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STUDIES ON STRUCTURAL PROPERTIES OF THE BINARY MIXTURES OF PHARMACEUTICAL INTERMEDIATES THROUGH DIELECTRIC INVESTIGATIONS

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ABSTRACT: The homo and hetero interaction in the binary mixtures of Ethyl acetate + n-Butylamine, Ethyl acetate + Cyclohexylamine and Ethyl acetate + Diethylamine has been investigated through the orientation of dipoles using dielectric polarization method. The dielectric and thermodynamic parameters such as Kirkwood correlation factor, Excess permittivity, Bruggemann factor and Dipolar excess free energy for the above systems have been calculated from the experimentally measured values of capacitance and refractive index of solutions, at temperatures 303K, 313K and 323K.In all the studied systems, the dielectric parameters obtained show systematic change in the molecular structure with the concentration of amine in the solution. It indicates that the β-multimer formation due to the presence of hetero interaction between the components of above mixtures.

INTRODUCTION: The pharmaceutical sciences are a group of interdisciplinary areas of study concerned with the design, action, delivery, disposition, inorganic, physical, biochemical and analytical biology, epidemiology, statistics, chemometrics, mathematics, physics and chemical engineering, and apply their principles to the study of drugs. Compounds used as medicines are most often mixture of organic compounds. Therefore it is seemed important to examine the molecular interaction studies on the mixture of organic liquids [1]. Dielectric studies are of great help in the assignment of the molecular structure or configurations, particularly those of organic compounds [2].

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In this study, Ethyl acetate has been used as a solvent and *n*-Butyl amine, Cyclohexylamine and Diethyl amine as solute. Ethyl acetate is a moderately polar solvent that has the advantage of being volatile, relatively non-toxic, and non-hygroscopic. It is a weak hydrogen bond acceptor, and is not a donor due to the lack of an acidic proton. In the pharmaceutical industry it is an important component in extractants for the concentration and purification of antibiotics. It is also used as an intermediate in the manufacture of various drugs. And amines are used in the production of pesticides, pharmaceuticals, rubber chemicals, emulsifiers [3] and also used as an intermediate in synthesis of other organic compounds [1]. A survey of literature shows that a few workers [4-5] have tried to investigate some binary systems taking amines as one of the constituent components in the binary mixtures. The objective of this paper is to investigate the molecular interaction between amine and ester molecules through dielectric study of the above systems at temperatures 303K, 313K and 323K.It makes one to understand the solute-solvent interaction and liquid structure [6].

THEORY: The determination of the structure and properties of associated liquids could provide deeper insight into the phenomena of the molecular interactions and is of great importance in Biology and Chemical Physics. The IR and NMR spectroscopic methods were extensively used for determining the nature of association. However, these methods could give only circumlocutory information regarding the alignment of neighboring molecules. This vital information could be obtained from dielectric measurements by virtue of its influence on the correlation between the permanent dipole moments in such a molecule. There are various mixture formulae with which one can correlate dielectric parameters with molecular activities in liquid.

The Kirkwood model: The Kirkwood correlation factor is a measure of the short- range interaction between the components in the liquid mixtures. For pure liquids and liquid mixtures, it can be described by the following expression[7-10]

$$\frac{4\pi N\mu^2\rho}{9kTM}g=\frac{(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty+2)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$\frac{4\pi N}{9kT}\left(\frac{\mu_A{}^2\rho_A}{M_A}X_A+\frac{\mu_B{}^2\rho_B}{M_B}X_B\right)g^{eff}=\frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \quad \ldots(2)$$

$$\frac{4\pi N}{9kT}\left(\frac{\mu_A{}^2\rho_A g_A}{M_A}X_A+\frac{\mu_B{}^2\rho_B g_B}{M_B}X_B\right)g_f=\frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \quad \ldots.(3)$$

Where μ is the dipole moment in the gas phase, ρ is the density at temperature T, M is the molecular weight, k is the Boltzmann constant, N is the Avogadro's number, ε_o is the static permittivity and ε_∞ is the static permittivity at high frequency, often represented by the square of refractive index corresponding to sodium D-line. X is the volume fraction and suffices m, A and B represents mixture, liquid A and liquid B respectively.

