

Microwave dielectric characterization of binary mixture of diethylene glycol monomethyl ether with N, N-dimethylformamide

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Abstract: Dielectric relaxation measurements of Diethylene Glycol Monomethyl Ether (DGME) – N,N-dimethylformamide (DMF) binary mixtures have been carried out at 11 concentrations at four temperatures 288K to 318K, over the frequency range 10 MHz to 20 GHz using time domain reflectometry (TDR) technique. The mixtures exhibit a principle dispersion of the Davidson - Cole relaxation type at microwave frequencies. Bilinear calibration method is used to obtain complex permittivity spectra $\epsilon^*(\omega)$ from reflection coefficient spectra $\rho^*(\omega)$. A non linear least square fit method was used to obtain the static dielectric constant (ϵ_s) and relaxation time (τ). Excess permittivity (ϵ_s^E), Excess Inverse Relaxation time ($1/\tau$)^E, Kirkwood correlation factor (g^{eff} and g_p), Bruggeman factor (f_B) and molar enthalpy of activation (ΔH)* are also calculated to study the solute – solvent interaction.

Keywords: Time domain reflectometry; diethylene glycol monomethyl ether; N, N-dimethylformamide; excess parameters; Kirkwood correlation factor; Bruggeman factor; Thermodynamic parameters

INTRODUCTION

The knowledge of frequency dependent dielectric properties of binary liquid mixtures is important both the fundamental studies of solvent structure determination and its dynamics as well as in the practical application of microwave heating process [1,2]. At a fundamental level, the frequency dependent dielectric behavior of a liquid mixture provides information on molecular interactions and mechanism of molecular process. 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 process in mixtures. There have been several investigations on the dielectric behavior of solvent mixtures in which dielectric spectra were used to examine molecular orientations, hydrogen bonded networks and microdynamics of these systems [3-9].

In this paper, we study the systematic investigations of dielectric relaxation in binary mixture of DGME with DMF at various concentrations and temperatures employing time domain reflectometry [10]. The dielectric relaxation spectra have been obtained for solutions of various compositions in the frequency range of 10 MHz to 20 GHz, at temperatures 288 K to 318 K. the experimental data are fitted to the three

different relaxation models [11] by the non-linear least squares fit method. It is observed that the Davidson-Cole model is adequate to describe major dispersion of the various solute and solvent mixtures over this frequency range. Static dielectric constant and relaxation time could be obtained by fitting the spectra to the Davidson-Cole model. The static dielectric constant and relaxation time have been used to determine the excess permittivity, excess inverse relaxation time, Kirkwood correlation factor and Bruggeman factor. Kirkwood correlation factor characterizes the dipole alignment within the solutions. The excess permittivity, excess inverse relaxation time and Bruggeman factor provide information related to molecular interaction. These parameters will provide useful description of the structure and dynamics of the binary mixtures.

EXPERIMENTAL

Chemicals

Diethylene Glycol Monomethyl Ether (DGME) and N,N-dimethylformamide (DMF) were purchased from Merk and of spectroscopic grade purity. These chemicals used without further purification. The solutions were prepared at 11 different volume percentage of DGME in steps of 10% from 0 to 100% (before mixing) at room temperature.

Using these volume percents the mole fraction is calculated as

$$X_1 = \frac{\frac{v_1 \rho_1}{m_1}}{\left(\frac{v_1 \rho_1}{m_1}\right) + \left(\frac{v_2 \rho_2}{m_2}\right)}$$

Where m_i , v_i , and ρ_i represent the molecular weight, volume percent, and density of the ith ($i = 1, 2$) solute –

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solvent liquids, respectively.

TDR Setup and Data acquisition

The complex permittivity spectra were studied using the time domain reflectometry (TDR) method as described in [12-14]. The Hewlett Packard HP 54750 sampling oscilloscope with HP 54754A TDR plug in module has been used. A fast rising step voltage pulse of about 39 ps rise time generated by a pulse generator was propagated through a coaxial line system of characteristic impedance 50 Ohm. Transmission line system under test was placed at the end of coaxial line in the standard military applications (SMA) coaxial connector with 3.5 mm outer diameter and 1.35 mm effective pin length. All measurements were carried out under open load conditions. The change in the pulse after reflection from the sample placed in the cell was monitored by the sample oscilloscope. In the experiment, time window of 5 ns was used. The reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were digitized in 1024 points in the memory of the oscilloscope and transferred to a PC through 1.44 MB floppy disk.

