

Practical Exercises in Physical Chemistry

Advanced Level

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Block III: Kinetic Dipole moment and molar refraction

1. Objectives:

Identify an unknown dichlorobenzene isomer using the experimentally obtained value of the molecular dipole moment μ .

2. Methods:

Measure the index of refraction of a liquid medium using Abbe's refractometer.

Measure the dielectric constant of a liquid dielectric using its effect on the capacitance of a capacitor. Measure the capacitance of the capacitor using the resonance frequency of an oscillator circuit.

3. Backgrounds of the problem:

When two charges +q and -q are separated by a distance R, they constitute an electric dipole. The dipole can be presented by a vector called the dipole moment $\vec{\mu}$ directed from the negative charge towards the positive, where $|\mu| = q \cdot R$. The dimension of the dipole moment is debye, where $1D = 3.336 \cdot 10^{-30} C \cdot m$. When the charge q has the magnitude of the electronic charge $(1.602 \cdot 10^{-19} C)$, and the distance R is of atomic dimensions $(10^{-10} m)$, the magnitude of the dipole moment is about 4.8 D. Dipole moments of small molecules are of this order, but generally somewhat smaller. Whether a polyatomic molecule has a permanent dipole or not depends on its symmetry. Molecules which have a permanent dipole are called polar molecules. The dipole moment of a molecule may be obtained from measurements of the relative permittivity of a bulk sample. Consider two plane, parallel plates depicted in Fig. 1a called capacitor.



Let the charges on the plates be +q and -q and their areas are A. We can write $q = \sigma \cdot A$, where σ is the surface charge density (the charge per unit area). On account of the charges, there is a potential difference $\Delta \phi$ between the plates. The capacitance of the capacitor is then defined as: $C = \frac{q}{\Delta \phi}$ or $C = \frac{\sigma \cdot A}{\Delta \phi}$. The electric field in the region between the plates is proportional to the charge density σ . The proportionality coefficient is the electric permittivity or dielectric constant of the medium between the plates. If the medium is a vacuum then the dielectric constant (called vacuum permittivity) is $\varepsilon_0 = 8.854 \cdot 10^{-12} \frac{C^2}{J \cdot m}$ and the electric field in the region between the plates sis: $E_0 = \frac{\sigma}{\varepsilon_0}$. If the medium is a dielectric then its dielectric constant is $\varepsilon = \varepsilon_r \cdot \varepsilon_0$, where the factor ε_r is the relative dielectric constant. Thus, the electric field between the plates of a capacitor filled with a dielectric is $E = \frac{\sigma}{\varepsilon_0 \cdot \varepsilon_r}$. The magnitude of the electric field is decreasing. The reason for that is the polarisation of the dielectric discussed below. The potential difference $\Delta \phi$ between the plates is proportional to the electric field and the distance d between the plates: $\Delta \phi = E \cdot d$. Therefore, in the absence of a dielectric the capacitance is $C_0 = \frac{\sigma \cdot A}{E_0 \cdot d} = \frac{\varepsilon_0 \cdot A}{d}$. In the presence of a dielectric it is $C = \frac{\varepsilon_0 \cdot \varepsilon_r \cdot A}{d}$. Therefore, since $\frac{C}{C_0} = \varepsilon_r$ the relative permittivity can be measured by measuring the capacitance of a capacitor with and without a dielectric present. Since the relative dielectric constant of dry air is close to that in a vacuum ($\varepsilon_r \approx 1.00053$) one does not need to evacuate the capacitor.

