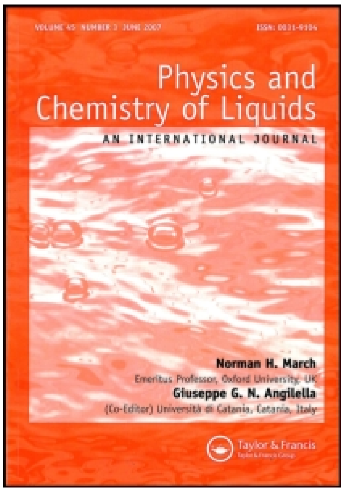

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S. K. Dash[a]; J. K. Das[ab]; V. Chakravortty[ac]; B. B. Swain[ad]
[a] Department of Physics, K.B.D.A.V. College, Nirakarpur, Orissa, India [b] Department of Physics, Stewart Science College, Cuttack, Orissa, India [c] Department of Chemistry, Utkal University, Bhubaneswar, Orissa, India [d] Department of Physics, Khallikote College, Berhampur, Orissa, India

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MOLECULAR INTERACTION IN BINARY MIXTURES OF TRI-N-BUTYL PHOSPHATE (TBP) AND ALIPHATIC ALCOHOLS-EFFECT OF FREE VOLUME AND INTERNAL PRESSURE

S. K. DASH, J. K. DAS[a], V. CHAKRAVORTTY[b] and B. B. SWAIN[c+]

Department of Physics, K.B.D.A.V. College
Nirakarpur-752019, Orissa, India
[a]*Department of Physics, Stewart Science College,*
Cuttack-753001, Orissa, India
[b]*Department of Chemistry, Utkal University,*
Bhubaneswar-751004, Orissa, India
[c]*Department of Physics, Khallikote College,*
Berhampur-760001, Orissa, India

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The ultrasonic velocity, density and viscosity in binary mixtures of TBP with a number of aliphatic primary alcohols viz. methanol, ethanol, 1-hexanol, 1-heptanol, 1-octanol and 1-decanol have been measured at frequency 3 MHz and at temperature 303.16 K. The data are used to compute excess internal pressure and excess enthalpy in these mixtures. The results corroborate the findings of these authors from dielectric studies that the interaction is maximum in 1 heptanol–TBP system and micro-heterogeneous β-clusters with antiparallel orientation of dissimilar molecules predominate in it.

KEY WORDS: Ultrasonic velocity, free volume, excess enthalpy.

1. INTRODUCTION

Tri-n-butyl phosphate (TBP) is an important commercial extractant used in the atomic energy industry for the separation of plutonium and uranium from fission–products and other nuclides[1]. A major disabling factor for its use however, is its high viscosity and high density. In order to improve upon its suitability for extraction purpose, therefore TBP is diluted with various organic solvents like benzene, carbon tetrachloride, kerosine etc. to alter its physico-chemical properties[2–4]. But the formation of a third mixed organic-aqueous phase[5] during extraction complicates the process. This third phase is eliminated by either addition of a modifier to the solvent (extractant and diluent) or by increasing the temperature of the system[6,7].

[+] Author to whom correspondence should be addressed: Plot 15, Chintamaniswar Area, Bhubaneswar-751006, Orissa, India.

Earlier we investigated[8,9] some basic properties of binary mixtures of TBP with a number of nonpolar solvents and also with a number of long-chain alcohols using dielectric measurements. Furthermore, in some of these mixtures, ultrasonic parameters such as intermolecular free length, accoustic impedance, isentropic compressibility, excess available volume etc. were evaluated to corroborate the results from dielectric studies. Recent reports[10,11] indicate increasing interest evinced in evaluation of internal pressure in the liquid as a tool for study of molecular interaction. Measurement of ultrasonic velocity in conjunction with other thermodynamic parameters like viscosity and density are used to evaluate the internal pressure[12] in the liquid state as well as in binary mixtures. In this paper we report measurements of ultrasonic velocity, density and viscosity in binary mixtures of TBP with a number of aliphatic primary alcohols viz. methanol, ethanol, 1-hexanol, 1-heptanol, 1-octanol and 1-decanol which will be used for evaluation of free volume and internal pressure. The data will also be used for estimation of excess internal pressure and excess enthalpy with a view to utilizing the data for obtaining information on molecular interactions of TBP with the alcohol in the mixtures.

