

# Dielectric Properties of Mixtures of Bromobenzene and 1-Heptanol at R.T.

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**Abstract-** About the molecular interactions between molecules. Kirkwood correlation factor  $g$  was also calculated to gain information. In this paper precisely measured values of static permittivity ( $\epsilon_0$ ) and permittivity at optical frequency ( $\epsilon_\infty$ ) of the binary mixtures of bromobenzene (BB) and 1- heptanol (1-HeOH) of varying concentration at 303 °C are reported.  $\epsilon_0$  and  $\epsilon_\infty$  were found to deviate from ideal behavior with concentration variation. The excess static permittivity was calculated from measured data. The character change of  $\epsilon_0$  is presented by its excess value as a function of composition of mixture. The excess property was qualitatively analyzed to gain valuable information regarding orientation of electric dipoles in polar liquids. Earlier reported results of the binary mixtures of BB + MeOH (methanol), BB + 1-PrOH (1-propanol) and BB + 1-BuOH (1-butanol) are compared with the data of BB + 1-HeOH. Effect of increase in chain length of primary alcohol on the dielectric properties of the mixtures of BB + alcohol is discussed. Measured static permittivity and refractive index data of BB + 1-HeOH mixtures are also compared with those estimated by different mixing rules.

**Keywords:** static permittivity, refractive index, bromobenzene, 1- heptanol, Kirkwood correlation factor.

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## I. Introduction

The properties of liquid-liquid mixtures are very important as a part of studies of thermodynamic acoustics and transport aspects. Dielectric studies of binary mixtures of polar molecules provide useful information about the intermolecular dipolar and hydrogen bonded interactions in the mixtures.

Recently we studied [1] dielectric properties of binary mixtures of bromobenzene (BB) with methanol (MeOH), 1-butanol (1-BuOH) and 1-propanol (1-PrOH) at 30 °C. In continuation of these studies dielectric properties of BB with 1- heptanol (1-HeOH) was conducted. Aim of this work is to gain valuable information about the molecular

interactions between molecules of the binary mixtures of BB and 1-HeOH.

## II. Experimental

### II.1. Materials

Analytical grade BB and 1-HeOH were procured from Ranbaxy Laboratories Limited (India) and SD Fine Chem. Limited (India) respectively. Binary mixtures of BB and 1-HeOH were prepared at 11 volume concentrations over the entire mixing range at room temperature. The mole fraction of BB of in the binary mixture was determined using the formula:

$$X_{BB} = \frac{\phi_{BB} \times \frac{\rho_{BB}}{M_{BB}}}{\phi_{BB} \times \frac{\rho_{BB}}{M_{BB}} + \phi_{1-HeOH} \times \frac{\rho_{1-HeOH}}{M_{1-HeOH}}} \quad (1)$$

where  $\phi$  is the volume fraction,  $\rho$  is the density,  $M$  is the molecular weight.

## II.2. Measurements

The values of static dielectric constant  $\epsilon_0$  of pure liquids, and  $\epsilon_{0m}$  of the binary mixtures were determined by using capacitive measurement method with a short compensation at 2 MHz. Agilent (4980-A) precision LCR meter with a four terminal liquid dielectric test fixture (Agilent, 16452-A) was used for the capacitance measurement of the cell without and with sample. The determined values of  $\epsilon_{0m}$  for different mole fractions of BB in 1-HeOH are presented in Table 1. The measurement accuracy of the static dielectric constant is  $\pm 0.3\%$ , which is estimated by the calibration of the cell with the standard liquids by comparing with their literature values. The high frequency limit dielectric constant  $\epsilon_\infty$  of pure liquids and  $\epsilon_{\infty m}$  of the binary mixtures was taken as square of the refractive index ( $n_D$ ), which was measured with an Abbe refractometer at wavelength of sodium – D light, and these values are also presented in Table-1. The maximum measurement error in high frequency limit dielectric constant values is  $\pm 0.02\%$ . All the measurements were carried out at  $30^\circ\text{C}$ .

## II.3. Data analysis

From the experimental values of static dielectric constant the excess static dielectric constant ( $\epsilon_0^E$ ) for binary mixtures were calculated using equation [2],

$$\epsilon_0^E = (\epsilon_{0m} - \epsilon_{\infty m}) - [(\epsilon_{0, BB} - \epsilon_{\infty, BB}) \cdot X_{BB} + (\epsilon_{0, 1-HeOH} - \epsilon_{\infty, 1-HeOH}) \cdot X_{1-HeOH}] \quad (2)$$

where  $X$  is the mole fraction and subscripts  $m$  represents the binary mixture.

From the dielectric relaxation parameters the information about the liquid structure, molecule's orientation, as well as the information regarding the orientation of electric dipoles in polar liquids could be obtained using the Kirkwood correlation parameter  $g$  [3].

