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TIME DOMAIN REFLECTOMETRY RESPONSE OF MONOHYDROXY ALCOHOL (ETHANOL) WITH POLAR LIQUIDS (DIMETHYL ACETAMIDE) AT HIGH FREQUENCY

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ABSTRACT

Dielectric Behavior of NN-Di-methyl Acetamide [C_4H_9NO] – Ethanol [C_2H_5OH] binary mixture at different temperatures 288,298,308 and 318 K have been determined over frequency range of 10 MHz to 20 GHz. Using the Time Domain Reflectometry Technique in reflection mode for 11 different concentrations of given binary system has been used to measure reflection coefficient. Further Fourier transform and least square fit method have been used to obtain dielectric parameters such as dielectric constant (ε_0) and relaxation time (τ). The dielectric constant decreased with an increase in temperature where as it increased with increase concentration of DMA in Ethanol. Relaxation time decreased with an increase in temperature and increases with the concentration of DMA in Ethanol. By using dielectric parameters excess permittivity (ε^E) and excess relaxation time $(1/\tau)^E$ are determined. (ε^E) has negative values for all concentrations and temperature indicates that total effective dipoles are decreases in the mixture. Excess inverse relaxation time $(1/\tau)^E$ has positive values for all concentrations and temperature indicates that formation of cooperative field which rotate dipole faster. Kirkwood factor (g^{eff}) g_f, and B_j coefficient gives systematic behavior of solute solvent for different concentrations and temperature at high frequency. Thermodynamic parameters enthalpy of activation (ΔH) and entropy of activation (ΔS) gives mixed nature.

KEYWORDS: Time domain reflectometry, Dielectric parameters, Excess parameters, Kirkwood correlation Factor and Bruggeman factor.

INTRODUCTION

a) Permittivity and Relaxation time

The frequency dependent complex permittivity ε*= ε'-j ε" data was obtained by using calibration process, by using dielectric parameters of raw data.[4] The static dielectric constant (ε_s) and relaxation time (τ) for the mixture obtained by fitting experimental data with the Debye equation[11] at four different temperatures have been given in "table(1)" and are shown in "figs (1&2)" respectively.[1,11]

Table 1: Temperature dependent dielectric parameters for binary mixture of Ethanol + NN Dimethyl acetamide.

Conc of DMA	ε				τ			
	288	**298**	**308**	**318**	**288**	**298**	**308**	**318**
0	26.5	24.52	23.66	20.64	146.2	126.3	115.1	105.2
0.0652	25.9	24.8	24.02	23.12	110.4	91.39	76.63	65.24
0.1356	26.68	25.88	25.23	24.35	86.03	73.32	60.12	53.24
0.2119	28.01	27.14	26.58	25.66	70	60.69	49.48	43.8
0.2949	29.41	28.64	27.89	27.11	58.65	49.86	42.17	37.28
0.3856	30.8	30.01	29.12	28.22	49.58	42.63	36.45	32.78
0.4849	32.58	31.89	31.02	30.01	42.24	37.12	31.82	28.17
0.5942	34.23	33.89	32.85	31.85	37.12	33.09	28.24	25.01
0.7151	36.51	35.89	34.88	33.65	33.28	30.17	25.2	22.45
0.8496	38.89	38.01	36.89	35.77	30.4	27.78	23.4	21.14
1	42.6	41.11	39.67	38.24	25.67	23.67	21.67	19.39

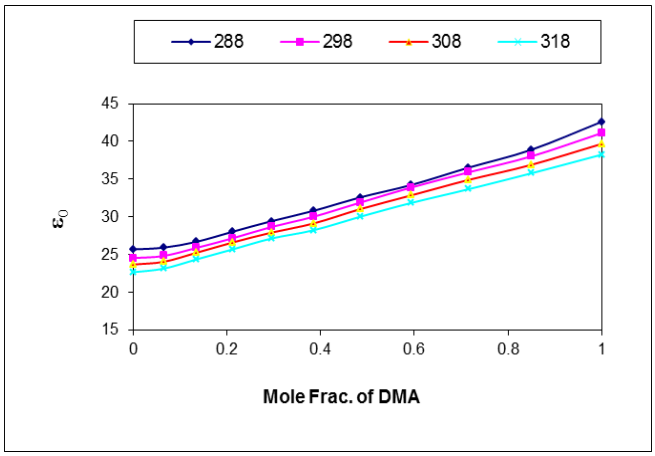


Figure 1: Variation of static dielectric constant (ε_0) as a function of mole fraction of NN Dimethyl acetamide at temperatures 288, 298, 308 and 318K.

