Dielectric studies of hydrogen bonded complexes – Methyl isobutyl ketone (MIBK) with aliphatic alcohols

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Received 22 May 2000; accepted 14 September 2000

The mechanism of dipolar complexation involving MIBK and three aliphatic alcohols namely 1-propanol, 1-butanol and 1-octanol in a non-polar benzene medium was investigated from dielectric measurements at frequency 455 kHz and at temperature 303.16 K. The dipole moment of the complex (μc), interaction dipole moment (Δμ) and induced polarization (P) for the thermodynamically most favoured geometry of 1:1 complexes of these systems were computed. The results show that complexation is due to partial proton transfer in all cases studied and the tendency of complex formation is maximum in 1-heptanol system.

1 Introduction

Methyl isobutyl ketone (MIBK) is used for extraction of protactinium-233 from HCl solution containing neutron-irradiated thorium nitrate at a neutron flux of $10^{12}$ n cm$^{-2}$ s$^{-1}$. The extractant MIBK can be used with water miscible diluents. Suitable physical properties are obtained by blending the extractant with suitable diluent for greater dispersal and more rapid phase disengagement in order to improve upon its extraction efficiency. Therefore, MIBK is diluted with various nonpolar solvents like benzene, CCl$_4$, p-xylene, kerosene, etc. to alter its physico-chemical properties. But the formation of a third organo-aqueous phase complicates the extraction process. This third phase can be eliminated by the addition of another polar liquid (modifier) to the solvent or by increasing the temperature of the system.

Earlier the authors have reported the utility of dielectric measurements while studying the molecular interaction in a binary mixture of liquids by assessing some parameters like Kirkwood Fröhlich linear correlation factor ($g$), mutual correlation factor ($g_{mn}$), excess molar polarization ($\Delta P$) and excess free energy of mixing ($\Delta G$). The present study is designed to extend our scope of investigation to another aspect of molecular dynamics at a microlevel by exploring the probability of complex formation due to molecular association between two polar molecules in the presence of a nonpolar solvent.

In mixtures of unlike polar liquids involving associated species a redistribution of electron density in the respective molecules takes place primarily due to electrostatic effect, polarization effect and charge transfer effect. The nature of such redistribution leading to possible complexation can be assessed by evaluating the dipole moment of the complex formed by proton donor and proton acceptor molecules. Pioneering work in this area were done by Sobczyk et al., Huysken and Jadzyn and Malecki. In H-bonded complexes the important characteristics of hydrogen bond is the increase in O-H bond length accompanied by an enhancement of the bond moment ($\Delta \mu$) which is useful on the analysis of the mechanism of such complexation. Besides the effects enumerated, reaction field effect of the environment is a major cause for the change in the dipole moment of the complexes in a polar medium.

Chelliah and Sabesan investigated the mechanism of complex formation in acetic acid aniline/pyridine systems. Similar study was done by Meyyappan et al. in phenol-ketone/aldehyde system.
systems. Complexes involving TBP-alcohols\textsuperscript{14}, alcohols-chloro benzene/bromobenzene\textsuperscript{15}, alcohols-amine\textsuperscript{16} were also investigated by the authors. The study of IR spectra of bromine-chlorobenzene in CCl\textsubscript{4} confirms the effect of complexation on the fundamental stretching frequency of diatomic electron acceptor molecules\textsuperscript{17}. Various physical and chemical studies of acetic acid in amines also lead to quantitative models predicting the existence of ionic complexes. In view of this, a survey of literature showed that the complexing ability of MIBK with alcohols is not yet investigated. As such the authors have undertaken the investigation of possibility of H-bonded complexes of MIBK with a number of aliphatic alcohols, viz. 1-propanol, 1-butanol, 1-octanol which are likely used as modifiers in the extraction technology.

Onsager's method has been followed, based on dipole-dipole interaction, which takes care of reaction field of the environment to estimate the enhancement of the dipole moment of the complex.

2 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 to an equation\textsuperscript{18}

\[
C_a \mu_a^2 + C_b \mu_b^2 + C_{ab} \mu_{ab}^2 = \frac{9kT}{4\pi N_A} \left[ \frac{(\varepsilon - n_a^2)(2\varepsilon + n_a^2)}{\varepsilon(n_a^2 + 2)^2} - \frac{C_a}{C_1} (\varepsilon_a - n_a^2)(2\varepsilon_a - n_a^2) \right] \]  

\text{... (1)}

where

- \( C_a \) = actual concentration of proton donor
- \( C_b \) = actual concentration of proton acceptor
- \( C_{ab} \) = actual concentration of 1:1 complex
- \( \varepsilon \) = relative permittivity of the solution
- \( n \) = refractive index of the solution
- \( \varepsilon_a \) = relative permittivity of the solvent
- \( n_a \) = refractive index of the solvent
- \( C_1 \) = concentration of the solvent in mol lit\textsuperscript{-1} of solvent itself

