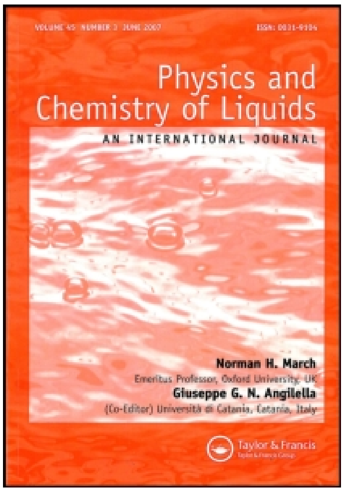


Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Evaluation of Excess Correlation Factor in Dilute Binary Mixtures of Tri-N-Butyl Phosphate (TBP) in Nonpolar Solvents

Suparna Ray[a]; Biswadas Mohanty[b]; Sandip Kumar Ray[b]; Gouri Sankar Roy[b]
[a] R. D. Women's College, Bhubaneswar [b] P. G. Department of Physics, Ravenshaw College, Cuttack

To cite this Article Ray, Suparna , Mohanty, Biswadas , Ray, Sandip Kumar and Roy, Gouri Sankar(1996) 'Evaluation of Excess Correlation Factor in Dilute Binary Mixtures of Tri-N-Butyl Phosphate (TBP) in Nonpolar Solvents', Physics and Chemistry of Liquids, 32: 4, 211 — 217

To link to this Article: DOI: 10.1080/00319109608030535

URL: http://dx.doi.org/10.1080/00319109608030535

Phys. Chem. Liq., 1996, Vol. 32, pp. 211–217
Reprints available directly from the publisher
Photocopying permitted by license only

EVALUATION OF EXCESS CORRELATION FACTOR IN DILUTE BINARY MIXTURES OF TRI-N-BUTYL PHOSPHATE (TBP) IN NONPOLAR SOLVENTS

SUPARNA RAY*, BISWADAS MOHANTY, SANDIP KUMAR RAY
and GOURI SANKAR ROY

P. G. Department of Physics, Ravenshaw College, Cuttack
**R. D. Women's College, Bhubaneswar*

(Received 13 February 1996)

Excess correlation factor δg in dilute binary mixtures of TBP in nonpolar solvents like tetrachloromethane, *n*-hexane, *n*-heptane, benzene, *p*-xylene, carbon disulphide and cyclohexane has been calculated. δg is found to be positive in binary mixtures of TBP-*p*-xylene, TBP-carbon disulphide and negative in TBP-*n*-hexane, TBP-benzene, TBP-cyclohexane mixtures. δg changes its sign from negative to positive in TBP-tetrachloromethane and TBP-*n* heptane. A sharp peak observed in TBP-carbon-disulphide indicates possibility of complexation.

Keywords: Excess correlation factor; Binary mixture; α and β multimer.

INTRODUCTION

Excess parameters [1–9] are often used to throw light on molecular interaction of binary mixtures of polar-polar and polar-nonpolar liquids. Linear correlation factor [10, 11] considered as a shape dependent parameter 'g' is a measure of short range intermolecular force leading to dipole-dipole interaction. The evaluation of 'g' on the basis of W.Q. equation [12] suitably modified for the purpose indicates that it should be either infinity or indeterminate when molefraction of solute tends to zero. Our observations [13] indicate that g increases in binary mixtures of TBP-tetrachloromethane, TBP-*n*-hexane, TBP-*n* heptane, TBP-benzene and decreases in TBP-*p*-xylene, TBP-carbondisulphide TBP-cyclohexane, when molefraction of solute tends to zero. Thus the evaluation of g does not properly reflect the nature of molecular interaction in binary as well as ternary mixtures. Therefore, we have considered excess correlation factor 'δg', the difference between experimentally determined g and its ideal value as a more appropriate parameter for such type of study.

