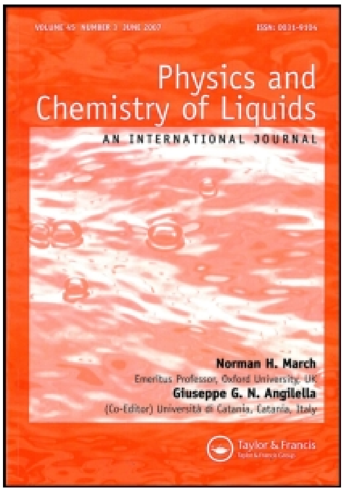

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Dielectric Studies of Hydrogen Bonded Association Complexes —Butanols with Aniline and Pyridine

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The mean square dipole moments of 1 : 1 complexes of *n*-butanol, *i*-butanol and *t*-butanol with aniline and pyridine in benzene are determined following two different methods: one uses Onsager's method based on dipole–dipole interaction and the other uses the help of modified Palit's method involving a limiting polarization measurement technique. The interaction dipole moments $\Delta\mu$ for the thermodynamically most favoured geometry of 1 : 1 complexes of the system involving butanol–aniline and butanol–pyridine were calculated. The value of $\Delta\mu$ indicated that complexation is due to polarization interaction. Furthermore, $\Delta\mu$ is found to be in the order pyridine > aniline. The dipole moment of the complexes involving butanol–aniline and butanol–pyridine is found to be in the order pyridine > aniline. These results have been used in interpreting of the structures of the complexes.

KEY WORDS: Dipole moment, polarization, hydrogen bond.

INTRODUCTION

Investigation of hydrogen bonded association solutions, in general, is a complicated phenomenon. It is usually undertaken by introduction of empirical parameters. As yet, there is no method of solving this problem univocally. The problem becomes increasingly intricate for binary mixtures involving donor and acceptor atoms where complex formation takes place. Composition of these complexes to a good approximation, can be determined for certain class of ternary solutions concerning two active components in a noninteracting medium.

In an earlier report on study of mutual correlation factor, one of the authors[1] suggested probable formation of hydrogen bonded complexes involving dissimilar molecules in binary mixtures of an alcohol–chlorobenzene and of an alcohol–aniline at nearly equimolar concentration range. We[2] have already investigated the mechanism of formation of OH···Cl complex in mixtures of butanols and chlorobenzene. Ekkehart Brandstädt[3] while studying the hydrogen bonding between pyrrole and amine indicated the formation of a charge transfer complex. Hassel and Hope[4] reported the formation of 1 : 1 charge transfer complex between iodine and pyridine. Hassel and Rømming[5] also prepared the crystalline pyridine–iodine monochloride complex and have shown that this has a linear arrangement of the pyridine ring with the acceptor molecule. Sabesan *et al.*[6] studied the complex formation of acetic acid with aniline and pyridine in a low dielectric solvent carbon tetrachloride and indicated the formation of a charge redistribution complex.

Thus there are ample evidences regarding complex formation involving alcohol, aniline and pyridine. Yet there is no report available in the literature regarding complex formation involving alcohol–aniline and alcohol–pyridine. As such we have undertaken the investigation of this aspect.

Of different methods, available for study of hydrogen bonded systems, the dielectric methods are highly suitable since the assumptions required for interpretation of these results are less arbitrary than while using other methods. Calculations and correct interpretation of the experimental results become feasible once the stoichiometry and geometry of the complexes are known.

In hydrogen bonding, a redistribution of electron density takes place mainly due to (a) electrostatic interaction, (b) polarization effect, (c) charge transfer effect. The experimental determination of dipole moment of complex and its associated parameters like interaction dipole moment etc. will indicate the manner in which complex is formed.

After the geometry of the complex is determined, its dipole moment resulting from vector addition of dipole moment of proton donor (μ_b) and proton acceptor (μ_c) can be calculated. The difference between the experimentally determined value μ_{bc} of the complex and the calculated value of complex, $\Delta\boldsymbol{\mu} = \boldsymbol{\mu}_{bc} - (\boldsymbol{\mu}_b + \boldsymbol{\mu}_c)$, is referred to as polarity of hydrogen-bond.

