Dipole Moment Studies in some Substituted Anilines with Alcohols

R.Priscilla\textsuperscript{a}, A.Deepika\textsuperscript{b} and R.Ida Malarselvi\textsuperscript{b}

\textsuperscript{a}Department of Physics, A.D.M. College for Women (Autonomous)
Nagapattinam– 611 001, Tamil Nadu, India,
\textsuperscript{b}Department of Physics, D G Government Arts College,
Mayiladuthurai – 609 001, Tamil Nadu, India.
Email ID: priscilla.arutchelvi@gmail.com, idamalarselvi@gmail.com

Abstract

Dipole moments have been determined by using the mixtures of diluted solutions of aniline, \(o\)-chloro aniline, \(p\)-chloro aniline, ethanol, 2-butoxy ethanol and 2-methoxy ethanol in carbon tetrachloride at 30°C based on Debye’s polarization method and Huysken’s method. The results are interpreted that the complex dipole moment for the halogen substitution of acceptor complexes is greater than the mono substituted acceptor complexes. But the case is reversed in halogen substitution of donor complexes.

Keywords: H-Bonding, Anilines, Ethanols, Dipole moment, Dipolar increment, Molar Polarization.

1. Introduction

Dielectric studies provide meaningful information about the mechanisms, which describe the intra-intermolecular orientations of these molecules. Among the physic-chemical methods used in the investigation of the nature of molecular complexes there are the phenomena of molecular orientation by a particular permanent electric field. Hoffman and Symth [1] have calculated the dielectric constant of \(n\)-docosyl bromide in the solid rotator phase applying Onsager’s equation and modifying extensively the theory of Fowler [2] that assured a fraction of the molecules to be rotating. This emphasizes the necessarily approximate character of the equations for the solvent effect that have been considered, but does not invalidate their use for the approximate calculation of the relatively small effects. Satheesh et al. [3] have measured the dielectric permittivity of binary mixtures of aniline, \(o\)-chloro aniline, \(p\)-chloroaniline, ethanol, 2-butoxyethanol and 2-methoxyethanol have been carried out at single frequency at 9.8 GHz and at 1 KHz. This result indicates that the presence of the double bond in allyl alcohol does not seem to influence appreciably on the complex formation and relaxation mechanics of the complexes. Dielectric measurements on acetophenone and its derivatives have been made by various workers [4-7].
Several authors [8,9] have studied the complexes of phenols and alcohols with ketones, esters, amides, aldehydes and amines in recent years using dielectric methods. The polarity of the hydrogen bonded complexes in non-polar solvents, represented by a dipolar increments $\Delta\mu$, shows a systematic dependence on the $\Delta pK_a$ that generally is sigmoidal. In this work, it is aimed to investigate the dipole moments for binary and complex systems by using mixtures of aniline, $o$-chloro aniline, $p$-chloroaniline, ethanol, 2-butoxyethanol and 2-methoxyethanol in CCI$_4$ at 303K from polarization and Huysken's method.

2. Experimental method

The dielectric measurements at static frequency 300 KHz were made using a Toshniwal R 1.09 type dipole meter. The cell temperature was maintained at 30 °C by circulating water through the glass jacket of the cell. The refractive indices were measured using Abbe’s refractometer; chemicals were purified by standard procedures and checked against their literature value.

Using the limiting polarization method the dipole moment of the solute ($\mu_b$) in a non-polar solvent can be calculated from the relation.

$$\mu_b = \frac{3kT}{4\pi N} \left[ (P_{2\infty} - R_D)T \right]^{1/2}$$

(1)

Where $K$ is the Boltzmann constant, $N$ is Avogadro’s number. $T$ is the absolute temperature, $P_{2\infty}$ is the molar polarization at infinite dilution and $R_D$ is molar refraction of the solute

$$R_D = \frac{(n^2 - 1)}{n_2^2 d_2^2} \frac{M_2}{d_2}$$

(2)

Here $n_2$, $d_2$ and $M_2$ are the refractive index, density and molecular weight of the solute.