The departure of Kirkwood correlation factor from unity is an indication for the molecular association. It means that if g >1 indicates the parallel orientation among the dipoles, g < 1 indicates the anti - parallel orientation among the dipoles and g = 1 represents an equilibrium between the multimers or non – association among the dipoles.

Excess permittivity (ε^E): The excess static permittivity is used to explain the formation of mutimers in the mixture[11-12]. It is defined as,

$$\varepsilon^E=(\varepsilon_{0m}-\varepsilon_{\infty m})-\left[(\varepsilon_{0A}-\varepsilon_{\infty A})\ X_A+(\varepsilon_{0B}-\varepsilon_{\infty B})\ X_B\right] \quad \ldots(4)$$

The excess permittivity provides qualitative information about multimer formation in the mixture as given below. If

ε^E = 0 indicates that there is no interaction between the unlike molecules.

ε^E < 0 indicates the interaction between the molecules in such a way that the effective dipoles get reduced. The two liquids mix in such way that the mixture may form multimers leading to the less effective dipoles.

ε^E > 0 indicates that the two liquids interact in such a way that the effective dipoles increase. This may be due to the formation of monomers and dimers.

Bruggeman factor (f_B): The Bruggeman factor is another parameter which may be used as an indicator of hetero interaction. The Bruggeman factor f_B is given by[13],

$$f_B=\left[\frac{\varepsilon_{0m}-\varepsilon_{0B}}{\varepsilon_{0A}-\varepsilon_{0B}}\right]\left[\frac{\varepsilon_{0A}}{\varepsilon_{0m}}\right]^{1/3}=(1-X_B) \quad \ldots\ldots\ldots\ldots\ldots..(5)$$

From equation (5), a linear relationship is expected when plotted f_B against X_B. Any deviation from this linear relation indicates molecular interactions. It is practically observed that in our experimental data for binary mixtures do not fit well with equation (5).To fit the experimental data, the equation (5) has been modified

$$f_B=1-\left[a-(a-1)X_B\right]X_B \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(6)$$

Where *a* is a numerical fitting parameter known as Bruggeman parameter. The value of *a* contain information regarding the nature of interaction between solute and solvent, as follows.

a > 1 indicates that the effective microscopic volume of solvent gets more than actual volume. The solute exerts a repulsive force in the system.

a < 1 indicates that the effective microscopic volume of solvent gets less than actual volume.

The solvent exerts an attractive macroscopic force in the system.

a = 1 indicates no change in effective microscopic volume of the system and corresponds to the ideal Bruggeman mixture factor.

Dipolar excess free energy (ΔF^E): The excess Helmholtz free energy of mixing ΔF^E is given by [14],

$$\Delta F^E = \frac{-N}{2}\left[\sum_{r=A,B}\mu_r^2 X_r\left(R_{fr}-R_{fr0}\right)+\sum_{r=A,B}\mu_r^2 X^2{}_r\left(g_{rr}-1\right)\left(R_{fr}-R_{fr0}\right)+X_A X_B\mu_A\mu_B\left(g_{AB}-1\right)\left(R_{fA}+R_{fB}-R_{fA0}-R_{fB0}\right)\right] = \Delta F_0{}^E+\Delta F_{rr}{}^E+\Delta F_{AB}{}^E \quad \text{.....(7)}$$

This 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 and

The third term $\Delta F_{AB}{}^E$ gives the excess dipolar energy due to short-range interaction between dissimilar molecules.

The term R_{fro} and R_{fr} which give the reaction field parameters in the pure liquid and in the mixture, are given by,

$$R_{fro} = \frac{8\pi N}{9Vr}\frac{(\varepsilon_r-1)(\varepsilon_{\infty r}+2)}{(2\varepsilon_r+\varepsilon_{\infty r})}$$

$$R_{fr} = \frac{8\pi N}{9Vr}\frac{(\varepsilon_r-1)(\varepsilon_{\infty r}+2)}{(2\varepsilon_{0m}+\varepsilon_{\infty r})}$$

It gives excess thermodynamic functions in binary mixtures that take into account the contribution due to both short-range and long-range dipolar interactions between both like and unlike molecules is adopted for polar-nonpolar mixtures.

