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Molecular interaction study of ethyl acetate with 1-butanol using Time Domain Reflectometry Technique

S.B. Kolhe[1], S.B. Sayyad[2], P.B. Undre[3] & P.W. Khirade[3]
[1]*Shivaji Arts, Commerce and Science College, Kannad-431103 (India)*
[2]*Miliya Arts, Science & Management Science College, Beed (India)*
[3]*Microwave Research Lab, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431004 (India)*

Abstract: Dielectric relaxation study has been carried out for ethyl acetate with 1-butanol binary mixtures over frequency range of 10 MHz to 20 GHz at different temperatures 288K, 298K, 308K, 318K using Time Domain Reflectometry (TDR) technique. Kirkwood correlation factor (g^{eff}), Bruggeman factor (f_B) and thermodynamic parameters such as the values of molar enthalpy of activation (ΔH) and the values of molar entropy of activation (ΔS) are obtained to yield information about intermolecular interaction.

Keywords: Time Domain Reflectometry, Kirkwood correlation factor, Bruggeman factor, thermodynamic parameters.

I. INTRODUCTION

Dielectric properties of substances lead to useful information about their molecular structure and intermolecular interactions. Many researchers have studied the dielectric properties of liquid by using various methods [1-10].

Objective of present paper is to report the study of dielectric parameters such as Bruggeman factor, Kirkwood Correlation factor and thermodynamic parameters such as molar enthalpy of activation (ΔH) and molar entropy of activation (ΔS) of Ethyl Acetate+1-Butanol binary system at four different temperatures by varying their volume concentration. 1-Butanol having one hydroxyl group. The C-O and O-H bonds of alcohol are polar. Another liquid is Ethyl Acetate which is aprotic with C = O group. The dielectric study of interaction between one aprotic and another protic solvent will give information about the intermolecular interactions in the mixture.

II. EXPERIMENTAL

2.1 Chemicals and Sample Preparation

The chemicals used in the present paper are Ethyl Acetate (Qualigens fine chemicals Mumbai) and 1-Butanol (Qualigens (ExcelaR)) and are used without further purification. The concentrations were prepared for 5 ml solution with the help of micropipette of 1 ml with accuracy of 99.5 %.

2.2 TDR Setup and Data Acquisition

The complex permittivity spectra were obtained by using a time domain reflectometry technique. Sampling oscilloscope is very precise instrument for digital data acquisition of instantaneous signals. The Hewlett Packard HP 54750 Sampling Oscilloscope with HP 54754A TDR plug in module has been used. A fast rising voltage pulse having 39 ps rise time was allowed to interact with the system under study. All measurements were carried out under open load conditions. The change in shape of the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In present work time window of 5 ns is used. The reflected pulse without sample R_1 (t) and with sample Rx (t) were digitized in 1024 points in the memory of the oscilloscope and transferred to a PC through 1.44 MB floppy diskette drive. The temperature controller system with water bath and a thermometer has been used to maintain constant temperature within accuracy limit of $\pm 1^{o}C$ by circulating constant water through heat insulating jacket surrounding sample cell. The data acquisition is carried out for 15 concentrations at 288,298, 308 and 318K.

III. DATA ANALYSIS

The time dependent data were processed to obtain complex reflection coefficient spectra ρ*(ω). It is related with dielectric response of the sample under study for the range of frequency from 10 MHZ to 20 GHZ.

$$\rho^*(\omega) = \frac{C}{i\omega d}\,\frac{p(\omega)}{q(\omega)} \quad (1)$$

Where p (ω) and q (ω) are Fourier transforms of R1 (t) + Rx (t) and R1 (t) - Rx (t) respectively, c is the speed of light, ω is is angular frequency, d is effective pin length and j = $\sqrt{-1}$

The complex permittivity spectra ε*(ω) were obtained from reflection coefficient spectra ρ*(ω) by using calibration method. The experimental values of ε*(ω) are fitted with Debye equation.