Dipole moment of the complex by Huysken’s method

The dielectric constant $\varepsilon$ and the refractive index for the sodium line $n_D$ of a ternary solution with formal concentrations $F_A$ of phenol and $o$-nitro phenol and $F_B$ of base in CCI$_4$ solution are measured first. The quantity $\Omega_B$ is then computed from the experimental data

$$\Omega_B = \frac{9kT \pi 10^{19}}{4\pi N_A} \frac{1}{F_B} \left[ \frac{(x-n\eta)(2x+n\eta)}{c(n\eta^2 + x)^2} \right]$$

(3)

$F_i^0$ is the formal concentration of the solvent in the pure state and $F_i$ its actual concentrations in the solution. The other subscripts refer to the pure solvent. If the internal index of refraction of the dissolved entities can be approximated as $n_0$ the theories of Onsager [10] and Froehlich [11] led to the following equation.

$$\Omega_B = \sum \mu_i^2 C_i$$

(4)

Where $\mu_i$ and $C_i$ are, respectively, the moment and the concentration of the entity $i$ present in solution. When only 1:1 complexes are formed in the ternary mixtures, this equation becomes,
\[ \Omega_B = \mu_B^2 C_a + \mu_B^2 C_b + \mu_{ab}^2 C_{ab}. \]  

The concentration \( C_b \) of the non-complexed base can be computed from \( F_A \) and \( F_B \) provided the complexation constant \( k_{ab} \) is known. For the complexes studied here, this quantity was determined by a calorimetric procedure.

\[ C_b = \left( F_A - F_B + k_{ab}^{-1} \right) + \sqrt{(F_A - F_B + k_{ab}^{-1}) - 4F_AF_B} \]  

The following quantities are then computed

\[ X = \left[ 1 + \frac{1}{k_{ab} C_b} \right]^{-1} F_A/F_B \]  

\[ \Omega_B = \Omega_B - \mu_B^2 (1 + k_{ab} C_b)^{-1} (F_A/F_B) \]  

The value of \( \mu_a \) is known from measurements on binary mixtures. From the previous equations it follows that \( \Omega_B \) and \( X \) are linearly related by the expression.

\[ \Omega_B = \mu_B^2 + (\mu_{ab}^2 - \mu_B^2) X \]  

Thus plotting \( \Omega_B \) against \( X \) gives straight line, the intercept of which gives \( \mu_B^2 \) and the slope, the difference \( \mu_{ab}^2 - \mu_B^2 \). If on the other hand \( \mu_B^2 \) is known, value for \( \mu_{ab}^2 \) can be computed for each value of \( \Omega_B \) which allows an estimation of the error on \( \mu_{ab}^2 \).

Seven determinations of \( \Omega_B \) were made for each system, the concentration \( F_B \) being of the order of 0.06 mol dm\(^{-3}\) and the ratio \( F_A/F_B \) varying in the range 0.03-0.18.

### 3. 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. The dipole moments of the binary and ternary interacting systems taken for study were determined in carbon tetrachloride and the corresponding values are given in Table 3.

From the binary systems, the observed polarization values for all substances decrease with increase of concentration of the solute in carbon tetrachloride and dilution decreases the polarization values in the order of aniline > o-chloro aniline > ethanol > 2-methoxy ethanol > 2-butoxy ethanol > p-chloro aniline. It is inferred from Table 3 that the dipole moment for the halogen substituted acceptor complexes are greater than for the mono substituted acceptor complexes. But the case is reversed in halogen substitution of donor complexes. This indicates that the polarization interactions only and it is not due to charge transfer interactions.

| Table -1 | Variation of related physical parameters with mole fraction |
### Aniline in carbon tetrachloride System

| Mole Fraction of the Solute $X_2$ (mol/L) | Dielectric Constant of the Solution $\varepsilon_{12}$ | Refractive Index of the Solution $n_{12}$ | Density of the Solution $d_{12}$ (g/cm$^3$) | $\Omega_B \times 10^{39}$ D$^2$ |
|------------------------------------------|-----------------------------------------------------|------------------------------------------|------------------------------------------|----------------------------------|
| 0.03                                     | 2.254                                               | 1.4577                                   | 1.626                                    | 3.03                             |
| 0.06                                     | 2.260                                               | 1.4510                                   | 1.619                                    | 0.81                             |
| 0.09                                     | 2.265                                               | 1.4458                                   | 1.607                                    | 0.44                             |
| 0.12                                     | 2.273                                               | 1.4432                                   | 1.595                                    | 0.20                             |
| 0.15                                     | 2.275                                               | 1.4402                                   | 1.565                                    | 0.16                             |
| 0.18                                     | 2.281                                               | 1.4316                                   | 1.551                                    | 0.13                             |