MATERIALS AND METHODS: Compounds used in the present study were of AR grade and were all procured from SRL, India. The static permittivity ε_{om} at 1 KHz was measured using a digital VLCR-7 meter supplied by M/S Vasavi electronics, India, after calibrating it for standard liquids like carbon tetrachloride, benzene, toluene and chlorobenzene.

The permittivity at optical frequency $\varepsilon_{\infty m}$ was obtained by squaring the refractive Index for sodium D-line, which was measured with the help of an Abbe's refractometer. The uncertainties in static permittivity, refractive index and density were ±0.0005, ±0.0002 and ±0.0001 g/cc respectively.

All measurements were made at 303±1K, 313±1K, and 323±1K using a water circulating thermostat arrangement.

RESULTS AND DISCUSSION: The dielectric and thermodynamic parameters such as static permittivity (ε_{om}), the static permittivity at high frequency ($\varepsilon_{\infty m}$), often represented by the square of refractive index corresponding to sodium D-line, Kirkwood correlation factor (g), Excess permittivity (ε^E), Bruggemann factor (f_B) and Dipolar excess free energy (ΔF^E) for the above systems are listed in tables 1-3 at temperatures 303K, 313K and 323K.

The value of ε^E is negative for the Ethyl acetate + *n*-Butyl amine system for all temperatures except Ethyl acetate + Cyclohexylamine and Ethyl acetate + Diethyl amine systems. In the case of Ethyl acetate + Cyclohexylamine and Ethyl acetate + Diethyl amine systems, ε^E was found to be positive in the amine-rich region. The negative excess permittivity value indicates the formation of multimer structure, which leads to a decrease in the total number of dipoles in the system whereas the positive value indicates formation of monomeric or polymeric structure, which increases the total number of dipoles in the system [6]. This change in structure occurs due to the interaction between the components of the mixture.

In all the systems, the g^{eff} value increases with the increase in concentration of amine in the solution. For pure Ethyl acetate, $g^{eff}<1$, indicates the anti-parallel orientation of dipoles. The g^{eff} values increase above unity in amine rich region indicating the parallel alignment of dipoles in this region. This indicates that intermolecular interaction between Ethyl acetate and amine increases with increase in the number of amine molecules in the solution. Similar behavior is observed at all temperatures for other amines used in this study. Thenappan *et al.*, [15] have concluded on similar lines for the mixture of ester and acid.

The interaction between the unlike molecules produces an electric field which makes the dipoles to have parallel orientations [16]. In all mixtures studied, the value of g_f is less than unity for all concentrations and temperatures. This may indicate the presence of a weak interaction between acetate and amine molecules [6].

The value of Bruggeman parameter is also nearly unity and do not vary much from unity. This also shows that the strength of the interaction between the components for all the systems is feeble and the Bruggeman parameters are listed in **table 4**. It also indicates the strength of the interaction is very small between the component molecules. Value of *a* is in the order of Cyclohexylamine > *n*-Butyl amine > Diethyl amine for the system with Ethyl acetate. The excess free energy ΔF^E for mixtures due to long range interaction ΔF_0^E, short range interaction between identical molecules ΔF_{rr}^E and short range interaction between dissimilar molecules ΔF_{AB}^E are reported in **tables 1 to 3** and the plots of ΔF_{rr}^E for the studied systems are shown in **figures 1 to 3**.

In all the systems, for all the three studied temperatures, values of ΔF_0^E, is positive indicating the existence of the long-range dipole-dipole interaction. The variation in the magnitude of ΔF_0^E value with concentration of one of the components and temperatures implies that the variation in the strength of the hetero interaction [17]. For all the systems at all the three studied temperatures, ΔF_{rr}^E value is negative. This indicates that the existence of short-range interaction between the amine molecules. Conclusion on similar lines has been reported by Thenappan *et al* [18].

