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DIELECTRIC RELAXATION STUDIES OF AMIDES WITH 2-METHOXYETHANOL AND 2-BUTOXYETHANOL USING TIME DOMAIN REFLECTOMETRY TECHNIQUE***Kumar, S., Periyasamy, P and Jeevanandham, P**

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Key words:Dielectric relaxation, Time Domain
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Complex dielectric permittivity measurements of amides like Formamide (FA), N-methylformamide (NMF) and N,N-dimethylformamide (DMF) with alcohols such as 2-methoxyethanol (2-ME) and 2-butoxyethanol (2-BE) has been carried out at different concentration in the frequency range of 10MHz to 30GHz using Time Domain Reflectometry (TDR). The least squares fit method has been used to obtain the static dielectric constant (ϵ_0), relaxation time (τ) and Bruggeman factor (f_B) for binary mixtures. The Bruggeman plot shows a deviation from linearity. This deviation was attributed to some sort of molecular interaction which may take place between the unlike molecules. The effective Kirkwood correlation factor (g^{eff}) and corrective Kirkwood correlation factor (g_r) of the mixtures have been determined and discussed to yield information on the structure and dynamics of the mixtures and it confirms the structural formation due to intermolecular interaction between amides with 2-ME and 2-BE. The relaxation time is increasing with increasing chain length of alcohols and is decreasing with increasing amide concentration. The excess static dielectric constant (ϵ^E) and excess inverse relaxation time ($1/\tau^E$) values are indicates that is a form of hydrogen bonding interaction between the 2-ME and 2-BE with amides systems, for all the mixtures dipoles are slowly rotated. The free energy of activation for relaxation time (ΔF_τ) is greater for initial concentration in all the system studied.

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INTRODUCTION

Advanced microwave techniques have been used as powerful tools for the measurement of complex permittivity of liquids and their mixtures over a wide frequency range from 10 MHz to 30 GHz in Time Domain Reflectometry technique (Mashimo *et al.*, 1989, Cole *et al.*, 1989, Kumbharkhane *et al.*, 1992). The importance of measuring the static permittivity of liquid lies in the fact that it provides valuable information about the ordering of the molecular interaction in a binary mixture. A great interest has been evidenced in the study of dielectric relaxation behavior in amide systems with a view to understanding the role of hydrogen bonding and NH_2 group in the system. The amides are an interesting class of liquids. Alcohols are versatile organic liquids used in chemical industries as solvents for oils, resins, and antifreeze for explosive. Amides are the simplest molecules containing a peptide linkage and a study of their hydrogen bonding ability yields insight into the nature of protein structure (Jeffrey *et al.*, 1991). The dielectric relaxation study of solute-solvent mixtures in the microwave frequency range gives information about the molecular polarization of the system. This is related to formation of multimers in dipoles and their rotations. The

earliest studies on the dielectric relaxation processes of mono alcohols (Jeffrey *et al.*, 1991, Dannhauser *et al.*, 1964, Grag *et al.*, 1965) have established that the magnitude of the primary dispersion is much greater than that of higher dispersion and has linear relaxation time which is attributed to the linear bond chain multimers (Dannhauser *et al.*, 1968).

A great variation in liquid state properties and dielectric relaxation is found among substituted amides. Complex permittivity spectra of a binary pyridine–amide mixture were reported by (Mehrotra and coworkers Ahire *et al.*, 1998). Thenappan and Sankar studied hydrogen-bonded complexes of alcohol with N, N-dimethylformamide (Thenappan *et al.*, 2006). The dielectric relaxation parameters for the mixtures of dimethylacetamide–2-ethoxy ethanol and dimethyl formamide–2-ethoxy ethanol at 298 K are reported by (Chaudhari *et al.*, 2001). These works provide information regarding solute–solvent interaction in liquids. The dielectric behavior of all these binary mixtures is found to agree well with the modified Bruggeman equation. In this work, we have reported the dielectric study on the mixtures of Formamide, N-methylformamide and N, N imethylformamide with 2-methoxyethanol (2-ME) and 2-butoxyethanol (2-BE). The dielectric parameters, viz. static dielectric constant and relaxation time have been

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determined. The static dielectric constant and relaxation time are also used to obtain the excess dielectric parameters, which give information related to the interaction between unlike molecules. The Kirkwood correlation factor for the binary mixtures has also been determined. 2-methoxyethanol and 2-butoxyethanol is an organic compound that are used mainly as solvents. 2-methoxyethanol is used as a solvent for many different purposes such as varnishes, dyes, and resins. It is also used as an additive in airplane deicing solutions. The main use of 2-butoxyethanol is as a solvent in paints and surface coatings, followed by cleaning products and inks. Alcohols have an O-H functional group.

