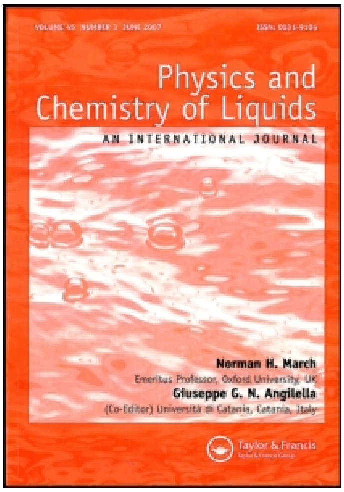

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EXCESS FREE ENERGY OF MIXING OF POLAR-NONPOLAR LIQUIDS – AN EXPERIMENTAL ASSESSMENT OF THE EFFICIENCY OF THE PROPOSED EQUATION

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Dipolar excess free energy of mixing in the binary mixture of polar-nonpolar liquid viz. *n*-butanol + tetrachloromethane and acetic acid + tetrachloromethane has been evaluated with the help of our proposed equation, which has been developed on the concept of thermodynamic ideality and the results have been compared with those of Sabesan *et al.*, evaluated with the help of Haskell's equation. The results indicate that though they agree qualitatively yet the magnitude differs. The maxima of dipolar excess free energy of mixing in the binary mixture of acetic acid + tetrachloromethane is found to be greater than that based on Haskell's equation whereas the trend is reversed in the binary mixture of *n*-butanol + tetrachloromethane.

KEY WORDS: Polarisation, excess correlation factor, dipolar excess free energy of mixing.

INTRODUCTION

Evaluation and analysis of dipolar excess free energy of mixing is useful in the interpretation of liquid structure. Though theoretical treatment suggested by Longuet–Higgins[1] is found useful in the interpretation of liquid structure involving weak interactions, it has its own limitation of not being applicable to hydrogen bonded systems. The reason for this may be attributed to the indistinguishability of the long-range force from that of the short-range one. In view of this limitation, experimental measurement of excess thermodynamic functions using the dielectric properties of liquids is found useful. In an attempt to determine directly the dipolar contribution to the excess thermodynamic function, Haskell[2] developed an expression for the dipolar excess free energy of mixing in the binary mixture of polar-nonpolar liquids from experimental values of dielectric constants. However this theory has the limitation of not considering the short range correlation among the similar as well as dissimilar molecules. Later Winkelmann–Quitzsch[3,4] extended the dielectric theory and developed the relation for the thermodynamic functions taking into account both long and short range interaction separately among the similar as well as dissimilar molecules. Roy and Swain and others[5–7] have studied the molecular interaction in the binary mixture of polar-nonpolar liquids using W.Q. equation. Subsequently we have analyzed[8] the concept of thermodynamic ideality proposed by Davis and Douheret[9,10] in the binary mixtures of polar liquids and developed an expression for two new terms[11,12]– excess correlation factor 'δg' and excess free energy of mixing (ΔF_{AB}) for the binary mixture of polar and nonpolar liquids.

Earlier Sabesan *et al.*[13,14] adopted Haskell's method to evaluate excess free energy of mixing F_P^E for a binary mixture of polar and nonpolar liquids, namely *n*-butanol + tetrachloromethane and acetic acid + tetrachloromethane. Our present study relates to the evaluation of excess free energy of mixing in the same set of mixtures with the help of our proposed equations & from those of Sabesan *et al.*[13,14].

THEORY

Winkelmann and Quitzsch[3,4] utilized the concept of structural correlation in the statistical theory of Ramshaw[15] and Wertheim[16] and have evaluated the expression for the correlation factor for the binary mixture of polar liquids.

For binary systems, one of which is non-polar it can be given as[5]

$$g_m = \frac{9kT\varepsilon_0}{N\mu_{gB}X_B} \cdot \frac{(2\varepsilon_m + \varepsilon_{\infty B})^2}{(\varepsilon_{\infty B}+2)^2(2\varepsilon_m+1)} \left[V\frac{\varepsilon_m - 1}{\varepsilon_m} - \frac{3X_A V_A(\varepsilon_A - 1)}{2\varepsilon_m + \varepsilon_A} - \frac{3X_B V_B(\varepsilon_{\infty B} - 1)}{2\varepsilon_m + \varepsilon_{\infty B}} \right] \quad (1)$$

where A refers to the nonpolar liquid and B refers to polar liquid.

