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DIELECTRIC RELAXATION STUDYOF BINARY MIXTURESOF DIMETHYL SULFOXIDEAND ETHANOL

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ABSTRACT : The dependence of dielectric relaxation on frequency, temperature, pressure and other external factors has been used to investigate the correlation between the morphology and electrical properties of macromolecules. Study of molecular interaction of Dimethyl Sulfoxide with Ethanol has been carried out at sampling frequency 12.4 GHz and at temperatures 15° C, 20° C, 25° C& 30° C. Time domain reflectometry (TDR) in reflection mode has been used as a technique. The static dielectric constant (ϵ_0), dielectric relaxation time (τ) and thermodynamic parameters of binary mixtures were obtained from complex reflection spectra.

KEYWORDS : Dimethyl Sulfoxide, Ethanol, Dielectric relaxation, Time domain reflectometry, Fourier transformation, Dielectric constant, Relaxation time.

I INTRODUCTION

Time domain reflectometry (TDR) is an effective approach to understand molecular interactions in liquid. It is very interesting to correlate dielectric parameters to molecular dynamics in aqueous solutions. Study of aqueous solutions to understand change in amount of hydrogen bonding, change in size of molecular entities as well as their speed of rotation, in presence of different types of solutes was carried out by many research groups in field of dielectric spectroscopy.

The basics of molecular interaction in solution are hydrogen bonding. Hydrogen bonding occurs between a proton donor and proton acceptor group. The hydroxyl (-OH) group is a proton donor as well as proton acceptor. Dimethyl sulfoxide (CH_3)₂SO an aprotic polar solvent is not a hydrogen bond donor because it does not have a hydrogen attached to an oxygen or to a nitrogen, so there are no positively charged hydrogens to form ion-dipole interactions. Aprotic polar solvents have a partial negative charge on the surface of their molecules that can solvate cations, but the partial positive charge is on the inside of the molecules, which makes it less accessible.

II EXPERIMENTAL

Time domain reflectometry (TDR) in reflection mode has been used as a technique. In TDR a fast rising step pulse of 25 ps is incident on the binary mixture kept in the cell. The binary mixtures were prepared at different volume percentage of Dimethyl sulfoxide (CH₃)₂SO in Ethanol in steps of 10 vol. % within a \pm 0.01 % error limit. The reflected pulse from the cell is sampled with incident pulse in sampling oscilloscope. The reflected pulse from sample contains the information regarding dielectric

behaviour of binary mixture. The reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were digitized in 1024 points and stored on disc.



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III DATA ANALYSIS

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ using Fourier transformation (Samulon [1]; Shannon [2]) as

$$\rho^*(\omega) = \frac{c \ p(\omega)}{j \omega d \ q(\omega)}$$

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 velocity of light, ω is the angular frequency, and d is the effective pin length.

The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by using the bilinear calibration method (Cole [3] et al.). The experimental values of $\varepsilon^*(\omega)$ are fitted with the Debye equation (Havriliak and Negami [4]; Cole and Cole [5]; Davidson and Cole [6])

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

with ε_0 , ε_∞ and τ as fitting parameters. A nonlinear least- squares fit method (Bevington [7]) was used to determine the values of dielectric parameters. The values of static dielectric constant (ε_0) and dielectric relaxation time (τ) are listed in table 1.

Table 1: Temperature dependent	dielectric parameters for	Dimethylsulfoxide –	Ethanol mixture
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Volume	15	^{0}C	20	0^{0} C	25	^{0}C	30	$O^{0}C$
fraction	ϵ_0	τps	ϵ_0	τps	ϵ_0	τps	ϵ_0	τps
of								
DMSO								
0.0	26.51	159.58	26.13	150.77	25.28	139.30	25.04	127.44
0.1	29.89	110.58	29.61	108.78	28.68	99.66	28.32	94.12
0.2	31.87	95.05	32.45	91.63	31.44	84.14	30.57	79.92
0.3	37.89	78.12	34.27	68.15	33.99	67.84	34.32	62.00
0.4	40.61	73.02	37.53	61.51	39.17	63.74	38.27	57.96
0.5	42.47	62.03	41.35	54.11	41.15	53.15	40.73	51.67
0.6	45.25	57.20	44.46	47.33	43.52	46.69	43.55	45.83
0.7	48.91	44.77	47.19	42.34	47.14	37.76	46.06	36.35
0.8	54.22	41.68	52.34	40.41	52.36	36.73	52.70	35.46
0.9	56.05	39.02	56.22	38.46	54.63	34.11	54.34	33.07
1.0	53.24	35.97	52.59	28.39	52.21	26.33	52.12	26.19

The thermodynamic parameters molar enthalpy of activation ΔH and the molar entropy of activation ΔS were obtained using equation

$$\tau = \frac{h}{KT} \exp[(\Delta H - T\Delta S) / RT]$$

and are listed in table 2.



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Table 2: Activation enthalpy and entropy of Dimethylsulfoxide – Ethanol mixture

Volume fraction of	Enthalpy (ΔH)	Entropy (ΔS)
DMSO	KJ/mole	J/ ⁰ Kmole
0.0	8.4645	-0.0277
0.1	5.8008	-0.0340
0.2	5.7329	-0.0325
0.3	7.6923	-0.0242
0.4	7.1188	-0.0255
0.5	5.8108	-0.0287
0.6	7.4713	-0.0221
0.7	8.2811	-0.0177
0.8	5.9610	-0.0252
0.9	6.4777	-0.0229
1.0	12.5608	-0.0125

IV RESULT AND CONCLUSION

The static permittivity increases with addition of Dimethylsulfoxide in Ethanol. This raise in permittivity is due to increase in effective dipole moment per unit volume in mixture. Relaxation time is very sensitive parameter related to molecular size as well as mobility of molecules in liquid. Relaxation time for aqueous solutions of Dimethylsulfoxide – Ethanol decreases rapidly up to 50 % concentrations and then deceases slowly with increase in volume fraction of solute in ethanol mixture. The variation in relaxation time shows that, the decrease in amount of hydrogen bonding between solute and solvent molecules, which leads to smaller molecular structures rotating fast.

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