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Temperature dependent dielectric relaxation studies of 2-nitrotoluene-dimethyl sulfoxide mixture using time domain reflectometry

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The dielectric relaxation measurements of 2-nitrotoluene (2-NT) with dimethyl sulfoxide (DMSO) for 11 different concentrations have been carried out in the frequency range from 10 MHz to 50 GHz using time domain reflectometry method. In this frequency range, a dielectric relaxation spectrum of 2-NT-DMSO mixtures shows Debye type relaxation behaviour. The static dielectric constant, dielectric relaxation time, Kirkwood correlation factor, excess dielectric properties have been determined from 20°C to 5°C. The excess dielectric and Kirkwood correlation factor gives the information about formation and orientation of electric dipoles in the mixture. As the concentration of 2-NT in DMSO increases, dipole changes its orientation from anti-parallel to parallel. The thermodynamic parameters (enthalpy, entropy and Gibbs free energy) have been determined from the relaxation time using least squares fit method.

Keywords: Static dielectric constant, Relaxation time, Excess parameters, Kirkwood correlation factor, Thermodynamic parameters, Time domain reflectometry

The dielectric relaxation studies of liquids are dependent on the composition, structure of molecule and on various factors such as temperature, density, viscosity, frequency of changing electric field etc. The information regarding frequency dependent dielectric properties of binary liquid mixtures has significant impact on both dynamics and structural variations at molecular level and are determined by using the time domain reflectometry (TDR) technique[1-7]. Using TDR technique over from 10 MHz to 50 GHz, it is possible to obtain both real and imaginary part of complex permittivity from which we can obtain static dielectric constant and relaxation time (in ps). External applied electric field causes disturbances in thermal distribution of dipoles due to which they are oriented in the direction of field such that the reorientation of dipoles after removal of electric field is the actual relaxation time of materials. Frequency dependent dielectric behaviour of liquid mixtures offer precious data concerning the occurrence of actual molecular processes and it helps in obtaining information regarding cooperative nature and intermolecular interactions between constituents of mixture[8-10].

2-Nitrotoluene (2-NT) is an organic compound having formula as [$CH_3C_6H_4NO_2$]. It is pale yellow liquid also named as ortho-nitrotoluene. Its IUPAC name is 1-methyl-2-nitrobenzene. It is used as a reagent in determination of prussic acid (hydrogen cyanide) content in the air, an intermediate for o-toludine synthesis, and has application in the dyestuff industry[11-14]. Dimethyl sulfoxide (DMSO) is an organosulfur compound with the formula $(CH_3)_2SO$. It is colourless liquid, important polar aprotic solvent that dissolves both in polar and nonpolar compounds and is soluble in a wide range of organic solvents as well as water. DMSO has the unusual property that many individuals distinguish a garlic-like taste in the mouth after contact with the skin[15-17].

Chaudhari et al.[18] obtained results of excess properties and explained the dielectric properties of 2-NT-DMSO using TDR in the frequency range of 10 MHz to 20 GHz. Mohan et al.[19] have studied and investigated thoroughly the effect of 2-NT with ethanol, 1-propanol, 1-butanol, 2-propanol and 2-butanol and revealed the concept of bonding between N-O group of 2-NT and O-H group of alcohols. Recently Nair et al.[20] worked on o-chlorotoluene and p-chlorotoluene with benzene solution and concluded that the o- and p-chlorotoluene with benzene shows increased dipoles in the microwave region and Karthik et al.[21-23] has investigated dielectric and FTIR Studies with the solutions of toluene with acetonitrile, butyonitrile and propionitrile thoroughly. In this work, the dielectric relaxation of 2-NT - DMSO mixtures with various concentrations and temperatures is reported in the frequency range of 10 MHz to 50 GHz. The static dielectric constant, relaxation time, excess permittivity, excess inverse relaxation, Kirkwood correlation factor have been determined. Arrhenius behaviour in the temperature range 20°C to 5°C and thermodynamic parameters have also been determined using least squares fit method.

Experimental Details

2-NT was obtained from Loba Chemie Pvt. Ltd. Mumbai with 99.00% of purity and DMSO was obtained from S D Fine-Chem Ltd. with 99.00% of purity. The solutions were prepared for 11 different concentrations. The solutions were prepared by mixing 2-NT and DMSO in volume fractions.

