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Evaluation of Excess Free Energy of Mixing in Binary Mixture of Polar-Nonpolar Liquids Using Dielectric Probe-an Experimental Assessment of the Efficiency of Proposed Equation

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EVALUATION OF EXCESS FREE ENERGY OF MIXING IN BINARY MIXTURE OF POLAR-NONPOLAR LIQUIDS USING DIELECTRIC PROBE – AN EXPERIMENTAL ASSESSMENT OF THE EFFICIENCY OF PROPOSED EQUATION

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Excess free energy of mixing ΔF_{total} , ΔF_{AB} in the binary mixtures of long chain alcohols and amines in nonpolar solvent carbon tetrachloride have been calculated with the help of our proposed equation. The novelty of our equation is that it involves separate estimation of excess free energy of mixing due to interaction between polar-polar molecules, polar-induced nonpolar molecules and induced nonpolar molecules and a picture of molecular interaction in these mixtures has been elicited with the help of these parameters.

Keywords: Binary mixtures; free energy of mixing

1. INTRODUCTION

Earlier [1] we have studied the molecular interaction in binary mixtures of *n*-butanol + tetrachloromethane and acetic acid + tetrachloromethane through evaluation of excess free energy of mixing based on our equation and compared the result with those of Sabesan *et al.* [2, 3]. In the present paper, we have investigated the same in two categories of binary mixtures viz. strongly associated liquid, long chain alcohols in nonpolar liquid tetrachloromethane and mildly associated

liquids, amines in same nonpolar liquid. We have evaluated ΔF_{total} and ΔF_{AB} for two categories of mixtures and tried to elicit a picture of molecular interaction in such systems.

Theory

The excess free energy of mixing [1] ΔF_{total} and ΔF_{AB} are given by

$$\Delta F_{\text{AB}} = -\frac{N}{2} [R_{fB} - R_{fB}^{\circ}] [X_B \mu_B^2 \{X_B(\delta g - 1) + 1\}] \quad (1)$$

$$\Delta F_{\text{total}} = -\frac{N}{2} [R_{fB} - R_{fB}^{\circ}] [X_B^2 \mu_B^2 g] \quad (2)$$

where

$$R_{fB}^{\circ} = -\frac{2N}{9\varepsilon_{\circ} V_B} \frac{(\varepsilon_B - 1)(\varepsilon_{\infty B} + 2)}{(2\varepsilon_B + \varepsilon_{\infty B})} \quad (3)$$

$$R_{fB} = -\frac{2N}{9\varepsilon_{\circ} V_B} \frac{(\varepsilon - 1)(\varepsilon_{\infty B} + 2)}{(2\varepsilon + \varepsilon_{\infty B})} \quad (4)$$

Experimental

The chemicals used were of anal grade and of reputed make and redistilled before use. The experimental arrangement used for the measurement of relative permittivity etc. is the same as used by Swain [4]. The relative permittivity measurements for the pure polar liquids and mixtures, were carried out by a wavemeter-oscillator combination at the frequency 455 kHz. The device was standardized with the help of standard liquids with known relative permittivity [5]. The cell temperature was controlled with an electronically regulated thermostatic arrangement at the regulated temperature by a Pulfrich refractometer at the sodium D-line. The density measurement was done by a semimicrobalance with a pycnometer of 25 cm³ volume. The reproducibility of relative permittivity measurement at the radio frequency was ± 0.003 and those of refractive index and density measurement were ± 0.00002 and ± 0.00002 gm cm⁻³ respectively.

For these maximum limits of variation, the value of ΔF_{AB} , ΔF_{AA} , ΔF_{BB} and ΔF_{total} could be measured accurately up to second decimal digit.

2. RESULTS AND DISCUSSION

The variation of ΔF_{AB} and ΔF_{total} with the molefraction of solute is depicted in Figures 1 and 2 and Table I.

