Investigation on Molecular Interaction in Binary Liquid Mixtures — Tri-n-butyl Phosphate with Both Polar and Nonpolar Liquids Using Viscosity and Ultrasonic Parameters

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Ultrasonic velocity and viscosity measurements, namely of TBP + methanol, TBP + ethanol, TBP + benzene, and TBP + CCl$_4$ have been used to study molecular interaction at 303 K. Grunberg—Nissan parameter (d), excess Gibbs energy (G^E), intermolecular free length (L_f), acoustic impedance (Z), isentropic compressibility (β), molar sound velocity (U_m), and available volume (V_a) have been calculated from these data. The excess parameters for the factors β, Z, and V_a are also evaluated. TBP—methanol and TBP—ethanol interaction leads to the formation of clusters of dissimilar molecules.

Tri-n-butyl phosphate (TBP) is extensively used as an extractant for actinide and lanthanide elements and it dominates in the chemical reprocessing of the nuclear fuel in the atomic energy industry. Major disabling factor for the use of TBP in nuclear industry is its high viscosity. Therefore, this extractant is diluted with organic solvents like benzene, CCl$_4$, kerosene, etc., to alter its physicochemical properties [1—5], to improve upon its suitability for extraction purposes. Earlier we have investigated the molecular interaction in some binary mixtures involving TBP using the dielectric method [6, 7]. Ultrasonic investigation, however, finds extensive applications in eliciting information concerning nature of molecular interactions in pure [8] as well as in binary and ternary mixtures [9—11] of liquids, and also the ionic interaction in aqueous electrolytic solutions [12, 13]. The present work aims at utilization of the ultrasonic method to study the behaviour of binary mixtures of TBP, with two nonpolar solvents, viz. benzene and CCl$_4$ and with two polar solvents, viz. methanol and ethanol. The results will be used to compare the nature of molecular interaction in these two groups of mixtures with a view examining the suitability of these solvents as diluents — modifiers. It is proposed to evaluate also certain parameters from viscosity measurements in these mixtures and use them for comparison with the results obtained from dielectric and ultrasonic studies.

THEORETICAL

Viscosity (η) of a liquid, using an Ostwald viscometer is

$$\eta = K\rho t \qquad (1)$$

where K is the viscometer constant, t is the time of efflux, and ρ is the density of the liquid.

The molar volume of a mixture is defined as

$$V_m = \overline{M}/\rho_m \qquad (2)$$

where $\overline{M}$, the average molar mass, is $x_1 M_1 + (1 - x_1)M_2$, M_i being molar mass of the i-th component, x_i is the mole fraction of component i in the mixture, and ρ_m is the density of the mixture. The molar excess Gibbs energy of activation of flow (G^E) is given by [14]

$$G^E = RT[\ln \{\eta V_m\} - x_1 \ln \{\eta_1 V_1\} - \\ - (1 - x_1) \ln \{\eta_2 V_2\}] \qquad (3)$$

where T is the absolute temperature, R is the universal gas constant. η, η_1, and η_2 represent viscosity of the mixture and that of the component 1 and 2, respectively, and V_1, V_2 represent molar volume of pure components 1 and 2.

Grunberg and Nissan [14] proposed an expression for binary liquid mixtures exhibiting nonideal behaviour

$$\ln\{\eta\} = x_1 \ln\{\eta_1\} + (1 - x_1) \ln \{\eta_2\} + \\ + x_1 (1 - x_1)d \qquad (4)$$

where d is termed as "interaction parameter" which is a measure of strength of interaction between the components in the mixture.

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From the measured ultrasonic velocity (u) and density (ρ_m) of the mixture, the isentropic compressibility (β) is computed [15] from eqn (5) and acoustic impedance (Z) is calculated [15] from eqn (6)

$$\beta = u^{-2} \rho_m \qquad (5)$$
$$Z = u \rho_m \qquad (6)$$

The molar sound velocity (U_m) and intermolecular free length (L_f) [16, 17] are calculated from eqns (7) and (8), respectively

$$U_m = V_m u^{1/3} \qquad (7)$$
$$L_f = C \beta^{1/2} \qquad (8)$$

where C is a temperature-dependent constant.