The complex dielectric permittivity spectra of mixtures have been measured using the TDR Technique[24]. TDR technique is used in the frequency range of 10 MHz to 50 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 pulse 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 method[25-26].

Results & Discussion

Complex permittivity spectra

Fig. 1 illustrates frequency dependent complex permittivity spectra for 2-NT- DMSO mixtures at 20°C. It can be seen from figure that the position of the peak is shifted towards lower frequency after the addition of 2-NT in DMSO, which shows increase in relaxation time. Also, the loss value of mixture decreases from DMSO to 2-NT which indicates the decreases in molecular interaction in system.

The complex permittivity spectra obtained using TDR is fitted by the non-linear least squares fit method to the Havriliak-Negami expression as[27-28],

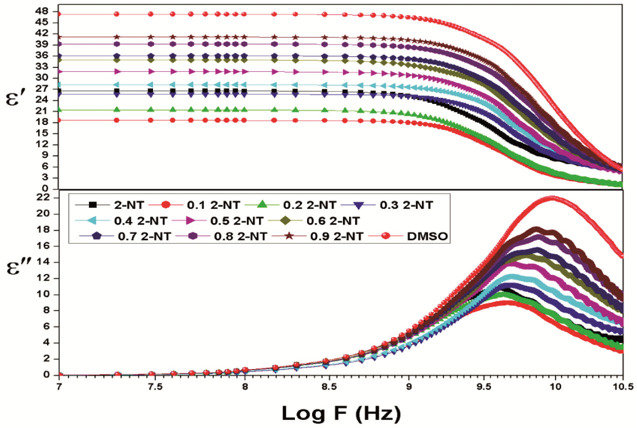

Fig. 1 — Frequency dependent (a) dielectric permittivity (ε’) and (b) dielectric loss (ε”) for 2-NT-DMSO mixtures at 20°C

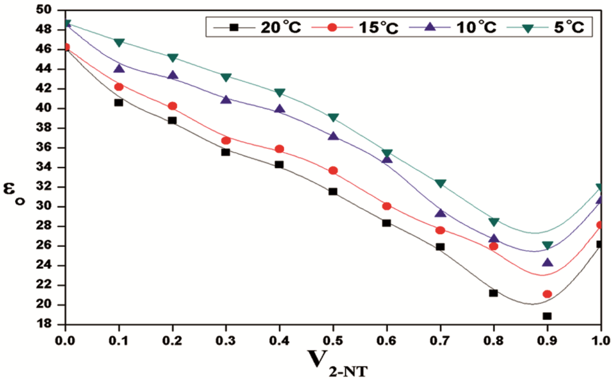

Fig. 2 — Static dielectric constant versus volume fraction of 2-NT

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

where ε_o is the static dielectric constant, ε_∞ is the permittivity at high frequency, τ is relaxation time and α & β are the distribution parameters. Eqn (1) includes the Debye[29] ($\alpha = 0$, $\beta = 1$), Cole-Cole[30] ($0 \le \alpha \le 1$ and $\beta = 1$) and Davidson–Cole[31] ($\alpha = 0$ and $0 \le \beta \le 1$). The static dielectric constants (ε_o), relaxation time (τ in ps) for 2-NT-DMSO binary mixtures at various temperatures are reported in Table 1.

Static dielectric constant and relaxation time

Fig. 2 shows that the value of static dielectric constant decreases non-linearly with increase in concentration of 2-NT, this indicates the number density of electric dipole decreases within mixture[32]. The decrease in values of static dielectric constant also suggest the net change in polarization configuration along with the transition of elongated molecular aggregation into spherical aggregation structure in mixtures for all concentrations[33]. In this mixture the values of ε_o suddenly decrease at

Table 1 — Dielectric relaxation parameters of 2-NT-DMSO mixtures at different temperatures

