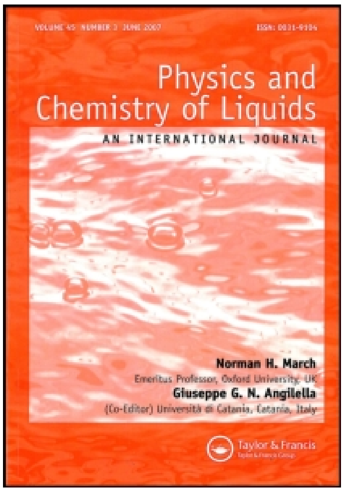

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Dipolar Complexation in Binary Mixtures of Tri-*n*-Butyl Phosphate (TBP) with Long-Chain Aliphatic Alcohols

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DIPOLAR COMPLEXATION IN BINARY MIXTURES OF TRI-*n*-BUTYL PHOSPHATE (TBP) WITH LONG-CHAIN ALIPHATIC ALCOHOLS

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The mean square dipole moments of the 1 : 1 complexes of tri-*n*-butyl phosphate (TBP) with 1-hexanol, 1-heptanol and 1-octanol in benzene are determined following two different methods *i.e.*, one based on Onsager's method and the other using modified Palit's method. The interaction dipole moment for the thermodynamically most favoured geometry of 1 : 1 complexes of the system involving 1-hexanol, 1-heptanol, 1-octanol as the first components and TBP as the second component is evaluated. The results indicate that complexation is predominantly due to polarization effect involving charge redistribution. Furthermore, the induced excess polarization and apparent complexation constant in these mixtures are calculated.

Keywords: Hydrogen-bonding; long-chain alcohol; TBP; interaction dipole moment

1. INTRODUCTION

Tri-*n*-butyl phosphate (TBP) is used in the solvent extraction process in atomic energy industry for extraction of actinide and lanthanide elements [1]. In view of high viscosity and density, TBP is mixed with a suitable diluent to increase the extraction efficiency. Furthermore, formation of a third phase (organo-aqueous) during the extraction of actinides by this extractant complicates the process [2–4]. This third phase can be eliminated by the addition of a modifier to the extractant and diluent or by increasing the temperature of the system [5, 6]. Iso-decanol, nonyl-phenol, tri-decyl alcohol, 2-ethyl hexanol, *etc.*, are reported to have been used as modifiers [7].

In an attempt to investigate the dielectric behaviour of certain possible modifiers, we investigated [8] the mechanism of mutual dipolar association. Therefore TBP is added into number of long-chain alcohols. The trend of variation of mutual correlation factor with number of binary mixtures indicates the probability of formation of hydrogen-bonded complexes between TBP and the alcohols. Chakravortty *et al.* [9] while exploring the ultrasonic behaviour in binary mixtures of alcohols and TBP also indicated complexation in these systems. Shi Xiukun *et al.* [10] also reported from dielectric studies formation of complexes in binary mixtures of TBP and water. Apart from these few reports, we have not come across any other report regarding complex formation involving TBP. Therefore, we have undertaken this study to examine the nature and extent of complexation. There are many reports [11–13] regarding complex formation due to hydrogen bonding in varieties of binary mixtures. In hydrogen-bonding of proton donor–acceptor complexes a redistribution of electron density takes place and the dipole moment of H-bonded system is no more a single vector. The most important characteristics of the hydrogen bond is the increase in the distance of O —H accompanied by an enhancement of the dipole moment $\Delta\mu$ [14], which will indicate the type of complex since dipolar increment is a function of ΔP and K. Pioneering work in this area was carried out by Sobczyk and coworkers [15] and Hyskens *et al.* [16]. Polarization effects [17] charge transfer effects [18], partial proton transfer effects [19] and complete proton transfer effects [20] were invoked to account for the excess dipole moment in many O —H...N and O —H...0 complexes. Here we report the results of our investigation regarding H-bonded complexes of TBP with 1-hexanol, 1-heptanol and 1-octanol by evaluating the dipole moment of complexes following two different methods, *viz.*, that of Onsager's method [21] based on dipole–dipole interaction and the modified Palit's method [22], which makes use of the infinite dilution technique based on fundamental Debye equation.

