

DIELECTRIC CHARACTERISTICS OF BINARY MIXTURES OF ESTERS WITH HYDROCARBONS AT 303K

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ABSTRACT

Dielectric permittivity, refractive indices and density were measured for the mixtures of aliphatic esters, like methyl acetate, ethyl acetate and butyl acetate with aromatic hydrocarbons like o-xylene, p- xylene and m-xylene at 303K. The measurements like excess permittivity, linear correlation factor, Bruggemann factor for six binary mixtures were measured for whole concentration range. These parameters were used to predict the nature of molecular interactions of same or different kinds of molecules and solute-solvent interactions. This shows the symmetric changes in dielectric behaviour with the variation of concentration. Further theoretical permittivity rules were calculated for the above five binary mixtures models. The relative merits of these models have been discussed in terms of standard deviation and percentage deviation.

Keywords: Dielectric constant, Refractive index, Kirkwood correlation factor, Bruggmann factor, excess permittivity, Theoretical permittivity model.

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INTRODUCTION

Dielectric studies of the binary mixtures of both polar and polar-non polar are important for understanding the intermolecular and intra molecular interactions due to the dipole interactions and hydrogen bonding.¹⁻³ the refractive index measurements in combination with density, boiling point , melting point and other analytical data have wide application in chemical analysis and industry⁴ .Static permittivity of a material is an intrinsic property which can play an important role in the solution⁵⁻⁷ . Measurement of relative permittivity has been shown to be a useful technique in characterizing the molecular structure, solute – solute and solute - solvent interactions in solutions state.⁸⁻⁹ many researchers¹⁰⁻¹¹ have carried out dielectric studies on mixtures of polar and non polar molecules. Some have reported the dielectric studies of binary polar and non polar binary systems liquids.¹²⁻¹³

The Kirkwood Froehlich theories of dipolar liquids define the short range of dipolar interactions. Determination of Kirkwood correlation factor provides the information on the orientation of dipoles in pure liquids and liquid mixtures. The effective Kirkwood correlation factor, the Bruggemann parameter and the excess permittivity on mixing provide the information on the interaction and orientation of the molecules in a binary polar-polar mixture.

Xylenes are widely used as solvent for dyes, colouring raw materials in plastic industry used to make synthetic fibres and for aircrafts and vehicles.¹⁴ Esters, find wide applications such as plasticizers in polymer processing industries in order to impact favourable thermoplastic behaviour and also in the flavour and fragrance industries¹⁵. In the present study the molecular interactions on binary mixtures of ester (methyl acetate, ethyl acetate, butyl acetate) with aromatic hydrocarbon (o-xylene, p-xylene, and m-xylene) have been studied at 303K. The values of refractive index and permittivity have been utilized to obtain the valuable information about heterogeneous molecular interaction. The Kirkwood correlation factor, Bruggeman factor and excess permittivity were used to discuss the molecular interaction and also predict the theoretical dielectric permittivity models of the binary mixtures and check the validity of the equations.

EXPERIMENTAL

The dielectric permittivities were measured at 303 K by using Toshniwal (RL09) dipole meter using a water circulating thermostat maintained at constant temperature. The refractive indices were measured using an Abbe's refractometer. Density has been measured by using a 25 ml specific gravity bottle. Chemicals methyl acetate, ethyl acetate, butyl acetate, o-xylene, p-xylene, and m-xylene are of AR grade.

Theory

The change in molecular orientation and molecular interaction in a mixture of two liquids can be analyzed by using dielectric measurements. The dielectric parameters are briefly described below.

Kirkwood Correlation Factor

The first relation between relative permittivity and dipole moment for pure polar liquid and liquid mixtures has been given by Onsager¹⁶. The Onsager theory applies only to systems where there is no orientation correlation between the individual molecules. Frohlich¹⁷ developed a theory, which included the short range correlation considered by Kirkwood¹⁸, and included the deformation polarizability of the molecules. Where g is the Kirkwood correlation factor and measure of the molecular association. The departure of g from unity indicates molecular association. If the high frequency dielectric constant, ϵ^∞ is taken to be given by the Maxwell relation, $\epsilon^\infty = n^2$, then the Kirkwood Frohlich equation is modified. The modified form of the Kirkwood equation Frohlich¹⁹ for the mixtures of two polar liquids may be written as-

$$\left(\frac{\mu_1^2 d_1^2}{M_1} X_1 + \frac{\mu_2^2 d_2^2}{M_2} X_2 \right) g^{\text{eff}} = \frac{9KT}{4\pi N_A} \frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2} \quad (1)$$