The magnitude of ΔF_{rr}^E suggests that the strength of the interaction is weak. Negative value of ΔF_{rr}^E shows the structure making property of the amine molecules. Similar views have been expressed by Thenappan *et al* [19-20]. The magnitude of ΔF_{AB}^E indicates the existence of a weak hetero interaction between the components in the mixtures. Values of ΔF^E for all the systems at all the three studied temperatures are positive, which implies the formation of β-multimers with anti-parallel orientation. The electric field created inside the mixture is such that it favors anti-parallel alignment between the dipoles. Similar views have been expressed by Gupta *et al* [4].

TABLE 1: VALUES OF ε_{0m} , $\varepsilon_{\infty m}$, g^{eff},g_f ,ε^E, f_B, ΔF_0^E, ΔF_{rr}^E, ΔF_{AB}^E AND ΔF^E OF BINARY MIXTURES OF ETHYL ACETATE WITH *n*-BUTYL AMINE AS A FUNCTION OF MOLE FRACTION AT 303K, 313K AND 323K

T/K	X_2	ε_{0m}	$\varepsilon_{\infty m}$	g^{eff}	g_f	ε^E	f_B	ΔF_0^E /Jmole^{-1}	ΔF_{rr}^E /Jmole^{-1}	ΔF_{AB}^E /Jmole^{-1}	ΔF^E /Jmole^{-1}
	0.00	6.1790	1.8662	0.9824	1.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
	0.10	5.9630	1.8720	1.0041	0.9870	-0.0603	0.8699	18.4395	-1.1175	0.1267	17.4486
	0.20	5.8010	1.8777	1.0410	0.9865	-0.0619	0.7704	28.1803	-3.1068	0.1793	25.2528
	0.30	5.6660	1.8838	1.0945	0.9898	-0.0461	0.6862	32.2032	-5.8412	0.1322	26.4941
	0.40	5.5310	1.8895	1.1570	0.9950	-0.0253	0.6007	34.3322	-8.8292	0.0471	25.5501
303	0.50	5.3960	1.8970	1.2316	0.9996	-0.0063	0.5139	34.2432	-11.6720	0.0016	22.5728
	0.60	5.1800	1.9102	1.2900	0.9787	-0.0740	0.3721	39.7625	-12.3205	-0.1204	27.3216
	0.70	4.9910	1.9160	1.3837	0.9693	-0.1074	0.2449	39.1776	-11.1544	-0.3904	27.6329
	0.80	4.8830	1.9218	1.5452	0.9831	-0.0597	0.1708	28.0697	-10.1512	-0.2234	17.6951
	0.90	4.7750	1.9335	1.7596	0.9941	-0.0179	0.0956	14.4911	-7.2101	-0.0565	7.2245
	1.00	4.6400	1.9421	2.0606	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.00	6.1250	1.8635	1.0052	1.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
	0.10	5.8820	1.8692	1.0206	0.9800	-0.0903	0.8507	22.3025	-0.6043	0.1839	21.8821
	0.20	5.7200	1.8725	1.0591	0.9801	-0.0926	0.7490	32.2634	-2.4139	0.2439	30.0934
	0.30	5.6120	1.8807	1.1184	0.9873	-0.0551	0.6803	33.1913	-5.2726	0.1590	28.0777
	0.40	5.4770	1.8846	1.1834	0.9929	-0.0355	0.5931	35.5291	-8.3882	0.0627	27.2036
313	0.50	5.3420	1.8953	1.2561	0.9941	-0.0228	0.5046	35.6169	-11.3785	0.0194	24.2579
	0.60	5.0990	1.9011	1.3117	0.9698	-0.1132	0.3417	44.1571	-11.3792	-0.2335	32.5443
	0.70	4.9100	1.9113	1.4004	0.9555	-0.1541	0.2115	43.5849	-9.7912	-0.6563	33.1375
	0.80	4.8290	1.9160	1.5770	0.9765	-0.0814	0.1546	29.8972	-9.4729	-0.3270	20.0973
	0.90	4.7480	1.9304	1.8065	0.9925	-0.0184	0.0972	14.2598	-7.6218	-0.0709	6.5672
	1.00	4.6130	1.9354	2.1206	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

