

EXPERIMENTAL AND THEORETICAL ESTIMATIONS OF DIPOLE MOMENTS OF MONOCYCLIC AND BICYCLIC AROMATIC COMPOUNDS

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Abstract

Estimation of electric dipole moment, polarizability and molar polarizability of monocyclic (aniline and acetophenone) and bicyclic (1-naphthol and 4-hydroxycoumarin) aromatic compounds were carried out. A standard solution of the solutes were prepared in double distilled solvents ranging from polar to non-polar solvents (acetic acid, ethanol, propan-2-ol, chloroform and n-hexane). The refractive indices and the dielectric constants of the samples were determined in these solvents. The refractive index was measured from digital table 9 volts alkaline battery refractometer which measures at temperature range of 10 - 50^oC. The dielectric constant was derived from the refractive index using the Maxwell and Debye equations. These two parameters (dielectric constant and refractive index) were used to estimate the aforementioned microscopic parameters (dipole moment, polarizability and molar polarizability). The results shows different variations of the dipole moments of the solutes as the solvent polarity increases from n- hexane to ethanol. However, constant decrease of the dipole moment of all the molecules was observed in acetic acid. This trend was also observed in the computational studies of the dipole moment of the aforementioned monocyclic and bicyclic aromatic compounds using Hartreefock (HF) simulation with the basis set being 6-31G*.

Keywords: Microscopic properties; Maxwell equation; cyclic compounds; Hartreefock simulation; basis set

INTRODUCTION

The macroscopic (bulk properties, such as relative permittivity, refractive index, density, thermodynamic characteristics) and microscopic (intermolecular forces including electron pair donating and accepting abilities) are important in determining the polarity of solvents and they also play a major role defining the solubility of solutes in various solvents (Katritzky *et al.*, 2004). The effect of solvents on the physical properties of solutes, especially in organic compounds, has been well documented in literature (Burke, 1984). The crucial role of these solvents in various processes and interactions taking place in solutions is significant in the understanding of the physicochemical properties of the solute. Polarity is an important solvent property for explaining solvent effects (cage effect) on many chemical processes (Barton, 1975).

A molecule as a whole, while still neutral, will have the properties of a small magnet, with equal but opposite poles, called dipoles. A molecule, because of its structure, can have several dipoles at once. These dipoles may be strong, weak and may cancel out. The resulting sum of all the dipoles is what is known as the dipole moment of the molecule (Burke, 1984). The polarity or non-polarity of a molecule is characterized by whether the molecule has a permanent dipole moment or not (Burrell, 1968). The strength of the molecular dipoles is the major determinant of the cohesive energy density and the solubility of solutes. However, the knowledge of dipole moment alone is not sufficient in solubility determination, as the overall polarity of a molecule is often the combined result of the contributing polar nature of molecule's environment (macroscopic).

In solutions, molecules of solutes arrange themselves in an organized manner. Non-covalent interactions, as well as hydrogen bonding contribute generally to the solubility and self-assembly of solutes in solvents. The self-assembling property of these solutes may be

dependent on the molecular rigidity and the competition between inter and intra molecular interactions taking place in the solution (Rehm and Schmuck, 2008). Non-polar solutes in polar solvents have the tendency to be polarized (induced polarity). In fact, any molecule even if nonpolar, will be temporarily polarized in the vicinity of a polar solvent, and the induced and permanent dipoles will be mutually attracted (Stark effect). These dipole-induced dipole forces are called Debye interactions (Feller, 1972).

The separation between opposite charges in classical systems, such as solute-solvent system is termed dipole moment. The separation of these charges in molecules usually arises due to electronegativity differences of the molecular constituents. Normally separated or induced dipole moments' measurements in molecules are vital in determining both the physical and chemical properties of molecular matter (Li et al., 2011). The dipole moment determination or measurement of heteronuclear dimers has been used to modify and steer chemical reactions (Ospelkaus et al., 2010). and exposes researchers to new trends in ultracold chemistry, quantum information science and quantum physics (Carr, DeMille, Krems, & Ye, 2009). Molecular polarizability describes the effect of an external field on the electron density of molecules (Miller, 1975). In electron transfer reactions, the rate of the reactions is mainly dependent on solvent polarizability because there is a significant effect of the solvent polarizability on the reaction activation barrier which is largely influenced by solvent reorganization energy (Gupta & Matyushov, 2004).

In this article, we estimate the effect of solvents of varying polarities on the experimentally and computationally determined dipole moments of monocyclic (Aniline and Acetophenone) and bicyclic (1-Naphthol and 4-hydroxycoumarin) aromatic compounds.

