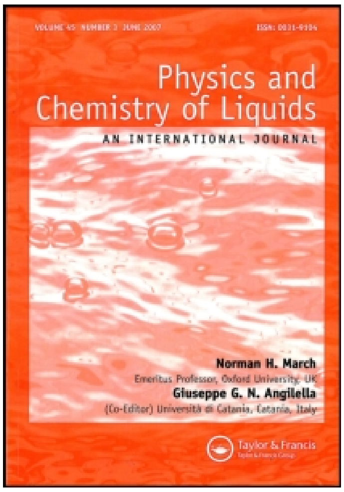

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Dipole Moment Studies of *n*-butanol, *i*-butanol and *t*-butanol with Chlorobenzene Complexes

U. S. Mohapatra[a]; G. S. Roy[b]; S. K. Dash[a]
[a] Department of Physics, K.B.D.A.V. College, Nirakarpur, Orissa, India [b] Pathani Samanta Planetorium, Bhubaneswar, Orissa, India

To cite this Article Mohapatra, U. S. , Roy, G. S. and Dash, S. K.(2001) 'Dipole Moment Studies of *n*-butanol, *i*-butanol and *t*-butanol with Chlorobenzene Complexes', Physics and Chemistry of Liquids, 39: 4, 443 — 451
To link to this Article: DOI: 10.1080/00319100108031675
URL: http://dx.doi.org/10.1080/00319100108031675

Phys. Chem. Liq., 2001, Vol. 39, pp. 443–451
Reprints available directly from the publisher
Photocopying permitted by license only

DIPOLE MOMENT STUDIES OF *n*-BUTANOL, *i*-BUTANOL AND *t*-BUTANOL WITH CHLOROBENZENE COMPLEXES

U. S. MOHAPATRA[a], G. S. ROY[b] and S. K. DASH[a,*]

[a]*Department of Physics, K.B.D.A.V. College, Nirakarpur-752019, Orissa (India);* [b]*Pathani Samanta Planetorium, Acharya Vihar, Bhubaneswar-751013, Orissa (India)*

(Received 19 May 2000)

The dipole moments of H-bonded complexes of *n*-butanol, *i*-butanol and *t*-butanol with chlorobenzene in benzene were investigated from dielectric measurements at 455 kHz and at temperature 303.16 K. The dipole moment of the complex (μ_{ab}), interaction dipole moment ($\Delta\mu$) and induced polarization (P_{ab}) for thermodynamically most favoured geometry of 1:1 complexes in these systems were determined. The results shows that the complexation is due to charge redistribution effect in all cases studied and the tendency of complex formation is maximum in *n*-butanol system.

Keywords: Relative permittivity; Butanols; Chlorobenzene; Interaction dipole moment; Induced polarization

INTRODUCTION

A dielectric technique has been widely used for studying the complex formation between two interacting solutes in an inert solvent. In hydrogen bonding of proton donor – acceptor complexes, a redistribution of electron density takes place and the dipole moment of the H-bonded system is no longer additive. The significant characteristics of the hydrogen bond is the increase in the distance of O—H

---

*Corresponding author.

accompanied by an enhancement of the bond moment [1], $\Delta\mu$. The determination of the dipole moment will indicate the type of complex. Pioneering work in this area was done by Jadzyn *et al.* [2] and Huysken *et al.* [3]. Polarization effects [4], charge transfer effects [5], partial proton transfer effects [6] and complete proton transfer effects [7] were invoked to account for the excess dipole moment in many H-bonded complexes.

In order to determine the presence of such complexes, nonlinear and linear dielectric methods have variously been adopted. Once the composition of solution is known, dielectric polarization results can serve for calculation of the dipole moment of the complex formed due to hydrogen bonding between proton donor and proton acceptor. Several investigators [8, 9] have determined the quantity $\Delta\mu$, the enhancement of dipole moment defined as

$$\Delta\mu = \mu_{\text{complex}} - (\mu_a + \mu_b)$$

where μ_a and μ_b are the dipole moment values of the components forming the hydrogen bond.

In the present work, we have adopted the evaluation of the dipole moment of complexes involving three butanols *viz.* *n*-butanol, *i*-butanol, *t*-butanol with chlorobenzene in a non-polar solvent (benzene) by Onsager's method [10]. Further we have evaluated the excess molar polarization in these systems. Such evaluation is useful to corroborate the picture that emerges from the study of $\Delta\mu$.

