EFFECT OF TEMPERATURE AND CONCENTRATION ON THERMODYNAMIC EXCESS PARAMETERS OF ISOPROPYL MYRISTATE WITH N -N DIETHYLANILINE IN BINARY MIXTURES

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ABSTRACT

By frequency technic method, the values of the static dielectric constant (ε_0), dielectric constant at optical frequency (ε_∞) for different molar ratios at different temperatures for binary system of Isopropyl myristate and N -N Diethylaniline have been measured. Based on the values thermodynamic excess parameters of Isopropyl myristate and N -N Diethylaniline ($\Delta F_{0p}^\varepsilon$, $\Delta F_{rr}^\varepsilon$, $\Delta F_{ab}^\varepsilon$ and ΔF^ε) have been calculated.

KEYWORDS: Isopropyl myristate, N -N Diethylaniline, Dielectric constant, Thermodynamic Excess Parameters

I   INTRODUCTION

The study of excess thermodynamically parameters [1-4] on mixing of two polar liquids give information about various interactions between the molecules such as long range electrostatic interaction, short range dipolar interaction between similar molecules and short range dipolar interaction between dissimilar molecules. The Molecular weight(M), Density (p), Refractive index (n_D), Dielectric constant (ε) of Isopropyl myristate is 270.46 g/mol, 0.8532 g/cm^3, 1.4325 (25°C), 3.124 (313.2 K), and N -N Diethylaniline is 149.24 g/mol, 0.933 g L^{-1}, 1.540 (20°C) and 5.15 (303.2 K) respectively. Values of Isopropyl myristate and N -N Diethylaniline of $\Delta F_{0p}^\varepsilon$, $\Delta F_{rr}^\varepsilon$, $\Delta F_{ab}^\varepsilon$ and ΔF^ε for all five different temperatures are reported.

II MATERIALS AND METHODS

Isopropyl myristate ($C_{17}H_{34}O_2$)and N -N Diethylaniline ($C_{10}H_{15}N$) was used. The molar fraction of the Bromoform with N -N Diethylaniline are 0,0.1,0.2,0.3… and 1.0.The static dielectric constant ε_0 measured by frequency technic at five different temperatures. The refractive index was measured by Abbe's refractometer .Using dipole meter (1MHz), the dielectric constant was

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measured. The errors in measurements of refractive index (n_D) is $\pm$ 0.002. Using Temperature controlled water circulating thermostat 0.1°C accuracy maintained for 298,303K, 308K, 313K and 318K. Isopropyl myristate ($C_{17}H_{34}O_2$) and N -N Diethylaniline ($C_{10}H_{15}N$) are purified by usual methods.

III THEORY

3.1 Excess permittivity

$$\varepsilon_0^E = (\varepsilon_0 - \varepsilon_\infty) - [(\varepsilon_{0A} - \varepsilon_{\infty A})X_A + (\varepsilon_{0B} - \varepsilon_{\infty B})X_B] \tag{1}$$

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

$\varepsilon^E = 0$ indicates that there is no interaction between the unlike Molecules.

$\varepsilon^E < 0$ 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 less effective Dipoles.

$\varepsilon^E > 0$ 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.

3.2 Thermodynamic Excess Functions

The excess free energy of mixing ΔF^E which is almost equal to the excess Gibbs free energy , ΔG^E for a matter in a condensed phase may be obtained from the reaction field factor of the two liquids (R_{fi}^0) and that of the solution R_{fi}.

$$\Delta F^E = \Delta F_O^E + \Delta F_{rr}^E + \Delta F_{ab}^E \tag{2}$$

$$= \frac{-N_A}{2}\left\{\sum_{r=1,2} x_r \mu_r^2 \left[R_{fr} - R_{fr}^0\right]\right\}$$

$$+ \frac{-N_A}{2}\left\{\sum_{r=1,2} x_r \mu_r^2 [g_{rr} - 1]\left[R_{fr} - R_{fr}^0\right]\right\}$$

$$+ \left\{\frac{-N_A}{2}\right\} x_1 x_2 \mu_1 \mu_2 (g_{12} - 1)\left[R_{f1} + R_{f2} - R_{f1}^0 - R_{f2}^0\right]$$

$$\Delta F_{OP}^E = \frac{-N_A}{2}\left\{\sum_{r=1,2} x_r \mu_r^2 \left[R_{fr} - R_{fr}^0\right]\right\} \tag{3}$$

$$\Delta F_{rr}^E = \frac{-N_A}{2}\left\{\sum_{r=1,2} x_r \mu_r^2 [g_{rr} - 1]\left[R_{fr} - R_{fr}^0\right]\right\} \tag{4}$$

$$\Delta F_{ab}^E = \frac{-N_A}{2} x_1 x_2 \mu_1 \mu_2 (g_{12} - 1)\left[R_{f1} + R_{f2} - R_{f1}^0 - R_{f2}^0\right] \tag{5}$$

The first term ΔF_O^E represents the excess dipolar energy due to long-range electrostatic interaction.