### Variation of related physical parameters with mole fraction p-Chloroaniline in carbon tetrachloride system

| Mole Fraction of the Solute $X_2$ (mol/L) | Dielectric Constant of the Solution $\varepsilon_{12}$ | Refractive Index of the Solution $n_{12}$ | Density of the Solution $d_{12}$ (g/cm$^3$) | $\Omega_B \times 10^{39}$ D$^2$ |
|------------------------------------------|-----------------------------------------------------|------------------------------------------|------------------------------------------|----------------------------------|
| 0.03                                     | 2.279                                               | 1.4316                                   | 1.652                                    | 3.03                             |
| 0.06                                     | 2.315                                               | 1.4325                                   | 1.6653                                   | 1.60                             |
| 0.09                                     | 2.365                                               | 1.4332                                   | 1.6787                                   | 0.81                             |
| 0.12                                     | 2.433                                               | 1.4341                                   | 1.692                                    | 0.50                             |
| 0.15                                     | 2.523                                               | 1.435                                    | 1.6987                                   | 0.40                             |
| 0.18                                     | 2.643                                               | 1.4366                                   | 1.722                                    | 0.40                             |

### Variation of related physical parameters with mole fraction o-Chloroaniline in carbon tetrachloride system

| Mole Fraction of the Solute $X_2$ (mol/L) | Dielectric Constant of the Solution $\varepsilon_{12}$ | Refractive Index of the Solution $n_{12}$ | Density of the Solution $d_{12}$ (g/cm$^3$) | $\Omega_B \times 10^{39}$ D$^2$ |
|------------------------------------------|-----------------------------------------------------|------------------------------------------|------------------------------------------|----------------------------------|
| 0.03                                     | 2.2938                                              | 1.4396                                   | 1.667                                    | 3.90                             |
| 0.06                                     | 2.2978                                              | 1.4436                                   | 1.6486                                   | 0.90                             |
| 0.09                                     | 2.319                                               | 1.4526                                   | 1.6373                                   | 0.40                             |
| 0.12                                     | 2.450                                               | 1.4557                                   | 1.6293                                   | 0.30                             |
| 0.15                                     | 2.475                                               | 1.4707                                   | 1.628                                    | 0.20                             |
| 0.18                                     | 2.586                                               | 1.4757                                   | 1.6107                                   | 0.16                             |

### Variation of related physical parameters with mole fraction Ethanol in carbon tetrachloride system

Variation of related physical parameters with mole fraction Ethanol in carbon tetrachloride system

| Mole Fraction of the Solute $X_2$ (mol/L) | Dielectric Constant of the Solution $\varepsilon_{12}$ | Refractive Index of the Solution $n_{12}$ | Density of the Solution $d_{12}$ (g/cm$^3$) | $\Omega_B \times 10^{39}$ D$^2$ |
|------------------------------------------|-----------------------------------------------------|------------------------------------------|------------------------------------------|----------------------------------|
| Mole Fraction of the Solute \(X_2\) (mol/L) | Dielectric Constant of the Solution \(\varepsilon_{12}\) | Refractive Index of the Solution \(n_{12}\) | Density of the Solution \(d_{12}\) (g/cm³) | \(\Omega_0 \times 10^{19}\) D² |
|------------------------------------------|-----------------|-----------------|-----------------|-----------------|
| 0.03                                    | 2.313           | 1.4396          | 1.6873          | 12.1            |
| 0.06                                    | 2.320           | 1.4356          | 1.6486          | 3.27            |
| 0.09                                    | 2.341           | 1.4336          | 1.6433          | 1.53            |
| 0.12                                    | 2.363           | 1.326           | 1.632           | 0.89            |
| 0.15                                    | 2.3711          | 1.4276          | 1.6107          | 0.65            |
| 0.18                                    | 2.398           | 1.4265          | 1.606           | 0.43            |

Variation of related physical parameters with mole fraction 2-Methoxyethanol in carbon tetrachloride system
| Mole Fraction of the Solute \(X_2\) (mol/L) | Dielectric Constant of the Solution \(\varepsilon_{12}\) | Refractive Index of the Solution \(n_{12}\) | Density of the Solution \(d_{12}\) (g/cm³) | \(\Omega_0 \times 10^{19}\) D² |
|------------------------------------------|-----------------|-----------------|-----------------|-----------------|
| 0.03                                    | 2.2401          | 1.3773          | 1.6027          | 4.1             |
| 0.06                                    | 2.255           | 1.3793          | 1.5679          | 0.1             |
| 0.09                                    | 2.354           | 1.4306          | 1.5613          | 0.4             |
| 0.12                                    | 2.396           | 1.4336          | 1.5547          | 0.2             |
| 0.15                                    | 2.443           | 1.4356          | 1.515           | 0.15            |
| 0.18                                    | 2.485           | 1.4366          | 1.4633          | 0.11            |