EXPERIMENTAL

AR grade chemicals such as Formamide, N-methylformamide and N, N-dimethylformamide, 2-methoxyethanol (2-ME) and 2-butoxyethanol (2-BE) were obtained commercially and used without further purification. The solutions were prepared by mixing of amides with alcohols by volume percentage. The solutions were prepared at different volume percentages of Formamide, N-methylformamide and N, N-dimethylformamide in alcohols from 0% to 100% in step of 25%, at 25°C. The dielectric spectra were obtained by the Time Domain Reflectometry (TDR) technique (Madhurima *et al.*, Chaudhari *et al.*, 2004). The Tektronix model no. DSA 8200 Digital Serial Analyzer sampling main frame along with the sampling module 80E08 has been used for the Time Domain Reflectometer (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 50Ω. Sampling oscilloscope monitors 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 digitized in 2000 points. The Fourier transformation of the pulses and data analysis were done earlier to determine complex permittivity spectra $\epsilon^*(\omega)$ using nonlinear least square fit method (Bevington *et al.*, 1969). The temperature of the sample was controlled with an accuracy of ±1°C. The processing of data was carried out to yield complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range of 10 MHz– 30 GHz. The complex permittivity spectra $\epsilon^*(\omega)$ were obtained from reflection coefficient spectra by applying a bilinear calibration method (Cole *et al.*, 1989). The static dielectric constant, static dielectric constant at optical frequency, and relaxation time were obtained by using the non-linear least-square fit method (Bevington *et al.*, 1969). The general form of the relaxation model is given by Havriliak–Negami equation (Havriliak *et al.*, 1966)

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{[1 + (j\omega\tau)^{1-\alpha}]^\beta} \dots\dots\dots (1)$$

where $\epsilon^*(\omega)$ is the complex reflection coefficient, ϵ_0 is the static dielectric constant, ϵ_∞ is the static dielectric constant at optical frequency, τ is the relaxation time, α and β are empirical parameters for the distribution of relaxation times with values between 0 and 1. The Havriliak - Negami

equation includes three relaxation modes as limiting forms. The Debye mode ($\alpha = 0$ and $\beta = 1$) implies a single relaxation time while Cole–Cole ($\alpha = 1$ and $\beta = 1$) and Cole Davidson ($\alpha = 0$ and $\beta = 1$) both suggest a distribution of relaxation times. The relaxation behavior of Amides with alcohols such as 2-ME and 2-BE system agrees with Debye model. Therefore the experimental values of $\epsilon^*(\omega)$ were fitted with the Debye model.

RESULT AND DISCUSSION

The static dielectric constant (ϵ_0), bruggeman factor (f_B), effective Kirkwood correlation factor (g^{eff}), corrective Kirkwood correlation factor (g_f), relaxation time (τ), excess static dielectric constant (ϵ^E) and free energy activation relaxation time (ΔF_τ) for a mixture of amides Formamide (FA), N-methylformamide (NMF) and N,N-dimethylformamide (DMF) with alcohols such as 2-methoxyethanol (2-ME) and 2-butoxyethanol (2-BE) are listed in Table 1, 2, 4 & 5. The volume fraction of amides increases static dielectric constant (ϵ_0) increases for 2-ME and 2-BE systems, in the case indicates that the parallel orientation of dipoles takes place. The modified Bruggeman equation (Bruggeman *et al.*, 1935) is another parameter, which may be used as an indicate for solute-solvent interaction. The Bruggeman factor f_B is given by,

$$f_B = \left(\frac{(\epsilon_{0m} - \epsilon_{02})}{(\epsilon_{01} - \epsilon_{02})} \right) \left(\frac{\epsilon_{01}}{\epsilon_{0m}} \right)^{1/3} = (1 - \phi_2) \dots\dots\dots (2)$$

