



DIELECTRIC STUDIES ON BINARY SYSTEMS – EFFECTIVE AVERAGE CORRELATION FACTOR AND EXCESS PERMITTIVITY OF ALCOHOLS AND PHTHALATES

Rm. Uma Maheshwari*

Sree Sevugan Annamalai College, Devakottai, Tamilnadu *Corresponding Author

K. Sathish Kumar

Sree Sevugan Annamalai College, Devakottai, Tamilnadu

M.Subramanian

Fatima Michael College of Engg. & Tech., Madurai, Tamilnadu

ABSTRACT The determination of the structure and properties of associated liquids could provide deeper insight into the phenomenon of the molecular interactions and is of great importance in biology and chemical physics. Dielectric constant measurements have been extensively used to obtain the electric dipole moment of molecules with the object of determining the polarities of their bonds, geometrical structures of the molecules and significant shifts of the electric charge in them. Dielectric parameters such as Kirkwood correlation factor, effective correlation factor, corrective correlation factor and thermo dynamical excess parameters for a mixture of diethyl phthalate dioctyl phthalate and octonal were determined at 303 k, 313 k and 323 k.

KEYWORDS :

1. INTRODUCTION

The electric permittivity often called the dielectric constant is a characteristic quantity, which can be easily measured. Dielectric constant measurements have been extensively used to obtain the electric dipole moment of molecules with the object of determining the polarities of their bonds, geometrical structures of the molecules and significant shifts of the electric charge in them. The calculation of molecular dipole moment from the measured dielectric constant of the bulk material depends upon the molecular interactions with their neighbors. The effect of these interactions in bulk can be theoretically traced to the effect of the internal field upon the dipoles.

An electric dipole is a pair of electric charges equals in size but opposite in sign and is very close to each other. The dipole moment is the product of one of the two charges and the distance between them. The system of positive and negative charges formed by the molecules may be treated as a single dipole or as a system of dipoles lying in molecular axis or bonds or groups having a vector sum, which is the molecular dipole moment. When an electric field acts on a molecule, it shifts to form an induced dipole, usually much smaller than the permanent dipole due to structural symmetry of the molecule. The dipole moment values are in the order of debye. Debye had related the dielectric constant and dipole moment with the molar polarization. But Debye's theory could be applied only to gaseous molecules. But Smyth had determined the dipole moment of dilute solutions of non-polar solvents to reduce the effects of internal field in the liquids. Onsager equation related the dipole moment and dielectric constant for pure liquids. But this model was found to be applicable only for non-associative pure liquids.

2. EXPERIMENTAL DETAILS

2.1 STATISTICAL MECHANICAL CONSIDERATIONS OF STATIC DIELECTRIC CONSTANT AND 'g' FACTOR

Consider a macroscopic cavity of volume V containing N molecules. Let E_0 be the mean macroscopic field due to the electric charges outside this volume, then the mean moment $\langle M_E \rangle$ at the volume in the direction of the field is given by

$$\langle M_E \rangle = \frac{\int \dots \int M_E \exp(-U(X_i, E_0) / K T) dx}{\int \dots \int \exp(-U(X_i, E_0) / K T) dx} \quad (1)$$

Where $\langle M_E \rangle$ is the moment associated with the given volume V and E and X_i $U(X_i, E_0)$ is the total potential energy of N particles and X is a set of co-ordinates allowing a complete description of the system. The energy U depends on all the interactions of all the particles with one another and also with the field E_0 , can be written as

$$M = \sum_i \left[\mu_i + \alpha \left(E_0 - \sum_k T_{ik} m_k \right) \right] \quad (2)$$

Here μ_i is the Permanent dipole moment of the isolated molecule.

α is the Polarizability involving both atomic and electronic deformation polarization.

$T_{ik} m_k$ is the tensor product representing the first approximation of the field created by k^{th} molecule in the region of the i^{th} molecule. In case of spherical volume located in its own medium, Onsager cavity field C^i is used

$$C^i = \frac{3\epsilon E_0}{2\epsilon + 1} \quad (3)$$

Since orientation effects and deformation effects could not be separated, a mean effective internal field is defined.

$$\text{Hence, } F = E_0 - \sum_{k \neq i} \langle (T_{ik} \cdot m_k) E \rangle \quad (4)$$

$$\langle M_E \rangle = \sum_i \langle (\mu_i)_E \rangle + \alpha F_i$$

This internal field F is split into the reaction field R and cavity C in the continuum approach of Onsager. R exists even when C is absent. Thus internal moment P comes into discussion, it is the sum of the moment of an isolated molecule and the moment due to the reaction field.

According to Kirkwood, dispersion forces are practically independent of E_0 . The total potential energy U consists of two parts.

$$U = U_1(X) + U_2(X, E_0) \quad (5)$$

Here U_1 is due to dispersion forces and U_2 is due to electrostatic interaction of the dipoles with external field.

$$U_1(X_1, E_0) = U_1(X)$$

$$U_2(X_1, E_0) = \sum_i P_i E_0 \quad (6)$$

P is the internal moment of a set of non-formable molecules in the cavity. P_i is different whenever the sphere contains more than one molecule. When such a number of molecules exceed the particular minimum, P_i will be independent of N , outside the cavity orientation effect of the representation molecule becomes too negligible. These short range-ordering effects could be well studied with the help of 'g' factor. Derivation of P_i is understood on these grounds.

