# DIELECTRIC AND THERMODYNAMIC STUDIES ON A BINARY MIXTURE OF ETHYLBROMIDE WITH OLEIC ACID

Indira .T1, Thenappan .T2

<sup>1</sup>Research Scholar, Alagappa University, Chennai, INDIA. <sup>2</sup>Alagappa University, Karaikudi, Chennai, INDIA. Email: <sup>1</sup>indirathangaraj@yahoo.in

#### Abstract

The molecular interaction of ethyl bromide with oleic acid (naturally occurring fatty acid) has been studied using standard dielectric methods. The permittivity at static and optical frequency (the sodium D-line) of a mixture of ethylbromide + Oleic acid was measured at three different temperatures. Kirkwood correlation parameters, the excess permittivity, the Bruggeman parameter and excess free-energy were determined for each concentration of the mixture. A negative value of excess permittivity was obtained for a mixture of ethylbromide and Oleic acid at all studied temperatures. Parallel and anti-parallel alignments of dipoles in the mixture were identified.

Keywords: Permittivity; Oleic Acid; Kirkwood correlation factor, H-Bonding

#### I. INTRODUCTION

Molecular interactions are the key to understanding the structure and properties of liquids. "Static and optical frequency permittivity studies" yield information about the structural properties of liquids through dielectric parameters, such as the effective Kirkwood correlation factor, the corrective Kirkwood correlation factor, excess permittivity, the Bruggeman parameter and excess freeenergy, and data on molecular interactions. Although many dielectric studies have been made on polar and non-polar liquids [1-3], very few have been undertaken on ethylbromide with polar liquids. Over the last few years, there has been some progress in dielectric studies on polar-polar mixtures [4, 5], but not on binary mixture of ethylbromide and Oleic acid. Ethylbromide is an example of an ester formed from an alcohol and an inorganic acid. Since hydrogen bromide is a gas, it is generated actually in the reaction mixture, where it rapidly esterifies without appreciable loss. Oleic acid is naturally occurring straightchain fatty acid, which is generally available in the esterified form in cells and tissues, and are rarely available in free form [6]. Oleic acid is utilized in the commercial production of esters, in perfumery and also in the manufacture of dyes.

## II. MATERIALS AND METHODS

Analar grades ethylbromide and Oleic acid were obtained from SISCO Research Laboratories and distilled before use. The binary mixtures were prepared at 10 different concentrations. The permittivity at static and optical frequency was measured at 1 KHz using the capacity of a condenser filled with liquids via a VLCR-7

Digital capacitance meter (Vasavi Electronics, Secunderabad, India) and an Abbey's refractometer, respectively [7]. The capacitance meter was calibrated using standard liquids of known static permittivity, which was computed from calibrated data [8]. The error in the capacity measurement was ± 1 pf and the uncertainty in the static permittivity value was ± 0.0249. The required temperature measured to within 1°C was maintained by water - circulating thermostat (Ragga Industries, Chennai, India). The dipole moments of the liquids in the gaseous state were taken from the CRC hand book [9] and density was measured using a 10 ml R.D Bottle and a K-Roy microbalance. Errors in density and refractive index measurements were 0.0001 g/cm<sup>3</sup> and 0.0001 respectively. The precision in the mole fraction was 0.0001.

### III. THEORY

The Kirkwood correlation factor (g) is a parameter that supplies information regarding the orientation of the electric dipoles in polar liquids. For pure liquids it is given by[10]:

$$\frac{4\pi N_A 2d}{9kTM}g = \frac{(\varepsilon - \varepsilon_{00})(2\varepsilon + \varepsilon_{00})}{\varepsilon(\varepsilon_{00} + 2)^2}$$
(1)

where  $\mu$  is the dipole moment in the gaseous phase;  $\epsilon$  is the permittivity at static frequency;  $\epsilon_{\infty}$  is the permittivity at optical frequency, which is the squared refractive index corresponding to the sodium D-line; d is the density; k is the Boltzmann constant;  $N_{\text{A}}$  is the Avagadro number;