The second term ΔF_{rr}^E gives the excess dipolar energy due to short-range interaction between identical molecules and

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The third term $\Delta F_{ab}^{\varepsilon}$ 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,

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

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

Where g_u is the Kirkwood's mutual correction factor for solvent and solute – solute interactions. The value of g_{12} is the correlation factor between the solute and the solvent.

IV RESULTS AND DISCUSSION

4.1 Static Permittivity (ε_{om})

In system ,the value of static permittivity decreases with the increasing of aniline concentrations. For all the studied, five temperatures, the static permittivity is found to decrease with rise of temperature. This behavior may be due to the fact that the rise in temperature causes thermal agitation which affects the equilibrium between the multimers present in the mixtures. This disturbance in equilibrium changes the orientation of the dipoles in such a way they have lesser parallel orientation. This behavior is found to exist in all the studied concentrations in Table 1 and Fig.1 This behavior is expected as per Debye's model.[5].

4.2 Variation Of The Excess Permittivity $\varepsilon^{\varepsilon}$

The information regarding hetero interaction in a mixture of two polar liquids may be obtained by the excess property related to the permittivity [6].Kande et al.[7] have pointed out that the study of the excess permittivity may provide some trend regarding the interaction between the two constituent liquids leading to the structural information of the mixture. Thus the study of parameter $\varepsilon^{\varepsilon}$ helps to understand the short range dipole- dipole interactions in two different component systems. The values of $\varepsilon^{\varepsilon}$ for all the systems at all different five temperatures are studied and reported in Table 1 and the variation of $\varepsilon^{\varepsilon}$ is plotted in the graph Fig.2.

From the Table1, it is found that $\varepsilon^{\varepsilon}$ deviates from zero for all the systems at all the concentrations and at all five temperatures studied. Rana et al.[8] have indicated that $\varepsilon^{\varepsilon}$ – variation as a function of concentration is due to the interaction between the dissimilar molecules which may cause an effect of structural change in the system. Negative or positive value of $\varepsilon^{\varepsilon}$ implies the interaction between unlike molecules[9].The negative value of $\varepsilon^{\varepsilon}$ may be due to

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creation of less polar structures leading to lower microscopic permittivity [10]. It is also pointed out that the negative ε^E values indicate that the molecules of the mixture may form multimers structures through hydrogen bonding in such a way that the effective dipole moment gets reduced. Thus the negative value of ε^E in system indicates that the interaction between the components in the mixture is such as to form multimeric structures with anti-parallel dipoles in the mixture. The negative value of ε^E is due to strong intercomponent H-bonding. Similar results reported by many researchers [11-17].

4.3 Long Range Electrostatic Interaction (ΔF_{0F}^E)

From the Table 2 and Fig 3 all the studied concentrations, the value of ΔF_{0F}^E is positive. ΔF_{0F}^E increases with increase of aniline /aniline concentrations and thereafter the value of ΔF_{0F}^E decreases. The increase of ΔF_{0F}^E with increasing of aniline concentration, results to increase the number of dipoles. Positive value of ΔF_{0F}^E implies that existence of long range dipole-dipole interaction and attractive forces between them. Conclusions on similar lines were reported by Thenappan et al [18] for anisole- aniline systems. Also the conclusions reported by Varadarajan et al [19].

4.4 Short Range Interaction between Similar Molecules

The excess dipolar energy due to the Short range dipolar interaction between similar molecules ΔF_{rr}^E varies with aniline/aniline concentration for each of all the systems at all the five temperatures. The values of ΔF_{rr}^E tabulated in Table 2, and the values of ΔF_{rr}^E are plotted in the graph Fig. 4. ΔF_{rr}^E is positive value, the rupture of H-bonding between the dipoles are implied. All the concentrations, ΔF_{rr}^E decreases with increase of temperature. ΔF_{rr}^E shows the positive value of system. This means positive value of ΔF_{rr}^E implies the rupture of H-bonding between the dipoles. As aniline/aniline concentration increases, the value of ΔF_{rr}^E increases. This implies that, with increasing concentration, the number of ruptured H-bonding increases. Results on similar lines are reported by Thenappan et al [20].