If θ_{ij} represents the angle between the orientation of i^{th} and j^{th} dipole, we can write

$$\langle \mu_i, P_i \rangle = \frac{\mu^2 \sum_{j=1}^N \int \cos \theta_{ij} \exp(-U_j / K T) dx}{\int \exp(-U_2 / K T) dx} \quad (7)$$

Here μ is the dipole moment of the representative molecule in the gaseous state. Defining 'g' as

$$g = \sum_{j=1} \langle \cos \theta_{ij} \rangle = \frac{1}{\mu^2} \int W(X_i) \mu_i P_i dx \quad (8)$$

Where $W(X_i)$ is the statistical weight factor of the i^{th} molecule,

$$\text{Now, } \langle \cos \theta_{ij} \rangle = \frac{\int \cos \theta_{ij} \exp(-U_2 / K T) dx_i dx_j}{\int \exp(-U_2 / K T) dx_i dx_j} \quad (9)$$

Here U_2 is the rotational intermolecular interaction energy of the molecules, dx_i, dx_j are co-ordinates to represent i^{th} and j^{th} molecules.

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon} = \frac{4\pi N_A}{3KT} W(X_i) \mu_i P_i dx \quad (10)$$

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon} = \frac{4\pi N_A}{3KT} g \mu^2 \quad (11)$$

Taking into account the deformation polarization, electronic as well as atomic.

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon} = \frac{4\pi N_A g \mu^2}{3KT V} + \frac{4\pi N_A \alpha}{3V} \quad (12)$$

Attempts to improve on the semi empirical super imposition of the deformation effect on the theory were only of partial success due to difficulty in enunciating boundary conditions. A model in which no such boundary effects need to be considered has been given by Frohlich [1]. He was able to replace the molecules by a set of non-deformable point dipoles of moment P , placed in continuous medium of dielectric constant ϵ . By treating the deformation polarization as a macroscopic phenomenon, he was able to show that this takes care of deformation effects. The moment of the spherical molecule is then

$$P = \left[\frac{\epsilon_\infty + \alpha}{3} \mu \right] \quad (13)$$

Hence one can write

$$\frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{3\epsilon} = \frac{4\pi N_A d}{3KT M} \langle P^1 M^* \rangle \quad (14)$$

Where N_A - Avogadro's number

d - Density of the medium

M - Molecular weight

M^* - Moment of the spherical cavity placed in a continuous dielectric medium with a moment defined by P^1 Therefore,

$$\langle P^1 M^* \rangle = \frac{KT M}{4\pi N_A d} \frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{3\epsilon} \quad (15)$$

If the fundamental unit is the molecule itself, then

$$\langle \mu M^* \rangle = g \mu^2 = \frac{9KT M}{4\pi N_A d} \frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{(\epsilon_\infty + 2)^2} \quad (16)$$

The dimensionless parameter 'g' in this equation reflects the average mutual orientation correlation between the representative dipolar molecule and its neighbors. According to this equation, 'g' is always positive; the phenomenological generalization of Kirkwood formula as given above was further refined by many workers [2-4]. Though they were able to provide the necessary ingredients for a correct microscopic theory, the phenomenological expressions given by the equation (16) completely holds good for polarizable species [5]. It is obvious that 'g' describes something about the orientation ordering of molecules in a liquid through the angular correlation of the neighboring dipoles and hence a measurement of 'g' could give useful information about the local structure of the liquid.

2.2 DIPOLAR EXCESS THERMODYNAMIC FUNCTIONS

In a binary associated mixture, the pure solute component may consist of monomers and their associates; the deviation from ideality in mixtures arises from differences between the intermolecular forces and the molecular sizes of the compounds. Meaningful information concerning the cohesive energy of a system by employing different experimental techniques can be obtained from these measurements of thermodynamic excess function and is found to be more significant since these functions have been utilized to interpret the solution models. The calorimetric or vapor pressure measurements yield the total excess heat. Excess free energy in the mixture consisting of the

components arising due to dipolar, dispersion and short-range forces. It is useful to determine the contribution made by each component individually. This could be achieved by an additive scheme of structural group contributions.

2.3 THERMODYNAMIC EXCESS FUNCTION DUE TO DIPOLAR INTERACTIONS

The energy of a polar molecule in a solution consists of

- i) An interaction energy ($-\mu R$) for a dipole in a field
- ii) An interaction energy ($\frac{1}{2}\mu R$) resulting from polarization of the surrounding molecules and
- iii) An energy ($\frac{1}{2}\alpha R^2$) arising from polarization of the surrounding molecules themselves.