3.1 Polarisation of a dielectric medium

Dielectric is a nonconducting medium polarizable in an external electric field. Polarization, P, is the average dipole moment per unit volume of the medium. The electric field generated by the polarisation partially compensates the electric field generated by the charges on the plates of the capacitor, Fig. 1b. Since the polarisation is the average dipole moment per unit volume we may formally write: $P = \frac{\langle \mu_d \rangle}{A \cdot R} = \frac{q_d \cdot R}{A \cdot R} = \frac{q_d}{A} = \sigma_d$, where σ_d is the surface charge density of the dielectric. The electric field between the plates of a capacitor filled with a dielectric can be expressed in two ways. One is to write it in terms of the relative permittivity : $E = \frac{\sigma}{\varepsilon_0 \cdot \varepsilon_r}$ or $\sigma = E \cdot \varepsilon_0 \cdot \varepsilon_r$. The other is to write it in terms of the net charge, which is reduced due to the polarization of the dielectric: $E = \frac{\sigma - \sigma_d}{\varepsilon_0} = \frac{\sigma - P}{\varepsilon_0}$ or $P = \sigma - E \cdot \varepsilon_0$. The latter equation can be rewritten as $P = \sigma - E \cdot \varepsilon_0 = E \cdot \varepsilon_0 \cdot \varepsilon_r - E \cdot \varepsilon_0 = (\varepsilon_r - 1) \cdot \varepsilon_0 \cdot E$.

It is useful to distinguish between two kinds of polarization. Even if the molecules are polar, i.e. possesses a permanent dipole moment, the mean dipole moment is zero in a fluid sample because a fast reorientation of the molecules. However, when an external electric field is present it forces the molecules to orient their dipole moments along the field. The generated nonzero mean dipole moment depends on the strength of the applied field and temperature. The associated with this nonzero mean dipole moment polarization is called the orientation polarization, P_0 . However, the external electric field does not only align the molecules in the most favourable direction. It also disturbs their electronic distributions and nuclear positions. As a result one observes the displacement polarisation. One distinguishes between electronic polarisation, P_e , (the charge centers of the electrons and nucleus, which normally coincide, are separated by some small distance) and ion or distortion polarisation, P_a , (negative and positive ions are separated). The

ion polarisation is also called atomic polarisation, since this kind of polarisation is also effective in molecules consisting of atoms with different electronegativities. The dipole moment induced because of the displacement polarisation does not depend on the presence of the permanent dipole moment and is proportional exclusively to the strength of the external field $\mu_{ind} = \alpha \cdot E$. The proportionality coefficient α is called polarizability of the molecule.

A single molecule of the dielectric in the external electric field experiences also a field that arises from other molecules. This external contribution to the local field is $\frac{P}{3 \cdot \varepsilon_0}$. Therefore, the total

field at the molecule is $E_{loc} = E + \frac{P}{3 \cdot \varepsilon_0} = \frac{P}{(\varepsilon_r - 1) \cdot \varepsilon_0} + \frac{P}{3 \cdot \varepsilon_0} = \frac{P \cdot (\varepsilon_r + 2)}{3 \cdot \varepsilon_0 \cdot (\varepsilon_r - 1)}$.

While the external electric field tends to align the molecules in the most favourable direction the thermal motion trends to randomize their orientations. Therefore, the orientation polarization strongly depends on temperature. For not too low temperatures and not too strong fields the mean molecular dipole moment is $\langle \mu \rangle_{perm} = \frac{\mu^2 \cdot E_{loc}}{3 \cdot k \cdot T}$, where μ is the permanent dipole moment, T is the absolute temperature in Kelvin (K) and k is the Boltzmann constant ($k = 1.381 \cdot 10^{-23} J \cdot K^{-1}$). In contrast the electronic and atomic polarisations do not depend on temperature. They do, however, depend on the frequency of the applied external electric field, Fig. 2.



Fig. 2 The dependence of the different polarizabilities on the frequency of the applied field. (accepted from [1])

A molecule takes about 10^{-12} s to rotate. Therefore, the permanent dipole moment cannot follow the external electric field oscillating at frequencies above 10^{12} Hz. The distortion polarisation demands bending and stretching of the molecules which cannot follow the field after the microwave region. In the visible region, only the electrons are light enough to follow the field. Finally, one should take into account that the polarisation is proportional to the concentration of

the molecules. Thus, the full polarisation of the sample is $P = N \cdot (P_0 + P_e + P_a)$, where N is the

number of molecules in the unit volume. Here, $P = \frac{3 \cdot \varepsilon_0 \cdot (\varepsilon_r - 1)}{(\varepsilon_r + 2)} \cdot E_{loc}$, $P_0 = \frac{\mu^2 \cdot E_{loc}}{3 \cdot k \cdot T}$ and