\( \mu_a \) = dipole moment of proton donor
\( \mu_b \) = dipole moment of proton acceptor
\( \mu_{ab} \) = dipole moment of 1:1 complex

\( \Omega_b \) = dipole moment dependent parameter
\( \Omega_a \) = concentration of proton acceptor in mol lit\textsuperscript{-1} for the complex in the solution
\( k \) = Boltzmann constant
\( N_A \) = Avogadro's number

If the concentration of proton acceptor is much greater than the concentration of proton donor for the complex in the solution, such that\textsuperscript{19}

\[ C_a - C_b \gg K^{-1} \]  

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\textsuperscript{19}

\[ \Omega_b = \mu_a^2 + (\mu_{ab}^2 - \mu_b^2) \left( \frac{C_a}{C_b} \right) \]  

\text{... (3)}

where, \( \mu_b \) = dipole moment of proton acceptor
\( \mu_{ab} \) = dipole moment of 1:1 complex

One can, therefore, obtain the dipole moment of the complex from the intercept of the curve \( \Omega_b - \frac{C_a}{C_b} \mu_{ab}^2 \) can be deduced from the slope.

However, the curve is no longer a straight line if there is higher order complex 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\textsuperscript{19}

\[ \mu_{ab} = (0.01281)(P_{ab})T \]  

\text{... (4)}

where, \( T \) is the temperature in Kelvin.

When a proton donor of dipole moment \( \mu_a \) forms an hydrogen bond with proton acceptor of dipole moment \( \mu_b \), the direction of \( \mu_a \) and \( \mu_b \) with respect to a-H...b axis can be defined by angles \( \theta_a \) and \( \theta_b \), respectively. If \( \theta_a \) and \( \theta_b \) differ from zero, one can define an azimuthal angle \( \phi \) which describes the rotation position of \( \mu_a \) around the hydrogen bond with respect to the plane formed by
this bond and \( \mu_r \). 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...O bridge which is different from the vector sum may be given by the expression:

\[
\mu^c = \mu_{on} + \mu_r + \Delta \mu \quad \ldots (5)
\]

where \( \Delta \mu \) is the interaction dipole moment of the complex. Keeping in mind the collinearity of hydrogen bond for the most favourable structure of 1:1 complex\(^{11} \), one can have:

\[
(\mu_{on})^2 = \mu_r^2 + \mu_r^2 + 2\mu_r (\Delta \mu \cos \theta_r + 2\mu_r (\Delta \mu \cos \theta_r + 2\mu_r \mu_r \cos \theta_r \pm \theta_r + 2\mu_r \mu_r \sin \Theta_r \sin \Theta_r \cos \phi)
\]

\ldots (6)

For more stable configuration\(^{20} \) in which potential energy is minimum, \( \varphi = \pi/2 \) and the interaction dipole moment of complex reduces to\(^{14} \)

\[
\Delta \mu = (\mu_r^2 - (\mu_r^2 \sin^2 \theta_r - \mu_r^2 \sin^2 \Theta_r))^{1/2} - \mu_r (\cos \Theta_r - \mu_r \cos \Theta_r), \quad \ldots (7)
\]

3 Experimental Details

The experimental arrangements used for the measurements of relative permittivity (\( \varepsilon \)), refractive index (\( n \)) and density (\( \rho \)) are the same as used by the authors earlier\(^{21} \). The accuracy of measurements is also the same. Chemicals are of AR grade and purified by standard procedures\(^{22,23} \) 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 MIBK were determined for all alcohols studied. The variation of relative permittivity refractive index and density with weight fraction of proton acceptor and limiting value of molar polarization in MIBK-benzene and MIBK-alcohol systems were evaluated.

4 Results and Discussion

The variation of relative permittivity (\( \varepsilon \)), refractive index (\( n \)) and density (\( \rho \)) with weight fraction of proton acceptor were evaluated in the systems containing MIBK and benzene in 1-propanol, 1-butanol and 1-octanol. The relevant data have been presented in Tables 1 and 2 and displayed in Fig. 1.

Bond angle data

(i) 1-propanol: Using R-O bond moment value 1.14 and O-H bond moment value 1.51, the R-OH angle is 103°, \( \mu_r = 1.68 \)D and \( \theta_r = 41^{10}/30' \)

(ii) 1-butanol: The R-O bond moment and O-H bond

![Fig. 1 — Variation of \( \Omega_0 = C_0/C_B \)](image-url)
alcohol exists in monomer-dimer equilibrium and 
O-H moment value the same as above, the R-OH angle is 
$10^\circ.4$, $\mu_0 = 1.66D$ and $\theta_0 = 42^\circ.36'$

(iii) 1-octanol: The O-O bond moment and O-H bond moment value are the same as above, the R-OH angle is $102^\circ.42^\circ$, $\mu_0 = 2.7D$ and $\theta_0 = 43^\circ.26^\circ$