The expression for 'g'

$$\frac{4\pi N \mu^2 \rho}{9kTM} g = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \quad (3)$$

where  $\rho$  is the density of liquid at temperature  $T$ ,  $M$  is the molecular weight,  $k$  is the Boltzmann constant,  $N$  is the Avogadro's number and  $\mu$  is the dipole moment of solutes in gas phase.  $\epsilon_\infty$  is taken as square of refractive index.

For the mixtures of two polar liquids, the effective averaged angular Kirkwood correlation factor ( $g^{eff}$ ) of two different molecules is evaluated from the modified Kirkwood equation [4]. The Modified Kirkwood equation for the binary mixture is expressed as:

$$\left( \frac{4\pi N}{9kT} \right) \left[ \frac{\mu_A^2 \rho_A}{M_A} V_A + \frac{\mu_B^2 \rho_B}{M_B} V_B \right] g^{eff} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad (4)$$

where suffices  $A$ ,  $B$  and  $m$  represent BB, 1-HeOH and mixture, respectively.

## III. Results and Discussion

Values of static permittivity, permittivity at optical frequency, Kirkwood correlation factor ( $g^{eff}$ ), and Bruggman parameter ( $f_B$ ) for binary mixtures of BB + 1-HeOH at 303 K are presented in Table 1.

TABLE I

Static permittivity ( $\epsilon_0$ ), permittivity at optical frequency ( $\epsilon_\infty$ ), Kirkwood correlation factor ( $g^{eff}$ ), and Bruggman parameter ( $f_B$ ) as a function of mol fraction of BB for binary mixtures of BB + 1-HeOH.

$X_{BB}$	$\epsilon_0$	$\epsilon_\infty$	$g^{eff}$	$f_B$
0	10.38	2.0664	3.28	1
0.131	9.13	2.0678	2.75	0.788
0.254	8.24	2.0993	2.34	0.627
0.368	7.53	2.1261	2.01	0.490
0.476	6.47	2.1895	1.55	0.273
0.576	6.05	2.2255	1.35	0.181
0.671	5.81	2.2455	1.23	0.127
0.760	5.64	2.2834	1.13	0.088
0.845	5.53	2.3104	1.05	0.061
0.925	5.44	2.3409	0.98	0.040
1	5.28	2.3978	0.88	0

Variation in static permittivity as a function of concentration of BB in the BB+ 1-HeOH mixture is

shown in Fig.1 (a). In the Figure our earlier [1] reported results of mixtures of BB + MeOH, BB + 1-PrOH and BB + 1-BuOH are also presented for comparison. From the figure it is clear that static permittivity decreases nonlinearly with the concentration of BB in all the alcohols. Static permittivity values are found to decrease with increase in the chain length of the alcohols, at all the mixture concentration. Further more it is observed that the variation in dielectric constant value of BB + 1-HeOH cannot be expressed by a simple mixing formula of the type  $\epsilon_{om} = X_{BB} \epsilon_{o, BB} + X_{1-HeOH} \epsilon_{o, 1-HeOH}$ , where X is mole fraction of the components,  $\epsilon_{om}$  is the static dielectric constant of the mixture. BB and 1-HeOH have nearly the same electric dipole moment. Therefore the internal field in the pure state would not be expected to be very different from the internal field in the mixed state. It is apparent that the BB molecules separate the polar alcohol molecules from each other decreasing the probability of those molecular orientations which exists in the pure liquid and tend to decrease the effective dipole moment and hence the dielectric constant. Variation in permittivity at optical frequency as a function of concentration of BB in the BB + 1-HeOH is shown in the Fig-1(b). From the figure it can be seen that permittivity of BB + 1- HeOH alcohol mixture varies nonlinearly with concentration of BB in 1-MeOH, as is the case with the mixtures of BB with other lower order alcohols (MeOH, 1-PrOH and 1-BuOH). This confirms that the electronic polarization is influenced by the interaction between the molecular species of the liquid mixture.

The  $\epsilon_0^E$  values of BB-1-HeOH mixtures are non zero and are all negative as shown in the Fig-2. The negative  $\epsilon_0^E$  values suggest that the polar associate forms with lower dipole due to orientation of some of the neighbouring dipoles in opposite direction in these systems. The different strength of H-bond interactions and net dipolar alignments is responsible for the divergent magnitude of  $\epsilon_0^E$  values in these mixtures. The magnitude of maximum values of  $\epsilon_0^E$  of BB- 1- HeOH system is 1.36, whereas the reported values[1] for BB + MeOH, BB + 1-PrOH and BB + 1-BuOH are 5.65, 3.68 and 2.42 respectively. These values clearly suggest that the magnitude of maximum values of  $\epsilon_0^E$  increases with the decreases in the carbon chain length of the alcohols. It appears that hydrogen bonded linear networks are more effectively dissociated on addition of BB to the lower order alcohols than to the higher order alcohols.