 $P_e + P_a = \alpha \cdot E_{loc}$ Using these equations we obtained the Debye equation:

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N}{3 \cdot \varepsilon_0} \cdot \left(\alpha + \frac{\mu^2}{3 \cdot k \cdot T}\right)$$

In terms of the density ρ of the sample using $N = \frac{\rho \cdot N_A}{M_m}$, where N_A is the Avogadro constant $(N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1})$ and M_m is the molar mass of the molecule, we may define the molar polarizability p_m :

$$p_m = \frac{N_A}{3 \cdot \varepsilon_0} \cdot \left(\alpha + \frac{\mu^2}{3 \cdot k \cdot T}\right) \text{ and } \frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{\rho \cdot p_m}{M_m}$$

All polarizabilities used below are the molar ones, so we omit the index m for the rest of the text.

3.2 Molar polarizability of mixtures

To determine the dipole moment of a single molecule, the interactions between the individual dipoles have to be as small as possible. Therefore, one uses highly dilute solutions in nonpolar solvents and extrapolates the obtained values to infinite dilution. The total polarizability of a complex medium, p^{mix} , is composed of the individual polarizabilities of the solvent, p^{sol} , and the dissolved substance, p^{sub} : $p^{mix} = x^{sol} \cdot p^{sol} + x^{sub} \cdot p^{sub}$, where x^{sol} is the mole fraction of the solvent, x^{sub} is the mole fraction of the substance and $x^{sol} + x^{sub} = 1$. Therefore, for this mixture $\frac{\varepsilon_r^{mix} - 1}{\varepsilon_r^{mix} + 2} = \frac{\rho^{mix}}{x^{sol} \cdot M_m^{sub} \cdot M_m^{sub}} \cdot (x^{sol} \cdot p^{sol} + x^{sub} \cdot p^{sub})$. The polarizability of a pure nonpolar

solvent can be directly calculated using the value of the dielectric constant of the pure solvent. Then the polarizability of the substance can be obtained using a value of the dielectric constant for a mixture at low concentration. In fact, interactions between polar molecules of the substance result in dependence of the substance polarizability on the concentration of the substance. To minimize this effect several values of p^{sub} , obtained for different concentrations of the substance, are plotted against the corresponding x^{sub} and extrapolated to $x^{sub} = 0$. We will call this limiting value of the substance polarizability $(p^{sub})_{x^{sub}}$.

3.3 Debye method to determine the permanent dipole moment and the polarizability of a substance

The polarizability of a polar substance depends on temperature. Namely:

$$\left(p^{sub}\right)_{x_0^{sub}} = \frac{N_A}{3 \cdot \varepsilon_0} \cdot \left(\alpha^{sub} + \frac{\left(\mu^{sub}\right)^2}{3 \cdot k \cdot T}\right) \text{ that can be written as: } \left(p^{sub}\right)_{x_0^{sub}} = b + m \cdot \frac{1}{T}.$$

If the value of $(p^{sub})_{x_0^{sub}}$ is known at several temperatures, they can be plotted against $\frac{1}{T}$. The slope of the curve $m = \frac{N_A \cdot (\mu^{sub})^2}{9 \cdot \varepsilon_0 \cdot k}$ gives the value of the permanent dipole moment while the intercept $b = \frac{N_A \cdot \alpha^{sub}}{3 \cdot \varepsilon_0}$ gives the value of the polarizability of the substance.

3.4 Lorenz & Lorentz method to determine the permanent dipole moment and the polarizability of a substance

The polarizability of a substance depends on the frequency of the external electric field. In the visible region, only the electrons are light enough to follow the direction of the oscillating electric field of the electromagnetic wave. The dielectric constant of a medium at a certain frequency of the oscillating external electric field is proportional to the square of its index of refraction at the same frequency. The proportionality coefficient is close to 1 for all non-ferromagnetic materials. This is the so called Maxwell equation for the index of refraction: $\varepsilon_r \approx n_r^2$, where n_r is the index of refractivity, R_m .