According to equation (2), a non linear relationship is expected between (f_B) and Vol. fraction of amides. The estimated values of (f_B) are shown in fig (1.a) and fig (1.b). This shows the non linear relation between (f_B) and Vol. fraction of amides. It can be seen from these figures that f_B is not a linear function of volume fraction of amides. The observed results indicate the existence of an intermolecular association between O-H group of alcohol and C=O group of amide. Similar interpretations are given by (Rana *et al.*, 2002) for aniline with alcohols. The Bruggeman factor (f_B) shows a negative deviation for all the amides with 2-ME and 2-BE systems, which indicate that the intermolecular interaction is taking place in the mixture. The maximum deviation from the linearity is observed for NMF and minimum deviation is occurred for DMF. It shows that NMF has more interaction than other amides in both the systems.

The structural information about the liquids from the dielectric relaxation parameter may be obtained using the Kirkwood correlation parameter ‘g’ (Frohlich *et al.*, 1949). This parameter is useful for obtaining information regarding orientation of electric dipoles in polar liquids.

Table 1 Variation of ϵ_0 , f_B , g^{eff} and g_f values with volume fraction of amides in 2-ME

Φ_2	ϵ_0	f_B	g^{eff}	g_f
Formamide+2-methoxyethanol				
0	17.81	1	1.27	1
0.25	42.08	0.55	1.33	1.26
0.50	66.24	0.30	1.21	1.23
0.75	88.12	0.14	1.05	1.10
1.00	110.57	0	0.92	1
N-methylformamide+2-methoxyethanol				
0	17.81	1	1.27	1
0.25	59.65	0.49	2.61	1.13
0.50	101.89	0.27	3.06	1.11
0.75	141.75	0.12	3.16	1.05
1.00	182.41	0	3.17	1
N,N-dimethylformamide+2-methoxyethanol				
0	17.81	1	1.27	1
0.25	24.11	0.61	1.28	1.04
0.50	29.90	0.33	1.27	1.06
0.75	33.86	0.15	1.21	1.02
1	37.72	0	1.17	1

Table 2 Variation of τ , ϵ^E , $(1/\tau)^E$ and ΔF_τ values with volume fraction of amides in 2-ME

Φ_2	τ (ps)	ϵ^E	$(1/\tau)^E$ ps ⁻¹	ΔF_τ (kJ/mol)
Formamide+2-methoxyethanol				
0	29.99	0	0	13.05
0.25	32.45	1.08	-0.0011	13.25
0.50	34.18	2.05	-0.0013	13.38
0.75	35.02	0.74	-0.0006	13.44
1	36.06	0	0	13.51
N-methylformamide+2-methoxyethanol				
0	29.99	0	0	13.05
0.25	45.00	0.69	-0.0049	14.06
0.50	76.32	1.78	-0.0078	15.38
0.75	80.02	0.49	-0.0022	15.50
1.00	118.49	0	0.0000	16.48
N,N-dimethylformamide+2-methoxyethanol				
0	29.99	0	0	13.05
0.25	21.54	1.38	-0.0029	12.23
0.50	20.00	2.21	-0.0154	12.04
0.75	12.45	1.17	-0.0012	10.86
1	10.23	0	0	10.37

The 'g' for the pure liquid may be obtained from the expression

$$\frac{4\pi N_A \mu^2 \rho}{9kTM} g = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \dots\dots\dots (3)$$

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_A is Avogadro's number. Modified forms of this equation have been used to study the orientation of electric dipoles in binary mixture of amides with 2-ME and 2-BE. Equation (3) is modified by assuming that for the mixture, g^{eff} has become effective Kirkwood correlation factor in the mixture. The Kirkwood equation for the mixture may be expressed as (Pawar *et al.*, 2005).

$$\frac{4\pi N_A}{9kT} \left(\frac{\mu_1^2 \rho_1}{M_1} \phi_1 + \frac{\mu_2^2 \rho_2}{M_2} \phi_2 \right) g^{eff} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})^2 \epsilon_{0m} + \epsilon_{\infty m}}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \dots\dots\dots (4)$$

where g^{eff} is the effective Kirkwood correlation factor for a binary mixture, with ϕ_1 and ϕ_2 as volume fractions of liquids 1 and 2 respectively.

