XIII

Electric and Magnetic Properties

EXPERIMENTS

30. Dipole moment of polar molecules in solution
31. Dipole moment of HCl molecules in the gas phase
32. Magnetic susceptibility
33. NMR determination of paramagnetic susceptibility

EXPERIMENT 30

Dipole Moment of Polar Molecules in Solution

When a substance is placed in an electric field, such as exists between the plates of a charged capacitor, it becomes to some extent electrically polarized. The polarization results at least in part from a displacement of electron clouds relative to atomic nuclei; polarization resulting from this cause is termed *electronic polarization.* For molecular substances, atomic polarization may also be present, owing to a distortion of the molecular skeleton. Taken together, these two kinds of polarization are called *distortion polarization.* Finally, when molecules possessing permanent dipoles are present in a liquid or gas, application of an electric field produces a small preferential orientation of the dipoles in the field direction, leading to *orientation polarization.*

The permanent dipole moment μ of a polar molecule, as a solute molecule in a liquid solution in a nonpolar solvent or as a molecule in a gas, can be determined experimentally from measurements of the *dielectric constant* κ. This quantity is the ratio of the electric permittivity ε of the solution or gas to the electric permittivity ε_0 of a vacuum (8.854×10^{-12} F m^{-1}):

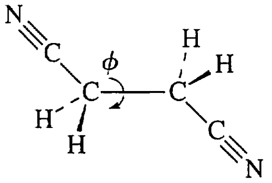
$$\kappa = \frac{\varepsilon}{\varepsilon_0} \tag{1}$$

For that reason the dielectric constant is also known as the *relative permittivity* (with symbol ε_r). The dielectric constant is determined with a capacitance cell, incorporating a capacitor of fixed dimensions in a suitable containment vessel. If C is the capacitance of the cell when the medium between the capacitor plates is the solution or gas of interest and C_0 is the capacitance when the medium is a vacuum, then[1]

$$\kappa = \frac{C}{C_0} \tag{2}$$

The present experiment deals with polar molecules in solution in a nonpolar solvent. Experiment 31 deals with polar molecules in a gas. The basic theoretical framework is the same for both.

Either of two systems can be studied in this experiment: (1) *o*- and *m*-dichlorobenzene, or (2) succinonitrile and propionitrile. In the first case, the results can be compared with the vector sum of C—Cl bond moments obtained from the known dipole moment of monochlorobenzene. In the second case, one obtains direct information about internal rotation in a simple 1,2-disubstituted ethane



The angle ϕ is defined so that $\phi = 180°$ when the two C≡N groups eclipse each other (on viewing the molecule along the C—C axis). Thus $\phi = 0$ corresponds to the most stable trans configuration, and $\phi = \pm 120°$ corresponds to two equivalent gauche configurations. Hindered rotation about the C—C sigma bond can be taken into account by defining temperature-dependent mole fractions in the trans, gauche plus, and gauche minus states. The dipole moment of each of these forms can be predicted from the C—C≡N bond moment measured in propionitrile (ethyl cyanide).

THEORY

An electric dipole[2] consists of two point charges, $-Q$ and $+Q$, with a separation represented by a vector $\mathbf{r}$, the positive sense of which is from $-Q$ to $+Q$. The electric dipole moment is defined by

$$\mathbf{m} = Q\mathbf{r} \tag{3}$$

A molecule possesses a dipole moment whenever the center of gravity of negative charge does not coincide with the center of gravity of positive charge. In an electric field, all molecules have an induced dipole moment (which is aligned approximately parallel to the field direction) owing to distortion polarization. In addition *polar molecules* have a *permanent dipole moment* (i.e., a dipole moment that exists independent of any applied field) of constant magnitude μ and a direction that is fixed relative to the molecular skeleton.