Therefore, for a mixture $R_m^{mix} = \frac{\left(n_r^{mix}\right)^2 - 1}{\left(n_r^{mix}\right)^2 + 2} \cdot \frac{x^{sol} \cdot M_m^{sol} + x^{sub} \cdot M_m^{sub}}{\rho^{mix}}$.

The index of refraction n_r^{mix} should be measured for several diluted solutions. That gives the corresponding values of the molar refractivity R_m^{mix} . The total molar refractivity of a complex medium is composed of the individual molar refractivities of the solvent and the dissolved substance: $R_m^{mix} = x^{sol} \cdot R_m^{sol} + x^{sub} \cdot R_m^{sub}$. This eq. can be rewritten as: $R_m^{mix} = R_m^{sol} + \left(R_m^{sub} - R_m^{sol}\right) \cdot x^{sub}$.

Thus, the value of R_m^{sub} can be obtained from the slope of the plot of R_m^{mix} as a function of x^{sub} .

It is worth to mention that the molar refractivity of a molecule can be estimated as a sum of contributions from the individual chemical bonds making up the molecule. Values of the molar refractivities for different chemical bonds and ions can be found in literature. You are expected to estimate the molar refractivity of dichlorobenzene using this approximation and to compare the theoretical and experimentally observed values.

The atomic polarizabilities of molecules are of the order of 10-15% of the electronic polarizabilities. Therefore, the displacement molar polarizability can be estimated to be $p_d^{sub} \approx 1.1 \cdot R_m^{sub}$. The difference between the molar polarizability $\left(p^{sub}\right)_{x_0^{sub}}$ obtained above and the displacement molar polarizability p_d^{sub} is equal to the orientation polarizability p_0^{sub} . Since

 $p_0^{sub} = \frac{N_A \cdot (\mu^{sub})^2}{9 \cdot \varepsilon_0 \cdot k \cdot T}$ one can calculate the value of the permanent dipole moment of the substance.

3.5 Hedestrand, Guggenheim & Smith method to determine the permanent dipole moment of a substance

For sufficiently diluted solutions another evaluation method was developed by Hedestrand, Guggenheim and Smith. At a given temperature the index of refraction n_r^{mix} and the dielectric constant ε_r^{mix} for solutions of different mole fractions were determined. They can be expressed as:

$$\begin{cases} \varepsilon_r^{mix} = x^{sol} \cdot \varepsilon_r^{sol} + x^{sub} \cdot \varepsilon_r^{sub} = \varepsilon_r^{sol} + x^{sub} \cdot \left(\varepsilon_r^{sub} - \varepsilon_r^{sol}\right) = \varepsilon_r^{sol} + x^{sub} \cdot a_{\varepsilon} \\ \left(\left(n_r^{mix}\right)^2 = \left(n_r^{sol}\right)^2 + x^{sub} \cdot \left(\left(n_r^{sub}\right)^2 - \left(n_r^{sol}\right)^2\right) = \left(n_r^{sol}\right)^2 + x^{sub} \cdot b_n \end{cases}$$

The value of a_{ε} can be obtained from the slope of the plot of ε_r^{mix} as a function of x^{sub} and the value of b_n can be obtained from the slope of the plot of $(n_r^{mix})^2$ as a function of x^{sub} . It was

shown^[2] that the dipole moment of the substance is determined by:

$$\left(\mu^{sub}\right)^{2} = \frac{27 \cdot M_{m}^{sub} \cdot \varepsilon_{0} \cdot k \cdot T}{\rho^{sol} \cdot \left(\varepsilon_{r}^{sol} + 2\right)^{2} \cdot N_{A}} \cdot \left(a_{\varepsilon} - b_{n}\right)$$

The advantage of this method is that one does not need to know the densities of the mixtures.

