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On The Dipole Moment of Polar Molecules

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Abstract: In this experiment, the dipole moments of 1,2- and 1,3-dichlorobenzene were explored. This was done indirectly, by measuring the frequency to obtain the dielectric constant, and the index of refraction. The dipole moment of both molecules was determined using these values, through Hegestrand's and Guggenheim's methods. The values obtained from Hegestrand's method were 2.77 D for 1, 2-dichlorobenzene and 1.89 D for 1, 3-dichlorobenzene. From Guggenheim's method, the values of 0.21 D and 0.14 D were obtained for 1, 2- and 1, 3-dichlorobenzne, respectively. The dipole moment was found to decrease as the substituent's been farther apart supporting the predictions. In addition, the data indicated that the experiment was performed with moderate success depicting its general trend.

Keywords: dipole moments, dichlorobenzene, polar molecules, Guggenheim's method, Hegestrand's method

INTRODUCTION

The electric dipole moment is a measure of the separation of negative and positive charges in a system; it is representative of the system's overall polarity.[1] An electric dipole is made up of two point charges, -Q and +Q separated by a distance r. The dipole moment, m, is given by **Equation 1:**

$$m = Qr \quad (1)$$

A dipole moment occurs in molecules where the center of gravity of the negative charge and the center of gravity of the positive charge do not coincide[2]. If placed in an electric field, all molecules have an induced dipole moment, aligned parallel to the field, due to polarization caused by distortion. Polar molecules, however, have a permanent dipole moment, which exists without an electric field. This is caused by partial opposite charges reside in the molecule, such as boron trifluoride, as shown in **Figure 1.**

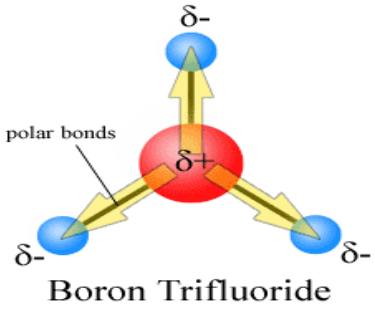

Fig. 1: Boron trifluoride[1]

The boron atom has a partial positive charge, and the fluorine atoms have a partial negative charge, giving it a charge asymmetry[1]. The charge asymmetry results in polar bonds in the molecule. The vector sum of the electric dipole moment of a medium per unit volume is called polarization, P. When a medium is uniform in all directions (isotropic), the polarization is parallel to the electric field (E) and is proportional to E in terms of its magnitude. For a pure substance, the polarization is given by **Equation 2:**

$$P = \bar{m}\frac{N_0}{\bar{V}} = \bar{m}\frac{N_0\rho}{M}, \quad (2)$$

where, $\bar{m}$ is the average dipole moment of each molecule, N_0 is Avogadro's number, $\bar{V}$ is the molar volume, ρ is the density, and M is the molar mass[2].

The dipole moment has not been measured directly in this experiment. Instead, a specific property of the material, known as the dielectric constant has been measured, in order to calculate the dipole moment. If a voltage difference is applied between a simple capacitor made up of two plates, charge builds up on the plates as the capacitor stores the charge[3]. Also, the area between the plates is filled with liquids that have different dielectric properties; the capacitors do not store the charge in the same manner. There is a difference in the charge storing ability, known as capacitance. Capacitance is directly related to the dielectric constant of the liquid placed between the capacitor plates. This relationship can be visualized in **Equation 3.**

$$k = \frac{C}{C_a}, \quad (3)$$

Where, k is the dielectric constant, C is the capacitance of the conductivity cell when it is immersed in a medium, and C_0 is the capacitance of the cell when that medium is a vacuum[2]. Additionally, an Abbe refractometer is used for the measurements. The investigation of dipole moments of substances by measuring the dielectric constant at a singular temperature necessitates the knowledge of the refractive indices. Refractometers are instruments which scientists used to determine the index of refraction of a liquid[2]. In an electric field, the index of refraction squared is equal to the dielectric constant of the material.

EXPERIMENTAL

Initially, the 25 mL picnometer was massed. The temperature bath was turned on to 25°C, and the water jacketed bath held the picnometer at a constant temperature. The power supply and the frequency counter to the capacitance cell were then connected. The system was allowed to stabilize and the frequency of air was measured, recorded, and the dielectric constant measurements were obtained thereafter. The sample container was filled with benzene, and the capacitor was fully submerged in the liquid. The experimental apparatus was set up as shown in **Figure 2**

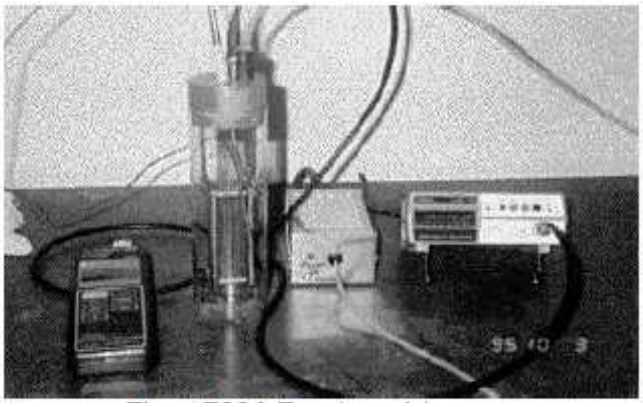

Fig. 2: The experimental apparatus was set up as shown in Figure
(Experimental apparatus)

