

## SHORT COMMUNICATIONS

### EXCESS THERMODYNAMIC FUNCTIONS OF MIXING IN BINARY MIXTURES OF ALCOHOLS AND TOLUENE

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THE Kirkwood-Fröhlich linear correlation factor<sup>1</sup>,  $g$ , and excess thermodynamic functions evaluated from the dielectric constant measurement give useful information regarding the dipole interaction forces between the molecules in a mixture. Such studies have been utilized to interpret structural composition in binary mixtures of a polar liquid in a nonpolar solvent<sup>2-4</sup>. Similarly, the dielectric constant measurement may be utilized for determining mutual correlation factor and excess thermodynamic parameters eventually to be used for analysis of structural composition in a binary mixture of polar liquids.

Winkelmann *et al*<sup>5</sup> developed a relation linking the dielectric constant of a binary mixture with those of the dielectric constants of the components in the mixture. The long-range as well as the short-range dipolar interaction between identical and also between dissimilar molecules are considered in formulating this relation. The mutual correlation factor,  $g_{ab}$ , in binary mixtures of some alcohols with toluene was evaluated<sup>6</sup> using this relation. The results indicate that in such mixtures voids present in alcohol structure<sup>7,8</sup> are gradually filled up by toluene molecules forming microheterogeneous clusters of these dissimilar molecules. Further, these clusters have predominance of antiparallel orientation of dissimilar molecules ( $\beta$ -clusters) where the value of  $g_{ab}$  is less than unity. Hence, it is worthwhile to examine if results from investigation on excess thermodynamic functions support this picture.

Winkelmann *et al*<sup>9</sup> further extended their dielectric theory of binary mixture<sup>5</sup> and developed a relation for excess thermodynamic functions of mixing. According to this relation, the excess Helmholtz free energy of mixing  $\Delta F^E$  which is almost equal to the excess Gibbs free energy  $\Delta G^E$  for a matter in a condensed phase is given by

$$\Delta F^E = -\frac{N}{2} \left[ \sum_{r=a,b} \chi_r m_r^2 (R_{fr} - R_{fr}^0) \right.$$

$$\left. + \sum_{r=a,b} \{ \chi_r^2 m_r^2 (g_{rr} - 1) (R_{fr} - R_{fr}^0) \} + \chi_a \chi_b m_a m_b (g_{ab} - 1) (R_{fa} + R_{fb} - R_{fa}^0 - R_{fb}^0) \right] \\ = \Delta F_0^E + \Delta F_{rr}^E + \Delta F_{ab}^E. \quad (1)$$

The first term  $\Delta F_0^E$  in (1) 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 dipolar interaction between similar molecules and the third term  $\Delta F_{ab}^E$  gives the excess dipolar energy due to short-range interaction between dissimilar molecules. The terms  $R_{fr}^0$  and  $R_{fr}$  representing the reaction field parameters in the pure liquid and that in the mixture respectively are given by

$$R_{fr}^0 = \frac{8\pi N}{9V_r} \frac{(\epsilon_r - 1)(\epsilon_{\infty r} + 2)}{(2\epsilon_r + \epsilon_{\infty r})}, \quad 2(i)$$

$$R_{fr} = \frac{8\pi N}{9V_r} \frac{(\epsilon_m - 1)(\epsilon_{\infty r} + 2)}{(2\epsilon_m + \epsilon_{\infty r})}. \quad 2(ii)$$