Our evaluation of dipole moment of complex involving butanols–aniline and butanols–pyridine in a nonpolar solvent is based on two methods, one with Onsager's method[7] based on dipole–dipole interaction and the other with the help of modified Palit's method[8–12] which makes use of infinite dilution technique. The results of both the methods are consistent.

Theory: Calculation of Dipole Moment of 1 : 1 Complex

Method I: (Based on the Onsager equation) The formation of multimers in a solution of polar liquid in a nonpolar solvent results in a different value of dipole moment of a molecule from its value in gas phase. The apparent value of square of molecular dipole moment $\langle\mu^2\rangle_{\text{app}}$ is an average over all types of multimers, that are present and can be written as,

$$\langle\mu^2\rangle_{\text{app}} = \sum_i \frac{C_i\langle\mu^2\rangle_i}{X} \tag{1}$$

The symbol $\langle\mu^2\rangle_i$ denotes the average of square of dipole moment of the multimer containing i molecules. C_i is the fraction of multimers containing i molecule with respect to total number of solvent molecules and monomeric units and $X = \sum iC_i$. The value of $\langle\mu^2\rangle_{\text{app}}$ is related to $\mu_{(\text{monomer})}$ as,

$$g = \frac{\langle\mu^2\rangle_{\text{app}}}{\mu^2_{(\text{mon})}} \tag{2}$$

where g is the linear correlation factor.

Huysken and Craco[13] obtained a relation for $\langle\mu^2\rangle_{\text{app}}$ using Onsager's treatment[7] based on dipole-dipole interaction, given by

$$\langle\mu^2\rangle_{\text{app}} = g\mu^2_{(\text{mon})} = \frac{9KT(2\varepsilon+\varepsilon_\infty)^2}{4\pi NX_b(\varepsilon_\infty+2)^2(2\varepsilon+1)} \times \left[V\frac{\varepsilon-1}{\varepsilon} - \frac{3X_aV_a(\varepsilon_a-1)}{2\varepsilon+\varepsilon_a} - \frac{3X_bV_b(\varepsilon_b-1)}{2\varepsilon+\varepsilon_b}\right] \tag{3}$$

where

μ	is the dipole moment of solute;
V	is the molar volume of mixture;
V_a and V_b	are molar volumes of solvent and solute respectively;
X_a and X_b	are mole fractions of solvent and solute respectively;
ε_∞	is taken as the square of refractive index n in the polar solute measured for sodium D line;
ε	is dielectric constant of the mixture;
ε_a	is the dielectric constant of a nonpolar solvent;
K	is Boltzmann constant;
T	is Temperature Kelvin;
N	is Avogadro number.

In a ternary system of mixed solvents Eq. (3) can be modified as

$$\langle\mu_{\text{exp}}^2\rangle = \frac{9KT}{4\pi N}V\left[\frac{\dfrac{\varepsilon-1}{\varepsilon}-3\left\{\dfrac{X_aV_a}{V}\left(\dfrac{\varepsilon_a-1}{2\varepsilon+\varepsilon_a}\right)+\left(1-\dfrac{X_aV_a}{V}\right)\left(\dfrac{n_{bc}^2-1}{n_{bc}^2+2\varepsilon}\right)\right\}}{X_{bc}(2\varepsilon+1)\left(\dfrac{n_{bc}^2+2}{n_{bc}^2+2\varepsilon}\right)^2}\right] \tag{4}$$

The term $\langle\mu_{\text{exp}}^2\rangle$ in Eq. (4) corresponds to mean square value of dipole moment of all solute molecules (proton donor + proton acceptor) in benzene. If molar concentrations of proton donor and proton acceptor be C_b and C_c respectively, then extension of Eq. (1) to the complexed molecule gives,

$$\langle\mu_{bc}^2\rangle(C_b+C_c)=\sum_i \mu_i^2 C_i \tag{5}$$

A more rigorous calculation to obtain the dipole moment of 1 : 1 complex (μ_{bc}) is possible only if the equilibrium constants for various associations are accurately known. However, a simplified procedure may be adopted for calculation of μ_{bc}.