The thermocouple tip was placed in the container, and the container was then placed into the water bath letting it to stabilize. The temperature and the frequency values were recorded afterward. Three additional replicate measurements were taken. A portion of the solution was added to the picnometer and placed into the water jacketed bath. The cap which contained a capillary was then placed onto the picnometer and was subsequently massed. As the solution was stabilizing, the refractive index of the solution was measured by placing a few drops on an Abbe refractometer, as shown in **Figure 3.**

Fig. 3: Abbe refractometer[1]

The next solution was prepared by adding 2 mL of 1, 2-dichlorobenzene into a 250 mL volumetric flask, and this was then diluted to the fiduciary mark with benzene. Three more solutions with a higher concentration of 1, 2-dichlorobenzene was made in the same manner and the procedure was repeated for the 1, 3-dichlorobenzene thereafter.

RESULTS AND DISCUSSION

The mole fractions of various solutions of 1, 2- and 1, 3-dichlorobezene used in the experiment are listed in **Table 1**. As expected the mole fraction values fall in between the range of 1-5%.

Calculating the mole fraction of dichlorinated benzene in all the solutions:
Sample calculation for 1, 2-dichlorobezene solution1

Moles of 1, 2-dichlorobenzene

$$Moles = \frac{(V_{1,2-d}) * (\rho_{1,2-d})}{MW_{1,2-d}} = \frac{(2ml) * (1.306\frac{g}{ml})}{147.01g} = 0.0178mol$$

Moles of Benzene

$$Moles = \frac{(V_{1,2-d}) * (\rho_{1,2-d})}{MW_{1,2-d}} = \frac{(248ml) * (0.874\frac{g}{ml})}{78.11g} = 2.77mol$$

Mole fraction

$$X = \frac{mol\ of\ 1,2dichlorobezene}{mol\ of\ bezene + mol\ of\ 1,2dchloronezene} = \frac{0.0178}{0.0178 + 2.77} = 0.64\%$$

Table-1: Solution mole fractions

Solution	Mole fraction (%)
1,2-Dichlorobenzene (2ml solution)	0.64
1,2-Dichlorobenzene (4ml solution)	1.26
1,2-Dichlorobenzene (6ml solution)	1.88
1,2-Dichlorobenzene (8ml solution)	2.50
1,3-Dichlorobenzene (2ml solution)	0.64
1,3-Dichlorobenzene (4ml solution)	1.26
1,3-Dichlorobenzene (6ml solution)	1.88
1,3-Dichlorobenzene (8ml solution)	2.50

The dielectric constant was determined for each of the solutions using **Equation 4** and the values are calculated as listed in **Table 2.**

$$\kappa = \frac{v_0}{v} \qquad (4)$$

Performing a Q-test for the replicate measurements and calculating the dielectric constant
Q-test for benzene:

$$Q = \frac{gap}{range} = \frac{393{,}500\ Hz - 393{,}553 Hz}{393{,}500\ Hz - 393{,}595\ Hz} = 0.56$$

$$Q_{95\%} = 0.97 > 0.56 = Q$$

Therefore, at 95% confidence, 392,768 Hz is not an outlier.

There was no outlier found in the data collected.

Calculating Dielectric constant for 1, 2-dichlorobenzene (2ml -solution 1):

$$\kappa = \frac{v_0}{v} = \frac{865{,}234\ Hz}{393550\ Hz} = 2.20$$

Table-2: Dielectric constant for all the solutions

Solution	Dielectric constant
1,2-Dichlorobenzene (2ml solution)	2.25
1,2-Dichlorobenzene (4ml solution)	2.30
1,2-Dichlorobenzene (6ml solution)	2.33
1,2-Dichlorobenzene (8ml solution)	2.38
1,3-Dichlorobenzene (2ml solution)	2.22
1,3-Dichlorobenzene (4ml solution)	2.24
1,3-Dichlorobenzene (6ml solution)	2.26
1,3-Dichlorobenzene (8ml solution)	2.27

The calculated dielectric constants and mole fractions of each solution were depicted in Figures 4 and 5. The plots of dielectric constant vs. solute mole fraction have a strong positive linear relationship. As the mole fraction of a solution increase the dielectric constant increases too. The best-fit lines were provided in **Figures 4** and **5.**