THEORY

Kirkwood-Fröhlich linear correlation factor [11] for the binary mixture of polar and non-polar liquid is expressed as

$$g = [9KT\varepsilon_0(2\varepsilon + \varepsilon_{\infty B})^2 / N\mu_B^2 X_B(\varepsilon_{\infty B} + 2)^2 (2\varepsilon + 1)]$$
$$[V(\varepsilon - 1)/\varepsilon - 3X_A V_A(\varepsilon_A - 1)/(2\varepsilon + \varepsilon_A) - 3X_B V_B(\varepsilon_{\infty B} - 1)/(2\varepsilon + \varepsilon_{\infty B})], \quad (1)$$

where A and B represent the nonpolar and polar liquid, respectively, X_A and X_B denote the mole fraction of nonpolar and polar liquid respectively, V, V_A, V_B denote the molar volume of mixture, nonpolar liquid and polar liquid, respectively, ε, ε_A denote the dielectric constant of mixture and non-polar liquid, respectively, $\varepsilon_{\infty B}$ is the square of the refractive index, μ_B is the dipole moment of polar liquid, K is Boltzmann constant, T is the temperature in Kelvin, N is Avogadro's number, ε_0 is the vacuum permittivity.

From Eqn. (1) it is observed that g increases with decrease of X_B. But in case of amines [18] g is found to decrease with the decrease of mole fraction of polar solute. In view of this, we have utilized the concept of Davis and Douheret [14] to define a new parameter δg known as excess correlation factor as:

$$\delta g = g - g_{\text{ideal}} = g - (X_A g_A + X_B g_B) \quad (2)$$

where g_A and g_B represent the correlation factor of pure nonpolar and polar liquid, respectively. In the binary mixture of polar and nonpolar liquids, the nonpolar molecules are slightly polarised. So the effective dipole moment as well as the gas phase dipole moment of nonpolar liquid are negligibly small. According to Oster and Kirkwood [15] the correlation factor for nonpolar liquid in the mixture can be written as

$$g = \lim_{\substack{\mu_{\text{eff}} \to 0 \\ \mu_g \to 0}} ({\mu_{\text{eff}}}^2/\mu_g^2) = 1 \quad (3)$$

In reality, the molecules of nonpolar liquid and very weakly polar liquids lack of correlation for which correlation factor approaches one.

Hence Eqn. (2) reduces to

$$\delta g = g - (X_A + X_B g_B) \qquad (4)$$

EXPERIMENTAL

The experimental device used for measurement of dielectric constant, refractive index etc. were the same as used by Roy [16]. The reproducibility of dielectric constant measurement at radio-frequency range was ± 0.003 with wavemeter-oscillator combination. The reproducibility of refractive index and density measurements were ± 0.00002 and ± 0.00002 gm/cm^3, respectively. For these minimum limits of variation, the value of g and δg show a change in only in the third decimal digit.

DISCUSSION

The experimentally determined value of δg in extremely dilute solution of TBP in seven nonpolar solvents at temperature 303 K has been presented in Table I and Figure 2.

TABLE I Variation of g and δg with the content of tri-*n*-butyl phosphate (TBP) in benzene, *n*-hexane, *n*-heptane, tetrachloromethane, *p*-xylene, cyclohexane and carbon disulphide at 303 K

X_2	g	g_{ideal}	δg
	benzene		
0.030	0.586	1.009	−0.423
0.035	0.636	1.011	−0.375
0.060	0.733	1.018	−0.285
0.076	0.820	1.023	−0.203
0.100	0.878	1.030	−0.152
	n-heptane		
0.010	0.701	1.003	−0.302
0.020	0.701	1.006	−0.305
0.030	0.702	1.009	−0.307
0.040	0.878	1.012	−0.134
0.050	0.982	1.015	−0.033
0.060	1.050	1.018	−0.032
0.070	1.096	1.021	0.075
0.080	1.130	1.024	0.106
0.090	1.157	1.027	0.130
0.100	1.178	1.030	0.148