	0.00	6.0440	1.8531	1.0267	1.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
	0.10	5.8280	1.8561	1.0498	0.9869	-0.0652	0.8622	19.5583	-0.1399	0.1213	19.5398
	0.20	5.6930	1.8589	1.0964	0.9931	-0.0445	0.7746	26.7578	-1.9143	0.0896	24.9330
	0.30	5.5310	1.8706	1.1396	0.9844	-0.0690	0.6676	34.8185	-4.5427	0.1799	30.4557
	0.40	5.4230	1.8780	1.2103	0.9935	-0.0305	0.5952	34.4699	-7.9292	0.0573	26.5980
323	0.50	5.3150	1.8895	1.2924	1.0004	0.0038	0.5219	32.2017	-11.4484	-0.0018	20.7515
	0.60	5.0180	1.8939	1.3297	0.9614	-0.1438	0.3153	47.1076	-10.2188	-0.3618	36.5270
	0.70	4.8290	1.9069	1.4148	0.9435	-0.1919	0.1796	46.9236	-8.1473	-0.9240	37.8523
	0.80	4.7480	1.9130	1.5904	0.9623	-0.1251	0.1204	33.3045	-7.3795	-0.5747	25.3504
	0.90	4.6130	1.9246	1.7919	0.9616	-0.1179	0.0203	21.8630	-1.5795	-0.4336	19.8499
	1.00	4.5860	1.9335	2.1718	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

TABLE 2: VALUES OF ε_{0m}, $\varepsilon_{\infty m}$, g^{eff}, g_f, ε^E, f_B, ΔF_0^E, ΔF_{rr}^E, ΔF_{AB}^E AND ΔF^E OF BINARY MIXTURES OF ETHYL ACETATE WITH CYCLOHEXYLAMINE AS A FUNCTION OF MOLE FRACTION AT 303K, 313K AND 323K

