Thermodynamic Parameters in the Dielectric Study of Methyl Acetate + Alcohol Systems

Shirke R. M.

Abstract— Three solute + solvent systems were prepared with methyl acetate in methanol, ethanol and propan-1-ol by increasing solvent in the steps of 10% at an accuracy of 0.01%. Time Domain Reflectometer in reflection mode (Cole et al, 1989) was used to obtain complex permittivity (ε*) values at 15, 25, 35 and 45°C. Relaxation time (τ) values were estimated by fitting them with Havriliak-Negami model of dynamic permittivity using non-linear least squares approximation. Activation enthalpy (ΔH) and entropy (ΔS) were estimated using Eyring rate equation. In case of all the systems, heat is liberated to the surrounding during mixture formation and there is more disorder in the molecules after mixing than that in the molecules before mixing.

Index Terms— Complex permittivity, relaxation time, dielectric loss, time domain reflectometer, reflection coefficient spectra, esters.

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1 INTRODUCTION

The dielectric relaxation of solute-solvent mixtures gives information about intermolecular interaction and hydrogen bonding in the system. The importance of measuring the relaxation time of liquid mixtures lies in the fact that it provides valuable information about kinetics of the dipoles during the mixture formation as well as about the ordering of the molecules in the liquid state i.e. it quantifies the extent of polarization of the medium. The relaxation time of some eaters is reported by Saxena et al (1981). The dielectric permittivity, dielectric loss and relaxation time of the ester are reported by Roy et al (1977), using frequency domain technique. The dielectric relaxation is used to estimate thermodynamic parameters using known theories.

2 EXPERIMENTAL

Methyl Acetate (AR grade, Sd-Fine chemicals Ltd., Bombay), Methanol, Ethanol (Spectroscopic grade, Fluka Chemicals, Fabrik, CH-9470 Buchs) and Propan-1-ol (AR grade, E Merck, India, Ltd., Bombay) were obtained commercially and used without further purification. The solutions were prepared at different volume percentage of methyl acetate in alcohols in

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step of 10 %, within 0.01% error limit. The complex permittivity spectra were studied using the HP 54754A time domain reflectometer.

3 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 (Shannon C. E.; 1949 and Samulon H. A.; 1951) as

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

where p(ω) and q(ω) are Fourier transforms of (R1(t) - Rx(t)) and (R1(t) + Rx(t)) respectively, c is the velocity of light, ω is angular frequency, d is the effective pin length and j= √ -1 .

The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying bilinear calibration method (Samulon H. A., 1951). The respective acetates and alcohols are used as calibrating liquids. The experimental values of $\varepsilon^*(\omega)$ are fitted with the Havriliak-Negami expression (Cole R. H. et. al., 1989)

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

with, ε_o, ε_∞, τ, α, β as fitting parameters.

Further the thermodynamic parameters ΔH and ΔS are estimated using Eyring rate equation in the form of macroscopic relaxation time τ as

$$\tau = \frac{h}{KT} \exp\left[\frac{\Delta H}{RT} \right] \exp\left[- \frac{\Delta S}{R} \right] \qquad (3)$$

where h is plank's constant, K is Boltzman's constant, R is gas

constant and ΔH and ΔS are fitting parameters. A nonlinear Least-Squares fit method (Havriliak et. al., 1966) was used to determine the values of dielectric parameters as well as thermodynamic parameters.

4 RESULT AND DISCUSSION

Table 1: Temperature dependent dielectric relaxation time and thermodynamic parameters for Methyl Acetate -Methanol binary system (Values inside the bracket indicate percentage error)

X_2	τ (ps)				ΔH (KJ/mole)	ΔS (J/K-mole)
	15 ⁰C	25 ⁰C	35 ⁰C	45 ⁰C		
00	10.51(20)	9.41(20)	8.87(19)	7.26(25)	6.33 (58)	0.21
10	13.90(23)	12.36(24)	11.98(22)	9.87(28)	5.50 (63)	0.21
20	18.81(30)	17.03(30)	14.66(28)	13.17(34)	6.75 (56)	0.21
30	24.64(41)	21.89(36)	19.05(35)	16.90(38)	6.89 (29)	0.21
40	28.41(47)	26.03(44)	22.72(42)	19.41(47)	7.18 (02)	0.21
50	33.12(56)	30.14(49)	26.32(48)	22.88(53)	6.93 (74)	0.20
60	36.84(55)	33.34(53)	29.46(50)	25.46(54)	6.83 (72)	0.21
70	41.83(63)	38.80(60)	33.24(53)	28.70(61)	7.22 (14)	0.20
80	50.18(76)	46.16(70)	38.78(60)	32.74(68)	8.51 (34)	0.21
90	54.37(73)	48.38(70)	39.32(62)	33.81(68)	9.88 (26)	0.21
100	60.00(76)	52.86(71)	41.87(64)	35.42(70)	11.26 (19)	0.21