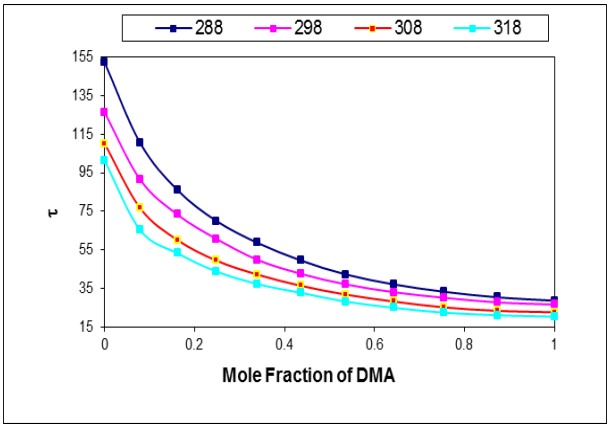


Figure 2: Variation of relaxation time (τ) as a function of mole fraction of NN Dimethyl Acetamide at temperatures 288, 298, 308 and 318K

b) Excess Permittivity and Excess inverse relaxation time

The excess permittivity is defined as

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

Where X is the weight fraction and suffices M, A, B represent mixture, liquid A and liquid B respectively the excess permittivity provides qualitative information about structure formation in the mixture as follows[2,3,5&8]

$\varepsilon^E = 0$ indicates the solute and solvent do not interact at all

$\varepsilon^E < 0$ indicates the solute and solvent interact in such a way that the total effective dipoles are reduced. The solute and solvent may be form multimers leading to the less effective dipoles.

$\varepsilon^E > 0$ indicates the solute and solvent interact in such a way that the total effective dipole moment increases. There is a formation of monomers and dimmers.

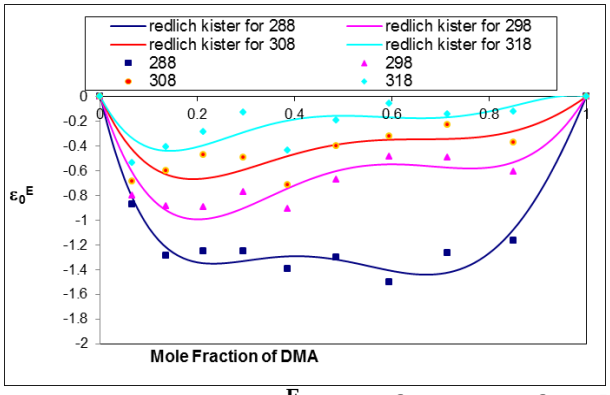


Fig. 3: Variation of excess permittivity (ε^E) as a function of mole fraction (x2) of NN DiMethyl Formamide at 288, 298, 308 and 318K.

"Fig. 3" shows the plot of excess permittivity against mole fraction of DMA for all four temperatures. In the present study excess permittivity values are found to be negative for all temperatures and concentrations, which indicates that the total effective dipoles are decreases in the mixture. This is due to antiparallel or opposite alignment of the dipoles of the two interacting solvent molecules. The curves are more deviated from zero at equal concentration region indicates strong intermolecular interaction in this region.

The excess inverse relaxation time is defined as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A X_A + (1/\tau)_B X_B]$$

Where $(1/\tau)^E$ is the excess inverse relaxation time, which represent the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening (which is the inverse of relaxation time) from resonant spectroscopy.[5,9&10]

The information regarding the dynamics of solute solvent interaction gives from this excess property is as follows:

1) $(1/\tau)^E = 0$ there is no change in the dynamics of solute solvent interaction
2) $(1/\tau)^E < 0$ the solute solvent interaction produces a field such that the effective dipoles rotate slowly.
3) $(1/\tau)^E > 0$ the solute solvent interaction produces a field such that the effective dipoles rotate faster i.e. the field facilitates rotation of dipoles.

The variation of $(1/\tau)^E$ with mole fraction of NMA at 15, 25, 35 and 45^0c and at 11 different concentrations as shown in following fig.