Table 3 Variation of thermodynamic parameters (ΔF_{0r}^E , ΔF_{rr}^E , ΔF_{12}^E and ΔF^E) values with volume fraction of amides in 2-ME

Φ_2	ΔF_{0r}^E (J/mol)	ΔF_{rr}^E (J/mol)	ΔF_{12}^E (J/mol)	ΔF^E (J/mol)
Formamide+2-methoxyethanol				
0	0	0	0	0
0.25	-141.72	-83.95	32.76	-192.92
0.50	58.33	-58.26	-22.68	-22.62
0.75	139.95	-25.34	-8.08	106.52
1	0	0	0	0
N-methylformamide+2-methoxyethanol				
0	0	0	0	0
0.25	-279.95	13.88	-139.23	-405.30
0.50	-98.08	114.87	-480.05	-463.26
0.75	15.41	120.78	-453.83	-317.63
1	0	0	0	0
N,N-dimethylformamide+2-methoxyethanol				
0	0	0	0	0
0.25	-84.18	-26.78	-0.83	-111.79
0.50	-18.00	-11.33	-26.58	-55.93
0.75	38.44	4.44	-22.83	20.05
1	0	0	0	0

The effective Kirkwood correlation factor (g^{eff}) calculated using equation (4) is given in table (1) and table (4) shown in fig (2.a) and fig (2.b). The (g^{eff}) value are approximately equational to one for Formamide with 2-ME and 2-BE and DMF with 2-ME and 2-BE whereas g^{eff} is upto 3 for NMF with 2-ME and 2-BE it shows a parallel alignment of dipoles are takes place except Formamide with 2-ME and 2-BE. The Kirkwood correlation factor g_f (Frohlich *et al.*, 1949) is also parameter for getting information regarding the orientation of electric dipoles in polar liquids. The g_f for pure liquid may be obtained by the expression,

$$\frac{4\pi N_A}{9kT} \left(\frac{\mu_1^2 \rho_1}{M_1} \phi_1 + \frac{\mu_2^2 \rho_2}{M_2} \phi_2 \right) g_f = \frac{(\epsilon_{0m} - \epsilon_{\infty m})^2 \epsilon_{0m} + \epsilon_{\infty m}}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \dots\dots\dots (5)$$

Where μ dipole moment is in gas phase, ρ is density at temperature T, M is molecular weight, K is Boltzmann constant, and N_A is Avogadro's number. The corrective Kirkwood correlation factor (g_f) calculated by using equation (5) at 25°C. The (g_f) values will remain close to unity if there is no interaction between amides with alcohols. The deviation from unity will indicate the interaction between amides with alcohols. The relaxation time values get increases as the concentration of amide increases in the case of FA+2-ME, NMF+2-ME and NMF+2-BE. The reverse is the case in other systems like DMF+2-ME, FA+2-BE and DMF+2-BE. The alcohols with NMF have higher τ values than the DMF. This may be due to the variation of inductive effect in secondary and tertiary amides (Kalaivani *et al.*, 2005). It is useful to compute the excess parameters related to (ϵ^E) and $(1/\tau)^E$, which provide information about the formation of multimers in the mixture. The excess permittivity is defined as (Kumbharkhane *et al.*, 1993).

$$\epsilon^E = (\epsilon_0 - \epsilon_\infty)_m - \{(\epsilon_0 - \epsilon_\infty)_1 X_1 + (\epsilon_0 - \epsilon_\infty)_2 X_2\} \dots\dots\dots (6)$$

Table 4 Variation of ϵ_0 , f_B , g^{eff} and g_f values with volume fraction of amides in 2-BE

