Study of Co-operative Dynamics in Cyclohexanol-Xylene Solutions using Dielectric Relaxation Spectroscopy

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ABSTRACT: *Cooperative dynamics in pure cyclohexanol (CYN), xylene and their binary solutions have been studied using dielectric relaxation spectroscopy (DRS) in 10 MHz to 30 GHz microwave frequency range. The dynamics in CYN-CYN, CYN-xylene molecules have been explained using concept of cooperative domains (CDs). Deviations in CYN-xylene binary solutions exist due to braking and making of bonds as well as self-association among the molecules. Kirkwood correlation factor authenticates CDs with diverse exchanges through hydrogen bonding. Luzar model offers moderately decent qualitative values of ε_o such that the theoretically calculated values found relatively good in comparison with experimental results.*

Keywords: complex permittivity spectra, dielectric properties, co-operative domains, Kirkwood correlation factor, Luzar model, time domain reflectometry

1.   INTRODUCTION

Cyclohexanol (CYN) [$HOCH(CH_2)_5$] is colourless, viscous and polar liquid with O-H group attached to it and xylene [$(CH_3)_2C_6H_4$] is an aromatic compound.[1–3] The investigation of cooperative dynamics between polycyclic CYN and xylene with non-ideal behaviour is carried out such that bonding among hydroxyl (O-H) group of CYN and methyl (CH_3) group of xylene contributes in essential physiochemical significance to comprehend inter and intra molecular configuration. Besides this

O-H group strongly affects physicochemical properties of CYN and is may be due to low π-electron density that is more electro negativity difference in R–O$^{\delta-}$–H$^{\delta+}$ and CYN-xylene forms a weaker bonded interaction as discussed in earlier article.[4] These molecules change their structural properties depending upon surrounding temperature, applied frequency and type of polarity that the molecule possesses. Interactions among CYN-CYN and CYN-xylene at molecular level are deliberated thereby finding thermo-dielectric relaxation parameters of CYN-xylene solutions. The raw complex spectra is obtained using time domain reflectometry (TDR) and is fitted by means of non-linear least square fit method.[5]

Concept of braking and making of bonds arises due to deviations as well as self-association among CYN-xylene hetero molecules in binary solution. A physical change in solution with increasing V_{CYN} reveals discrepancies in structure with dipole-dipole interactions and is associated with formation of dimmers and multimers. Recently dielectric and thermodynamic parameters of CYN-xylene solutions using dielectric relaxation spectroscopy (DRS) were studied in previous article.[6] The present article aims to investigate and provide more relevant data concerning dynamics of CYN-xylene exchanges in binary solutions. The study conveys exhaustive discussion concerned to cooperative domains (CDs) and is explicated thereby comparing experimentally observed relaxation time (τ_{obs}), theoretical relaxation time (τ_{theor}), their ratio (τ_{ratio}) and Kirkwood correlation factor using Luzar model. $\tau_{ratio} = (\tau_{obs}) / (\tau_{theor})$ reflects dissimilarity among experimentally obtained and theoretical τ values.

2.   EXPERIMENTAL

2.1   Materials

CYN and xylene both were obtained commercially from Merck Life Sciences Ltd., Mumbai, India with 99.0% of purity and used without further purification.

2.2   Measurements

The dielectric spectra were obtained by the TDR technique in the frequency range of 10 MHz to 30 GHz at different temperatures with an accuracy of ±0.1°C.[6–9] Tektronix model number DSA 8200 Digital Serial Analyser sampling mainframe along with the sampling module 80E08 has been used for the TDR. A repetitive fast rising voltage pulse with 18 ps incident pulse rise time and 20 ps reflected pulse rise time was fed through coaxial line system of impedance 50 Ω. Sampling oscilloscope monitor changes in step pulse after reflection from the end of line.

Reflected pulse without sample $R_1(t)$ and with sample $R_X(t)$ were recorded in time window of 2 ns and digitised in 2,000 points. Fourier transformation of both these pulses and data analysis was completed to find out complex permittivity spectra $\varepsilon^*(\omega)$ by means of non-linear least square fit method.[6–9]

3.   RESULTS AND DISCUSSION

Temperature dependent complex permittivity spectra (CPS) of pure CYN is shown in Figure 1, maximum loss is observed at 0.1 GHz such that due to decrease in polarisation with rising frequency, the permittivity gets affected.[13] Values of ε_o, ε_∞ and τ were achieved by fitting CPS to Debye relaxation model ($\alpha = 0$ & $\beta = 1$) in Havriliak-Negami equation,[9–12]