2. THEORY

Method I

Due to intermolecular association leading to multimerization, the dipole moment of a molecule measured in a solution of the associated polar liquid in a non polar medium differs from its value in vapour state. The apparent value of the square of the molecular dipole moment $<\mu^2>_{\mathrm{app}}$ is the mean square of dipole moment of all types of multimers that are present and can be written as [23].

$$<\mu^2>_{\mathrm{app}} = \frac{\sum_i C_i <\mu^2>_i}{X}$$

where $<\mu^2>_i$, denotes the average of the dipole moments of the multimers, containing i molecules, C_i denotes the fraction of multimers containing i molecules with respect to that number of solvent molecules and monomeric units and

$$X = \sum_i iC_i \qquad (1)$$

Using Scholte's theory as developed by Weaver and Parry, a relation can be established between $<\mu^2>_{\mathrm{app}}$ for associated molecule determined from Onsager's formula and the molecular properties of successive multimers. Based on Onsager's treatment, Huysken and Craco [24] developed a relation for $<\mu^2>_{\mathrm{app}}$ or $<\mu^2>_{\mathrm{exp}}$ which reduces to the following form in case of a ternary system (polar + polar + nonpolar) of mixed solvent [25, 26].

$$<\mu^2>_{\mathrm{exp}} = \frac{9kT}{4\pi N} \frac{V\left[\frac{\varepsilon-1}{\varepsilon} - 3\frac{X_a V_a}{V}\left(\frac{\varepsilon_a-1}{2\varepsilon+\varepsilon_a}\right) + \left(1-\frac{X_a V_a}{V}\right)\left(\frac{n_{bc}^2-1}{n_{bc}^2+2\varepsilon}\right)\right]}{X_{bc}(2\varepsilon+1)\left(\frac{n_{bc}^2+2}{n_{bc}^a+2\varepsilon}\right)^2} \qquad (2)$$

where

V and V_a	are the molar volume of the mixture (polar + polar) and the solvent (nonpolar) respectively,
n_{bc}	is the refractive index of the mixture of polar solutes measured at sodium D-line,

X_a and X_{bc}	are molefractions of the solvent and mixture of polar solute respectively,
ε and ε_a	are dielectric constants of the mixture and nonpolar solvent, respectively,

k is Boltzmann's constant,
N is Avogadro's number,
T is the temperature (K)

The term $<\mu^2>_{\exp}$ in Eq. (2) corresponds to the value for solute molecules (alcohol + TBP) in nonpolar solvents. If C_b and C_c are molar concentrations of alcohol (proton donor) and TBP (proton acceptor), respectively, in the solution, then extension of Eq. (1) to the complexed molecule gives,

$$<\mu_{bc}^2> (C_b + C_c) = \sum_i \mu_i^2 C_i \tag{3}$$

Since it is difficult to assess accurately the equilibrium constant for the various associations, instead of adopting rigorous calculations a simplified procedure is usually adopted for calculation of μ_{bc}. In the concentration range of TBP < 1 mole, the contribution to the total dipole moment is mainly due to 1 : 1 complex.

Defining the quantity

$$\mu_m^2 = \frac{\mu_{\exp}^2(C_c + C_b) - \mu_c^2(C_c - C_b)}{C_b} \tag{4}$$

in a domain of concentration where most of the molecules predominantly exist in 1 : 1 complexed state it can be shown that $\mu_m = \mu_{bc}$ where $C_b \gg C_c$.

Method II

This method uses the fundamental Debye equation for determination of the dipole moment of solute using the infinite dilution method. Prakash, after critical examination of various limiting polarization methods [27–29], showed that modified Palit's method [22] which reduces to Higasi [28] and Guggenheim's relation as special cases was the most satisfactory. According to this,

$$P_{2\mu} = M_2\left\{\frac{3(\varepsilon_{01} - n_a^2)}{d_1(\varepsilon_{01} + 2)(n_1^2 + 2)}\left(1 - \frac{\beta_{ow}}{d_1}\right)\right\} + M_2\left\{\frac{3\alpha_{ow}}{d_1(\varepsilon_{01} + 2)}\right\} - M_2\left\{\frac{6n_1\gamma_{ow}}{d_1(n_1^2 + 2)}\right\} \quad (5)$$

where

$$\alpha_{ow} = \left(\frac{\varepsilon_{12}}{W_2}\right)_{w_2 \to 0} \quad (6a)$$

$$\beta_{ow} = \left(\frac{d_{12}}{W_2}\right)_{w_2 \to 0} \quad (6b)$$

$$\gamma_{ow} = \left(\frac{n_{12}}{W_2}\right)_{w_2 \to 0} \quad (6c)$$

where subscripts 1 and 2 refer to the solvent and solute, respectively; ε, d, n are the dielectric constant, density and refractive index of the solution for the sodium D-line respectively. $P_{2\mu}$ is the molar orientation polarization of the solute.