According to the available volume concept in the case of a liquid, where the available volume is only a fraction of the total volume, the compressibility and viscosity of a liquid is generally influenced by the amount of space in which the molecules are free to move [18]. The relative amount of available volume should be the same for all the liquids at their boiling points as required by the van der Waals equation

$$(P + P_o) (V_m - V_o) = RT \qquad (9)$$

where P is the pressure exerted by the liquid at T(K), P_o is the correction factor for pressure, and V_o is the van der Waals constant.

Measurement of ultrasonic velocity (u) in liquids leads to the idea of the size of molecules of liquid, which on the other hand, determines V_o [17, 19] as

$$V_o = V_m \left[1 - \frac{RT}{\overline{M}u^2} \left(\sqrt{1 + \frac{\overline{M}u^2}{3RT}} - 1 \right) \right] \qquad (10)$$

where $\overline{M} = (x_1 M_1 + x_2 M_2)$.

The available volume (V_a) [18] is defined as

$$V_a = V_m - V_o \qquad (11)$$

The excess functions are obtained from the following equation

$$A^E = A_m - (x_1 A_1 + x_2 A_2) \qquad (12)$$

where A^E is the excess function, A_m is the mixture property, and A_1, A_2 are pure component properties.

EXPERIMENTAL

In the present investigation the chemicals used are of anal. grade, purified by standard procedures [20—23] and redistilled before use. The purity of the samples was checked by comparing the measured densities with those reported in the literature [24]. Density was determined with a pyknometer of 25 cm^3 capacity calibrated at 303 K with deionized doubly

distilled water. At a fixed temperature, the densities were determined with an error of one in 10^4. Ultrasonic velocity was measured by a single crystal variable-path interferometer operating at a frequency of 2 MHz. Circulating water from thermostatically regulated bath around the sample holder with double wall maintains the temperature of the liquid constant with a precision of ± 0.1 °C. Viscosity of the mixtures was measured by Ostwald viscometer, immersed in a constant temperature water bath. Viscosity could be measured with an accuracy of ± 10^{-6} Pa S.

RESULTS AND DISCUSSION

Ultrasonic velocity (u), density (ρ_m), and viscosity (η) of the binary mixture of TBP—benzene, TBP—CCl$_4$, TBP—methanol, and TBP—ethanol were measured at 303 K. The experimental data are used to calculate isentropic compressibility (β), acoustic impedance (Z), molar sound velocity (U_m), intermolecular free length (L_f), available volume (V_a), and Grunberg—Nissan parameter (d) in these mixtures. The excess Gibbs energy (G^E), excess isentropic compressibility (β^E), excess acoustic impedance (Z^E), and excess available volume (V_a^E) are also calculated. Some of the relevant data are displayed graphically in Figs. 2—6 and recorded in Tables 1 and 2.
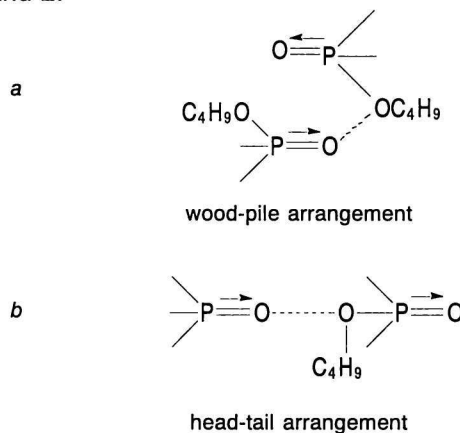

wood-pile arrangement

head-tail arrangement

Fig. 1. Wood-pile and head-tail arrangements of TBP molecules.