$V_{2\text{-NT}}$	20°C			15°C		
	ε_o	τ (ps)	ε_∞	ε_o	τ (ps)	ε_∞
0.0	46.14 (7)	16.80 (5)	1.61 (3)	46.24 (7)	19.31 (5)	2.20 (2)
0.1	40.58 (4)	20.63 (4)	3.03 (1)	42.19 (5)	21.87 (4)	3.27 (1)
0.2	38.75 (5)	21.40 (6)	2.99 (2)	40.25 (7)	22.03 (7)	2.81 (2)
0.3	35.51 (6)	22.59 (7)	2.80 (2)	36.71 (6)	23.56 (7)	2.93 (2)
0.4	34.25 (7)	23.83 (9)	2.95 (2)	35.86 (8)	25.66 (1)	3.28 (2)
0.5	31.49 (5)	26.11 (8)	2.80 (2)	33.68 (6)	28.07 (1)	3.00 (2)
0.6	28.30 (7)	26.33 (1)	3.26 (2)	30.03 (7)	30.16 (1)	3.36 (2)
0.7	25.89 (6)	28.53 (1)	3.15 (2)	27.59 (6)	31.52 (1)	3.45 (6)
0.8	21.17 (4)	36.56 (1)	3.04(1)	25.96 (6)	43.05 (1)	2.02 (1)
0.9	18.81 (2)	36.41 (7)	2.28 (7)	21.09 (2)	39.92 (9)	1.87 (8)
1.0	26.16 (1)	36.46 (1)	3.78 (2)	28.13 (1)	38.75 (1)	4.43 (3)
		10 °C			5 °C	
0.0	48.60 (1)	19.71 (7)	2.32 (4)	48.74 (1)	19.80 (8)	2.39 (4)
0.1	43.97 (7)	23.56 (6)	2.25 (2)	46.81 (1)	24.81 (1)	2.25 (4)
0.2	43.31 (9)	23.99 (9)	2.26 (3)	45.26 (1)	25.96 (1)	2.55 (5)
0.3	40.78 (1)	24.29 (1)	2.35 (4)	43.25 (1)	26.72 (1)	3.00 (6)
0.4	39.89 (1)	26.21 (1)	3.02 (5)	41.70 (1)	28.90 (1)	3.71 (6)
0.5	37.09 (1)	29.43 (1)	3.15 (3)	39.16 (1)	31.61 (1)	4.04 (5)
0.6	34.76 (1)	32.46 (1)	4.61 (5)	35.51 (1)	31.82 (1)	5.03 (6)
0.7	29.24 (7)	35.36 (1)	3.85 (2)	32.44 (1)	35.59 (1)	5.04 (5)
0.8	26.67 (6)	45.03 (1)	3.17 (1)	28.52 (2)	51.69 (1)	2.73 (2)
0.9	24.21 (4)	43.56 (1)	3.52 (1)	26.13 (7)	47.95 (1)	3.67 (2)
1.0	30.61 (1)	40.44 (1)	4.83 (5)	32.03 (1)	44.04 (1)	5.38 (6)

Numbers in the bracket denotes uncertainties in least significant digit obtained by least square fit method e.g. 26.16 (1) means 26.16±0.01

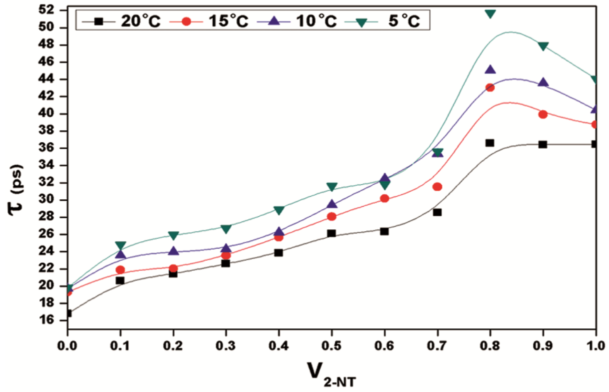

Fig. 3 — Relaxation time versus volume fraction of 2-NT

0.9 volume fraction of 2-NT, which may be due to formation of heterogeneous cluster in the mixtures.

Relaxation time depends upon the viscosity, molecular size, and functional group of molecules. Fig. 3 shows the relaxation time increases with the concentration of 2-NT, which may be due to the increase in hetero-molecular interaction in mixture. The relaxation time increases suddenly for 0.8 volume fraction of 2-NT, which indicates that in mixture molecular dipolar interaction is stronger and formation of complex molecular structure is due to hydrogen bonding[-35].

