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DIELECTRIC CORRELATION AND EXCESS ENERGY STUDIES OF MIXTURES OF ANILINE AND BROMOBENZENE

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Abstract:

The dielectric correlation and excess energy studies of the mixtures of aniline and bromobenzene have been studied for various mole ratios for 303K, 313K and 318K. From the values of static permittivity and refractive index, the dielectric parameters such as Kirkwood parameter, Bruggeman parameter, excess permittivity and thermodynamic excess free energy of the binary mixtures of polar-polar liquids are obtained and each parameter is discussed briefly. Dielectric parameters and excess values obtained were interpreted in terms of molecular interactions between molecular species in the liquid mixtures.

Key Words: Dielectric Constant, Polarization Effect, Proton Donor & Proton Acceptor

1. Introduction:

The magnitude of molecular dipole moment depends on the size and symmetry of the molecule. Molecular dipole moment is obtained from the permittivity of the liquids, which depends upon the molecular structure. The importance of measuring the permittivity of liquid lies in the fact that it provides valuable information about the ordering of the molecule in the liquid state. Large number of work concerning the dielectric behavior of dilute solutions of polar solute in non-polar solvents has been worked using Debye, Onsager, Kirkwood and Frohlich theories. Studies of binary polar mixture have been carried out [1] and have modified the Kirkwood parameter and also used the Bruggeman and excess parameters to explain the dielectric behavior of the liquid mixture containing polar-polar liquids. Effective Kirkwood correlation parameter explains the dipole alignment in liquid and intermolecular interaction between the components of the mixture in explained by corrective Kirkwood correlation parameter [2]. Bruggeman factor and excess permittivity can also give information on the interaction between the dissimilar molecules [3, 4]. Excess free energy due to mixing is used to explain the long- range and short-range interactions existing between similar and dissimilar liquids [5].

2. Materials and Methods:

The dielectric constants were measured at 1 kHz using aVLCR-7meter supplied by Vasavi Electronics, India. The temperature was maintained at 303K,313K and 318K with accuracy ±1 K with the help of a water circulating thermostat.The refractive indices were measured with Abbe′srefractometer. Densities were determined using a 10 ml specific gravity bottle and a K-Roy micro balance. BD grade of aniline and bromobenzene were obtained from Sisco Research Laboratories, Limited, Mumbai, were distilled, the distillates were collected at their boiling temperatures and used. The uncertainties in dielectric constants, refractive indices and densities were ±0.0005, ±0,0.0002 and 0.0001 g/cc respectively.

3. Theory:

Dielectric Parameters Related to Molecular Interaction: There are different formulas with which one can correlate dielectric parameters with molecular activities in liquids. The correlation between dielectric parameters and molecular interactions 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.

3.1 Kirkwood Correlation Factor: Orientation and short-range interaction between the electric dipoles in pure polar liquid in gaseous state could be explained by Kirkwood correlation factor, which is given by the equation given below [6].

$$\frac{4\pi N_A \mu^2 \rho}{9kTM} g = \frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(\varepsilon_\infty + 2)^2} \qquad (1)$$

For a binary mixture of polar liquids, the above equation is modified [7-9] and the modified forms are

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

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

The values of g^{eff} describes the orientation of electric dipoles in the mixture. Where g_f is known as corrective correlation factor.The value of is unity for an ideal liquid and deviation from unity may indicate interaction between the two components in the mixture.

3.2 Bruggeman Parameter: According to the Bruggeman [7] mixture formula of static permittivity, the Bruggeman dielectric factor f_B is given by equation (4).

$$f_B=\left(\frac{\varepsilon_m-\varepsilon_B}{\varepsilon_A-\varepsilon_B}\right)\left(\frac{\varepsilon_A}{\varepsilon_m}\right)^{\frac{1}{3}}=(1-\phi_B) \quad (4)$$

This Bruggeman equation assumes that orientation of the solvent molecules does not change in the mixture. This is only true for the non-polar solvents. When both solvent and solute happen to be polar liquids, the Bruggeman equation has to be modified as [8]

$$\left(\frac{\varepsilon_m-\varepsilon_B}{\varepsilon_A-\varepsilon_B}\right)\left(\frac{\varepsilon_A}{\varepsilon_m}\right)^{\frac{1}{3}}=1-[a-(a-1)\phi_B]\phi_B \quad (5)$$

Where ‘ a ’ is Bruggeman parameter. The deviation of Bruggeman factor from unity, may be due to change in volume signifies the structural rearrangement of solute molecules. The change in volume is due to the hetero interaction between the components in the mixture.