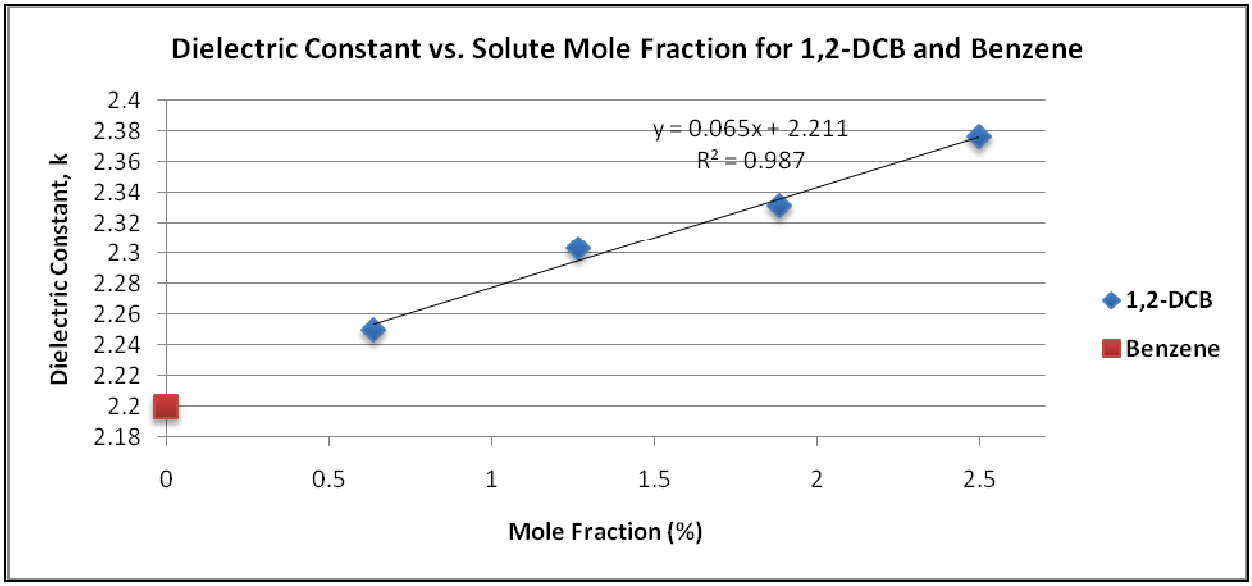

Fig. 4: Plot of dielectric constant vs. mole fraction for 1, 2-dichlorobenzene

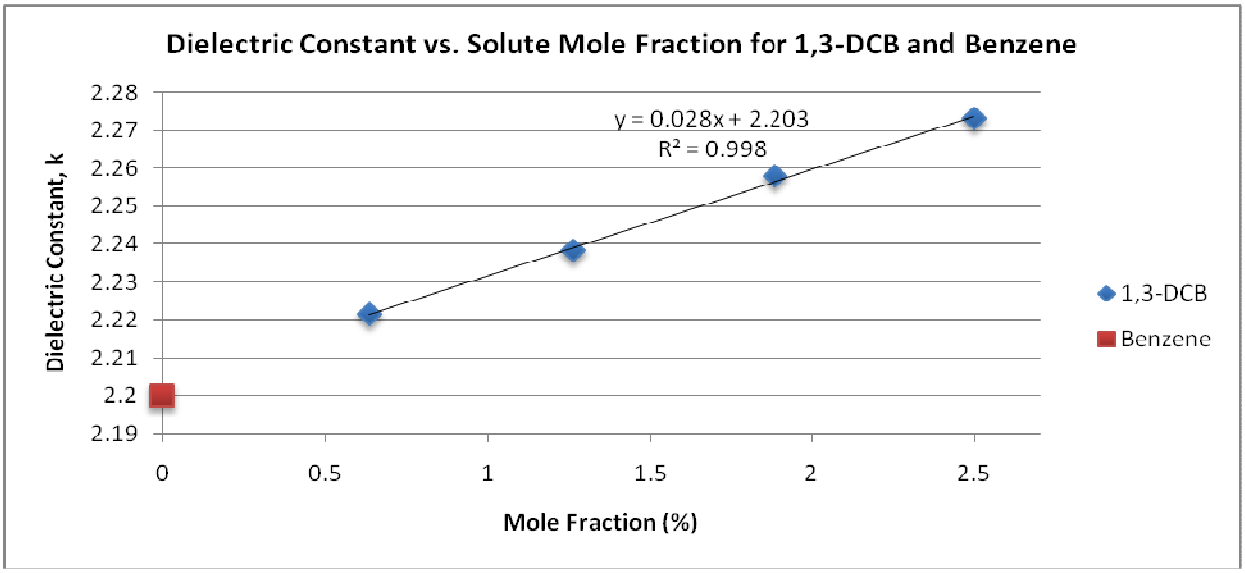

Fig. 5: Plot of dielectric constant vs. mole fraction for 1, 3-dichlorobezene

The weight differences between the empty and filled picnometer and the density of each of the solutions was determined and listed in **Table 3**. These densities were plotted against mole fractions in **Figures 4** and **5**. From observing these plots it can be understood that as the mole fraction increases the density of the solution also increases. The best-fit line was also determined from these graphs.