Excess properties

The contribution of hydrogen bonds to dielectric properties of the mixture is also studied in terms of the excess permittivity (ε_o^E), which can be written as[36-37],

$$\varepsilon_o^E = (\varepsilon_o)_m - [(\varepsilon_o)_2 V_2 + (\varepsilon_o)_1 (1 - V_2)] \qquad \dots (2)$$

The excess inverse relaxation provides information associated to structural changes in the mixture and are determined by using the equation[38],

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_1 V_2 + \left(\frac{1}{\tau}\right)_1 (1 - V_2)\right] \quad \dots (3)$$

where, suffix m, 1 and 2 represents mixture, 2-NT & DMSO, respectively, $(\varepsilon_o)^E$ is excess permittivity, $(1/\tau)^E$ is the excess inverse relaxation time.

The plot of excess permittivity versus the volume fraction of 2-NT is shown in Fig. 4. The values of excess permittivity for 2-NT-DMSO binary mixtures are negative over the entire concentration range which indicates that DMSO acts as a structure breaker for 2-NT39. Thus the dipoles in 2-NT are oriented in opposite direction with reduction in total effective dipoles. The negative peak values of excess permittivity are observed at V2-NT ≈ 0.9 which

Table 2 — Enthalpy, entropy and average Gibb's free energy for 2-NT-DMSO mixture

$V_{2\text{-NT}}$	Enthalpy ΔH ($kJ\ mol^{-1}$)	Entropy ΔS ($J\ mol^{-1}K^{-1}$)	Average Gibb's free energy ($kJ\ mol^{-1}$)
0.0	5.391	0.209	5.330
0.1	5.562	0.208	5.501
0.2	5.901	0.209	5.840
0.3	5.783	0.208	5.723
0.4	6.074	0.209	6.013
0.5	6.762	0.210	6.701
0.6	7.323	0.212	7.262
0.7	8.111	0.214	8.049
0.8	11.040	0.222	10.976
0.9	8.944	0.215	8.882
1.0	6.013	0.205	5.954

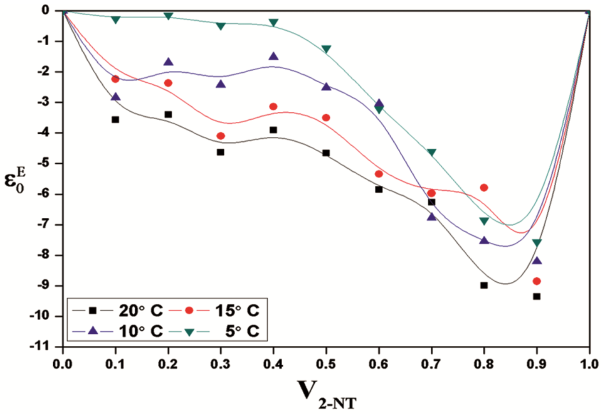

Fig. 4 — Excess permittivity versus volume fraction of 2-NT

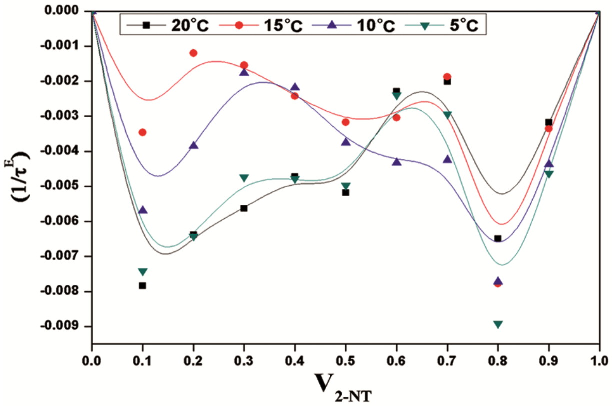

Fig. 5 — Excess inverse relaxation versus volume fraction of 2-NT

indicates that the formation of maximum complexes through H-bonding40 at this concentration. Higher value of (ε_o^E) represents stronger, long-range H-bond molecular interactions between unlike molecules and vice-versa. In 2-NT-DMSO binary mixture, hydrogen bonded structures that is polymeric structures[41-42] were formed due to slower rotation of dipoles and this is due to the negative values of excess inverse relaxation. This change in (1/τ)E with volume fraction of 2-NT is shown in Fig. 5.