M is the molecular weight and T is the temperature in Kelvin units. Mehrotra and co-workers [11, 12] modified equation (1) for a binary mixture of polar liquids with some assumptions. Assuming that g<sup>eff</sup> is the effective Kirkwood correlation factor for the mixture; the Kirkwood equation can be expressed as:

$$\frac{4\pi N_A}{9kT} \left( \frac{\mu_A^2 d_A}{M_A} X_A + \frac{\mu_B^2 d_B}{M_B} X_B \right) g^{eff} = \frac{(z_m - z_{00m})(2z_m + z_{00m})}{z_{m(z_{00m} + z)^2}}$$
(2)

Where X is the mole fraction of the liquid and subscripts A and B represent the two liquids.  $g^{\text{eff}} = 1$  indicates the state of no association between like molecules in the liquids, whereas  $g^{\text{eff}} > 1$  refers to the case of dipoles in the mixture with parallel orientation and  $g^{\text{eff}} < 1$  denotes the case of dipoles in the mixture with antiparallel orientation. The value of  $g^{\text{eff}}$  may change from  $g_{\text{A}}$  to  $g_{\text{B}}$  as the mole fraction of liquid B is increased from zero to one.

Assuming that dipole moments of both liquids are affected by the same amount of g' in the mixture (g<sub>r</sub> is known as corrective Kirkwood correlation factor), the Kirkwood equation can be expressed as:

$$\frac{4\pi N_A}{9kT} \left( \frac{\mu_{BgAdA}^2}{M_A} X_A + \frac{\mu_{BgBdB}^2}{M_B} X_B \right) g_f = \frac{(\varepsilon_m - \varepsilon_{\varpi m})(2\varepsilon_m + \varepsilon_{\varpi m})}{\varepsilon_{m(\varepsilon_{\varpi m} + 2)^2}}$$
(3)

The value of g<sub>i</sub> is unity for pure polar liquids and will remain close to unity if there are no interactions. Data related to heterogeneous interactions between the components of a mixture may be obtained from one of the dielectric parameters, namely the excess permittivity, defined as[13]:

$$\varepsilon^{\bar{\varepsilon}} = (\varepsilon - \varepsilon_{z})_{m} - [(\varepsilon - \varepsilon_{z})_{A}X_{A} + (\varepsilon - \varepsilon_{z})_{\bar{\varepsilon}}X_{\bar{\varepsilon}}]$$
 (4)

The excess permittivity provides qualitative information regarding multimer formation in the mixture, as follows:

- (a)  $\epsilon^E$  =0 indicates that there are no interactions between the components in the mixture.
- (b) ε<sup>E</sup> <0 reveals that components in the mixture may form closed multimers leading to fewer effective dipoles owing to interactions between the components.
- (c) ε<sup>E</sup>>0 denotes that components in the mixture interact in such a way that the effective dipole moment is increased. There is a possibility of multimer formation.

The hetero (A-B) interaction between the components of the mixture can also be obtained from the Bruggeman equation [14]. The Bruggeman factor  $f_B$  is related to the volume fraction of one of the components as:

$$f_{B=\left(\frac{\varepsilon_{m}-\varepsilon_{B}}{\varepsilon_{A}-\varepsilon_{B}}\right)\left(\frac{\varepsilon_{A}}{\varepsilon_{m}}\right)^{1/3}=(1-\emptyset_{B})}$$
(5)

In equation (5),  $f_{\scriptscriptstyle B}$  may varey from one to zero as  $\Phi B$  varies from zero to one. If there is no interaction between the components in the mixture, then  $f_{\scriptscriptstyle B}$  should have a linear relationship with  $\Phi_{\scriptscriptstyle B}$ . If there is interaction between the components in the mixture, then equation (5) is modified as [15]:

$$\left(\frac{\varepsilon_{m}-\varepsilon_{B}}{\varepsilon_{A}-\varepsilon_{B}}\right)\left(\frac{\varepsilon_{A}}{\varepsilon_{m}}\right)^{1/3}=1-\left[\alpha-(\alpha-1)\emptyset_{B}\right]\emptyset_{B} \tag{6}$$

Where "a" is the Bruggeman parameter, which gives valuable information about any heterogeneous interaction between the molecules. It is assumed that the volume fraction of the solute in the mixture is modified by a factor of  $[-a(a-1)\Phi_{_B}]$   $\Phi_{_B}.$  This modification of volume may be due to structural rearrangement of the solute molecules in the mixture. Using a least-squares fitting method, the value of 'a' was obtained.