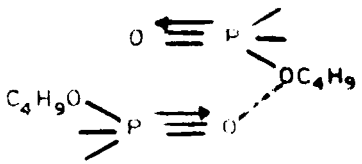
TABLE I (*Contd.*)

	p-xylene		
0.022	1.945	1.007	0.938
0.060	1.232	1.018	0.214
0.080	1.181	1.024	0.157
0.100	1.120	1.030	0.090
0.150	1.000	1.045	−0.045
	n-hexane		
0.010	0.065	1.003	−0.938
0.020	0.344	1.006	−0.662
0.030	0.437	1.009	−0.572
0.050	0.484	1.015	−0.531
0.070	0.471	1.021	−0.550
0.100	1.020	1.030	−0.010
	tetrachloromethane		
0.019	0.880	1.006	−0.126
0.030	0.925	1.009	−0.084
0.040	0.962	1.012	−0.050
0.050	1.108	1.015	0.093
0.060	1.164	1.018	0.146
0.070	1.159	1.021	0.138
0.082	1.360	1.025	0.335
	cyclohexane		
0.030	0.930	1.009	−0.079
0.050	0.890	1.015	−0.125
0.070	0.835	1.021	−0.186
0.080	0.810	1.024	−0.214
0.090	0.755	1.027	−0.272
0.102	0.720	1.031	−0.311
	carbondisulphide		
0.020	1.455	1.006	0.449
0.030	1.384	1.009	0.375
0.040	1.360	1.012	0.348
0.050	1.578	1.015	0.563
0.060	1.493	1.018	0.475
0.070	1.409	1.021	0.388
0.080	1.385	1.024	0.361
0.090	1.401	1.207	0.374

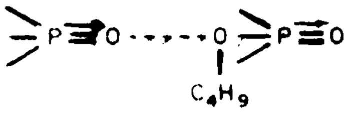
It is observed that δg is mostly positive in TBP-*p*-xylene and TBP-carbondisulphide binary mixtures. In case of *p*-xylene, δg decreases and approaches a negative value with increase in molefraction of solute. In case of carbondisulphide δg decreases and then increases showing a sharp peak around $X_2 = 0.05$ and thereafter decreases with molefraction of solute approaching 0.1. Excess correlation factor is mostly negative in case of binary mixtures of TBP-cyclohexane, TBP-benzene and TBP-*n* hexane. However in the first case it decreases and in the other two cases, it increases with increase in molefraction of solute. In case of binary mixtures of TBP-*n* heptane and TBP-tetrachloromethane δg is negative initially and approaches a positive value when $X_2 \rightarrow 0.05$.

TBP is a mildly associated liquid ($g = 1.3$) which can remain in wood pile (Fig. 1a) and head tail structure [17] (Fig. 1b). Head tail structure results in α-multimers and wood pile structure results in β-multimers. In TBP-cyclohexane mixtures, TBP molecules are trapped in the fold of the chair structure of cyclohexane molecules and probably accomodated in head tail linkage while with increase in number they find it convenient to pile over each other. In the case of benzene and *n*-hexane, the situation is different. When the concentration of TBP is less, the scarce TBP molecules are surrounded by a cage of nonpolar molecules. The isolated TBP molecules, therefore, fail to establish any correlation among themselves of their own. Also the solvent molecules do not help in reinforcing angular correlation. With increase in concentration of TBP, the polar molecules start to establish correlation among themselves of their own. Consequently the value of δg increases.

In case of *p*-xylene, 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. Consequently δg is very high. With increase in concentration of polar liquid, neither the solute molecule establish correlation among themselves nor the solvent molecules



