_1}{\mu_2}\right) \quad \ldots(4)$$

where, Z_{11} =2 $\langle n^{11}_{HB}\rangle$, Z_{12}=2 $\langle n^{12}_{HB}\rangle$ and Z_{21} =2 $\langle n^{21}_{HB}\rangle$ (1-Vx)/Vx are average number of hydrogen bonds with *n*-BA-*n*-BA and *n*-BA-Xylene pairs respectively. Φ_{11}, Φ_{12} and Φ_{21} signify angles among adjacent dipoles of diverse molecules.

Formation of average number of hydrogen bonds *i.e.* (n^{11}_{HB}) and (n^{12}_{HB}) per *n*-BA molecule for 1i pairs (i =1 or 2) has been derived using the equation as[27,28],

$$n^{1i}_{HB} = n^{1i}_{HB} n_{1i} \omega^{1i} / n_1 \quad \ldots(5)$$

where, $\omega^{1i} = 1/[1+ \alpha^{1i}\exp(\beta E^{1i})]$ signifies the chance of formation of bonding between the molecule of *n*-BA and Xylene. n_1 is density of *n*-BA molecule, β =1/kT and α^{1i} are statistical volume ratios of two sub-volumes of phase space related to hydrogen-bonded and hydrogen non-bonded pairs. E^{11} and E^{12} are energy levels for 11 and 12 pairs.

Increasing $V_{n\text{-BA}}$ cause increase in n^{11}_{HB} with decreasing n^{12}_{HB}[28,29], as shown in Fig. 5 (a). Feasible values of molecular parameters bids good qualitative values of dielectric permittivity such that theoretical and experimentally calculated ε_o values using Luzar model found to be good in agreement, as tabulated in Table 3 and shown in Fig. 5 (b).

Table 2 — Kirkwood correlation factors g_1 and g_2 for *n*-BA-Xylene binary solutions at 25°C.

$V_{n\text{-BA}}$	g_1	g_2
0.0	-	1.00
0.1	1.08	1.16
0.2	1.12	1.32
0.3	1.16	1.50
0.4	1.20	1.67
0.5	1.24	1.85
0.6	1.29	2.04
0.7	1.33	2.23
0.8	1.38	2.41
1.0	1.48	-

Table 3 — Molecular parameters used in computation of static dielectric constant (ε_o) at 25°C.

Molecular Parameters	
Effective dipole moment[a] of *n*-BA	1.88
Effective dipole moment[a] of Xylene	0.34
Polarizability[b] of *n*-BA	6.2
Polarizability[b] of Xylene	13
Binding energy[c] of *n*-BA-*n*-BA	−7
Binding energy[c] of *n*-BA-Xylene	−9
Enthalpy[c] of *n*-BA-*n*-BA	30
Enthalpy[c] of *n*-BA-Xylene	45
Number of Hydrogen Bond	03

[a]Unit : Debye; [b]Unit : A^{03}; [c]Unit: kJ/mol

Temperature dependent τ value described and analyzed by Arrhenius[30-32], as shown in Fig. 6 and the chemical rate theory in relation with dielectric relaxation was explained by Eyring, given by equation as[30-33],

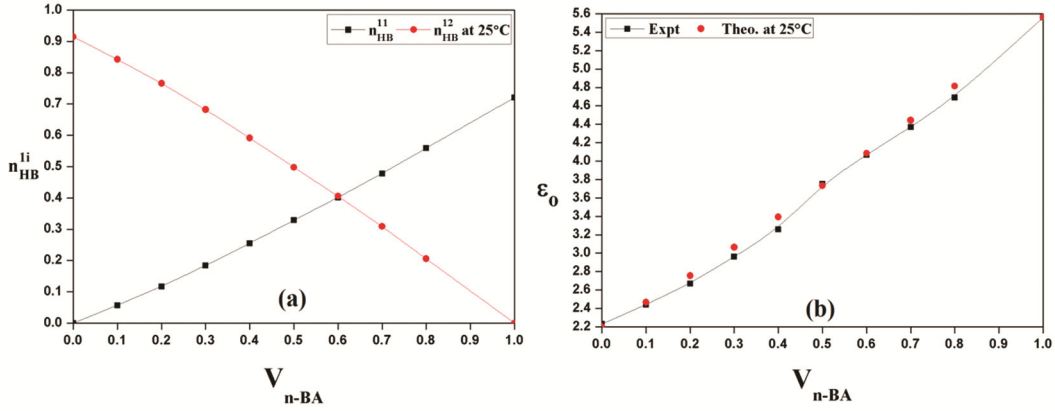

Fig. 5 — (a) Plots of the average number of hydrogen bonds per unit volume (b) Experimental and theoretical values of ε_o*vs*.$V_{n\text{-BA}}$.

