Microwave Dielectric Characterization of Binary Mixtures of 3-Nitrotoluene with Dimethylacetamide, Dimethylformamide and Dimethylsulphoxide

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Dielectric relaxation measurements on 3-nitrotoluene (3-NT) mixture of dimethylacetamide (DMA), dimethylformamide (DMF) and dimethysulphoxide (DMSO) have been carried out across the entire concentration range using Time domain reflectometry technique at 15, 25, 35 and 45 °C over the frequency range from 10 MHz to 20 GHz. For all the mixtures, only one dielectric loss peak was observed in this frequency range and the relaxation in these mixtures can be well described by a single relaxation time using Debye model. Bilinear calibration method is used to obtain complex permittivity $\varepsilon^*(\omega)$ from complex reflection coefficient $\rho^*(\omega)$ over frequency range 10 MHz to 20 GHz. The excess permittivity, excess inverse relaxation time, Kirkwood correlation factor, molar energy of activation are also calculated for these mixtures to study the solute-solvent interaction.

Key Words : Dielectric relaxation, Mixture, Excess properties, Time domain reflectometry

Introduction

Microwave energy has been directly applied in many fields especially in scientific research such as communication, microwave-assisted chemistry and in food industry.[1,2] The successful application of microwaves is directly associated with the dielectric properties of the materials. An accurate measurement and working knowledge of these properties are key factors in better understanding the interaction of microwaves with the materials. Dielectric relaxation spectroscopy, for instance, is a powerful tool for examining the underlying physics of solvent systems and for exploring the molecular dynamics of liquids, which are characterized by inter- and intramolecular structures that vary rapidly with time.

Studies on the relaxation properties of the mixture of solvent have provided some interesting insights into the volumes implicated by the Debye expression and the nature of the mixing process. If the solvents are chemically similar and mix well at the molecular level then the mixture will often exhibit a single relaxation time at an average position, which reflects the molar ratios of the two components. However, if the solvents do not mix well at the molecular level, then two distinct relaxation times are observed and they do not differ greatly from those of the pure solvents.

The knowledge of frequency dependent dielectric properties of solvent systems, is important both in fundamental studies of solvent structure and dynamics and in practical application of microwave heating processes.[1] At a fundamental level, the frequency dependent dielectric behavior of solvent mixtures provides information on molecular interactions and mechanism of molecular processes. The dielectric relaxation behavior of mixtures of polar molecules under varying conditions of compositions is very important as it helps in obtaining information about relaxation processes in mixtures. There have been several investigations on the dielectric behavior of solvent mixtures in which dielectric relaxation spectra were used to examine molecular orientations, hydrogen bonded networks and microdynamics of these systems.[3-20]

In this paper, we report a systematic investigation of dielectric relaxation in binary mixture of 3-NT with DMA, DMF and DMSO at various concentration and temperature employing Time Domain Reflectometry (TDR).[21-23] We have measured the dielectric relaxation spectra for the solutions at various compositions in the frequency range of 10 MHz-20 GHz, over a temperature range of 15 °C to 45 °C. We fitted the experimental data to the three different relaxation models by the non-linear least squares fit method and determined that the Debye relaxation model[24-27] is sufficient to describe the major dispersion of the various solvents and solvent mixtures over this frequency range. These mixtures exhibit a principal dispersion of the Debye type at microwave frequencies and dielectric relaxation time and static permittivity could be obtained by fitting the spectra to Debye model. We have used the relaxation time constant to determine relevant thermodynamic parameters for the dipolar polarization process and the static permittivity to determine Kirkwood correlation factor that characterize the dipolar alignment within the solutions. The excess permittivity and excess inverse relaxation time are also obtained, which give information related to molecular interaction. These parameters will provide useful description of the structures and molecular dynamics of the solvent mixtures.