4. Work program:

In this work you are requested to obtain a value of the molecular dipole moment of an unknown dichlorobenzene isomer dissolved in decaline using three different methods. To do that you should experimentally measure: i) the relative dielectric constant of pure decaline and dilute solutions of the dichlorobenzene isomer in decaline of three different concentrations at three different temperatures; ii) the index of refraction of pure decaline and the same dilute solutions of the dichlorobenzene isomer in decaline near 20 °C. The table of the temperature dependent densities of decaline and the used solutions is available to copy.

Experimental measurement of the relative dielectric constant

One of the methods to measure the dielectric constant of a liquid dielectric medium is to define the effect of the medium on the capacitance of a capacitor. When the dielectric is introduced between the plates of the capacitor its capacity is changed since $C \sim \varepsilon_r$. The capacitance can be measured with high accuracy using the resonance frequency, v_{res} , of an oscillator circuit. Indeed, the resonance frequency of the oscillator circuit depicted in Fig. 3 is $v_{res} = \frac{1}{2 \cdot \pi \cdot \sqrt{L \cdot C}}$, where L is the inductivity of the coil and C is the capacitance of the capacitor.



The principal scheme of a device used in this work for capacitance measurements is depicted in Fig. 4. The frequency generator (Gen) generates the precision frequency signal of 2 MHz (v_{ref}). The frequency mixer (Mix) subtracts the frequency generated by the oscillator circuit (v_{res}) from

the reference frequency. The output frequency ($\Delta v = v_{ref} - v_{res}$) is transmitted to the oscilloscope (Osc). When the output frequency is high one observes on the oscilloscope screen a straight line. When the output frequency becomes low one observes on the oscilloscope screen fascinating Lissajou figures. When the frequency generated by the oscillator circuit becomes equal to the reference frequency, i.e. $\Delta v = v_{ref} - v_{res} = 0$, the figures are again collapsed in a straight line. At this condition the resonance frequency of the oscillator circuit is precisely 2 MHz.



Fig. 4 The principal scheme of a dipolemeter operating at a frequency of 2 MHz. Amp - amplifier, Gen – reference frequency generator, Mix – frequency mixer, Oscoscilloscope.

The scheme includes two quasi-independent oscillator circuits. The first one operates when the switcher "S" is in the position "K" (it is called "correction" or "Korr"). The first circuit includes the inductive coil L, the variable capacitor C_K and the reference capacitor C_R . You should tune the capacitor C_K so that the resonance frequency of the first circuit becomes precisely 2 MHz. When the switcher "S" is in the position "M" (it is called "measurement" or "MI") the reference capacitor C_R is substituted on the variable capacitor C_T and the capacitor C_M which contains between its plates the dielectric whose dielectric constant should be measured. In Fig. 5 is schematically depicted the measuring cell used in this work. It is a cylindrical capacitor whose temperature can be varied. You should tune the capacitor C_T so that the resonance frequency of the second circuit becomes precisely 2 MHz. At this condition the known capacitance of the

reference capacitor C_R is equal to the total capacitance of the capacitors C_T and C_M . Since the capacitance of the capacitor C_T is known the capacitance of the capacitor C_M and the dielectric constant of the medium between its plates can be calculated. In fact, due to some mechanical imperfections you will need to tune and match the circuits step by step. The read values of the capacitor C_T should be corrected using the correction curve which is available to copy. Then the corrected values, $C_T^{corrected}$ should be converted into ε values using eq.: $\varepsilon = 1.831 \cdot 10^{-3} \cdot C_T^{corrected} + 1.190$.



Fig. 5 Scheme of the measuring cell

Experimental measurement of the index of refraction

One of the methods to measure the index of refraction of a liquid dielectric medium is to define the critical angle of the total reflection. When a light ray passes from one medium into another it changes its direction. Lets the angle between the ray direction in the first medium and the normal to the boundary surface to be α . Then the value of the same angle in the second medium is defined by eq.: $\sin \beta = \frac{n_1}{n_2} \cdot \sin \alpha$, where n_1 is the index of refraction in the first medium and n_2 is the index of refraction in the second medium. If the first medium is optically denser there is a limit on the values of the angle β . Indeed, $|\sin \beta| \le 1$ that means the product $\frac{n_1}{n_2} \cdot \sin \alpha$ must be less than 1 or $\sin \alpha \le \frac{n_2}{n_1}$. Rays falling on the surface under bigger angles α are reflected back