Φ_2	ϵ_0	f_B	g^{eff}	g_f
Formamide+2-butoxyethanol				
0	9.99	1	1.92	1
0.25	33.01	0.51	1.55	1.35
0.50	55.25	0.31	1.23	1.21
0.75	82.35	0.13	1.06	1.11
1	110.57	0	0.92	1
N-methylformamide+2-butoxyethanol				
0	9.99	1	1.92	1
0.25	51.95	0.43	3.34	1.46
0.50	92.35	0.24	3.04	1.28
0.75	138.45	0.10	2.77	1.15
1	182.31	0	2.43	1
N,N-dimethylformamide+2-butoxyethanol				
0	9.99	1	1.92	1
0.25	15.81	0.67	1.63	1.16
0.50	20.57	0.48	1.35	1.06
0.75	30.12	0.18	1.34	1.11
1	37.72	0	1.17	1

Table 5 Variation of τ , ϵ^E , $(1/\tau)^E$ and ΔF_τ values with volume fraction of amides in 2-BE

Φ_2	τ (ps)	ϵ^E	$(1/\tau)^E$ ps ⁻¹	ΔF_τ (kJ/mol)
Formamide+2-butoxyethanol				
0	47.86	0	0	14.22
0.25	44.91	-2.12	-0.0003	14.06
0.50	45.00	-5.03	-0.0021	14.06
0.75	39.01	-3.07	-0.0004	13.71
1	36.06	0	0	13.51
N-methylformamide+2-butoxyethanol				
0	47.86	0	0	14.22
0.25	65.61	-1.12	-0.0025	15.00
0.50	92.00	-3.80	-0.0038	15.85
0.75	101.11	-0.78	-0.0016	16.08
1	118.86	0	0	16.49
N,N-dimethylformamide+2-butoxyethanol				
0	47.86	0	0	14.22
0.25	36.00	-0.00	-0.0100	13.51
0.50	25.00	-1.99	-0.0166	12.60
0.75	15.53	0.18	-0.0124	11.41
1	10.23	0	0	10.37

where X_1 and X_2 volume fraction and suffices m, 1, 2 represents mixture, liquid 1 (2-ME) & (2-BE) and liquid 2 (FA, NMF and DMF) respectively. The excess static dielectric constant may provide qualitative information about multimers formation in the mixture as follows:

1. $\epsilon^E = 0$ indicates that there is no interaction between the components in the mixture.
2. $\epsilon^E < 0$ reveals that components in the mixture may form closed multimers leading to the less effective dipoles due to the interaction between the components in such a way that the effective dipole moment gets reduced.
3. $\epsilon^E > 0$ denotes that components in the mixture interact in such a way that the effective dipole moment is increased. There is a probability for the formation of linear multimers.

In an ideal mixture of polar liquids if the molecules are interacting, a non linear variation in dielectric constant and relaxation time occurs.

Table 6 Variation of thermodynamic parameters (ΔF_{0r}^E , ΔF_{rr}^E , ΔF_{12}^E and ΔF^E) values with volume fraction of amides in 2-BE

Φ_2	ΔF_{0r}^E (J/mol)	ΔF_{rr}^E (J/mol)	ΔF_{12}^E (J/mol)	ΔF^E (J/mol)
Formamide+2-butoxyethanol				
0	0	0	0	0
0.25	-23.30	-202.36	99.83	-125.83
0.50	206.28	-123.28	-4.03	78.96
0.75	215.13	-45.30	-7.28	162.54
1	0	0	0	0
N-methylformamide+2-butoxyethanol				
0	0	0	0	0
0.25	-161.79	-111.96	-47.42	-321.17
0.50	1.95	62.10	-305.26	-241.20
0.75	57.25	97.55	-269.45	-114.64
1	0	0	0	0
N,N-dimethylformamide+2-butoxyethanol				
0	0	0	0	0
0.25	5.47	-55.94	36.18	-14.28
0.50	162.08	1.61	-3.89	159.80
0.75	127.63	15.63	-21.59	121.67
1	0	0	0	0