Though the trend of variation of ΔF_{AB} and ΔF_{total} for the two categories of mixtures is same, yet some distinct features are observed. In the higher concentration range ΔF_{total} overrides ΔF_{AB} . It is

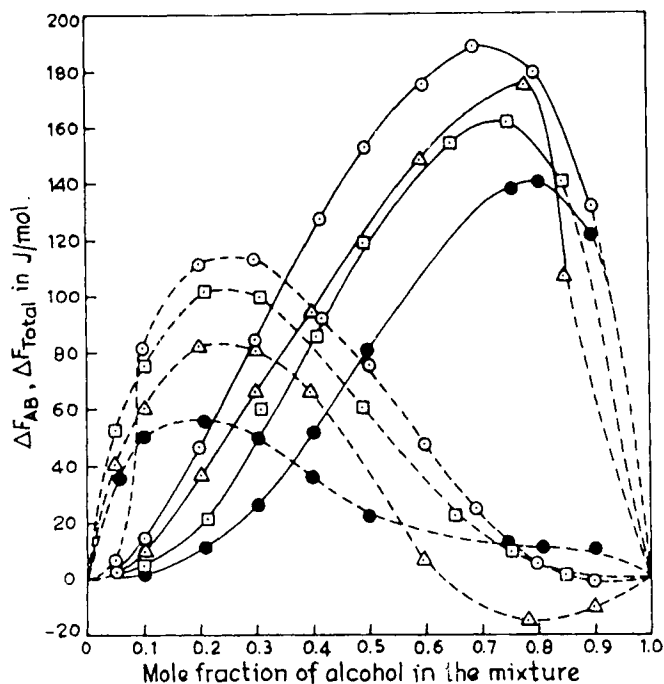


FIGURE 1 Variation of ΔF_{AB} , ΔF_{total} with the mole fraction of alcohol in the binary mixture of alcohol and carbontetrachloride at 303°K.

Plots: ΔF_{AB} —, ΔF_{total} ---, pentanol \circ , hexanol Δ , heptanol \square , octanol \bullet .

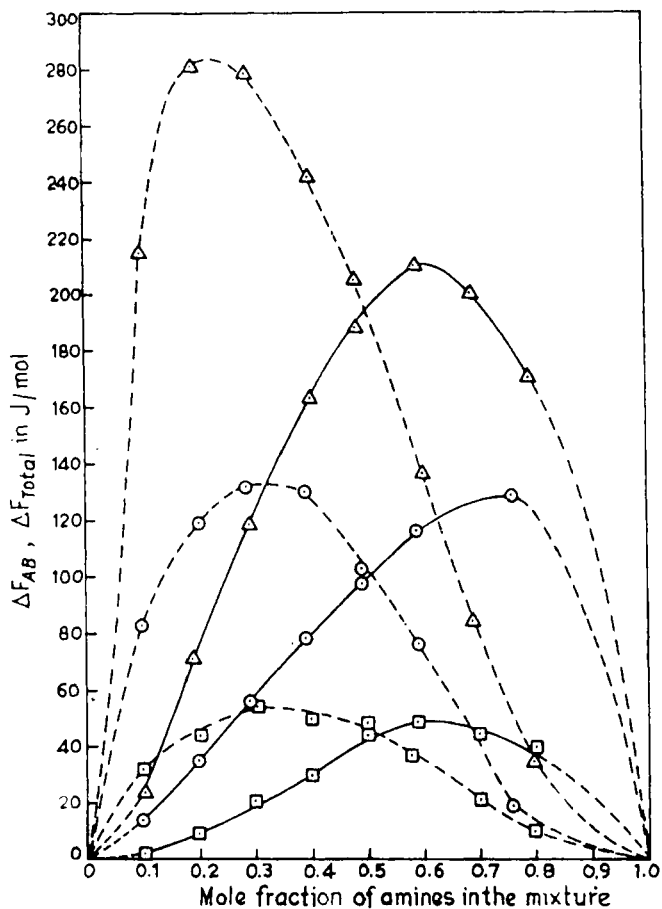


FIGURE 2 Variation of ΔF_{AB} , ΔF_{total} with the mole fraction of amine in the binary mixture of amine and carbontetrachloride at 303°K.