Kirkwood correlation factor for pure BB is close to unity (0.88), which confirms its non-associative behavior and that of 1- HeOH is greater than unity (3.28), which

confirms the existence of H-bonded molecular multimers with parallel dipole alignments. The effective correlation factor  $g^{eff}$  of the binary mixtures is evaluated using Eq. (4) and are presented in Table 1.  $g^{eff}$  values are found to decrease nonlinearly with the increase in the mol fraction of BB.

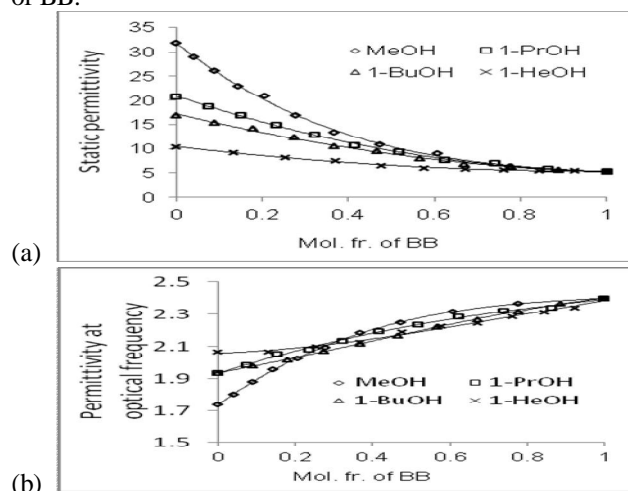


Fig.1: Variation in (a) static permittivity and (b) permittivity at optical frequency with mol. fraction of BB in different alcohols (MeOH, 1-PrOH, 1-BuOH and 1- HeOH). (Solid line shows trend line).

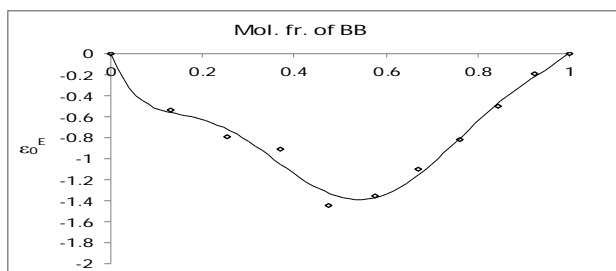


Fig.2: Plots of  $\epsilon_0^E$  against mole fraction of BB,  $X_{BB}$  for BB-1-HeOH binary mixtures at 303<sup>o</sup>K. Solid line is non-linear fit.

The information related to the solute-solvent interaction is given by the Bruggeman factor ( $f_B$ ). According to the Bruggeman,  $\epsilon_{om}$ ,  $\epsilon_{oA}$  and  $\epsilon_{oB}$  may be related to the volume fraction of BB ( $\phi_B$ ) by the following formula [5], assuming ideal mixing behavior:

$$f_B = \frac{(\epsilon_{om} - \epsilon_{oA})}{(\epsilon_{oB} - \epsilon_{oA})} \left( \frac{\epsilon_{oB}}{\epsilon_{om}} \right)^{\frac{1}{3}} = 1 - \phi_B \quad (5)$$

yielding a linear relationship between Bruggeman factor  $f_B$  and volume fraction of solute.

The Bruggeman plot for BB + 1-HeOH mixtures is shown in Fig.3. The  $f_B$  is not a linear function of volume fraction (Fig.3). To fit the experimental data, Eq. (5) has been modified as follows [6]:

$$f_B = 1 - [a - (a - 1)\phi] \phi \quad (6)$$

where 'a' is a numerical fitting parameter.

The value of 'a' for BB + 1-HeOH mixture is 2.0636. For BB + 1-HeOH mixtures  $a > 1$ . This suggests that the effective volume of 1-HeOH in BB has decreased which indicates stronger molecular interaction in this system.