In the concentration range less than one mole, alcohol exists in monomer-dimer equilibrium and O-H proton in alcohol forms a hydrogen bonded complex with proton acceptor (MIBK). When a proton donor of dipole moment $\mu_d$ forms a H-bond with a proton acceptor of dipole moment $\mu_a$, the dipolar increment arising due to displacement of hydrogen atom on H-bonding is given by

\[
\Delta \mu = \varepsilon (r_{d-H} - r_{o-H}^0)
\]

where, $r_{d-H}$ and $r_{o-H}^0$ were the bond lengths in H-bonded and non-H-bonded configuration, respectively. If a single H-bond is formed between proton donor and proton acceptor, 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 ($C_A$) and are recorded in Table 1. In the condition $C_A > C_B$, the values of $\Omega_B$ computed through eq. (1) are plotted against $C_A / C_B$. From the nature of variation of $\Omega_B$ it is observed that the plots are straight line for the concentration $C_B$ of proton acceptor at 3 and 3.5 mol lit$^{-1}$. This suggests that there is 1:1 complexes between MIBK + 1-propanol, MIBK + 1-butanol and MIBK + 1-octanol systems.

In these systems, the complex formation is likely to occur between $H^{8+}$ of alcohols and $O^-$ of $C=O$ group of MIBK. Oxygen atom is $Sp^3$ hybridised and in the MIBK structure there is a lot of voids available for O-H to penetrate and enter into complexation.

A perusal of Table 2 shows that for $C_A = 3.5$ mole lit$^{-1}$ the value of $\mu_{ab}$ decreases in the order,

1-octanol (4.22D) $>$ 1-butanol (3.65D) $>$ 1-propanol (3.35D)

This trend indicates that the tendency of complex formation in higher chain alcohol, i.e. 1-octanol is relatively more. Because of steric
hindrance it is likely that long chain alcohols will have greater probability of complex formation due to head-tail linkage, whereas for relatively smaller alcohols the tendency is weakened due to switching mechanism prevalent in alcohol system. However, in lower alcohols like 1-propanol and 1-butanol $\mu_{ab}$ is maximum for $C_N = 3$ mol lit$^{-1}$. But it has got no apparent linkage with chain length of alcohols.

The trend of variation of $P_{ab}$ is observed to be also in the same order as that of $\mu_{ab}$. This may be compared with results of our earlier corroborative work involving ultrasonic and dielectric measurements in these systems. It is observed that the mutual correlation factor $g_{ab}$, excess isentropic compressibility $\beta^E$, excess acoustic impedance $Z^E$ and excess intermolecular free length $L^I$ decreases in the order

1-octanol > 1-butanol > 1-propanol

The point of inflexion of these parameters is relatively sharp in 1-octanol system. 1-octanol is not only a bigger molecule compared to 1-butanol and 1-propanol, its viscosity is also high. Hence the findings of those corroborative studies also supports the contention that higher alcohols are in advantageous position in getting involved in complex formation.

Furthermore, the value of $\Delta \mu$ also decreases in the order:

1-octanol (3.14D) > 1-butanol (2.33D) > 1-propanol (1.83D)

at $C_N = 3.5$ mol lit$^{-1}$. But the order is altered to 1-butanol (2.82D) > 1-propanol (2.39D) > 1-octanol (2.33D) for $C_N = 3$ mol lit$^{-1}$. The O-H bond induces a moment in highly polarizable lone pair charge cloud in C=O group and this induced polarization moment should count for $\Delta \mu$. Shannugundaram$^{[2]}$ have shown that by employing the minimized distances of 1.03Å and 1.04Å for free and H-bonded O-H, and the maximum order of displacement of 0---O distance as 0.025Å, the magnitude of $\Delta \mu$ should be between 0.3D to 0.4D. Furthermore, calculation based on Frank’s method$^{[22]}$ also shows that contribution of induced polarization effect is of the order of 0.1D-0.15D. The values of $\Delta \mu$ determined by the authors are higher than both of these. As such it could not be solely arising out of interaction moment induced by the charge cloud. This may lead to the following possibilities.

(i) The formation complex of higher stoichiometry, like

\[
\begin{array}{c}
\text{R} \quad \text{H} \quad \text{O} \quad \text{H} \quad \text{R} \\
\text{R} \quad \text{O} \quad \text{H} \quad \text{R} \\
\end{array}
\]

(ii) Partial proton transfer, in which an equilibrium between ion pairs exist, i.e. electron delocalisation is more predominant than proton transfer. Delocalisation and dispersion interactions accompanying the partial proton transfer complex may be the physical model of the hydrogen bonded complexes between MIBK and alcohol molecules. In such a physical model $\Delta \mu$ have two components – one coming from induced dipole moment and another due to presence of charge transfer in the ground state. It is worthwhile to mention here that though the nature of plots between $\Omega_{II}$ and $C_N$ is linear as per requirement of 1:1 complexes, the
existence of higher order complexes can not be ruled out.

Acknowledgement

The authors SKD and JKD are thankful to the University Grant Commission, New Delhi, for the award of financial assistance for a minor Research Project.

References