4.5 Short Range Interaction between Dissimilar Molecules

The excess dipolar energy due to short range interaction between dipolar interactions between dissimilar molecules given by the value of ΔF_{ab}^E [21].Swain [22] has reported the negative value of ΔF_{ab}^E may indicate the formation of micro heterogeneous β-clusters with anti-parallel alignment between dissimilar molecules may lead to the destruction of angular correlation between them and thereby the external energy gets decreased. From the Table 3 and Fig.5, the value of ΔF_{ab}^E is negative. The aniline concentration increases, the value of ΔF_{ab}^E changes from negative to positive. That means the formation of micro heterogeneous β-clusters with anti-parallel alignment between dissimilar molecules may lead to the destruction of angular correlation between them and thereby the internal energy decreased. The aniline region is

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increased; the micro heterogeneous β-clusters changes to hetero association, leads to the formation of linear multimers.

The temperature increases, the value of $\Delta F_{ab}^{\varepsilon}$ decreases in all the studied concentrations, at all the five temperatures. From the Table 3 and Fig.6, it can be seen that ΔF_0^{ε} is greater than $\Delta F_{rr}^{\varepsilon}$ and $\Delta F_{ab}^{\varepsilon}$. This indicates that long range interaction contributes more to the free energy than short range interactions. Conclusions on similar lines have been reported by Parthipan et al.[23]

Table 1 Variation of ε_{0m} & ε^{E} with the concentration of the N- N diethylaniline (X2) at different temperatures.

X_2	ε_{0m}					ε^{E}				
	298 K	303 K	308 K	313 K	318 K	298 K	303 K	308 K	313 K	318 K
0.00	3.2935	3.2849	3.2678	3.2510	3.2342	0.0000	0.0000	0.0000	0.0000	0.0000
0.10	3.3107	3.2935	3.2763	3.2678	3.2421	-0.1900	-0.1846	-0.1812	-0.1684	-0.1732
0.20	3.3537	3.3451	3.3365	3.3221	3.3163	-0.3424	-0.3302	-0.3108	-0.2960	-0.2666
0.30	3.4920	3.4902	3.4706	3.4510	3.4314	-0.3839	-0.3592	-0.3426	-0.3266	-0.3066
0.40	3.6486	3.6399	3.6225	3.6050	3.5701	-0.4113	-0.3879	-0.3638	-0.3415	-0.3276
0.50	3.8065	3.8168	3.7938	3.7709	3.7479	-0.4405	-0.3900	-0.3691	-0.3429	-0.3198
0.60	3.9744	3.9980	3.9739	3.9497	3.9257	-0.4651	-0.3948	-0.3695	-0.3405	-0.3092
0.70	4.1527	4.1646	4.1294	4.0941	4.0589	-0.4858	-0.4190	-0.3976	-0.3691	-0.3440
0.80	4.4048	4.3686	4.3415	4.2874	4.2379	-0.432	-0.409	-0.374	-0.359	-0.341

						6	2	8	3	1
0.90	4.6692	4.6417	4.5868	4.5412	4.5002	-0.3817	-0.3396	-0.3253	-0.2985	-0.2710
1.00	5.2260	5.1527	5.0770	4.9987	4.9180	0.0000	0.0000	0.0000	0.0000	0.0000

Table 2 Variation of ΔF^{E}_{OF} & ΔF^{E}_{rr} with the concentration of the N- N diethylaniline (X2) at different temperatures

X_2	ΔF^{E}_{OF} joules/mole					ΔF^{E}_{rr} joules/mole				
	298 K	303 K	308 K	313 K	318 K	298 K	303 K	308 K	313 K	318 K
0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.10	18.2064	18.6196	18.2660	17.0737	17.5289	0.7262	0.7884	0.7547	0.5728	0.6824
0.20	33.6080	32.7395	31.1328	30.1030	28.0791	3.0432	2.8408	2.5691	2.3329	1.9676
0.30	38.8872	36.8699	35.9457	34.9925	33.8869	5.9171	5.3612	5.0410	4.6456	4.2792
0.40	41.8066	40.0229	38.4430	36.8076	36.7166	9.6601	8.9505	8.4104	7.7452	7.3946
0.50	44.1590	40.0727	38.5789	36.9950	35.1870	13.8322	12.5668	11.9268	11.1173	10.3576
0.60	45.1421	39.3815	37.5356	35.5760	33.3414	17.6754	15.8407	15.0394	14.0308	13.0692
0.70	44.8258	39.7273	38.4575	37.0622	35.3810	20.5543	18.6277	17.9066	16.9436	16.0249
0.80	37.6786	36.4112	33.9164	33.6718	32.7470	19.9970	19.1192	17.9818	17.3748	16.6617
0.90	29.7211	27.1103	26.4556	24.8222	22.4889	16.6570	15.3149	14.8470	13.8373	12.6647
1.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