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Experimental Section

DMF, DMSO, DMA and 3-NT were obtained commercially with 99.9% purity and were used without further purification. The solutions were prepared at different volume percentage of 3-NT in DMA, DMF and DMSO in step of 10% at room temperature. The dielectric measurements were carried out using TDR. Detail explanation for the apparatus and the measurement procedure have already been reported in previous paper.[21-23,28]

Results and Discussion

The density and static permittivity values of pure liquids used along with literature values are given in Table 1. The complex permittivity spectra measured using TDR are fitted by the nonlinear least-squares fit method to the Havriliak-Negami expression[24] to obtain various dielectric parameters

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[1 + (j\omega\tau)^{1-\alpha}]^\beta} \qquad (1)$$

where $\varepsilon^*(\omega)$ is the complex permittivity at an angular frequency ω, ε_∞ is the permittivity at high frequency, ε_0 is the static permittivity, τ is the relaxation time of the system, α is the shape parameter representing symmetrical distribution of relaxation time and β is the shape parameter of an asymmetric relaxation curve.

Equation (1) includes Cole-Cole $(\beta = 1)$,[25] Davidson-Cole $(\alpha = 0)$[26] and Debye $(\alpha = 0, \beta = 1)$[27] relaxation models. It has been found that all the mixtures obey the Debye dispersion model. Therefore, it can be concluded that in the mixture of 3-NT+DMA, 3-NT+DMF and 3-NT+DMSO, the individual principal relaxation processes of the components coalesce and hence the mixtures exhibits a single relaxation time. Table 2, 3 and 4 reports the values of dielectric parameters obtained from fitting eq. (1) for 3-NT+DMA, 3-NT+DMF and 3-NT+DMSO systems, respectively. It can be seen that with an increasing concentration of 3-NT in the respective liquid, the static permittivity values are decreased whereas relaxation time values are increased. These values,

Table 1. Comparison of data for the pure liquids used with literature values at 25 °C

Liquid	ε_0		Density (g-cm^{-3})	
	This Work	Lit.	This Work	Lit.
3-NT	22.80	23[a] (at 20 °C)	1.1514	1.1571[a] (at 20 °C)
DMA	40.20	39.97[b]	0.9372	0.9366[c]
DMF	39.48	40.21[b]	0.9450	0.9487[d]
DMSO	48.09	48.4[e]	1.0959	1.09537[c]

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Table 2. Dielectric relaxation parameters for 3-NT-DMA mixtures

Vol. Fraction of 3-NT	ε_0	ε_∞	τ (ps)	ε_0	ε_∞	τ (ps)
		15 °C			25 °C	
0.0	42.69(1)	2.24	25.38(2)	40.20(7)	2.02	18.39(3)
0.1	41.98(3)	2.16	32.62(1)	39.90(2)	2.06	26.34(1)
0.2	40.06(2)	2.07	33.53(5)	37.07(1)	2.01	28.96(1)
0.3	37.93(1)	2.06	36.35(1)	34.19(3)	2.11	32.26(2)
0.4	35.27(2)	2.34	37.26(4)	33.11(1)	2.12	32.70(1)
0.5	33.16(5)	2.22	38.87(1)	31.19(6)	2.16	33.38(2)
0.6	31.91(1)	2.60	41.61(2)	29.13(3)	2.06	37.42(1)
0.7	29.69(1)	2.00	50.52(3)	27.12(1)	2.12	45.42(1)
0.8	29.08(3)	2.01	51.92(6)	26.90(1)	2.34	47.58(1)
0.9	25.07(1)	2.12	59.99(1)	24.75(3)	2.11	53.57(4)
1.0	23.87(2)	1.67	74.04(2)	22.80(2)	1.68	63.56(3)
		35 °C			45 °C	
0	37.26(2)	2.46	15.87(2)	35.22(1)	3.10	11.70(7)
0.1	34.61(1)	2.22	22.76(2)	34.07(0)	2.46	20.32(1)
0.2	33.94(1)	2.07	24.54(1)	32.19(0)	2.11	22.53(2)
0.3	30.89(3)	2.20	25.40(2)	29.12(1)	2.06	22.98(1)
0.4	29.56(1)	2.41	27.44(1)	27.91(0)	2.34	23.38(4)
0.5	28.67(2)	2.46	28.58(1)	26.67(1)	2.07	25.22(2)
0.6	26.91(3)	2.19	31.20(2)	25.45(1)	2.16	27.19(5)
0.7	26.19(1)	2.19	38.61(7)	24.17(1)	2.07	32.79(8)
0.8	25.87(4)	2.67	41.53(4)	23.92(1)	2.07	34.62(2)
0.9	24.01(6)	2.13	48.42(1)	22.76(0)	2.13	41.81(3)
1.0	22.45(1)	1.66	54.87(5)	22.09(0)	1.74	50.71(3)