The excess Gibbs energy (G^E) and Grunberg—Nissan parameter (d) are evaluated from viscosity measurements. It has been observed [2, 25, 26] that in the case of mixtures where strong specific interactions between unlike molecules are predominant there is a distinct maximum in the viscosity vs. composition curves. Also excess Gibbs energy and Grunberg—Nissan parameter are all positive in such cases. Results from this investigation show that viscosity (η) increases with increasing TBP concentration in all mixtures. Grunberg—Nissan parameter (d)
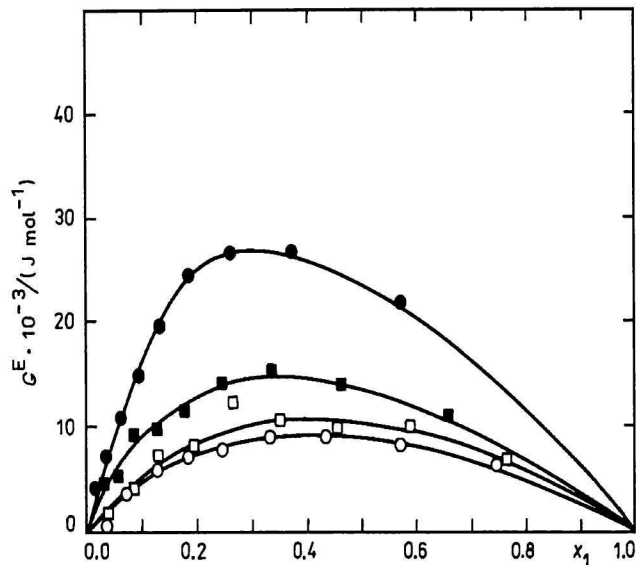
Fig. 2. Variation of G^E with the mole fraction of TBP (x_1): ● methanol, ■ ethanol, ○ benzene, □ CCl_4.

is positive in all systems being maximum for the TBP—methanol system followed by the TBP—ethanol one. The exception, however, is seen in the TBP—benzene system where at a very low concentration of TBP it is slightly negative. The relatively higher value of d in the mixtures containing alcohols indicates the presence of strong interaction between unlike molecules. This observation is also corroborated from our finding on G^E. G^E in the case of the TBP—methanol mixture is maximum and it is in the same order as d. TBP—alcohol interaction is due to the hydrogen bonding

$$P{=}O{-}H{-}O{\overset{R}{\diagup}}$$
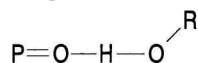
between one of the oxygen atoms of TBP and the hydroxyl group of alcohol. Besides dipole—dipole interaction, the dipole-induced—dipole interaction between unlike molecules has a major role in deciding the difference between the strength of interaction in these binary systems [27]. Because of the high dipole moment value, its effect is likely to be greater in the case of alcohols. Further, the interaction in methanol being stronger than that in ethanol reflects on greater steric hindrance experienced by ethanol molecules.