3.3 Excess Permittivity and Excess Free Energy: In the mixture, formation of multimers was detected by one of the dielectric parameters namely the excess permittivity and it is defined as [9,10]

$$\varepsilon^E=(\varepsilon-\varepsilon_\infty)_m-[(\varepsilon-\varepsilon_\infty)_A X_A+(\varepsilon-\varepsilon_\infty)_B X_B] \quad (6)$$

The excess Helmholtz free energy is given as [25,26]

$$\Delta F^E=-\frac{N_A}{2}\{\sum_{r=A,B}X_r\mu_r^2(R_{fr}-R_{fr}^0)+\sum_{r=A,B}X_r^2\mu_r^2(g_{rr}-1)(R_{fr}-R_{fr}^0)+X_AX_B\mu_A\mu_B(g_{AB}-1)(R_{fA}+R_{fB}-R_{fA}^0-R_{fB}^0)\} \quad (7)$$

Where

$$\Delta F^E=\Delta F_0^E+\Delta Frr_0^E+\Delta F_{AB}^E,\ R_{fr}^0=\left(\frac{8\Pi N_A}{9V_r}\right)\frac{(\varepsilon_r-1)(\varepsilon_{\infty r}+2)}{(2\varepsilon_r+\varepsilon_{\infty r})},R_{fr}=\left(\frac{8\Pi N_A}{9V_r}\right)\frac{(\varepsilon_m-1)(\varepsilon_{\infty r}+2)}{(2\varepsilon_m+\varepsilon_{\infty r})} \quad (8)$$

Table 1: Variation of ε_0,ε_∞ and g^{eff} with mole fraction of bromobenzene at three different temperatures.

X_2	ε_0			ε_∞			g^{eff}		
	303K	313K	318K	303K	313K	318K	303K	313K	318K
0	6.8095	6.5980	6.5200	2.5002	2.4838	2.3470	1.79	1.78	1.94
0.100	6.2991	6.0755	5.9654	2.4909	2.4746	2.4659	1.46	1.45	1.44
0.304	5.9102	5.7770	5.7134	2.4721	2.4560	2.4477	1.14	1.15	1.16
0.501	5.7886	5.7272	5.6126	2.4540	2.4382	2.4301	0.98	1.00	0.99
0.699	5.5942	5.5282	5.5622	2.4359	2.4203	2.4125	0.83	0.85	0.88
0.772	5.3754	5.3540	5.3605	2.4292	2.4137	2.4060	0.75	0.78	0.80
1	5.3511	5.2047	5.1337	2.4211	2.4000	2.3846	0.67	0.67	0.67

Table 2: Variation of g_f ,f_B and ε^E values with mole fraction ofbromobenzene at three different temperatures

X_2	g_f			f_B			ε^E		
	303K	313K	318K	303K	313K	318K	303K	313K	318K
0	1.00	1.00	1.00	1.00	1.00	1.00	0.00	0.00	0.00
0.100	0.92	0.91	0.84	0.67	0.64	0.62	-0.36	-0.38	-0.53
0.304	0.90	0.91	0.85	0.40	0.43	0.44	-0.45	-0.39	-0.47
0.501	0.94	0.96	0.90	0.32	0.39	0.36	-0.28	-0.17	-0.28
0.699	0.96	0.98	0.98	0.18	0.25	0.33	-0.19	-0.09	-0.03
0.772	0.92	0.96	0.95	0.02	0.11	0.17	-0.30	-0.16	-0.12
1	1.00	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 3: Variation of ΔF_{01}^E, ΔF_{02}^E and ΔF_{11}^E values with mole fraction of bromobenzene.