Variation of related physical parameters with mole fraction 2-Methoxyethanol in carbon tetrachloride system
| Mole Fraction of the Solute \(X_2\) (mol/L) | Dielectric Constant of the Solution \(\varepsilon_{12}\) | Refractive Index of the Solution \(n_{12}\) | Density of the Solution \(d_{12}\) (g/cm³) | \(\Omega_0 \times 10^{19}\) D² |
|------------------------------------------|-----------------|-----------------|-----------------|-----------------|
| 0.03                                    | 2.2169          | 1.4753          | 1.5863          | 1.02            |
| 0.06                                    | 2.225           | 1.4711          | 1.5638          | 0.367           |
| 0.09                                    | 2.233           | 1.4433          | 1.5343          | 0.4             |
| 0.12                                    | 2.256           | 1.4390          | 1.5257          | 0.268           |
| 0.15                                    | 2.262           | 1.4213          | 1.5109          | 0.22            |
| 0.18                                    | 2.270           | 1.3555          | 1.4409          | 0.028           |
### Table 2

| Solute          | Limiting Polarization Method $P_2\alpha$ | Molar Refraction $R_D$ | Limiting Polarization Method $P_2\mu$ |
|-----------------|------------------------------------------|------------------------|---------------------------------------|
| Aniline         | 17.003                                   | 11.9307                | 5.0693                                |
| o-Chloroaniline | 20.2                                     | 13.702                 | 6.498                                 |
| p-Chloroaniline | 20.89                                    | 11.2096                | 9.6804                                |
| Ethanol         | 11.8                                     | 5.4794                 | 6.3206                                |
| 2-Butoxyethanol | 25.362                                   | 13.31                  | 12.052                                |
| 2-Methoxyethanol| 17.0                                     | 8.5719                 | 8.4281                                |

### Table 3

| Solute          | Dipole moment in Carbon tetrachloride | Reference Value $\mu_b$ | Reference |
|-----------------|--------------------------------------|--------------------------|-----------|
|                 | Debye’s Method | Huysken’s Method |                 |            |
| Aniline         | 1.59                              | 1.5                      | 1.5        | 103        |
| o-Chloroaniline | 1.79                              | 1.81                     | 1.69       | 54         |
| p-Chloroaniline | 3.11                              | 2.911                    | 2.99       | 54         |
| Ethanol         | 1.77                              | 1.687                    | 1.69       | 103        |
| 2-Butoxyethanol | 2.44                              | 2.14                     | 2.14       | 103        |
| 2-Methoxyethanol| 2.048                             | 2.04                     | 2.04       | 103        |

### 4. Conclusion
The increase of density describes a hydrogen bond formation and specific interaction in amino group. The hydrogen bonding formation and molecular interaction in halogen substituted acceptor complexes are greater than mono substituted acceptor complexes. The dipole moments for all systems are in the order of 1.5D >1.69D >1.69D > 2.04D > 2.14D > 2.99D, Which again supports the above conclusion. On the basis of Eq. (1) it is possible to calculate the above dipole moment values. It is inferred from Table3 that the dipole moment for the halogen substituted acceptor complexes are greater than for the mono substituted acceptor complexes. But the case is reversed in halogen substitution of donor complexes.

Reference:

[1] J.D.Hoffman, C.P.Smyth, J. Am. Chem. Sc. 72 (1950) 171.
[2] R.H. Fowler, Proc. R. Soc. Lond. 1 (1935) 149.
[3] V. Satheesh, M. Jeyaraj, J. Sobhanadri, J. Mol. Liq. 64 (1995) 247.
[4] M. Malathi, R. Sabesan and S. Krishnan, J. Mol. Liq., 109, 11 (2004).
[5] P. Krishnamurthy, PhD Thesis, Department of Physics, Annamalai University, India, 2003.
[6] A. Unamaheswari, S. Balamuralikrishnan, J. Annamalai Univ., Sci. (2004) 85.
[7] K.K. Gupta, A. K. Bansal, P. J. Singh, K. S. Sharma, Indian J. Pure Appl. Phys. 41 (2003) 57.
[8] J. W. Smith, Electric Dipole Moment, Butter Worth, Scientific Publications, London, 1955.
[9] P. L. Huyskens and H. M. Vanbrabant-Govaerts, J. Mol. Struct., 84, 141 (1982).
[10] Onsagar L., J. Am. Chem., 58, 1486 (1936).
[11] H. Fröhlich, Trans. Faraday Soc., 44 (1948) 238.
[12] S. Glasstone, Textbook of Physical Chemistry, Second ed., Mc Milan India Ltd., 1990, p. 552.
[13] K.K. Gupta, P. J. Singh, Pramana-J. Phys. 62 (5) (2004) 1129.
[14] S. Balamuralikrishnan, PhD Thesis, Department of Physics, Annamalai University, India, 1992.