In ternary system of proton donor–proton acceptor in an inert solvent for 1 : 1 complex stochiometry, if $(P_{b\mu})_a$ and $(P_{c\mu})_a$ are molar orientation polarization of proton donor and proton acceptor in the solvent and $(P_{b\mu})_{ca}$ is the polarization of proton donor in the mixed solvent, the induced polarization (ΔP) due to H-bonding is given by the relation;

$$\frac{1}{(P_{b\mu})_{ca} - (P_{b\mu})_a} = \frac{1}{\Delta P} + \frac{1}{K\Delta P}\frac{1}{C_c} \quad (7)$$

where K is the apparent complex formation constant of the complex.

Hence the plot of $(1/((P_{b\mu})_{ca} - (P_{b\mu})_a))$ *against* $(1/C_c)$ will give ΔP and K.

$$(P_{b\mu})_a = (P_{b\mu})_a + (P_{c\mu})_a + \Delta P \quad (8)$$

and

$$\mu_{bc} = 0.01281\sqrt{(P_{bc\mu})_a T} \tag{9}$$

Dipole moment of the hydrogen bridge O—H...0 is given by

$$\mu^* = \mu_{\mathrm{OH}} + \Delta\mu + \mu_c \tag{10}$$

where $\Delta\mu$ is the interaction dipole moment and can be calculated as follows. If the azimuthal angle between two dipoles of the complex is θ_b, the angle which proton donor dipole (μ_b) makes with O—H...O axis and θ_c is the angle which proton acceptor dipole makes with 0—H...O axis then

$$\begin{aligned}(\mu_{bc})^2 &= \mu_b^2 + \mu_c^2 + (\Delta\mu)^2 + 2\mu_b(\Delta\mu)\cos\theta_b + 2\mu_c(\Delta\mu)\cos\theta_c \\ &\quad + 2\mu_b\mu_c\cos\theta_b\cos\theta_c + 2\mu_b\mu_c\sin\theta_b\sin\theta_c\cos\phi\end{aligned} \tag{11}$$

For the most stable configuration in which the potential energy is minimum, $\phi = \pi/2$, and the expression for interaction dipole moment of the complex reduces to

$$\Delta\mu = (\mu_{bc}^2 - \mu_b^2\sin^2\theta_b - \mu_c^2\sin^2\theta_c)^{1/2} - \mu_b\cos\theta_b - \mu_c\cos\theta_c. \tag{12}$$

3. EXPERIMENTAL

The experimental arrangement used for the measurement of dielectric constant, refractive index, density *etc.*, is the same as used by the authors earlier [8]. The accuracy of measurement is also the same. The chemicals are AR grade and redistilled by using the standard procedures [30 – 32] before use. The temperature of all measurements was maintained at 303.16 ± 1 K using a water circulating thermostat.

4. RESULTS AND DISCUSSION

The relevant data have been presented in Tables I, II and III, and displayed in Figure 1.

TABLE I Properties of three long-chain alcohols with TBP in benzene $\mu_c = 3$ (Debye), $(P_{c\mu})_a = 355.964\,\text{cm}^3\,\text{mol}^{-1}$

Liquids	μ *(Debye)*	μ_{bc} *(Debye)*		*Mean* μ_{bc} *(Debye)*	$\Delta\mu$ *(Debye)*	ΔP $(gcm^3\,mol^{-1})$	K $(cm^3\,mol^{-1})$	$(P_{b\mu})_{ca}$ $(cm^3\,mol^{-1})$	μ^* *(Debye)*
		Method *I*	*Method* *II*						
1-hexanol	1.55	4.803	5.019	4.911	0.557	77.82	0.064	72.620	5.067
1-heptanol	1.71	4.264	5.146	4.705	0.730	108.58	0.02	67.854	5.240
1-octanol	1.68	4.141	5.063	4.602	0.680	65.574	0.01	93.756	5.190

