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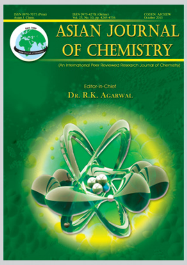

Hydrogen Bond Dynamic Properties of Ethanol-Methanol Mixtures Studied by The Complex Permittivity

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The complex permittivity of ethanol-methanol mixtures, over the entire concentration range, have been measured using resonant cavity perturbation method at 293, 303 and 313 K. The observed values of the permittivity gradually increased with increasing concentration of methanol in ethanol, whereas the relaxation time decreased with increasing concentration and temperature. The increase in the dielectric relaxation time in ethanol-methanol mixtures is attributed to the spatial constraints of ethanol molecules on the hydrogen-bond network, the reorientation processes in pure liquids and mixtures are controlled by enthalpic rather than by entropic factors.

Key Words: Ethanol-methanol mixtures, Permittivity, Debye equation, Hydrogen-bond.

INTRODUCTION

Microwave heating has attracted interest in the chemical industry for its ability to provide targeted heating of liquids rapidly and uniformly[1]. For better application of microwaves in the chemical industry, the interaction between microwaves and the mixtures needs to be further studied. Usually, the permittivity describes a material's ability to absorb, transmit and reflect electromagnetic energy. Thus, it is important to know the permittivity of liquid mixtures at microwave frequencies. Alcohols play an important role in many chemical reactions due to the ability undergo self-association with manifold internal structures and are in wide use in industry and science and reagents, solvents and fuels[2]. Sivagurunathan *et al.*[3], reported the dielectric parameters for acrylic esters with alcohol (primary alcohols) at different temperatures and concentration. Many people have studied the dielectric properties of binary mixtures using time domain reflectometry (TDR) in order to understand their intermolecular interactions and dynamics[2-9]. Chaudhari *et al.*[4], studied the dielectric properties of tetrahydrofuran (THF) in methanol and ethanol at different temperatures in the frequency range 10 MHz to 10 GHz. Lone *et al.*[9], have made similar measurements for various concentrations of methanol-ethanol mixtures over the frequency range from 10 MHz to 20 GHz by time domain reflectometry. The experimental results of these binary systems were found to obey the Debye model. The present paper reports the dielectric relaxation studies of methanol with ethanol mixtures using resonant cavity perturbation method and study of their hydrogen bonding ability yields insight into the nature of heating dynamics.

EXPERIMENTAL

Methanol (99.5 %) and ethanol (99.5 %) were purchased from the Chengdu Kelong Chemical Factory. The measurement system consists of a vector network analyzer Agilent E8362 BandaH105 rectangular resonant wave guide cavity. The rectangular resonant cavity technique is based on the electromagnetic field perturbation of a resonant cavity by the insertion of a small sample and is a popular technique for measuring the permittivity by using the perturbation formula[6]. A temperature controller system with a water bath and thermostat was used to maintain the temperature constant within ± 0.5 K. The sample cell was surrounded by a heat insulating container through which the constant temperature water was circulated. The temperature at the cell was checked using a thermometer sensor. The dielectric properties of ethanol-methanol mixtures with different volume ratios were measured at 293, 303 and 313 K. The experimental dielectric spectra were fitted in a complex nonlinear least-squares routine by using various models represented by the Havriliak Negami function[7].

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

where ε_0 is the static permittivity, ε_∞ is the high-frequency limiting permittivity and τ is the relaxation time. α and β are

TABLE-1
REAL AND IMAGINARY PARTS OF THE RELATIVE PERMITTIVITY (DIELECTRIC CONSTANT) FOR ETHANOL-METHANOL A BINARY MIXTURES (AT 2.45 GHz) AT DIFFERENT TEMPERATURES

x	293 K				303 K				313 K			
	ε' ± 0.3		ε'' ± 0.3		ε' ± 0.5		ε'' ± 0.3		ε' ± 0.3		ε'' ± 0.3	
	E	C	E	C	E	C	E	C	E	C	E	C
0	6.72	5.18	6.43	7.37	7.87	6.08	6.32	7.86	9.14	7.10	6.28	8.19
0.1	7.70	5.91	7.30	8.19	8.88	6.96	7.08	8.64	10.21	8.05	6.83	8.85
0.2	8.50	6.77	7.83	9.03	10.07	8.00	7.78	9.41	11.56	9.25	7.39	9.52
0.3	9.25	7.79	8.72	9.87	11.42	9.18	8.49	10.15	12.73	10.34	7.89	10.08
0.4	11.07	8.97	9.60	10.70	12.89	10.51	9.15	10.83	14.55	12.03	8.32	10.63
0.5	11.65	10.31	10.02	11.48	14.54	11.98	9.70	11.43	16.03	13.46	8.72	11.04
0.6	13.64	11.81	10.97	12.93	16.26	13.57	10.19	11.93	17.63	14.97	8.93	11.35
0.7	15.26	13.45	11.40	12.80	18.09	15.27	10.54	12.31	19.27	16.55	9.09	11.56
0.8	17.06	15.22	11.65	13.29	19.93	17.04	10.84	12.57	20.92	18.16	9.15	11.67
0.9	18.21	17.08	12.20	13.63	21.37	18.41	11.12	12.78	22.56	19.79	9.13	11.67
1.0	20.25	19.15	12.51	13.79	22.03	20.67	12.17	12.80	24.22	21.43	9.04	11.58