The resultant (vector sum) electric moment of the medium per unit volume is known as the *polarization* **P**.[3] For an isotropic medium, **P** is parallel to the electric field intensity **E**, and to a first approximation it is proportional to **E** in magnitude. For a pure substance, **P** is given by

$$\mathbf{P} = \bar{\mathbf{m}}\frac{N_0}{\tilde{V}} = \bar{\mathbf{m}}\frac{N_0\rho}{M} \tag{4}$$

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

The moment of a polarized dielectric is equivalent to a moment that would result from electric charges of opposite sign on opposite surfaces of the dielectric. In a capacitor these "polarization charges" induce equal and opposite charges in the metal plates that are in contact with them. These induced charges are in addition to the charges that would be present at the same applied potential for the capacitor with a vacuum between the plates. Accordingly, the capacitance is increased by the presence of a polarizable medium. Thus the dielectric constant κ is greater than unity. By electrostatic theory it can be shown[4] that

$$\mathbf{D} = \varepsilon\mathbf{E} = \varepsilon_0\mathbf{E} + \mathbf{P} \tag{5a}$$

or

$$\kappa\mathbf{E} = \mathbf{E} + \frac{1}{\varepsilon_0}\mathbf{P} \tag{5b}$$

where $\mathbf{D}$ is the electric displacement and $\mathbf{E}$ is the electric field strength.

The average dipole moment $\overline{\mathbf{m}}$ for an atom or molecule in the medium is given by

$$\overline{\mathbf{m}} = \alpha\mathbf{F} \tag{6}$$

where we denote by $\mathbf{F}$ the *local* electric field and α is the polarizability (which is independent of field intensity if the field is not so intense that saturation is incipient). To a good approximation, $\mathbf{F}$ may be taken as the electric field intensity at the center of a spherical cavity in the dielectric within which the atom or molecule is contained. Thus $\mathbf{F}$ is the resultant of $\mathbf{E}$ and an additional contribution due to the polarization charges on the surface of the spherical cavity; electrostatic theory[4] gives

$$\mathbf{F} = \mathbf{E} + \frac{1}{3\varepsilon_0}\mathbf{P} \tag{7}$$

Combining this with Eq. (5*b*) we obtain

$$\mathbf{F} = \frac{\kappa + 2}{\kappa - 1}\frac{1}{3\varepsilon_0}\mathbf{P} \tag{8}$$

and using Eqs. (4) and (6) we obtain, for a pure substance,

$$\frac{\kappa - 1}{\kappa + 2}\frac{M}{\rho} = \frac{1}{3\varepsilon_0}N_0\alpha \equiv P_M \tag{9}$$

This is the *Clausius–Mossotti* equation. The quantity P_M is called the *molar polarization* and has the dimensions of volume per mole.

If the molecules have no permanent dipole moment, only distortion polarization takes place. The corresponding polarizability is denoted by α_0. If each molecule has a permanent dipole moment of magnitude μ, there is a tendency for the moment to become oriented parallel to the field direction, but this tendency is almost completely counteracted by thermal motion, which tends to make the orientation random. The component of the moment in the field direction is $\mu \cos \theta$, where θ is the angle between the dipole orientation and the field direction. The potential energy U of the dipole in a local field of intensity $\mathbf{F}$ is $-(\mu \cos \theta)F$, which is small in comparison with kT under ordinary experimental conditions. By use of the Boltzmann distribution, the average component of the permanent moment in the field direction is found to be

$$\overline{m}_\mu = [\mu \cos \theta \, e^{-U/kT}]_{\text{av}} = [\mu \cos \theta \, e^{\mu F \cos \theta / kT}]_{\text{av}}$$

$$\cong \mu\left[\cos \theta\left(1 + \frac{\mu F \cos \theta}{kT}\right)\right]_{\text{av}}$$

where the average is taken over all orientations in space. The average of cos θ vanishes, but the average of its square is $\frac{1}{3}$; accordingly, as found by Debye,

$$\overline{m}_\mu = \frac{\mu^2}{3kT}F \tag{10}$$

Thus the total polarizability is given by

$$\alpha = \alpha_0 + \frac{\mu^2}{3kT} \tag{11}$$

and the molar polarization can be written in the form

$$\begin{aligned} P_M = \frac{\kappa - 1}{\kappa + 2}\frac{M}{\rho} &= \frac{1}{3\varepsilon_0}N_0\left(\alpha_0 + \frac{\mu^2}{3kT}\right) \\ &= P_d + P_\mu \end{aligned} \tag{12}$$

where P_d and P_μ are, respectively, the distortion and orientation contributions to the molar polarization:

$$P_d = \frac{1}{3\varepsilon_0}N_0\alpha_0 \qquad \text{and} \qquad P_\mu = \frac{1}{3\varepsilon_0}N_0\frac{\mu^2}{3kT} \tag{13}$$

Equation (12) is known as the *Debye–Langevin equation.*

Immediately it is clear that a plot of P_M versus $1/T$ utilizing measurements of κ as a function of temperature will yield both α_0 and μ. This technique is readily applicable to gases. In principle it is applicable to liquids and solutions also, but it is seldom convenient owing largely to the small temperature range accessible between the melting point and boiling point.