EXPERIMENTAL

MATERIALS AND METHODS

MATERIALS

Solvents such as n-Hexane, chloroform, acetic acid, propan-2-ol, ethanol, Solutes (Aniline, 1-Naphthol, Acetophenone and 4-hydroxycoumarin), Abbe refractometer, digital weighing balance and distilled water for refractometer calibration

APPARATUS

Retort stand, non- digital micro pipette (plastic), volumetric flask and beakers, distillation kit

EXPERIMENTAL METHOD

All the solutes (aniline, acetophenone and 1-naphthol) were sourced locally, except 4-hydroxycoumarin which was purchased from Sigma Aldrich company in Germany. The solvents used (n-hexane, chloroform, propan-2-ol, ethanol and acetic acid) were products of British Drug Houses limited, (BDH) and were double distilled prior to their usage. 0.001M solutions of the solutes were prepared in each of the solvents and the refractive indices of the resulting solutions were determined with the use of calibrated Abbe refractometer. Using Maxwell equation (eqn. 1) and Debye equation (eqn. 2), the dielectric constants and the dipole moment of each of the solutes in different solvents with varying polarities were determined.

$$n = \epsilon^{1/2} \quad (1)$$

Therefore:

$$\epsilon = n^2 \quad (2)$$

Where n is the refractive index and ϵ is the dielectric constant

Inserting the value of the dielectric constant into the Debye equation:

$$\frac{\epsilon-1}{\epsilon+2} = \frac{\rho P_m}{M} \quad (3)$$

Equation 3 can be rearranged to give:

$$P_m = \frac{M(\epsilon-1)}{\rho(\epsilon+2)} \quad (4)$$

where ρ is the mass density of the sample in the volume of the solvent. The density of the samples was obtained from the formula: $\rho = \frac{\text{mass (g)}}{\text{volume (dm}^3\text{)}}$. For solid samples, i.e. 1-naphthol and 4-hydroxycoumarin, the masses of the solutes dissolved in 250 ml of each solvent was used. For liquid samples, i.e. aniline and acetophenone, the mass equivalences were obtained from the amount and molar masses of the liquid samples dissolved in each solvent, i.e.

$$\text{Amount (mol)} = \frac{\text{mass (g)}}{\text{molar mass (g mol}^{-1}\text{)}} \quad (5)$$

The amount, which is obtained by using 0.001M concentration prepared and 250 ml of the solvents used, is calculated to be 0.00025 mol. Therefore, ρ for aniline, acetophenone, 1-naphthol and 4-hydroxycoumarin were calculated as: 0.093, 0.120, 0.144 and 0.162 g/dm³ respectively.

M is the molar mass of the molecules, and P_m is the molar polarization, which may also be defined as:

$$P_m = \frac{N_A}{3\epsilon_0} \left(\alpha + \frac{\mu^2}{3KT} \right) \quad (6)$$

ϵ_0 is the permittivity of vacuum = 8.85×10^{-12}

N_A = Avogadro's constant = 6.02×10^{23}

μ = dipole moment, K = Boltzmann constant = 1.38×10^{-23} J/K, T = Temperature = 298 K

$$\alpha = \text{polarizability given by: } \frac{3M\epsilon_0(\epsilon-1)}{\rho N_A(\epsilon+2)} \quad (7)$$

Rearranging equation (5) gives the dipole moment to be:

$$\mu = \sqrt{3KT \left(\frac{P_m 3\epsilon_0}{N_A} - \alpha \right)} \quad (8)$$

The dipole moments of the aniline, acetophenone, 1-naphthol and 4-hydroxycoumarin were then estimated by substituting the values of molar polarization and polarizability into equation (8).

COMPUTATIONAL METHOD

The computational evaluation of the dipole moments of the four compounds (aniline, acetophenone, 1-naphthol and 4-hydroxycoumarin) in solvents of varying polarities was carried out using Spartan 14 software by wave function Inc., USA. Hartree fock method of computation was adopted in the calculations using 6-31G* basis set. The results of computation were compared with those of experiment.