x is the volume fraction of methanol, E is the experimental value of the relative permittivity and C is the corresponding value calculated by eqn. 2.

TABLE-2
REAL AND IMAGINARY PARTS OF THE RELATIVE PERMITTIVITY (DIELECTRICCONSTANT) FOR ETHANOL-METHANOL A BINARY MIXTURES (AT 5.8 GHz) AT DIFFERENT TEMPERATURES

x	293 K				303 K				313 K			
	ε' ± 0.3		ε'' ± 0.3		ε' ± 0.5		ε'' ± 0.3		ε' ± 0.3		ε'' ± 0.3	
	E	C	E	C	E	C	E	C	E	C	E	C
0	4.17	2.68	3.45	3.56	4.15	2.90	3.80	4.01	4.20	3.27	3.97	4.63
0.1	4.31	2.84	3.91	4.07	4.42	3.12	4.34	4.58	4.69	3.57	5.38	5.22
0.2	4.61	3.05	4.38	4.64	4.70	3.41	4.85	5.21	4.83	3.97	6.10	5.93
0.3	4.85	3.31	5.04	5.28	4.98	3.76	5.92	5.91	5.11	4.37	6.77	6.58
0.4	5.07	3.65	5.81	5.99	5.13	4.20	6.48	6.67	5.48	4.91	7.57	7.34
0.5	5.50	4.06	6.43	6.77	5.54	4.75	6.77	7.50	6.03	5.55	8.37	8.14
0.6	6.01	4.57	7.10	7.62	6.49	5.42	8.35	8.39	7.01	6.31	9.27	8.99
0.7	6.52	5.20	8.14	8.54	7.72	6.22	8.62	9.33	8.62	7.21	10.10	9.86
0.8	7.30	5.97	9.02	9.51	7.97	7.18	9.30	10.31	9.62	8.25	10.84	10.75
0.9	8.14	6.89	9.91	10.54	9.39	8.32	10.00	11.30	10.40	9.44	11.98	11.62
1	9.25	8.09	11.23	11.66	10.46	9.63	10.96	12.28	11.21	10.80	12.89	12.46

x is the volume fraction of methanol, E is the experimental value of the relative permittivity and C is the corresponding value calculated by eqn. 2.

shape parameters describing symmetric and asymmetric distribution of relaxation times, respectively.

We used dielectric "mixing rules" that have been developed by Lou *etc.*[7], to estimate three Debye parameters. Those mixing rules describe the frequency-dependent dielectric properties of the solvent mixture based on solution composition and the dielectric parameters for the solution components. It was noticed that the permittivity gradually increased with increasing concentration of methanol in ethanol,whereas the relaxation time decreased with increasing concentration and temperature.

RESULTS AND DISCUSSION

The structure factor g through the following[7] expression:

$$\varepsilon_0 - \varepsilon_\infty = \frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon_\infty}\frac{4\pi N}{3k_B TV}\frac{(\varepsilon_\infty + 2)^2\mu^2}{3\varepsilon} g \qquad (2)$$

where μ is the dipole moment in the vapour phase, N is the Avagadro number, V is the molar volume and ε is a constant whose value depends on the system of units used. ε_∞ is the dielectric constant at a frequency that is sufficiently low for atomic and electronic polarization. The expression for g derived by Suresh and Naik[10], analogous to theoretical equation that relates the density and temperature of the system with the average number of hydrogen bond per molecule.