2. THEORY

The free volume[13], V_f and internal pressure[14], π_i, in a liquid are evaluated by using the following equations,

$$V_f = \left[\frac{MU}{K_a \eta}\right]^{3/2} \tag{1}$$

$$\pi_i = bRT\left[\frac{K_a \eta}{U}\right]^{1/2} \frac{\rho^{2/3}}{M^{7/6}} \tag{2}$$

where

M is the molar mass of the liquid,
U is ultrasonic velocity in it,
K_a is a constant having a value of 4.28×10^9 independent of temperature and the nature of the liquids,
η is the viscosity and ρ is the density of the liquid
b is the space packing factor being equal to 2 in the present case[15],
R is the gas constant and
T is temperature Kelvin.

Equation (1) and (2) are also used for a mixture where the parameters such as M, U, η and ρ correspond to those of the mixtures.

The excess internal pressure of a binary mixture is obtained using

$$\pi_i^E = (\pi_i)_{\text{mix}} - [\lambda_1(\pi_i)_1 + \lambda_2(\pi_i)_2] \tag{3}$$

where λ_1 and λ_2 refer to the molefractions of components 1 and 2 in the mixture.

The excess enthalpy[16] of a binary mixture is obtained from the fundamental definition of internal pressure as:

$$H^E = \lambda_1(\pi_i)_1 V_1 + \lambda_2(\pi_i)_2 V_2 - (\pi_i)_{\text{mix}} V_m \tag{4}$$

where V_m denote the molar volume of the mixture.

3. EXPERIMENTAL

The experimental arrangement used for measurement of ultrasonic velocity (U) at 3 MHz frequency at 303.16 K is the same as employed by one of authors earlier[5]. All the chemicals used were of analytical grade, purified by standard procedures[17,18]. Viscosity of the mixtures was measured by an Ostwald viscometer. The density measurement was carried out using a semimicrobalance with pyknometer of 25 ml capacity. The reproducibility of viscosity and density were ± 0.002 ($\times 10^3$ NS m^{-2}) and ± 0.00002 g cm^{-3}, respectively.

4. RESULTS AND DISCUSSION

Ultrasonic velocity (U), viscosity (η) and density (ρ) of the binary mixtures of TBP with six polar liquids viz. methanol, ethanol, 1-hexanol, 1-heptanol, 1-octanol and 1-decanol were measured at 303.16 K. The experimental data were used to compute the value of $(V_f)_{\text{mix}}$, $(\pi_i)_{\text{mix}}$, $(\pi_i^E)_{\text{mix}}$ and H^E in these mixtures. Some of the relevant data are displayed graphically in Figures 1–2 and presented in Table 1.

It is observed that, the free volume increases with increase in concentration of TBP in all the mixtures. On the other hand, internal pressure decreases with increase in TBP molefraction. However, this change is significant for the mixtures containing methanol and ethanol only in the TBP-rich region. Both TBP and alcohols are associated liquids. When TBP is added to alcohol, the more active $0^{\delta-}$ in $P=0$ breaks the hydrogen bond in alcohol molecules resulting in alcohol monomers. As a result due to hydrogen bonding between $o^{\delta-}$ of TBP and $H^{\delta+}$ of alcohols, microheterogenous clusters of the unlike molecules are formed. Furthermore, alcohol monomers are also enclosed in the voids of TBP structure leading to close packing, which is responsible for continuous increase in free volume and consequent decrease in internal pressure in all the six sets of mixtures. The excess internal pressure is negative over the entire range of concentration in all the mixtures. The magnitude of the excess parameters reflects upon the strength of interaction though Despande *et al.*,[19] associate the negative sign of π_i^E with weak interaction. On the other hand, according to Fort and Moore[20], Piotrowska[21] and Kalgud[22], negative values of excess functions are indicative of complexation between the unlike liquid components in the mixture and are influenced by their interactions. From dielectric studies in alcohol-TBP mixtures, we reported[9] that alcohol-TBP association results in a mutual correlation factor $g_{ab} < 1$ signifying the predominance of antiparallel orientation forming β-clusters for long chain alcohols