This confirms that the intermolecular association is taking place in the system. The excess property related to static dielectric constant and relaxation time provides significant information regarding interaction between the polar – polar liquid mixtures. In the case of amides with 2-ME systems, positive value of excess static dielectric constant (ϵ^E) is obtained. The positive values of excess static dielectric constant (ϵ^E) indicates that molecules of the mixtures may form monomers or dimmers structures in such a way that the number of effective dipoles increases. The negative values of excess static dielectric constant are obtained for all the selected amides with 2-BE systems. The negative value of (ϵ^E) indicates that molecules of the mixtures may form multimer structures via hydrogen bonding in such a way that the effective dipoles get reduced (Chaudhari *et al.*, 2001, Parthipan *et al.*, 2007). The excess dielectric constant (ϵ^E) of mixtures was calculated using equation (6) and its variation with mole fraction of amides in 2-ME & 2-BE at 25°C shown in fig (3.a) and fig (3.b). The excess inverse relaxation time is defined as

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left\{ \left(\frac{1}{\tau}\right)_1 X_1 + \left(\frac{1}{\tau}\right)_2 X_2 \right\} \dots \dots \dots (7)$$

where $(1/\tau)^E$ is excess inverse relaxation time which represents the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening which is inverse of the relaxation time in the resonant spectroscopy (Mehrotra *et al.*, 1977). The information regarding the dynamic of liquids 1 and 2 interaction from this excess property is as follows:

- (i) $(1/\tau)^E = 0$: there is no change in the dynamics of liquids 1 and 2 interaction.
- (ii) $(1/\tau)^E < 0$: the liquids 1 and 2 interaction produces a field such that the effective dipoles rotate slowly.