Table 2 : Temperature dependent dielectric relaxation time and thermodynamic parameters for Methyl Acetate - Ethanol binary system

X_2	τ (ps)				ΔH (KJ/mole)	ΔS (J/K-mole)
	15 0C	25 0C	35 0C	45 0C		
00	10.51(20)	9.41(20)	8.87(19)	7.(25)	6.33 (58)	0.21
10	16.84(24)	15.38(21)	14.30(19)	12.4(23)	5.90 (93)	0.20
20	24.27(35)	21.92(29)	19.89(22)	17.4(23)	6.80 (57)	0.20
30	35.86(58)	31.57(42)	28.15(33)	23.80(27)	7.69 (78)	0.21
40	46.81(75)	40.79(56)	37.09(50)	30.3(36)	8.14 (28)	0.21
50	57.86(58)	54.71(73)	48.01(57)	38.2(46)	7.88 (28)	0.20
60	63.81(75)	60.70(81)	58.41(68)	46.7(55)	4.88 (49)	0.19
70	81.72(91)	78.92(88)	68.41(71)	54.2(63)	7.854 (53)	0.20
80	96.04(10)	92.21(92)	83.41(77)	65.3(68)	6.94 (66)	0.20
90	123.9(10)	114.9(93)	103.39(81)	79.4(77)	8.53 (56)	0.20
100	159.9(10)	130.4(94)	110.78(83)	87.9(77)	12.39 (86)	0.21

Table 3: Temperature dependent dielectric relaxation time and thermodynamic parameters for Methyl Acetate –Propan-1-ol binary system

X_2	τ(ps)				ΔH (KJ/mole)	ΔS (J/K-mole)
	15 ⁰C	25 ⁰C	35 ⁰C	45 ⁰C		
00	10.51(20)	9.41(20)	8.87(19)	7.26(24)	6.33 (58)	0.21
10	14.74(39)	12.96(20)	11.86(21)	10.00(20)	6.69 (94)	0.21
20	22.06(61)	19.15(37)	16.68(32)	14.21(22)	8.56 (45)	0.21
30	34.88(82)	29.87(58)	24.86(44)	20.89(35)	10.57 (51)	0.22
40	48.85(11)	42.27(88)	33.26(60)	26.88(43)	12.91 (29)	0.22
50	62.17(13)	51.85(10)	40.31(75)	33.06(54)	13.80 (84)	0.22
60	88.31(17)	75.54(14)	57.05(99)	45.47(73)	14.73 (53)	0.22
70	115.02(18)	94.63(15)	72.39(11)	56.35(88)	15.78 (13)	0.23
80	161.77(17)	141.76(14)	103.86(13)	79.09(10)	16.11 (36)	0.22
90	237.45(18)	214.26(17)	142.58(14)	100.41(12)	20.10 (94)	0.23
100	358.08(23)	280.68(19)	195.20(16)	130.70(13)	23.17 (40)	0.24
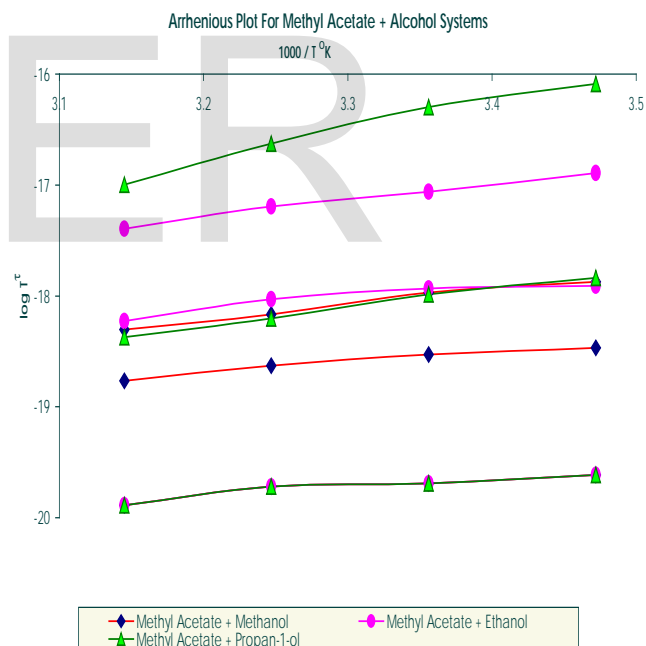
5. Conclusions:

The relaxation time shows systematic change with concentration and temperature. Positive values of ΔH shows that heat is liberated by the system to the surroundings during the mixture formation while non-zero values of ΔS shows that there is more disorder in the molecules after mixing than that of before mixing.

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