RESULTS AND DISCUSSIONS

Experimental Method

The values of refractive indices, dielectric constants and dipole moments of the four compounds (aniline, acetophenone, 1-naphthol and 4-hydroxycoumarin) are as shown in the tables below:

Aniline

Table 1: Experimental and Theoretical Estimation of Dipole moment of Aniline

Solvents	Refractive index	Dielectric constant	Dipole moment	
			Experimental	Computational
n-hexane	1.44	2.07	3.23	1.67
Chloroform	1.43	2.06	3.18	1.76
Propan-2-ol	1.42	2.02	3.08	1.79
Ethanol	1.41	2.00	3.06	1.79
Acetic acid	1.40	1.96	2.96	1.73

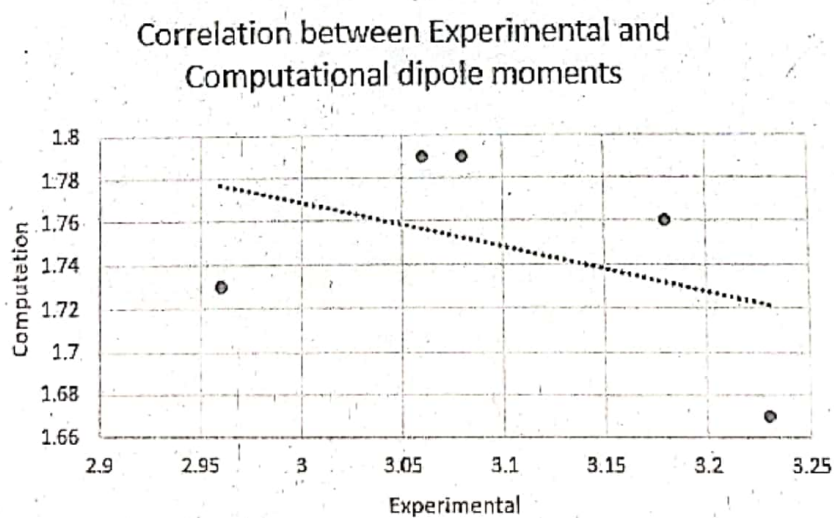


Figure 1: Correlation between Experimental and Computational values of Aniline

r^2 value of Aniline = 0.1863

Acetophenone

Table 2: Experimental and Theoretical Estimation of Dipole moment of Acetophenone

Solvents	Refractive index	Dielectric constant	Dipole moment	
			Experimental	Computational
n-hexane	1.45	2.10	3.30	3.53
Chloroform	1.47	2.16	3.42	3.85
Propan-2-ol	1.48	2.20	3.50	4.19
Ethanol	1.49	2.23	3.55	4.25
Acetic acid	1.50	2.26	3.62	3.25

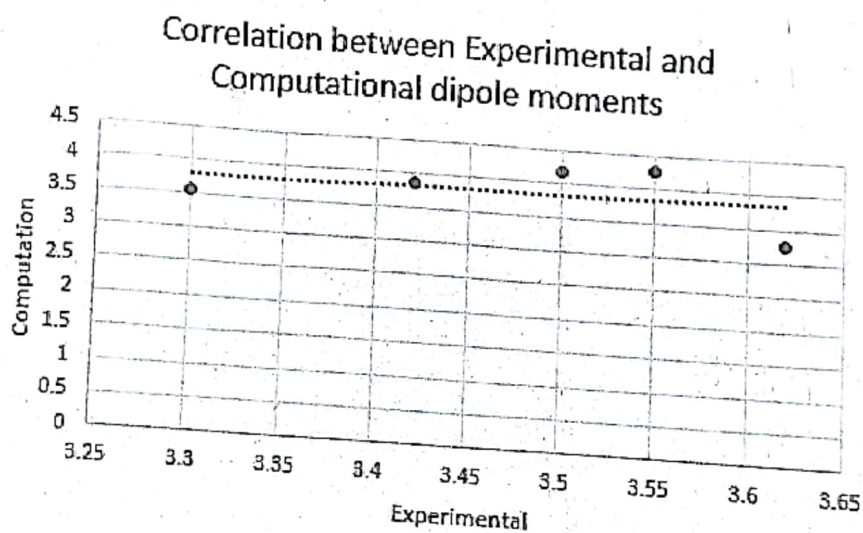


Figure 2: Correlation between Experimental and Computational values of Acetophenone

r^2 value = 0.0015

1-naphthol

Table 3: Experimental and Theoretical Estimation of Dipole moment of 1-Naphthol

Solvents	Refractive index	Dielectric constant	Dipole moment	
			Experimental	Computational

		Dielectric constant	Experimental	Computational
n-hexane	1.41	1.99	3.04	1.77
Chloroform	1.45	2.09	3.26	1.87
Propan-2-ol	1.43	2.05	3.17	1.94
Ethanol	1.46	2.12	3.33	1.95
Acetic acid	1.44	2.07	3.22	1.89