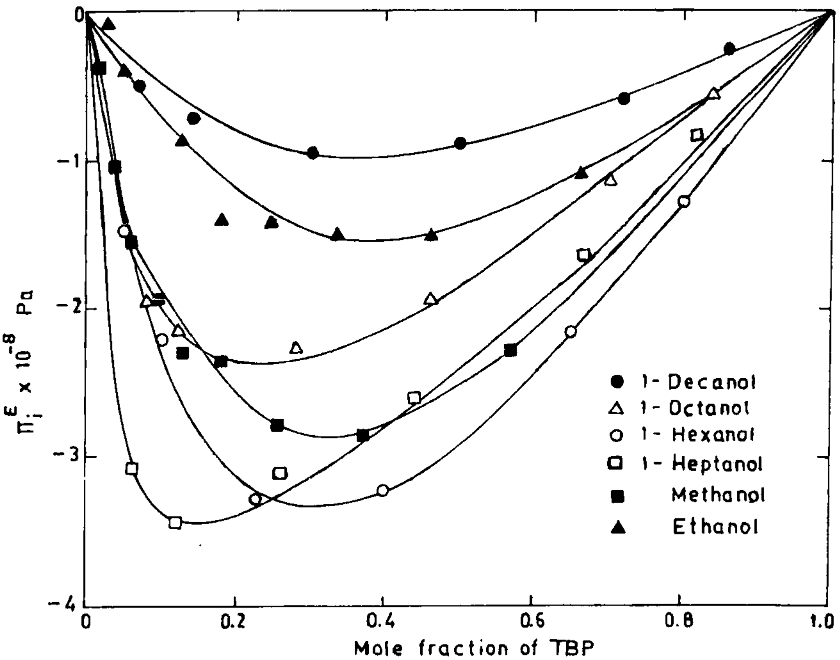

Figure 1 Variation of π_i^E with mole fraction of TBP

while smaller alcohols resulted in predominance of α-clusters with $g_{ab} > 1$. The magnitude of the deviation of g_{ab} from unity, which reflects upon the degree of interaction, shows an identical trend with that of π_i^E. As such we associate a negative value of π_i^E with formation of β-clusters and as a corollary, positive values of π_i^E with α-clusters representing parallel orientation between dissimilar molecules. The magnitude of π_i^E value for 1 heptanol-TBP system is maximum. The point of inflexion in this system is sharp and occurs at a TBP molefraction of 0.125. This agrees with our earlier finding[9] that the intermolecular attraction for 1 heptanol-TBP is maximum. On the other hand, in TBP-1 decanol system, the magnitude of π_i^E is minimum and the curve is relatively shallow. It is worth mentioning here that in the mixtures with long chain alcohols, because of high viscosity and in the presence of greater steric hindrance, a relatively stable structure due to linear linkage between TBP and alcohol molecules is likely to occur, as such antiparallel orientation is a greater probability in this case. On the other hand in order to maintain parallel orientation both unlike molecules are required to maintain a strained structure which is possible for smaller alcohol molecules like methanol and ethanol with low steric hindrance. The switching mechanism[23,24], occurs more easily in this case making possible prevalence of relatively unstable strained structure with co-operative orientation of dipoles.

The excess ethalpy H^E is found to be positive over the entire range of concentration of TBP in the four sets of mixtures with higher chain alcohols, while it is negative for methanol and ethanol. For 1 heptanol-TBP it is also maximum at