In the foregoing derivation, a static (dc) electric field was assumed. The equations apply also to alternating (ac) fields, provided the frequency is low enough to enable the molecules possessing permanent dipoles to orient themselves in response to the changing electric field. Above some frequency in the upper radio-frequency or far-infrared range, the permanent dipoles can no longer follow the field and the orientation term in Eq. (12) disappears. At infrared and visible frequencies, the dielectric constant cannot be measured by the use of a capacitor. However, it is known from electromagnetic theory that, in the absence of high magnetic polarizability (which does not exist at these frequencies for any ordinary materials),

$$\kappa = n^2$$

where n is the *index of refraction.* We then obtain from Eq. (12) the relation of Lorentz and Lorenz:

$$R_M \equiv \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho} = \frac{1}{3\varepsilon_0}N_0\alpha_0 = P_d \tag{14}$$

where R_M is known as the *molar refraction.* Thus the distortion polarizability α_0 can in principle be obtained from a measurement of the refractive index at some wavelength in the far infrared where the distortion polarization is virtually complete. However, it is not experimentally convenient to measure the index of refraction in the infrared range. The index of refraction n_D measured with the visible sodium D line can usually be used instead. Although the atomic contribution to the distortion polarization is absent in the visible, and the electronic contribution is not in all cases at its dc value, these variations in the distortion polarization are small and usually negligible in comparison with the orientation polarization. The measurement of n_D can be made conveniently in an Abbe or other type of refractometer (see Chapter XX). Thus P_d can be measured independently from P_M, and P_μ can be determined by difference. By this means μ can be determined from measurements made at a single temperature.

Measurements in Solution. We are concerned here with a dilute solution containing a polar solute 2 in a nonpolar solvent 1. The molar polarization can be written

$$P_M = X_1 P_{1M} + X_2 P_{2M} = \frac{\kappa - 1}{\kappa + 2} \frac{(M_1 X_1 + M_2 X_2)}{\rho} \tag{15}$$

where the X's are mole fractions, M's are molar masses, and κ and ρ (without subscripts) pertain to the solution. Since a nonpolar solvent has only distortion polarization, which is not greatly affected by interactions between molecules, we can take P_{1M} to have the same value in solution as in the pure solvent:

$$P_{1M} = \frac{\kappa_1 - 1}{\kappa_1 + 2} \frac{M_1}{\rho_1} \tag{16}$$

We can then get P_{2M} from

$$P_{2M} = \frac{1}{X_2} (P_M - X_1 P_{1M}) \tag{17}$$

obtained by rearrangement of Eq. (15).

Values of P_{2M} calculated using Eq. (17) are found to vary with X_2, generally increasing as X_2 decreases. This effect arises from strong solute–solute interactions due to the permanent dipoles. This difficulty can be eliminated by extrapolating P_{2M} to infinite dilution ($X_2 = 0$) to obtain P^0_{2M}. Although this could be done by plotting P_{2M} for each of a series of solutions against X_2, it is easier and more accurate to follow the procedure of Hedestrand,[5] which is given below.

Let us assume a linear dependence of κ and ρ on the mole fraction X_2:

$$\kappa = \kappa_1 + aX_2 \tag{18}$$

$$\rho = \rho_1 + bX_2 \tag{19}$$

On writing out Eq. (17) explicitly and using Eqs. (16), (18), and (19), it is possible to rearrange terms and obtain the *limiting* expression

$$P^0_{2M} = \frac{3M_1 a}{(\kappa_1 + 2)^2 \rho_1} + \frac{\kappa_1 - 1}{(\kappa_1 + 2)\rho_1} \left(M_2 - \frac{M_1 b}{\rho_1} \right) \tag{20}$$

Thus measurements on solutions of the *slope* of κ versus X_2 and the *slope* of ρ versus X_2 enable us to calculate the limiting molar polarization of the solute in solution. If we assume that the molar distortion polarization in an infinitely dilute solution is equal to that in the pure solute, then

$$P^0_{2d} = R_{2M} = \frac{n_2^2 - 1}{n_2^2 + 2} \frac{M_2}{\rho_2} \tag{21}$$

where n_2 is the index of refraction and ρ_2 is the density measured for the solute in the pure state. From these two expressions, we can obtain the molar orientation polarization of the solute at infinite dilution:

$$P^0_{2\mu} = P^0_{2M} - P^0_{2d} = \frac{1}{3\varepsilon_0} N_0 \frac{\mu^2}{3kT} \tag{22}$$