TABLE II Mean dipole moment of the solute species of alcohol + TBP in benzene

C_c ($mol\ l^{-1}$) 1	C_b ($mol\ l^{-1}$) 2	ε 3	n_{bc} 4	d ($g\ cm^{-3}$) 5	μ_m (Debye) 6
(a) 1-hexanol + TBP in benzene					
0.4	2	4.663	1.3921	0.868	4.094
	2.5	5.569	1.3923	0.867	4.220
	3	6.221	1.3932	0.863	4.226
	3.5	6.800	1.3933	0.861	4.203
0.6	2	5.109	1.3919	0.872	4.180
	2.5	6.096	1.3921	0.871	4.310
	3	6.825	1.3930	0.867	4.320
	3.5	7.469	1.3932	0.863	4.374
0.8	2	5.681	1.3917	0.876	4.312
	2.5	6.775	1.3919	0.875	4.438
	3	7.603	1.3928	0.871	4.450
	3.5	8.356	1.3929	0.867	4.444
1.0	2	6.927	1.3911	0.885	4.693
	2.5	8.247	1.3915	0.884	4.800
	3	9.313	1.3924	0.881	4.805
	3.5	10.345	1.3925	0.876	4.803
(b) 1-heptanol + TBP in benzene					
0.4	2	4.882	1.4203	0.871	4.120
	2.5	5.287	1.4200	0.867	4.085
	3	6.109	1.4198	0.864	4.155
	3.5	7.045	1.4196	0.860	4.255
0.6	2	5.501	1.4201	0.876	4.263
	2.5	6.109	1.4199	0.873	4.265
	3	7.053	1.4198	0.869	4.330
	3.5	8.134	1.4195	0.864	4.398
0.8	2	6.192	1.4200	0.882	4.453
	2.5	6.920	1.4198	0.879	4.430
	3	7.991	1.4196	0.874	4.491
	3.5	9.205	1.4194	0.869	4.561
1.0	2	6.866	1.4199	0.887	4.601
	2.5	7.724	1.4197	0.884	4.588
	3	8.909	1.4194	0.879	4.643
	3.5	10.262	1.4193	0.874	4.715
(c) 1-octanol + TBP in benzene					
0.4	2.0	4.650	1.4206	0.869	4.050
	2.5	5.006	1.4208	0.864	3.991
	3.0	5.629	1.4214	0.859	4.022
	3.5	6.372	1.4216	0.855	4.159
0.6	2.0	5.143	1.4202	0.874	4.149
	2.5	5.665	1.4204	0.868	4.122
	3.0	6.301	1.4211	0.864	4.132
	3.5	7.038	1.4212	0.860	4.161
0.8	2.0	5.668	1.4197	0.878	4.254
	2.5	6.179	1.4200	0.874	4.203
	3.5	0.867	1.4207	0.869	4.210
	3.5	7.689	1.4207	0.865	4.244
1.0	2.0	6.158	1.4193	0.884	4.439
	2.5	6.849	1.4195	0.879	4.327
	3.0	7.859	1.4204	0.875	4.342
	3.5	8.205	1.4202	0.870	4.298

TABLE III Data for estimation of molar polarization of alcohol and TBP in benzene

W_2	d ($g\ cm^{-3}$)	ε	n
		(a) Solute 1-hexanol	
0.005	0.8742	2.67	1.4943
0.009	0.8740	2.69	1.4937
0.017	0.8736	2.72	1.4928
0.035	0.8726	2.72	1.4907
0.049	0.8718	2.84	1.4892
0.065	0.8710	2.90	1.4872
0.077	0.8704	2.95	1.4857
0.093	0.8696	3.02	1.4838
		(b) Solute 1-heptanol	
0.010	0.8784	2.72	1.4972
0.020	0.8781	2.76	1.4964
0.040	0.8775	2.80	1.4944
0.050	0.8771	2.85	1.4934
0.060	0.8768	2.88	1.4924
0.070	0.8765	2.92	1.4914
0.086	0.8750	2.98	1.4902
		(c) Solute 1-octanol	
0.010	0.8720	2.60	1.4924
0.020	0.8718	2.64	1.4916
0.035	0.8716	2.70	1.4906
0.053	0.8712	2.77	1.4888
0.065	0.8708	2.82	1.4878
0.080	0.8705	2.88	1.4866
0.090	0.8702	2.64	1.4850
		(d) Solute TBP	
0.010	0.8732	2.68	1.4874
0.020	0.8740	2.75	1.4868
0.032	0.8752	2.83	1.4862
0.046	0.8764	2.93	1.4854
0.065	0.8782	3.06	1.4842
0.075	0.8792	3.13	1.4832
0.085	0.8802	3.19	1.4830

Bond-angle Data

(i) **Alcohols**– Using R—O bond moment values of 1.14, O—H bond moment values 1.51, for 1-hexanol R—OH angle = 110°; $\theta_b = 43°$ 43.4′, for 1-heptanol R—OH angle = 101°, $\theta_b = 40°53.2'$ and for 1-octanol R—OH angle = 102°42′, $\theta_b = 41°27'$.