A study of thermodynamic free-energy can also give information on the interaction between the components in the mixture through the breaking mechanism of the H-bonds. The excess free energy due to mixing is given as [16, 17]:

[16, 17]:  

$$\Delta F^{E} = \frac{N_{A}}{2} \left\{ \sum_{r=A,S} X_{r} \mu_{r}^{2} \left( R_{fr} - R_{fr}^{0} \right) + \sum_{r=A,S} X_{r}^{2} \mu_{r}^{2} \left( g_{rr} - 1 \right) \left( R_{fr} - R_{fr}^{0} \right) + X_{A} X_{S} \mu_{A} \mu_{S} \left( g_{AS} - 1 \right) \left( R_{fA} + R_{fS} - R_{fA}^{0} - R_{fS}^{0} \right) \right\}$$

$$\Delta F^{E} = \Delta F_{0}^{E} + \Delta F_{rr}^{E} + \Delta F_{AB}^{E}$$
(7)

Where 
$$R_{fr}^{0} = \left(\frac{8\pi N_{A}}{9V_{r}}\right) \frac{(\varepsilon_{r}-1)(\varepsilon_{\varpi r}+2)}{(2\varepsilon_{r}+\varepsilon_{\varpi r})} \quad \text{and} \quad R_{fr} = \left(\frac{8\pi N_{A}}{9V_{r}}\right) \frac{(\varepsilon_{r}-1)(\varepsilon_{\varpi r}+2)}{(2\varepsilon_{r}+\varepsilon_{\varpi r})}$$

Here V is the molar volume of the components and  $\epsilon_{\infty_\Gamma}$  is the permittivity at optical frequency of the pure liquid, which is the squared refractive index with respect to the sodium D-line. This formula is applicable only for a mixture of liquids. The first term  $\Delta F_0^E$  in equation (7) represents the excess dipolar energy due to long-range electrostatic interaction. The second term  $\Delta F_{rr}^E$  gives the excess dipolar energy due to short-range interaction between identical molecules. The third term  $\Delta F_{AB}^E$  gives the excess free energy due to short-range interaction between dissimilar molecules. The terms  $R_{fr}^0$  and  $R_{fr}$  give the reaction field parameters in the pure liquid and mixture, respectively.

### IV. RESULTS AND DISCUSSION

The permittivity at static and high frequency for various concentrations of Oleic acid + ethylbromide were

measured and the effective Kirkwood correlation factor, corrective Kirkwood correlation factor, excess permittivity, Bruggeman parameter, and other thermodynamic parameters were computed. The values of  $\epsilon, \epsilon \infty$ ,  $g^{\text{eff}}$  and gf are reported in Table-1. The values of excess free-energy are reported in Table-2.

Table 1.Variation in  $\epsilon_{0}$ ,  $\epsilon_{\infty}$ ,  $g^{\text{eff}}$  and  $g_{\text{f}}$ ,  $f_{\text{m}}$ ,  $\epsilon^{\text{E}}$  with mole fraction of oleic acid in Ethylbromide. At 303K

$\mathbf{X}_{B}$	ε,	٤	g <sup>eff</sup>	g <sub>f</sub>	$f_{m}$	εE
0.00	2.35	2.11	0.46	1.01	1.00	0.00
0.09	2.40	2.11	0.27	0.41	0.99	-0.54
0.20	2.60	2.11	0.28	0.38	0.93	-1.05
0.28	2.72	2.10	0.27	0.35	0.90	-1.46
0.38	2.90	2.10	0.27	0.34	0.86	-1.93
0.48	3.10	2.10	0.28	0.34	0.81	-2.38
0.58	3.66	2.09	0.35	0.43	0.69	-2.46
0.69	3.87	2.09	0.34	0.41	0.65	-2.98
0.79	4.88	2.07	0.38	0.55	0.48	-2.60
0.88	4.54	2.05	0.46	0.65	0.43	-2.28
1.00	8.81	2.03	0.84	1.00	0.00	0.00