T/K	X_2	ε_{0m}	$\varepsilon_{\infty m}$	g^{eff}	g_f	ε^E	f_B	ΔF_0^E /Jmole^{-1}	ΔF_{rr}^E /Jmole^{-1}	ΔF_{AB}^E /Jmole^{-1}	ΔF^E /Jmole^{-1}
	0.00	6.1790	1.8662	0.9824	1.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
	0.10	5.8550	1.8777	0.9675	0.9661	-0.1620	0.8110	28.3359	-0.9218	0.3419	27.7560
	0.20	5.7200	1.9102	0.9757	0.9634	-0.1363	0.7304	31.9740	-1.7725	0.4860	30.6875
	0.30	5.6120	1.9332	1.0026	0.9723	-0.0840	0.6651	30.2507	-2.8988	0.3603	27.7122
	0.40	5.4230	1.9569	1.0128	0.9622	-0.1134	0.5488	36.9772	-4.0041	0.2117	33.1848
303	0.50	5.2340	1.9718	1.0325	0.9583	-0.1339	0.4299	41.7605	-4.7530	-0.1828	36.8247
	0.60	5.0720	1.9985	1.0554	0.9535	-0.1393	0.3258	41.2257	-5.0652	-0.6090	35.5515
	0.70	4.9100	2.0195	1.0893	0.9536	-0.1390	0.2196	38.5219	-4.5963	-0.9127	33.0129
	0.80	4.8290	2.0343	1.1677	0.9849	-0.0514	0.1656	24.7445	-4.4068	-0.2751	20.0627
	0.90	4.7210	2.0701	1.2347	0.9958	-0.0119	0.0927	12.1338	-3.0915	-0.0538	8.9884
	1.00	4.5860	2.1066	1.3100	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.00	6.1250	1.8635	1.0052	1.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
	0.10	5.8010	1.8728	0.9905	0.9662	-0.1634	0.8076	29.0247	-0.1794	0.3344	29.1797
	0.20	5.6660	1.8780	1.0177	0.9810	-0.1141	0.7255	32.9713	-1.0027	0.2440	32.2125
	0.30	5.5040	1.8923	1.0380	0.9821	-0.1107	0.6253	38.3260	-2.1620	0.1813	36.3454
	0.40	5.3690	1.9160	1.0623	0.9840	-0.0898	0.5405	38.5764	-3.5056	0.0769	35.1477
313	0.50	5.1530	1.9421	1.0657	0.9635	-0.1522	0.4018	47.0204	-4.2095	-0.2525	42.5584
	0.60	4.9910	1.9572	1.0979	0.9653	-0.1496	0.2953	46.6474	-4.5843	-0.5461	41.5170
	0.70	4.8830	1.9805	1.1495	0.9783	-0.1012	0.2231	37.8190	-4.8239	-0.4201	32.5749
	0.80	4.7750	1.9836	1.2328	1.0096	-0.0326	0.1499	27.1747	-4.3138	0.1841	23.0450
	0.90	4.6940	2.0133	1.3214	1.0334	0.0364	0.0942	11.9045	-3.4840	0.4233	8.8438
	1.00	4.5590	2.0944	1.3532	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.00	6.0440	1.8531	1.0267	1.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
	0.10	5.7740	1.8643	1.0218	0.9749	-0.1176	0.8340	22.9138	0.3678	0.2599	23.5415
	0.20	5.6390	1.8722	1.0477	0.9868	-0.0775	0.7493	27.5619	-0.4390	0.1801	27.3030
	0.30	5.4230	1.8865	1.0538	0.9730	-0.1345	0.6110	40.6352	-1.4489	0.2368	39.4231
	0.40	5.3150	1.9069	1.0880	0.9822	-0.0895	0.5405	37.9941	-3.1260	0.0809	34.9490
323	0.50	5.0990	1.9335	1.0900	0.9591	-0.1588	0.3969	47.1609	-3.9041	-0.2994	42.9573
	0.60	4.9370	1.9421	1.1276	0.9634	-0.1562	0.2865	47.3954	-4.3955	-0.5960	42.4039
	0.70	4.8020	1.9480	1.1857	0.9787	-0.1237	0.1928	42.2021	-4.2869	-0.4533	37.4620
	0.80	4.7210	1.9614	1.2718	1.0081	-0.0448	0.1357	28.8750	-4.1853	0.1589	24.8486
	0.90	4.6400	1.9836	1.3707	1.0350	0.0253	0.0780	13.9980	-3.1752	0.4532	11.2760
	1.00	4.5320	2.0742	1.4054	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

TABLE 3: VALUES OF ε_{0m}, $\varepsilon_{\infty m}$, g^{eff}, g_f, ε^E, f_B, ΔF_0^E, ΔF_{rr}^E, ΔF_{AB}^E AND ΔF^E OF BINARY MIXTURES OF ETHYL ACETATE WITH DIETHYL AMINE AS A FUNCTION OF MOLE FRACTION AT 303K, 313K AND 323K

