2.10 DETERMINATION OF DIPOLE MOMENT FROM RELATIVE PERMITTIVITY AND REFRACTIVE INDEX
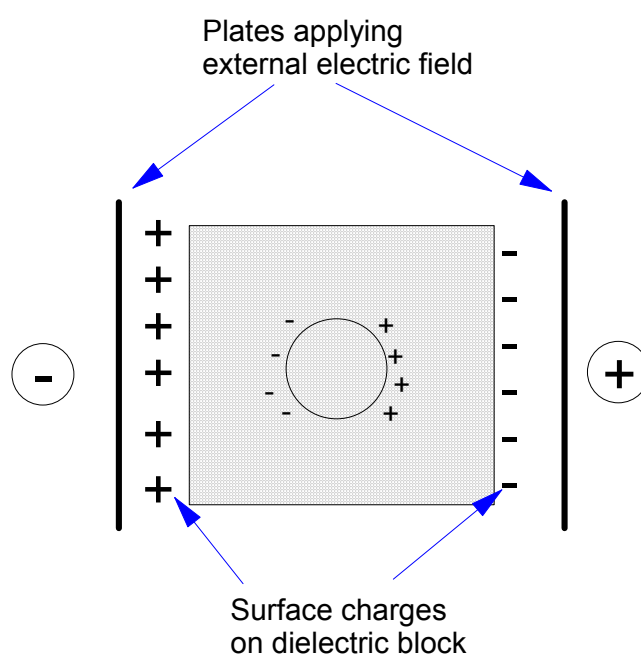
(4 points)

Figure 1. Polarization in a liquid.

1   Outline

In this experiment you will measure the relative permittivity (dielectric constant) and refractive index of solutions of one of the isomers of chloronitrobenzene, dissolved in cyclohexane. From these data the dipole moment of the sample is obtained, and from this you can deduce whether your sample is ortho, meta or para substituted.

2 Safety

Chloronitrobenzenes are poisonous: avoid skin contact and inhalation. Use the fume cupboard when you prepare the solutions and wear disposable gloves whenever you are handling the solid or any solution of it. Clean up all waste after use and any spills immediately.

Cyclohexane-air mixtures are explosive; dispose of cyclohexane solutions in the residues bottle provided. To encourage the solid to dissolve, you may warm the cyclohexane/chloronitrobenzene mixture, but do this using hot water, not a Bunsen burner (cyclohexane is highly flammable!)

The URL for this experiment is http://ptcl.chem.ox.ac.uk/~hmc/tlab/experiments/210.html

3 Theory

In most molecules the centre of negative charge due to the electrons does not coincide with the centre of positive charge due to the nuclei. These molecules possess a permanent electric dipole moment p. If charges $-q$ and $+q$ are separated by a distance r, the dipole moment has magnitude

$$p = q\,r \tag{1}$$

The dipole is drawn from positive to negative charge, indicating the direction of electron drift. The polarization P of a sample is the average dipole moment per unit volume. In a dielectric sample, (or just "dielectric"), induction of electric charge occurs when the substance is placed in an electric field. If the molecules in the dielectric are oriented randomly, P will be zero. However in the presence of an electric field they tend to line up so as to counteract the applied field, as shown in Figure 1. As the dipole moment per unit volume is equal to the charge per unit area, surface charges appear on a block of polarized dielectric.

The relative permittivity ε_r of a sample is the ratio of the field strength in vacuum to that in the material for the same distribution of charge. ε_r is equal to $\varepsilon/\varepsilon^o$, where ε is the permittivity of the sample, and ε^o the permittivity of a vacuum (which is almost equal to that of air). ε_r is also equal to the ratio of the capacitance C of a cell filled with sample to the capacitance C^o of the cell when evacuated.

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon^o} = \frac{C}{C^o} \tag{2}$$

Capacitance is increased by the presence of a polarizable medium; typical values of ε_r are 1.00 (air), 5.94 (chlorobenzene) and 15.5 (liquid ammonia). Water has the unusually high value of 80, and this high value has important consequences for the rate of reactions between charged species in aqueous solution, since the field around an ion falls away very rapidly with distance if the dielectric constant is high.