On substituting the numerical values of the physical constants, we obtain

$$\mu = 42.7(P_{2\mu}^0 T)^{1/2} \times 10^{-30}\ \text{C m} \tag{23a}$$

$$= 12.8(P_{2\mu}^0 T)^{1/2}\ \text{debye} \tag{23b}$$

where $P_{2\mu}^0$ is given in $m^3\ mol^{-1}$ units and T is in kelvin. The unit of molecular dipole moment universally used by chemists is the debye (D), historically defined as 10^{-18} esu cm, where esu is the electrostatic unit of charge having the value 3.33564×10^{-10} C. Thus 1 D $= 3.33564 \times 10^{-30}$ C m.

An alternative expression for $P_{2\mu}^0$ has been given by Smith,[6] who improved a method of calculation first suggested by Guggenheim.[7] This expression presupposes knowledge of the index of refraction n of the *solution,* and assumes that

$$n^2 = n_1^2 + cX_2 \tag{24}$$

where c, like a and b, is a constant determined by experiment. It follows[6] that

$$P_{2\mu}^0 = \frac{3M_1}{\rho_1}\left[\frac{a}{(\kappa_1 + 2)^2} - \frac{c}{(n_1^2 + 2)^2}\right] \tag{25}$$

This expression is an approximate one that holds when $\kappa_1 - n_1^2$ is small (as in the case of benzene, where it is 0.03) and M_2 and b are not too large. It is a useful form when the index of refraction n_2 of the pure solute is inconvenient to determine; this is often the case when the pure solute is solid. Note also that Eq. (25) does not require a knowledge of the densities of the solutions.

Solvent Effects. The values of P_{2M}^0 obtained from dilute solution measurements differ somewhat from P_M values obtained from the pure solute in the form of a gas. This effect is due to solvent–solute interactions in which polar solute molecules induce a local polarization in the nonpolar solvent. As a result μ as determined in solution is often smaller than μ for the same substance in the form of a gas, although it may be larger in other cases. Usually the two values agree within about 10 percent. A discussion of solvent effects is given in Ref. 4.

METHOD

A capacitance cell suitable for work with liquids or solutions is shown in Fig. 1; it is made with a small variable-air capacitor of the type formerly in common use in radios and electronic circuits. It should have a maximum capacitance of 50 to 200 pF. This device is more convenient than a fixed-plate capacitor, since with the latter device it is necessary to measure separately the stray capacitance due to electrical leads, etc. In the cell shown, the variable capacitor is used in two positions: fully closed (maximum capacitance) and fully open (minimum capacitance); these positions are defined by mechanical stops for the pointer on the knob that rotates the capacitor shaft.† The difference ΔC between the closed (b) and open (a) positions is independent of the stray capacitance. Thus the dielectric constant of the liquid or solution is given by

