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CHARACTERIZATION OF INTERACTION IN BINARY MIXTURES BY DIELECTRIC ANALYSIS.

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ABSTRACT

The density (ρ), refractive index (n_D), dielectric constant (ε_s) and relaxation time (τ) of binary mixture of Allyl Bromide (AB) with polar protic solvent 2-Butanol including those of the pure liquids, were measured over the complete composition range. The experimental data is used to calculate excess molar volumes (V_m^E), excess dielectric constant (ε_s^E), excess inverse relaxation time $(1/\tau)^E$, excess molar refraction $(R_m)^E$, Bruggeman factor (f_B). The variation of these parameters with composition and the effect of bonding in new chemical species were discussed from the point of view of intermolecular interactions in these mixtures. The decrease in excess molar volume (V_m^E) is attributed to the formation of hydrogen bonded associated species formed between unlike molecules.

KEYWORDS: **dielectric constant, relaxation time, intermolecular interactions**

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INTRODUCTION

The study of physical & chemical properties of binary mixture of polar liquids is important in many fields. The study provides qualitative information on molecular dynamics and molecular interactions in liquid mixture. Dielectric relaxation studies of binary mixtures of polar liquids in microwave frequency region provide useful information about self association, intermolecular interactions between solute and solvent [1-11]. Hydrogen bonding in polar protic liquid has been the focus of interest in liquid state physics, because of its significance in quite different sphere of biology and chemistry. The objective of present paper is to report the experimental dielectric parameters along with density and refractive index for 2-butanol (proton donors) + Allyl bromide (AB) (proton accepters) mixture at temperature 303K and determine structural properties through experimental data.

2. EXPERIMENTAL

2.1. CHEMICALS

The chemicals used in the present paper (2-butanol & AB) are of spectroscopic grade. The solutions were prepared at eleven different volume percentage of AB (from) 0% to 100% in steps of 10% within 0.02% error limit.

2.2. MEASUREMENTS

The Hewelt Packard HP 54750A sampling oscilloscope with HP54754A plug-in model has been used for dielectric measurements [12]. The detail experimental procedure and data analysis is same as earlier[1-3]. Refractive indices (at Sodium D line) were measured by using Abbe's Refractometer. Density is measured using Anton Paar Denstometer DMA 5000.

3 THEORY

All excess parameters were calculated by using following relation,

$$A^E = A_m - (X_1 A_1 + X_2 A_2) \quad (1)$$

A is parameter and m, 1, 2 indicates mixture, pure components one and two respectively.
The excess molar volumes (V_m^E) were calculated by using the following relation [13]

$$V_m^E = x_1 M_1 \left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + x_2 M_2 \left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \quad (2)$$

where M is the molecular mass.
Molar refraction is given by the formula [14-15].

$$R_m = \frac{n_D^2 - 1}{n_D^2 + 2} V_m \quad (3)$$

The Bruggeman factor f_B is given by

$$f_B = \left(\frac{\varepsilon_{sm} - \varepsilon_{s2}}{\varepsilon_{s1} - \varepsilon_{s2}}\right)\left(\frac{\varepsilon_{s1}}{\varepsilon_{sm}}\right)^{\left(\frac{1}{3}\right)} = 1 - V \quad (4)$$

RESULT & DISCUSSION

The values of density, refractive index, dielectric constant and relaxation time of binary mixture are tabulated in table 1. The density and refractive index of the binary mixture of AB with 2-butanol increases as the volume fraction of AB in the mixture is increasing. Both two parameters are in good agreement with each other. The value of dielectric constant decreases with increase in volume fraction of AB. This can be attributed to the decrease in polarity in the mixture. Relaxation time decreases as concentration of AB increases. The decrease in the relaxation time may be due to the decrease in the effective radius of the rotating unit. [16]. This results in the faster rotation of molecules which decreases relaxation time. The negative variation of excess molar volume (Fig 1) in AB + *2-butanol* mixtures indicates the structural contribution arising from proper geometrical fitting in this case i.e. a better interstitial accommodation of solute and solvent in the system. The molecules of AB cooperate with 2-butanol. This cooperation becomes the cause for decrease in molar volume of the mixture. This leads to the formation of tightly packed hydrogen-bonded aggregates between unlike molecules. Negative value shows that solute acts as a structure maker. The strong peak of excess molar volume shows the strength of hydrogen bond interaction. The negative value (Fig 2) of excess dielectric constant indicates that the solute solvent interaction takes place in such a manner that it reduces the dipole moment and may form multimers leading to less effective dipoles.