Suppose that a unit positive charge in the dielectric medium is situated at the centre of a small empty sphere. The size of this sphere, exaggerated in Figure 1, is large compared to molecular

dimensions but is small in relation to the distance between the plates, so the material beyond it can be treated as a continuum. The local field intensity acting on this unit charge is

$$F = 4\pi\sigma - 4\pi P + \frac{4}{3}\pi P \tag{3}$$

The three components of F are, respectively, the force due to the charges on the plates with charge density σ, the induced charges on the material facing the plates which partly counteract the applied field, and the charges on the surface of the small spherical cavity which enhance the applied field.

From this can be derived the Clausius-Mosotti equation:

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2}\frac{M}{\rho} = P = \frac{4\pi L}{3}\alpha \tag{4}$$

where M is the molar mass of the sample, ρ its density, and L is Avogadro's constant. Because of thermal motion, the molecules do not orientate themselves in a completely ordered fashion, but instead take up a range of positions at an angle θ to the electric field. The potential energy U of each molecule is given by

$$U = -pE\cos\theta \tag{5}$$

According to Boltzmann's law, the number of molecules distributed with the axes of their dipoles pointing in the directions within the solid angle $d\Omega$ is $Ae^{-U/kT}d\Omega$, where A is proportional to the number of molecules. From this we may obtain the average moment per molecule as a series expression. Taking the first non-zero term only, and considering the relation between the mean moment and the polarization, we obtain the Debye equation:

$$P_{or} = \frac{4\pi L p^2}{kT} \tag{6}$$

The polarization caused by the alignment of molecules with permanent dipole moments is termed the orientation polarization, P_{or}. It is one of three effects which contribute to the total polarization, P. A second effect, the electronic polarization P_{el}, arises from displacement of the electron cloud by the field, while the third, distortion polarization P_d, arises from the stretching and bending of the nuclear framework caused by the field.
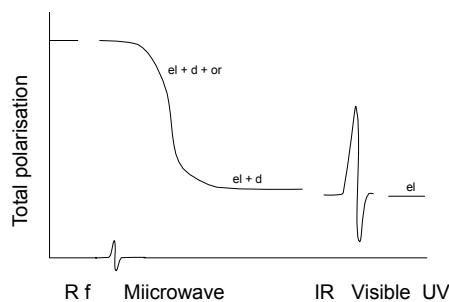

Fig. 2. The change of polarization with frequency.

The dependence of the three components of the polarization on frequency of the applied field is shown in Figure 2.

At low frequencies, all three effects are present. As the frequency is increased into the infrared region, molecules no longer have time to orient, and the P_{or} contribution drops out. In the visible region, the applied frequency is too high for molecular distortion to contribute to the polarization, and only P_{el} remains.

At X-ray frequencies even the electronic contribution drops out. Consequently, the refractive index of materials for X-rays is almost unity, and direct X-ray microscopy is made impractical because no lenses are available.

At optical frequencies P_{el} is the only component of the polarization and there is a simple relationship between relative permittivity and refractive index:

$$\varepsilon_r = n^2 \tag{7}$$

(Note that equation (7) applies only when P_{el} is the sole contributor to the polarization.) P_{el} may therefore be obtained by substituting this expression into the Clausius-Mosotti relation (4), to give the Lorentz equation:

$$P_{el} = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} \tag{8}$$

As P is the sum of the orientation, electronic and distortion polarization

$$P = P_{or} + P_{el} + P_d \tag{9}$$

it follows from equation (6) that

$$P - P_{el} = P_{or} + P_d = \frac{1}{4\pi\varepsilon^o} \frac{4\pi L p^2}{9kT} + P_d \tag{10}$$

