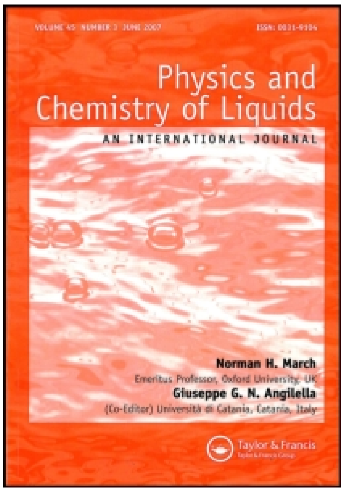

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Evaluation of dipole moment of hydrogen bonded complexes of long-chain alcohols with acetic acid and chlorobenzene

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To cite this Article Dash, S. K.(2008) 'Evaluation of dipole moment of hydrogen bonded complexes of long-chain alcohols with acetic acid and chlorobenzene', Physics and Chemistry of Liquids, 46: 3, 312 — 318
To link to this Article: DOI: 10.1080/00319100701211421
URL: http://dx.doi.org/10.1080/00319100701211421

Physics and Chemistry of Liquids
Vol. 46, No. 3, June 2008, 312–318

Evaluation of dipole moment of hydrogen bonded complexes of long-chain alcohols with acetic acid and chlorobenzene

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(*Received 12 January 2007; in final form 20 January 2007*)

The formation of 1 : 1 complexes involving *n*-pentanol-acetic acid, *n*-hexanol-chlorobenzene and *n*-heptanol-chlorobenzene in a non-polar solvent tetrachlormethane have been studied at the frequency of 455 kHz and at the temperature of 303.16 K. The dipole moment of 1 : 1 complex μ_{ab}, molar polarisation P_{ab}, and interaction dipole moment $\Delta\mu$ in all these ternary mixtures have been evaluated. The results indicate that complexation is due to polarisation effect.

Keywords: H-bonded complex; Relative permittivity; μ_{ab}; $\Delta\mu$; P_{ab}

1. Introduction

The formation of complex in hydrogen-bonded systems is an interesting phenomenon as it gives a firm insight into liquid structure. In hydrogen bonding of proton donor–acceptor complexes, a redistribution of electron density occurs primarily due to three factors, namely electrostatic, polarisation and charge transfer interactions. Further dipole moment of the H-bonded system is no more additive. The most important characteristic of the hydrogen bond is the increase in the distance of O–H accompanied by an enhancement of the bond moment $\Delta\mu$ [1] which will indicate the type of complex and nature of interaction involved in the formation of complex. The mechanism of complexation was investigated in acetic acid–aniline/pyridine system by Sabesen *et al.* [2], in phenol–triethyl amines system by Jadzyn *et al.* [3] and in phenol–amine system by Huyskens *et al.* [4] studies on IR spectra on bromine–chlorobenzene in tetrachloroethane confirms the effect of complexation of the fundamental stretching frequency of diatomic electron acceptor molecules [5]. Various physio-chemical studies of acetic acid in amines led to qualitative models predicting the existence of ionic complexes. Keefer *et al.* [6] and Buckles *et al.* [7] have adopted spectroscopic methods for studying the complexation in alcohol–iodine and acetic acid–iodine system. Study of mutual correlation factors in binary mixtures of long chain alcohols, and chlorobenzene

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Physics and Chemistry of Liquids
ISSN 0031-9104 print/ISSN 1029-0451 online
DOI: 10.1080/00319100701211421

indicated the formation of β-clusters with predominance of antiparallel orientation. The agreement in the value of $\Delta\mu$ probably owes to the fact that the bond formation is identical in both the cases and relative orientation of unlike molecules does not influence it. We have also investigated the formation of OH–Cl complex in butanol–chlorobenzene system [8] in an inert solvent benzene. In view of this, we have used Onsager's method to investigate the complexation in n-pentanol + acetic acid, n-hexanol + chlorobenzene and n-heptanol + chlorobenzene system in an inert solvent tetrachloromethane through evaluation of dipole moment.