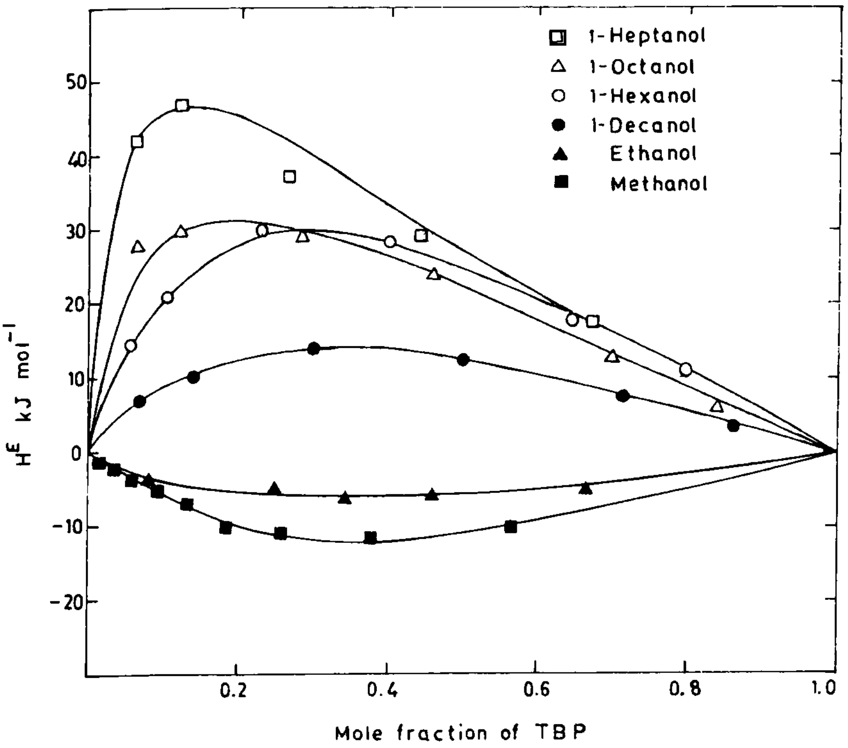

Figure 2 Variation of H^E with mole fraction of TBP

Table 1 Variation of Free volume and Internal Pressure with molefraction of TBP

$(\lambda_2)_{TBP}$	ρ $kg\,m^{-3}$	$\eta \times 10^3$ $N.S.m^{-2}$	U $m\,s^{-1}$	$V_f \times 10^8$ $m^3\,mol^{-1}$	$\pi_i \times 10^{-8}$ Pa
(1)	(2)	(3)	(4)	(5)	(6)
(a) Solvent-Methanol					
0.000	791	0.581	1147	5.682	11.116
0.016	806	0.670	1149	5.467	10.591
0.036	824	0.733	1154	5.745	9.739
0.060	843	0.839	1161	5.754	9.063
0.090	867	0.979	1176	5.758	8.399
0.129	880	1.181	1185	5.577	7.712
0.182	909	1.512	1205	5.186	7.153
0.257	923	1.767	1226	5.783	6.052
0.373	939	2.126	1233	6.610	4.954
0.572	956	2.677	1238	7.599	3.830
1.000	970	2.820	1240	14.312	2.281
(b) Solvent-Ethanol					
0.000	785	1.007	1190	5.459	8.104
0.023	810	1.181	1199	4.977	8.035
0.051	831	1.225	1202	5.495	7.400
0.084	861	1.445	1206	5.055	7.260

Table 1 (*Contd.*)

$(\lambda_2)_{TBP}$	ρ $kg\,m^{-3}$	$\eta \times 10^3$ $N.S.m^{-2}$	U $m\,s^{-1}$	$V_f \times 10^8$ $m^3\,mol^{-1}$	$\pi_i \times 10^{-8}$ Pa
(1)	(2)	(3)	(4)	(5)	(6)
0.125	868	1.530	1210	5.566	6.531
0.177	877	1.558	1214	6.636	5.679
0.244	899	1.838	1222	6.530	5.260
0.334	917	2.097	1231	6.990	4.654
0.963	937	2.321	1233	8.138	3.923
0.659	955	2.524	1237	9.300	3.223
1.000	970	2.820	1240	14.312	2.281
(c) Solvent-1 Hexanol					
0.00	812.15	9.56	1284.00	0.574	11.211
0.05	839.80	7.48	1279.57	0.927	9.283
0.10	853.36	6.58	1274.68	1.244	8.109
0.23	880.84	4.80	1266.32	2.533	5.851
0.40	909.60	3.98	1260.56	4.377	4.413
0.65	939.60	3.44	1254.12	7.504	3.257
0.80	954.84	3.16	1248.60	10.008	2.776
1.00	970.00	2.82	1240.00	14.312	2.281
(d) Solvent-1 Heptanol					
0.00	815.75	9.53	1305.90	0.717	9.582
0.06	843.156	4.35	1302.56	2.593	6.073
0.12	871.579	3.92	1298.40	3.347	5.247
0.26	885.547	3.80	1294.02	4.340	4.579
0.44	913.750	3.56	1287.90	6.046	3.762
0.67	942.320	3.30	1269.60	8.602	3.041
0.82	956.224	3.33	1256.70	9.825	2.763
1.00	970.00	2.82	1240.00	14.312	2.281
(e) Solvent-1 Octanol					
0.00	821.86	9.45	1345.65	0.902	8.270
0.06	835.36	5.47	1331.12	2.207	7.911
0.12	849.68	4.98	1315.70	2.721	7.551
0.28	878.90	4.20	1298.88	4.242	6.593
0.46	912.80	3.70	1294.08	6.255	5.515
0.70	939.62	3.40	1271.75	8.748	4.078
0.84	954.80	3.30	1257.50	10.159	3.239
1.00	970.00	2.82	1240.00	14.312	2.281
(f) Solvent-1 Decanol					
0.00	825.45	9.35	1375.32	1.269	6.499
0.07	839.92	7.77	1357.81	1.758	5.721
0.14	853.92	6.89	1337.59	2.206	5.202
0.30	881.68	5.48	1310.60	3.478	4.286
0.50	910.46	4.45	1296.40	5.493	3.500
0.72	940.40	3.65	1271.48	8.422	2.890
0.86	956.00	3.36	1256.99	10.288	2.622
1.00	970.00	2.82	1240.00	14.312	2.281