The excess dielectric constant values of the binary mixtures of polar solvents is commonly used to obtain insight into the strength of hetero-molecular H-bonded structures and dipolar ordering, and also the stoichiometric composition corresponding to the formation of a stable complex adduct. The concentration, X_{AB} corresponding to the maximum magnitude of excess permittivity, at 0.50 (Fig. 3) suggesting the formation of a stable complex with a 1:1 mole ratio, which governs their molecular dielectric polarization. The excess inverse relaxation time gives information regarding the dynamics of solute-solvent interaction. Fig 3 describes negative excess inverse relaxation time, which indicates that the solute-solvent interaction produces a field such that the effective dipoles rotate slowly. It is known that the molar refraction is primarily dependent on composition, is little affected by temperature or pressure, and is almost independent of the physical state of the substance [17–19] . Figure 4 shows that excess molar refraction (R_m^E) is negative. This nonlinear behavior indicates solute solvent interaction within the system. The typical deviation from ideality shown by the molar refraction is large [20]. This large deviation indicates solute and solvent are linked by strong intermolecular bonding. All excess parameters were fitted to the Redlich –Kister (RK) equation [21]. The Bruggeman factor [22] is another parameter, which may be used as an indicator of inter-molecular interactions between solute and solvent. The nonlinear deviation (fig 5) from ideal line in Bruggeman plot indicates solute solvent interaction in the given system.

Table 1
Static dielectric constant, Relaxation time (ps), Density (gm/cm^3) and Refractive index of 2-Butanol +AB system 303K

Volume fraction of AB	Dielectric constant	Relaxation time	RI	Density
0	15.75	354.00	1.397	0.79835
0.1	14.50	329.14	1.399	0.87178
0.2	13.48	300.00	1.414	0.99123
0.3	12.30	277.00	1.422	1.09843
0.4	11.10	231.13	1.424	1.17967
0.5	9.99	200.00	1.432	1.26899
0.6	8.87	134.00	1.446	1.31879
0.7	8.12	100.00	1.451	1.33168
0.8	7.39	71.00	1.452	1.34013
0.9	6.96	35.00	1.456	1.35924
1	6.68	12.59	1.460	1.37348