T/K	X_2	ε_{0m}	$\varepsilon_{\infty m}$	g^{eff}	g_f	ε^E	f_B	ΔF_0^E /Jmole^{-1}	ΔF_{rr}^E /Jmole^{-1}	ΔF_{AB}^E /Jmole^{-1}	ΔF^E /Jmole^{-1}
303	0.00	6.1790	1.8662	0.9824	1.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
	0.10	5.7740	1.8698	0.9580	0.9634	-0.1670	0.8485	34.4513	-1.1921	0.6569	33.9160
	0.20	5.6660	1.8722	1.0015	0.9934	-0.0359	0.8071	28.4174	-2.4103	0.1915	26.1986
	0.30	5.4230	1.8744	1.0143	0.9953	-0.0326	0.7121	38.4671	-4.1531	0.1336	34.4476
	0.40	5.2340	1.8783	1.0516	1.0051	0.0051	0.6365	36.9767	-6.2722	-0.1222	30.5823
	0.50	5.1530	1.8813	1.1222	1.0534	0.1667	0.6036	21.9537	-8.6587	-1.1118	12.1832
	0.60	4.9100	1.8893	1.1493	1.0534	0.1586	0.5030	23.1353	-10.3590	-0.4002	12.3762
	0.70	4.6130	1.8912	1.1665	1.0407	0.1042	0.3758	27.2503	-10.6555	0.3317	16.9265
	0.80	4.1270	1.8945	1.1012	0.9518	-0.1393	0.1560	49.6564	-6.1056	-1.3377	42.2130
	0.90	3.9650	1.9025	1.1808	0.9723	-0.0704	0.0790	27.4020	-3.9091	-0.5643	22.9285
	1.00	3.8030	1.9058	1.2992	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
313	0.00	6.1250	1.8635	1.0052	1.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
	0.10	5.7470	1.8591	0.9908	0.9735	-0.1356	0.8571	31.6095	-0.2686	0.4839	31.8248
	0.20	5.6120	1.8616	1.0290	0.9968	-0.0350	0.8047	29.3669	-1.6014	0.0924	27.8580
	0.30	5.3420	1.8649	1.0333	0.9898	-0.0634	0.6978	43.3502	-3.2965	0.2734	40.3272
	0.40	5.1530	1.8665	1.0719	0.9996	-0.0270	0.6210	42.0385	-5.7191	0.0082	36.3276
	0.50	5.0990	1.8722	1.1496	1.0524	0.1554	0.5987	23.6244	-8.7704	-1.0509	13.8031
	0.60	4.8830	1.8772	1.1886	1.0617	0.1738	0.5082	21.9709	-11.0211	-0.4949	10.4549
	0.70	4.5320	1.8802	1.1830	1.0278	0.0607	0.3558	32.7373	-10.8892	0.2961	22.1442
	0.80	4.3700	1.8893	1.2536	1.0542	0.1319	0.2830	17.9283	-11.5260	0.8213	7.2235
	0.90	4.1540	1.8923	1.3314	1.0655	0.1483	0.1832	3.7993	-9.7540	0.9320	-5.0226
	1.00	3.7760	1.8948	1.3387	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
323	0.00	6.0440	1.8531	1.0267	1.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
	0.10	5.6930	1.8575	1.0107	0.9721	-0.1225	0.8641	29.0485	0.5067	0.5121	30.0673
	0.20	5.5580	1.8602	1.0490	0.9945	-0.0273	0.8106	27.3488	-0.8589	0.1593	26.6492
	0.30	5.2610	1.8605	1.0472	0.9814	-0.0849	0.6900	45.6773	-2.3662	0.4800	43.7911
	0.40	5.0990	1.8635	1.0922	0.9961	-0.0278	0.6225	41.3933	-5.1972	0.0845	36.2805
	0.50	5.0180	1.8646	1.1661	1.0436	0.1270	0.5883	26.5789	-8.6063	-0.8071	17.1655
	0.60	4.8290	1.8665	1.2166	1.0620	0.1703	0.5071	22.2634	-11.3651	-0.4787	10.4196
	0.70	4.5050	1.8720	1.2177	1.0332	0.0766	0.3633	30.6514	-11.6228	0.3242	19.3529
	0.80	4.3160	1.8750	1.2834	1.0536	0.1217	0.2764	19.4852	-12.0363	0.8408	8.2897
	0.90	3.9650	1.8810	1.2831	1.0016	-0.0051	0.1083	20.5671	-6.3093	0.0299	14.2877
	1.00	3.7490	1.8871	1.3736	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

TABLE 4: VALUES OF BRUGGEMAN FACTOR *A* FOR THE SYSTEMS AT 303K, 313K AND 323K

System	Value of *a*		
	303K	313 K	323 K
Ethyl acetate + *n*-Butyl amine	1.04	1.11	1.15
Ethyl acetate + Cyclohexylamine	1.21	1.31	1.39
Ethyl acetate + Diethyl amine	0.61	0.63	0.64