The temperature controlled system with water bath and a thermostat has been used to maintain the constant temperature within the accuracy limit of $\pm 0.2^\circ\text{C}$. The sample cell is surrounded by a heat insulating container through which the water of constant temperature using temperature controller system is circulated. The temperature at the cell is checked using the electronic thermometer.

DATA ANALYSIS

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range from 10 MHz to 20 GHz using Fourier transformation [15-16] as

$$\rho^*(\omega) = (c / j\omega d) [p(\omega) / q(\omega)] \quad (1)$$

where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $[R_1(t)-R_x(t)]$ and $[R_1(t)+R_x(t)]$ respectively, c is the speed of light, ω is the angular frequency d is effective pin length and $j = \sqrt{-1}$. It is related with dielectric response of the sample under study.

The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by using the bilinear calibration method [17], 1-Hexanol and 1-Propanol were used as calibrating liquids. A sample spectra $\varepsilon^*(\omega)$ is shown in fig. (1), for a mixture of 50% DGME and 50% DMF at 308K. The experimental values of $\varepsilon^*(\omega)$ are fitted with the Havriliak – Negami expression [18].

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{\left[(1 + j\omega\tau)^{(1-\alpha)} \right]^\beta} \quad (2)$$

where ε_s , ε_∞ , τ , α and β are fitting parameters. In equation (2), ε_s is the static permittivity, ε_∞ is the static permittivity at high frequency, τ is the relaxation time of the system α is the shape parameter representing symmetrical distribution of relaxation time, β is the shape parameter of an asymmetric

relaxation curve and ω is the angular frequency. The value of ε_∞ is not sensitive to ε^* [19] and taken to be fixed as 3 while fitting this data. Equation (2) includes Cole-Cole ($\beta=1$) [20], Davidson-Cole ($\alpha=0$) [21] and Debye ($\alpha=0$, $\beta=1$) [22] relaxation models.

RESULT AND DISCUSSION

Complex permittivity spectra for 50% DMF in DGME – DMF binary mixture is shown in fig. (1). From the Cole – Cole plot shown in fig. (2), the dielectric model for fitting dielectric parameters suitable for present system is Davidson – Cole model. Therefore, the complex permittivity spectra have been fitted in Davidson – Cole model. A non linear least square fit method [23] was used to determine the values of dielectric parameters.

The static dielectric constants and relaxation time values are shown in Table 1.

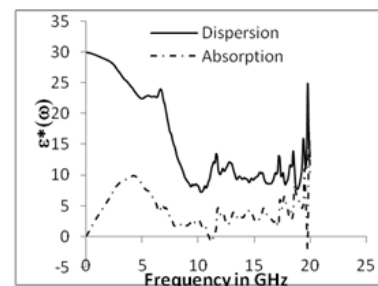


Figure 1. Complex Permittivity spectra for 50% DMF in DGME – DMF binary mixture

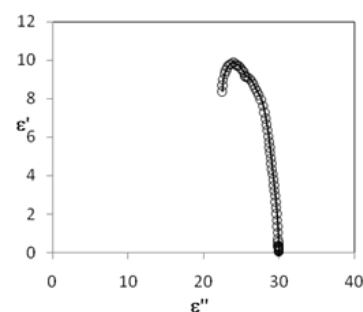


Figure 2. Cole – Cole Plot of 50% DMF in DGME – DMF binary mixture

The static dielectric constant for the mixtures increases towards the dielectric constant of DMF. The increase of dielectric constant is probably due to the transition of spherical molecular aggregates into elongated aggregates giving rise to parallel orientation of the dipoles [24-25]. It is found that in the DMF rich region the dielectric constant for the mixtures increases, whereas when the concentration of DGME dominates in the mixture the static dielectric constant decreases. There is a non linear relationship between the values of static dielectric constant (ε_s) relaxation time (τ) in the mixtures (Fig. 3) and (4). These values, static dielectric constant as well as relaxation time are decreased with an increase in temperature.

This may be due to the increase in the molar volume and the increase in the effective length of the dipole with increase

in temperature and also due to thermal agitation and partly due to decrease in the viscosity [26-27].