Calculating the density and plotting it against mole fraction:

Sample calculation for benzene

$$Density = \frac{37.928\ g - 16.0563\ g}{25\ mL} = 0.875\ \frac{g}{mL}$$

Table-3: Density measurements

Solution	Density (g/ml)
1,2-Dichlorobenzene (2ml solution)	0.883
1,2-Dichlorobenzene (4ml solution)	0.884
1,2-Dichlorobenzene (6ml solution)	0.885
1,2-Dichlorobenzene (8ml solution)	0.886
1,3-Dichlorobenzene (2ml solution)	0.880
1,3-Dichlorobenzene (4ml solution)	0.882
1,3-Dichlorobenzene (6ml solution)	0.883
1,3-Dichlorobenzene (8ml solution)	0.884

Also, the measured refractive index values were squared and then plotted against the mole fraction values to observe any linear relationship between them as in **Figures 6** and **7**. The plots indicated that as the mole fraction increases the refractive index increases.

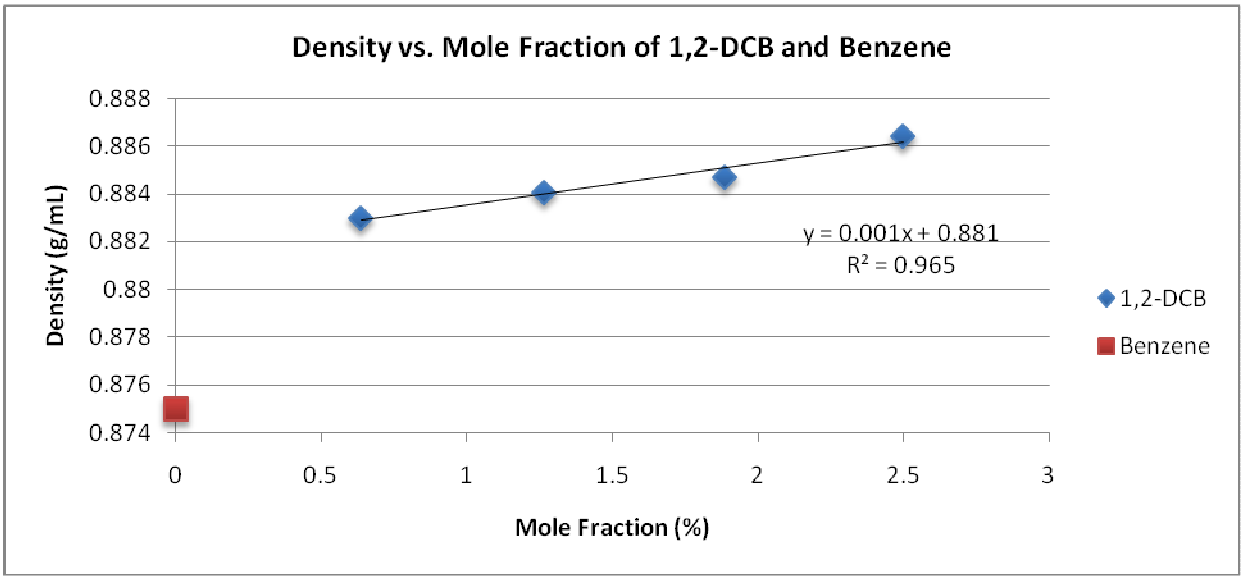

Fig. 6: Density vs. mole fraction plot for 1,2-dichlorobezene

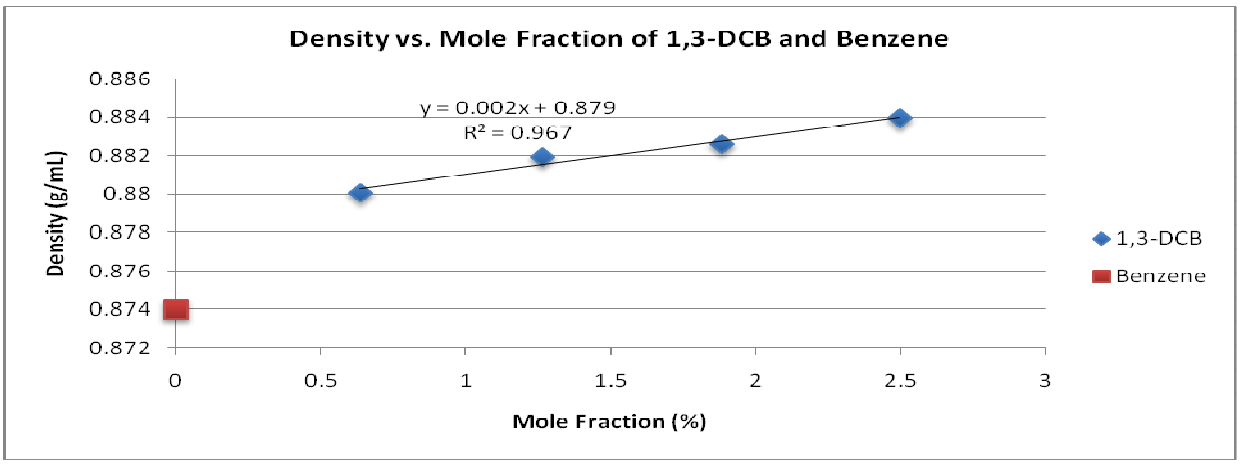

Fig.7: Density vs. mole fraction plot for 1,3-dichlorobezene.