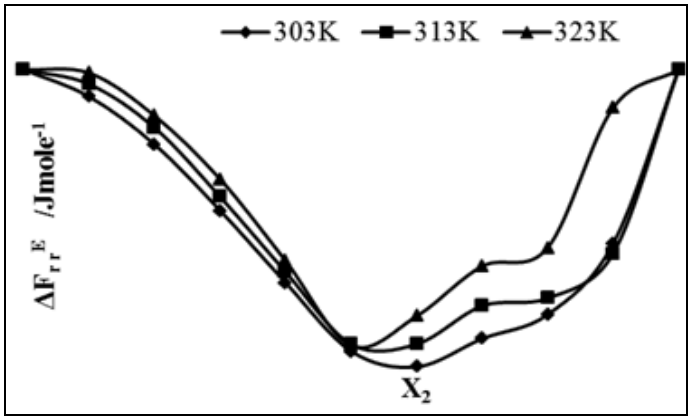

FIGURE 1: VARIATION OF EXCESS FREE ENERGY ΔF_{rr}^{E} WITH % MOLE FRACTION OF ETHYL ACETATE + *n*-BUTYL AMINE BINARY MIXTURES AT DIFFERENT TEMPERATURES

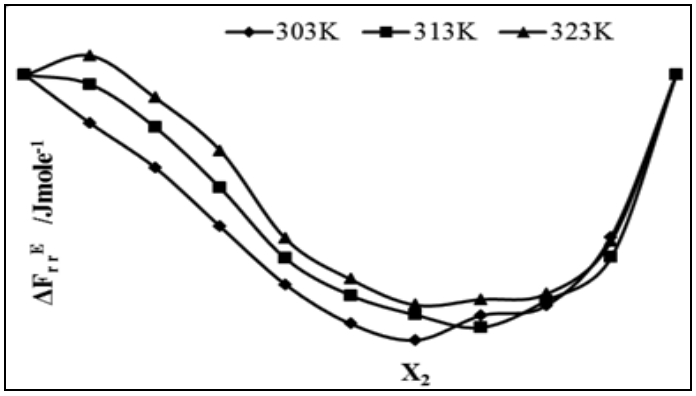

FIGURE 2: VARIATION OF EXCESS FREE ENERGY ΔF_{rr}^{E} WITH % MOLE FRACTION OF ETHYL ACETATE + CYCLOHEXYLAMINE BINARY MIXTURES AT DIFFERENT TEMPERATURES

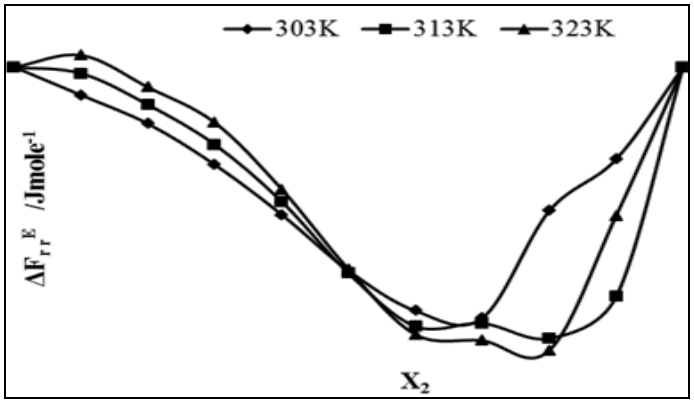

FIGURE 3 VARIATION OF EXCESS FREE ENERGY ΔF_{rr}^{E} WITH % MOLE FRACTION OF ETHYL ACETATE + DIETHYL AMINE BINARY MIXTURES AT DIFFERENT TEMPERATURES

CONCLUSIONS: Values static permittivity, ε_{0m} and the permittivity at optical frequency, $\varepsilon_{\infty m}$, which was by square of the refractive Index for sodium D-line, for ester – amine mixtures, are used to evaluate Kirkwood linear correlation factor, excess permittivity, Bruggeman factor and dipolar excess free energy of mixing. The values of these parameters have been reported for various temperatures and concentrations. These results are used to interpret liquid structure in above mixtures.

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