Haskell [6] developed a thermodynamic model that treats explicitly the dipole-dipole and dipole - induced dipole interactions based on Onsager's theory. For a binary mixture, it is possible to develop a suitable partition function and calculate Helmholtz free energy change on mixing due to the dipolar interactions based on Onsager's theory. For a binary mixture, it is possible to develop a suitable partition function and calculate Helmholtz free energy as a function of concentration and temperature.

However the model does not include the effect of dispersion forces and the short-range correlations due to association. Winklemen and Quitsch[7] utilized the concept of correlation in the statistical theory of RamShaw[8], Wortheim's [9] mean spherical model and formulate a thermodynamical equation for the calculation of the dipolar excess thermodynamic functions. This theory includes mutual correlation between like and unlike polar molecules. Davis and Douheret [10] used the four-segment composition model and estimated the dielectric properties of polar liquids. Tripathy and Swain [11], Ray and Roy [12] and Sabesan et al.[13] found that Winklemann and Quitsch expression is the most appropriate one for the study of dipolar excess thermodynamic properties of associated liquids in an inert solvent in the study. We have attempted to calculate the dipolar excess free energy using our values of the linear correction factor 'g'. A survey of literature shows that no such studies have been for the systems which we have taken. The excess Helmholtz free energy of mixing due to the dipolar interaction is given by

$$\Delta F^E = \frac{-N_A}{2} \left[(R_{f2} - R_{f20}) X_2 \mu^2 (1 + X_2 (g - 1)) \right] \quad (17)$$

Where

$$R_{f20} = \frac{8\pi N_A}{9V_2} \frac{(\epsilon_2 - 1)(\epsilon_\infty + 2)}{(2\epsilon_2 + \epsilon_\infty)} \quad \text{and}$$

$$R_{f2} = \frac{8\pi N_A}{9V_2} \frac{(\epsilon - 1)(\epsilon_\infty + 2)}{(2\epsilon + \epsilon_\infty)} \quad (18)$$

The dipolar excess free energy of mixing is positive in the entire concentration range. It is found that at high dilution, the contributions due to long-range interactions are given by the value of ΔF_0^E .

The interaction arising due to short-range interactions are indicated by the value of ΔF_{22}^E .

$$\Delta F_0^E = \frac{-N_A}{2} \left[(R_{f2} - R_{f20}) X_2 \mu^2 \right] \quad (19)$$

$$\Delta F_{22}^E = \frac{-N_A}{2} \left[(R_{f2} - R_{f20}) X_2 \mu^2 (g - 1) \right] \quad (20)$$

$$\Delta F^E = \Delta F_0^E + \Delta F_{22}^E \quad (21)$$

2.4 SCOPE OF THE PRESENT WORK

It is proposed to study the dielectric parameters such as Kirkwood correlation factor, effective correlation factor, corrective correlation factor and thermo dynamical excess parameters for a mixture of the following binary liquids.

- 1) diethyl phthalate + octanol
- 2) dioctyl phthalate + octanol

It is proposed to measure dielectric constant at a static frequency,

refractive index corresponding to sodium D-line and density of the mixture at different concentrations. The solution is prepared for different concentrations in terms of mole fraction. The experiment is carried out at the temperatures 303 K, 313 K and 323K.

2.5 MATERIALS AND METHODS

2.5.1 Purification of Chemicals

i) benzene

The BDH Analar variety of benzene was first treated with anhydrous calcium chloride, filtered and then dried over sodium. Then it was distilled. The liquid collected was redistilled after treating it with phosphorous pentoxide and collected at 80°C.

ii) diethyl phthalate

Aldrich quality of diethyl phthalate obtained from Sisco Research Lab., Mumbai, was used without further purification.

iii) dioctyl phthalate

Aldrich quality of dioctyl phthalate obtained from Sisco Research Lab., Mumbai, was used without further purification.

iv) octanol

Aldrich quality of octanol obtained from Sisco Research Lab., Mumbai, was used without further purification.

2.5.2 DIELECTRIC CONSTANT MEASUREMENTS

The dielectric constant was determined by the measurement of the capacity of a cylindrical cell (with and without liquid) at 1 KHZ by a digital LCR meter (VLCR 7) supplied by Ms. Vasavi Electronics, Secunderabad. The temperature was maintained constant using thermostat supplied by Ms. Raagaa Industries, Chennai. The fluctuation in temperature was $\pm 0.05^\circ\text{C}$. From the readings of VLCR, the dielectric constant was calculated using the calibrated data. The scale of the instrument was calibrated using standard liquids like carbon tetrachloride, benzene, toluene and chlorobenzene.

2.5.3 DIPOLE MOMENT MEASUREMENTS

Various methods are available for the determination of the dipole moment from the solution data.

- (i) Halverstadt and Kumler method
- (ii) Higasi formula
- (iii) Modified Higasi formula
- (iv) Palit and Banarjee method

Let us describe the first method, which is used to determine the dipole moment of the liquids.