The equations derived so far strictly apply only to gases, since interactions between molecules have been ignored. If this approximation is applied to a dilute solution of polar molecules in a non-polar solvent, then both ε_r and $1/\rho$, where ρ is the density of the solution, are almost linear functions of solute concentration. Therefore

$$P = x_1 P_1 + x_2 P_2 = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \frac{x_1 M_1 + x_2 M_2}{\rho} \tag{11}$$

where x is the mole fraction, and the subscripts 1 and 2 refer to the solvent and solute respectively. Employing the same reasoning used to obtain equation (8), we find that

$$x_1 P_{el,1} + x_2 P_{el,2} = \frac{n^2-1}{n^2+2} \frac{x_1 M_1 + x_2 M_2}{\rho} \tag{12}$$

The concentration of solvent, c_1, is related to its mole fraction by

$$c_1 = \frac{x_1 \rho}{x_1 M_1 + x_2 M_2} \tag{13}$$

and there is a corresponding relation for c_2. From equations (11), (12) and (13) :

$$(P_1 - P_{el,1})c_1 + (P_2 - P_{el,2})c_2 = \frac{\varepsilon_r-1}{\varepsilon_r+2} \frac{n^2-1}{n^2+2} = \frac{3(\varepsilon_r - n^2)}{(\varepsilon_r+2)(n^2+2)} \tag{14}$$

Applying equation (10) to each component in equation (14), and noting that for the solvent there is no dipole moment,

$$\frac{3(\varepsilon_r - n^2)}{(\varepsilon_r+2)(n^2+2)} = \frac{1}{4\pi\varepsilon^o} \frac{4\pi L p_2^2}{9kT} c_2 + P_{d,1}c_1 + P_{d,2}c_2 \tag{15}$$

The distortion polarization terms are assumed to be small and nearly constant. Thus a plot of the term on the left of equation (15) against c_2 (in mol m^{-3}) will yield a line from whose slope we can obtain the dipole moment.
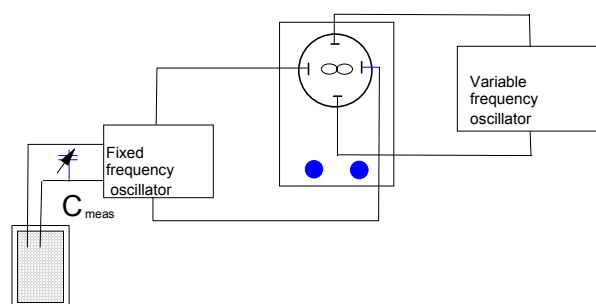

Figure 3. Apparatus used for the heterodyne beat method.

4   Procedure

You will measure capacitance using the heterodyne beat method. An oscillator provides a fixed frequency of 100 kHz, which is fed to the Y plates of an oscilloscope. A second oscillator, connected to the X plates of the scope, provides a variable frequency which is adjusted until a figure 8 (known as a Lissajous figure - see the link on the web page for this experiment) is traced on the oscilloscope screen. At this point the variable frequency is exactly double the fixed frequency.

The variable frequency is controlled by the total capacitance C_{tot} of an external circuit, as shown in the figure. C_{tot} is equal to the sum of the capacitance of the cell, C_{cell}, that of the precision

measuring capacitor C_{meas}, and the residual capacitance C_{resid} of the leads and of the measuring capacitor at its zero position:

$$C_{tot} = C_{cell} + C_{meas} + C_{resid} \tag{16}$$

When the Lissajous figure 8 is displayed, we know that C_{tot} has reached a fixed value. C_{resid} is also constant, so from equations (2) and (16) it follows that

$$C_{cell} + C_{meas} = C^0 \, \varepsilon_r + C_{meas} = \text{constant} \tag{17}$$

where C^0 is the capacitance of the empty cell and ε_r is the relative permittivity of the sample. The measuring capacitor is an earthed stepped rod which can be moved axially within a live cylinder by a micrometer screw. Its capacity C_{meas} is directly proportional to the micrometer reading R. If the proportionality constant is k', then

$$C^0 \, \varepsilon_r \; + \; k' \, R = \text{constant} \tag{18}$$

We measure R for air (R_o), the pure solvent (R_1) and the solution (R). It follows from equation (18) that:

$$\frac{R_o - R}{R_o - R_1} = \frac{\varepsilon_r - \varepsilon_{r,0}}{\varepsilon_{r,1} - \varepsilon_{r,0}} \tag{19}$$

This equation allows the relative permittivity of the solution ε_r to be obtained from the capacitance readings R, given the relative permittivities of the pure components, $\varepsilon_{r,0}$ and $\varepsilon_{r,1}$.