into the first medium. The angle α which satisfies the eq. $\sin \alpha = \frac{n_2}{n_1}$ is called the critical angle of the total reflection. If the second medium is optically denser there is again a limit on the values of the angle β . Indeed, $\sin \beta = \frac{n_1}{n_2} \cdot \sin \alpha \le \frac{n_1}{n_2} \cdot \sin 90^\circ = \frac{n_1}{n_2} \prec 1$. For example, when $n_1 = 1.333$ (pure water at 20 °C) and $n_2 = 1.890$ (heaviest flint glass) a ray of light passing from water into glass practically parallel to the boundary surface, i.e. Ray 3 in Fig. 6 ($\alpha \approx 90^\circ$), will be bent towards the normal to the angle $\beta \approx 45^\circ$. As a result, if the refractive index of the glass is known one can measure the refractive index of the first medium looking on the position of the borderline between the bright and dark regions on a detector scale, Fig. 6.



Fig. 6

Refraction of light passing from a less into a more optically dense transparent medium.

This optical scheme is used in the Abbe's refractometer, Fig. 7. A thin layer of a liquid sample is placed between two prisms. The incident light goes through the first, illuminating prism, the bottom surface of which is dim. This surface scatters the incident light in all directions so that the substance is uniformly illuminated. The second, measuring prism is made of a glass with a high index of refraction. Samples with different refractive indexes will produce different angles of refraction which define the position of the borderline between the bright and dark regions on a scale. When not monochromatic light is used, the borderline will be colored due to the dispersion of the index of refraction. To eliminate this effect, a set of compensating prisms is included after

the measuring prism. These compensating prisms are designed to correct the dispersion and to reproduce the refractive index which would correspond to the monochromatic light of 589 nm, the sodium Fraunhofer D line. From the compensator position we can estimate the mean dispersion of the index of refraction, so-called Abbe number.



Fig. 7 The principal scheme of Abbe's refractometer

The execution order of the work

Results with sufficient accuracy are only obtained when the accuracy of the measurements is sufficient.

The dipolemeter must be switched on in advance since it takes half an hour to warm it up. The measuring cell should be filled until the lid is covered. It takes about 5 min. until the temperature of a sample stabilizes. Do not rinse the measuring cell between experiments at the same temperature; start each set of these experiments with pure decaline and keep the trend towards increasing concentration of dichlorobenzene; after the set of experiments at room temperature rinse the cell with petrol ether and after the sets at 50 $^{\circ}$ C and 80 $^{\circ}$ C with toluene; use hot air from a dryer to dry the cell (do not put the stream directly into the cell!). Use the higher heat step of the thermostat for heating up and to maintain a constant temperature. Check that there is enough water in the thermostat. It is hard to get precisely 50 $^{\circ}$ C or 80 $^{\circ}$ C; measure the dielectric constant at any stable temperature in the intervals $50 \pm 5 \,^{\circ}$ C and $75 \pm 5 \,^{\circ}$ C.

The prisms of the refractometer should be rinsed with petrol ether; wait until they are totally dry; do not touch the surface of the prisms with hard objects to avoid scratches and offensive comments of your follows.

Pay attention to the working instructions for handling chemical substance. Pour the waste only in the corresponding, marked bottles. Clean up the working place at the end.

- a) Measure the index of refraction of amyl alcohol at room temperature. Compare the obtained value to the reference value of 1.409.
- b) Measure the index of refraction of decaline and three solutions of dichlorobenzene in decaline at room temperature.
- c) Measure the dielectric constant of decaline and three solutions of dichlorobenzene in decaline at room temperature.
- d) Heat up the dipolemeter up to 50 ± 5 ⁰C.
- e) Measure the dielectric constant of decaline and three solutions of dichlorobenzene in decaline at this temperature.
- f) Heat up the dipolemeter up to 75 ± 5 ⁰C.
- g) Measure the dielectric constant of decaline and three solutions of dichlorobenzene in decaline at this temperature.