Plots ΔF_{AB} ---, ΔF_{total} —, aniline \circ , pyridine Δ , dimethyl aniline \square .

probably due to the fact that when an appreciable amount of solute is added (i.e. in the higher concentration range) it facilitates interaction between the induced nonpolar liquid molecules causing excess free energy [the departure of $(F_{AA})_{expt}$ from $(F_{AA})_{ideal}$] less. Consequently $\Delta F_{total} > \Delta F_{AB}$ beyond 0.3 to 0.4 mole fraction range of solute. But the situation is reverse in the lower concentration range, where the nonpolar molecules are not properly induced to have any interaction

TABLE I Variation of ΔF_{total} , ΔF_{AB} in J/mol with the mole fraction of polar liquid in carbon tetrachloride at 303°K

	$X_B - \Delta F_{\text{total}} - \Delta F_{\text{AB}}$		$X_B - \Delta F_{\text{total}} - \Delta F_{\text{AB}}$		$X_B - \Delta F_{\text{total}} - \Delta F_{\text{AB}}$		$X_B - \Delta F_{\text{total}} - \Delta F_{\text{AB}}$				
	(i) Pentanol	(ii) Hexanol	(iii) Heptanol	(iv) Octanol	(v) Aniline	(vi) Pyridine	(vii) Dimethyl amine				
.050	.46	4098	.057	2.98	40.51	.056	1.54	52.06	.059	0.38	35.75
.099	14.66	81.38	.099	9.80	59.55	.097	5.19	75.86	.100	2.43	49.70
.200	46.85	111.85	.200	37.25	82.69	.209	21.12	102.79	.210	10.42	56.97
.299	84.51	112.93	.300	66.08	80.72	.310	60.87	100.63	.300	26.01	49.09
.421	126.79	91.40	.399	94.37	65.18	.399	85.89	81.49	.401	52.45	36.96
.495	151.79	75.90	.599	147.22	5.16	.488	119.15	60.55	.499	80.34	22.29
.596	175.73	48.83	.785	176.06	-15.09	.655	154.54	22.45	.759	138.54	11.27
.689	187.78	24.48	.853	106.79	-14.59	.750	161.26	10.40	.810	140.09	13.13
.800	179.42	5.03				.850	140.52	.03	.899	122.24	11.49
.899	131.33	0.48									
.099	13.19	93.07	.098	23.33	215.83	.103	1.59	31.49			
.197	34.64	119.26	.194	71.31	281.62	.200	8.92	43.04			
.293	56.63	132.69	.292	118.35	279.16	.299	20.21	53.68			
.393	77.79	125.62	.400	163.65	242.01	.399	29.18	49.44			
.490	97.83	102.96	.480	188.38	205.57	.498	44.44	48.97			
.587	116.29	75.80	.590	209.13	136.05	.582	47.59	37.07			
.761	127.91	17.68	.685	199.74	84.75	.698	44.71	20.94			
			.797	165.47	35.23	.798	39.63	10.33			

among themselves. Further, in case of alcohols, $(\Delta F_{\text{total}})_{\text{max}} > (\Delta F_{\text{AB}})_{\text{max}}$, whereas in case of amines $(\Delta F_{\text{AB}})_{\text{max}} > (\Delta F_{\text{total}})_{\text{max}}$. This is due to the fact that the strength of hydrogen bonding is more in case of alcohol in comparison to amines. As such alcohol molecules help in better interaction among the induced nonpolar molecules resulting in less value of ΔF_{AA} in the binary mixtures of alcohols in nonpolar solvents.