Kirkwood correlation factor

The information regarding the orientation of electric dipoles in liquids is given by the Kirkwood correlation factor. The Kirkwood correlation factor for binary mixtures (g^{eff}) gives information of dipole-dipole correlation in associating binary mixture is calculated from the modified Kirkwood equation[43-44],

$$\frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} = \frac{4\pi N}{9kT}\left[\frac{\mu_2^2\rho_2}{M_2}V_2 + \frac{\mu_1^2\rho_1}{M_1}(1-V_2)\right]\times g^{eff} \qquad \ldots (4)$$

where, g^{eff} is the effective Kirkwood correlation factor, μ_2 is the dipole moment of DMSO, μ_1 is the dipole moment of 2-NT, N is Avogadro's number, ρ_2, ρ_1 are the densities of DMSO and 2-NT, respectively. ε_{om} is static dielectric constant of mixture, k is Boltzmann's constant, M_2 is the molecular weight of DMSO and M_1 is the molecular weight of 2-NT, T is the temperature.

The effective Kirkwood correlation factor 'g^{eff}' for DMSO at 20°C is found to be 1.92 which is less than the value of 2-NT which is 0.62. It seen that lower concentration g^{eff} values is > 1 indicating parallel orientation of dipoles with formation of multimers and higher concentration dipoles rotate in antiparallel mode such that g^{eff} values decreases below unity[45], The Kirkwood correlation factor for 2-NT is less than that of DMSO, suggests the self-association is weaker in 2-NT than DMSO. g^{eff} value decreases confirming the heterogeneous interaction between 2-NT-DMSO molecules at all temperatures as shown in Fig. 6.

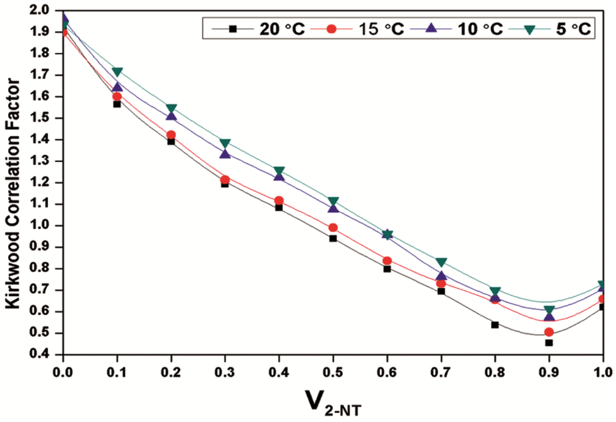

Fig. 6 — Kirkwood correlation factor versus volume fraction of 2-NT

Thermodynamic parameters

Thermodynamic parameter such as enthalpy of activation (ΔH) and entropy of activation (ΔS) were determined from Eyring equation using least squares fit method as[46],

$$\tau = (h/kT) \exp(\Delta H/RT) \exp(-\Delta S/R) \qquad \ldots (5)$$

where ΔH is enthalpy in kJ/mole, ΔS is the entropy, τ is the relaxation time in ps, k is the Boltzmann's constant, h is the Plank's constant and T is the temperature in K. Gibb's free energy (ΔG) is related to enthalpy (ΔH) and entropy (ΔS) of activation by following relation,

$$\Delta G = \Delta H - T * \Delta S \qquad \ldots (6)$$

Positive values of enthalpy for all concentrations show endothermic interaction in the system and positive values of entropy for all concentrations indicate less orderedness[47] in product than reactant. Gibbs free energy of activation 2-NT is found to be smaller than DMSO.

Conclusion

The excess dielectric and excess relaxation times were negative suggest strong intermolecular interactions with slower rotation of electric dipoles within the 2NT-DMSO mixtures. Kirkwood correlation factor g^{eff} for 2-NT less than unity indicates anti-parallel orientation of dipoles and is greater than unity for DMSO which increases the parallel orientation of dipoles. The Thermodynamic parameters are also reported for 2NT-DMSO mixtures.

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