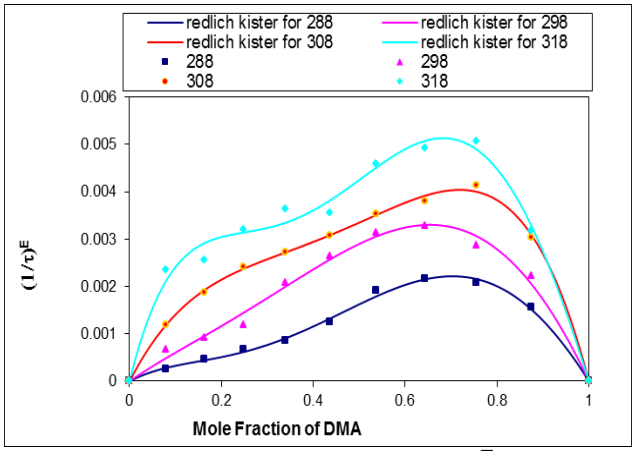


Fig. 4: Variation of excess inverse relaxation time $(1/\tau)^E$, as a function of mole fraction (x2) of NN Dimethyl Acetamide at 288, 298, 308 and 318K.

From "fig.(4)" it seen that, for all temperatures excess inverse relaxation values are positive and have maximum values at 70% region of DMA, it indicates the formation of spherical structure which rotates dipoles faster, under the influence of an external varying field dipole align themselves in the direction of field i.e. Parallel alignment of dipole occurred and the dipoles are rotate such that the effective field facilitate total dipoles due to which it rotates faster.

The variation of Excess permittivity (ε^E) "fig.(3)" and Excess inverse relaxation time $(1/\tau)^E$ "fig.(4)" with change in mole fraction of DMA at different temperatures is shown in "fig.(3)" and "fig (4)". The experimental values of both the excess parameters were fitted to the Redlich - Kister equation to obtain B_j coefficients at different temperatures. Using these B_j values excess parameters at various concentrations were calculated and used to draw the smooth curves. The estimated values of B_j are given in "table(2)".[5&6]

Table 2: The estimated values of Bj coefficients in Redlich-Kister equation for ethanol - NN Di Methyl Acetamide mixture at different temperatures.

Parameter	B_j coefficient	Temperature			
		288 K	298 K	308 K	318 K
$(\varepsilon_s)^E$	B_0	-5.3129	-2.3549	-1.5215	-0.6212
	B_1	-1.4461	1.7219	1.1364	-0.0076
	B_2	-7.8841	-7.06	-4.3213	-2.8442
	B_3	5.0896	1.2838	1.8857	4.1686
$(1/\tau)^E$	B_0	0.0065	0.0116	0.0134	0.017
	B_1	0.0093	0.0093	0.0086	0.0142
	B_2	0.0038	0.0021	0.0146	0.0181
	B_3	-0.0042	-0.0024	0.0004	-0.0187

c) The kirkwood correlation factor

The values of g^{eff} are given in "table (3)" and gf shown in "fig.(4)".

The variation in g_f with change in volume fraction of NN Di methyl acetamide are given in "table (4)" and shown in "fig.(5)". The amount of solute-solvent interaction can be accessed using these parameters.[5&6]

Table no. 3: Kirkwood correlation factor g^{eff} values for ETH+DMA.

Vol. frac. of DMA	288	298	308	318
0	1.00	0.95	0.92	0.88
0.1	0.95	0.91	0.88	0.84
0.2	0.92	0.89	0.87	0.84
0.3	0.92	0.89	0.87	0.84

0.4	0.91	0.89	0.87	0.84
0.5	0.91	0.89	0.86	0.83
0.6	0.92	0.90	0.87	0.84
0.7	0.92	0.91	0.88	0.85
0.8	0.94	0.92	0.89	0.86
0.9	0.95	0.93	0.90	0.87
1	1.00	0.96	0.93	0.89

Table no. 4: Kirkwood correlation factor gf values for ETH+DMA.