X_2	ΔF_{01}^E J/mole			ΔF_{02}^E J/mole			ΔF_{11}^E J/mole		
	303K	313K	318K	303K	313K	318K	303K	313K	318K
0.100	28.56	29.22	31.71	-13.05	-12.58	-12.31	20.25	20.50	22.57

0.304	42.19	37.01	36.96	-24.64	-26.17	-26.99	23.13	20.08	20.34
0.501	36.06	28.38	30.29	-32.27	-39.59	-37.22	14.19	11.05	11.96
0.699	26.95	21.66	19.44	-25.74	-35.21	-46.82	6.40	5.09	4.63
0.772	24.49	19.54	18.33	-2.94	-18.44	-28.24	4.40	3.47	3.30

Table 3: Variation of $\Delta F_{22}^E, \Delta F_{12}^E$ and ΔF^E values with mole fraction of bromobenzene

X_2	ΔF_{22}^E J/mole			ΔF_{12}^E J/mole			ΔF^E J/mole		
	303K	313K	318K	303K	313K	318K	303K	313K	318K
0.100	0.43	0.42	0.41	0.27	0.27	0.41	36.46	37.82	42.79
0.304	2.47	2.63	2.71	-0.80	-0.45	-0.65	42.36	33.11	32.37
0.501	5.33	6.54	6.15	-1.06	-0.32	-1.01	22.24	6.06	10.16
0.699	5.93	8.12	10.79	-1.01	-0.31	-0.26	12.55	-0.66	-12.22
0.772	0.75	4.70	7.20	-2.13	-0.84	-0.79	24.57	8.44	-0.20

Table 4: Bruggeman Factors

Systems	**Value of \`a\` parameter**
aniline + bromobenzene	4.99

Figure 1: Plot of static permittivity versus concentration at three different temperatures.

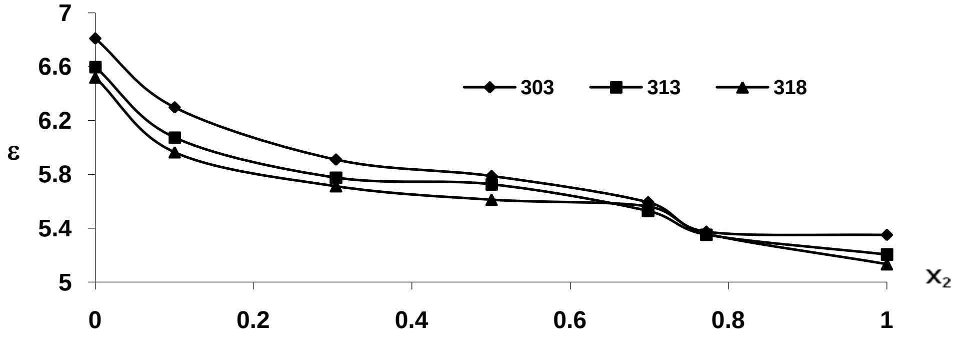
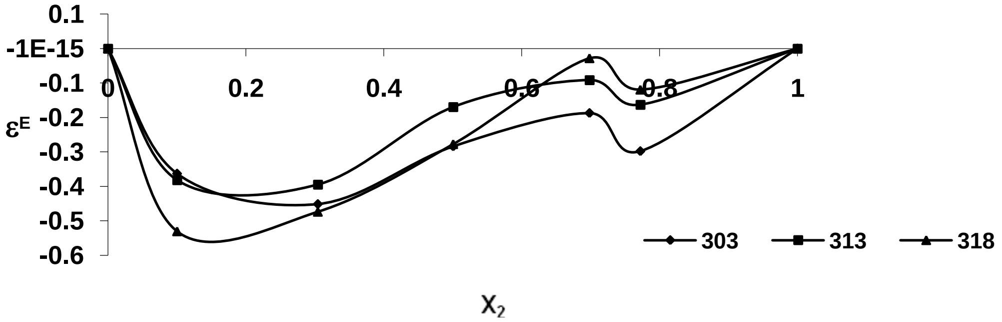


Figure 2: Plot of excess permittivity versus concentration of at three different temperatures