5. Questions to the work

- A capacitor of capacitance C is connected to a cell of emf V. Calculate: the potential difference Δφ between the plates and the charge q accumulated on the plates of the capacitor. How Δφ and q change if a dielectric of relative permittivity ε is introduced between the plates?
- 2) A capacitor of capacitance C was loaded from a cell of emf V and disconnected from it. Calculate: the potential difference Δφ between the plates and the charge q accumulated on the plates of the capacitor. How Δφ and q change if a dielectric of relative permittivity ε is introduced between the plates?
- 3) For which light the refractive index is greater blue or red?
- 4) Does the value of the refractive index depend on temperature?
- 5) Calculate the critical angle of the total reflection for the system water:air ($n_{water} \approx 1.3$, $n_{air} \approx 1$).
- 6) Why the Maxwell equation $\varepsilon_r \approx n_r^2$ is valid for benzene ($\varepsilon = 2.3$, $n \approx 1.5$) but not for water ($\varepsilon = 78$, $n \approx 1.3$)?
- 7) What are Van-der-Waals forces? How are they connected with the molecular

polarizability α and the permanent dipole moment μ ?

6. Data analysis:

- a) Using the experimentally obtained values of the complex dielectric constant ε_r^{mix} estimate graphically the values of the substance polarizabilities $\left(p^{sub}\right)_{x_0^{sub}}^{T_1}$, $\left(p^{sub}\right)_{x_0^{sub}}^{T_2}$ and $\left(p^{sub}\right)_{x_0^{sub}}^{T_3}$ for three temperatures and their margin of error.
- b) Using the calculated values of the substance polarizabilities $(p^{sub})_{x_0^{sub}}^{T_1}$, $(p^{sub})_{x_0^{sub}}^{T_2}$ and $(p^{sub})_{x_0^{sub}}^{T_3}$ estimate graphically the values of the permanent dipole moment μ^{sub} and the molecular polarizability α^{sub} of the dichlorobenzene isomer with the help of the Debye method. Both values must be reported together with their margin of error.
- c) Using the experimentally obtained values of the complex index of refraction n_r^{mix} estimate graphically the value and the margin of error of the molar refractivity of the dichlorobenzene isomer R_m^{sub} with the help of the Lorenz & Lorentz method. Calculate the values of the permanent dipole moment μ^{sub} and the molecular polarizability α^{sub} of the dichlorobenzene isomer. Both values must be reported together with their margin of error. Compare the obtained value of the molar refractivity to a value estimated as a sum of contributions from the individual chemical bonds making up the molecule. Do the values agree within the margin of error of the first value?
- d) Using the experimentally obtained values of the complex index of refraction n_r^{mix} and dielectric constant ε_r^{mix} calculate the value of the permanent dipole moment μ^{sub} of the dichlorobenzene isomer with the help of the Hedestrand, Guggenheim & Smith method. Estimate the margin of error of this value.
- e) Compare the values of the permanent dipole moment μ^{sub} of the dichlorobenzene isomer obtained with the help of different methods. Do the values agree within the margin of error? If not, can you explain why? Is the accuracy of your experiments sufficient to identify the dichlorobenzene isomer?
- f) Compare the values of the molecular polarizability obtained with the help of different methods. Do the values agree within the margin of error? If not, can you explain why?

7. Data presentation:

You are demanded to include in you report the following tables. The second columns of Table 1 and Table 2 must be filled out during the work.

x^{sub}	$n_r^{mix} \pm \Delta$	$(n_r^{mix})^2 \pm \Delta$	R_m^{mix} \pm Δ
0			
0.03			
0.06			
0.10			

Table 1. Experimental values of the complex index of refraction.

Table 2. Experimental values of the complex dielectric constant.