2. Theory

Onsager's relation [9] for dipole moment of a liquid in terms of dielectric constant takes care of the reaction field of the environment and leads to equation (1) [10]

$$C_a\mu_a^2 + C_b\mu_b^2 + C_{ab}\mu_{ab}^2 = \frac{9kT}{4\pi N}\left[\frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2+2)^2} - \frac{C_s}{\overline{C}_s}\frac{(\varepsilon_s - n_s^2)(2\varepsilon_s + n_s^2)}{\varepsilon_s(n_s^2+2)^2}\right] = \Omega_B C_B \qquad (1)$$

where

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 ML^{-1} in the solution
$\overline{C}_s$ = concentration of pure solvent in ML^{-1} of solvent itself
Ω_B = dipole moment dependant parameter
C_B = concentration of proton acceptor in ML^{-1} for the complex in the solution.
k = Boltzmann's constant
N = Avogadro's number

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

$$C_B - C_A \gg K^{-1} \qquad (2)$$

where K is the equilibrium constant of 1 : 1 complexation. If the non-interacting solvent has zero dipole moment then equation (1) reduces to

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

where

μ_b is the dipole moment of proton acceptor
μ_{ab} is the dipole moment of 1 : 1 complex.

The value of μ_{ab}^2 can be deduced from slope of the curve Ω_B *versus* C_A/C_B. However, the curve is no longer a straight line if there is higher order complexation in addition to 1 : 1 complex. This fixes a criterion for choosing the proper concentration of C_A and C_B for 1 : 1 complexation. The effective molar polarisation is obtained from the relation

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

where T is the temperature in Kelvin.

When a proton donor of dipole moment μ_a forms a H-bond with a proton acceptor of dipole moment μ_b, the direction of μ_a and μ_b with respect to *a*–H–*b* axis can be defined by angle 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. Consequently the dipole vector of H–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 [11], we have

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

For most stable configuration [12] in which potential energy is minimum, $\Phi = \pi/2$ and interaction dipole moment of the complex [13] reduces to

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

3. Experimental

The experimental arrangement used for the measurement of relative permittivity (ε), refractive index (n) and density (ρ) are the same as used by the author earlier [14]. The accuracy of the measurement is also the same. Chemicals are of AR grade and purified by standard procedure [15,16]. The temperature of all the measurements was maintained at 303.16 K using a water circulating thermostat.

4. Results and discussion

The relevant data have been presented in tables 1 and 2.

4.1. *Bond angle data [17]*

***n*-Pentanol.** Using R–O bond moment value as 1.14, O–H bond moment value 1.51, R–OH angle is 105°33′, $\mu_a = 1.63$ D, θ_a is found to be 42°22′.

Table 1. Values of concentration of alcohols (C_A), dielectric constant (ε) refractive index (n) density (ρ) and Ω_B.