In the concentration range <1 mole, butanols exist in a monomer dimer equilibrium[14] and OH proton forms a hydrogen bonded complex with proton acceptor N^-. With increase in concentration of proton acceptor, the concentration of uncomplexed proton donor decreases. Under this condition, the contribution to the total dipole moment is mostly due to 1 : 1 complex.

Let us define a new quantity $\mu_m{}^{22}$ as,

$$\mu_m^2=\frac{\mu_{\text{exp}}^2(C_c+C_b)-\mu_c^2(C_c-C_b)}{C_b} \tag{6}$$

in a domain of concentrations, where most of the molecules exist as 1 : 1 complex. It can be shown that

When $C_c \gg C_b$

$$\mu_m=\mu_{bc} \tag{7}$$

where μ_{bc} is the dipole moment of 1 : 1 complex of proton donor and acceptor in the inert solvent. It indicates that the number of molecules in the 1 : 1 complexed state depends on the excess of proton acceptor and hence the most coherent set of values of μ_m in a said domain gives μ_{bc}.[15]

Method II: (Based on the Debye equation) Dipole moment of 1:1 complex can also be determined using Debye's equation involving infinite dilution technique. In this method, the molar orientation polarization of solute $P_{2\mu}$ is given by,

$$P_{2\mu} = M_2\left\{\frac{3(\varepsilon_{01} - n_1^2)}{d_1(\varepsilon_{01} + 2)(n_1^2 + 2)}\left(1 - \frac{\beta_{0w}}{d_1}\right)\right\} + M_2\left\{\frac{3\alpha_{0w}}{d_1(\varepsilon_{01} + 2)^2}\right\} - M_2\left\{\frac{6n_1\gamma_{0w}}{d_1(n_1^2 + 2)^2}\right\} \tag{8}$$

where M_2 is the molecular weight of solute.

$$\alpha_{0w} = \left(\frac{\partial\varepsilon_{12}}{\partial w_2}\right)_{w_2\to 0} \tag{8a}$$

$$\beta_{0w} = \left(\frac{\partial d_{12}}{\partial w_2}\right)_{w_2\to 0} \tag{8b}$$

$$\gamma_{0w} = \left(\frac{\partial n_{12}}{\partial w_2}\right)_{w_2\to 0} \tag{8c}$$

and suffixes 1, 2 represent the solvent and solute respectively. ε, d and n represent the dielectric constant, density and refractive index of the solution for sodium D line.

In a ternary system of proton donor and acceptor in an inert solvent for 1:1 complex stoichiometry it has been shown that induced polarization (ΔP) due to H bonding is given by

$$\frac{1}{(P_{b\mu})_{Ca} - (P_{b\mu})_a} = \frac{1}{\Delta P} + \frac{1}{K_{\text{APP}}\,\Delta P}\cdot\frac{1}{C_c} \tag{9}$$

where $(P_{b\mu})_a$ and $(P_{b\mu})_{Ca}$ are the molar orientation polarization of proton donor in the solvent and in the mixed solvent respectively. K_{APP} is the apparent complex formation constant and C_c is the concentration of proton acceptor expressed in mole/litre. Reciprocal of the intercept of the plot between $1/(P_{b\mu})_{Ca} - (P_{b\mu})_a$ and $1/C_c$ will give ΔP.

Now

$$(P_{bc\mu})_a = (P_{b\mu})_a + (P_{C\mu})_a + \Delta P \tag{10}$$

and

$$\mu_{bc} = 0.01281\sqrt{(P_{bc\mu})_a T} \tag{11}$$

where T is temperature Kelvin. Dipole moment of the bridge OH···N is given by

$$\boldsymbol{\mu}^* = \boldsymbol{\mu}_b + \Delta\boldsymbol{\mu} + \boldsymbol{\mu}_c \tag{12}$$

Table 1 Mean dipole moment of solute species of butanol + aniline in benzene.