The excess entropy being a temperature-dependent quantity is given as,

$$\Delta S^E = -\frac{\partial}{\partial T} (\Delta F^E). \quad (3)$$

This term can also be separated into three separate terms as in (1)

$$\Delta S^E = \Delta S_0^E + \Delta S_{rr}^E + \Delta S_{ab}^E \quad 3(i)$$

Here  $a$  and  $b$  refer to the molecules of variety  $a$  and  $b$ ,  $\chi_r$  denotes the respective molefraction of the components in the mixture,  $V_r$  and  $V_m$  denote the molar volumes of the components and the mixture respectively,  $N$  is the Avogadro number,  $K$  is the Boltzmann constant,  $T$  denotes temperature (K),  $m_r$  denotes the gasphase dipole moment of the component,  $\epsilon_m$  is the dielectric constant of the mixture,  $\epsilon_{\infty r}$  is taken as the square of the refractive index of the component,  $g_{rr}$  refers to the linear correlation factor between identical molecules and  $g_{ab}$  is the mutual correlation factor between dissimilar molecules.

All measurements were at 34°C and 45°C. The experimental details are the same as described earlier<sup>6</sup>. The  $g_{ab}$  values reported earlier have been used (table 1).

In the mixtures studied here, the microheterogeneous  $\beta$ -clusters with antiparallel orientation are

Table 1 Excess Thermodynamic functions in binary mixture at 307 K.

Mole fraction of the alcohol in the mixture	$g_{ab}$	$\Delta F_{ab}^E$ cal. mol <sup>-1</sup>	$\Delta F^E$ cal. mol <sup>-1</sup>	$T\Delta S_{ab}^E$ cal. mol <sup>-1</sup>	$T\Delta S^E$ cal. mol <sup>-1</sup>
(1) <i>n</i> -Butanol + toluene					
0.115	-0.04	-5.75	+34.98	-3.91	+29.21
0.226	-0.73	-9.40	+68.07	+26.06	-1.71
0.334	-0.72	-0.32	+90.97	+84.24	-155.22
0.438	-1.24	+7.00	+117.13	+88.26	-133.83
0.539	-0.86	+14.48	+114.85	+48.39	-122.39
0.637	-0.59	+16.00	+103.40	+16.99	-17.22
0.732	-0.07	+11.25	+76.06	-0.42	+118.14
0.824	+0.73	+1.25	+40.62	-1.11	+270.56
(2) Methanol + toluene					
0.220	-0.54	-25.78	+154.46	+115.62	-329.07
0.389	-1.44	-26.81	+253.96	+106.83	-238.77
0.522	-1.60	-1.73	+280.57	+153.75	-594.31
0.629	-1.38	+13.85	+262.13	+45.76	-259.54
0.718	-1.62	+20.41	+250.52	+15.83	-77.66
0.793	-0.90	+16.77	+184.45	-15.24	+374.23
0.856	-0.79	+14.37	+116.30	-22.37	—
(3) <i>n</i> -Propanol + toluene					
0.039	+0.55	-0.51	+17.30	-0.11	+4.39
0.091	+0.02	-5.46	+40.16	-5.50	+22.89
0.220	-0.85	-15.81	+86.35	+37.34	-30.55
0.331	-1.07	-7.22	+120.79	+51.35	-53.22
0.429	-1.37	+2.02	+148.50	+72.21	-111.32
0.503	-1.15	+10.41	+150.31	+43.85	-86.46
0.549	-0.85	+13.89	+142.80	+39.82	-141.29
0.601	-0.52	+14.33	+130.56	+21.45	-98.24
0.642	-0.31	+13.55	+120.06	+10.87	-37.59
0.730	+0.44	+6.08	+83.22	+2.01	+61.90
0.827	+0.71	+2.71	+55.41	-2.35	—
0.869	+0.74	+1.96	+41.93	0.0	—
0.914	+1.00	+0.00	+25.56	0.0	—

predominant over  $\alpha$ -clusters. Antiparallel alignment in  $\beta$ -clusters necessitates decrease in internal energy of the system due to destruction of angular correlation between dissimilar molecules. Hence it is expected to result in increase in the value of  $\Delta F_{ab}^E$ . The present study shows that  $\Delta F_{ab}^E$  changes from negative to positive suggesting gradual formation of  $\beta$ -clusters with increase in alcohol concentration. As expected, this value attains a maximum in nearly equimolar concentration range. With further increase in alcohol concentration it decreases presumably due to the fact that a smaller number of toluene molecules are available for the formation of  $\beta$ -clusters. The value of  $\Delta F^E$  in all the mixtures studied remain positive over the entire concentration range. However, for a meaningful interpretation of this aspect, relative con-

tribution from  $\Delta F_{ab}^E$  and  $\Delta F_{\pi}^E$  should be taken into account. This, however, is not relevant to our present report.