Where g^{eff} is the effective correlation factor for binary mixture values of which measured from the above expression. g^{eff} refers to effective Kirkwood correlation factor which provides the following information²⁰-

1. $g^{\text{eff}} = 1$, indicates that there is no interaction between solute-solvent
2. $g^{\text{eff}} < 1$ indicates that the solute and solvent interactions in a manner that the total number of effective dipoles is reduced. The two liquid mixtures may form multimers, leading to the smaller dipoles
3. $g^{\text{eff}} > 1$ indicates that the unlike molecules interact in a manner that the effective dipole increases.

Bruggeman factor

According to the Bruggemann²¹ mixture formula between unlike molecules for the static permittivity may also be obtained from the modified Bruggeman equation²²-

$$f_B = \left(\frac{\epsilon - \epsilon_2}{\epsilon_1 - \epsilon_2} \right) \left(\frac{\epsilon_1}{\epsilon} \right)^{\frac{1}{3}} = (1 - \phi_2) \quad (2)$$

The ϕ_2 is the volume fraction of one of the components in the binary mixture. The Bruggeman equation has to be modified to²³-

$$\left(\frac{\epsilon - \epsilon_2}{\epsilon_1 - \epsilon_2} \right) \left(\frac{\epsilon_1}{\epsilon} \right)^{\frac{1}{3}} = 1[a - (a - 1)\phi_B] \phi_B \quad (3)$$

The parameter 'a' is the Bruggeman factor Deviation of the Bruggeman parameter 'a' from unity is a measure of the interaction between unlike molecules in the mixtures.

Excess permittivity

In the mixtures the formation of multimers was detected through one of the dielectric parameters known as excess permittivity²⁴ -

$$\epsilon^E = (\epsilon - n^2)_{12} - ((\epsilon - n^2)_1 x_1 + (\epsilon - n^2)_2 x_2) \quad (4)$$

The subscripts 12, 1, and 2 denote the mixture, solvent, and solute respectively. ϵ^E - refers to excess permittivity which provides the following information.

1. $\epsilon^E = 0$, indicates that there is no interaction between solute-solvent,
2. $\epsilon^E < 0$ indicates that the solute and solvent interactions in a manner that the total number of effective dipoles is reduced. The two liquid mixtures may form multimers, leading to the smaller dipoles. ,
3. $\epsilon^E > 0$ indicates that the unlike molecules interact in a manner that the effective dipole increases.

Permittivity models

In this work, the experimental data of relative permittivity for the binary mixtures were compared with those estimated by five mixing rules which were proposed by-

Looyenga [L]²⁵
$$\epsilon = [\epsilon_1^{\frac{1}{3}} + \phi_2 (\epsilon_2^{\frac{1}{3}} - \epsilon_1^{\frac{1}{3}})]^3 \quad (5)$$

Böttcher-Bordewijk [B-B]²⁶
$$\frac{3\epsilon_1}{2\epsilon + \epsilon_1} \phi_1 + \frac{3\epsilon_2}{2\epsilon + \epsilon_2} \phi_2 = 1 \quad (6)$$

Bruggemann asymmetric [BA]²⁷

$$\frac{\epsilon_2 - \epsilon}{\left(\frac{\epsilon}{\epsilon_1}\right)^{\frac{1}{3}}} = (1 - \phi_2)(\epsilon_2 - \epsilon_1) \quad (7)$$

Kraszewski [K]²⁸
$$\epsilon^{\frac{1}{2}} = \phi_1 \epsilon_1^{\frac{1}{2}} + \phi_2 \epsilon_2^{\frac{1}{2}} \quad (8)$$

Peon-Iglesias [P-I]²⁹
$$\epsilon = \epsilon_1^{\phi_1} \epsilon_2^{\phi_2} \quad (9)$$

Where ϕ_1 and ϕ_2 are the volume fractions of the components of a mixture.