Table: 1: Temperature dependent dielectric parameters for binary mixture of DGME-DMF

Mole Fraction of DMF	288K		298K		308K		318K	
	ϵ_s	τ (ps)	ϵ_s	τ (ps)	ϵ_s	τ (ps)	ϵ_s	τ (ps)
0	16.49	41.85	16.18	34.42	15.72	27.23	15.28	25.37
0.1442	22.52	41.22	21.42	30.2	21.05	24.06	20.24	20.53
0.2749	26.28	36.43	25.17	26.05	24.58	20.38	23.50	17.03
0.3940	28.68	32.89	27.04	22.76	26.08	18.14	24.81	15.13
0.5028	30.28	30.33	28.56	20.57	27.76	15.47	26.47	13.41
0.6027	31.67	25.31	29.94	18.73	28.87	14.67	27.73	12.45
0.6947	33.72	24.18	31.30	17.52	29.43	13.23	28.60	12.08
0.7797	34.34	19.46	33.24	15.64	31.20	12.07	29.96	10.55
0.8585	35.89	16.89	34.48	14.53	32.26	11.35	31.14	10.37
0.9317	38.67	13.82	37.52	12.25	36.45	10.12	34.13	9.39
1	42.42	11.17	40.96	10.75	39.47	9.3	38.02	8.5

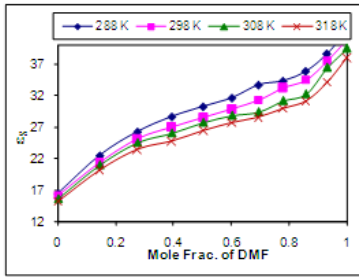


Figure 3. Variation of estimated static permittivity as function of mole fraction of DMF in DGME at different temperatures

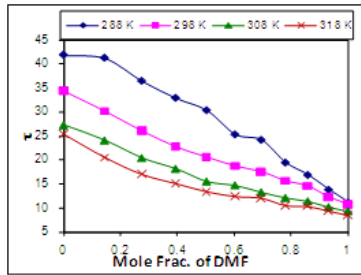


Figure 4. Variation of estimated relaxation time as function of mole fraction of DMF in DGME at different temperatures

The structural information about the liquid by the dielectric relaxation parameter may be obtained using the Kirkwood correlation parameter g [28]. This factor is also a parameter for obtaining information regarding orientation of electric dipoles in polar liquids. The g for the pure liquid may be obtained using the expression

$$\frac{4\pi N \mu^2 \rho}{9kTM} g = \frac{(\epsilon_s - \epsilon_\infty)(2\epsilon_s + \epsilon_\infty)}{\epsilon_s(\epsilon_\infty + 2)^2} \quad (3)$$

where μ is the dipole moment in the gas phase, ρ is the density at temperature T , M is the molecular weight, k is the Boltzmann constant, and N is Avogadro's number.

For the mixture of two polar liquids A and B, equation (3) is modified [29-32] using the following assumption:

For the mixture, g^{eff} is the effective correlation factor in the mixture. The Kirkwood equation for the mixture may be expressed as

$$\begin{aligned} \frac{4\pi N}{9kT} \left(\frac{\mu_A^2 \rho_A}{M_A} X_A + \frac{\mu_B^2 \rho_B}{M_B} X_B \right) g^{\text{eff}} \\ = \frac{(\epsilon_s - \epsilon_\infty)(2\epsilon_s + \epsilon_\infty)}{\epsilon_s(\epsilon_\infty + 2)^2} \end{aligned} \quad (4)$$

where g^{eff} is the effective Kirkwood correlation factor for a binary mixture, with X_A and X_B as the volume fractions of liquids A and B, respectively. The Kirkwood correlation factor, g^{eff} , gives angular correlation between the molecules of the system.

In the mixtures the values of g^{eff} show decreasing trend with the increasing concentration of DMF molecules in the mixtures. This indicates the decrease in interaction between the molecules of the system with increase in volume fraction of DMF in the solution. This is because DGME have more hydrogen bonding which gives more interaction of the molecules of the system in DGME rich region. The values of g^{eff} are greater than unity for all the concentration and all four

temperatures suggesting parallel orientation of electric dipoles.

The another way to visualize variation in Kirkwood correlation factor is to assume that correlation factors for molecules A and B in mixture contribute to effective (g) in proportion to their pure liquid values g_A and g_B . Under this assumption Kirkwood equation for the mixture can be written as.

$$\frac{4\pi N}{9kT} \left(\frac{\mu_A^2 \rho_A g_A}{M_A} X_A + \frac{\mu_B^2 \rho_B g_B}{M_B} X_B \right) g_f$$

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

where g_f is correlation factor for mixture. The values of g^{eff} in equation (4) will change from g_A to g_B as the fraction of component B increases from zero to unity. In equation (5), g_f is unity for pure liquids and will remain close to unity if there is no interaction between A and B.