Roy *et al.*[17] while studying the dielectric behaviour of extremely dilute solutions of alcohols and amines in nonpolar solvents observed that the correlation factor increases in case of alcohols while it decreases in case of amines. Further the correlation factor does not vary linearly with the molefraction of solute[18(a,b)]. Therefore we consider the deviation of this parameter from the ideal value to be more suitable for studying molecular interaction (hydrogen bonding) between the molecules of two liquids[19]. To obtain on expression for 'δg' we proceed as follows:

The correlation factor for ideal liquid mixture can be written as:

$$g_{\text{ideal}} = X_A\, g_{AA} + X_B\, g_{BB} \quad (2)$$

According to Oster and Kirkwood[21] the correlation factor for a pure polar liquid can be defined as

$$g = \mu_{\text{eff}}^2/\mu_g^2 \quad (3)$$

Where μ_{eff} is the effective dipole moment of the polar liquid. However, in the binary mixture of polar and non polar liquids,

$$g_{AA} = \text{Lim}\,\frac{\mu_{\text{eff}\cdot A}^2}{\mu_{gA}^2} = 1 \quad (4)$$

$$\mu_{\mathrm{eff}\cdot A} \rightarrow 0$$

$$\mu_{gA} \rightarrow 0$$

From Eqn. (2) and (4)

$$g_{\mathrm{ideal}} = X_A + X_B\, g_{BB} \tag{5}$$

By utilizing the theoretical concept of Davis and Douheret[9,10] we have defined the excess correlation factor 'δg'[11,12] whose magnitude is taken as the departure from ideality.

$$\delta g = g_m - (X_A + X_B\, g_{BB}) \tag{6}$$

For the binary mixture of polar and nonpolar liquids, Winkelmann and Quitzsch equation[3,4] for the dipolar excess free energy of mixing can be expressed as

$$\Delta F = -\frac{N}{2}(R_{fB} - R^o_{fB})\, X_B\, \mu^2_{gB}\, [X_B(g_{BB} - 1) + 1] \tag{7}$$

where,

$$R^o_{fB} = \frac{2N}{9V_B\varepsilon_0}\;\frac{(\varepsilon_B - 1)(\varepsilon_{\infty B} + 2)}{(2\varepsilon_B + \varepsilon_{\infty B})}$$

$$R_{fB} = \frac{2N}{9V_B\varepsilon_0}\;\frac{(\varepsilon_m - 1)(\varepsilon_{\infty B} + 2)}{(2\varepsilon_m + \varepsilon_{\infty B})}$$

Here '*B*' refers to the molecules of pure polar liquid.

The expression in the square bracket of Eqn. (7) on simplification reduces to g_{ideal}. Hence the expression for dipolar excess free energy of mixing refers to ideal condition only. On the other hand, with the substitution of 'δg' in place of 'g_{BB}', We have the expression for dipolar excess free energy of mixing[11,12] as:

$$\Delta F_{AB} = -\frac{N}{2}(R_{fB} - R^o_{fB})\, X_B\, \mu^2_{gB}\, [X_B(\delta g - 1) + 1] \tag{8}$$

The terms in the square bracket of Eqn. (8) on expansion becomes

$$= X_B\, g_m - X_B^2\, g_{BB} + X_A^2$$

Hence Eqn. (9) can be written as

$$\Delta F_{AB} = -\frac{N}{2}(R_{fB} - R^o_{fB})\, X_B\, \mu^2_{gB}\, (X_B g_m - X_B^2 g_{BB} + X_A^2) \tag{9}$$

$$= \Delta F_{\mathrm{total}} + \Delta F_{AA} - \Delta F_{BB}$$

or,

$$\Delta F_{\text{total}} = \Delta F_{AB} + \Delta F_{BB} - \Delta F_{AA}$$

$$\Delta F_{AA} = -\frac{N}{2}(R_{fB} - R^{o}_{fB})\, X_B X_A^2 \mu_{gB}^2$$

$$\Delta F_{BB} = -\frac{N}{2}(R_{fB} - R^{o}_{fB})\, X_B^3 g_{BB} \mu_{gB}^2$$

$$\Delta F_{\text{total}} = -\frac{N}{2}(R_{fB} - R^{o}_{fB})\, X_B^2 \mu_{gB}^2\, g_m$$

EXPERIMENTAL

The experimental arrangement used for the measurement of dielectric constant is same as used by Swain[20]. The relative permittivity measurements for the pure substance and mixtures were carried out by a wavemeter oscillator at 455 KHz. The chemical used were anal grade, purified and redistilled before use. The cell temperature was controlled with an electronically regulated thermostat arrangement with temperature variation of ± 0.1 °C. The refractive indices were measured at the regulated temperature by a pulfrich refractometer at Sodium D-line. The density measurement was done in semimicrobalance with a pyknometer of 25 cm^3 volume. The reproducibility of relative permittivity and density measurements were ± 0.003 and ± 0.002 gm cm^{-3} respectively. Within this maximum limit of variation the value of 'δg' and 'ΔF_{AB}', could be measured accurately. The values of dipolar excess free energy of mixing used by Sabesan[13,14] have been taken from reference for comparison.