Vol. frac. of DMA MF	288	298	308	318
0	1	1	1	1
0.1	0.95	0.95	0.95	0.96
0.2	0.92	0.94	0.95	0.95
0.3	0.92	0.93	0.94	0.95
0.4	0.91	0.93	0.94	0.95
0.5	0.91	0.92	0.93	0.94
0.6	0.92	0.93	0.94	0.95
0.7	0.92	0.94	0.95	0.96
0.8	0.94	0.95	0.96	0.96
0.9	0.95	0.97	0.97	0.98
1	1	1	1	1

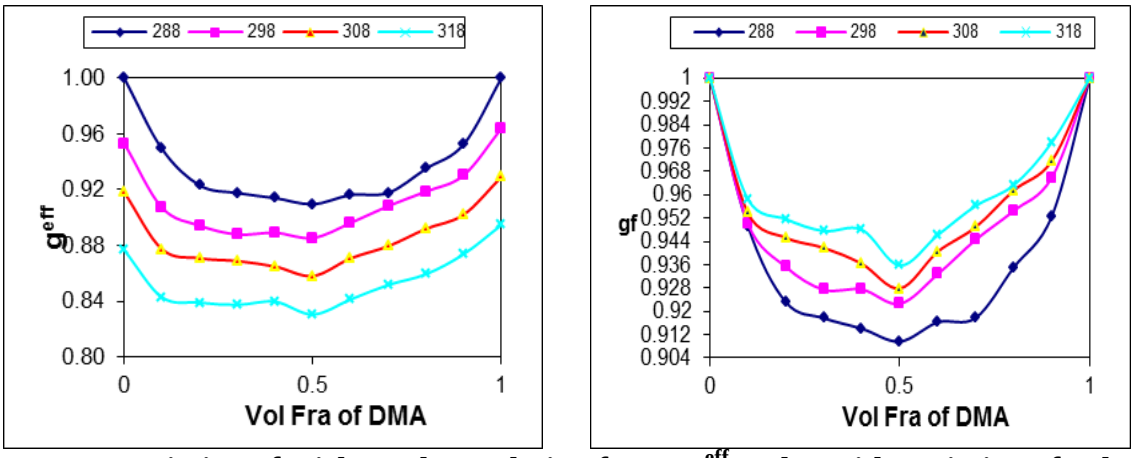


Fig. no. 5: Variation of Kirkwood correlation factor g^{eff} and g_f with variation of volume fraction of DMA at various temperatures.

d) Thermodynamic parameters

The values of molar enthalpy of activation (ΔH) and molar entropy of activation (ΔS) at different concentrations determined using Eyring rate equation[13] are listed in "table (5)". The variation of molar enthalpy of activation and molar entropy of activation with increase in volume fraction of DMA in the mixture are shown in "fig.(6)". The Arrhenius plot for ETH+DMA system is shown in "fig.(7)"[5&12]

Table no. 5: The activation enthalpy (ΔH) entropy (ΔS) of ETH+DMA binary mixture for various concentrations.

Vol Fr. DMA	Enthalpy	Entropy
0	7886.54	-29.12
0.1	10850.6	-16.32
0.2	9969.58	-17.33
0.3	9752.48	-16.41
0.4	9123.79	-17.05
0.5	8145.23	-19.04
0.6	7909.25	-18.6
0.7	7702.33	-18.28
0.8	7832.5	-16.97
0.9	7077.65	-18.83
1	6484.45	-20.44

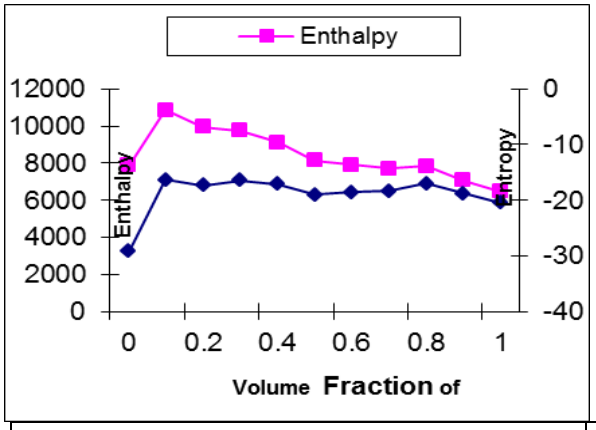
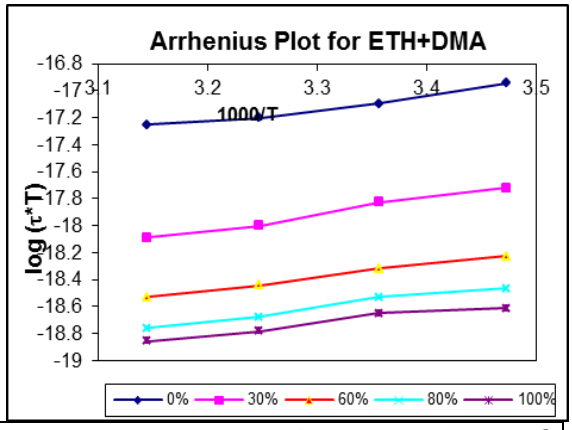