Your sample is a chloronitrobenzene of molar mass 157.5 g mol^{-1}. Prepare four solutions as follows: <u>First put on a clean pair of protective gloves</u>. Accurately weigh about 2g sample in a weighing bottle. Tip the contents into a clean, dry 100 cm^3 volumetric flask and re-weigh the weighing bottle. Dissolve the solid in about 50 cm^3 cyclohexane. Dissolution is slow in cold cyclohexane but rapid if the temperature is raised a few degrees.

ON NO ACCOUNT SHOULD YOU HEAT THE CYCLOHEXANE OVER A BUNSEN BURNER!

Instead, dip the flask into a beaker of hot water. Make up to the mark once the solid has dissolved. Prepare further solutions containing roughly 3g, 4g and 5g solid in 100 cm^3 cyclohexane.

Measure the relative permittivities of air, the solvent and the solutions as follows:

1.   Switch on the capacity meter and water bath and allow them 30 minutes to warm up. The water bath should be set to a temperature within the range 24 - 30 C.

2.   Switch on the oscilloscope. Do not use the scope with brightness greater than necessary, or the screen may be burnt.

3.   Clamp a volumetric flask containing cyclohexane and the flasks containing the sample solutions in the water bath to equilibrate. Place a clean, empty tall 50 cm^3 beaker in the

brass thermostat jacket and carefully bring it up under the cylindrical plates of the cell. Rest the beaker and jacket on the wooden block provided. Be careful not to move the cell itself, or you will change the capacity of the leads. Wait for five minutes for thermal equilibrium, then adjust the measuring condenser using the knobs on the right hand side to give a figure 8 on the oscilloscope. Make all final adjustments in the same direction to minimize backlash errors. The meter is sensitive to vibration and it readily picks up the minute changes in capacitance caused by your body, so it may not be possible to tune a precisely stationary figure 8. Record the air reading, R_o (this will be approximately 38).

4.   Fill the beaker with pure cyclohexane (taken from your thermally equilibrated supply) through a funnel inserted in the hole at the top of the cell. The liquid should reach to the lower edges of the vents cut in the outer tube of the cell under the lid, so that the inner tube is fully immersed. Allow a couple of minutes for thermal equilibrium to be re-established, then take the cyclohexane reading.

5.   Withdraw the beaker of cyclohexane in the jacket from the cell. Replace the beaker by a clean one and repeat the procedure with the chloronitrobenzene solutions, washing the cell with cyclohexane between readings.

6.   While waiting for thermal equilibrium to be attained, measure the refractive indices of the solutions using the refractometer provided. You will find it helpful to use the refractometer first with water, which readily gives a clear image. The solutions you will later measure are slightly (but not much) more difficult to measure, as they evaporate more readily. Use the refractometer as follows:

Turn on the adjustable lamp and position it so it illuminates the back of the prism assembly. Open the prism box and place a few drops of liquid on the ground surface of the lower prism. Close and fasten the prism box, so that the liquid is squeezed into a thin film; to obtain a good reading the film should extend across the entire closed region of the prism.

Focus the crosswires of the eyepiece, adjust the illumination if necessary, then gently turn the prism box using the rear knurled wheel until a coloured band appears in the field of view. By turning the milled wheel at the base of the telescope, a position will be found at which the coloured band will be eliminated, the field of view being partly light and partly dark, with a sharp dividing line. Bring this sharp line into coincidence with the intersection of the crosswires and read the refractive index by means of the magnifier. The scale is divided to the third decimal place, the fourth being obtained by estimation.