C_A (ML^{-1})	C_B (ML^{-1})	ε	n	ρ (g cm^{-3})	Ω_B
n-Pentanol + acetic acid + tetrachloromethane					
0.4	2	3.2	1.439	1.442	4.1550
0.6		3.14	1.438	1.435	3.9530
0.8		3.26	1.436	1.428	4.4224
1.0		3.39	1.436	1.422	4.8900
0.4	2.5	3.28	1.437	1.404	3.5972
0.6		3.47	1.435	1.397	4.1689
0.8		3.61	1.434	1.392	4.5783
1.0		3.75	1.434	1.384	4.9705
0.4	3	3.55	1.434	1.365	3.6880
0.6		3.88	1.432	1.354	4.4808
0.8		4.04	1.431	1.347	4.8608
1.0		4.18	1.430	1.342	5.1933
0.4	3.5	4.15	1.431	1.319	4.3923
0.6		4.35	1.429	1.311	4.8038
0.8		4.47	1.428	1.305	5.0469
1.0		4.51	1.427	1.301	5.1363
n-Hexanol + chlorobenzene + tetrachloromethane					
0.4	2	3.259	1.444	1.407	4.2912
0.6		3.284	1.447	1.395	4.3317
0.8		3.315	1.449	1.382	4.4100
1.0		3.330	1.451	1.368	4.4304
0.4	2.5	3.466	1.442	1.375	4.0663
0.6		3.475	1.445	1.363	4.0510
0.8		3.511	1.447	1.348	4.1218
1.0		3.553	1.449	1.337	4.2156
0.4	3	3.618	1.440	1.330	3.7823
0.6		3.695	1.443	1.317	3.9258
0.8		3.761	1.444	1.305	4.0663
1.0		3.801	1.446	1.291	4.1340
0.4	3.5	3.941	1.438	1.290	3.9142
0.6		3.975	1.441	1.279	3.9483
0.8		4.001	1.447	1.267	3.9337
1.0		4.312	1.445	1.253	4.5513
n-Heptanol + chlorobenzene + tetrachloromethane					
0.4	2	3.34	1.476	1.386	4.0637
0.6		3.40	1.478	1.380	4.2379
0.8		3.44	1.479	1.368	4.3586
1.0		3.47	1.501	1.361	4.1087
0.4	2.5	3.65	1.474	1.333	4.1428
0.6		3.73	1.476	1.322	4.3295
0.8		3.81	1.478	1.312	4.5149
1.0		3.86	1.479	1.300	4.6330
0.4	3	3.92	1.472	1.282	4.0918
0.6		4.05	1.475	1.273	4.3393
0.8		4.14	1.477	1.260	4.5100
1.0		4.24	1.477	1.247	4.7264
0.4	3.5	4.35	1.471	1.231	4.3348
0.6		4.44	1.473	1.217	4.4775
0.8		4.54	1.475	1.213	4.6370
1.0		4.66	1.476	1.198	4.8434

Table 2. Variation of μ_{ab}, P_{ab}, μ^* and $\Delta\mu$ of aliphatic alcohols with acetic acid, chlorobenzene in tetrachloromethane.

Liquids							
Proton donor	Proton acceptor	μ_a (Debye)	μ_b (Debye)	μ_{ab} (Debye)	P_{ab} ($\mathrm{g\,cm^3\,mol^{-1}}$)	μ^* (Debye)	$\Delta\mu$ (Debye)
n-Pentanol	Acetic acid	1.63	1.74	2.743	151.245	2.284	−0.966
n-Hexanol	Chlorobenzene	1.55	1.69	2.826	160.537	3.004	−0.196
n-Heptanol	Chlorobenzene	1.71	1.69	3.152	99.711	3.165	−0.035

n-Hexanol. Here R–O bond moment value and O–H bond moment value are the same as in *n*-pentanol and R–OH angle is 110°, $\mu_a = 1.55\,\mathrm{D}$, θ_a is found to be 43°43′.

n-Heptanol. Here R–O bond moment value and O–H bond moment value are the same as in *n*-pentanol and R–OH angle is 101°, $\mu_a = 1.71\,\mathrm{D}$, θ_a is found to be 40°53′.

Acetic acid. Using the same R–O and O–H bond moment values as in case of above alcohols, the C=0 bond moment value is 2.5, $\mu_b = 1.74$ D, $\theta_b =$ is found to be 66°.

Chlorobenzene. The dipole moment of chlorobenzene is directed along hydrogen bond, $\theta_b = 0°$ and $\mu_b = 1.69$ D.

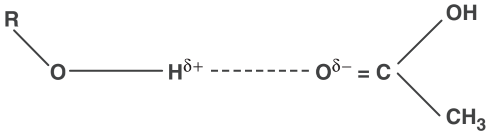
In the concentration range less than 1 M, alcohol exists in monomer–dimer equilibrium and O–H proton of it forms a H-bonded complex with acetic acid and chlorobenzene (proton acceptor). The formation of the H-bond is influenced by the dipole moment of the molecules involved in H-bonding and the displacement of the electron. As a result the dipolar vector of the complex is different from the sum of their components. The dipolar increment due to the displacement is given as

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

where $r_{a\text{–H}}$ and $r^0_{a\text{–H}}$ are the bond lengths in H-bonded and non-H-bonded configuration. If a single H-bond is formed between proton donor and proton acceptor, it can be presumed that $\Delta\mu$ has the direction of H-bond. The dipole moment increment $\Delta\mu$ serves as an indicator of nature of interaction.