THEORY

Onsager's relation for dipole moment of a liquid in terms of dielectric constant takes care of the reaction field of the environment and leads us to the equation [11]

$$\begin{aligned} C_a\mu_a^2 + C_b\mu_b^2 + C_{ab}\mu_{ab}^2 &= \frac{9kT}{4\pi N_A}\left[\frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2+2)^2}\right. \\ &\qquad \left. - \left(\frac{C_S}{\bar{C}_S}\right)\frac{(\varepsilon_s - n_s^2)(2\varepsilon_s - n_s^2)}{\varepsilon_s(n_s^2+2)^2}\right] \\ &= \Omega_B C_B \qquad (1) \end{aligned}$$

The symbols used in Eq. (1) are as follows:

C_a = actual concentration of proton donor
C_b = actual concentration of proton acceptor
C_{ab} = actual concentration of 1:1 complex
ε = relative permittivity of the solution
n = refractive index of the solution
ε_S = relative permittivity of the solvent
n_S = refractive index of the solvent
C_S = concentration of the solvent in mol lit^{-1} in the solution
$\bar{C}_S$ = concentration of the pure solvent in mol lit^{-1} of solvent itself
Ω_B = dipole moment dependent parameter
C_B = concentration of proton acceptor in mol lit^{-1} for the complex in the solution
k = Boltzmann constant
N_A = Avogadro's number

If the concentration of proton acceptor C_B is much greater than the concentration C_A of proton donor such that,

$$C_B - C_A \gg K^{-1} \tag{2}$$

where K is the equilibrium constant of 1:1 complexation and if the non-interacting solvent has zero dipole moment, then Eq. (1) reduces to [12]

$$\Omega_B = \mu_b^2 + (\mu_{ab}^2 - \mu_b^2)\left(\frac{C_A}{C_B}\right) \tag{3}$$

where, μ_b = dipole moment of proton acceptor μ_{ab} = dipole moment of 1:1 complex.

One can, therefore, obtain the dipole moment of the complex from the intercept of the curve Ω_B *versus* $\frac{C_A}{C_B}$ and μ_{ab}^2 can be deduced from the slope. However, the curve is no longer a straight line if there is higher order complexing in addition to 1:1 complex. This fixes a criterion for choosing the proper concentration C_A and C_B for 1:1 complexation.

In a ternary system of proton donor – proton acceptor in an inert solvent for 1:1 complex stoichiometry, the effective molecular polarization is obtained from the relation [19]

$$\mu_{ab} = (0.01281)\sqrt{(P_{ab})T} \tag{4}$$

where, T is the temperature in degrees Kelvin.

When a proton donor of dipole moment μ_a forms a hydrogen bond with proton acceptor of dipole moment μ_b, the direction of μ_a and μ_b with respect to a—H$\cdots b$ axis can be defined by angles θ_a and θ_b, respectively. If θ_a and θ_b differ from zero, one can define an azimuthal angle Φ which describes the rotation position of μ_b around the hydrogen bond with respect to the plane formed by this bond and μ_a. The formation of the H-bond is accompanied by the dipole moment of the molecules involved in H-bonding and the displacement of electron. As a consequence the dipole vector of the H $\cdots$ O bridge which is different from the vector sum may be given by the expression:

$$\mu^* = \mu_{\mathrm{OH}} + \mu_b + \Delta\mu \tag{5}$$

Keeping in mind the collinearity of hydrogen bond, the most favourable structure of 1:1 complex [14], we have

$$\begin{aligned}(\mu_{ab})^2 &= \mu_a^2 + \mu_b^2 + 2\mu_a(\Delta\mu)\cos\theta_a + 2\mu_b(\Delta\mu)\cos\theta_b \\ &\quad + 2\mu_a\mu_b\cos\theta_a\cos\theta_b + 2\mu_a\mu_b\sin\theta_a\sin\theta_b\cos\phi \end{aligned} \tag{6}$$

For more stable configuration [15] in which potential energy is minimum, $\phi = \frac{\pi}{2}$ and the interaction dipole moment of complex [16] reduces to

$$\Delta\mu = [\mu_{ab}^2 - (\mu_a^2\sin^2\theta_a - \mu_b^2\sin^2\theta_b)]^{1/2} - \mu_a\cos\theta_a - \mu_b\cos\theta_b \tag{7}$$