The results from ultrasonic investigations show that the variation of L_f is linear in the TBP-rich region in all mixtures. However, in the TBP-deficient region, it is nonlinear in all mixtures, though for methanol and ethanol the nonlinearity is distinctly more evident when compared to others. From linear correlation factor (g) evaluated in dielectric studies [7] it is observed that TBP is a mildly associated liquid (g = 1.3) indicating predominance of α-multimers with parallel orientation. TBP molecules can remain either
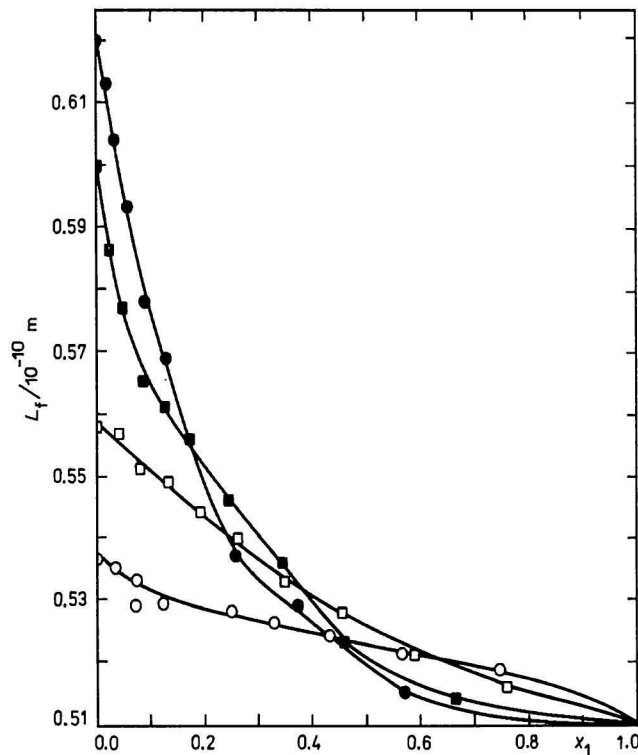

Fig. 3. Variation of L_f with the mole fraction of TBP (x_1): ● methanol, ■ ethanol, ○ benzene, □ CCl_4.
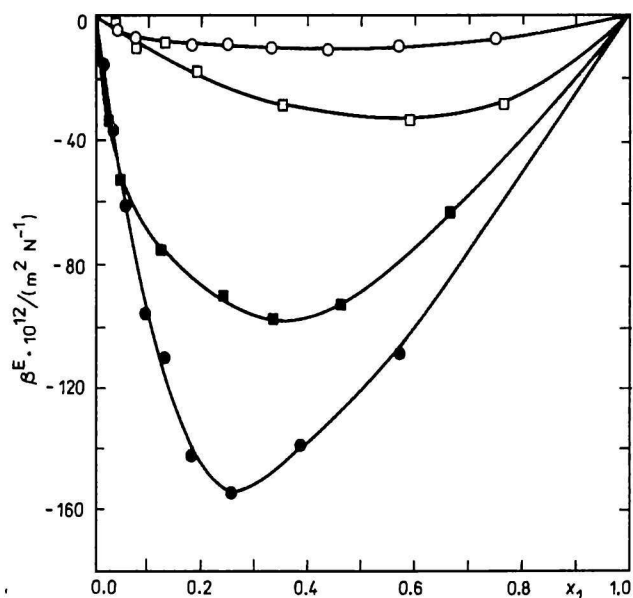

Fig. 4. Variation of β^E with the mole fraction of TBP (x_1): ● methanol, ■ ethanol, ○ benzene, □ CCl_4.

in "wood-pile" (Fig. 1a) or as "head-tail" (Fig. 1b) configuration [28]. Head-tail structure results in α-multimers and wood-pile structure results in β-multimers. In the first group of binary mixtures (viz. TBP—benzene and TBP—CCl_4) TBP—TBP interaction is present throughout and no significant change in cluster formation involving dissimilar molecules is expected.
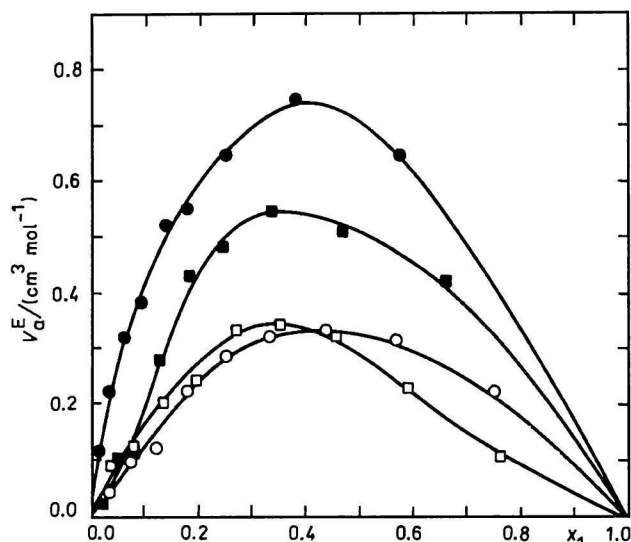
Fig. 5. Variation of V_a^E with the mole fraction of TBP (x_1): ● methanol, ■ ethanol, ○ benzene, □ CCl$_4$.