Figure 6: Enthalpy (ΔH) and Entropy (ΔS) of ETH+DMA Binary mixture



: Figure 7: Arrhenius plot of ETH+DMA Binary mixture

Arrhenius plot of ETH+DMA Binary mixture

The Arrhenius plot of log(1/t) vs (1000/T) are plotted in "fig.(7)" for various concentrations. The log(1/T) values increase with increase in concentration of DMA all plots having almost similar result (slope), which indicates that at all concentrations the activation energy remain almost same.

DISCUSSION

Static Permittivity and Relaxation time

From "fig.(1)" it can be seen that there is a linear relationship between the values of static dielectric constant (εs) and concentration of DMA in the mixture's static dielectric constant increases with increase in concentration of DMA. And from "fig.(2)" it can be seen that the relationship for the relaxation time is non-linear. This suggests strong intermolecular interaction due to exposed charge distribution in ETH and DMA molecules.

Excess parameters

From "fig.(3)" it can be seen that $(\varepsilon_s)^E$ is negative for all concentration of DMA in the mixture for all temperatures. This indicates that the molecules of mixture may form multimers structures in such a way that the effective dipoles get reduced. With increase in temperature the no. of dipoles get increases slowly.

The values of $(1/\tau)^E$ positive for all concentration and temperature this suggest that the molecular interaction produces a co-operative field and the effective dipoles have more freedom of rotation and total effective dipoles are rotate faster. from "fig.(4)" it can be seen that as temperature increases there is increase in cooperative field so curve is more positive.

Kirkwood correlation factor

The value of g^{eff} is 1 for ETH at 288 K which decreases to 0.88 at 318 K. The values confirm the formation of hydrogen bonding in pure ETH system. These values are near to unity or less than unity at all temperatures suggesting quite anti parallel orientation of electric dipoles. The corresponding values for DMA are 1.00 and 0.89 respectively indicating negligible or weak dipole-dipole interaction resulting formation of antiparallel dipoles in the pure system of DMA. From "table (4)" the value of gf is unity for an ideal mixture and deviation from unity may indicate interaction between two components of the mixture. The gf value less than one indicates that the dipoles of mixture will be oriented in such a way that the effective dipole will be less than the corresponding values of pure liquid. It is seen that there is very small deviation for all concentrations and temperature.

Thermodynamic parameters

From "table (5)" it is to be seen that molar enthalpy of activation (ΔH) having nonlinear nature on addition of DMA in ethanol first it increases and then decreases with increase in concentration of DMA in ETH it shows mixed nature. This means that the required energy for group dipole reorientation is more for 10% DMA and less with increase in volume fraction of DMA in the mixture. All negative value of molar entropy of activation (ΔS) with volume fraction of DMA indicates relatively high ordered arrangement of molecules in the activated state at equal concentration. Arrhenius plot for the system is shown in "fig.(7)". The Arrhenius plot is almost linear for this system. The linear nature of Arrhenius plot shows that equivalent incremental change in temperature causes equivalent changes in values of activation enthalpy (ΔH) in temperature range under consideration. The slope of Arrhenius

plot changes with concentration, which shows the change in activation energy of the system. The temperature dependence of relaxation time follows Arrhenius behavior.

CONCLUSION

Dielectric parameter(ε_0), Excess parameters $(1/\tau)^E$, $(\varepsilon)^E$, the Kirkwood correlation factor have been reported for ETH-DMA mixture for different concentrations and temperatures. These data provide information regarding solute solvent interaction in liquid. The investigated values of dielectric parameter show systematic change in dielectric values with increase in temperature and concentration. The negative excess dielectric parameter values indicate the slower rotation of effective dipoles of the system. The dielectric constant and relaxation time increases with increase in concentration of DMA whereas decrease with increase in temperature.

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