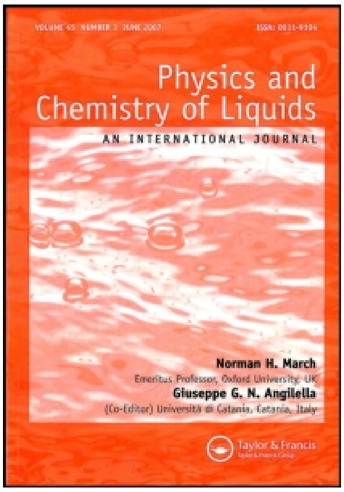

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EVALUATION OF EXCESS GIBBS ENERGY OF MIXING IN EXTREMELY DILUTE SOLUTIONS OF TRI-N-BUTYL PHOSPHATE IN NONPOLAR SOLVENTS

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The excess gibbs energy of mixing in binary mixtures of TBP in nonpolar solvents viz. benzene, carbon disulphide, cyclohexane, *n*-heptane, *n*-hexane, *p*-xylene, tetrachloromethane at temperature 303°K is studied. The excess free energy of mixing (ΔG_{AB}) is in the order, *n*-hexane < *n*-heptane < benzene < cyclohexane < *p*-xylene < CCl_4 < CS_2. The results corroborate the findings obtained through evaluation of the excess correlation factor.

Keywords: Gibbs energy; molecular interactions; nonpolar solvents

1. INTRODUCTION

Dielectric studies of binary mixtures of hydrogen bonded liquid, especially polar-nonpolar liquids in extremely dilute solution, represents an interesting field of investigation. Evaluation of '*g*' in the dilute state in the Winkelmann Quitzsch equation indicates that it should increase when the mole fraction of the polar solute tends to zero. Tripathy *et al.* [1] observed that it increases in alcohols and decreases

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in amines. Identical results have been obtained in the binary mixtures of TBP in nonpolar solvents [2]. In view of this, we have defined the excess correlation factor [3, 4] and evaluated the excess gibbs energy of mixing in these binary mixtures in extremely dilute states. This parameter helps in forming a better picture of molecular interaction as compared to that obtained through the evaluation of 'g'. Further the Winkelmann-Quitzsch equation for the excess gibbs energy of mixing for polar and nonpolar liquids indicates that it is applicable to an ideal condition [5]. On the other hand, the modified equation proposed in Refs. [6, 7] shows that it is an equation of a general kind as it involves all the possible types of interaction as revealed in the theory. Therefore we have evaluated the excess gibbs energy of mixing in dilute solution of TBP in nonpolar solvents using our equation. We have chosen tri-*n*-butyl phosphate as a polar liquid for its utility as an important commerical extractant in the atomic energy industry for separation of plutonium [8, 9].

2. THEORY

The excess correlation factor 'δg' whose magnitude is taken as a departure from its ideal value is given by [3, 6, 7, 10]

$$\delta g = g_m - (X_A + X_B\, g_{BB}) \tag{1}$$

where
$$g_m = \frac{9KT\varepsilon_o(2\varepsilon_m + \varepsilon_{\infty B})^2}{N\mu_{gB}^2 X_B(\varepsilon_{\infty B}+2)^2(2\varepsilon_m+1)}$$

$$X\left[V_m\frac{\varepsilon_m - 1}{\varepsilon_m} - \frac{3X_A V_A(\varepsilon_A - 1)}{2\varepsilon_m + \varepsilon_A} - \frac{3X_B V_B(\varepsilon_B - 1)}{2\varepsilon_m + \varepsilon_{\infty B}}\right]$$

and
$$g_{BB} = \frac{9KT\varepsilon_o(2\varepsilon_B + \varepsilon_{\infty B})^2}{N\mu_{gb}^2 X_B(\varepsilon_{\infty B}+2)^2(2\varepsilon_B+1)}\left[V_B\frac{\varepsilon_B - 1}{\varepsilon_B} - \frac{3X_B V_B(\varepsilon_{\infty B}-1)}{2\varepsilon_B + \varepsilon_{\infty B}}\right].$$

X_A and X_B denote the mole fraction of nonpolar and polar liquids; V_m, V_A and V_B denote the molar volume of mixture, nonpolar liquid and polar liquid respectively, ε_m and ε_B are the dielectric constant of the mixture and polar liquid, μ_{gB} is the gas phase dipole moment of the polar liquid. N is Avogadro's number, K is the Boltzmann constant, ε_o is the vacuum permittivity and T is the temperature in kelvin. 'g_m' is the correlation factor for the binary mixture of polar and nonpolar liquids and g_{BB} is the Kirkwood correlation factor of the pure polar liquid.