RESULTS AND DISCUSSION

The experimentally measured values of permittivity (ϵ_{12}), refractive index (n_{12}) of the solutions are presented in table-1. From the experimental values calculated effective Kirkwood correlation factor are also shown in table-1 and effective Kirkwood correlation factor and Bruggemann factor (f_B), excess permittivity (ϵ^E) also evaluated and plotted with concentration as mole fraction unit as shown in fig.-1 to fig.3 whole concentrations range of all the binary mixtures at 303 K.

In the present investigation to access the molecular interactions between Esters (MA), Ethyl (EA) and Butyl acetate (BA) with aromatic hydro carbon (o-xylene (OX), p-xylene (PX), m-xylene (MX)). From the equation 5 to 9 the theoretical permittivity of binary mixtures are determined and find the percentage of deviation using theoretical and experimental permittivity and also checked the validity of these equations. The calculated values of g^{eff} are tabulated in table-1. It can be seen from table-1 that, g^{eff} values are less than unity for pure liquids indicating anti parallel orientation of electric dipoles. It can also be seen that the g^{eff} values are increased with an increasing concentration of acetates (MA, MA, BA). These values are less than unity at all concentrations suggesting parallel orientation of electric dipoles..In all the binary mixtures, the value of g^{eff} are less than unity indicating weak dipole – dipole interaction, resulting

in the formation of anti parallel orientation in the pure liquids. The g^{eff} is less than unity, which suggests that the addition of xylene (o, p, and m) break large amount of hydrogen bond long range order of acetates (methyl, ethyl, and butyl) structures.

Table -1: Experimental values ϵ_{12} , n_{12} , g^{eff} esters with aromatic hydro carbon.

X2	ϵ_{12}	n_{12}	g^{eff}	ϵ_{12}	n_{12}	g^{eff}	ϵ_{12}	n_{12}	g^{eff}
MA+OX				MA+PX			EA+PX		
0.1	2.983	0.85	0.85	2.713	1.4865	0.6	2.643	1.4876	0.57
0.2	3.19	0.88	0.88	2.935	1.4795	0.7	2.8295	1.4811	0.68
0.3	3.396	0.74	0.74	3.156	1.4725	0.58	3.016	1.4747	0.58
0.4	3.603	0.77	0.77	3.378	1.4656	0.65	3.2025	1.4683	0.66
0.5	3.809	0.8	0.8	3.599	1.4586	0	3.389	1.4619	0.72
0.6	4.222	0.74	0.74	4.042	1.4446	0.67	3.762	1.449	0.69
0.7	4.635	0.78	0.78	4.485	1.4307	0.73	4.135	1.4362	0.76
0.8	5.048	0.82	0.82	4.928	1.4168	0.78	4.508	1.4234	0.81
0.85	5.461	0.84	0.84	5.371	1.4028	0.82	4.881	1.4105	0.85
0.9	5.874	0.87	0.87	5.814	1.3889	0.85	5.254	1.3977	0.89
EA+MX				BA+OX			BA+PX		
0.1	2.733	1.4847	0.69	2.823	1.4959	0.85	2.553	1.49	0.51
0.2	2.9145	1.4784	0.78	2.9495	1.4904	0.89	2.6945	1.4847	0.63
0.3	3.096	1.4722	0.66	3.076	1.4848	0.78	2.836	1.4795	0.55
0.4	3.2775	1.4659	0.72	3.2025	1.4793	0.82	2.9775	1.4743	0.63
0.5	3.459	1.4596	0.77	3.329	1.4737	0.85	3.119	1.4691	0.7
0.6	3.822	1.4471	0.73	3.582	1.4626	0.8	3.402	1.4586	0.69
0.7	4.185	1.4346	0.79	3.835	1.4515	0.85	3.685	1.4482	0.77
0.8	4.548	1.4221	0.83	4.088	1.4404	0.89	3.968	1.4378	0.83
0.85	4.911	1.4096	0.87	4.341	1.4293	0.92	4.251	1.4273	0.88
0.9	5.274	1.397	0.9	4.594	1.4182	0.94	4.534	1.4064	0.91