Halverstadt and Kumler method:-

Halverstadt and Kumler assumed linear variation of ϵ and the specific volume v with concentration

$$\epsilon = \epsilon_1 + \alpha W_2 \quad (22)$$

$$v = v_1 + \beta w_2 \quad (23)$$

2.6 INTRODUCTION OF EFFECTIVE CORRELATION FACTOR

The Kirkwood correlation factor g is also a parameter affording information regarding orientation of electric dipoles in polar liquids. The Kirkwood correlation factor (g) for the pure liquid is given by the expression.

$$\frac{4\pi N_A \mu^2 \rho}{9KT M} g = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)} \quad (24)$$

where μ the dipole moment in the gas phase. ρ is the density at a temperature T , M is the molecular weight, K is the Boltzmann constant and N_A is the Avogadro's number. The corresponding equation for binary mixture is not available in literature. However, for a mixture of two polar liquids say A and B the equation is modified by Kumbharkhane using some assumptions.

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

$$\frac{4\pi N_A}{9KT} \left(\frac{\mu_A^2 \rho_A}{M_A} X_A + \frac{\mu_B^2 \rho_B}{M_B} X_B \right) g^{\text{eff}} = \frac{(\epsilon_m - \epsilon_\infty)(2\epsilon_{0m} + \epsilon_\infty)}{\epsilon_m(\epsilon_\infty + 2)} \quad (25)$$

Where X_A and X_B are the volume fractions of liquids A and B respectively and g^{eff} is the effective Kirkwood correlation factor for a binary mixture.

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

$$\frac{4\pi N_A}{9KT} \left(\frac{\mu_A^2 \rho_A g_A}{M_A} X_A + \frac{\mu_B^2 \rho_B g_B}{M_B} X_B \right) g_r = \frac{(\epsilon_m - \epsilon_\infty)(2\epsilon_{0m} + \epsilon_\infty)}{\epsilon_m(\epsilon_\infty + 2)} \quad (26)$$

Where g_r is the correlation factor for mixture. The value of g^{eff} in equation will change from g_A to g_B as the fraction of component B increases from zero to unity. In equation (26) g_r is unity for pure liquids and will remain close to unity if there is no interaction between A and B.

2.7 DIELECTRIC PARAMETER RELATED TO MOLECULAR BEHAVIORS

There are different formulae with which one can correlate dielectric parameters with molecular activities in liquid. The correlation between dielectric parameters and molecular interaction as well as the structural changes in mixture can be explored to some extent by using various theories. In the absence of exact theory exploring these quantities, available theories with some assumptions can provide the trend regarding interactions and the structural changes.

3. EXCESS PARAMETER

Studying the excess dielectric properties can access the useful information regarding the structural changes in binary mixture. Let A and B be two molecular systems with measurable macroscopic properties P_A and P_B . If we prepare the mixture of A and B having mole fraction X_A and $X_B = 1 - X_A$, the excess macroscopic property P^E corresponding to mixture is defined as

$$P^E = P_{AB} - (P_A X_A + P_B X_B) \quad (27)$$

where P_{AB} is the measured value of property P for mixture. The value of P^E provides information regarding interaction between A and B. $P^E > 0$ indicates that interaction between A and B leads to increase in the value of property P. Similarly, $P^E < 0$ indicates decrease in macroscopic property P.

In the present work, excess dielectric properties are determined corresponding to static permittivity and molar volume. The excess permittivity (ϵ^E) is defined as

$$\epsilon^E = (\epsilon - \epsilon_\infty)_m - [(\epsilon - \epsilon_\infty)_A X_A + (\epsilon - \epsilon_\infty)_B X_B] \quad (28)$$

where X is the mole fraction and the subscripts m, A and B represent mixture, solvent and solute respectively. The excess permittivity ϵ^E may provide qualitative information about the multimer formation in mixtures as follows.

1. $\epsilon^E = 0$ indicates the liquid A and B do not interact at all.
2. $\epsilon^E < 0$ indicates the liquid A and B interact in such a way that the total effective dipole gets reduced. The liquids A and B may form multimers leading to the less effective dipoles. In general, the negative excess permittivity indicates the formation of multimers in the binary mixtures.
3. $\epsilon^E > 0$ indicates the liquids A and B interact in such a way that the total effective dipole moment increases. There is a tendency to form multimers, dipoles aligned in parallel direction. The excess molar volume may be defined as

$$V^E = V_m - (V_A X_A + V_B X_B) \quad (29)$$

If V^E is positive then it refers to the breaking of H-bonds and hence demolition of multimers. Negative values of V^E refer to the association due to dipole-dipole interaction.

4. Conclusion:

From the Tables, it is found that values of ϵ_m have a non-linear variation with the concentration for all the systems studied. The non-linear

variation of ϵ_0 confirms the presence of the interaction between the unlike molecules. Similar results were reported by Kroeger [14]. Vyas et al. [15] have pointed out that a non-linear variation of dielectric constant with concentration may be due to interaction between the molecules.

For the system diethyl phthalate + octanol, values of g^{eff} vary from g_a to g_b as the concentration of B is increased from 0 to 100 %. As the concentration increases, g^{eff} decreases indicating that more anti parallel orientation is favoured. Similar results were reported by Madhumohan et al. [16]. This shows that addition of alcohol makes the alignment of the dipoles more anti parallel. This may be due to the heterogenous interaction between the unlike molecules. The same trend happens at all temperatures.