4. Results and Discussions:

From the values of static permittivity and refractive index, the dielectric parameters such as Kirkwood parameter, Bruggeman parameter, excess permittivity and thermodynamic excess free energy of the binary mixtures of polar-polar liquids (aniline with bromobenzene) are obtained and each parameter is discussed briefly. For the above liquids, from the values of ε and ε_∞ the values of g^{eff}, g_f, f_B, a, $\varepsilon^E \Delta F^E$ and are obtained using equations (2) (3), (4), (5), (6) and (8) respectively .The values of ε , ε_∞, g^{eff}, g^f, f_B and ε^E are presented in Tables 1and 2. The values of ΔF_{0r}^E, ΔF_{rr}^E, ΔF_{12}^E and ΔF^E for the systems at all the three studied temperatures are given in Table 3. The values of Bruggeman parameter for the systems studied are given in Table 4.

The measured values of static permittivity for aniline and bromobenzene for all temperatures fairly agree with literature values [11]. A non- linear variation in permittivity with concentration is found to occur for all studied temperatures. This non-linear variation of permittivity with concentration indicates the existence of the interaction between the two liquids in the mixture.The static permittivity decreases with increase in temperature for all concentrations. Decrease in the permittivity value may be due to the decrease in the number of dipoles forming the cluster. Anon linear variation of static permittivity with concentration may be due to inter association between the solute molecules. Hence it may be concluded that a weak hetero interaction is exist. values of ε decreases with increasing concentration of the second component. This goes to say that ellipsoidal aggregates on getting converted into spherical aggregates. Thus the addition of second component in the system produces a structural change in the molecule [12].

The value of g^{eff} varies from g_1 to g_2 as the concentration of liquid 2 is varied from 0 to 1, where g is the Kirkwood correlation factor for pure liquids and suffix 1 and 2 denotes component 1 and 2 respectively. Values of g^{eff} for aniline is greater than unity and is less than unity for bromobenzene, which implies the parallel orientation of the dipoles in pure liquid state for aniline and anti- parallel alignment of dipoles in pure state of bromobenzene. The value of g^{eff} decreases with the increasing concentration of the bromobenzene, which indicates that the interaction between aniline decreases with increasing concentration of the bromobenzene [13].

The values of g_f is less than unity. This indicates the interaction between the molecules of aniline and bromobenzene be present. The deviation increases with increasing concentration of bromobenzene. In aniline rich region, deviation is more indicating more hetero interaction. Existence of interaction between aniline and bromobenzene has been reported [14] from the study of excess Gibb's free energy. The interaction between the components may be between the bromine atom of bromobenzene and C-H of aniline through H-bonding. This is generally a weak H-bond.

Negative values of ε^E indicate the formation of multimeric structures which leads to the decrease in total number of dipoles in the mixture. This implies the formation of closed multimers with anti-parallel orientation of dipoles. Thus the conclusion arrived from the study of g_f is confirmed by the study of excess parameters.

The value of *a* is greater than unity, hence it may be concluded that there is an increase in the volume of the second component due to the addition of the first component.

When two liquids are mixed together energy may be observed or released due to the formation or breaking of H-bonding between the components. The parallel alignment of dipoles leads to destruction of angular correlation between unlike molecules decreasing internal energy which results in the increase of ΔF_{12}^{E} values [15]. The values are small indicates a weak interaction. The values of ΔF_{11}^{E} and ΔF_{22}^{E} are positive with small magnitude. This indicates the rupture of small number of bonds or rupture of weak H-bonds between the molecules. Positive values of ΔF_{0r}^{E} indicates the existence of attractive force between the dipoles of unlike molecules, whereas negative values of ΔF_{0r}^{E} indicates the repulsive force between the dipoles of the unlike molecules.

5. Conclusion:

Using the values the dielectric parameters such as Kirkwood parameter, Bruggeman parameter, excess permittivity and thermodynamic excess free energy of the binary mixtures of polar-polar liquids (aniline with bromobenzene) is studied. The dielectric correlation and excess energy studies conforms the interaction between the molecules and the interaction is found to be weak.

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