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Table 3 Variation of ΔF^E_{12} & ΔF^E with the concentration of the N- N diethylaniline (X2) at different temperatures

| X_2	ΔF^E_{12} joules/mole					ΔF^E joules/mole				
	298 K	303 K	308 K	313 K	318 K	298 K	303 K	308 K	313 K	318 K
0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.10	-2.3753	-2.2376	-2.2068	-2.0215	-2.1127	16.5574	17.1704	16.8139	15.6250	16.0986
0.20	-6.4851	-6.1831	-5.7299	-5.4001	-4.6590	30.1661	29.3972	27.9720	27.0358	25.3876
0.30	-6.9975	-6.3784	-6.0233	-5.6950	-5.2321	37.8068	35.8527	34.9635	33.9431	32.9340
0.40	-6.1481	-5.6852	-5.2198	-4.8242	-4.5968	45.3186	43.2882	41.6336	39.7287	39.5144
0.50	-4.8611	-3.9630	-3.7061	-3.3460	-3.0542	53.1301	48.6765	46.7996	44.7663	42.4903
0.60	-3.3017	-2.4003	-2.1815	-1.9258	-1.6478	59.5158	52.8218	50.3935	47.6809	44.7628
0.70	-1.7619	-1.2477	-1.1588	-1.0281	-0.9155	63.6182	57.1073	55.2053	52.9778	50.4904
0.80	-0.1804	-0.1532	-0.0715	-0.0838	-0.0735	57.4951	55.3772	51.8267	50.9628	49.3351
0.90	0.3751	0.3671	0.3580	0.3491	0.3545	46.7532	42.7923	41.6605	39.0086	35.5080
1.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
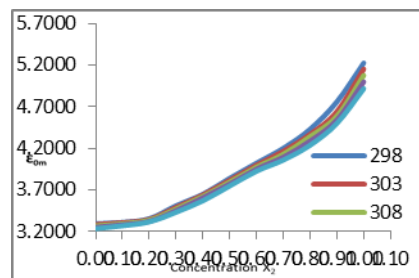
Fig.1
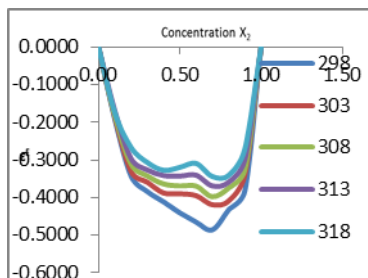
Fig.2
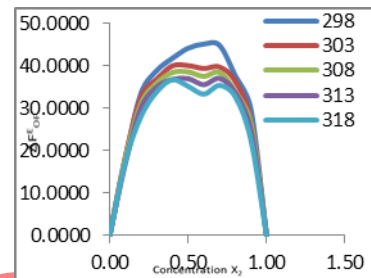
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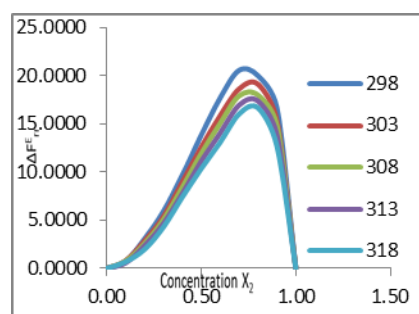
Fig.4
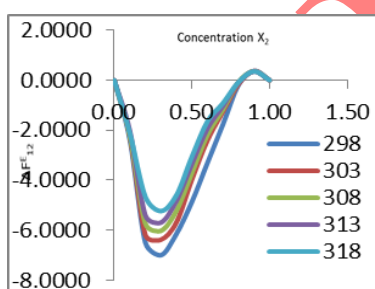
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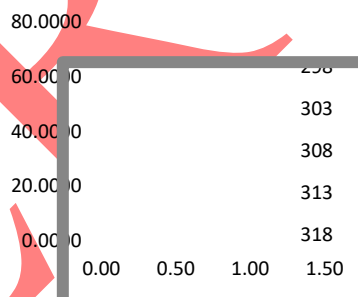

Fig.6

V CONCLUSIONS

In all the studied systems, at all the range of concentrations studied and all the five temperatures, existence of $\varepsilon_{om}, \Delta F_{cp}^E, \Delta F_{\tau\tau}^E, \Delta F_{ab}^E$ and ΔF^b are identified. These interactions are found to be concentration and temperature dependent.

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