C_c m/L	C_b m/L	W_2	ε	n_{bc}	d gm/cm^3	V cm^3/mole	n	$\langle \mu^2_{\text{exp}} \rangle$ (Debye^2)	μ_m (Debye)
1	2	3	4	5	6	7	8	9	10
(a) n-butanol + aniline in benzene									
2.5	0.6	0.048	4.26	1.5001	0.824	98.55	1.5046	2.52	2.37
	0.8	0.063	4.38	1.4980	0.823	98.57	1.503	2.51	2.32
	1.0	0.080	4.48	1.4942	0.822	98.59	1.5016	2.55	2.33
3.0	0.6	0.048	4.56	1.5020	0.833	98.17	1.5065	2.45	2.31
	0.8	0.063	4.70	1.5004	0.832	98.20	1.5049	2.48	2.31
	1.0	0.080	4.80	1.4991	0.830	98.22	1.5036	2.46	2.27
3.5	0.6	0.048	4.95	1.5076	0.842	97.84	1.5120	2.48	2.37
	0.8	0.063	5.03	1.5054	0.840	97.88	1.519	2.44	2.28
	1.0	0.080	5.15	1.5033	0.839	97.92	1.508	2.43	2.26

				(b) *i*-butanol + aniline in benzene					
2.5	0.6	0.048	4.28	1.4989	0.8225	98.73	1.5038	2.55	2.4
	0.8	0.063	4.39	1.4969	0.8206	98.75	1.5017	2.53	2.34
	1.0	0.080	4.50	1.4931	0.8192	98.77	1.4995	2.51	2.3
3.0	0.6	0.048	4.59	1.5011	0.8322	98.30	1.5058	2.51	2.39
	0.8	0.063	4.71	1.4993	0.8313	98.33	1.5037	2.49	2.32
	1.0	0.080	4.82	1.4979	0.8302	98.37	1.5018	2.48	2.29
3.5	0.6	0.048	4.97	1.5066	0.8411	97.98	1.5109	2.50	2.4
	0.8	0.063	5.05	1.5039	0.8396	98.07	1.5087	2.47	2.32
	1.0	0.080	5.17	1.5021	0.8386	98.11	1.5069	2.46	2.28
				(c) *t*-butanol + aniline in benzene					
2.5	0.6	0.048	4.19	1.4998	0.8236	98.60	1.5043	2.44	2.28
	0.8	0.063	4.3	1.4978	0.8227	98.62	1.5023	2.42	2.24
	1.0	0.080	4.41	1.4940	0.8218	98.65	1.4985	2.42	2.23
3.0	0.6	0.048	4.5	1.5018	0.8329	98.22	1.5062	2.41	2.26
	0.8	0.063	4.61	1.5001	0.8316	98.23	1.5046	2.24	2.23
	1.0	0.080	4.72	1.4989	0.8303	98.25	1.5033	2.38	2.2
3.5	0.6	0.048	4.87	1.5074	0.8418	97.90	1.5117	2.42	2.29
	0.8	0.063	4.96	1.5051	0.8403	97.99	1.5085	2.41	2.25
	1.0	0.080	5.07	1.5030	0.8394	98.01	1.5066	2.39	2.21

Table 2 Mean dipole moment of solute species of butanol + pyridine in benzene.

C_c m/L	C_b m/L	W_2	ε	n_{bc}	d gm/cm^3	V cm^3/mole	n	$\langle\mu^2_{\text{exp}}\rangle$ (Debye^2)	μ_m (Debye)
1	2	3	4	5	6	7	8	9	10
				(a) *n*-butanol + pyridine in benzene					
2.5	0.6	0.048	7.24	1.4805	0.8167	95.75	1.4884	4.60	2.93
	0.8	0.064	7.36	1.4765	0.8158	95.77	1.4875	4.51	2.9
	1.0	0.080	7.48	1.4727	0.8150	95.78	1.4867	4.42	2.87
3.0	0.6	0.048	8.10	1.4819	0.8189	95.52	1.4890	4.72	3.02
	0.8	0.064	8.21	1.4792	0.8180	95.55	1.4881	4.62	2.96
	1.0	0.080	8.32	1.4756	0.8175	95.58	1.4872	4.53	2.92
3.0	0.6	0.048	9.04	1.4897	0.8219	95.25	1.4897	4.75	3.04
	0.8	0.064	9.16	1.4887	0.8202	95.27	1.4887	4.65	2.97
	1.0	0.080	9.28	1.4878	0.8195	95.31	1.4878	4.59	2.94