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

Where $\varepsilon_s, \varepsilon_\infty$ and τ as fitting parameters, ω angular frequency. In the equation (2), ε_s is the static dielectric constant, τ is the relaxation time of the system and ε_∞ is the high frequency dielectric constant. The value of ε_∞ was kept fixed as 3.0 while fitting this data. A non linear least square fit method was used to determine the values of these parameters.

IV. RESULT AND DISCUSSIONS

We have determined values of static dielectric constant ε_s and relaxation time τ for Ethyl Acetate +1-Butanol binary mixture for solutions of different concentrations of alcohols which are already reported in our previous paper [11]. Static dielectric constant and relaxation time decreases with increase in volume fraction of Ethyl Acetate in the mixture. Dielectric absorption ε' and dielectric loss ε'' for ethyl acetate +1-butanol binary mixtures is shown in fig.1 & 2 respectively. Using these values Kirkwood correlation factor (g^{eff}) and Bruggeman factor (fB) parameters and thermodynamic parameters such as molar enthalpy of activation (ΔH) and molar entropy of activation (ΔS) are obtained.

4.1 Bruggeman Factor

The Bruggemen factor which is the ratio of theoretical value of static dielectric constant computed from Bruggemen mixture formulae and practically obtained values has been obtained. A linear relationship has been expected from the Bruggemen factor values, which gives a straight line when fB plotted against volume fraction. The straight line from (0,1) to (1,0) represents non interaction between solute – solvent system [12].

The Bruggeman mixture formulae [13,14] can be used as first evidence of molecular interactions in binary mixture. The Bruggeman factor fB is given by

$$f_B = \left(\frac{\varepsilon_{sm} - \varepsilon_{sB}}{\varepsilon_{sA} - \varepsilon_{sB}}\right)\left(\frac{\varepsilon_{sA}}{\varepsilon_{sm}}\right)^{1/3} = 1 - V \qquad (3)$$

This formula states that static permittivity of binary mixture (εsm), solute A (εsA) and solvent B (εsB) can be related to volume fraction of solvent (V) in mixture. The values of Bruggeman factor for all four temperatures are plotted in fig.3. The Bruggeman factor deviates from linear values for all concentrations and temperatures [15]. Negative shift in Bruggeman factor suggests that the effective volume of complex increases. This increase in complex volume indicates weak intermolecular interaction between Ethyl Acetate and 1-Butanol molecules. The trend is same for all temperatures which shows molecular interaction is temperature dependent also [16].

4.2 Kirkwood Correlation Factor

The Kirkwood correlation factor ‘g’ [17, 18] is also a parameter containing information regarding orientation of electric dipoles in polar liquids. The g for the pure liquid is given by the following expression

$$\frac{4\pi N\mu^2\rho}{9KTM}g=\frac{(\varepsilon_s-\varepsilon_\infty)(2\varepsilon_s+\varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty+2)^2} \quad (4)$$

where μ is dipole moment in gas phase, ρ is density at temperature T, M is molecular weight, K is Boltzmann constant and N is Avogadro's number. For mixture of two polar liquids say A and B, above equation can be modified using some assumptions.

Assume that (g) for mixture is expressed by an effective averaged correlation factor (g^{eff}) such that Kirkwood equation for the mixture can be expressed as

$$\frac{4\pi}{9KT}\left(\frac{\mu_A^2\rho_A}{M_A}X_A+\frac{\mu_B^2\rho_B}{M_B}X_B\right)g^{eff}=\frac{(\varepsilon_{sm}-\varepsilon_{\infty m})(2\varepsilon_{sm}+\varepsilon_{\infty m})}{\varepsilon_{sm}(\varepsilon_{\infty m}+2)^2} \quad (5)$$

where XA and XB the volume fractions of liquids A and B respectively.