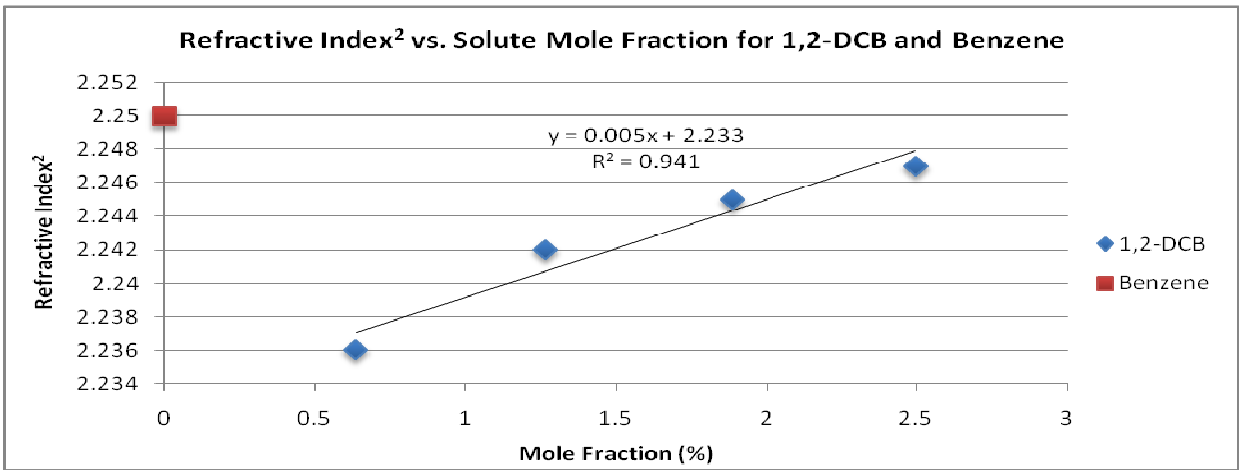

Fig. 8: Refractive index squared vs. mole fraction for 1,2-dichlorobezene

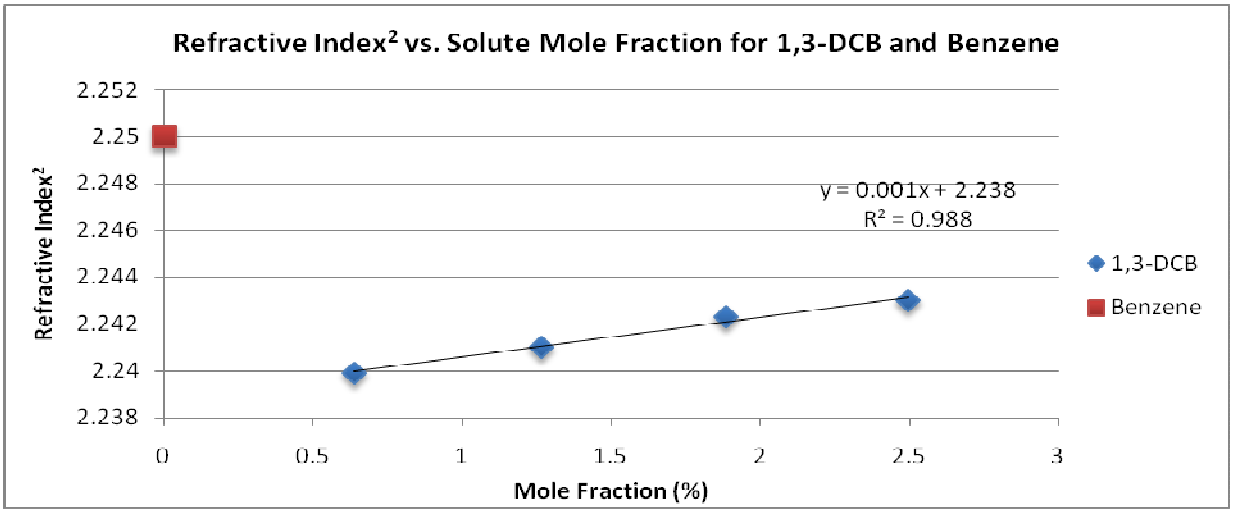

Fig. 9: Refractive index squared vs. mole fraction for 1,3-dichlorobezene

Using Hegestrand's method, the molar polarization, molar distortion polarization, and molar orientation polarization at an infinite dilution were determined in **Table 4**. The calculated dielectric constant and the density plots were used in this method. The molar polarization was calculated using **Equation 5**, molar distortion polarization was calculated using **Equation 6** and molar orientation polarization was calculated using **Equation 7.**

$$P_{2M}^{0} = \frac{3M_1 a}{(\kappa_1 + 2)^2 \rho_1} + \frac{\kappa_1 - 1}{(\kappa_1 + 2)\rho_1}\left(M_2 - \frac{M_{1b}}{\rho_1}\right) \quad (5)$$

$$P_{2d}^{0} = R_{2M} = \frac{n_2^2 - 1}{n_2^2 + 2} * \frac{M_2}{\rho_2} \quad (6)$$

$$P_{2\mu}^{0} = P_{2M}^{0} - P_{2d}^{0} \quad (7)$$

Calculating the molar polarization molar distortion polarization and molar orientation polarization of the solute at infinite dilution using the Hegestrand's method:

Sample calculation for 1,2-dichlorobezene

$$P_{2M}^{0} = \frac{3M_1 a}{(\kappa_1 + 2)^2 \rho_1} + \frac{\kappa_1 - 1}{(\kappa_1 + 2)\rho_1}\left(M_2 - \frac{M_{1b}}{\rho_1}\right)$$

$$= \left(\frac{3 * 78.11\ g * 0.0659}{(2.200 + 2)^2 * 0.884\ g/mL} + \frac{2.200 - 1}{(2.200 + 2) * 0.884\ g/mL}\right)\left(147.01\ g - \frac{78.11\ g * 0.0017}{0.884\ g/mL}\right)$$

= 192.9 mL/mol

$$P_{2d}^{0} = R_{2M} = \frac{n_2^2 - 1}{n_2^2 + 2} * \frac{M_2}{\rho_2} = \frac{1.5510^2 - 1}{1.5510^2 + 2} * \frac{147.01\ g}{1.306\ g/mL} = 35.91\ \text{mL/mol}$$

$P_{2\mu}^{0} = P_{2M}^{0} - P_{2d}^{0}$ = 192.9 mL/mol – 35.91 mL/mol = 156.99 mL/mol

Table-4: Polarization values

	P_{2M}^0 (ml/mol)	P_{2d}^0(ml/mol)	$P_{2\mu}^0$(ml/mol)
1,2-dichlorobezene	192.8998	35.91	156.9898
1,3-dichlorobezene	108.9928	36.14	72.8528

Using Guggenheim's method the molar orientation polarization was calculated. Instead of using the density plots, the refractive index plots were used in tandem with dielectric constant were used in method using **Equation 8.**

$$P_{2\mu}^0 = \frac{3M_2}{\rho_2}\left[\frac{\alpha}{(\kappa_2+2)^2} - \frac{\sigma}{(n_2^2+2)^2}\right] \quad (8)$$

Calculating the molar orientation polarization at infinite dilution using Guggenheim's method: Sample calculation for 1,2-dichlorobenzene

$$P_{2\mu}^0 = \frac{3M_2}{\rho_2}\left[\frac{\alpha}{(\kappa_2+2)^2} - \frac{\sigma}{(n_2^2+2)^2}\right] = \frac{3 * 78.11\ g}{0.884\ g/mL}\left[\frac{0.0659}{(2.200+2)^2} - \frac{0.0058}{(1.494^2+2)^2}\right] = 0.903\ mL/mol$$

Table-5: Molar orientation polarization using Guggenheim's method

	$P_{2\mu}^0$(ml/mol)
1,2-dichlorobezene	0.903
1,3-dichlorobezene	0.396

Using the molar orientation polarization values calculated by Hegestrand's and Guggenheim's methods the dipole moments for each of the two dichlorobenzene molecules were calculated using **Equations 9** and **10** and listed in **Table 6**.

$$\mu = 42.7\left(P_{2\mu}^0 T\right)^{1/2} x\ 10^{-30} C\ m \quad (9)$$

$$\mu = 12.8\left(P_{2\mu}^0 T\right)^{\frac{1}{2}} Debye \quad (10)$$

Calculating the dipole moment: Sample calculations for 1,2-dichlorobenzene

$$\mu = 42.7\left(P_{2\mu}^0 T\right)^{1/2} x\ 10^{-30} C\ m = 42.7(99.21\ mL/mol * 297.9\ K)^{1/2} x\ 10^{-30}$$

$$= 7.341 \times 10^{-27}\ C\ cm = 7.341 \times 10^{-30}\ C\ m$$

$$\mu = 12.8\left(P_{2\mu}^0 T\right)^{\frac{1}{2}} Debye = 12.8(99.21\ mL/mol * 297.9\ K)^{\frac{1}{2}} = 2200.48/1000 = 2.20\ D$$

Table-6: Calculated dipole moments

	Hegestrand's method		Guggenheim's method	
	μ (Cm)	μ (Debye)	μ (Cm)	μ (Debye)
1,2-dichlorobezene	9.23E-27	2.77	7.00E-28	0.21
1,3-dichlorobezene	6.29E-27	1.89	4.64E-28	0.14

The geometry and the position and properties of the attached functional groups in a molecule can be used to predict the dipole moment. The structures of the molecules studied are displayed in **Figures 10** and **11.**