Numbers in brackets represents errors. For e.g. 42.69 (1) means 42.69 ± 0.01.

Table 3. Dielectric relaxation parameters for 3-NT+DMF mixtures

Vol. Fraction of 3-NT	ε_0	ε_∞	τ (ps)	ε_0	ε_∞	τ (ps)
		15 °C			25 °C	
0	42.51(1)	2.07	12.10(2)	39.48(1)	2.01	10.30(3)
0.1	40.96(2)	2.16	17.62(3)	36.98(1)	3.74	15.93(1)
0.2	38.79(1)	2.90	21.48(3)	36.06(0)	2.94	20.78(2)
0.3	37.66(5)	2.17	23.39(1)	33.12(0)	2.01	22.42(1)
0.4	35.55(2)	4.12	26.30(5)	31.27(1)	2.74	24.46(1)
0.5	34.04(3)	3.94	34.80(2)	30.68(1)	2.94	31.35(6)
0.6	32.09(2)	3.79	38.52(4)	29.19(0)	4.01	35.46(2)
0.7	30.15(1)	2.19	41.09(4)	27.29(0)	2.96	38.14(4)
0.8	28.56(4)	3.96	49.88(2)	26.52(1)	3.74	46.38(5)
0.9	26.97(3)	3.16	61.89(1)	25.23(1)	2.94	55.23(2)
1.0	23.87(2)	1.67	74.04(2)	22.80(2)	1.68	63.56(3)
		35 °C			45 °C	
0	37.03(2)	1.96	9.20(3)	35.23(8)	2.00	8.12(2)
0.1	35.34(1)	2.14	14.24(4)	33.14(2)	2.74	11.89(1)
0.2	33.49(1)	3.15	17.74(1)	31.69(0)	3.16	15.71(3)
0.3	31.10(3)	2.96	21.21(2)	30.56(0)	2.74	18.88(1)
0.4	30.16(1)	3.14	22.85(3)	29.06(1)	3.24	19.05(2)
0.5	29.09(1)	3.78	24.81(1)	27.56(0)	2.69	20.82(3)
0.6	27.07(5)	2.81	30.59(4)	26.06(1)	3.08	27.01(6)
0.7	26.37(1)	3.19	33.09(3)	25.51(0)	2.89	29.03(2)
0.8	25.65(2)	2.86	36.38(5)	24.19(1)	3.42	30.57(4)
0.9	24.82(1)	2.56	46.36(1)	23.06(1)	2.51	38.25(1)
1.0	22.45(1)	1.66	54.87(5)	22.09(0)	1.74	50.71(3)