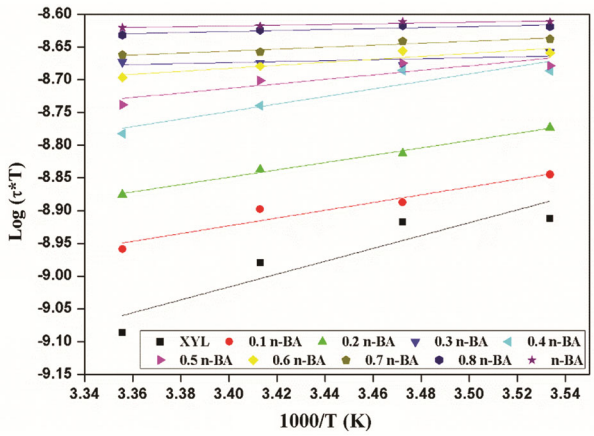

Fig. 6 — Plot of (Log τ*T) *versus* 1000 / T for *n*-BA-Xylene mixture.

$$\tau = \left(\frac{h}{kT}\right) \exp\left(\frac{\Delta H}{RT}\right) \exp\left(\frac{-\Delta S}{R}\right) \quad \ldots(6)$$

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

$$\Delta G = \Delta H - T * \Delta S \quad \ldots(7)$$

where, ΔS is entropy, ΔH is enthalpy of activation, τ is relaxation time, T is temperature, k is the Boltzmann's constant and h is Planck's constant.

Positive values of enthalpy (ΔH) reveal endothermic reaction[33,34] *i.e*. heat is absorbed during dipole reorientation. To reorient dipoles, Xylene requires 18.806 kJ mol^{-1} of energy and *n*-BA requires 1.111 kJ mol^{-1} of energy as tabulated in Table 4. Other meaning of these values is stated that a positive ΔH means that energy has to be taken to achieve the activated state along the relaxation coordinate. As for 0.3 *n*-BA the relaxation is close to that of a single entity with only a very little alteration required in its surroundings. The small value of ΔH indicates that there may be a proton moving between two minima in a hydrogen bond as it might be expected of pure *n*-BA.

Entropy (ΔS) is measure of ordered nature of system, found to be positive for all mixtures representing that the system is less ordered which point outs non-cooperative environment[33,34]. Positive ΔS means that the activated state has higher entropy than the ground state, *i.e*. it is more disordered than the ground state. Large values of positive ΔS refer to a large disordering in the achievement of the activated state. Thus there are a large number of alternative routes to enter this state from the ground state, *i.e*. there is no preferred order in the sequence of molecular movements required to enter the activated state.

Equilibrium state of an activated system is described using Gibb's free energy of activation (ΔG)[35]. With increasing $V_{n\text{-BA}}$, molecular interaction in the binary mixture decreases such that ΔG for *n*-BA is found to be 0.788. The plot of Log τ*T *versus* 1000/T for *n*-BA-Xylene mixture is shown in Fig. 6.

Bruggeman provides information concerning to static permittivity of binary mixture using the relation as[36],

$$f_B = \left[\frac{(\varepsilon_{om} - \varepsilon_{oX})}{(\varepsilon_{o\,n-BA} - \varepsilon_{oX})}\right]\left[\frac{\varepsilon_{o\,n-BA}}{\varepsilon_{om}}\right]^{\frac{1}{3}} = 1 - V_{n-BA} \quad \ldots(8)$$

The Bruggeman equation has been modified for binary liquid mixtures[37] as,

$$f_B = \left[\frac{(\varepsilon_{om} - \varepsilon_{oX})}{(\varepsilon_{o\,n-BA} - \varepsilon_{oX})}\right]\left[\frac{\varepsilon_{o\,n-BA}}{\varepsilon_{oo}}\right]^{\frac{1}{3}} = 1 - [a - (a-1)V_{n-BA}]V_{n-BA} \quad \ldots(9)$$

where, $f_B$is Bruggeman factor, ε_{om}, $\varepsilon_{on\text{-}BA}$, ε_{oX} are static dielectric constants corresponding to mixture, *n*-BA and Xylene respectively, $V_{n\text{-BA}}$ is volume fraction of *n*-BA and 'a' is interaction parameter.