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

where ε_o is static dielectric constant, ε_∞ is high frequency dielectric constant, ω is angular frequency and τ is relaxation time. Diverse binary solutions of CYN-xylene point out variation in ε_o and more parallel alignment of dipoles such that ε_o and τ rises with increasing V_{CYN} and decreasing temperature. Temperature dependent values of ε_o, τ and ε_∞ are tabulated in Table 1.[6]
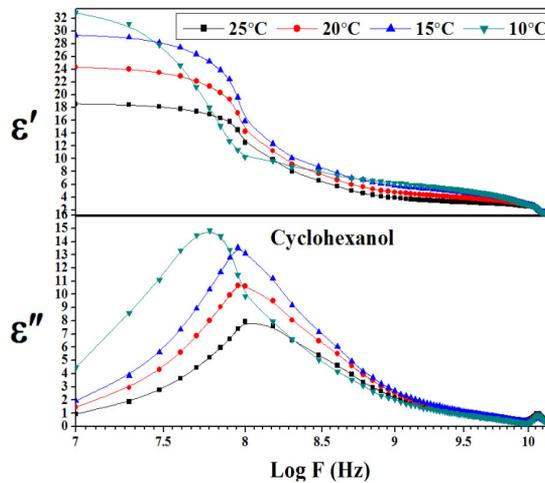

Figure 1: Temperature dependent CPS of pure CYN.

Table 1: Dielectric relaxation parameters for pure CYN and xylene at different temperatures.[6]

Liquid	ε_o	τ (ps)	ε_∞	ε_o	τ (ps)	ε_∞
		25°C			20°C	
CYN	18.62 (6)	1,057.59 (16)*	2.90 (2)	24.43 (1)	1,249.49 (21)	3.46 (3)
Xylene	2.23 (6)	2.75 (6)	1.74 (1)	2.40 (1)	3.58 (1)	2.02 (2)
		15°C			10°C	
CYN	29.81 (1)	1,405.31 (28)	4.14 (4)	33.21 (1)	2,783.26 (70)	4.28 (5)
Xylene	2.81 (3)	4.20 (2)	2.57 (4)	3.50 (1)	4.33 (5)	2.75 (2)

*Numbers in the bracket denotes uncertainties in least significant digit obtained by using least square fit method e.g., 1,057.59 (16) means 1,057.59±0.016

For CYN-xylene binary solutions, theoretical τ is evaluated using the relation as,[14–15]

$$\tau_{theor} = \tau_{Xyl} V_{Xyl} + \tau_{CYN} (1 - V_{Xyl}) \tag{2}$$

where, τ_{Xyl} and τ_{CYN} are relaxation time of xylene and CYN, V_{Xyl} is volume fraction of xylene.

Comparatively greater τ values validate the existence of self-associated molecular structure in pure CYN. The τ value for CYN is 1,057.59 ps and that of xylene is 2.75 ps correspondingly and such difference occurs because of larger size of CYN molecule than that of xylene. Heterogeneous structures of CYN and xylene with their hetero-intermolecular interactions in binary solution gives rise to a dynamics, which is revealed with CDs in which reorientation of molecules takes place.[14–15]

At all temperatures, deviation of τ_{obs} from τ_{theor} with ideal behaviour isn't observed due to heteromolecular interactions arising in binary solutions thereby confirming existence of $CD_{CYN-XYL}$ such that τ_{ratio} replicates variance between τ_{obs} from τ_{theor} values as shown in Figure 2.[14–16]