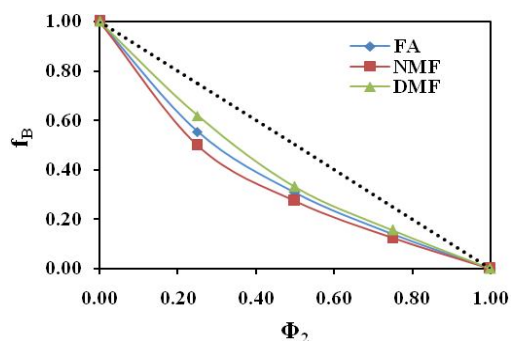


Fig.1 (a) Plot of Bruggemann factor Vs volume fraction of amides in 2-ME

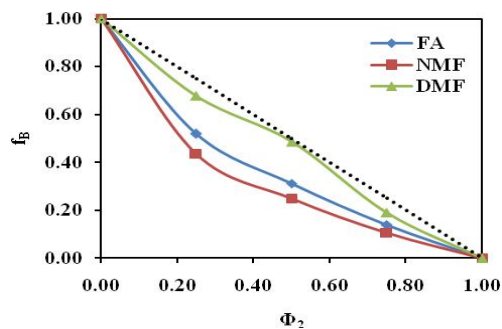


Fig.1 (b) Plot of Bruggemann factor Vs volume fraction of amides in 2-BE

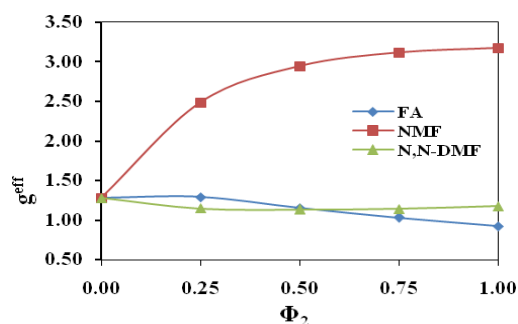


Fig.2 (a) Plot of effective Kirkwood factor Vs volume fraction of amides in 2-ME

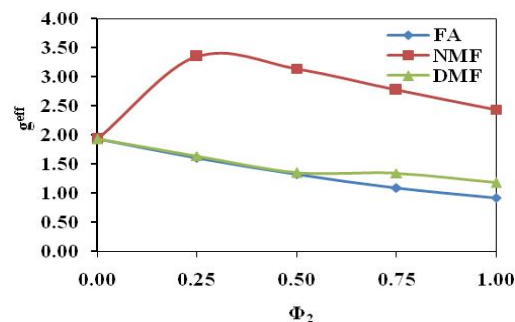


Fig.2 (b) Plot of effective Kirkwood factor Vs volume fraction of amides in 2-BE

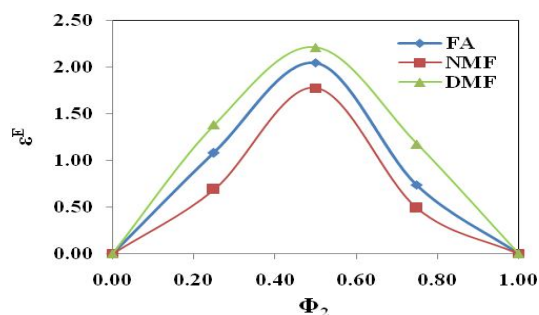


Fig.3 (a) Plot of excess permittivity Vs volume fraction of amides in 2-ME

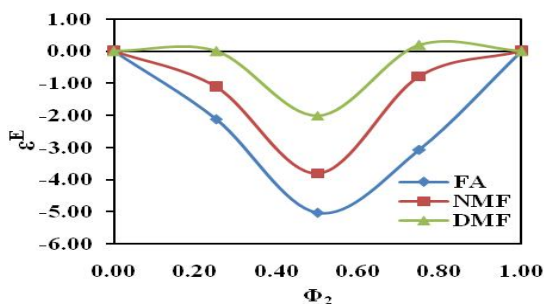


Fig.3 (b) Plot of excess permittivity Vs volume fraction of amides in 2-BE

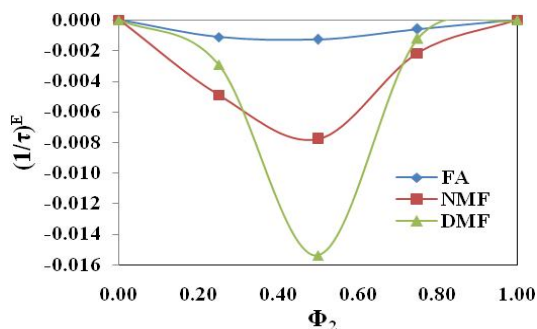


Fig.4 (a) Plot of excess inverse relaxation time Vs volume fraction of amides in 2-ME

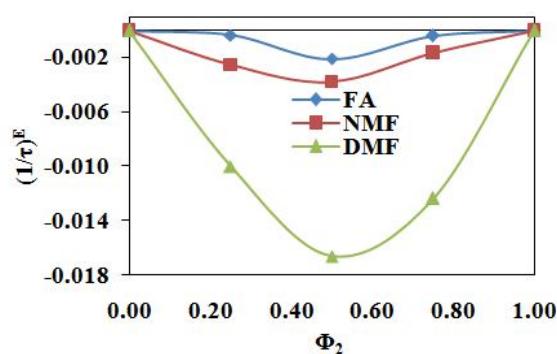


Fig.4 (b) Plot of excess inverse relaxation time Vs volume fraction of amides in 2-BE

- (iii) $(1/\tau)^E > 0$: the liquids 1 and 2 interaction produces a field such that the effective dipoles rotate fastly (i.e.) the field will cooperate in the rotation of dipoles.

The variation of $(1/\tau)^E$ with volume fraction of amides calculated using equation (7) at 25°C as shown in fig (4.a) and fig (4.b). As seen from the plots, $(1/\tau)^E$ is negative for volume fraction of amides with 2-ME and 2-BE. This indicates that the addition of amides with 2-ME and 2-BE has created a hindering field such that the effective dipole rotates slowly. The excess inverse relaxation time values are negative for all the amides at 25°C. The negative value of excess inverse relaxation time indicates slower rotation of the dipoles of the system. The free energy of activation for relaxation time (ΔF_r) is greater at initial concentration of amides in DMF+2-ME, FA+2-BE and DMF+2-BE systems. The free energy of activation for relaxation time (ΔF_r) is greater at final concentration of amides is FA+2-ME, NMF+2-ME and NMF+2-BE systems. The activation for relaxation time (ΔF_r) is greater for NMF with 2-ME and 2-BE where compared with other two amides systems. The excess Helmholtz free energy (ΔF^E) is a good parameter to evaluate the interaction between the components in the mixture through breaking mechanism of hydrogen bond and is expressed (Gupta *et al.*, 2005) as,

