Dipole moment studies of substituted Benzaldehyde with alcohols

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Abstract

Dipole moments have been determined by using the mixture of Benzaldehyde, O-Chlorobenzaldehyde, P-Chlorobenzaldehyde, 1-propanol and 1-Butanol with non-polar CCl4 at 303K. Dielectric constant density and refractive index from the dielectric data based on Polarization and Huysken’s method. The result were interpreted in the liquid mixtures have been explained on the basis of dipole moment.

Keywords: Dielectric Parameters, dipole moment, Huysken’s method, Polarization Benzaldehyde, O-Chlorobenzaldehyde, P-Chlorobenzaldehyde

1.1 INTRODUCTION

Dipole moments have been generally used to discuss about the molecular interaction between the same or differ liquid system. The nature of solute – solvent (polar or non-polar) interaction and the structure of the liquids in pure and mixtures can be explained from dielectric measurements. These gain information relating to the alignment of neighboring molecule and the ability to interact with them. Dipole moment is one of the physical properties made used to study of interaction taking place between the same or different liquids. Benzaldehyde are important industrial chemicals and are widely used as perfume and flavoring compounds and it is also used in the preparation of certain aniline(1). Alcohols have found in various
application and widely use in industry and excellent proton donors (2). Dielectric studies about binary mixtures are important to understand the intermolecular interactions (3). Several researchers (4-9) have studied the complexes of alcohols and phenols with aldehydes, ketones, esters in recent years using dielectric methods. The present work is aimed to study the dipole moments for binary by using mixtures of Benzaldehyde, O-Chlorobenzaldehyde, P-Chlorobenzaldehyde, 1-propanol and 1-Butanol with non-polar CCl4 at 303K.

2. MATERIALS AND METHOD

2.1 Measurement of density

Density values of liquid and liquids mixture were measured using a specific gravity of bottle 5 ml. A digital electronic balance were used to measured density. For all the measurement, temperature were controlled by circulating water through an ultra-thermostat with an accuracy ± 0.15K.

2.2 Measurement of refractive index

Refractive index of the pure and binary liquid mixture was measured by Abbe’s refractometer. From the measured values of the refractive index of the dielectric constant at infinite dilution or dielectric constant at article frequency have been measured ($\varepsilon_\infty = n_D$)

2.3 Measurement of Dielectric constant ($\varepsilon_0$)

Dipole meter is an instrument that is uses to measure the dielectric constant of liquids. In the equipment a particular circuit has been developed for audio oscillator that produce stabilized wave. In this experiment dielectric cell is standardized using reference liquid having known dielectric constant by immersing the dielectric cell assembly in to reference liquid then experimental liquid whose dielectric constant has to be determine. Is immersed into liquid resulting in change in frequency. From the resulting shift capacitance of cell in unknown of liquid is calculated (c) Dielectric constant of unknown liquid is calculated using the relation

$$\varepsilon_o + \frac{(\varepsilon_o - \varepsilon_x)}{(\varepsilon_o - \varepsilon_r)} (\varepsilon_r - 1)$$

Where $c_o$ = capacitance of air, $c_r$ = capacitance of standard liquids, $c_x$ = capacitance of test liquids

$\varepsilon_r$ = dielectric constant of standard liquid
3. DETERMINATION OF DIPOLE MOMENT

a) Polarization method (PM)

According to limiting polarization method in dilute solutions, the molar polarization of the solution \( P_{12} \) is expressed as

\[
P_{12} = \left( \frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} \right) \left( \frac{m_1 x_1 + m_2 x_2}{d_{12}} \right)
\]

(1)

Where the suffixes 1, 2 and 12 refer the solvent, solute and solution respectively, \( P \) the molar polarization, \( x \) the mole fraction, \( m \) the molecular weight, \( \varepsilon \) the dielectric constant and \( \rho \) the density and \( P_{12} \) is the sum of the polarization contributions of the two components.

\[
P_{12} = P_1 x_1 + P_2 x_2
\]

(2)

\( P_1 \) and \( P_2 \) are the molar polarization of the solvent and solute respectively. From equations (1) and (2) we can write,

\[
P_2 = \left[ \frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} \right] \left( \frac{m_{12}}{d_{12}} \right) - P_1 X_1 \left( \frac{1}{X_2} \right)
\]

(3)

Where \( m_{12} = m_1 x_1 + m_2 x_2 \) is the molecular weight of the solution. \( P_2 \) may be plotted against \( x_2 \) and the resultant curve may be extrapolated to \( X_2 = 0 \) to obtain the polarization at infinite dilution \( P_2^\infty \). This value of \( P_2^\infty \) includes the contribution of electronic and atomic polarizations also which taken into consideration gives the orientation polarization of the solute molecule and thereby the value of the dipole moment from the following relation.