For the system, dioctyl phthalate + octanol,, g^{eff} exhibits a steady decreasing tendency as the concentration of alcohol goes on increasing. It favours the anti parallel orientation of the dipoles. This happens when X_b is about 70%. After this, g^{eff} increases indicating that more parallel orientation is favoured. Initially anti parallel orientation is favoured. When the concentration is more than 70%, the molecular dipole orientation is changed from anti parallel to parallel at all temperatures studied [17].

Deviation of g_r from unity indicates the interaction between the components in the mixture. For an ideal non interacting mixture g_r must be unity and the magnitude of the deviation of g_r from unity indicates the magnitude of interaction between the compounds. A greater deviation from unity means a larger strength of interaction [18].

For the system diethyl phthalate + octanol, the strength of the interaction between unlike molecules is maximum when X_b is about 40%. In octanol rich region, deviation of g_r from unity is small compared to phthalate rich region, indicating a weak hetero interaction. When the temperature is increased, the same thing happens at higher concentration. When the temperature is increased, there is no appreciable change in the shift [19].

For the system dioctyl phthalate + octanol, the strength of the interaction between unlike molecules is maximum when X_b is about 40 %. The deviation of g_r from unity is large in phthalate rich region than in the alcohol rich region. This indicates a weak hetero interaction. The same trend repeats at all temperatures. Moreover, value of g_r indicates that, the effective dipoles in the mixture are smaller than the average of those in the pure compounds [20].

The excess permittivity is a dielectric parameter which provides valuable information regarding the interaction between the unlike molecules of the polar-polar liquid mixtures. The change in the value of ϵ^E with concentration is due to the interaction between dissimilar molecules, which may produce structural changes. For all the systems, it is found to vary with X_b .

For the systems diethyl phthalate + octanol and dioctyl phthalate + octanol, the excess permittivity values are negative over the entire range of solute mole fractions at all temperatures studied. The negative value of ϵ^E indicates that the molecules in the mixture form multimers through H-bonding in such a way that the effective dipole moment gets reduced. Our results are in good agreement with those reported by Mehrotra et.al.[21].

The hetero interaction and homo interaction between the components of a liquid mixture can be studied by the determination of excess free energy on mixing. Values of excess free energy (ΔF_0^E) explains the long-range dipole-dipole interaction between the molecules. The short-range interaction due to hydrogen bonding between the solute molecules is reflected by ΔF_{12}^E values. Values of ΔF_0^E suggest the presence of long-range dipole-dipole interaction. The increasing rate of ΔF_0^E with X_2 indicates that the strength on the interaction also increases. This may probably be due to the increasing number of molecules of one component with its increasing concentration. For all the systems studied, values of ΔF_0^E increase with concentration indicating the increase in the strength of the interaction [22].

For the system dioctyl phthalate + octanol, value of ΔF_{12}^E is positive and increases with concentration and is maximum when X_b is about 40%. This shows the breakage of H-bonding [28]. After this, ΔF_{12}^E decreases. This shows the formation of H-bonding. When the temperature is

increased, the shift of breaking of H-bonding into formation of H-bonding takes place at lower concentrations. Conclusion on similar lines has been reported by Thenappan et al. [23].

For the system diethyl phthalate + octanol, value of ΔF_{12}^E is negative and increases with concentration and is maximum when X_b is about 50%. This shows the breakage of H-bonding. After this, ΔF_{12}^E decreases. This shows the formation of H-bonding. When the temperature is increased, the shift of breaking of H-bonding into formation of H-bonding takes place at lower concentrations.

The other dielectric parameter determined in the present study is Bruggeman parameter (f_b), which gives information on the interaction between the components in the mixture. For all the system studied the values are found to vary non – linearly with volume fraction at all temperatures as shown in figures, which indicates that there is an interaction between the components [24].

Table.1 Variation of g^{eff} , g_r , ϵ^E and f_b with X_2 of Diethyl Phthalate + Octanol