TABLE-3
ENTHALPY (ΔH) AND ENTROPY (ΔS) OF ACTIVATION

x	ΔH (KJ/mol)	ΔS (KJ/mol)
0	6.09	-0.027
0.1	6.18	-0.020
0.2	4.55	-0.030
0.3	6.92	-0.027
0.4	6.09	-0.030
0.5	7.57	-0.020
0.6	7.70	-0.020
0.7	9.09	-0.020
0.8	10.07	-0.020
0.9	10.74	-0.019
1.0	13.36	-0.012

$$g = 1 + \frac{2\sqrt{1+8\rho K} - 1}{\sqrt{1+8\rho K} + 2} \qquad (3)$$

where $K = e^{-(\Delta H - T\Delta S)/k_B T}$ is the equilibrium constant for bond formation. ρ is the system density in g/cm^3.

$$P = \frac{K}{1+K}, \quad \langle n_{HB} \rangle = 4P = \frac{4(\sqrt{1+8\rho K}-1)}{\sqrt{1+8\rho K}+1} \qquad (4)$$

where P is the probability that a given association site on a central molecule, is bonded at a certain instant of time, thus $\langle n_{HB} \rangle$ is the average number of hydrogen bonds per molecule,

Figs. 1 and 2 indicate that there exist strong hydrogen bonds interactions between methanol and ethanol molecules. The dielectric relaxation can be treated as a rate process[7] involving a path over a potential barrier. The energy of activation for the dielectric relaxation process, ΔG, can be calculated from the dielectric relaxation time by using the Eyring equation:

$$\Delta G = RT \ln\left(\frac{k_B T\tau}{h}\right) \qquad (5)$$

where T is the absolute temperature and h, k_B and R are Plank's constant, Boltzmann's constant and the molar gas constant, respectively. A plot of ΔG *versus* T(ΔG = ΔH – TΔS) can yield the enthalpy ΔH and entropy ΔS of activation for the dielectric relaxation process. These parameters characterize the molecular interactions and dynamics of the components and their mixtures.

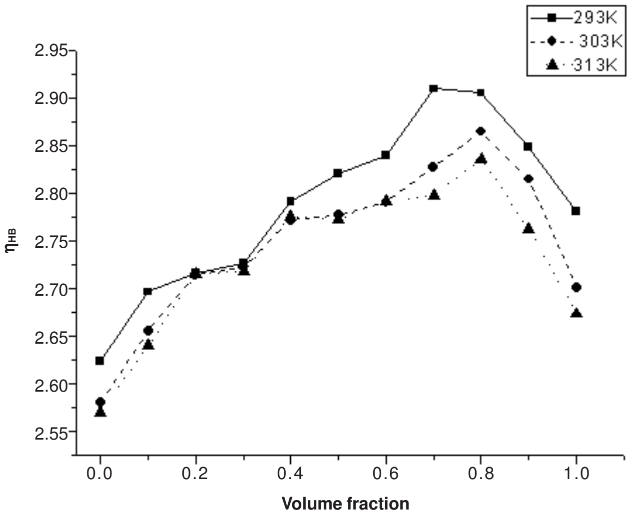

Fig. 1. Average number of hydrogen bonds per molecule in the methanol-ethanol mixtures as a function of the solution composition at 293, 303 and 313 K

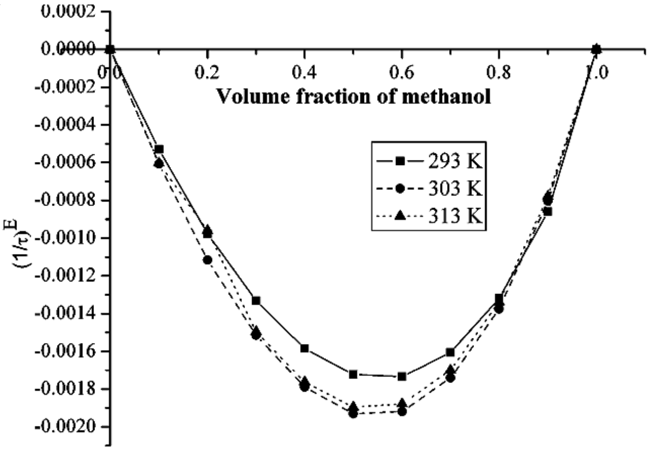

Fig. 2. Variation of the excess inverse relaxation time (1/τ) *versus* the volume fraction of methanol inethanol at 293, 303 and 313 K

For most mixtures, ΔH > |TΔS|, indicating that the reorientation processes in pure liquids and mixtures are controlled by enthalpic rather than by entropic factors.

Conclusion

The temperature dependence of the dielectric relaxation behaviour at microwave frequencies of ethanol-methanol were measured and are reported over the whole composition range at 293, 303 and 313 K. It was noticed that the permittivity gradually increased with increasing concentration of methanol in ethanol, where as the relaxation time decreased with increasing concentration and temperature. The observed values of the dielectric parameters confirm that H-bonded molecular interactions decrease the number of effective parallel aligned dipoles with the formation of complexes in liquid ethanol + methanol mixtures. Reorientation processes in pure liquids and mixtures are controlled by enthalpic rather than by entropic factors.

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