 $T_1 = __{0}C$

x^{sub}	Units $\pm \Delta$	${\cal E}_r^{mix}~\pm\Delta$	$ ho^{mix}\pm\Delta$	$p^{sol}\pm\Delta$	$p^{sub} \pm \Delta$
0					
0.03					
0.06					
0.10					

 $T_2 = __{0}^{0}C$

x^{sub}	Units $\pm \Delta$	${\cal E}_r^{mix}~\pm\Delta$	$ ho^{mix}\pm\Delta$	$p^{sol}\pm\Delta$	$p^{sub} \pm \Delta$
0					
0.03					
0.06					
0.10					

 $T_3 = __{0}C$

x^{sub}	Units $\pm \Delta$	$\mathcal{E}_r^{mix} \pm \Delta$	$ ho^{mix}\pm\Delta$	$p^{sol}\pm\Delta$	$p^{sub} \pm \Delta$
0					
0.03					
0.06					
0.10					

Table 3. Evaluation table.

$\left(p^{sub} ight)^{T_1}_{x_0^{sob}} \pm \Delta$	$\left(p^{sub} ight)_{x_{0}^{sob}}^{T_{2}} \pm \Delta$	$\left(p^{sub} ight)_{x_{0}^{sob}}^{T_{3}}\pm\Delta$	$R_{_{m}}^{sub} \pm \Delta^{\mathrm{exp}}$	$R_{_{m}}^{sub} \pm \Delta^{ m calc}$

^{exp} - the value of molar refractivity observed experimentally;

^{calc} - the value of molar refractivity estimated as a sum of contributions from chemical bonds.

Table 4. Values of the permanent dipole moment and the molecular polarizability of dichlorobenzene isomer

	Debye	L&L	H&G&S
$\mu^{sub}\pm\Delta$			
$\alpha^{sub} \pm \Delta$			

8. Error analysis

Remember:

- a) Experimental uncertainties should be rounded to one significant figure.
- b) In calculations, the intermediate uncertainties should be kept with two significant figure and rounded to one significant figure at the end.
- c) The last significant figure in the final value should be in the same decimal position as the uncertainty.

In this work some values and their margin of error should be estimated graphically. Since the margin of error of the experimental values obtained in your measurements are quite big as compared to the difference between different values you should be very careful with the graphical estimation of the errors. Namely, you will need to find coefficients m and b of a linear dependence $y = m \cdot x + b$, where y and x are some experimental values. It is advisable to use the Method of the Least Square to estimate these coefficients:

$$m = \frac{N\sum_{i=1}^{N} y_i x_i - \sum_{i=1}^{N} y_i \sum_{i=1}^{N} x_i}{N\sum_{i=1}^{N} x_i^2 - (\sum_{i=1}^{N} x_i)^2} \qquad b = \frac{\sum_{i=1}^{N} x_i^2 \sum_{i=1}^{N} y_i - \sum_{i=1}^{N} x_i \sum_{i=1}^{N} y_i x_i}{N\sum_{i=1}^{N} x_i^2 - (\sum_{i=1}^{N} x_i)^2}, \text{ where } N \text{ is the number of the}$$

experimental pairs (y_i, x_i) .

The margin of errors for these coefficients can be estimated using Eqs.:

$$\Delta b = \sqrt{\frac{\sigma_y^2 \sum_{i=1}^N x_i^2}{N \sum_{i=1}^N x_i^2 - (\sum_{i=1}^N x_i)^2}} \qquad \Delta m = \sqrt{\frac{N \cdot \sigma_y^2}{N \sum_{i=1}^N x_i^2 - (\sum_{i=1}^N x_i)^2}}, \text{ where } \sigma_y^2 = \frac{\sum_{i=1}^N (y_i - m \cdot x_i - b)^2}{N - 2}$$

Otherwise you can use a suitable computer program.

9. Literature

- [1] P.W. Atkins. "Physical Chemistry", 3th ed., Oxford University Press, Oxford 1987.
- [2] E.A.Guggenheim. "The computation of electric dipole moments", *Trans. Faraday Soc.* 1951, 47, 573-576.

This script was corrected by Dr. I. Shenderovich in SS 2006. Comments/corrections are welcome.