Table 4. Dielectric relaxation parameters for 3-NT+DMSO mixtures

Vol. Fraction of 3-NT	ε_0	ε_∞	τ (ps)	ε_0	ε_∞	τ (ps)
		15 °C			25 °C	
0	50.76(3)	1.75	23.84(4)	48.09(1)	2.37	21.14(3)
0.1	47.67(2)	1.97	33.59(1)	46.06(2)	2.75	28.75(1)
0.2	45.18(3)	3.14	34.87(1)	45.00(1)	2.94	30.80(0)
0.3	43.15(3)	4.06	39.75(1)	40.96(2)	3.74	34.72(0)
0.4	40.26(5)	4.17	40.07(1)	38.16(1)	4.17	35.46(0)
0.5	37.67(2)	3.16	43.00(0)	35.15(2)	3.16	35.48(2)
0.6	34.16(2)	2.66	43.01(0)	32.95(1)	3.17	38.68(0)
0.7	31.06(5)	2.17	46.89(0)	30.15(2)	3.94	40.47(0)
0.8	27.87(4)	3.14	51.25(0)	27.05(2)	3.14	44.46(1)
0.9	26.02(1)	4.12	63.79(0)	25.76(5)	4.17	57.58(0)
1.0	23.87(1)	1.67	74.04(2)	22.80(2)	1.68	63.56(3)
		35 °C			45 °C	
0	45.91(1)	2.13	18.86(1)	45.02(6)	2.2	15.12(6)
0.1	44.61(2)	3.10	27.23(3)	42.94(1)	3.74	25.37(2)
0.2	42.67(1)	3.18	28.87(1)	40.15(2)	4.17	25.82(1)
0.3	40.15(4)	3.17	31.52(2)	38.74(2)	4.06	27.34(3)
0.4	36.66(2)	2.12	31.70(4)	35.69(4)	3.14	28.05(3)
0.5	33.95(2)	3.96	32.71(1)	32.90(5)	2.94	28.23(2)
0.6	31.15(3)	3.74	32.89(3)	30.56(1)	2.26	29.95(4)
0.7	29.87(3)	4.17	36.09(1)	28.25(3)	3.74	33.08(1)
0.8	26.95(2)	3.14	41.73(6)	25.61(2)	2.34	37.77(1)
0.9	24.49(1)	2.72	50.77(5)	23.05(1)	2.94	46.24(5)
1.0	22.45(1)	1.66	54.87(5)	22.09(3)	1.74	50.71(3)

Figure 1. Excess permittivity (ε^E) for (a) 3-NT+DMA. (b) 3-NT+DMF. (c) 3-NT+DMSO systems.

static permittivity as well as relaxation time, are decreased with an increase in temperature.
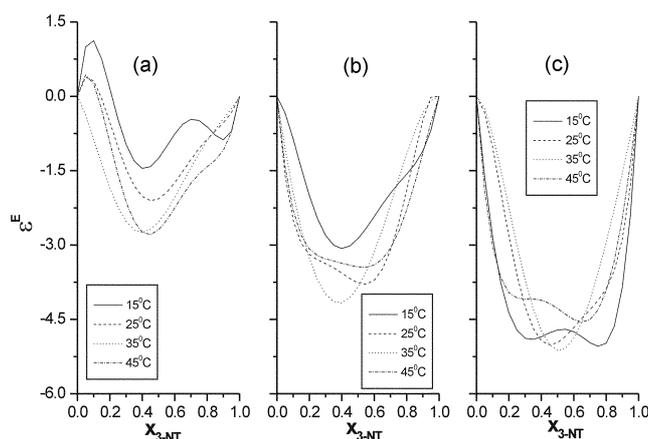
The excess parameters[4,29] related to ε_0 and τ provide valuable information regarding interaction between the polar-polar liquid mixtures. These properties are also useful for detection of the cooperative domain in the mixture and may evidence formation of multimers in the mixture due to intermolecular interaction. The excess permittivity is defined as

$$\varepsilon^E = (\varepsilon_0 - \varepsilon_\infty)_m - [(\varepsilon_0 - \varepsilon_\infty)_A x_A + (\varepsilon_0 - \varepsilon_\infty)_B x_B] \qquad (2)$$

where x-mole fraction and suffices m, A, B represents mixture, solvent A and B respectively. The excess permittivity provides qualitative information about multimers formation in the mixture as follows :

i) $\varepsilon^E = 0$ indicates that the two solvent do not interact at all.

ii) $\varepsilon^E < 0$ indicates that the solvent and solvent interaction act so as to reduce total effective dipoles. This suggests that the two solvents mixture may form multimers leading to the less effective dipoles.

iii) $\varepsilon^E > 0$ indicates that the two solvents interact in such a way that the effective dipole moment increases. There is formation of multimers and dimers.