Table 4 — Enthalpy, Entropy and Gibb's free energy of activation for *n*-BA-Xylene mixture.

$V_{n\text{-BA}}$	Enthalpy ΔH (kJ mol^{-1})	Entropy ΔS (J mol^{-1}K^{-1})	Gibb's Free Energy ΔG(kJ mol^{-1})
0.0	18.806	0.268	18.728
0.1	11.335	0.241	11.265
0.2	10.726	0.238	10.659
0.3	1.435	0.203	1.376
0.4	10.983	0.236	10.914
0.5	6.627	0.221	6.563
0.6	4.357	0.221	4.293
0.7	2.871	0.207	2.811
0.8	1.435	0.202	1.376
1.0	1.111	0.200	0.788

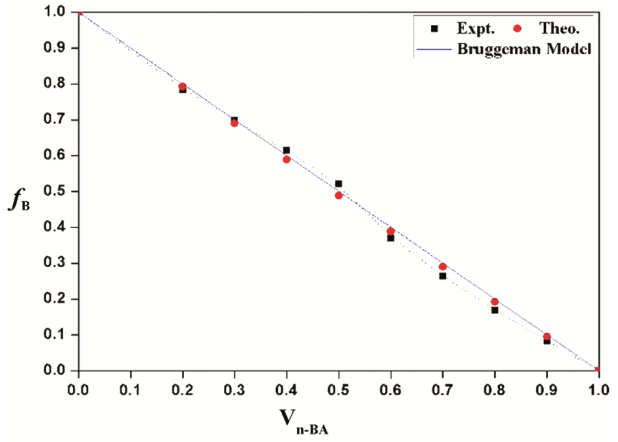

Fig. 7 — Variation of Bruggeman Factor *vs* $V_{n\text{-BA}}$ at 25°C.

Bruggeman factor (f_B) for *n*-BA-Xylene mixture is quite linear as predicted[38,39] and is shown in Fig. 7. Interaction parameter 'a' obtained experimentally and is found to be 1.03 at 25°C.

Conclusions

The present study concluded with CPS of *n*-BA-Xylene mixture using TDR technique in 0.1<ν/GHz<50 frequency range. Increasing $V_{n\text{-BA}}$ causes $\varepsilon_o$and τ to increases slowly. Presence of CD_{nBA}, $CD_{n\text{-BA-XYL}}$ and CD_{XYL} in a definite proportion is confirmed and g^{eff} reveals impact of CDs through hydrogen bonding with diverse interactions between *n*-BA and Xylene molecules. Correlation factors g_1 and g_2 rises with increasing $V_{n\text{-BA}}$. Theoretical $\varepsilon_o$values are well in accordance with the measured experimental ε_o values such that Luzar model provides a theoretical basis for the computation of molecular parameters. Molecules of *n*-BA-Xylene in the mixture show positive values of enthalpy and entropy for all concentrations. Bruggeman factor confirms the quite linear nature as predicted.