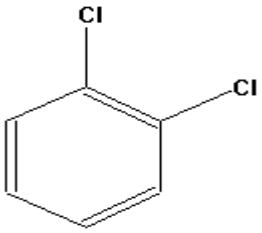

Fig.10: 1, 2-dichlorobenzene[5]

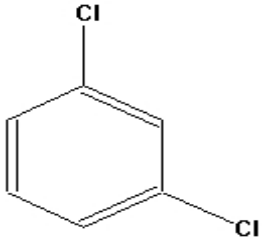

Fig.11: 1, 3-dichlorobenzene[5]

The dipole moment of di-substituted benzene molecules though vector addition of the moments of the singular bonds can be approximated. Let us call μ_1 and μ_2 the single dipole moments for the specific bonds that contain the substituents. The process by which the dipole moment is calculated is shown in **Figure 12.**

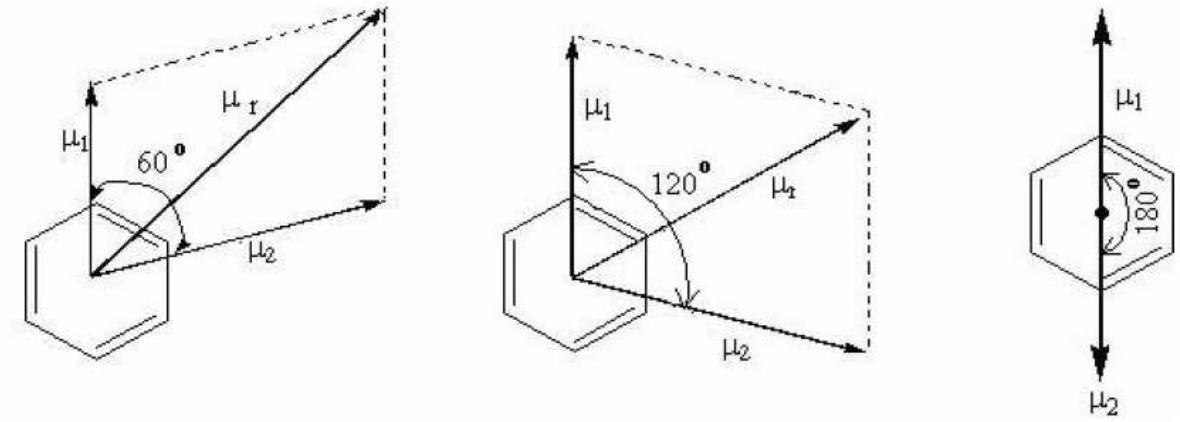

Fig. 12: Dipole moment prediction process[5]

The calculation is done through the law of cosines, as shown below, where the resultant vector, μ_r is the predicted dipole moment of the molecule.

$$\mu_r = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 cos\theta} \qquad (11)$$

The carbon-chlorine bond is known to have a dipole moment[5] of 1.55 D. An application of the law of cosines, for 1, 2-dichlorobenzene, assuming the angle of 60° between the two substituent bonds is made. This yields a predicted dipole moment of 2.68 D. For the 1, 3-dichlorobenzene, application of the same rule is made, but the angle between the substituent bonds is 120°, resulted in a predicted dipole moment of 1.55 D. The values obtained from the Hegestrand's method were 2.77 D for 1, 2-dichlorobenzene and 1.89 D for 1, 3-dichlorobenzene. The differences between the predicted and experimental values were 3.36% and 21.94% for 1, 2- and 1,3-dichlorobenzne, respectively. From the Guggenheim's method, values of 0.21 D and 0.14 D were obtained for 1, 2- and 1, 3-dichlorobenzne, respectively, resulting in 92.16% and 90.97% differences.

The values for the Hegestrand's method were reasonably close to the predicted values, but the Guggenheim's method resulted in values which were very different. This may have resulted from inadequate equilibration time when taking measurements. Additionally, if the capacitor plates were not completely submerged, this may have affected measurements of the dielectric constant. If the thermocouple had been touching the capacitor plates, it would have affected the frequency measurements, and would have affected the time at which the frequency measurements were taken.

The thermocouple may not have actually equilibrated and would actually be measuring the temperature of the capacitor plates. The reading of the refractive index may have been incorrect from the Abbe refractometer if not observed properly. If the readings of the refractive index were inaccurate, the slope obtained from the graph would also reflect inaccuracies, resulting in smaller values for the dipole moment. The primary source of error arose from the calculation itself where the mole fractions were expressed as percentages. This may have led to inaccurate quantities by an order of magnitude.

The molecule 1, 4-dichlorobenzene is similar to the other two molecules studied in the experiment, except that the two chlorine functional groups are present on the 1st and 4th carbons. This can be visualized in **Figure 13.**

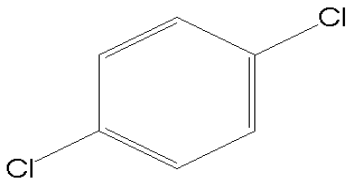

Fig. 13: 1, 4-dichlorobenzene[5]

If the dipole moment using the law of cosines was to be predicated, the angle between the substituent bonds is 180°. This would give us a dipole moment which would equal zero, because $\cos(180^{\circ}) = 0$. As the dipole moments of the two carbon-chlorine bonds go in opposing directions, and the molecule is geometrically symmetrical, the two dipole moments cancel themselves out, resulting in no net dipole moment[6].