7.   At the end of the experiment leave the instruments clean. Switch off all power.

5 Useful information

The relative permittivity of air, $\varepsilon_{r,0}$ is 1.00, and that of cyclohexane, $\varepsilon_{r,1}$ is [2.023 - 0.0016 (*t*-20)], in which *t* is the temperature in °C. The dipole moment of chlorobenzene is 1.60D (in which direction must this be?), and that of nitrobenzene is 4.01D in the direction $C \rightarrow NO_2$. 1 Debye = 3.38×10^{-30} C m.

6 Calculations

Calculate the relative permittivity of the solutions using equation (19). Use your calculated values of relative permittivity and your measurements of refractive index to calculate the dipole moment of the chloronitrobenzene (equation 15). Calculate the dipole moments of ortho, meta and para chloronitrobenzene by vector addition and thus determine whether your sample is ortho, meta or para. Discuss sources of error in this experiment, and their magnitude.

7 References

1.   *Dielectric Behaviour and Structure*, C.P.Smyth, McGraw-Hill, New York (1955), ch. 1. or Determination of Dipole Moments, C.P.Smyth; in *Techniques of Chemistry* (ed. A.Weissberger and B.W.Rossiter), Vol. IV, 397, Wiley Interscience, New York, 1972.
2.   *Some Electrical and Optical Aspects of Molecular Behaviour*, M.Davies, Pergamon Press, (Oxford (1965), ch. 1 - 3.
3.   The determination of dipole moments in solution, H.B. Thompson, *J. Chem. Educ.*, **43**, 66 (1966).
4.   *Determination of Organic Structures by Physical Methods*, ed. E.A.Braude and F.C.Nachod, Academic Press, New York (1955), ch. 9 by L.E.Sutton.

8   <u>Problems and solutions</u>

Observation	Indicates	Solution
Lissajous figure completely absent	Connections to oscilloscope faulty or 'scope not turned on	(i) Check connections. (ii) Check that 'scope is plugged in and turned on. (iii) Check that intensity or brightness control is turned up.
Trace appears on scope but Lissajous figure will not remain fixed or the trace appears to be smudged.	Tuning of capacitance meter is not exact	The display on the 'scope is extremely sensitive to changes in capacitance. (i) Move away from the region close to the sample so that your body does not affect the readings. (ii) Try first using a beaker with no liquid in it; the air reading should be near to 38. When you have turned the moveable slider to a figure close to this, scan quite slowly, watching the display as you do so; it is easy to scan through the point at which the figure appears.
No boundary can be seen on the refractometer	Refractometer incorrectly adjusted or insufficient sample present	(i) The refractive index for water is around 1.33. Adjust the prism position to a value close to this and check that the boundary has appeared. (ii) Check that liquid covers the prism area at the back of the instrument. If the glass plate is only partly covered the boundary will be weaker. (iii) Check that the light providing rear illumination is positioned so as to shine on the prism.
Lissajous figure appears but is not stable; constant readjustment of the slider is required	Capacitance of the sample is changing	(i) Move away from the region close to the sample - your body may be affecting the results. (ii) The sample has not reached thermal equilibrium - check that the water bath is not heating up without limit.

9   <u>Summary of symbols used in the theory</u>

Sub and superscripts o and 1 refer to air (or vacuum) and solvent respectively.

p	electric dipole moment
q	charge
r	charge separation
P	polarization
P_{or}	orientation polarization
P_{el}	electronic polarization
P_d	distortion polarization
R	micrometer reading, sample
R_o	micrometer reading, air
R_1	micrometer reading, pure cyclohexane
E	electric field
ε_r	relative permittivity
ε	permittivity
ε^o	permittivity of vacuum
C^b	capacitance of evacuated cell
C_{cell}	capacitance of cell
C_{rot}	capacitance of external circuit
C_{resid}	residual capacitance
C_{meas}	capacitance of measuring capacitor
F	local field density
σ	charge density on plates
M	molar mass of sample
ρ	density of sample
L	Avogadro's constant
θ	angle to electric field
U	potential energy of molecule
n	refractive index
x	mole fraction
c	concentration