Fig. 6. Variation of Z^E with the mole fraction of TBP (x_1): ● methanol, ■ ethanol, ○ benzene, □ CCl$_4$.

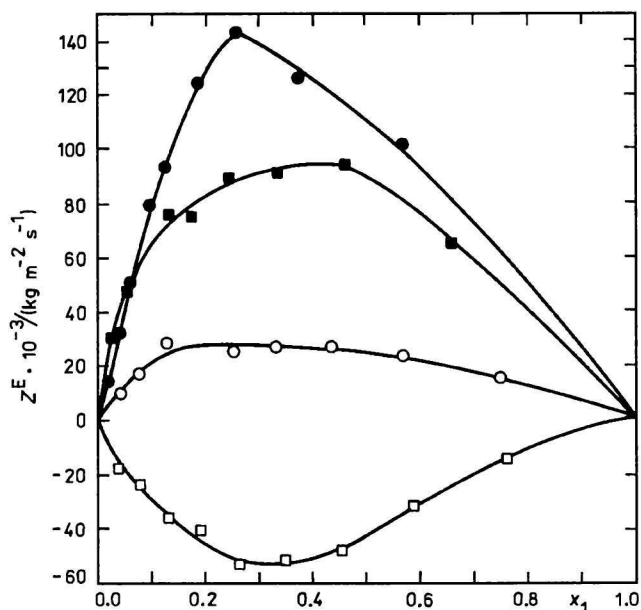The slight increase in the value of L_f on dilution may be attributed to the solvent effect. Due to high pola-

Table 1. Variation of ρ, η, d, u, and U_m with the Content of TBP in Nonpolar Solvents at 303 K

	Benzene						CCl$_4$				
x_1	ρ / kg m^{-3}	η / 10^{-3} Pa S	d	u / m s^{-1}	U_m / cm$^{3.3}$ mol^{-1} s$^{-1/3}$	x_1	ρ / kg m^{-3}	η / 10^{-3} Pa S	d	u / m s^{-1}	U_m / cm$^{3.3}$ mol^{-1} s$^{-1/3}$
0.000	862	0.582	–	1268	4555	0.000	1565	0.899	–	906	4416
0.035	876	0.614	– 0.124	1264	4856	0.038	1501	0.976	0.970	927	4767
0.076	888	0.725	1.354	1260	5219	0.082	1442	1.095	1.302	955	5171
0.124	903	0.844	1.567	1257	5627	0.133	1382	1.290	1.748	979	5630
0.180	908	0.932	1.633	1253	6176	0.193	1322	1.404	1.382	1011	6185
0.248	918	1.031	0.899	1248	6796	0.264	1249	1.662	1.540	1048	6924
0.331	928	1.240	0.980	1247	7563	0.349	1187	1.816	1.256	1088	7767
0.433	938	1.466	0.876	1246	8517	0.455	1136	2.012	1.055	1122	8706
0.569	949	1.779	0.776	1245	9745	0.588	1081	2.400	1.149	1167	9942
0.748	959	2.313	0.854	1244	11396	0.763	1026	2.709	1.061	1210	11552
1.000	970	2.967	–	1257	13827	1.000	970	2.967	–	1257	13827

Table 2. Variation of ρ, η, d, u, and U_m with the Content of TBP in Polar Solvents at 303 K