about 0.125 molefraction of TBP. It corroborates our findings on π_i^E suggesting that physical interaction is endothermic[25], i.e. energy is required to disperse the molecules of the two components in higher chain alcohols-TBP mixtures while it is exothermic in methanol and ethanol.

References

1. A. Naylor and H. Eccles, *Int. Solvent Ext. Conf.*, Moscow, **1**, 31 (1988).
2. A. K. De, S. M. Khopkar and R. A. Chalmers, Solvent extraction of metals (Van Nostrand-Reinhold, London, 1970).
3. R. J. Fort and W. R. Moore, Trans. Faraday Soc. (GB), **61**, 2102 (1965).
4. M. V. Kalgud, Acoustica, **10**, 2102 (1965).
5. B. K. Rout, V. Chakravortty and D. Behera, *Ind. J. of Tech.*, **31**, 745 (1993).
6. P. R. Vasudev Rao and T. G. Srinivasan, Proc. Int. Symp. on Radiochemistry and Radiation Chemistry, BARC Bombay (1991).
7. G. M. Ritcey and A. W. Ashbrook, Solvent extraction, Part II (Elsevier New York, 1979).
8. S. K. Dash, V. Chakravortty and B. B. Swain, Acta Chim. Hung. (Under Publication).
9. S. K. Dash and B. B. Swain, *Jpn. Jour. of Appl. Phys.*, **32**, 2753 (1993).
10 B. P. Shukla, L. K. Jha and G. P. Dubey, *Ind. J. of Pure and Appl. Phys.*, **30**, 754 (1992).
11. B. P. Shukla, A. P. Srivastava, A. P. Upadhyaya and S. N. Dubey, *J. of Pure and Appl. Ultrason.*, **12**, 12 (1990).
12. C. V. Suryanarayan, *J. of Acoust. Soc. of India*, **7**, 131 (1979).
13. C. V. Suryanarayan and J. Kuppusami, *J. of Acoust. Soc. of India*, **4**, 75 (1976).
14. C. V. Suryanarayan, *Ind. J. of Pure and Appl. Phys.* **27**, 751 (1989).
15. A. N. Kannapan and V. Rajendran, *Ind. J. of Pure and Appl. Phys.*, **31**, 354 (1993).
16. K. Malakondaiah, V. Hyder Khan and S. V. Subramanyam, *Ind. J. of Chem.*, **16A**, 733 (1978).
17. K. Alcock, S. S. Grimbly, T. V. Healy, J. Kennedy and A. C. McKay, Trans. Faraday Soc. **52**, 56 (1956).
18. A. Weissberger, Technique of Organic Chemistry, Interscience, New York, **7** (1955).
19. D. D. Deshpande and L. G. Bhatgadde, *J. Phys. Chem.*, **72**, 261 (1968).
20. R. J. Fort and W. R. Moore, Trans. Faraday Soc. (GB), **62**, 1112 (1966).
21. A. Piotrowska, Rocz Chem., **39**, 437 (1965).
22. M. V. Kalgud, *Z. Phys. Chem.*, (Germany) **36**, 365 (1963).
23. F. X. Hassion and R. H. Cole, *J. Chem. Phys.*, **23**, 1756 (1955).
24. F. X. Hassion and R. H. Cole, *Nature*, **172**, 212 (1953).
25. O. Prakash, A. Srivastava and S. Prakash, *Ind. J. of Pure and Appl. Phys.*, **24**, 306 (1986).