The value of g_f is unity for an ideal mixture and deviation from unity may indicate interaction between two components of the mixture. The g_f values greater than one indicate that the dipoles of mixture will be oriented in such a way that the effective dipole will be greater than the corresponding values of pure liquid.

The calculated values of g^{eff} and g_f are tabulated in Table 2.

Table 2: Kirkwood Correlation factor (g^{eff}) and g_f for DGME - DMF

Mole Fraction of DMF	288K		298K		308K		318K	
	g^{eff}	g_f	g^{eff}	g_f	g^{eff}	g_f	g^{eff}	g_f
0	4.09	1	4.15	1	4.15	1	4.16	1
0.1	3.23	1.19	3.17	1.16	3.22	1.18	3.19	1.17
0.2	2.65	1.23	2.62	1.20	2.64	1.22	2.60	1.20
0.3	2.23	1.19	2.17	1.16	2.16	1.15	2.11	1.13
0.4	1.91	1.14	1.86	1.10	1.87	1.11	1.84	1.09
0.5	1.69	1.08	1.65	1.05	1.64	1.05	1.62	1.04
0.6	1.55	1.06	1.49	1.01	1.44	0.98	1.44	0.99
0.7	1.39	0.99	1.39	0.99	1.35	0.96	1.33	0.96
0.8	1.30	0.96	1.29	0.96	1.24	0.93	1.24	0.93
0.9	1.26	0.97	1.27	0.97	1.27	0.98	1.23	0.95
1	1.27	1	1.26	1	1.26	1	1.25	1

There is no appropriate molecular theory available in the literature which correlated dielectric relaxation parameters to solute-solvent interaction. The excess parameters [33] related to static dielectric constant and relaxation time provides valuable information regarding interaction between the solute-solvent (polar-polar) liquid mixtures. These properties are also useful for detection of the cooperative domain in the mixture due to intermolecular interaction.

The excess permittivity (ϵ_s^E) is defined as

$$\epsilon_s^E = (\epsilon_s - \epsilon_{\infty})_m - [(\epsilon_s - \epsilon_{\infty})_1 x_1 + (\epsilon_s - \epsilon_{\infty})_2 x_2] \quad (6)$$

Where x - mole fraction and suffices m , 1, 2 represents mixture, liquid 1(DGME) and liquid 2 (DMF) respectively.

The excess permittivity may provide qualitative information about multimers, monomers and dimmers formation in the mixtures as follows:

(i) $\epsilon_s^E = 0$ indicates the solute and solvent do not interact at all.

(ii) $\epsilon_s^E < 0$ indicates the solute and solvent interaction in such a way that the total effective dipoles get reduced. This suggests that the solute and solvent mixture may form multimers leading to the less effective dipoles.

(iii) $\epsilon_s^E > 0$ indicates the solute and solvent interaction in such a way that the total effective dipole moment increases. There is a tendency to form monomers and dimmers, dipole aligned in parallel direction.

The plot of excess permittivity plotted against mole fraction of DMF for all temperatures is shown in fig. (5).

In this study, the excess permittivity values are positive only up to high concentration of DGME in the mixture. The excess permittivity value is negative in DMF rich region; it indicates the addition of DMF results solute and solvent interaction in such a way that the total effective dipoles get reduced due to formation of multimer structure in the mixture.

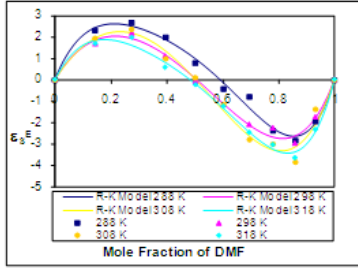


Figure 5 Variation of estimated excess permittivity as function of mole fraction of DMF in DGME at different temperatures.