At this stage it is appropriate to study the behaviour of ΔF_{AB} rather than ΔF_{total} since it results from the interaction of the polar molecules with induced nonpolar molecules. Further the study of cluster formation, multimerisation etc. can be effectively studied through evaluation of ΔF_{AB} rather than through ΔF_{total} .

In the both category of mixtures, $(\Delta F_{\text{AB}})_{\text{max}}$ occurs in the lower concentration range. It is due to the fact that in the lower concentration range, formation of β -clusters (antiparallel orientation of molecular dipoles) results in an increase of ΔF_{AB} [6, 7, 8, 9]. With gradual increase of polar liquids, a stage is reached when α -clusters (parallel orientation of dipoles) are formed which results in decrease of ΔF_{AB} . Further conversion of β -cluster to α -cluster in the lower concentration range agree with spontaneous polarisation in dilute solution [10]. The conversion of β -cluster to α -cluster in case of amines in relatively lower concentration is due to low value of correlation factor of amines.

It is observed from Figure 1 that the excess free energy of mixing for odd long chain alcohols is more in comparison to even long chain alcohols (Pentanol > Heptanol > Hexanol > Octanol).

It indicates that the interaction between odd long chain alcohols with nonpolar solvents is less compared to that between even long chain alcohols with nonpolar solvents. It is due to the fact that in case of even long chain alcohols the matching is more effective due to the fitting of one molecular chain in the vacant space of another chain and the proximity of molecular chain is favourable for greater interaction. In case of odd number alcohols, this type of fitting between molecular chain is not effective leading to less interaction. It is further observed that interaction is less in pentanol in comparison to heptanol in odd long chain alcohols, and in hexanol compared to octanol in even long chain alcohols. Since the interacting group-OH is common to all the

alcohols, the difference in strength of interaction and the value of excess free energy of mixing is probably due to the difference in the value of g of pure alcohols. [$g_{\text{pentanol}}^{(3.25)} > g_{\text{heptanol}}^{(2.43)} > g_{\text{hexanol}}^{(3.92)} > g_{\text{octanol}}^{(3.08)}$] at 303°K]

The negative value of ΔF_{AB} in the higher concentration range of alcohols (beyond 0.65 molefraction of solute) is probably due to the saturation of the fitting of molecular chain of polar molecules in the vacant space of molecular chain of nonpolar solvents.

From Figure 2, it is observed that ΔF_{AB} is in the order, pyridine > aniline > dimethyl aniline. The reason for this may be explained as follows. In case of dimethyl aniline due to the inductive effect (+I effect) of two methyl groups, electron density is more concentrated on the nitrogen atom which brings about greater repulsion between solute and solvent electronic orbit. Hence induced polarisation of electron cloud in case of nonpolar solvent is more prominent resulting in stronger induced dipole. Hence interaction between the polar solute and induced nonpolar dipole molecules is maximum. In case of aniline, the lone pair of electrons of nitrogen enters into resonance with benzene ring and results in three ionic resonating structures. The resonance hybrid describing the actual state of the molecule is more polar than the nonionic structures. Thus there is an appreciable ionic character developed on the solute molecules. Also the electronic orbitals of the nonpolar solvent molecules are appreciably polarised. This results in moderate interaction between partially ionic molecules and induced dipoles of solvent molecules. But the situation is completely different in case of pyridine, where the lone pair electrons of nitrogen atom cannot enter into the resonance with aromatic ring thereby reducing the ionic character. Therefore weak dipole of pyridine cannot effectively polarise the electronic orbital of solvent molecules leading to minimum interaction between its molecules and carbon tetrachloride. Consequently the departure of $(F_{AB})_{\text{expt}}$ from $(F_{AB})_{\text{ideal}}$ becomes maximum in case of pyridine.

Thus the evaluation of ΔF_{AB} plays an important role in the study of cluster formation, multimerisation as well as in the interaction of solute solvent molecules in the binary mixture of polar and nonpolar liquids.

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