Temp K	X_2	E	ϵ_0	g^{eff}	g_r	ϵ^E	f_b
303	0.0	7.3351	2.2180	0.8485	1.0000	0.000	1.0000
	0.1	7.5792	2.1978	0.8233	0.9874	-0.051	0.9074
	0.2	7.8603	2.1739	0.8091	0.9851	-0.061	0.8035
	0.3	8.1416	2.1533	0.7962	0.9822	-0.074	0.7021
	0.4	8.4125	2.1421	0.7800	0.9735	-0.107	0.6069
	0.5	8.7131	2.1188	0.7748	0.9769	-0.098	0.5037
	0.6	9.0151	2.0984	0.7698	0.9796	-0.091	0.4026
	0.7	9.3456	2.0742	0.7705	0.9885	-0.051	0.2946
	0.8	9.6541	2.0432	0.7728	0.9990	-0.026	0.1961
	0.9	9.9396	2.0263	0.7677	0.9990	-0.039	0.1068
1.0	10.2888	2.0215	0.7637	1.0000	0.000	0.0000	
313	0.0	7.3325	2.2186	0.8758	1.0000	0.000	1.0000
	0.1	7.5763	2.1986	0.8497	0.9872	-0.051	0.9075
	0.2	7.8564	2.1762	0.8341	0.9838	-0.064	0.8038
	0.3	8.1401	2.1549	0.8215	0.9817	-0.073	0.7015
	0.4	8.4111	2.1436	0.8049	0.9730	-0.106	0.6063
	0.5	8.6052	2.1206	0.7875	0.9618	-0.204	0.5393
	0.6	8.8531	2.0997	0.7775	0.9583	-0.250	0.4554
	0.7	9.3021	2.0759	0.7907	0.9826	-0.092	0.3074
	0.8	9.5511	2.0449	0.7876	0.9860	-0.127	0.2275
	0.9	9.9224	2.0275	0.7909	0.9969	-0.053	0.1109
1.0	10.2844	2.0215	0.7885	1.0000	0.000	0.0000	
323	0.0	7.3305	2.2192	0.9031	1.0000	0.000	1.0000
	0.1	7.5742	2.1997	0.8759	0.9870	-0.052	0.9075
	0.2	7.8538	2.1772	0.8599	0.9836	-0.065	0.8041
	0.3	8.1389	2.1565	0.8468	0.9813	-0.074	0.7014
	0.4	8.4098	2.1448	0.8299	0.9730	-0.106	0.6061
	0.5	8.6041	2.1219	0.8119	0.9617	-0.204	0.5392
	0.6	8.8511	2.1009	0.8015	0.9581	-0.251	0.4556
	0.7	9.3008	2.0771	0.8153	0.9826	-0.092	0.3074
	0.8	9.5483	2.0464	0.8117	0.9857	-0.129	0.2280
	0.9	9.9208	2.0288	0.8154	0.9968	-0.054	0.1111
1.0	10.2836	2.0227	0.8130	1.0000	0.000	0.0000	

Table.2 :- Variation of Thermo dynamic excess free energies with X_2 of Diethyl Phthalate + Octanol

Temp K	X_2	ΔF_0^E J/mole	ΔF_{22}^E J/ mole	ΔF_{12}^E J/ mole	ΔF^E J/ mole
303	0.1	2450	-54	-381	2015
	0.2	2039	-65	-290	1684
	0.3	1418	-80	-192	1146
	0.4	931	-91	-103	737
	0.5	533	-97	-14	422
	0.6	-26	-73	88	-11
	0.7	-470	-51	176	-345
	0.8	-707	-46	234	-519
	0.9	-960	-25	291	-694
313	0.1	3510	-251	-679	2580
	0.2	2286	-202	-354	1730
	0.3	1496	-183	-203	1110
	0.4	1071	-184	-107	780
	0.5	236	-143	31	124
	0.6	-340	-79	101	-318

	0.7	-560	-75	136	-499
	0.8	-641	-154	203	-592
	0.9	-744	-184	221	-704
323	0.1	4361	-285	1776	2300
	0.2	3189	-212	1187	1790
	0.3	1943	-138	593	1212
	0.4	1247	-82	368	797
	0.5	532	-13	-102	417
	0.6	-37	-82	-60	-179
	0.7	-251	-145	-67	-463
	0.8	-331	-181	-98	-610
	0.9	-698	-230	-195	-733

Table.3 Variation of g^{eff} , g_p , e^E and f_b with X_2 of Diethyl Phthalate + Octanol