There are two types of dipolar polarization, known as distortion polarization and orientation polarization. As was mentioned earlier, molecules can have either a permanent or induced dipole, based on the polarity of the molecules.[2] Polarization which is inherent to these polar molecules is known as orientation polarization, while polarization which can be induced in any type of molecule where the nuclei are asymmetrically distorted is known as distortion polarization. Orientation polarization arises from the existence of a permanent dipole; for example, if there exists a 120° angle

between the substituent bonds of a molecule, the molecule has polarization even without the existence of an external electric field. The experiment distinguished between them through the use of a capacitor[3]. The electric field was placed between the two capacitor plates, and the benzene molecule was distorted. This allowed us to calculate the dielectric constant values. The Abbe refractometer was used to measure the index of refraction for each of the samples. More distinction between the two types of polarization was accounted for in the data analysis. The Hegestrand's method has been used once again to calculate the orientation polarization using the dielectric constant. The Abbe refractometer accounted for the energies in the IR and visible range; that could not have been done this with only the capacitor method[2].

The freezing point of benzene is 278.7 K. If the experiment was carried out by freezing the sample, the temperature would have been greatly from the original experimental conditions. The temperature is inversely related to the orientation polarization. If the temperature is decreased, the orientation polarization increases. According to the equation below, the orientation polarization is directly proportional to the dipole moment.

$$P_{\mu} = \frac{1}{3\varepsilon_0} N_0 \frac{\mu^2}{3kT} \qquad (12)$$

In effect, the decreased temperature increases the dipole moment. It is important to note that the square root of temperature is also directly proportional to dipole moment, but the temperature has a larger effect on the orientation polarization and small changes in temperature affect the orientation polarization greatly. The decreased temperature would decrease the magnitude of the dipole moment vectors, and this would result in an increased overall dipole moment measurement. Experimental data, however, has shown that as the temperature decreases below the freezing point, the dipole moment also decreases. This would occur because the solvent, benzene, would exist in a crystalline structure causing impaired dipole calculations. By studying the data, it can be predicted that lowering the temperature would decrease the dipole moment.[7] Based on this observation, it can be stated that freezing the solvent would decrease the dipole moment measured for both dichlorobenzene molecules used[6].

CONCLUSION

In this experiment, the dipole moment of polar molecules was explored. The dipole moment was calculated indirectly by measuring the frequency to obtain the dielectric constant, and the index of recfraction of the solutions. The dipole moments of 1, 2- and 1, 3-dichlorobenzene was calculated through the use of Hegestrand's and Guggenheim's methods. The values obtained from the Hegestrand's method were 2.77 D for 1, 2-dichlorobenzene and 1.89 D for 1, 3-dichlorobenzene. The differences between the predicted and experimental values were 3.36% and 21.94% for 1, 2-dichlorobenzene and 1, 3-dichlorobenzne, respectively. From the Guggenheim's, the values of 0.21 D and 0.14 D for 1, 2- and 1, 3-dichlorobenzne was obtained, respectively, resulting in 92.16% and 90.97% differences. The values for the Hegestrand's method were reasonably close to the predicted values, but the Guggenheim's method resulted in values which were very different. As the concentration of the chemical was increased in the solution, the frequency increased, and subsequently, the dielectric constant value increased, with values near 2.20 and 2.30. As the concentration of the chemical was increased in solution, the density also slightly increased, staying near 0.88 g/mL for each of the dichlorobenzene molecules. Compared to literature values, these values had approximately a 30% difference. The refractive index for both 1,2-dichlorobenzene and 1,3-dichlorobenzene also increased as the mole fraction increased. The refractive index for 1,2-

dichlorobenzene was found near 1.497, and the refractive index of 1,3-dichlorobenzne was found near 1.496. Compared to literature values, the two molecules had 3.48% and 3.23% differences, for 1, 2- and 1, 3-dichlorobenzene, respectively. These trends were consistent with expectations.

Based on the experimental data, the Hegestrand's method was found to be the more accurate calculation of the dipole moment. The values from the Guggenheim's method had values which were, on average, 92% smaller. This can be attributed to inaccurate frequency and refractive index measurements, as both are used in the calculation. However, it is important to note that the density values obtained were significantly different from literature values, suggesting error from the mass measurements has occurred. Additionally, issues arose with the use of the mole faction units in the computation leading to inaccurate results. The Dipole moments have significance, especially in the field of spectroscopy. Infrared spectroscopy often uses the change in dipole moment to characterize molecules[8]. In this way, chemists are able to find what an unknown type of chemical is. Additionally, chemical engineers may need to consider the dipole moment of various chemicals to make sure chemicals dissolve in the pipelines they build.

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