RESULTS AND DISCUSSION

The relevant data have been represented in Figure 1 & Table 1. It is seen in Figure 1 that the trend of variation of dipolar excess free energy of mixing evaluated on the basis of two different approaches with the mole fraction of solute in both the set of binary mixtures are similar thus confirming the qualitative agreement between the proposed equation and Haskell's equation. For a given nonpolar solvent tetrachloromethane, the change of dipolar excess free energy of mixing with the mole fraction of solute is in the order of acetic acid > *n*-butanol. This is due to the fact that the value of 'g' for acetic acid 0.635 at 306 °K ($g < 1$) indicating the predominance of β-multimers with antiparallel orientation. On the other hand, the value of g for *n*-butanol is 3.26 ($g > 1$) which indicates the predominance of α-multimers with parallel dipolar orientation.

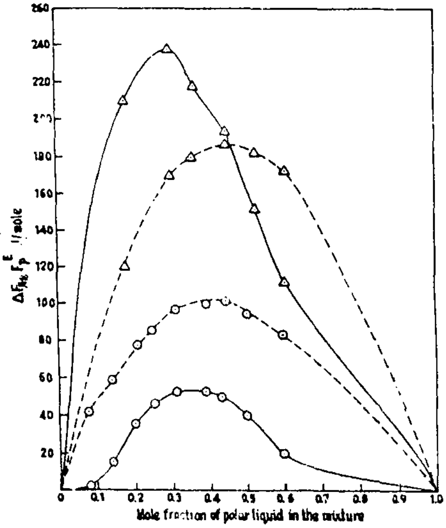

Figure 1 Variation of ΔF_{AB} and F_P^E with the mole fraction of polar liquids in the binary mixtures. Plots:⊙ *n*-butanal + CCl_4,Δ acetic acid + CCl_4, ——ΔF_{AB}, ------F_P^E.

Table 1 Variation of ΔF_{total}, ΔF_{AA}, ΔF_{BB}, ΔF_{AB}, and F_P^E in Joul/mole with the mole fraction of solute in tetrachloromethane at 306 K.

Mole fraction of solute							
X_B	g_m	δg	ΔF_{total}	ΔF_{AA}	ΔF_{BB}	ΔF_{AB}	F_P^{E*}
			(i) *n*-butanol				
.078	.82	−.356	0.11	1.42	.06	1.47	42
.135	.85	−.455	2.41	15.69	1.98	16.12	59
.198	.89	−.557	9.13	33.33	6.60	35.96	77
.245	1.00	−.554	17.99	41.85	14.39	45.45	85
.310	1.10	−.601	35.38	49.39	32.48	52.29	97
.390	1.44	−.441	69.62	46.13	62.46	53.29	100
.430	1.54	−.432	87.11	42.31	78.91	50.51	103
.500	1.72	−.410	119.39	34.71	113.15	40.95	95
.600	1.98	−.376	139.41	18.77	137.36	20.42	84
			(ii) acetic acid				
.182	.10	−.834	5.72	210.45	6.63	209.54	120
.300	.33	−.561	44.33	219.43	25.52	238.24	170
.361	.36	−.508	65.24	204.99	41.30	228.93	180
.450	.40	−.435	99.11	166.56	70.76	194.91	188
.532	.46	−.346	130.51	116.81	95.86	151.46	183
.611	.51	−.267	154.35	74.96	117.96	111.94	173

*Source - Ref No. 13, 14

In case of acetic-acid $(\Delta F_{AB})_{\max}$ is found to be more than $(F_P^E)_{\max}$ whereas in case of *n*-butanol $(\Delta F_{AB})_{\max}$ is found to be less than $(F_P^E)_{\max}$. This is due to the fact that in evaluation of F_P^E, the short range correlation between similar molecules has not been considered. As such, the energy from these interactions has not been taken into account. When a nonpolar solvent is added to strongly associated liquid like alcohol, the nonpolar molecules are polarised due to induction. As a result, interaction between induced molecules is facilited, which causes the excess free energy ΔF_{AA} [departure of F_{AA} from $(F_{AA})_{\text{ideal}}$] less. Therefore, ΔF_{AB} is considerably lowered in case of *n* butanol-tetrachloromethane liquid mixture. On the other hand when the nonpolar solvent is added to acetic acid, the degree of polarisation by induction being less, ΔF_{AA} is considerably higher. Consequently $(\Delta F_{AB})_{\max}$ is higher in case of binary mixture of acetic acid-tetrachloromethane.

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