(a) Wood - pile arrangement



(b) Head - tail arrangement

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

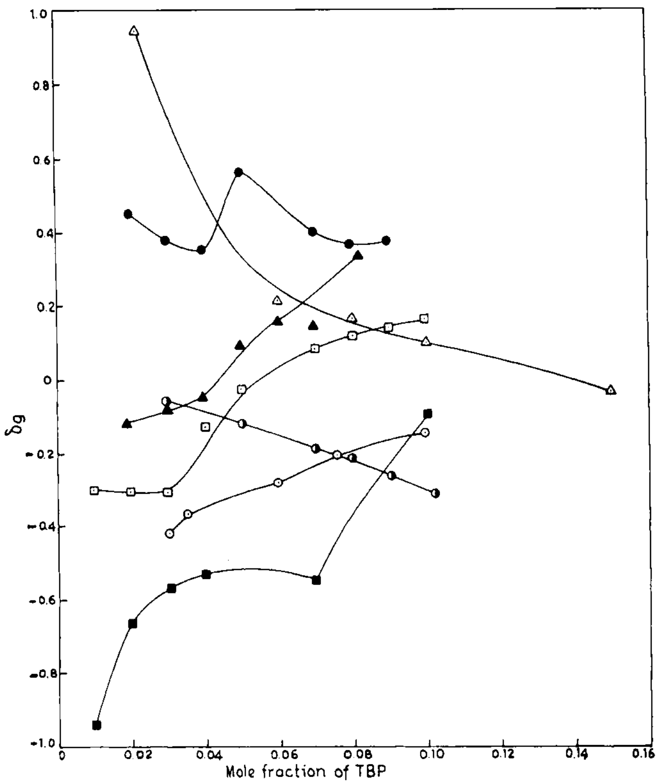


FIGURE 2 Variation of excess correlation factor of TBP in non-polar solvents with mole fraction of solute at 303 K. Plots: ○ Benzene, Δ *p*-xylene, □ *n*-heptane, ● CS_2, ▲ CCl_4, ■*n*-hexane, ◑ Cyclohexane.

help in reinforcing angular correlation. Consequently 'δg' decreases. In *n*-heptane environment, the increase in δg is probably due to the fact that TBP molecules reinforce angular correlation among themselves trying to attain head tail structure. In case of tetrachloromethane, the interaction between TBP-CCl_4 increases with increasing TBP concentration due to interaction of oxygen atom of phosphoryl group with chlorine atom of tetrachloromethane due to their electronegativity leading to saturation of moities followed by replacement of tetrachloromethane molecules by TBP molecules at higher concentration of TBP.

The sharp peak observed in case of TBP-Carbondisulphide mixture is due to favourable interaction between π electron of C=S of Carbondisulphide with O of phosphoryl group of TBP leading to possibility of complexation. I-R spectra of this mixture can confirm the possibility of complexation.

Thus our proposition of 'δg' satisfactorily explains order ($\delta g > 0$) – disorder ($\delta g < 0$) transition and possibility of complexation in binary mixtures of polar-nonpolar liquids.

References

[1] Dash, S. K., Das, J. K., Chakrovarty, V. and Swain, B. B. (1995). *Phys. Chem. Liquid*, **29**, 299.

[2] Ray, S. K. and Roy, G. S. *Phys. Chem. Liquid* (Accepted for publication).

[3] Ray, S. K. and Roy, G. S. Acta Chim Hung–132(6)–1995 (Accepted for publication).

[4] Dash, S. K. and Swain, B. B. (1994). *Chem. Papers*, **48**(3), 146.

[5] Subramanian, V., Bellubi B. S. and Sobhandri, J. Pramana (1993). **41**, 9.

[6] Tripathy, S., Roy, G. S., Dash S. K. and Swain, B. B. (1995). *Ultra Scientist*, **7**(2), 162.

[7] Garabadu K. and Swain, B. B. (1993). *Ind. J. Pure Appl. Phys.*, **31**, 741.

[8] Ray, S. K. and Roy, G. S. (1993). *Proc. Indian nath Sci. Acad.*, **59A**(2), 205.

[9] Ray, S. K. and Roy, G. S. (1994). *Proc. Indian nath Sci Acad.*, **60A**(4), 619.

[10] Kirkwood, J. G. (1939). *J. Chem. Phys.*, **1**, 911.

[11] Frohlich, H. (1949). *Trans. Farad Soc.*, **44**, 238.

[12] Dash, S. K., Chakrovorty, V. and Swain, B. B. (1994). *Acta Chim Hung*, **131**(6), 799.

[13] Roy, G. S., Dash, S. K., Dash, J. K., Tripathy, S. and Swain, B. B. (1995). *Bol. Soc. Chil. Quim.*, **40**, 305.

[14] Davis, M. I. and Douheret, G. (1986). *Thermochim Acta.*, **104**, 203.

[15] Oster, G. and Kirkwood, J. G. (1943). *J. Chem. Phys.*, **11**, 175.

[16] Swain, B. B. and Roy, G. S. (1986). *Jpn. J. Appl. Phys.*, **25**, 209.

[17] Aforin, M. A., Komarov, E. V., Korolev, V. V., Schpunt, L. B., Scherebakov V. A. and Kopylov, E. A. (1989). In Proc. Actinides-89, *Int. Lint.Taskent*, VSSR.

[18] Tripathy S. and Swain, B. B. (1991). Chemical Papers, **45**, 321.