Figure 1 shows the plot of excess permittivity plotted against mole fraction of 3-NT for all the three systems. In this study, the excess permittivity values are found to be negative for all the three systems, for all temperatures and

concentrations, except near DMA rich region at 15 °C, 25 °C and 35 °C, indicates that the total number of dipoles decreases in the mixtures. This is due to the apposite alignment of the dipoles of the two interacting solvent molecules. For all the three systems, the curves are more deviated from zero at and near equal concentration region than near the pure component region indicates strong intermolecular interaction in this region. The positive values of ε^E for 3-NT+DMA system near DMA rich region at 15 °C, 25 °C and 35 °C indicate formation of monomeric or polymeric structures which increases the total number of dipoles in the system.

The excess inverse relaxation time is defined as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A x_A + (1/\tau)_B x_B] \qquad (3)$$

where $(1/\tau)^E$ is excess inverse relaxation time. The information regarding the dynamics of solute-solvent interaction from this excess property is as follows.

i) $(1/\tau)^E = 0$: There is no change in the dynamics of solvent-solvent interaction.

ii) $(1/\tau)^E < 0$: The solvent-solvent interaction produces a field such that the effective dipoles rotate slowly.

iii) $(1/\tau)^E > 0$: The solvent-solvent interaction produces a field such that the effective dipoles rotate fastly *i.e.* the field
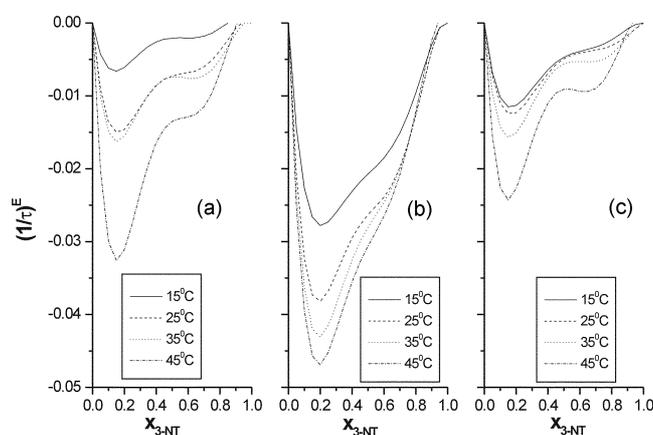
Figure 2. Excess inverse relaxation time $(1/\tau)^E$ for (a) 3-NT + DMA. (b) 3-NT + DMF. (c) 3-NT + DMSO systems.

will co-operate in rotation of dipoles.

The variation of $(1/\tau)^E$ with mole fraction of 3-NT for all the three systems is shown in Figure 2. From Figure 2, it can be seen that, for all the three systems, the excess inverse relaxation time values are negative which indicate the formation of linear structures, which rotate slowly under the influence of an external varying field. It indicates that addition of 3-NT to DMA, DMF and DMSO has created a hindering field such that the effective dipoles rotate slowly.

The structural information about the liquids by dielectric relaxation parameter can be obtained by Kirkwood correlation parameter.[30] The Kirkwood correlation factor g is also a parameter for affording information regarding orientation

of electric dipoles in polar liquids. The g for pure liquid can be obtained by the expression,

$$\frac{4\Pi\mu^2\rho}{9kTM}g = \frac{(\varepsilon_0 - \varepsilon_0)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} \quad (4)$$

where m is dipole moment in gas phase, ρ is density at temperature T, M is molecular weight, k is Boltzmann constant, N is Avogadros number. The dipole moment in gas phase is 3.86, 3.72, 3.86 and 3.90 Debye for 3-NT, DMA, DMF and DMSO, respectively.

The effective angular correlation (g^{eff}) between molecules is calculated using modified form of eq. (4).[4,31] g^{eff} has been used to study the orientation of electric dipoles in binary mixtures. The value of this parameter changes from Kirkwood correlation factor of one pure liquid to that of second liquid. The Kirkwood equation for the mixture may be expressed as;[4,31]

$$\frac{4\Pi N}{9kT}\left(\frac{\mu_A^2\rho_A}{M_A}\Phi + \frac{\mu_B^2\rho_B}{M_B}\Phi_B\right)g^{eff}$$

$$= \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2} \quad (5)$$

where g^{eff} is the effective Kirkwood correlation factor for a binary mixture, with ϕ_A and ϕ_B as volume fractions of liquids A and B respectively. g^{eff} varies between g_A and g_B.