EXPERIMENTAL

The experimental arrangements used for the measurements of relative permittivity (ε), refractive index (n) and density (ρ) are the same as used by earlier authors [17]. The accuracy of measurement is also the same. Chemicals are of AR grade and purified by standard procedures [18, 19] before use. Benzene was repeatedly refluxed with sodium and then fractionally distilled under anhydrous conditions. The temperature of all measurements was maintained at 303.16 K using a water circulating thermostat. The apparent molecular polarization at zero concentration in solvents containing varying amount of chlorobenzene was determined for all butanols studied. The variation of relative permittivity, refractive index and density with weight fraction of proton acceptor and limiting value of molar polarization in chlorobenzene + butanol systems were evaluated.

RESULTS AND DISCUSSION

The relevant data have been presented in Tables I and II and structure of the complex is indicated in Figure 1.

TABLE I Values of concentration of alcohol (C_A), dielectric constant (ε), refractive index (n), density (ρ) and Ω_B

C_A $mol\,l^{-1}$ (1)	C_B $mol\,l^{-1}$ (2)	ε (3)	n (4)	ρ $kg\,m^{-3}$ (5)	Ω_B (6)
(i) *n*-butanol (A) + chlorobenzene (B) + benzene					
0.4	2.0	3.82	1.4974	0.9226	5.840
0.6		3.84	1.4941	0.9218	5.956
0.8		3.87	1.4918	0.9210	6.089
1.0		3.89	1.4894	0.9200	6.192
0.4	2.5	4.28	1.4983	0.9328	5.832
0.6		4.30	1.4952	0.9320	5.925
0.8		4.32	1.4927	0.9311	6.010
1.0		4.35	1.4901	0.9301	6.122
0.4	3.0	4.75	1.4900	0.9446	5.945
0.6		4.77	1.4957	0.9437	5.906
0.8		4.80	1.4935	0.9431	5.995
1.0		4.82	1.4908	0.9422	6.070
0.4	3.5	5.20	1.5001	0.9558	5.760
0.6		5.23	1.4970	0.9549	5.848
0.8		5.25	1.4948	0.9544	5.908
1.0		5.27	1.4920	0.9535	5.976
(ii) *i*-butanol (A) + chlorobenzene (B) + benzene					
0.4	2.0	3.89	1.5000	0.9562	6.021
0.6		3.90	1.4925	0.9553	6.179
0.8		3.93	1.4875	0.9541	6.359
1.0		3.95	1.4780	0.9528	6.589
0.4	2.5	4.31	1.5025	0.96670	5.845
0.6		4.33	1.4966	0.9560	5.980
0.8		4.36	1.4899	0.9648	6.154
1.0		4.38	1.4836	0.9635	6.297

TABLE I (Continued)

C_A $mol\,l^{-1}$ (1)	C_B $mol\,l^{-1}$ (2)	ε (3)	n (4)	ρ $kg\,m^{-3}$ (5)	Ω_B (6)
0.4		4.86	1.5039	0.9797	5.981
0.6		4.88	1.4987	0.9785	6.090
0.8	3.0	4.92	1.4935	0.9767	6.240
1.0		4.93	1.4862	0.9752	6.360
0.4		5.36	1.5063	0.9901	5.956
0.6	3.5	5.38	1.5006	0.9888	6.060
0.8		5.40	1.4971	0.9872	6.137
1.0		5.42	1.4924	0.9858	6.230
(iii) *t*-butanol (A)+chlorobenzene (B)+benzene					
0.4		3.84	1.4957	0.9052	5.933
0.6	2.0	3.86	1.4943	0.9038	6.018
0.8		3.89	1.4932	0.9024	6.130
1.0		3.90	1.4913	0.901	6.192
0.4		4.25	1.4988	0.9184	5.749
0.6	2.5	4.27	1.4966	0.9170	5.829
0.8		4.29	1.4946	0.9158	5.906
1.0		4.31	1.4924	0.9149	5.986
0.4		4.70	1.4993	0.9282	5.717
0.6	3.0	4.72	1.4979	0.9269	5.774
0.8		4.75	1.4952	0.9255	5.869
1.0		4.79	1.4935	0.9240	5.972
0.4		5.20	1.5016	0.9334	5.741
0.6	3.5	5.22	1.4688	0.9322	5.808
0.8		5.24	1.4955	0.9308	5.882
1.0		5.25	1.4935	0.9292	5.922