\[
\mu_2 = \left[ \frac{9kT}{4\pi N} P_2^\infty T \right]^{1/2}
\]

(4)

Where \( P_2 \mu = P_2^\infty - R_D \) and \( R_D \) is the molar refraction.

\[
R_D = \left( \frac{n_2^2 - 1}{n_2^2 + 2} \right) \left( \frac{m_2}{d_2} \right)
\]

(5)

Insertion of the appropriate values for the constants leads to

\[
\mu_2 = 0.01281 \times 10^{-18} [P_2 \mu T]^{1/2}
\]

(6)
The Debye equation starts from the assumption that the internal field of the solution is the Lorentz field. Consequently, in highly diluted solution, the molecules of polar substances must behave just as in the vapour state and must become freely oriented in the applied field.

b) Palit and Bannerjee

According to Palit and Bannerjee method determine the value of $P_2^\infty$ can be determined with the help of the following relation.

$$P_2^\infty = \frac{3M_2\alpha^2V_i}{(\varepsilon_i + 2)^2} + M_1(V_i + \beta^2)\left(\frac{\varepsilon_i - 1}{\varepsilon_i + 2}\right)$$

(7)

Where $P_2^\infty = \frac{4\pi N\mu^2}{9KT}$, $\varepsilon = \varepsilon_i + \alpha W_2$ and $V = V_i + \beta W_2$

They have claimed advantages for the use of specific volumes ($v=1/d$) rather than densities.

c) Huyskens Method (HM)

The difficulty the molecular shape and inadequately of the Lorentz treatment of the local field acting on the molecules were taken up by Onsager(10-11). This method assumed the molecules to be spherical and the neighborhood of each solute molecule to be a continuum without discrete structure.

Huyskens computed the experimental quantity $\mathbf{\Omega}$ from the relative dielectric constant $\varepsilon_{12}$, the refractive index for sodium line $n_{12}$, the density $d_{12}$ of the system and its average molecular weight $M_{12}$

$$\mathbf{\omega} = \left[\frac{9KT}{4\pi N}\right] \left|\frac{(\varepsilon_{12} - n_{12}^2)(2\varepsilon_{12} + n_{12}^2)}{\varepsilon_{12}(n_{12}^2 + 2)^2}\right| \frac{M_{12}}{d_{12}}$$

(8)

Where $\mathbf{\Omega}$ is a molar quantity derived from the theory of Onsager. It is related to the apparent dipole moments ($\mu_F$) of the formal components of the system
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**Table 1** Variation of $\varepsilon_{12}$, $n_{12}$, $d_{12}$, $P_2$, and $\bar{\omega}$ with mole fraction benzaldehyde in carbon tetrachloride system

<table>
<thead>
<tr>
<th>Mole fraction of the solute $X_2$</th>
<th>Dielectric constant of the solution $\varepsilon_{12}$</th>
<th>Refractive index of the solution $n_{12}$</th>
<th>Density of the solution $d_{12}$ (gm/cc)</th>
<th>$P_2$</th>
<th>Molar polarization of the solute $P_2$ (gm/cm³)</th>
<th>$\bar{\omega} \times 10^{-37}$</th>
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<td>2.2542</td>
<td>1.468</td>
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<tr>
<th>Systems</th>
<th>Polarization Method</th>
<th>Huysken’s Method</th>
<th>Palit and Bannerjee</th>
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</table>

4. RESULTS AND DISCUSSION.

Dielectric constant, refractive index and density of the solutions were measured at 303 K and these experimental data were used to compute the values with various parameters. Their relevant trends are displayed in (Fig 1-2). Fig 1 shows polarization plotted against concentration of solute. Fig 2 represent the plot of $\bar{\omega}$ vs $X_2$ for the given solutes with alcohols in the dilute solution of carbon tetrachloride.

Table 2: Dipole moment results of the analysis of binary mixtures system taken for varying concentrations.
Fig 1 shows polarization plotted against concentration of solute.

Fig 2 represents the plot of $\bar{\omega}$ vs $X_2$. 
The dipole moments of the binary systems taken for study were determined in carbon tetrachloride and the corresponding values are given in Table 1.

From the binary systems, the observed polarization values for the all substances decrease with increase of concentration of the solute in carbon tetrachloride and dilution decrease the polarization values. On the other hand binary systems, the observed huyskens values for the all substances decrease with increase of concentration of the solute in carbon tetrachloride and dilution increase the huyskens values. The dipole moment have been computed in various methods and these methods analysed. It is found that the dipole moment for all systems are in the order of o-chloro benzaldehyde > benzaldehyde > p-chloro benzaldehyde > 1-propanol > 1-butanol.

5. CONCLUSION

In the present work we have calculated the dielectric parameters like density, refractive index, dielectric constant, dipole moment using polarization, huysken’s and palit and bannerjee method. In general a good agreement between experiment and calculated value have been observed.

REFERENCES