$$\kappa = \frac{\Delta C(\text{liq})}{\Delta C(\text{air})} \tag{26}$$

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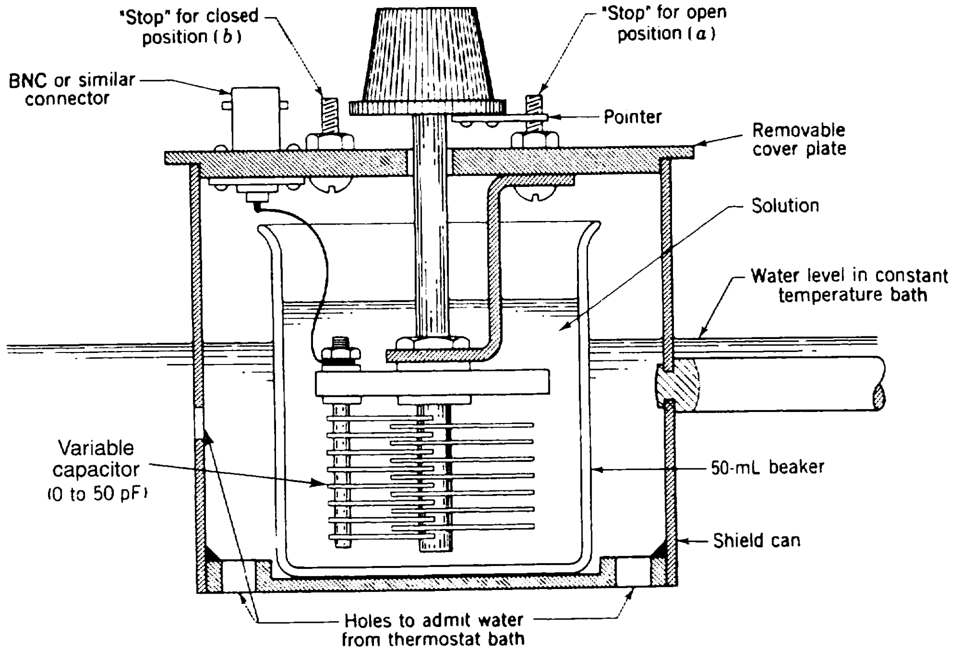
†For high-precision work with very stable electronics, a fixed-plate capacitor cell is preferable, since it eliminates any error due to lack of reproducibility in setting a variable capacitor. However, in this case, one must determine the capacitance of the leads from measurements on a material of known dielectric constant.

FIGURE 1
Variable-capacitance dielectric cell for solutions.



where $\Delta C = C_b - C_a$. For liquids and solutions it is possible to use air instead of vacuum, since the dielectric constant of air is very close to unity.

We now turn our attention to methods of measuring the capacitance. A very precise method, and one that is particularly useful when the liquid or solution has a high conductance, involves the use of a capacitance bridge.[8] For the present system, in which the conductance is small, less expensive instruments can be used. Among these are digital capacitance meters made by a variety of manufacturers (see listings given by Tucker Electronics Co., Garland, TX) with capacitance ranges down to 1 to 200 pF, readability of ±0.1 pF, and accuracy of 1 pF or better. These are very simple to operate, give capacitance readings directly, and are suitable for use in the present experiment, but their use gives little insight into the physical principles involved in capacitance measurement.

Several traditional methods are based on use of an electrical oscillator incorporating an inductance L and a capacitance C in parallel; this combination is known as a "tank" circuit. The frequency of such an oscillator is given by

$$f = \frac{1}{2\pi\sqrt{LC}} \tag{27}$$

The inductance L is fixed, while the capacitance C is the sum of several separate capacitances: that of the conductance cell, C_X; that of a separate variable tank capacitor incorporated in the oscillator, C_T (if present); and stray capacitances due to leads, etc., C_S. Also present in some methods is a precision air capacitor C_P graduated directly in capacitance units (generally picofarads), used when the equipment is operated in a null mode. In this mode the precision air capacitor is used to bring the frequency f to the same value in each measurement, and the change in reading of the precision air capacitor is then equal in magnitude to the change in capacitance of the cell.

An important and precise traditional method of measuring capacitance for dipole moment determinations is the *heterodyne beat* method, a particular form of the null method mentioned above. The output of an LC oscillator incorporating the capacitance cell and a precision variable air capacitor is mixed with the output of a fixed-frequency oscillator to produce a difference frequency in the audio range. This is typically applied to the vertical plates of an oscilloscope while the fixed-frequency output of a stable audio oscillator is applied to the horizontal plates. In each determination the precision air capacitor is adjusted so that the two audio frequencies are equal, as indicated by the appropriate Lissajous figure (circle, ellipse, or slant line) on the oscilloscope screen; see Fig. XX-6. An instrument that has been widely used for this purpose, incorporating the fixed oscillator, the variable oscillator, and the mixer, is the WTW Dipolmeter, model DM01. This instrument unfortunately is no longer produced; however, such instruments are present in many physical chemistry laboratories. This instrument requires the minor modification of removing an existing capacitor from the tank circuit and introducing connections for leads for external capacitors, namely, the capacitance cell and the precision air capacitor (such as GenRad 1304B).