### At 313K

Хв	ε,	€	g <sup>eff</sup>	g <sub>f</sub>	f <sub>m</sub>	εE
0.00	2.31	2.11	0.39	1.01	1.00	0.00
0.09	2.35	2.11	0.24	0.39	0.99	-0.50
0.20	2.42	2.11	0.19	0.27	0.97	-1.11
0.28	2.51	2.10	0.19	0.26	0.94	-1.50
0.38	2.76	2.10	0.24	0.31	0.87	-1.87
0.48	2.99	2.09	0.26	0.33	0.82	-2.25
0.58	3.17	2.09	0.26	0.33	0.77	-2.69
0.69	3.73	2.09	0.33	0.41	0.65	-2.79
0.79	4.50	2.07	0.42	0.52	0.51	-2.62
0.88	4.25	2.05	0.62	0.72	0.46	-2.43
1.00	8.37	2.03	0.81	1.01	0.00	0.00

#### At 323K

$\chi_{\text{B}}$	ε	ε	geff	g <sub>f</sub>	fm	εE
0.00	2.29	2.11	0.37	0.99	1.00	0.00
0.09	2.31	2.11	0.21	0.34	0.99	-0.49
0.20	2.47	2.10	0.22	0.32	0.94	-0.96
0.28	2.56	2.10	0.22	0.30	0.92	-1.33
0.38	2.67	2.10	0.21	0.29	0.89	-1.79
0.48	2.94	2.09	0.25	0.33	0.81	-2.09
0.58	3.05	2.09	0.24	0.32	0.79	-2.54
0.69	3.12	2.09	0.22	0.29	0.77	-3.10
0.79	4.21	2.07	0.38	0.49	0.54	-2.58
0.88	4.00	2.04	0.45	0.84	0.49	2.38
1.00	7.95	2.03	0.79	1.00	0.00	0.00

Table 2. Variation in  $\Delta F_0^E$ ,  $\Delta F_{ii}^E$ ,  $\Delta F_{AB}^E$ ,  $\Delta F^E$  with mole fraction of oleic acid in Ethylbromide. At 303K

$X_B$	ΔF <sub>0</sub> <sup>E</sup>	ΔFii <sup>E</sup>	$\Delta F_{AB}^{E}$	ΔFE
0.09	165.98	-81.56	-15.27	69.14
0.20	145.91	-63.03	-31.32	51.56
0.28	131.32	-51.06	-41.33	38.94
0.38	113.08	-37.86	-48.91	26.31
0.48	94.84	-26.63	-51.69	16.52
0.58	76.60	-17.37	-43.44	15.79
0.69	56.54	-9.46	-39.53	7.54
0.79	38.30	-4.34	-23.36	10.60
0.88	25.67	-2.09	-17.15	13.45

### At 313K

$\chi_{B}$	$\Delta F_0^E$	ΔFii <sup>E</sup>	ΔF <sub>AB</sub> E	ΔFE
0.09	162.60	-90.26	-15.41	56.93
0.20	142.94	-69.76	-35.98	37.20
0.28	128.65	-56.50	-45.86	26.29
0.38	110.78	-41.90	-50.00	18.88
0.48	92.91	-29.47	-51.38	12.06
0.58	75.04	-19.23	-50.23	5.59
0.69	55.39	-10.47	-38.68	6.24
0.79	37.52	-4.81	-24.53	8.19
0.88	23.45	3.12	18.23	11.18

## At 323K

XB	$\Delta F_0^E$	ΔFii <sup>E</sup>	ΔF <sub>AB</sub> E	$\Delta F^{E}$
0.09	160.82	-92.20	-16.31	52.31
0.20	142.90	-72.02	-33.19	37.69
0.28	137.66	-62.44	-46.13	29.09
0.38	122.69	-47.92	-57.21	17.56
0.48	107.02	-35.06	-58.88	13.08
0.58	93.65	-24.78	-63.95	4.91
0.69	71.13	-13.89	-60.26	-3.02
0.79	48.97	-6.48	-33.93	8.56
0.88	29.14	-5.54	20.27	10.25

A non-liner variation in permittivity with concentration and temperature was found in this system, indicating an interaction between the two liquids in the mixture. Vyas et al. [18] reported that a non-linear relationship of static permittivity with concentration may arise from an association between the solute molecules. Table 1 clearly shows that the non-linear variation in system.