(ii) **TBP**– Assuming the dipole moment μ_c directed along P—O bond, $\theta_c = O^0$.

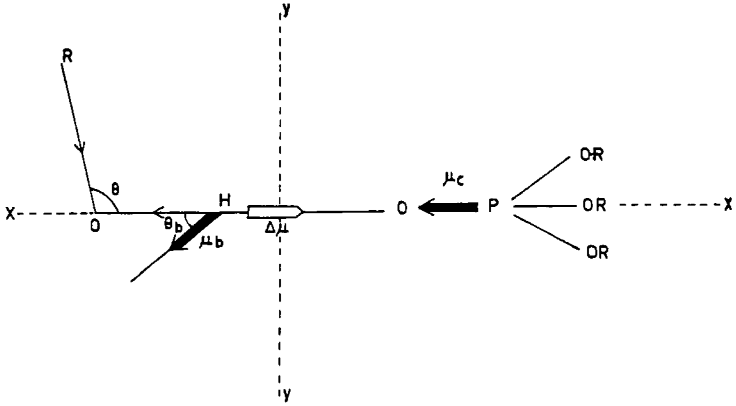

FIGURE 1 The geometry of 1 : 1 complex of TBP + alcohol.

In the concentration range less than one mole, TBP, exists in a monomer–dimer equilibrium and O—H proton in long-chain aliphatic alcohols forms a hydrogen-bonded complex with proton acceptor P → O. When a proton donor of dipole moment μ_b forms a H-bond with a proton acceptor of dipole moment μ_c, the direction of μ_c and μ_b with respect to b—H...c axis can be defined by θ_b and θ_c respectively. The formation of the H-bond is influenced by the dipole moment of the molecules involved in H-bonding and the displacement of the electrons. As a consequence the dipolar vector of the complex is different from the vector sum of the components and may be given by μ^*. If a single H-bond is formed between the protons, it can be presumed that $\Delta\mu$ has the direction of the hydrogen bond.

In the systems studied, complex formation is likely between the $H^{\delta+}$ of alcohol and $O^{\delta-}$ of TBP. Since O-atom is SP^3 hybridised and shape of TBP is almost pyramid-like, there is lot of space available for the O—H to penetrate and enter into the complexation. It is observed that the dipole moment of the complex μ_{bc}(TBP + alcohol) decreases in the order 1-hexanol (4.911 D) > 1-heptanol (4.705 D) > 1-octanol (4.602). The probable reason for this may be the increase in steric hindrance with increase in chain length. Furthermore, the value of $\Delta\mu$ decrease in order 1-heptanol (0.73 D) > 1-octanol (90.68 D) > 1-hexanol (0.557 D). The small magnitude of $\Delta\mu$ indicates that complexation is due to polarization effect involving charge distribution and does not involve charge transfer interaction, in which case $\Delta\mu$

should be around 10 D [33]. Further this low value of $\Delta\mu$ rules out the likelihood of formation of complexes of higher order. The value of $\Delta\mu$ being maximum for 1-heptanol-TBP system probably corroborates our earlier inference [8] that 1-heptanol is a more efficient modifier. It is worthwhile here to compare our results with systems involving smaller alcohols. In, butyl alcohol – chlorobenzene system $\Delta\mu$ is of the order of 4D [33]. It is probable that the presence of complexation is more favoured in smaller alcohols while it is reduced due to steric hindrance in long-chain alcohols.

The trend of variation of induced polarization ΔP is observed to be in the same order as that of $\Delta\mu$. It agrees with the trend observed by us for excess molar polarization evaluated through different technique in the TBP-alcohol systems.

Apparent complex formation constant in the systems is found to decrease in the order 1-hexanol (0.064) > 1-heptanol (0.02) > 1-octanol (0.01). It further supports our findings that complexation is more hindered with increases in chain-length due to steric factors. While evaluating mutual correlation factor, g_{ab}, in these systems [8] we observed that β-clusters with antiparallel orientation are predominant in them. The geometry of the complex that we have adopted do perhaps need modification in that context. The presumption that $\theta_c = 0°$ should be revised to the extent that TBP dipole moment may be inclined to the OH axis instead of lying along it. However, this change will not necessitate any significant alteration in the nature and the value of $\Delta\mu$ so that our conclusion that the complexation is due to charge redistribution is still valid.

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