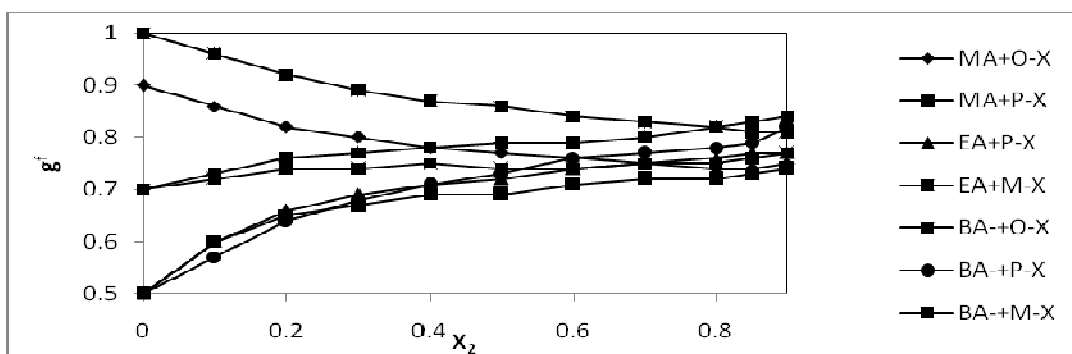


Fig.-1: Mole fraction Vs g^f

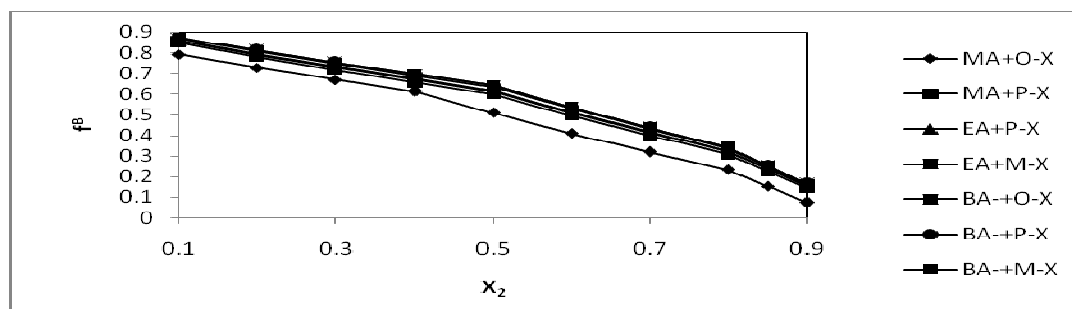


Fig.-2: Mole fraction Vs f^B

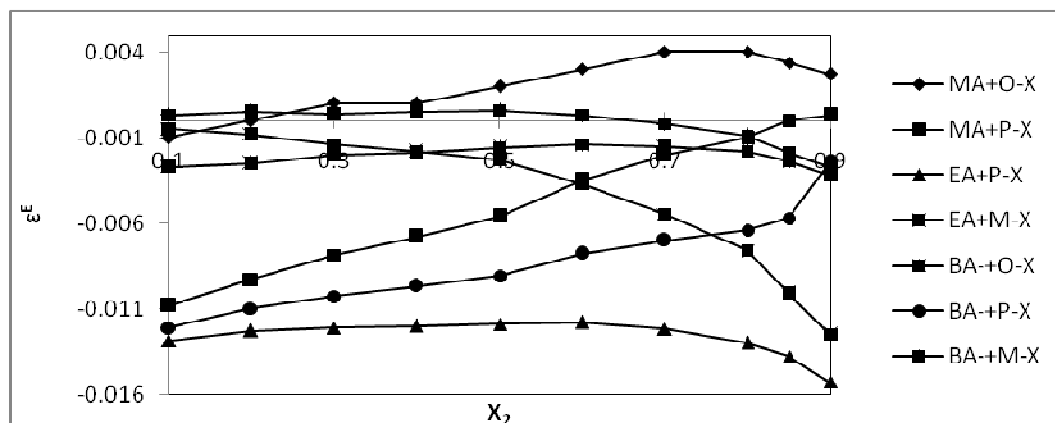


Fig.-3: Mole fraction Vs excess permittivity

The values of g^{eff} calculated from equation given in table-1 for the binary mixtures. The ' g^{eff} ' value increase with increasing concentration of acetate reach and it reaches maximum unity, indicating weak dipole – dipole interaction resulting in the formation of anti parallel dipoles in the pure system. The g^{eff} values are less than unity, which suggest that the addition of small amount of acetate breaks large amount of H-bonded long-range ordered acetate structures.