Another way to visualize variation in Kirkwood correlation factor is to assume that correlation factors for molecules A and B in mixture contribute to effective (g) in proportion to their pure liquid values gA and gB. Under this assumption Kirkwood equation for the mixture can be written as

$$\frac{4\pi}{9KT}\left(\frac{\mu_A^2\rho_A g_A}{M_A}X_A+\frac{\mu_B^2\rho_B g_B}{M_B}X_B\right)g_f=\frac{(\varepsilon_{sm}-\varepsilon_{\infty m})(2\varepsilon_{sm}+\varepsilon_{\infty m})}{\varepsilon_{sm}(\varepsilon_{\infty m}+2)^2} \quad (6)$$

where gf is correlation factor for mixture. The values of geff in equation (5) will change from gA to gB as the fraction of component B increases from zero to unity. In equation (6), gf is unity for pure liquids and will remain close to unity if there is no interaction between A and B. The calculated values of g^{eff} are tabulated in Table 1 and variation of correlation factor gf against volume fraction of Ethyl Acetate is shown in fig.4. The values of effective correlation factor decrease with increase in volume fraction of Ethyl Acetate in the mixture. This indicates decrease in interaction between the molecules of the system with increase in concentration of Ethyl Acetate in the mixture [19]. There may be parallel alignment of electric dipoles in alcohol rich region [20]. The gf values for pure liquids are unity as expected for this system and deviation from unity may indicate interaction between two components of the mixture. The gf value less than one indicates that the dipoles of the mixture will be oriented in such a way that the effective dipoles will be less than the corresponding value of pure liquid [21].

4.3 Thermodynamic Parameters

According to Eyring rate equation [22] the relation between activation enthalpy, entropy and relaxation time τ is given by,

$$\tau=(h/kT)\exp[(\Delta H-T\Delta S)/RT] \quad (7)$$

Where, ΔH is the molar enthalpy of activation and ΔS is the molar entropy of activation for the dipole reorientation process. ΔH is obtained from the slope of ln (τT) versus 1/T. If ΔH & ΔS are independent of temperature, then the plot of ln(τT) Vs T^{-1} is linear.

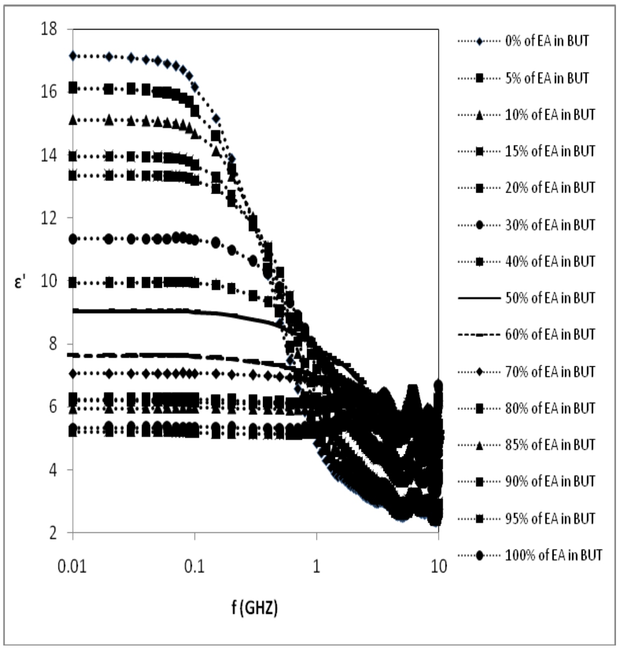
$$\Delta H-T\Delta S=RT(\ln\tau)-RT[\ln(h/kT)] \quad (8)$$

The order of magnitude of the enthalpy of activation can give some clue to the molecular energy involved in the relaxation process.

The values of molar enthalpy of activation (ΔH) and the values of molar entropy of activation (ΔS), at different concentrations determined using Eyring rate equation are listed in table 2. The Arrhenius plot for Ethyl Acetate + 1-Butanol is shown in fig. 5.