The excess inverse relaxation time is defined as

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_1 x_1 + \left(\frac{1}{\tau}\right)_2 x_2\right] \quad (7)$$

The inverse relaxation time $\left(\frac{1}{\tau}\right)^E$ analogy is taken from spectral line broadening (which is inverse of the relaxation time) from the resonant spectroscopy [34]. The information regarding the dynamic of solute solvent interactions from this excess property is as follows:

- (i) $(1/\tau)^E = 0$ There is no change in the dynamics of solute and solvent interaction.
- (ii) $(1/\tau)^E < 0$ The solute and solvent interaction produces a field such that the effective dipoles rotate slowly.
- (iii) $(1/\tau)^E > 0$ The solute and solvent interaction produces a field such that the effective dipoles rotate fastly i.e. the field will co-operate in rotation of dipoles.

The plot of excess inverse relaxation time plotted against mole fraction of DMF for all temperatures is shown in fig. (6).

It can be seen that for all temperatures, the excess inverse relaxation time values are negative. It indicates that addition of DMF has created a hindering field such that the effective dipoles rotate slowly due to formation of linear structures.

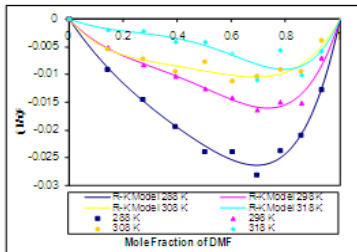


Fig. 6. Variation of estimated excess inverse relaxation time as function of mole fraction of DMF in DGME at different temperatures.

The Bruggeman equation [35] is another parameter which may be used an indicator of solute- solvent interaction. The Bruggeman factor f_B is given by,

$$f_B = \left[\frac{\epsilon_{Sm} - \epsilon_{SB}}{\epsilon_{SA} - \epsilon_{SB}} \right] \left[\frac{\epsilon_{SA}}{\epsilon_{Sm}} \right]^{1/3} = (1 - \Phi_B) \quad (8)$$

Where Φ_B is the volume fraction, ϵ_{Sm} , ϵ_{SA} and ϵ_{SB} are the values of static dielectric constant corresponding to mixture, solvent and solute respectively.

According to equation (8), a linear relationship is expected which will give a straight line when plotted f_B against ϕ_B .

The values of Bruggeman factor for all concentrations and all four temperatures are plotted in in fig. (7). The Bruggeman factor deviates from the ideal values for all concentrations of DMF in the solution. The deviation is more in DGME rich region. This confirms the strong intermolecular interaction in the DGME rich region.

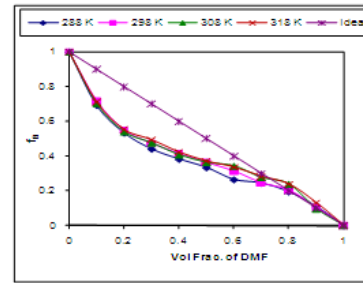


Figure 7. Variation of estimated values of Bruggeman factor as a function of mole fraction of DMF in DGME at different temperatures.

The values of molar enthalpy of activation (ΔH) obtained from Eyring rate equation [36] at different concentrations is tabulated in Table 3.

$$\tau = \left(\frac{h}{kT}\right) \exp \left[\frac{(\Delta H^* - T\Delta S^*)}{RT} \right] \quad (9)$$

These values are positive for all the concentrations. The activation energy increases as increasing the percentage of DMF in the mixture. This means that more energy is needed for group dipole reorientation with increase in volume fraction of DMF in the mixture.

Table 3. Molar enthalpy of activation (ΔH^*) of DGME – DMF system.

Volume Fraction of DMF	Molar enthalpy ΔH^* (KJ/mole)
0	10.76
0.1	15.2
0.2	16.79
0.3	17.03
0.4	18.41
0.5	15.61
0.6	15.58
0.7	13.47
0.8	10.53
0.9	7.784
1	4.797

CONCLUSION

The dielectric relaxation parameters, the Kirkwood correlation factor, the excess properties, the Bruggeman factor and molar enthalpy of activation have been reported for DGME –DMF binary mixture for different concentrations and temperatures. In the mixture the static dielectric constant increases with increase in concentration of DMF in the mixture.

The relaxation time of the mixture is found higher in DGME rich region. The higher relaxation time may be due to more association through hydrogen bonding of –OH group in DGME. Kirkwood correlation factor have been reported in this system. These data provide information regarding orientation of molecules in liquids. The negative excess relaxation time values indicate the slower rotation of effective dipoles of the system. There is a deviation in Bruggeman factor from linearity shows molecular interaction in the mixture. Molar enthalpy of activation shows more energy is needed for group dipole reorientation.

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