The excess gibb's energy of mixing for the binary mixture of polar and nonpolar liquids can be expressed as [3, 5, 7]

$$\Delta G_{AB} = -\frac{N}{2}[R_{fB} - R_{fB}{}^{\circ}][X_B\mu^2 g_B\{X_B(\delta g - 1) + 1\}] \tag{2}$$

where

$$R^{\circ}_{fB} = -\left(\frac{2N}{9\varepsilon_o V_B}\right)[(\varepsilon_B - 1)(\varepsilon_{\infty B} + 2)/(2\varepsilon_B + \varepsilon_{\varepsilon fty B})]$$

$$R_{fB} = -\left(\frac{2N}{9\varepsilon_o V_B}\right)[(\varepsilon_m - 1)(\varepsilon_{\infty B} + 2)/(2\varepsilon_m + \varepsilon_{\varepsilon fty B})]$$

We have also found

$$\Delta G_{\text{total}} = \Delta G_{AB} - \Delta G_{AA} + \Delta G_{BB} \tag{3}$$

where

$$\Delta G_{\text{total}} = -\left(\frac{N}{2}\right)[R_{fB} - R^{\circ}_{fB}][X_B{}^2\mu^2_{gB}g_m]$$

$$\Delta G_{AA} = -\left(\frac{N}{2}\right)[R_{fB} - R^{\circ}_{fB}][X_A{}^2 X_B\mu^2_{gB}]$$

$$\Delta G_{BB} = -\left(\frac{N}{2}\right)[R_{fB} - R^{\circ}_{fB}][X_B{}^3 g_{BB}\mu^2_{gB}].$$

The negative sign of ΔG_{AA} in equation [3] indicates that the excess gibb's energy of mixing between the nonpolar molecules arises due to their induction effect in an environment of polar solute molecules.

3. EXPERIMENTAL

The chemicals used were of anal. grade and manufactured by Merck. They were redistilled before use [11, 12]. The experimental arrangement used for the measurement of relative permittivity etc. was the same as used by Swain [13]. The relative permittivity measurements for pure substances and mixtures were carried out by means of a wave meter-oscillator combination at frequency 455 KHz. The device was standardized with the help of standard liquids (tetrachloromethane, benzene) with known relative permittivity [14]. The cell temperature was controlled with an electronically regulated thermostatic arrangement at the regulated temperature. The refractive index was determined by a Pulfrich refractometer at sodium D-line. The density measurement was done by a semimicrobalance with a pyknometer of 25 cm^3 volume. The reproducibility of the relative permittivity measurements at the radio frequency was ± 0.003 and those of refractive index and density measurements were ± 0.00002 and ± 0.00002 gm cm^{-3} respectively. The values of ΔG_{AA}, ΔG_{AB} and ΔG_{total} could be measured up to the second decimal digit.

4. RESULTS AND DISCUSSION

The experimental values of the excess gibbs energy of mixing in the binary mixture tri-*n*-butyl phosphate in nonpolar solvents (i.e. benzene, carbon disulphide, cyclohexane, *n*-heptane, *n*-hexane, *p*-xylene, tetrachloromethane) at 303°K have been presented in Table I. We have observed earlier [7] that the study of cluster formation and molecular association can be effectively studied through the evaluation of ΔG_{AB} rather than through ΔG_{total}.

It is observed that the variation of dielectric constant in these binary mixtures with the mole fraction of polar liquids is nonlinear [15].

TABLE I Variation of ΔG_{total}, ΔG_{AA} and ΔG_{AB} in J Mol^{-1} with the mole fraction of TBP in nonpolar solvents at 303°K

X_B	ε^*_m	ΔG_{total}	ΔG_{AA}	ΔG_{AB}
(1)	(2)	(3)	(4)	(5)
		(a) TBP + benzene		
.030	2.450	0.14	7.62	7.75
.035	2.496	0.27	11.52	11.77
.060	2.550	0.99	19.89	20.77
.076	2.873	2.33	31.94	33.98
.100	3.100	4.94	45.64	49.85
		(b) TBP + Carbon disulphide		
.020	3.150	0.34	11.10	11.43
.030	3.350	0.79	17.87	18.64
.040	3.550	1.48	25.20	26.62
.050	4.070	3.14	35.92	38.93
.060	4.100	4.31	42.51	47.61
.070	4.200	5.66	49.69	54.98
.080	4.350	9.09	62.04	70.41
.090	4.550	10.00	65.68	74.83
		(c) TBP + Cyclohexane		
.030	2.454	0.28	9.49	9.96
.050	2.600	0.88	17.81	18.62
.070	2.720	1.79	2.66	28.19
.080	2.750	2.53	33.11	35.31
.090	2.780	2.81	34.33	36.70
.102	2.802	0.39	38.61	41.50
		(d) TBP + *n*-heptane		
.010	2.100	0.012	1.68	1.69
.020	2.150	0.055	3.78	3.83
.030	2.200	0.093	4.16	4.24
.040	2.300	0.042	9.91	10.27
.050	2.400	0.769	14.14	14.85
.060	2.500	1.34	18.83	19.98
.070	2.600	2.11	23.83	25.48
.080	2.700	3.12	29.26	32.09
.090	2.800	4.38		38.77
		(e) TBP + *n*-hexane		
.010	1.900	0.40	0.59	5.96
.020	1.950	0.22	3.04	3.06
.030	2.000	0.05	3.34	3.38
.050	2.150	0.36	13.57	9.10
.070	2.430	0.75	19.75	20.35
.100	2.700	4.40	35.00	38.89