Temp K	X_2	E	ϵ_n	g^{eff}	g_p	e^E	f_b
303	0.0	4.8661	2.1747	0.7951	1.0000	0.0000	1.0000
	0.1	4.9327	2.1677	0.6757	0.9192	-0.2446	0.9735
	0.2	5.0186	2.1530	0.5986	0.8641	-0.4622	0.9397
	0.3	5.2880	2.1439	0.5692	0.8607	-0.5018	0.8366
	0.4	5.2977	2.1211	0.5141	0.8071	-0.7876	0.8330
	0.5	5.8171	2.1144	0.5314	0.8603	-0.5796	0.6452
	0.6	5.8866	2.1086	0.4922	0.8176	-0.8225	0.6210
	0.7	6.2174	2.1005	0.4885	0.8294	-0.8018	0.5087
	0.8	6.5941	2.0578	0.5010	0.8669	-0.7006	0.3860
	0.9	7.2610	2.0455	0.5304	0.9330	-0.3396	0.1803
	1.0	7.8826	2.0093	0.5604	0.9999	0.0000	0.0000
313	0.0	8.7848	2.1624	0.8316	0.9999	0.0000	1.0000
	0.1	9.0718	2.1585	0.7207	0.9307	-0.2072	0.9501
	0.2	9.3588	2.1524	0.6361	0.8668	-0.4506	0.9150
	0.3	9.6458	2.1410	0.5790	0.8225	-0.6685	0.8733
	0.4	9.9328	2.1336	0.5335	0.7837	-0.8900	0.8321
	0.5	10.2198	2.1150	0.5150	0.7775	-0.9995	0.7578
	0.6	10.5068	2.1005	0.5003	0.7729	-1.1008	0.6817
	0.7	10.7938	2.0805	0.5019	0.7906	-1.0919	0.5751
	0.8	11.0808	2.0673	0.4957	0.7939	-1.1470	0.4899
	0.9	11.3678	2.0309	0.5539	0.9001	-0.6001	0.2437
	1.0	11.6548	2.0076	0.6076	1.0000	0.0000	0.0000
323	0.0	11.6548	2.1559	0.8859	1.0000	0.0000	1.0000
	0.1	11.6548	2.1506	0.7570	0.9222	-0.2446	0.9660
	0.2	11.6548	2.1497	0.6702	0.8648	-0.4626	0.9212
	0.3	11.6548	2.1407	0.5968	0.8055	-0.7437	0.9027
	0.4	11.6548	2.1246	0.5510	0.7711	-0.9662	0.8660
	0.5	11.6548	2.1092	0.5277	0.7606	-1.0954	0.7974
	0.6	11.6548	2.0973	0.5211	0.7701	-1.1214	0.6950
	0.7	11.6548	2.0745	0.5288	0.7981	-1.0576	0.5716
	0.8	11.6548	2.0693	0.5120	0.7870	-1.1788	0.5046
	0.9	11.6548	2.0315	0.5781	0.9026	-0.5685	0.2368
	1.0	11.6548	2.0011	0.6316	1.0000	0.0000	0.0000

Table.4 :- Variation of Thermo dynamic excess free energies with X_2 of Diethyl Phthalate + Octanol

Temp K	X_2	ΔF_0^E J/mole	ΔF_{22}^E J/ mole	ΔF_{12}^E J/ mole	ΔF^E J/ mole
303	0.1	13718	17	-10	13725
	0.2	10632	2320	-936	12016
	0.3	8911	2796	-156	11551
	0.4	7195	3357	40	10591
	0.5	4027	2873	302	7202
	0.6	3346	2934	184	6463
	0.7	1971	2499	-54	4417
	0.8	769	1893	-467	2195
	0.9	417	861	-148	1130
313	0.1	14168	1563	-1106	14625
	0.2	10702	2781	-555	12928
	0.3	8960	3575	-58	12477
	0.4	7511	4097	165	11773
	0.5	5752	4163	348	10263
	0.6	4153	3915	278	8347
	0.7	2515	3292	14	5821
	0.8	1544	2822	-329	4037
	0.9	2152	1341	-1235	2258
323	0.1	14120	1618	-696	15042
	0.2	10493	2866	-155	13204

	0.3	9209	3802	119	13130
	0.4	7826	4401	342	12569
	0.5	6143	4531	456	11131
	0.6	4205	4113	349	8667
	0.7	3426	3362	15	6803
	0.8	1651	3013	-318	4346
	0.9	3090	1362	-1312	3140