The calculated values of g^{eff} are tabulated in Table 5. It can be seen from Table 5 that, g^{eff} values are less than unity for 3-NT indicating antiparallel orientation of electric dipoles. But these values are very close to unity indicating no dipole correlation. For all the three systems studied here, it can be seen that the g^{eff} values are increased with an increasing concentration of respective liquid in 3-NT. These values are greater than unity for all the mixtures and at all temperatures suggesting parallel orientation of electric dipoles.

The values of molar enthalpy of activation (ΔH^*) obtained from Eyring's rate equation[32] for the three systems at different concentrations are tabulated in Table 6.

Table 5. Kirkwood correlation factor 3-NT + DMA, 3-NT + DMF and 3-NT + DMSO mixtures

Vol. fraction of A[a]	g^{eff}			
	15 °C	25 °C	35 °C	45 °C
3-NT + DMA				
0	0.98	0.98	0.95	0.94
0.1	1.09	1.04	1.02	1.01
0.2	1.10	1.08	1.03	1.02
0.3	1.19	1.16	1.07	1.06
0.4	1.22	1.20	1.14	1.11
0.5	1.29	1.27	1.18	1.15
0.6	1.38	1.34	1.24	1.21
0.7	1.38	1.37	1.31	1.29
0.8	1.39	1.45	1.34	1.31
0.9	1.48	1.49	1.40	1.35
1.0	1.57	1.54	1.45	1.40
3-NT + DMF				
0	0.98	0.98	0.95	0.94
0.1	1.01	1.01	1.00	1.00
0.2	1.05	1.04	1.01	1.00
0.3	1.09	1.08	1.05	1.02
0.4	1.12	1.11	1.09	1.05
0.5	1.15	1.16	1.09	1.04
0.6	1.19	1.16	1.12	1.10
0.7	1.26	1.24	1.23	1.19
0.8	1.37	1.35	1.32	1.28
0.9	1.45	1.44	1.44	1.38
1.0	1.02	0.98	0.95	0.93
3-NT + DMSO				
0	0.98	0.98	0.95	0.94
0.1	1.05	1.05	1.02	1.01
0.2	1.09	1.07	1.04	1.03
0.3	1.07	1.06	1.05	1.03
0.4	1.11	1.10	1.07	1.08
0.5	1.15	1.14	1.12	1.11
0.6	1.21	1.21	1.20	1.19
0.7	1.29	1.27	1.28	1.25
0.8	1.35	1.32	1.31	1.29
0.9	1.37	1.35	1.33	1.31
1.0	1.43	1.40	1.36	1.35

[a]A is DMA/DMF or DMSO

Table 6. Molar energy of activation for 3-NT + DMA, 3-NT + DMF and 3-NT + DMSO systems

Vol. Fract. of 3-NT	Molar enthalpy ΔH^* (KJ/mole)		
	DMA	DMF	DMSO
0	18.9 (2)	18.9 (4)	27.1 (1)
0.1	6.68 (5)	5.50 (1)	5.03 (7)
0.2	4.47 (6)	5.38 (9)	5.18 (8)
0.3	3.04 (8)	8.58 (9)	5.21 (6)
0.4	2.06 (7)	9.11 (3)	7.19 (9)
0.5	4.51 (5)	7.42 (2)	7.83 (2)
0.6	5.09 (5)	8.74 (1)	7.68 (1)
0.7	1.21 (8)	9.74 (7)	5.94 (5)
0.8	1.81 (9)	7.85 (1)	5.54 (8)
0.9	2.25 (9)	9.45 (1)	4.34 (1)
1.0	9.51 (1)	9.51 (1)	9.51 (1)

$$\tau = (h/kT) \exp{[(\Delta H^* - T\Delta S^*)/RT)]} \qquad (6)$$

These values are positive for all the concentrations and for all the three systems suggest endothermic interaction. The temperature dependence of the relaxation time follows the Arhenius behaviour.

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