			(b) *i*-butanol + pyridine in benzene						
2.5	0.6	0.048	7.31	1.4798	0.8150	95.95	1.4879	4.67	2.99
	0.8	0.064	7.42	1.4756	0.8137	96.01	1.4867	4.57	2.94
	1.0	0.080	7.56	1.4719	0.8124	96.08	1.4862	4.50	2.93
3.0	0.6	0.048	8.15	1.4814	0.8188	95.54	1.4886	4.76	3.06
	0.8	0.064	8.24	1.4786	0.8178	95.57	1.4879	4.65	2.98
	1.0	0.080	8.35	1.4749	0.8167	95.62	1.4871	4.56	2.94
3.5	0.6	0.048	9.06	1.4834	0.8205	95.35	1.4894	4.78	3.08
	0.8	0.064	9.18	1.4797	0.8194	95.37	1.4885	4.72	3.03
	1.0	0.080	9.29	1.4771	0.8184	95.38	1.4878	4.62	2.97
			(c) *t*-butanol + pyridine in benzene						
2.5	0.6	0.048	7.08	1.4802	0.8162	95.79	1.4882	4.47	2.8
	0.8	0.064	7.14	1.4761	0.8151	95.84	1.4872	4.34	2.78
	1.0	0.080	7.19	1.4724	0.8136	95.94	1.4866	4.21	2.75
3.0	0.6	0.048	7.86	1.4817	0.8190	95.53	1.4893	4.55	2.85
	0.8	0.064	7.91	1.4790	0.8179	95.57	1.4882	4.42	2.79
	1.0	0.080	7.95	1.4753	0.8170	95.59	1.4874	4.29	2.75
3.5	0.6	0.048	8.80	1.4837	0.8211	95.29	1.4897	4.61	2.88
	0.8	0.064	8.85	1.4801	0.8194	95.30	1.4888	4.49	2.82
	1.0	0.080	8.89	1.4777	0.8182	95.32	1.4882	4.38	2.78

Table 3 Properties of three butanols with aniline and pyridine in benzene.

Liquid (proton acceptor)	Liquid (proton donor)	μ_c (Debye)	μ_b (Debye)	μ_{bc} (Debye)		Mean (Debye)	μ (Debye)	μ^* (Debye)	$(P_{c\mu})_a$ cm^3 mole^{-1}	$(P_{b\mu})_a$ cm^3 mole^{-1}
				Meth. I	Meth. II					
aniline	*n*-butanol	1.53	1.66	2.31	2.23	2.27	3.12	6.31	25.34	63.7
	i-butanol		1.64	2.32	2.27	2.30	3.17	6.34		65.2
	t-butanol		1.66	2.25	2.26	2.26	3.10	6.29		61.2
pyridine	*n*-butanol	2.19	1.66	2.97	2.58	2.73	5.92	9.77	56.2	63.7
	i-butanol		1.64	2.98	2.62	2.80	5.99	9.82		65.2
	t-butanol		1.66	2.78	2.65	2.71	5.90	9.75		61.2

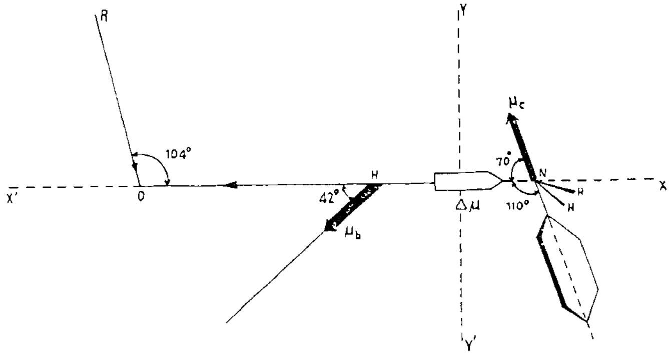

Figure 1 Geometry of 1 : 1 complex of butanol + aniline.

where μ_b and μ_c are the dipole moments of proton donor and proton acceptor respectively, and $\Delta\mu$ is the interaction dipole moment given by

$$\Delta\mu = \sqrt{\mu_{bc}^2 - \mu_b^2 \sin^2 \theta_b - \mu_c^2 \sin^2 \theta_c} - \mu_b \cos \theta_b - \mu_c \cos \theta_c \quad (13)$$

where θ_b is the angle which proton donor dipole makes with axis of bridge and θ_c is the angle which proton acceptor dipole makes with axis of bridge.