	Methanol						Ethanol				
x_1	ρ / kg m^{-3}	η / 10^{-3} Pa S	d	u / m s^{-1}	U_m / cm$^{3.3}$ mol^{-1} s$^{-1/3}$	x_1	ρ / kg m^{-3}	η / 10^{-3} Pa S	d	u / m s^{-1}	U_m / cm$^{3.3}$ mol^{-1} s$^{-1/3}$
0.000	791	0.581	–	1147	1967	0.000	785	1.007	–	1190	2886
0.016	806	0.667	6.267	1149	2162	0.023	810	1.181	5.759	1199	3116
0.036	824	0.733	4.936	1154	2389	0.051	831	1.225	2.782	1202	3405
0.060	843	0.839	4.667	1161	2667	0.084	861	1.445	3.353	1206	3713
0.090	867	0.979	4.441	1176	3004	0.125	868	1.530	2.389	1210	4198
0.129	880	1.181	4.281	1185	3481	0.177	877	1.558	1.528	1214	4805
0.182	909	1.512	4.270	1205	4063	0.244	899	1.838	1.665	1222	5505
0.257	923	1.767	3.453	1226	4971	0.334	917	2.097	1.483	1231	6495
0.373	939	2.126	2.741	1233	6324	0.463	937	2.321	1.114	1250	7902
0.572	956	2.677	2.135	1255	8696	0.659	955	2.823	1.043	1259	10044
1.000	970	2.967	–	1257	13827	1.000	970	2.967	–	1257	13827

rizability benzene molecules develop induced dipoles which interact with the dipolar molecules of TBP. As a result benzene molecules come closer to each other forming planar stacks sandwiching (clustering) TBP molecules. This leads to a slight increase in intermolecular free length in the mixtures. On the

other hand, in the second group of mixtures (viz. TBP—methanol and TBP—ethanol) TBP—alcohol interaction is a possibility due to the hydrogen bonding. Evaluation of mutual correlation factor (g_{ab}) in TBP—alcohol mixtures, using dielectric measurements [6] showed that g_{ab} in such mixtures departed from unity indicating formation of microheterogeneous clusters. In the present work data from viscosity studies also lead to the identical conclusion. As such L_f is likely to increase. The nonlinear characteristic of L_f vs. TBP mole fraction curve on increasing alcohol concentration probably indicates a rapid change of nature and extent of clusters. The degree of variation of L_f is greater in TBP—methanol than in TBP—ethanol system probably due to a relatively low steric hindrance of methanol molecules where a greater number of alcohol molecules establish favourable correlation with TBP.

Ultrasonic velocity (u) and molar sound velocity (U_m) exhibit similar trend in the entire range of concentration of TBP. Ultrasonic velocity is governed by the combined effect of intermolecular free length and density. Since the difference between density of CCl_4 and TBP is maximum while L_f in both the cases are very close to each other, the ultrasonic velocity in the TBP—CCl_4 mixture is expected to undergo a very large range of variation which is supported from the experimental findings. On the other hand, both L_f and ρ for TBP are close to those of benzene. As a consequence the change in ultrasonic velocity is rather insignificant over the entire composition range in the TBP—benzene mixture. Likewise variation in the case of methanol and ethanol is also of the same type, which could be explained by similar considerations.

The excess available volume (V_a^E) in all the mixtures is positive. Its magnitude is maximum for methanol followed by ethanol. For both benzene and CCl_4, its magnitude is relatively small. We have observed earlier that methanol molecules find it convenient to form clusters of dissimilar molecules (TBP), which makes more free space available. The clustering effect being less in ethanol, the magnitude of available volume is also reduced. Since benzene and CCl_4 molecules do not enter into any mutual interaction with TBP molecules, the magnitude of V_a^E is influenced mainly by the solvent effect.