TABLE II Properties of three alcohols with chlorobenzene in benzene

Liquids	μ_a (*Debye*)	P_{ab} ($g\,cm^3\,mol^{-1}$)	μ_{ab} (*Debye*)	$\Delta\mu$ (*Debye*)
n-butanol	1.66	115.877	2.399	2.187
i-butanol	1.64	94.415	2.165	1.956
t-butanol	1.66	74.353	1.922	1.763

Bond Angle Data [20]

(i) *Butanol*

Using R—O bond moment value of 1.14D and O—H bond moment value of 1.51D, R—OH angle = 104°, $\mu_{\text{butanol}} = 1.66\text{D}$, θ_a is found to be equal to 42°

(ii) *Chlorobenzene*

Assuming the dipole moment μ_b of chlorobenzene directed along hydrogen bond it is found that $\theta_b = 0$.

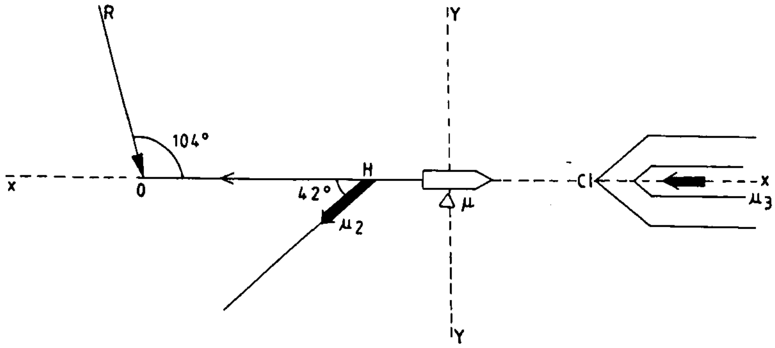

FIGURE 1 The geometry of 1 : 1 complex of butanol + chlorobenzene.

In the concentration range less than one mole, alcohol exist in monomer-dimer equilibrium and O—H proton of it form H-bonded complex with chlorobenze (proton acceptor). The dipolar increment due to the displacement of hydrogen atom in H-bonding is given by

$$\Delta\mu = e(r_{a\text{—H}} - r^0_{a\text{—H}})$$

where, $r_{a\text{—H}}$ and $r^0_{a\text{—H}}$ are the bond lengths in H-bonded and non H-bonded configuration, respectively. If a single H-bond is formed between proton donor (butanol) and proton acceptor (chlorobenzene) it can be presumed that $\Delta\mu$ has the direction of the hydrogen bond.

The values of relative permittivity, refractive index were measured with varying concentrations of proton donor (butanol) and are recorded in Table I. In the condition $C_B \gg C_A$, the values of Ω_B are computed through Eq. (1) are plotted against C_A/C_B. From the nature of variation of Ω_B it is observed that the plots are straight line for proton acceptor concentration (C_B) at 3.5 mol/lit in *n*- and *i*-butanol systems while at 2.5 mol/lit in *t*-butanol system. This suggests there is 1 : 1 complexes between *n*-butanol + chlorobenzene, *i*-butanol + chlorobenzene, and *t*-butanol + chlorobenzene systems. The complex formation is likely to occur between $H^{\delta+}$ of alcohol and $Cl^{\delta-}$ of chlorobenzene.

A perusal of Table II shows that the value of μ_{ab} and P_{ab} decrease in the order:

n-butanol > *i*-butanol > *t*-butanol

This trend indicates that the tendency of complex formation in *n*-chain alcohol is relatively more. Because of the steric factor it is likely that *n*-chain alcohol will have greater possibility of complex formation due to head–tail linkage [21], whereas for branched chain alcohols the tendency is weakened due to a switching mechanism [22]. Furthermore, the value of $\Delta\mu$ also decreases in the order:

$$n\text{-butanol } (2.19\text{D}) > i\text{-butanol } (1.95\text{D}) > t\text{-butanol } (1.76\text{D})$$

The hydrogen bond induces a moment in highly polarizable lone pair charge cloud in Cl atom and this induced polarization moment should account for $\Delta\mu$. Shanmugasundaram [15] have shown that by employing the minimised distances of 1.03 Å and 1.04 Å for free and H-bonded O—H and the maximum order of displacement of O···O distance as 0.025 Å, the magnitude of $\Delta\mu$ should be around 0.3D and 0.4D. Furthermore, calculation based on Frank's method [23] also shows that the contribution of induced polarization effect is of the order of 0.1 D to 0.15 D. The values of $\Delta\mu$ determined by us are higher than both of these.