Acknowledgements

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References

1 Murthy S S N, *J PhyChem*, 100 (1996) 8508.
2 Shirke RM, Chaudhari A, More N M &Patil P B, *J ChemEng Data*, 45 (2020) 917.
3 Manjunath M S &Sannappa J, *Int J Pure App Phy*, 4 (2008) 71.
4 Sen D J, *World J Pharm Res*, 4 (2015) 1.
5 Santos K A O, DantasNeto A A, Moura M C P A & Castro Dantas T N, *Brazilian J Petro Gas*, 5 (2011) 255.
6 Birajdar S S, Vagshette N D, Birajdar S S, Suryawanshi D B & Lathi A R, *VidhyabIntInterdis Res J*, 12 (2021) 125.
7 Chaudhari A, Shirke R M, More N M &Patil P B, *J Sol Chem*, 31 (2002) 4.
8 Thenappan T &Prabakar D A, *J Mol Liq*, 123 (2006) 72.
9 Meenachi M &Krishnamurthi P, *Rasayan J Chem*, 8 (2015) 98.
10 Cole R H, Berberian J G, Mashimo S, Chryssikos G, Burns A &Tombari E, *J App Phy*, 66 (1989) 793.
11 Kumbharkhane A C, Puranik S M & Mehrotra S C, *J ChemSoc Faraday Trans*, 87 (1991) 1569.
12 Birajdar S S, Deshmukh A R, Kumbharkhane A C & Suryawanshi D B, *PolycyAro Comp*, 43 (2023) 5227.
13 Kaatze U, *Radiat Phys Chem*, 45 (1995) 549.
14 Debye P, *Polar molecules*, (Chemical Catalog, New York)1929.
15 Guerra K D L S &Eiras J A, *J Phys Condens Matter*, 19 (2007) 386217.
16 Deshmukh A R & Kumbharkhane A C, *Indian J Phys*, 96 (2022) 3105.
17 Joshi Y S, Kanse K S, Rander D N & Kumbharkhane A C, *IJPAP*, 54 (2016) 621.
18 Birajdar S S, Suryawanshi D B, Deshmukh A R, Shinde R V, Ingole S A & Kumbharkhane A C, *Phys ChemLiq*, 59 (2021) 503.

19 Karthick N K, Arivazhagan G, Kumbharkhane A C, Joshi Y S &Kannan P P, *J Mol Struc*, 1108 (2015) 203.
20 Lide D R, *J Am ChemSoc*, 129 (2007) 724.
21 Bhadane P B, Rander D N, Kanse K S, Joshi Y S & Kumbharkhane A C, *PhyChemLiq*, 59 (2021) 657.
22 Sudo S, Shinyashiki N, Kitsuki Y &Yagihara S, *J Phy Chem A*, 106 (2002) 458.
23 Sengwa R J, Madhvi A & Sankhla S, *Indian J Pure App Phys*, 44 (2006) 943.
24 Kirkwood J G, *J Chem Phy*,7 (1939) 911.
25 Joshi Y S & Kumbharkhane A C, *Fluid Phase Equilibria*, 317 (2012) 96.
26 Luzar A, *J Mol Liq*, 46 (1990) 221.
27 Kumbharkhane A C, Joshi Y S, Mehrotra S C, Yagihara S &Sudo S, *Physica B: Cond Matt*, 421 (2013) 1.
28 Sudo S, Oshiki N, Shinyashiki N, Yagihara S, Kumbharkhane A C & Mehrotra S C, *J PhyChem A*, 111 (2007) 2993.
29 Birajdar S S, Deshmukh A R, Suryawanshi D B & Kumbharkhane A C, *Indian J Chem Sect*, 60A (2021) 72.
30 Eyring H, *J Chem Phys*, 4 (1936) 283.
31 Laider K J, *Pure ApplChem*, 68 (1996) 142.
32 Glasstone S, Laider K J & Eyring H, *The Theory of Rate Processes*, (McGraw Hill, New York) 1941.
33 Birajdar S S, Kumbharkhane A C,Hallale S N, Hudge P G & Suryawanshi D B, *Poly Arom Comp*, 43 (2023) 1619.
34 Ingole S A, Deshmukh A R, Shinde R V & Kumbharkhane A C,*J Mol Liq*, 272 (2018) 450.
35 Chiodelli A &Magistris A, *Solid State Ionics*, 18 (1986) 356.
36 Bruggeman D A G, *Ann Der Phys*, 24 (1935) 636,
37 Puranik S M, Kumbharkhane A C & Mehrotra S C, *J Mol Liquids*, 59 (1994) 173. 38 Chaudhari A, Patil C S, Shankarwar A G, Arbad B R & Mehrotra S C, *J Korean ChemSoc*, 45 (2001) 201.
38 Birajdar S S, Deshmukh A R, Kumbharkhane A C & Suryawanshi D B, *J Indian ChemSoc*, 99 (2022) 100733.