$$(\Delta F^E) = (\Delta F_{0r}^E) + (\Delta F_{rr}^E) + (\Delta F_{12}^E) \dots \dots \dots (8)$$

where (ΔF_{0r}^E) represents the excess dipolar energy due to long range electrostatic interaction. (ΔF_{rr}^E) represents the excess dipolar energy due to short range interaction between identical molecules and (ΔF_{12}^E) represents the excess free energy due to short range interaction between dissimilar molecules. The above terms are given in detail in equation (8):

$$\Delta F^E = - \left[\frac{N_A}{2} \right] \left\{ \left[\sum_{r=1,2} X_r^2 \mu_r^2 (R_{fr}^0 - R_{fr}^E) \right] + \left[\sum_{r=1,2} X_r^2 \mu_r^2 (g_{rr}-1) (R_{fr}^0 - R_{fr}^E) \right] \right\} \dots \dots \dots (9)$$

$$R_{fr}^0 = \left(\frac{8\pi N_A}{9V_r} \right) \frac{(\epsilon_r - 1)(\epsilon_{\infty r} + 2)}{(2\epsilon_r + \epsilon_{\infty r})}$$

$$R_{fr}^E = \left(\frac{8\pi N_A}{9V_r} \right) \frac{(\epsilon_m - 1)(\epsilon_{\infty r} + 2)}{(2\epsilon_m + \epsilon_{\infty r})}$$

$g_{12} = g_{21}$ and V_r is the molar volume of the components. ϵ_r and $\epsilon_{\infty r}$ are the static dielectric constant and static dielectric constant at optical frequencies, of the pure liquids, respectively.

The long range and short range interaction between dipoles can be studied from the thermodynamic parameter, excess Helmholtz free energy (ΔF^E). The different components of (ΔF^E) such as (ΔF_{0r}^E) , (ΔF_{rr}^E) and (ΔF_{12}^E) are given in Table 3 and Table 6. The values of (ΔF_{0r}^E) represent the long range interaction between the dipoles in the mixture. The values of (ΔF_{0r}^E) are positive at higher concentrations and negative at lower

concentrations of amides with 2-ME and 2-BE systems except DMK+2-BE. This shows that the strength of dipole-dipole interaction depends on the concentration and temperature of the mixture. This may be due to the interaction of the compounds in the mixture which produces structural changes. The values are all the concentration positive values of DMF+2-BE system. This shows the existence of dipole-dipole interaction between DMF molecules. The second term (ΔF_{rr}^E) gives the excess free energy due to short range interaction between the like molecules. As the concentration of amide increases (ΔF_{rr}^E) values are negative for FA+2-ME and FA+2-BE systems. It indicates the non specific interaction for the systems. The (ΔF_{rr}^E) values of NMF+2-ME system all the concentrations are positive it indicating that the strong short range interaction through H-bonding except FA, DMF with 2-ME and 2-BE systems. The magnitude of (ΔF_{12}^E) gives information on the strength of interactions between unlike molecules. Finally the high negative values of (ΔF^E) were observed for the NMF+2-ME and NMF+2-BE systems, which indicate the formation of α -clusters with parallel alignment of dipoles. In FA+2-ME, DMF+2-ME, FA+2-BE and DMF+ 2-BE systems there is both negative and positive values of (ΔF^E) . It indicates that the formation of α -clusters to β -clusters with parallel and anti-parallel alignment of dipoles takes place (Parthipan *et al.*, 2008)

CONCLUSION

The dielectric complex permittivity of amides with 2-ME and 2-BE systems have been studied using Time Domain Reflectometry technique in the frequency range of 10 MHz to 30 GHz. The Bruggeman factor (f_b) shows a negative deviation for all the amides with 2-ME and with 2-BE which indicates that the intermolecular interaction is taking place in the mixture. The maximum deviation from the linearity is observed for NMF and minimum deviation is occurred for DMF. It shows that the NMF has more interaction than other amide systems. The molecular interaction are confirmed by the excess static dielectric constant (ϵ^E), excess inverse relaxation time $(1/\tau)^E$ and excess dipolar free energy.

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