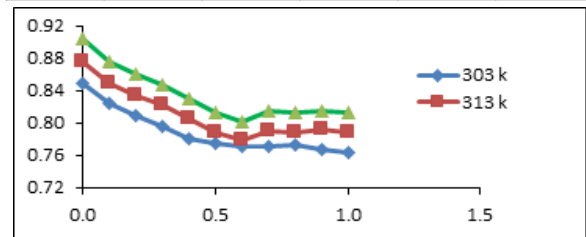


Fig.1 Variation of g^{eff} with X_2 for Diethyl Phthalate + Octanol

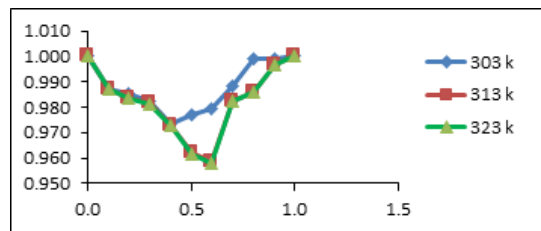


Fig.2 Variation of g with X_2 for Diethyl Phthalate + Octanol

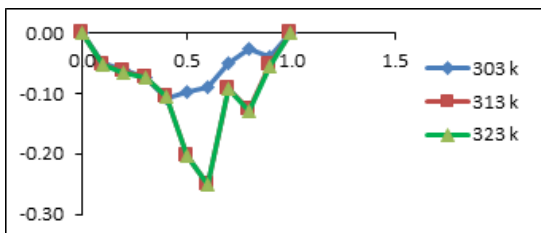


Fig.3 Variation of e^E with X_2 for Diethyl Phthalate + Octanol

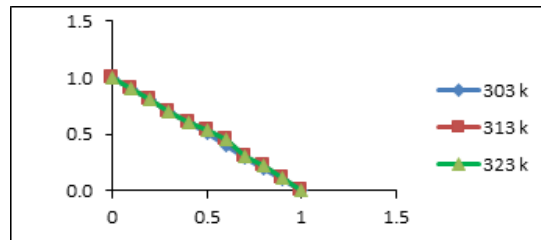


Fig.4 Variation of f_b with X_2 for Diethyl Phthalate + Octanol

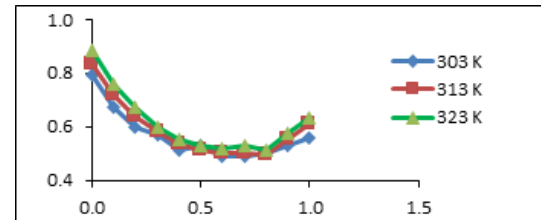


Fig.5 Variation of g^{eff} with X_2 for Diethyl Phthalate + Octanol

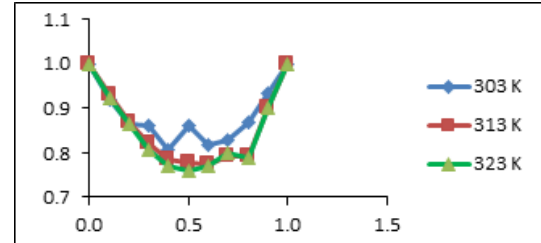


Fig.6 Variation of g with X_2 for Diethyl Phthalate + Octanol

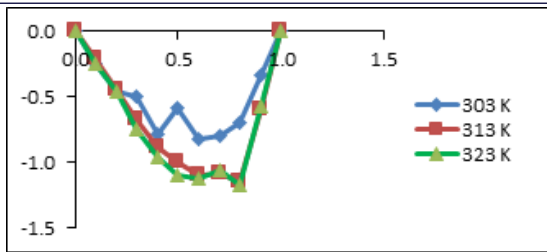


Fig.7 Variation of ϵ' with X_2 for Diocetyl Phthalate + Octanol

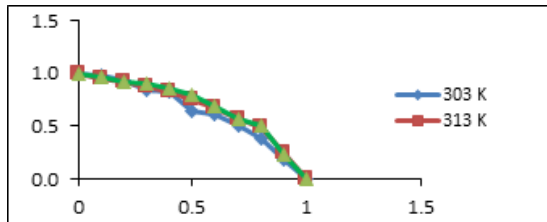


Fig.8 Variation of f_b with X_2 for Diocetyl Phthalate + Octanol

5. REFERENCES:

1. Frohlich H, Theory of Dielectrics Clarendon Press, Oxford, 1958.
2. Hoye, J S and Stell, G J Chem Phys, 65 (1976) 18.
3. Ramshaw, J D, J Chem Phys, 64 (1976) 11.
4. Werthim, M S, J Mol Phys, 33(1977)95.
5. Bordewijk, P, J Chem Phys, 33 (1978) 451.
6. Hasekell, R W, J Phys Chem, 73 (1969) 2916.
7. Winkleman, J and Quitzsch, K, J Phys Chem, 257 (1976) 45.
8. Ramshaw, J D, J Che Phys, 57 (1972) 2684.
9. Werthim, M S, J Mol Phys, 26(1973)1425.
10. Davis, M I and Douheret, G, Thermo Chemica Acta, 104 (1986) 203.
11. Tripathy, S and Swain, B B, Chem Paper, 45 (1991) 321.
12. Ray, S K and Roy, G S, Proc Indian Nati Sci Acad, 59 (1993) 205.
13. Sabesan, R, Thiagarajan, V and Srinivasan, S, Acta Chim Hungarica, 127 (1990) 149.
14. Kroeger, M K, J Mol Liqs, 36(1987) 101.
15. Vyas, A D, Rana, V A, J Mol Liqs, 103(2002) 379.
16. Madhu Mohan, T, Sreehari Sastry, S, and Murthy, V R K, Ind J of Pure and Appl Phy, 48 (2010) 668-675.
17. Liakath Ali Khan, F, Sivagurunathan, P, Raja Mohamed Kamil, S, and Mehrotra, S C, Ind J Pure and Appl Phys, 45 (2007) 754-758.
18. Chaudhari, A, Anita, D, Raju, G, Chaudhari, H, Prakash, K, Navinkumar, N, Suresh, M, Proc Nat Sci Counc, Roc, A25 (2001) 205-210.
19. Prathima, A, Karthikeyan, S, Prabhakaran, M, and Thenappan, T, Int J Phar Sc and Res, 4 (2013) 2753-2760.
20. Pawar, V P, Patil, A R, Mehrotra, S C, J Mol Liq, 122 (2005) 88-93.
21. Hosamani, M T, Fattepur, R H, Dhaspande, D K, Mehrotra, S C, J. Chem Soc Faraday Tran, 91(4)(1995)623.
22. Varadarajan, R, and Rajagopal, A, Ind J Pure and Appl Phys, 36 (1998) 113-118.
23. Thenappan, T and Sankar, U, J Mol Liqs, 126 (2006), 38-42.
24. Sivagurunathan, P, Dharmalingam, K, Ramachandran, K, Prabhakar, U B, Khirade, P W and Mehrotra, S C, J Mol Liq 133 (2007) 139-145