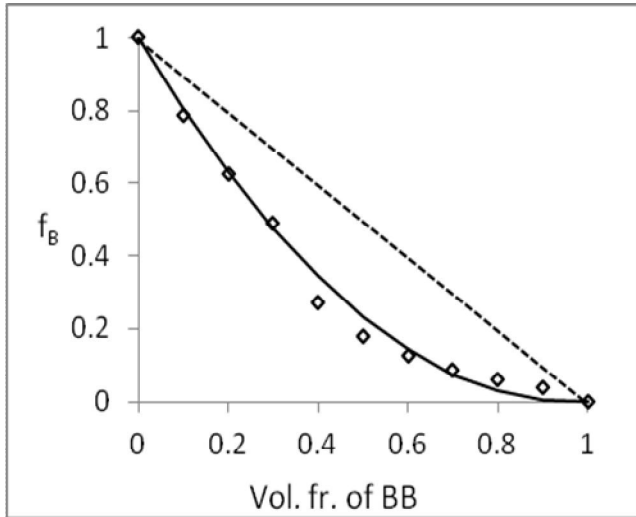


Fig.3: Bruggeman plots for BB + 1-HeOH

In this work measured experimental permittivity data of the BB + 1-HeOH binary mixtures are compared to those estimated by five mixing rules which were proposed by Looyenga[7], Kraszewski et al[8], Lichtenecker-Rother [9], Iglesias-Peon [10] and Bottcher[11], in Table 2.

The Standard deviation or Root Mean Square Deviation (R.M.S.D.) of these models compared to our experimental results are also given in Table-2. This deviation is calculated using equation

$$R.M.S.D. = \left[ \frac{1}{m \sum (\varepsilon_{exp} - \varepsilon_{cal})^2} \right]^{\frac{1}{2}} \quad (7)$$

Here  $m$  is the number of data points.  $\varepsilon_{exp}$  and  $\varepsilon_{cal}$  are experimental and calculated values of relative permittivity, respectively.

Very low values of  $R.M.S.D.$  indicate that relative permittivity values for mixtures are predicted with high accuracy by all models except Iglesias-Peon.

Measured refractive index values of the BB + 1-HeOH binary mixture are also compared with those estimated by four mixing rules which were proposed by Gladstone–

TABLE II

Comparison of the experimental relative permittivities from those estimated by the mixing rules proposed by Looyenga(Lg), Kraszewski(Kz), Iglesias-Peon(I-P), Lichtenecker–Rother(L-R) and Bottcher(B) for binary mixture of BB and 1-HeOH at 303 K temperature.

$X_{BB},$ $\phi_2$	Exp.	Lg	Kz	I-P	L-R	B
0.000	10.38	10.14	10.38	10.38	10.38	10.38
0.131	9.129	9.54	9.79	9.86	9.70	9.78
0.254	8.239	8.97	9.22	9.34	9.07	9.19
0.368	7.527	8.42	8.67	8.80	8.47	8.62
0.476	6.469	7.90	8.14	8.27	7.92	8.07
0.576	6.05	7.39	7.62	7.73	7.40	7.55
0.671	5.812	6.91	7.12	7.20	6.92	7.04
0.760	5.645	6.45	6.63	6.68	6.47	6.56
0.845	5.531	6.01	6.16	6.18	6.04	6.11
0.924	5.444	5.59	5.71	5.71	5.65	5.68
1.000	5.28	5.19	5.28	5.28	5.28	5.28
R.M.S.D.		0.1099	0.0905	1.0853	0.1062	0.0949

TABLE III

Comparison of the experimental refractive index values with those estimated using the mixing rules proposed by Gladstone – Dale (G-D), Newton (Nw), Arago- Biot (A-B), Heller (H) for binary mixture of BB and 1- HeOH at 303 K temperature.

$X_{BB},$ $\phi_2$	Exp.	G-D	Nw	A-B	H
0.000	1.437	1.437	1.437	1.437	1.437
0.131	1.438	1.448	1.449	1.448	1.448
0.254	1.4489	1.459	1.460	1.459	1.459
0.368	1.4581	1.470	1.471	1.470	1.470
0.476	1.4797	1.482	1.483	1.482	1.481
0.576	1.4918	1.493	1.494	1.493	1.492
0.671	1.4985	1.504	1.505	1.504	1.503
0.760	1.5111	1.515	1.516	1.515	1.514
0.845	1.52	1.526	1.527	1.526	1.525
0.924	1.53	1.537	1.538	1.537	1.536
1.000	1.5483	1.548	1.548	1.548	1.547
RMSD		0.0067	0.0073	0.0067	0.0062

Dale(G-D) [12], Newton (Nw) [13], Arago- Biot (A-B) [14] and Heller (H) [15] (Table-3). The Standard deviation or Root Mean Square Deviation (R.M.S.D.) of these models is also calculated and presented in the Table (3). This deviation is calculated using the equation

$$R.M.S.D. = \left[ \frac{1}{m \sum (n_{exp} - n_{cal})^2} \right]^{\frac{1}{2}} \quad (8)$$

Here  $m$  is the number of experimental data points.  $n_{exp}$  and  $n_{cal}$  are experimental and calculated values of refractive index.

The R.M.S.D values of different mixing rules for refractive index suggests that the best predictions are observed for the Heller followed by G-D, A-B and then by Nw.

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