The value of  $T\Delta S_{ab}^E$  remains positive almost over the entire concentration range in these mixtures. This further reinforces the idea of destruction of angular correlation between dissimilar molecules. The value of  $T\Delta S^E$ , however, remains mostly negative. According to Branin and Smyth<sup>10</sup>, negative entropy suggests reduced number of configurations, that is, the mixture as a whole is more ordered compared to the individual components.

The value of  $\Delta F^E$  and  $T\Delta S^E$  calculated in this investigation could be used to evaluate the excess enthalpy of mixing  $\Delta H^E$ .

In mixtures (not reported here) of toluene with some



non-associated liquids such as chlorobenzene, methylbenzoate and ethylbenzoate, the value of  $\Delta F_{ab}^E$  is almost nil supporting the fact that there is no tendency for clustering of dissimilar molecules in such mixtures.

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these solvents was tested by gas chromatography, density and refractive index. The impurity did not exceed 0.005 mol%. The density and the refractive index values varied in the fifth decimal place as compared to literature values. The mixtures were made up in special stoppered weighing bottles to prevent preferential evaporation losses. For each pair, the solvent mixtures were prepared by varying 2 volume percent in composition and the average of these two compositions is reported.

The dependence of mutual diffusion coefficients on composition of the mixture is exhibited in figures 1 and 2. Judging from the scatter of experimental points, the maximum deviation in  $D$  for any of the runs is about 3%, while the average deviation from the curve is somewhat less than 1 to 2%. In figure 1 are plotted the diffusion data for mixtures of cyclohexane-carbon tetrachloride, carbon tetrachloride-benzene and bromobenzene-chlorobenzene for the reason that these mixtures are nearly ideal. The present data are in good agreement with literature findings<sup>7,11-13</sup>.

In figure 2 are plotted the diffusion data for mixtures of carbon tetrachloride-methanol and carbon tetrachloride-ethanol. The differences from literature values are due to the involvement of an anisotropic solvent, namely, methanol or ethanol as one of the components of the mixture. Of these, the carbon