Similar results were reported by Kroeger et al.[19] for a mixture of alcohol-polar liquids. Hence, it may be concluded that a weak hetero interaction exists in system. The value of geff was less than unity for all concentrations and all temperatures, indicating that molecular dipoles have anti-parallel orientation. For the mixtures of acid with Ethylbromide, the value of geff shows a decreasing trend with the increasing concentration of acid in mixtures. It is due to the transition of parallel orientation of the electric dipoles to anti-parallel orientation. Similar results were reported by Chaudhari et al [20] for the mixtures of acid with alcohol.

The value of g<sub>r</sub> depends on the concentration, but the temperature dependence is small. Krishnan et al [21] noticed that the value of g<sub>r</sub> will remain close to unity if there is no interaction between the component molecules. If the value of g<sub>r</sub> is less than unity, the dipoles of both molecules will be oriented in such a way that the effective dipoles will be less than the corresponding average value of the pure liquids. If the value of g<sub>r</sub> is greater than unity, the effective dipole in the mixture will be more than the corresponding average value in the pure liquids. In this mixture, the values of g<sub>r</sub> is less than unity for all concentrations and temperatures, Fig.1. This shows that the interaction between the unlike molecules is weak due to the fact that more acid molecules are in involved in self association [22].

The excess permittivity  $(\epsilon^E)$  also provides information on the interaction between the components in the mixture. Negative values of  $\epsilon^E$  are observed, which indicate that the molecules in the mixture may form multimers through H-bonding in such a way that the number of effective dipoles is reduced [23] .Vyas et al[1] pointed out that the change in the value of  $\epsilon^E$  with concentration is due to the interaction between dissimilar molecules, which may produce a structural change in the system. The variation in  $\epsilon^E$  with concentration of the acid is given in Fig.1. The excess permittivity results are in good agreement with results obtained from the corrective Kirkwood Correlation factor.

The Bruggeman parameter (a) is the dielectric parameters that can provide information on the interaction between components in the mixture in terms of volume changes. In this mixture, the values of 'a' are 3.1667, 3.0210, 2.614 are obtained at temperatures 303K, 313K and 323K respectively. The value of 'a' for all temperatures is positive and greater than unity. Chaudhari et al [24] and Thenappan et al [25] noticed that value of 'a' is positive and greater than unity indicating that the effective volume of the solvent increases as the size of the solute molecule increases.

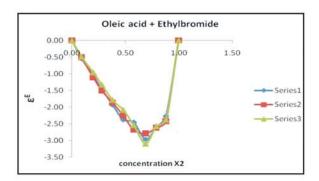


Fig. 1. Plot of excess permittivity Vs mole concentration of Oleic acid at three different temperatures

Our results are in close agreement with the above results. Plot of  $f_{\mbox{\tiny B}}$  Vs concentration of acid for this system is given in Fig 2.

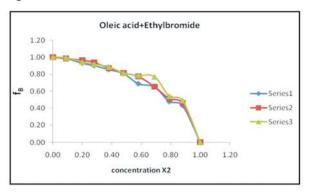


Fig. 2. Plot of Bruggeman factor Vs mole concentration of Oleic acid at three different temperatures.

Information on long and short-range interactions between dipoles can be obtained from studies of thermodynamic parameter such as the excess free energy [26]. The long range interaction between the dipoles in the mixture can be identified [27] from the values of  $\Delta F_0^E$ . Positive values of  $\Delta F_0^E$  indicates the existence of attractive forces between the dipoles. In this system,  $\Delta F_{o}^{E}$ . decreases with the concentration of oleic acid. Values of  $\Delta F_0^E$  supply information on the short-range interaction between similar molecules [28]. Negative values of  $\Delta Fii^E$  are observed which indicates that the formation of H-bonds. Swain et al. [29] reported the formation of micro heterogeneous clusters between dissimilar molecules in an alcohol / alcohol mixture. Increasing values of  $\Delta F_{_{AB}}{^{^{E}}}$  with concentration indicate the formation of β-clusters with anti-parallel alignment. The αcluster is said to have a parallel alignment, while the 1clusters has an anti-parallel alignment. In the present case, the value of  $\Delta F_{AB}^{E}$  shows no appreciable increase or decrease, but varies only slightly with concentration and temperature. This demonstrates that the molecules are not greatly involved in hetero association. Gupta et al. [17] pointed out that negative values of  $\Delta F^{\text{E}}$  indicate the formation of  $\alpha$ -clusters, while positive values of  $\Delta F^{\text{E}}$  reveal the formation of  $\beta$ -clusters with anti-parallel alignment. In this system,  $\Delta F^{\text{E}}$  is positive owing to the larger contribution of long-range interactions and the smaller contribution of short-range interactions between dissimilar molecules.