EXPERIMENTAL

The experimental set up used for measurement of dielectric constant, refractive index, density are the same as used by one of the authors.[1] The accuracy of measurement is also the same.

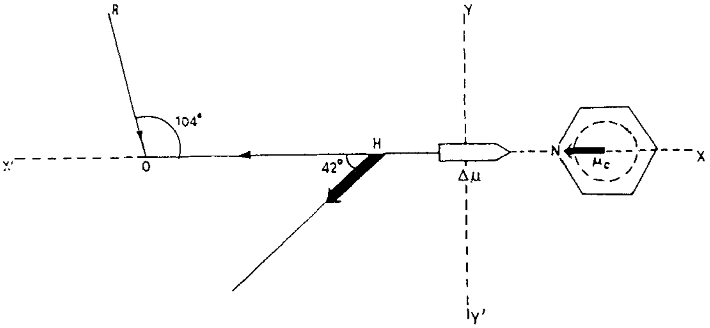

Figure 2 Geometry of 1 : 1 complex of butanol + Pyridine.

RESULT AND DISCUSSION

The relevant data have been presented in Tables 1, 2 and 3 and structures of complexes are indicated in Figures 1 and 2.

Bond angle data:

i) Butanol[16]—Using R—O bond moment value of 1.14 and O—H bond moment value of 1.51 and R—OH = 104° $\mu_{\text{butanol}} = 1.66$, θ_b is found to be equal to 42°.

ii) (a) Aniline[16,17]—Angle between lone pair direction and 1,4 axis = 110°. Angle between dipole vector and 1,4 axis = 142°, θ_c is found to be 70°. (b) Pyridine—Assuming dipole moment of pyridine, μ_c, directed along hydrogen bond we write $\theta_c = 0$.

A review of our data in Table 3 with the aim of reaching a decision as to the state of proton in the hydrogen bridge, that is, of deciding between delocalization and localization of proton indicates that complex formations in both the cases of butanol-aniline and butanol-pyridine are due to polarization interaction. Had it been a case of charge transfer interaction, $\Delta\mu$ would have been greater than 10 D.[18] Sobczyk and Skyrin[19] also determined interaction dipole moment $\Delta\mu$ for complexes involving pyridine and obtained a very low value of the order of 0.5 D. They were of the opinion that it was probably due to relatively low polarity of strong hydrogen bonds.

The value of $\Delta\mu$ in Table 3 for butanol-pyridine and butanol-aniline is found to be in the order, pyridine > aniline. The dipole moment of the complexes, μ_{bc}, involving butanol-pyridine and butanol-aniline are also found to be in the same order (Tables 1 and 2). It is due to greater tendency of intermolecular hydrogen bond formation in case of pyridine. This is probably due to the differences in nucleophilicity of contributing atoms of pyridine and aniline towards intermolecular hydrogen bond formation with butanol. As is known from resonance principle,[16] the nitrogen atom of pyridine is more nucleophilic, being an integral part of ring current and thereby the ease of formation of charge redistribution complex with butanol hydrogen is more probable than nitrogen atom of aniline.

The dipole moment of complex, μ_{bc}, involving butanol-chlorobenzene reported earlier[2] is found to be less than the dipole moment of complexes involving butanol-aniline and butanol-pyridine reported now. The reduced tendency of hydrogen bond formation is probably due to the fact that chlorobenzene is relatively neutral in character, the lone pair of electrons over chlorine atom is more inclined towards benzene nucleus and so is least available for coordination with butanol hydrogen.

It is worthwhile to note that the dipole moment of the complex reported by Sabesan *et al.*[6] is more than that of pyridine-butanol complex. The same order is also maintained for aniline. This difference is expected because the tendency of hydrogen bond formation of an acid with either aniline or pyridine is higher due to differential resonance stabilization of their respective conjugate bases.

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