

THERMODYNAMIC EXCESS PARAMETERS OF POLAR- POLAR LIQUID MIXTURES OF N- BUTYL IODIDE WITH ISOVALERIC ACID

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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 have been measured. Based on the values thermodynamic excess parameters have been calculated.

KEYWORDS: N-Butyl iodide, isovaleric acid, Dielectric constant, Thermodynamic Excess Parameters.

I. INTRODUCTION

Davis and Douheret [1] used the four – segment composition model and estimated the excess dielectric properties. The theory gave a reasonable link between the thermodynamics and the dielectric properties of polar liquids. Tripathy and Swain [2], Roy and Roy[3]and Sabesan et al. [4] found that Winklenmann and Quitzsch expression is the most appropriate one for the study of dipolar excess thermodynamic properties of associated liquid in an inert solvent.

Molecular interactions are the key to understand the structure and properties of liquids, gases and solids. In addition, they provide some understanding of the fundamental problems concerned with the mechanisms of chemical and biological catalysis and the paths of chemical reactions. For theoretical studies of molecular interactions one can use perturbation theory as well as the vibrational approaches of quantum mechanics.

In the theoretical point of view, it is convenient to classify molecular interactions in to long range and short – range interactions. In practice however, the precise boundary between these two types cannot be pinpointed accurately. Amongst aggregations involving short – range interactions one can distinguish molecular complexes formed by hydrogen bond and electron donor – acceptor (Charge – transfer) interactions (EDA interactions.). The essential difference between long range and short – range interactions is that in the former the principle of in distinguish ability of electrons in the interactions in the interaction pair may be neglected. In the latter type this assumption is no longer valid since the overlap of electron clouds of two interacting molecules is of great significance and consequently the total wave function must be anti – symmetrical with respect to the exchange of pair of electrons.

II.MATERIALS AND METHODS

N-Butyl iodide and isovaleric acid was used. The molar fraction of the n-Butyl iodide with isovaleric acid 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 measured. The errors in measurements of refractive index (n_D) is ± 0.002 . Using Temperature controlled water circulating thermostat 0.1°C accuracy maintained for 298,303K, 308K, 313K and 318K.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

III.THEORY

3.1 Excess permittivity

$$\epsilon_0^E = (\epsilon_0 - \epsilon_\infty) - [(\epsilon_{0A} - \epsilon_{\infty A})X_A + (\epsilon_{0B} - \epsilon_{\infty B})X_B] \quad (1)$$

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

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

$\epsilon^E < 0$ 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.

$\epsilon^E > 0$ 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_{fr}^0) and that of the solution R_{fi} .

$$\Delta F^E = \Delta F_{0F}^E + \Delta F_{FF}^E + \Delta F_{ab}^E \quad (2)$$

$$\begin{aligned} &= \frac{-N_A}{2} \{ \sum_{r=1,2} x_r \mu_r^2 [R_{fr} - R_{fr}^0] \} \\ &+ \frac{-N_A}{2} \{ \sum_{r=1,2} x_r \mu_r^2 [g_{rr} - 1] [R_{fr} - R_{fr}^0] \} \\ &+ \{ \frac{-N_A}{2} \} x_1 x_2 \mu_1 \mu_2 (g_{12} - 1) [R_{f1} + R_{f2} - R_{f1}^0 - R_{f2}^0] \end{aligned}$$

$$\Delta F_{0F}^E = \frac{-N_A}{2} \{ \sum_{r=1,2} x_r \mu_r^2 [R_{fr} - R_{fr}^0] \} \quad (3)$$

$$\Delta F_{FF}^E = \frac{-N_A}{2} \{ \sum_{r=1,2} x_r \mu_r^2 [g_{rr} - 1] [R_{fr} - R_{fr}^0] \} \quad (4)$$

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

The first term ΔF_{0F}^E represents the excess dipolar energy due to long-range electrostatic interaction.