CD size changes with variations in the interactions, such that stronger interactions create large CD.[14–16] τ_{ratio} is extreme at $V_{CYN} = 0.9$ and least around $V_{CYN} = 0.3$, advises that the $CD_{CYN-XYL}$ occupants are highest at these compositions as shown in Figure 3. In CYN-xylene solutions, magnitude of $CD_{CYN-XYL}$ is more diverse at $V_{CYN} = 0.3$ owing co-occurrence of CD_{CYN}, $CD_{CYN-XYL}$ and CD_{XYL} in definite extents.
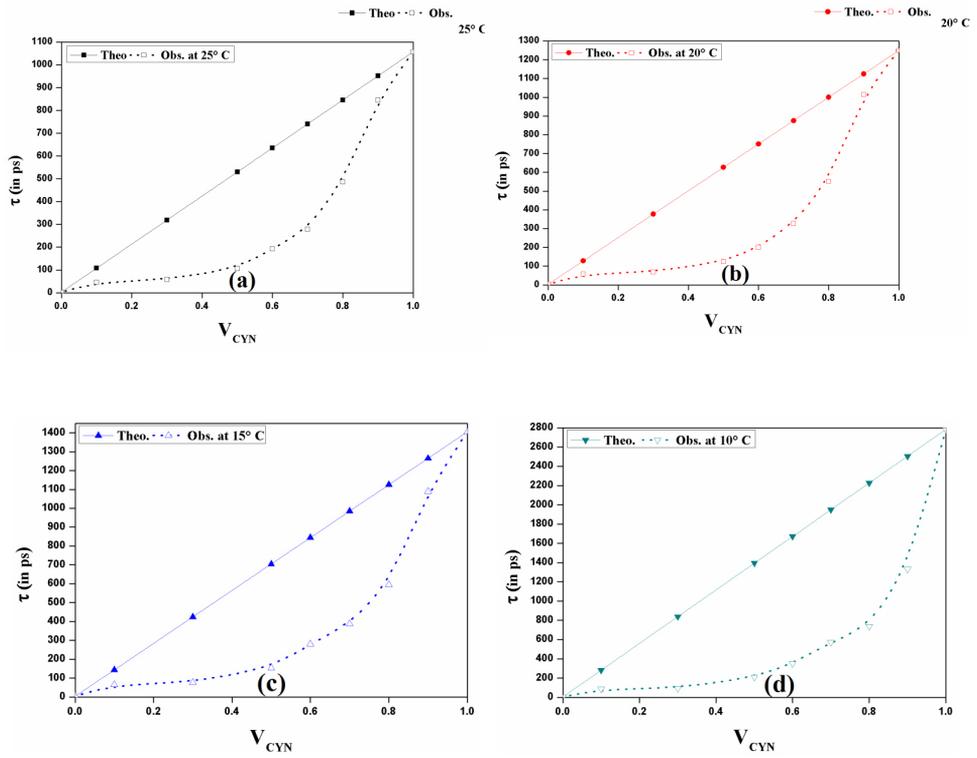
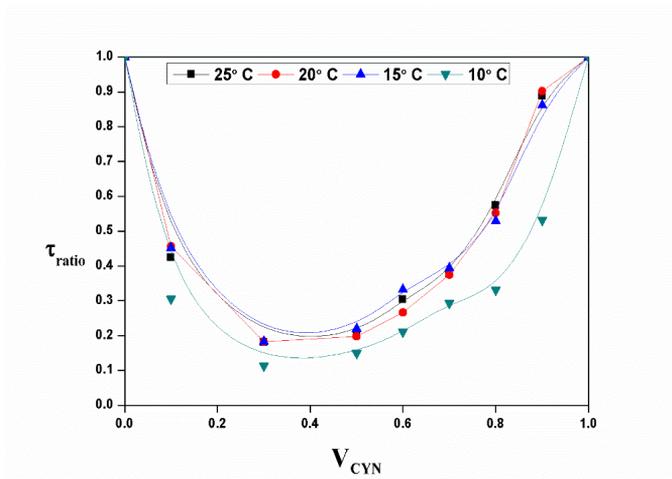Figure 2: Relaxation times (in ps) vs. V_{CYN} at different temperatures.

Figure 3: τ_{ratio} vs. V_{CYN}.

Kirkwood clarifies the facts concerned to dipole-dipole orientation which is a measure of molecular self-association among interacting molecules. Information concerning alignment of dipoles and intermolecular interaction in pure CYN and xylene given by Kirkwood correlation factor and is obtained using Kirkwood-Frohlich equation:[17–19]

$$\frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} = g\mu^2 \frac{4\pi N\rho}{9kTM} \tag{3}$$

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

Role of hydrogen bonding in association with dipole-dipole correlation revealed using Luzar model. Splitting of average correlation factors g_1 and g_2 is difficult from a single value of ε_0 such that for separate class i = 1 and i = 2 these values are obtained by using succeeding equations as:[21,22]

$$g_1 = 1 + z_{11}\cos\Phi_{11} + z_{12}\cos\Phi_{12}\left(\frac{\mu_2}{\mu_1}\right) \tag{4}$$

$$g_2 = 1 + z_{21}\cos\Phi_{21}\left(\frac{\mu_2}{\mu_1}\right) \tag{5}$$

where, $Z_{11} = 2 < n^{11}_{HB} >$, $Z_{12} = 2 < n^{12}_{HB} >$ and $Z_{21} = 2 < n^{21}_{HB} > (1-Vx)/Vx$ are average number of hydrogen bonds with CYN-CYN and CYN-xylene pairs, respectively. Φ_{11}, Φ_{12} and Φ_{21} signify angles among adjacent dipoles of diverse molecules. n^{11}_{HB} and n^{12}_{HB} are average number of hydrogen bonds formed per CYN molecule for 1i pairs (i = 1 or i = 2) and have been calculated using the equation as,[21,22]