#### V. CONCLUSION

The dielectric parameters, Kirkwood correlation parameters, the excess permittivity, the Bruggeman parameter and excess free-energy for Oleic acid + Ethylbromide at various concentrations and temperatures of the mixture have been determined. The formation of  $\alpha$  and -clusters in the mixture were identified. Parallel and anti-parallel alignments of dipoles in the mixtures were identified.

## REFERENCES

- [1] A.Ghanadzadeh, H. Ghanadzadeh, R.Sariri, 2005, J.Chem.Thermodyn. 37 357.
- [2] A.Ghanadzadeh and M.S.Beevers, J.Mol.Liq, 2003,102365.
- [3] T. Thenappan, M.Subramanian, 2001, Indian J.Pure Appl. Phys., 39 694.
- [4] V.P.Pawar and S.C.Mehrotra, 2004, J.Mol.Liq. 115-17.
- [5] R.M.Siirke, A.Chaudhari, N.M.More, 2001, J.Mol.Liq. 94 27 (2001)
- [6] T.Thenappan and U.Sankar, 2007, Indian J.pure Appl. Phys. 42 435 (2004).
- [7] T. Thenappan, Studies on fluid structure and molecular interaction of mono alcohols and monolayer's of fatty alcohols, Ph.D. thesis, Alagappa University 1994).
- [8] A.C.Kumbharkhane, S.M.Puranik and S.C.Mehrotra, 1992, J.Mol.Lig. 51 261.
- [9] S.M.Puranik, A.C.Kumbharkhane and S.C.Mehrotra, J.Mol.Liq. 50,143 (1991)

- [10] A.C.Kumbharkhane, S.M.Puranik and S.C.Mehrotra, J.Mol.Liq. 59 173 (1994)
- [11] G. Parthipan and T. Thenappan, J. Mol. Liq. 133 (207) 1.
- [12] K.K. Gupta, A.K. Basal, P.J. Singh, et.al. Indian J. Phys, 79 (2005) 147
- [13] V.A. Rana, A.D. Vyas and S.C. Mehrotra, J. Mol. Liq., 102 379 (2002).
- [14] M.K. Kroeger, J. Mol. Liq.36 101 (1987).
- [15] Ajay Chaudhari, Harish Chaudhari, Suresh Mehrotra, Fluid Phase Equilibria 201 (2002) 107
- [16] D. Balamurugan, S. Kumar and S. Krishnan, J. Mol. Liq., 122 (2005) 11
- [17] G. Parthipan, T.Thenappan, J.Mol.Liq. 138 (2008) 20.
- [18] I.G. Shere, V.P. Pawar, S.C. Mehrotra, J.Mol.Liq. 133 (2007) 116.
- [19] A.Chaudhari, S.Ahire, M.Lokhande, et al., Proc.Natl.Acad.Sci.India A71 75 (2001).
- [20] T.Thenappan and A.Prabakar Devaraj, J. Mol. Liq.12372 (2006).
- [21] G. Parthipan and T. Thenappan, J. Mol. Liq. 133 (207) 1.
- [22] R. Varadarajan, A. Rajagopal and Indian J., Pure Appl. Phys. 36 (1998) 113.
- [23] B.B. Swain, Curr. Sci.54 (1985) 504.
- [24] T. Thenappan and U.Sankar, J. Mol. Liq. 126 (2006) 23.



Indira.T is a research scholar in Alagappa University, Karaikudi. She is pursuing research on "Molecular interaction and fluid structure of Liquid Mixture" in the field "Dielectrics". She has published one paper in the International Journal of Elsevier.