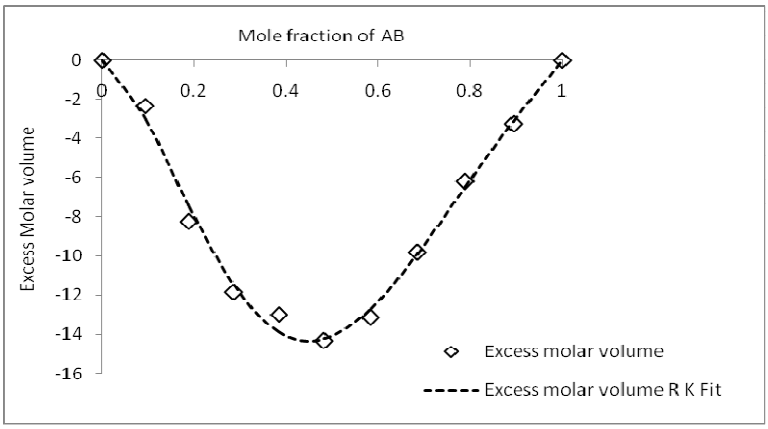

Figure 1
Excess molar volume of 2-butanol + AB

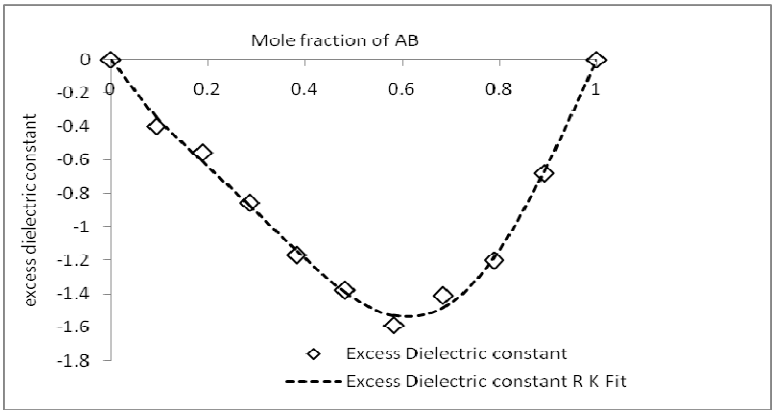

Figure 2
Excess dielectric constant of 2-butanol +AB

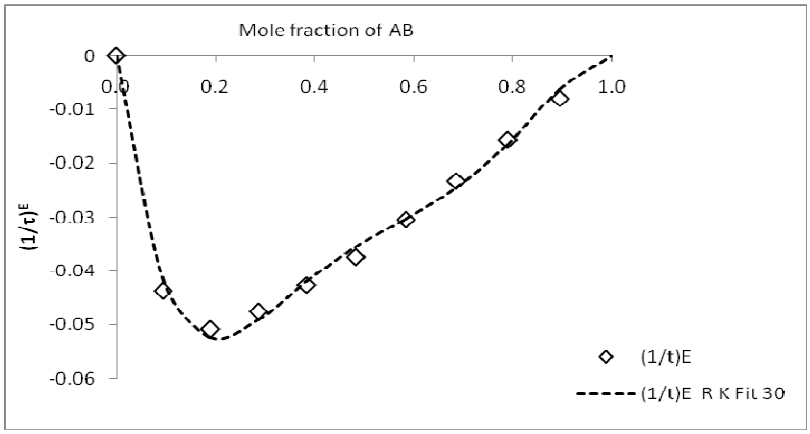

Figure 3
Excess inverse relaxation time of 2-butanol +AB

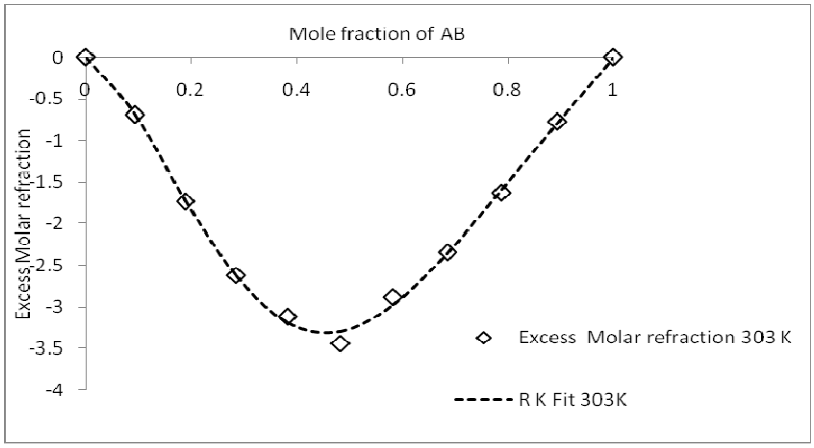

Figure 4
Excess molar refraction of 2-butanol +AB

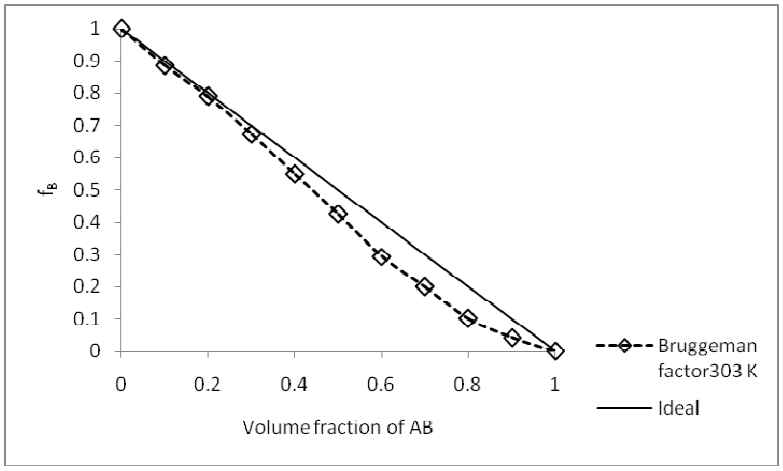

Figure 5
Bruggeman factor of 2-butanol +AB

CONCLUSIONS

The dielectric constant, relaxation time, density and refractive index of 2-butanol + AB have been studied at 303.15K. The values of refractive index and density are increasing with increase in volume fraction of AB. The value of ϵ_s decreases as the concentration of AB increases. The negative value of excess dielectric constant means the interaction of solute solvent in reduction of dipole moment and may form multimers leading to less effective dipoles. Negative excess inverse relaxation time, indicates the solute-solvent interaction produces a field such that the effective dipoles rotate slowly. Negative excess molar volume i.e. contraction of volume indicates hydrogen bonding between solute and solvent. Nonlinear deviation in Bruggeman plot also indicates solute solvent interaction in the given system.

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