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

The third term ΔF_{ab}^E gives the excess dipolar energy due to short-range interaction between dissimilar molecules.

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

$$R_{fro}^0 = \frac{8\pi N_A (\epsilon_r - 1)(\epsilon_{\infty r} + 2)}{9V_r (2\epsilon_r + \epsilon_{\infty r})}$$

$$R_{fir} = \frac{8\pi N_A (\epsilon_r - 1)(\epsilon_{\infty r} + 2)}{9V_r (2\epsilon_m + \epsilon_{\infty r})}$$

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

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 DISCUSSIONS

4.1 Variation Of The Excess Permittivity ϵ^E

The information regarding hetero interaction in a mixture of two polar liquids may be obtained by the excess property related to the permittivity [5]. Kande et al. [6] 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 ϵ^E helps to understand the short range dipole- dipole interactions in two different component systems. The values of ϵ^E for all different five temperatures are studied and reported in Table 1 and the variation of ϵ^E is plotted in the Chart 1

From the Table 1, it is found that ϵ^E deviates from zero at all the concentrations and at all five temperatures studied. Rana et al. [7] have indicated that ϵ^E – variation as a function of concentration is due to the interaction between the dissimilar molecules which may affect a structural change in the system. Negative or positive value of ϵ^E implies the interaction between unlike molecules [8]. According to Hosamani [9] the negative value of ϵ^E may be due to creation of less polar structures leading to lower microscopic permittivity. 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.

Pawar et al. [10] have noted that, the negative value of ϵ^E indicates that the number of dipoles in the mixture less than the sum of the number of dipoles in pure liquids. This may be due to opposite alignment of the dipoles of the two interacting liquids [11]. Thus the negative value of ϵ^E in system indicate 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 Nakmishi et al. [12], And many researchers [13-16]. From Table 1 for pure liquids $\epsilon^E = 0$. for all temperatures, ϵ^E is decreases with increase of temperature.

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

From table 2 the value of ΔF_{0F}^E is positive. ΔF_{0F}^E increases with increase of acid concentrations and thereafter the value of ΔF_{0F}^E decreases. 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 [17] for anisole- acid systems. Also the conclusions reported by Varadarajan et al [18]. The increase of ΔF_{0F}^E with increasing of acid concentration results to increase the number of dipoles and the variation of ΔF_{0F}^E is plotted in the Chart 2.

International Journal of Innovative Research in Science, Engineering and Technology

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Chart-1 to 4 Variation of excess dielectric constant ϵ^E , ΔF_{OF}^E , ΔF_{rr}^E and ΔF^E with the concentration of the Isovaleric acid (X2) at different temperatures. System : n-Butyl iodide (X1) + Isovaleric acid (X2)