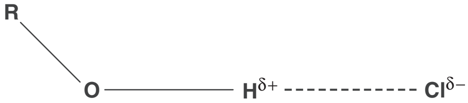
A perusal of table 1 shows the value of relative permittivity, refractive index for varying concentrations of proton donor (alcohol). In the condition, $C_B \gg C_A$ the values of Ω_B are computed by using equation (1). From the nature of variation of Ω_B *versus* C_A/C_B it is observed that the plots are straight line for proton acceptor concentration $C_B = 2.5\,\mathrm{ML^{-1}}$ in *n*-pentanol + acetic acid system, while at $3\,\mathrm{ML^{-1}}$ in *n*-hexanol + chlorobenzene and *n*-heptanol + chlorobenzene system. This suggests 1 : 1 complexation in all the three systems.

The complexation between alcohol and acetic acid is due to the linkage between $H^{\delta+}$ of alcohol and $O^{\delta-}$ of acid represented.



The hydrogen of alcoholic OH group is proton donor while the oxygen in C=0 group in acetic acid is proton acceptor. The negative charge on oxygen in carbonyl group resides due to the polarisation of the π bond. As a result there is a formation of hydrogen bond between $H^{\delta+}$ proton of alcohol and carbonyl ($C{=}O^{\delta-}$) oxygen of acid. Hydroxyl oxygen of acid cannot form bonds with alcohol as it is a part of donor group. As such carbonyl oxygen is more suitable in formation of hydrogen bond with $OH^{\delta+}$ proton of alcohol.

As regards to chlorobenzene the complexation is due to the linkage between $OH^{\delta+}$ of alcohol and $Cl^{\delta-}$ of chlorine represented as



The π electron in aromatic ring of chlorobenzene is delocalised resulting an electron cloud over benzene. In the pauling scale [18], chlorine is more electronegative than carbon, and the bond between C–Cl is polarised. As a result negative charge develops on chlorine. So hydrogen bond is formed between $OH^{\delta+}$ of alcohol and $Cl^{\delta-}$ of chlorobenzene.

A review of our data in table 2 indicates that the complex formation in the present study is due to the polarisation interaction. For charge transfer interaction [19] $\Delta\mu$ should exceed 10 D, hence its possibility is ruled out as the magnitude of $\Delta\mu$ in all the three systems studied is much less than 10 D.

Besides this, the values of μ_{ab}, P_{ab} and μ^* decreases in the order *n*-heptanol > hexanol > *n*-pentanol system. This trend indicates that the complexation in *n*-heptanol + acetic acid system is more in comparison with other two systems. This is probably due to the comparatively greater tendency of hydrogen bond formation in chlorobenzene system than with acetic acid system. The value of $\Delta\mu$ also decreases in the same order as *n*-heptanol + chlorobenzene > *n*-hexanol + chlorobenzene > *n*-pentanol + acetic acid.

In heptanol system, oxygen atom is less electronegative when compared to hexanol due to the less inductive effect because of the more number of carbon atoms. As a result H^+ is easily separated and the degree of polarity becomes more when compared to pentanol and hexanol which is in favour of the higher value of $\Delta\mu$ in heptanol system.

Shanmugasundaram and Mohan [13] have shown by employing a minimum distances of 1.03 Å and 1.04 Å for free and H-bonded OH and the maximum order of displacement of O–O distance as 0.025 Å. The magnitude of $\Delta\mu$ should be around 0.3 D and 0.4 D. Chelliah and Sabesan [10] calculated $\Delta\mu$ in a complex involving alcohol and amine. They obtained the value of $\Delta\mu$ less than 0.5 D and suggested the existence of polarisation interaction. The values of $\Delta\mu$ calculated in this report are in good agreement with that of Chelliah and Sabesan, which indicates the probable nature of complex and type of interaction between unlike polar molecules.

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