Molar enthalpy of activation (ΔH) values are positive for all concentrations. This shows endothermic interactions. The values of molar entropy of activation (ΔS) are negative for all concentrations. This indicates the activated state is more ordered. The plot of log (τ*T) versus (1000/T) is almost linear. The slope of the graph gives the activation energy of the system. The slope of these plots changes with concentrations, which shows change in activation energy of the system. The linear nature of Arrhenius plot indicates that equivalent incremental change in temperature causes equivalent change in values of activation enthalpy (ΔH) in temperature range under consideration.

V. FIGURES AND TABLES



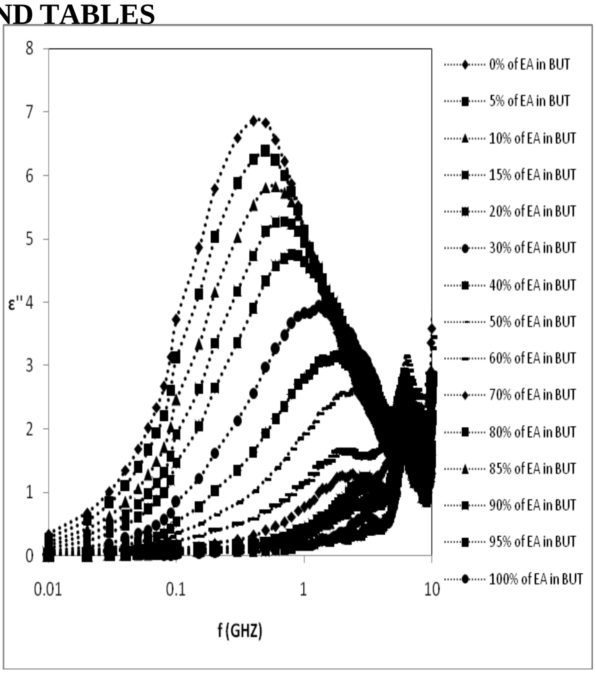
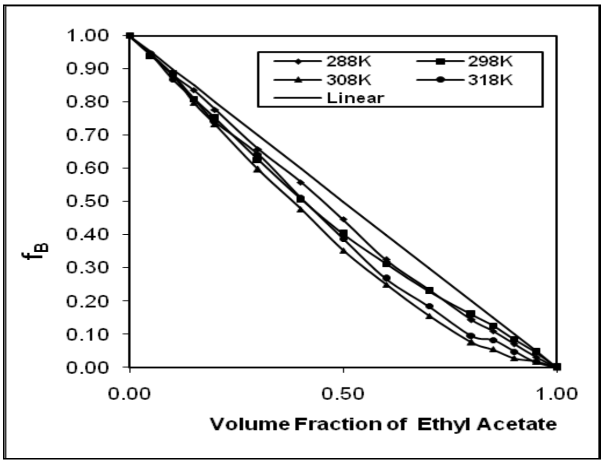


Fig.1-Frequency dependent dielectric permittivity (ε') Ethyl Acetate +1-Butanol system at 298K.

Fig.2 - Frequency dependent dielectric loss (ε'') for for Ethyl Acetate + 1-Butanol system at 298K