$$n^{1i}_{HB} = n^{1i}_{HB} n_{1i}\omega^{1i}/n_1 \tag{6}$$

where $\omega^{1i} = 1/[1 + \alpha^{1i}\exp(\beta E^{1i})]$ represents the chance of formation of bonding among CYN and xylene molecule. n_1 is density of CYN molecule, $\beta = 1/kT$, 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. Values of n^{11}_{HB} and n^{12}_{HB} depend on density of CYN and xylene and CYN-CYN pair of molecules, respectively.[22]
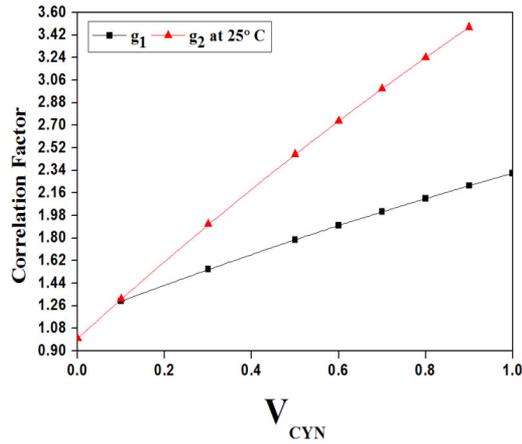
Figure 4: Variation of correlation factor (g_1 and g_2) vs. V_{CYN} at 25°C.

For different binary solutions, values of g_1 and g_2 increases with V_{CYN}, as represented in Figure 4. At $V_{CYN} = 0.5$, closely same bonds were formed whereas increasing V_{CYN} causes decrease in CYN-xylene bonding such that n^{11}_{HB} value increases with decrease in n^{12}_{HB}, as shown in Figure 5.[19,20] For CYN-Xylene binary solutions, Luzar model offers moderately decent qualitative values of ε_o such that the theoretically obtained values in comparison with experimental values found good as shown in Figure 6 and the values of theoretical ε_o are calculated using feasible molecular parameters, as tabulated in Table 2.
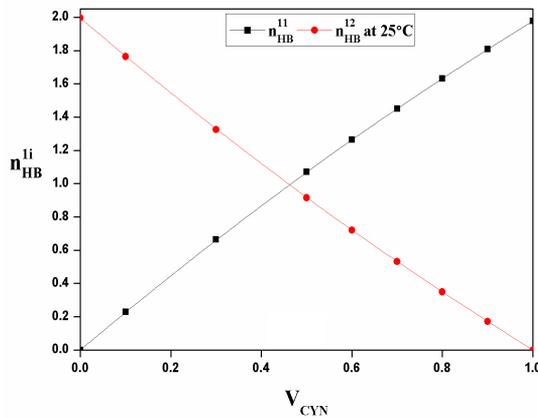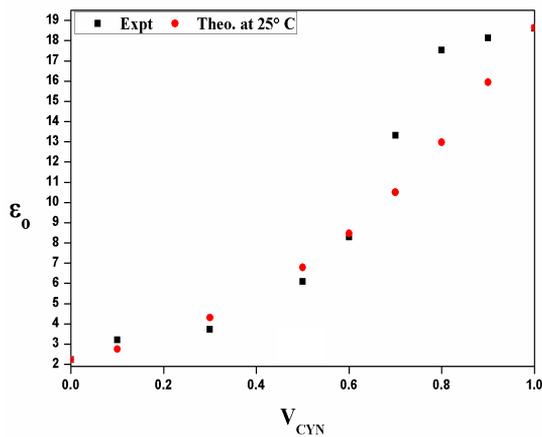

Figure 5: n^{1i}_{HB} vs. V_{CYN} at 25°C.

Figure 6: Theoretical and experimental ε_o values vs. V_{CYN} at 25°C.

Table 2: Molecular parameters used for computation of ε_o at 25°C.

Molecular parameters	
Effective dipole moment[a] of CYN	1.47
Effective dipole moment[a] of xylene	0.36
Polarizability[b] of CYN	19.80
Polarizability[b] of xylene	13.20
Binding energy[c] of CYN-CYN	−19.50
Binding energy[c] of CYN-xylene	−24.50
Enthalpy[c] of CYN-CYN	30.0
Enthalpy[c] of CYN-xylene	45.0
Number of hydrogen bond	02

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

4.   CONCLUSION

The temperature dependent CPS for CYN-xylene solutions have been revealed to study co-operative dynamics using DRS in 10 MHz to 30 GHz frequency. The dielectric parameters were used to study the presence of CD_{CYN}, $CD_{CYN-XYL}$ and CD_{XYL}. Kirkwood correlation factor confirms the impact of CDs through hydrogen bonding with diverse interactions. Luzar model offers moderately decent qualitative values of ε_o such that the theoretical and experimental values are relatively good.

5.   ACKNOWLEDGEMENTS

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