The parameter 'a' is the interaction parameter, which gives information about heterogeneous interaction between the molecules. Figure-2 shows the plot of the Bruggemann factor f^{B} versus mole fraction of the acetate (the mole fraction x_2 is used in place of the volume fraction).

The plots for f^{B} also deviate from linearity, which shows the existence deviation of the Bruggeman parameter 'a' from unity, which is a measure of the interaction between unlike molecules in the mixtures. The value of 'a' was determined by the least-squares method. For the binary mixtures of MA+OX, MA+PX, EA+PX, EA+MX, BA+OX, and BA+PX are 0.85, 0.97, 0.89, 0.91, 0.82, and 0.84 respectively at $T = 303 \text{ K}$.

The deviation of interaction parameters of the investigated dipole increases in order of BA+OX, BA+PX < MA+OX < EA+MX < MA+PX, EA+PX, and the findings also confirm the importance of position of the carbonyl groups along the chains of these molecules.

From the fig.-2 Bruggeman factor deviates from the ideal values for all concentrations of acetate in the solution. The deviation is less for all the mixtures this confirms the weak intermolecular interaction in the acetate rich region.

The plot of excess permittivity plotted against mole fraction of acetate for all concentration is shown in fig.-3. In this study, the excess permittivity values are negative in acetate rich region; it indicates the addition of acetate results solute and solvent interaction in such a way that the total effective dipoles get reduced due to formation of multimer structure in the mixture.

The experimental and theoretical permittivity for liquid mixtures of methyl acetate, ethyl acetate, Butyl acetate with xylene (o,m,p) are determined and also the evaluated the percentage deviations are listed in table-2.

For both the binary mixtures, the prediction ability of these theoretical models is almost similar. This similarity might be the same for all the type of binary mixtures. The Looyenga mode presents the best results and the Kraszewski and Bruggeman are not accurate for all the binary mixtures. Intermediate results are obtained by the Looyenga and Böttcher-Bordewijk models. By contrast, for the mixture of methyl acetate with p-xylene, the Kraszewski and Bruggeman model offers the best result and the Iglesias-Peon model is inaccurate.

The equations of Looyenga and Böttcher-Bordewijk make the intermediate predictions. As a typical example, table-2 shows the relative permittivity increments for the mixture of acetate and xylene at 303K. As can be seen, the relative permittivity increments are negative for both the systems and reach a minimum when the composition is approximately 0.5.

CONCLUSION

From the present investigation, it is eventually concluded that there is existence of weak dipole-dipole interaction between esters (methyl, ethyl, and butyl) and hydrocarbon (o, p, and m). The standard deviation of dielectric permittivity, excess permittivity has been reported. The linear correlation factor, Bruggmann factor have also been calculated.

From these parameters weak intermolecular interaction among the components of binary mixtures leads to dipole – dipole or polarization interaction between unlike molecules and confirm the interaction between esters and hydrocarbon. Further it can be concluded that the standard deviation of theoretical models on the whole, all the theoretical models fairly close to the experimental value and for **six** binary systems reported in this work, thus showing the validity of these theoretical models for binary mixtures.

Table -2: Relative Permittivity ϵ_{12} , for the binary mixtures of methyl, ethyl and butyl acetate with o,p,m-xylenes for different permittivity models.

S.No	System	L	B	K	L	PI
1	Ethyl acetate+ <i>o</i> -xylene	0.195	0.2	0.202	0.185	0.302
2	Ethyl acetate+ <i>p</i> -xylene	0.208	0.216	0.216	0.2	0.351
3	Ethyl acetate+ <i>m</i> -xylene	0.204	0.211	0.211	0.195	0.333
4	Methyl acetate+ <i>o</i> -xylene	0.225	0.233	0.234	0.216	0.377
5	Methyl acetate+ <i>p</i> -xylene	0.239	0.25	0.248	0.232	0.437
6	Methyl acetate+ <i>m</i> -xylene	0.307	0.312	0.281	0.36	0.557
7	Butyl acetate+ <i>o</i> -xylene	0.143	0.146	0.149	0.135	0.201
8	Butyl acetate+ <i>p</i> -xylene	0.154	0.158	0.16	0.146	0.237
9	Butyl acetate+ <i>o</i> -xylene	0.153	0.156	0.158	0.144	0.225

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[RJC-1234/2015]