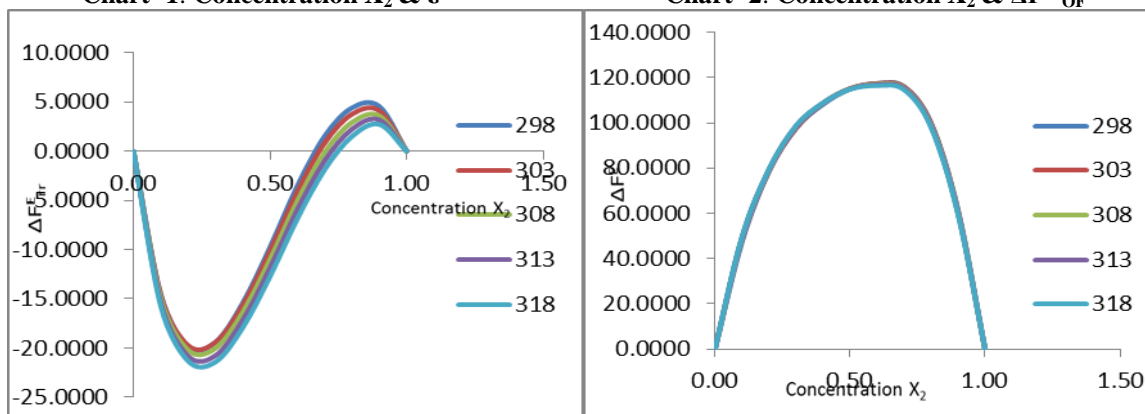
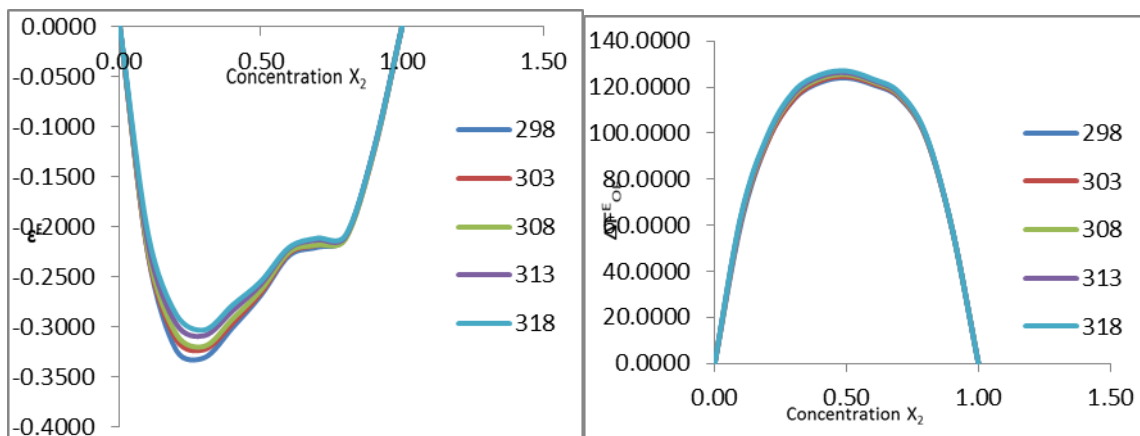


Chart -3: Concentration X_2 & ΔF_{rr}^E **Chart -4: Concentration X_2 & ΔF^E**
Table:1 Variation of ϵ_0^E at different mole fractions of n-Butyl iodide (X1) in isovaleric acid (X2) with the concentration of isovaleric acid (X2) at different temperatures

X_2	ϵ^E				
	298 K	303 K	308 K	313 K	318 K
0.00	0.0000	0.0000	0.0000	0.0000	0.0000
0.10	-0.2276	-0.2272	-0.2239	-0.2165	-0.2070
0.20	-0.3235	-0.3127	-0.3073	-0.2971	-0.2877
0.30	-0.3308	-0.3227	-0.3194	-0.3088	-0.3031
0.40	-0.3007	-0.2963	-0.2920	-0.2839	-0.2781
0.50	-0.2684	-0.2661	-0.2632	-0.2574	-0.2544
0.60	-0.2288	-0.2267	-0.2252	-0.2215	-0.2205
0.70	-0.2203	-0.2183	-0.2181	-0.2131	-0.2113
0.80	-0.2106	-0.2103	-0.2121	-0.2097	-0.2083
0.90	-0.1225	-0.1256	-0.1251	-0.1229	-0.1232
1.00	0.0000	0.0000	0.0000	0.0000	0.0000

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

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4.3 Short Range Interaction between Similar Molecules

ΔF_{rr}^E is positive value, the rupture of H-bonding between the dipoles are implied. ΔF_{rr}^E is the negative value, confirms the formation of H-bonding. In the system, it shows the partially negative value and increase of acid concentrations ΔF_{rr}^E changes to positive value. ΔF_{rr}^E varies marginally with rise of temperature in the halide region. This may be due to a small change in the random orientation of the dipoles [19].