## MUTUAL DIFFUSION COEFFICIENTS OF BINARY LIQUID MIXTURES

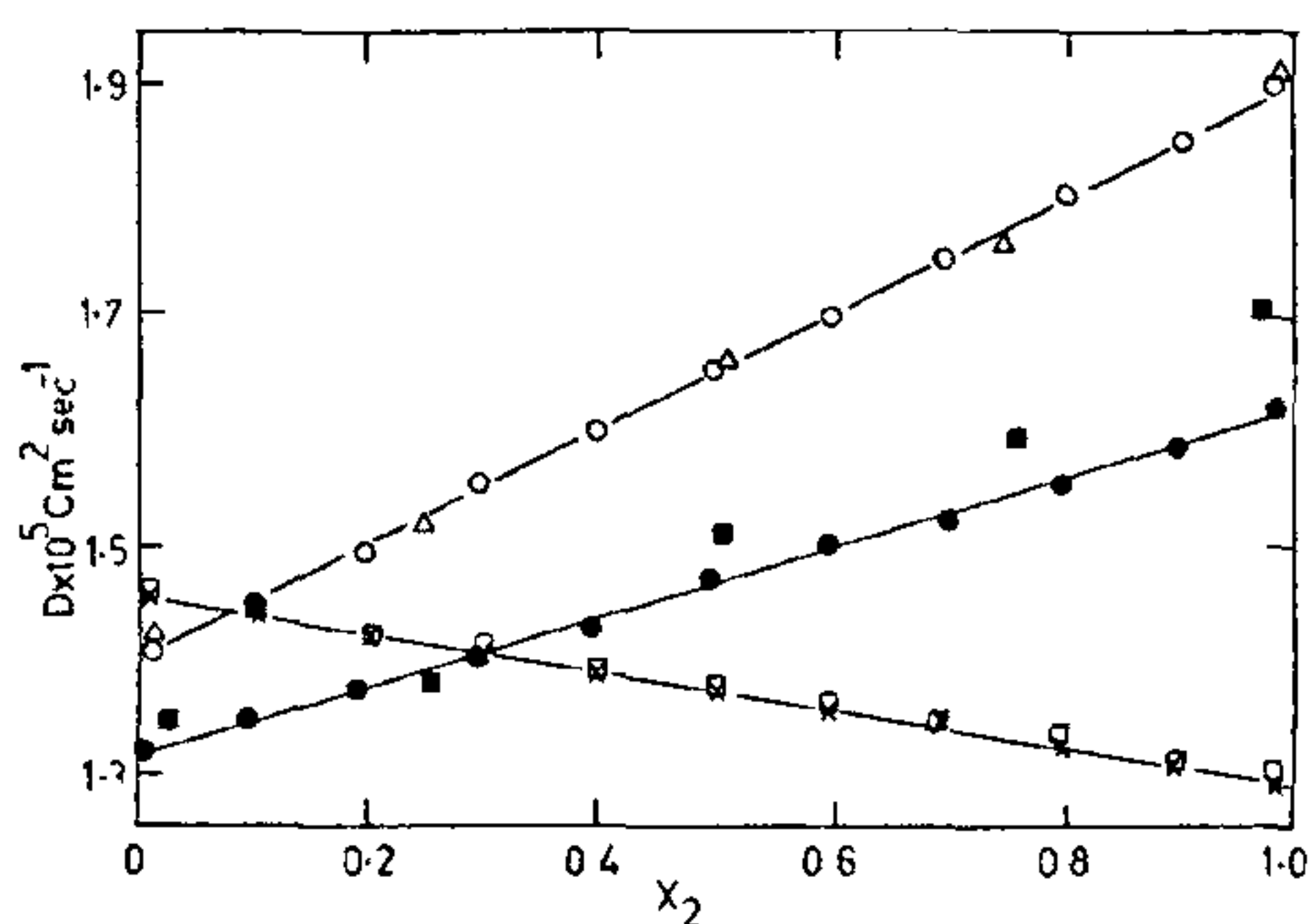
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RECENTLY, considerable effort has been bestowed on the study of mutual diffusion coefficients  $D$  from both experimental and theoretical points of view<sup>1-3</sup>. Of the several experimental techniques<sup>4-9</sup> to study the diffusion coefficients, analytical ultracentrifuge has rarely been used<sup>1,10</sup>. In this study we present data for mutual diffusion coefficients in five sets of liquid mixtures comprising cyclohexane, carbon tetrachloride, benzene, bromobenzene, chlorobenzene, ethanol and methanol.

The reagent grade solvents used were purified by fractionation through a five feet column. The purity of



**Figure 1.** Mutual diffusion coefficient as a function of composition for cyclohexane (1)-carbon tetrachloride (2), carbon tetrachloride (1)-benzene (2) and bromobenzene (1)-chlorobenzene (2) systems. Symbols: X present data (25°C), □ data from ref. 16 (25°C) for  $C_6H_{12}-CCl_4$ ; ○ present data (25°C) △ data from ref. 13 (25.26°C) for  $CCl_4-C_6H_6$  and ● present data (25°C), ■ data from ref. 13 (26.78°C) for  $C_6H_5Br-C_6H_5Cl$ .