The study of the mutual correlation factor in the binary mixture of alcohols and chlorobenzene indicated the formation of β clusters [24] with predominance of antiparallel orientation. The geometry of the complex that we have adopted here perhaps needs modification in that context. The presumption that $\theta_b = 0$ should be revised to the extent that chlorobenzene dipole moment may be inclined to the axis of the hydrogen bonding 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 will remain valid.

Acknowledgement

The author (SKD) is thankful to UGC, India for the award of financial assistance through project (PS-0-2/98) to complete this work.

References

[1] Smyth, C. P., *Molecular interactions*, Edited by Ratajczak, *et al.* (John Wiley, New York, 1981), **II**, 305.
[2] Jadzyn, J. and Malecki, J. (1972). *Acta Phys. Poln.*, **41**, 559.

[3] Zeegers-Huyskens, Th. and Huyskens, P., *Molecular interactions*, Vol. II, Edited by Ratajczak, *et al.* (John Wiley, New York, 1981).

[4] Tripathy, S., Roy, G. S. and Swain, B. B. (1993). *Indian J. Pure and Appl. Phys.*, **31**, 1828.

[5] Dash, S. K. and Swain, B. B. (1996). *J. Phys. Soc. Jpn.*, **65**, 3366.

[6] Shanmugasundram, V. and Mohan, R. (1982). *Indian J. Pure and Appl. Phys.*, **20**, 867.

[7] Siegel, G. G. and Herrera, F. (1990). *J. Mol. Liq.*, **44**, 175.

[8] Dash, S. K. (2000). *Phys. Chem. Liq.*, **38**, 49.

[9] Fainberg, V. S. and Ksido, L. L. (1974). *Zh. Fiz. Khim* (*USSR*), **48**, 997.

[10] Onsager, L. (1936). *J. Am. Chem. Soc.*, **58**, 1486.

[11] Chelliah, N. and Sabesan, R. (1994). *Indian J. Pure and Appl. Phys.*, **32**, 425.

[12] Garabadu, K., Roy, G. S., Tripathy, S. and Swain, B. B. (1997). *Czech. J. Phys.*, **47**, 765.

[13] Sabesan, R., Varadarajan, R. and Sargurumoorthy, M. (1979). *Indian J. Pure and Appl. Phys.*, **17**, 229.

[14] Roy, G. S. and Swain, B. B. (1988). *Phys. Chem. Liq.*, **18**, 61.

[15] Shanmugasundaram, V. and Mohan, R. (1980). *Adv. Mol. Relax. Int. Process* (*Netherlands*), **18**, 157.

[16] *Intermolecular Forces*, Edited by Huyskens, P. *et al.* (Springer Verlag, Berlin, 1991).

[17] Das, J. K., Dash, S. K., Acharya, S. and Swain, B. B. (1996). *Jpn. J. Appl. Phys.*, **35**, 453.

[18] Weisberger, A. (1955). *Technique of Organic Chemistry*, Interscience, New York.

[19] Riddich, J. A. and Bunger, W. B. (1970). *Organic Solvents* (Wiley Interscience, New York).

[20] Smyth, C. P. (1955). *Dielectric behaviour and structure*, McGraw-Hill Book Company.

[21] Dash, S. K. and Swain, B. B. (1993). *Jpn. J. Appl. Phys.*, **32**, 2753.

[22] Baba, K. and Shi Kamiyo, K. (1979). *Jpn. J. Appl. Phys.*, **18**, 1639.

[23] Frank, F. C. (1936). *Proc. R. Soc. London Ser A.* (*GB*), **152**, 171.

[24] Swain, B. B. (1984). *Acta Chim. Hung*, **117**, 383.