4.4 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 [20]. Swain [21] 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. the variation of ΔF_{of}^E is plotted in the Chart 3. Table 3 shows the value of ΔF_{ab}^E changes from positive to negative. The acid concentration increases, the value of ΔF_{ab}^E changes from positive to negative. This shows that the heterogeneous formation of linear multimers in the positive value changes to micro heterogeneous β -clusters.. The temperature increases, the value of ΔF_{ab}^E decreases in all the five temperatures in the halide region. It can be seen that ΔF_{of}^E is greater than ΔF_{rr}^E and ΔF_{ab}^E . 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. [22]

Table:2 Variation of ΔF_{of}^E & ΔF_{rr}^E at different mole fractions of n-Butyl iodide (X1) in isovaleric acid (X2) with the concentration of isovaleric acid (X2) at different temperatures

X ₂	ΔF_{of}^E joules/mole					ΔF_{rr}^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	60.8828	62.3286	63.3380	63.9537	64.5207	-14.5249	-14.6444	-14.9577	-15.3834	-15.7135
0.20	96.2191	96.3676	97.5778	98.3745	99.1061	-19.8565	-19.7485	-20.2043	-20.8236	-21.3248
0.30	114.7156	114.9909	116.3623	117.3112	118.1855	-19.4143	-19.4278	-20.0344	-20.7811	-21.4266
0.40	122.1058	122.8252	123.7173	124.6168	125.4461	-15.4390	-15.6731	-16.3677	-17.1823	-17.9370
0.50	124.0572	124.7167	125.5230	126.3121	127.0394	-9.7559	-10.1737	-11.0146	-11.8756	-12.7262
0.60	121.1149	121.6743	122.3455	122.9799	123.5635	-3.5370	-4.1249	-5.0767	-5.9518	-6.8625
0.70	115.4890	116.0058	116.6150	117.1909	117.7197	1.5257	0.8380	-0.1380	-0.9761	-1.8729
0.80	98.3290	98.6754	99.0680	99.4262	99.7510	4.3985	3.7558	2.9216	2.2359	1.4956
0.90	58.4704	58.5612	58.6481	58.7008	58.7432	4.5382	4.1044	3.5808	3.1675	2.7174
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_{ab}^E & ΔF^E at different mole fractions of n-Butyl iodide (X1) in isovaleric acid (X2) with the concentration of isovaleric acid (X2) at different temperatures

X_2	ΔF_{12}^E 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	0.9199	0.8819	0.8527	0.7874	0.6637	47.2778	48.5661	49.2330	49.3577	49.4709
0.20	2.2390	2.0742	1.9928	1.8509	1.7066	78.6017	78.6933	79.3663	79.4018	79.4879
0.30	2.2532	2.1518	2.1184	1.9378	1.8915	97.5545	97.7150	98.4463	98.4678	98.6503
0.40	1.5102	1.4620	1.4310	1.3278	1.2652	108.1771	108.6141	108.7806	108.7622	108.7743
0.50	0.6336	0.6191	0.5971	0.5469	0.5218	114.9349	115.1621	115.1055	114.9834	114.8350
0.60	-0.1332	-0.1555	-0.1935	-0.2276	-0.2788	117.4447	117.3939	117.0753	116.8004	116.4221
0.70	-0.9729	-1.0062	-1.1240	-1.1245	-1.2052	116.0418	115.8376	115.3530	115.0903	114.6416
0.80	-2.6710	-2.7788	-3.0171	-3.0980	-3.1977	100.0566	99.6523	98.9725	98.5642	98.0489
0.90	-1.6115	-1.8059	-1.8538	-1.8442	-1.9276	61.3972	60.8596	60.3752	60.0241	59.5330
1.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

V.CONCLUSION

In all the range of concentrations studied and all the five temperatures, existence of short and long range, homo and hetero interactions identified. These interactions are found to be concentration and temperature dependent. The hetero interaction results in the formation of linear as well as closed multimers in the mixture. Due to the existing interactions, structural changes are found to take place.

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