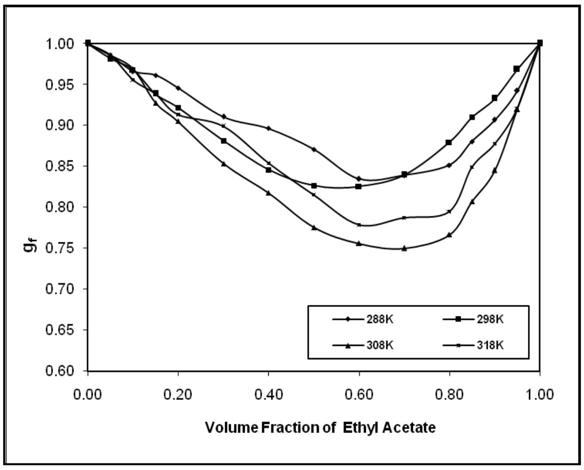


Fig. 3 - Bruggeman factor for (Ethyl Acetate+1-Butanol) binary system

Fig. 4 -: Correlation factor for (Ethyl Acetate+1-Butanol) binary system

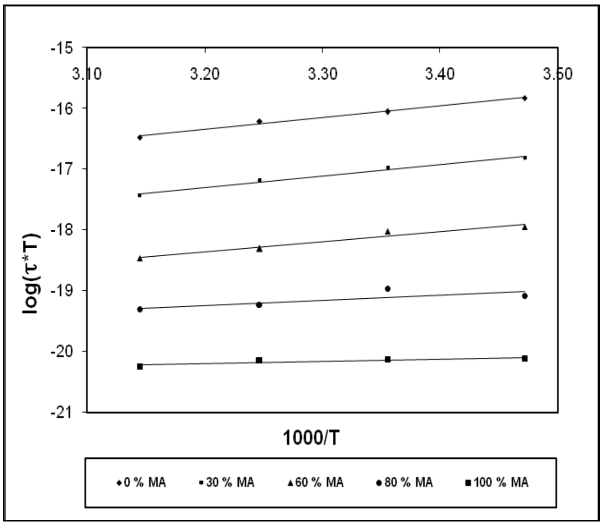


Fig. 5 - Arrhenius plot for (Ethyl Acetate+1-Butanol) system

Table 1: Kirkwood Correlation Factor (g^{eff}) for Ethyl Acetate +1-Butanol

Volume Fraction of Ethyl Acetate	**288 K**	**298 K**	**308 K**	**318 K**
0.00	3.08	3.03	2.96	2.86
0.05	2.91	2.86	2.80	2.71
0.10	2.74	2.70	2.64	2.52
0.15	2.61	2.51	2.42	2.37
0.20	2.45	2.36	2.26	2.21
0.30	2.15	2.05	1.94	1.98
0.40	1.91	1.78	1.68	1.70
0.50	1.65	1.55	1.42	1.45
0.60	1.40	1.37	1.23	1.23
0.70	1.22	1.21	1.06	1.08
0.80	1.05	1.09	0.92	0.93
0.85	1.00	1.03	0.89	0.91
0.90	0.93	0.96	0.85	0.86
0.95	0.87	0.89	0.83	0.81
1.00	0.82	0.82	0.80	0.78

Table 2: Thermodynamic Parameters for (Ethyl Acetate+1-Butanol) system

Volume Fraction of Ethyl Acetate	Molar Enthalpy (ΔH) KJ /mole	Molar Entropy (ΔS) KJ/mole
0.00	16.00	-0.0104
0.05	16.26	-0.0084
0.10	16.06	-0.0078
0.15	17.54	-0.0015
0.20	15.03	-0.0083
0.30	15.59	-0.0038
0.40	12.87	-0.0100
0.50	12.06	-0.0097
0.60	13.70	-0.0010
0.70	11.57	-0.0042
0.80	7.16	-0.0147
0.85	10.51	-0.0019
0.90	5.03	-0.0165
0.95	5.66	-0.0134
1.00	3.00	-0.0200

VI. CONCLUSION

Bruggeman factor for this system confirms the change in volume during intermolecular interaction. It has been observed that there is increase in volume during intermolecular interaction. The g^{eff} values decrease with increase in volume fraction of Ethyl Acetate in the mixture. The gf value less than unity indicates that the effective dipoles will be less than the corresponding value of pure liquid. Thermodynamic parameters show the intermolecular interactions for this system are endothermic and entropy of activated state is less. System studied shows Arrhenius behavior.

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