TABLE I (Continued)

X_B	ε_m^*	ΔG_{total}	ΔG_{AA}	ΔG_{AB}
(1)	(2)	(3)	(4)	(5)
		(f) TBP + *p*-xylene		
.022	2.623	3.83	8.51	9.04
.060	2.850	2.14	25.69	27.69
.080	3.000	4.02	36.09	39.77
.100	3.190	6.60	47.75	53.59
		(g) TBP + tetrachloromethane		
.019	2.397	0.10	5.70	5.79
.030	2.500	0.29	10.02	10.30
.040	2.600	0.61	14.55	15.12
.050	2.815	1.30	21.33	22.56
.060	2.900	2.10	26.57	28.52
.070	3.000	3.02	32.27	35.06
.082	3.303	4.74	42.90	48.15

*Source - Ref. No. 2.

It was reported earlier by Swain and Roy [16] that nonlinear variation of dielectric constant signifies that the process of multimerisation undergoes a change with the change in concentration of polar liquids. The extent of nonlinearity is probably an indicator of the rate of multimerisation involved in association of polar molecules in the binary mixture of polar and nonpolar liquids. Swain [17] also reported that the nonlinear variation could be attributed to short range interaction present in the associated liquid. In view of this, we are of the opinion that the findings drawn from the excess gibbs energy of mixing between polar and nonpolar molecules of the binary mixtures can be corroborated with the findings drawn from the variation of dielectric constant of these binary mixtures.

It is observed that in almost all the mole fraction of TBP, the variation of dielectric constant is in the order, *n*-hexane < *n*-heptane < benzene < cyclohexane < *p*-xylene < CCl_4 < CS_2 which fairly agrees with the variation of excess gibbs energy of mixing (ΔG_{AB}). TBP is a mildly associated liquid ($g = 1.3$) which can remain either in wood pile or head tail structure (Fig. 1). Head tail structure results in α-multimers and wood pile structure results in β-multimers . In the low concentration range, TBP molecules are surrounded in an environment of non-polar molecules. In the case of binary mixtures

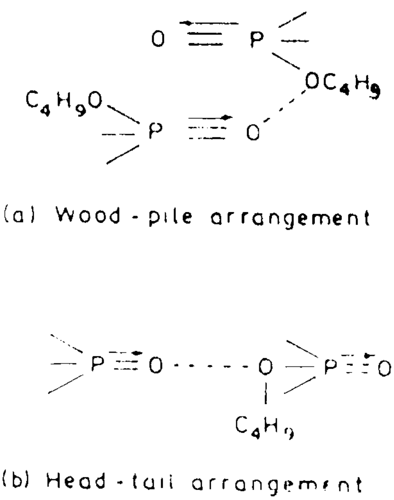

FIGURE 1 Head-tail and wood-pile arrangements of TBP molecules.

of TBP $+CS_2$, it is the interaction between π-electron of CS_2 with '0' of phosphoryl group of TBP which results in formation of β-clusters and consequently decrease the internal energy [14]. Therefore the excess gibbs energy of mixing ΔG_{AB} increases and becomes maximum. Our earlier findings [18] on 'δg' corroborates this. In the case of the binary mixture of TBP $+CCl_4$, the interaction is due to '0' of phosphoryl group of TBP with 'Cl' atom of tetrahedral CCl_4. But in TBP + *p*-xylene mixture, greater delocalization found in benzene ring through the hyperconjugative effect of $-CH_3$ group is a possible factor for reinforcing greater angular correlation with TBP molecules. The relatively high value of the excess correlation factor [16] is an indicator of favourable interaction leading to formation of β-clusters. In the binary mixture of TBP + cyclohexane, TBP molecules are trapped in the cleavage of the chair structure of cyclohexane molecules and probably accommodated in head-tail linkage. In case of the binary mixture of TBP + benzene, the π-electron in the benzene ring inhibits correlation due to unfavourable interaction with lone pair of oxygen of TBP. Consequently, excess free energy of mixing is relatively less. In case of *n*-hexane and *n*-heptane, the situation is different when the concentration of TBP is very low, the isolated TBP molecules fail to establish any correlation among themselves nor the solvent molecules help in reinforcing angular correlation. As a result, the excess gibbs energy of mixing (ΔG_{AB}) is comparatively low in this case.

In view of the above findings, we conclude that the expression for the excess gibbs energy of mixing suggested by us reflects molecular association in binary mixtures of polar-nonpolar liquids even in an extremely dilute state in a better way than obtained from equations proposed earlier and merits further consideration.

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