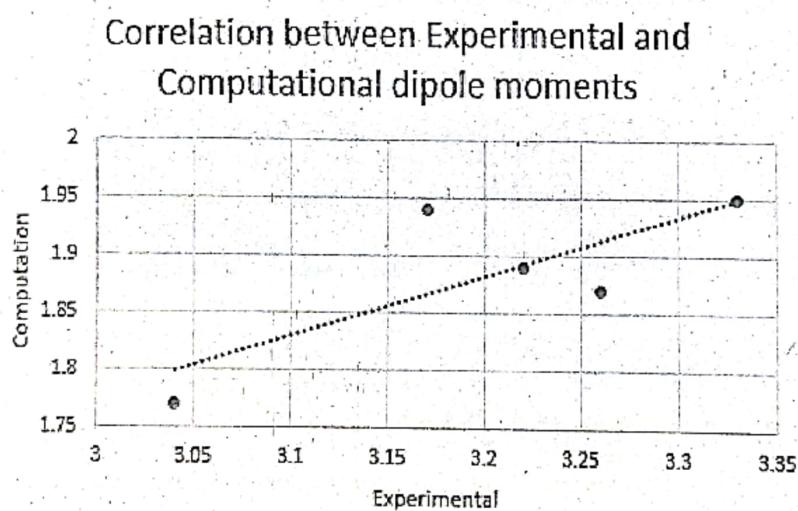


Figure 3: Correlation between Experimental and Computational values of 1-Naphthol

r^2 value = 0.6082

4-hydroxycoumarin

Table 4: Experimental and Theoretical Estimation of Dipole moment of 4-hydroxycoumarin

Solvents	Refractive index	Dipole moment
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		Aromatic and Bicyclic Aromatic Compounds		
		Dielectric constant	Experimental	Computational
n-hexane	1.45	2.10	3.28	5.54
Chloroform	1.44	2.07	3.22	6.19
Propan-2-ol	1.40	1.97	2.99	6.93
Ethanol	1.41	1.99	3.05	7.07
Acetic acid	1.38	1.91	2.85	6.80

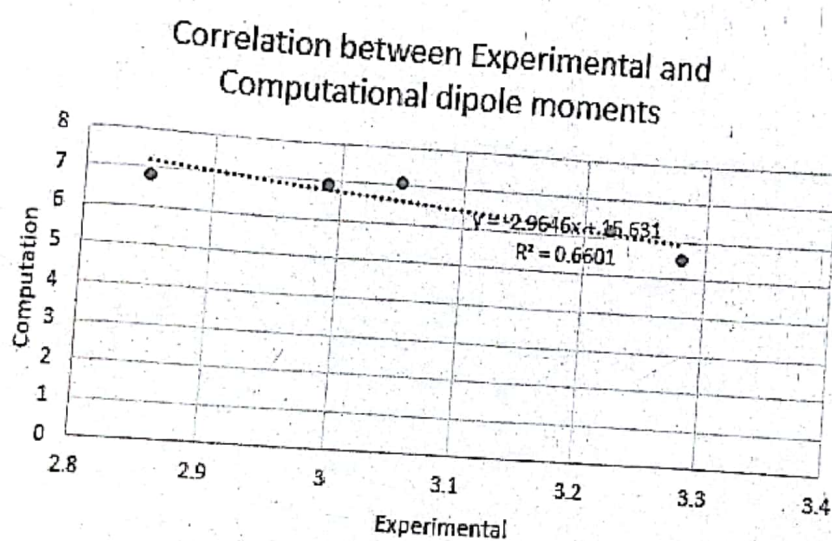


Figure 4: Correlation between Experimental and Computational values of 4-hydroxycoumarin

R^2 value = 0.6601

DISCUSSION

Examination of the results of the dipole moments of the solutes in solvents of varying polarities reveals an anomalous variation of the dipole moment values. In aniline and 4-hydroxycoumarin, the experimental values of the dipole moments decreases as the polarity of

the solvent increases from n-hexane to chloroform, while the values (dipole moment) increases as the polarity of solvents increases in solutions of acetophenone and 1-naphthol.

Furthermore, the comparison of the dipole moments of both experiment and computation showed a direct proportionality for both acetophenone and 1-naphthol and an inverse proportionality for aniline and 4-hydroxycoumarin. Additionally, both experimental and computational analysis revealed an increase in the value of dipole moments until acetic acid (the most polar solvent used), where the value of dipole moment decreased sharply. The dipole moment in the most polar solvent, which is the acetic acid, does not follow the pattern observed for other solvents.