The excess acoustic impedance (Z^E) is negative only in the case of mixtures containing CCl_4 and in the rest of the cases it is positive. For benzene the magnitude is relatively small and remains flat over a large range of concentration. For alcohols the magnitude is appreciable being maximum for TBP—methanol mixtures. It is probably due to the formation of the charge-redistribution complex due to hy-

drogen bonding for methanol and ethanol. While for benzene the dipole-induced—dipole interaction leads only to stacking of benzene molecules, no such interaction is expected in CCl_4 and hence CCl_4 stands apart. The excess isentropic compressibility (β^E) is negative in all cases, the magnitude being maximum for the TBP—methanol system and minimum for the TBP—benzene system. It agrees with our earlier observation that the change in L_f is maximum for TBP—methanol mixtures and minimum for the TBP—benzene system.

REFERENCES

1. De, A. K., Khopkar, S. M., and Chalmers, R. A., Solvent Extraction of Metals. Van Nostrand—Reinhold, London, 1970.
2. Fort, R. J and Moore, W. H., Trans. Faraday Soc. 61, 2102 (1968).
3. Kaulgud, M. V., Acustica 10, 316 (1960).
4. Prasad, N., Singh, R., Prakash, O., and Prakash, S., Indian J. Pure Phys. 14, 676 (1976).
5. Prakash, S., Acta Chem. 88, 371 (1976).
6. Dash, S. K. and Swain, B. B., Jpn. J. Appl. Phys. 32, 2753 (1993).
7. Dash, S. K., Chakravortty, V., and Swain, B. B., Acta Chim. Hung., in press.
8. Tabhane, V. A., Acoust. Lett. (G. B.) 6, 120 (1983).
9. Kannappan, A. N. and Rajendran, V., Indian J. Phys., B 65, 266 (1991).
10. Srinivasulu, V. and Ramachandra Naidu, P., Indian J. Pure Appl. Phys. 29, 576 (1991).
11. Kannappan, A. N. and Rajendran, V., Indian J. Pure Appl. Phys. 29, 465 (1991).
12. Pankaj, R. and Sharma, C., Ultrasonics (GG) 29, 344 (1991).
13. Kannappan, A. N. and Rajendran, V., J. Mol. Liq. (Netherlands) 54, 27 (1992).
14. Grunberg, L. and Nissan, A. H., Nature 164, 799 (1949).
15. Wan Choo, R. K., Rattan, V. K., Singh, S., and Sethi, B. P. S., Acustica 62, 172 (1986).
16. Rao, M. R., J. Chem. Phys. 9, 682 (1941).
17. Freyer, E. B., Hubbard, J. C., and Andrews, D. H., J. Acoust. Soc. Am. 51, 759 (1929).
18. Narayana, L., Ph. D. Thesis. Utkal University, India, 1983.
19. Hogfeldt, E., Ark. Kemi 7, 315 (1954).
20. Alcock, K., Grimbly, S. S., Healy, T. K., Kenedy, J., and Mackay, A. C., Faraday Discuss. Chem. Soc. 52, 52 (1956).
21. Vogel, A. I., Text Book of Practical Organic Chemistry. Third Edition. Longmans, London, 1957.
22. Riddich, J. A. and Bunger, W. B., Organic Solvents. Wiley—Interscience, New York, 1970.
23. Weissberger, A., Technique of Organic Chemistry. Vol. VII. Interscience, New York, 1955.
24. Handbook of Chemistry and Physics. 60th Edition. CRC Press, Ohio, 1979—1980.
25. Assarsson, P. and Elrich, F. R., J. Phys. Chem. 72, 2710 (1968).
26. Solimo, H. N., Rigglo, R., Davollo, F., and Katz, M., Can. J. Chem. 53, 1258 (1975).
27. Singh, S., Indian J. Pure Appl. Phys. 18, 254 (1980).
28. Afonin, M. A., Komarov, E. V., Korolev, V. V., Shchpunt, L. B., Shcherbakov, V. A., and Kopylov, E. A., Actinides '89. Int. Conf., Tashkent, USSR, 1989.