The correlation values between experimental and computational (r^2 value), which is higher in the bicyclic compounds (1-Naphthol and 4-hydroxycoumarin) than in the monocyclic compounds showed that the computational method (HF/6-31G) used in this research is better applicable to bicyclic aromatic compounds than for monocyclic aromatic compounds. This observation showed a better convergence of basis set (6-31G) in bicyclic aromatic compounds than in monocyclic compounds. The basis set convergence or non-convergence may be due to inter electronic coulomb singularity which is more pronounced in bicyclic aromatic compounds than in monocyclic compounds. However, the Hartree Fock method is excellent in comparing the experimental dipole moment with the computationally estimated dipole moment (Halkier, Klopper, Helgaker, & Jørgensen, 1999).

CONCLUSION

The dipole moments of aniline, acetophenone, 1-naphthol and 4-hydroxycoumarin has been analysed both experimentally and computationally in solvents of different polarities. The dipole moment value increases as the polarity of solvents increases for both aniline and 4-hydroxycoumarin, while it varies inversely with polarity for acetophenone and 1-naphthol. The results of these variations provide an insight to the structural correlation of both aniline and 4-hydroxycoumarin as well as both acetophenone and 1-naphthol. An unusual decrease was observed in the dipole moment of the compounds in acetic acid. With this unusual behaviour, it can be inferred that the dipole moment tends to converge (goes to a minimum) as the polarity of the solvent is further increased. This observation is related to the submission of Parkanyi and Aaron (Párkányi & Aaron, 1998).

The computational results of dipole moments in these solvents (n-hexane to ethanol) showed direct and inverse proportionality as compared to the experiment. It also revealed the decrease of the dipole moments in acetic acid for all solutes. This showed an optimum polarity at which the dipole moment of molecules is said to vary directly or inversely with the polarity of solvents. The computational observation is the same as the experimental observation in terms of the maximum at which polarity varies with the dipole moment. A further investigation on dipole moments of aromatic compounds using computational method with time dependent / density functional theory (TD/DFT) needs to be carried out as this provides a more accurate and parameterized basis set for heterocyclic compounds such as 4-hydroxycoumarin (Laurent & Jacquemin, 2013).

REFERENCES

- Barton, A. F. M. (1975). Solubility parameters. *Chemical Reviews*, 6(75), 731–753.
- Burke, J. (1984). Solubility parameters: Theory and application. *The Book and Paper Group Annual*, 102(4), 42–50.
- Burrell, H. (1968). The challenge of the solubility parameter concept. *Journal of Paint Technology*, 520(40), 197–208.
- Carr, L. D., DeMille, D., Krems, R. V., & Ye, J. (2009). Cold and ultracold molecules: Science, technology and applications. *New Journal of Physics*, 11(5), 49–55.
- Feller, R. L. (1972). The Relative Solvent Power Needed to Remove Various Aged Solvent Type Coatings. In *Preprints of the Lisbon Congress IIC*.
- Gupta, S., & Matyushov, D. V. (2004). Effects of Solvent and Solute Polarizability on the Reorganization Energy of Electron Transfer. *The Journal of Physical Chemistry A*, 2(108), 2087–2096.
- Halkier, A., Klopper, W., Helgaker, T., & Jørgensen, P. (1999). Basis-set convergence of the molecular electric dipole moment. *Journal of Chemical Physics*, 10(111), 4424–4430.
- Katritzky, A. R., Fara, D. C., Yang, H. F., Tamm, K., Tamm, T., Karelson, M. Tamm, K. (2004). Quantitative Measures of Solvent Polarity. *Chemical Reviews*, 1(104), 175–798.
- Laurent, A. D., & Jacquemin, D. (2013). TD-DFT benchmarks: A review. *International Journal of Quantum Chemistry*, 17(113), 2019–2039.
- Li, W., Pohl, T., Rost, J. M., Rittenhouse, S. T., Sadeghpour, H. R., Nipper, J., ... Pfau, T. (2011). A homonuclear molecule with a permanent electric dipole moment. *Science*, 6059(334), 1110–1114.
- Miller, T. M. (1978). Atomic and Molecular Polarizabilities. *Physical Chemistry, Series Two*, 1(13), 1–55.
- Ospelkaus, S., Ni, K. K., Wang, D., De Miranda, M. H. G., Neyenhuis, B., Quémener, G., ... Ye, J. (2010). Quantum-state controlled chemical reactions of ultracold potassium-rubidium molecules. *Science*, 5967(327), 853–857. <https://doi.org/10.1126/science.1184121>
- Párkányi, C., & Aaron, J. J. (1998). Dipole moments of aromatic heterocycles. *Theoretical and Computational Chemistry*, 5, 233–258.
- Rehm, T., & Schmuck, C. (2008). How to achieve self-assembly in polar solvents based on specific interactions. Some general guidelines. *Chemical Communications*.801-813