With the advent of inexpensive, fast frequency counters, which count the individual cycles over a precisely fixed period (usually 1 s) and display the frequency digitally, it is more convenient to connect the radio-frequency output of the variable-frequency oscillator directly to the frequency counter and determine the total capacitance with the aid of Eq. (27). This technique is highly suitable for the present experiment if a WTW Dipolmeter or another *LC* oscillator is available or can be constructed. (With the Dipolmeter only the variable-frequency oscillator is used.) A simple *LC* oscillator circuit that can be constructed from inexpensive components has been described by Bonilla and Vassos:[9] this circuit, with a small modification to provide for one side of the tank to be grounded, is shown in Fig. 2. In this circuit, as in the WTW Dipolmeter circuit, all tank capacitances are in *parallel*. [This is *not* true of the circuit described in Ref. 4 of Exp. 31, as that circuit incorporates some *series* capacitance. If that circuit is employed, Eqs. (28) to (30) are not valid and Eqs. (31-3) to (31-5) must be used instead, unless the null mode is employed.]

It follows from Eq. (27) that

$$C = C_X + C_T + C_S = \frac{1}{4\pi^2 L f^2} \tag{28}$$

The capacitance of the cell can be determined from measurements of the frequency at the closed (*b*) and open (*a*) positions using the following equation, in which the capacitances C_T and C_S cancel out since they are held constant:

$$C_X = C(b) - C(a) = \frac{1}{4\pi^2 L}\left(\frac{1}{f_b^2} - \frac{1}{f_a^2}\right) \tag{29}$$

To eliminate the apparatus constant $1/4\pi^2 L$ and determine the dielectric constant, we combine this with Eq. (26) and obtain

$$\kappa = \left(\frac{1}{f_b^2} - \frac{1}{f_a^2}\right)_{\text{sample}} \Big/ \left(\frac{1}{f_b^2} - \frac{1}{f_a^2}\right)_{\text{air}} \tag{30}$$

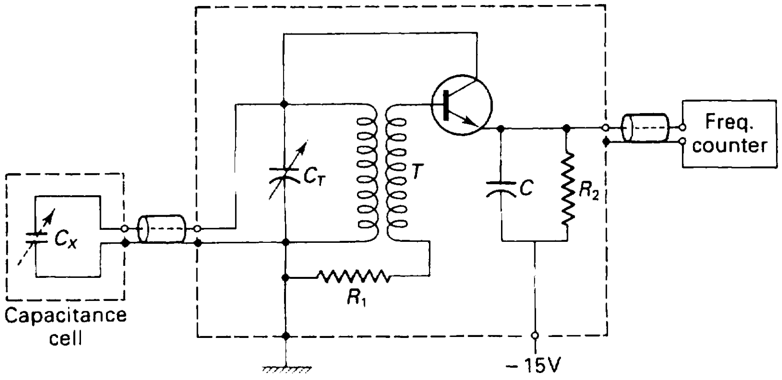
Another type of electronic circuit, the relaxation oscillator, can be used to measure capacitance; a simple apparatus for this purpose has been described by Kurtz, Anderson, and Willeford.[10]

EXPERIMENTAL

Although several methods for making the capacitance measurements have been suggested, we will limit our discussion to the use of the *LC* oscillator and frequency counter shown in Fig. 2.

FIGURE 2

A simple oscillator circuit for capacitance measurements, adapted from Bonilla and Vassos.[9] The transistor is 1N3904 or a similar type. Suggested parameters: radio-frequency transformer T, 0.6 mH; R_1 and R_2, 12 kΩ; C, 300 pF; C_T, 0 to 100 pF. The circuit should be housed in a metal box for shielding, and connections with the capacitance cell and the frequency counter should be made with shielded coaxial cable with BNC or similar connectors.



With the cell capacitor and cell beaker clean and dry, assemble the cell and mount it in a constant-temperature bath set at 25°C. Set the cell capacitor at the open position (*a*). Turn on the oscillator and the frequency counter, and adjust the tank capacitance C_T to yield a frequency in the range of 1.3 to 1.5 MHz. Wait a while to make sure that the apparatus is operating stably and not drifting in frequency. Determine the frequencies f_a and f_b in alternation at intervals of 30 s by alternating the position of the pointer knob between (*a*) and (*b*) until four to six frequency values have been recorded at each position. Make certain that you do not alter C_T or move the leads so as to affect C_S during either set of measurements.

Rinse the cell beaker and variable capacitor with the pure nonpolar solvent, fill the cell beaker to a level that will completely immerse the capacitor plates, and reassemble the cell. Make measurements in the open and closed positions as described above. Repeat this procedure with all the solutions of the polar solute in the nonpolar solvent. Note the temperature of the bath.

Handle the capacitor with care; damage to the plates will affect the frequency values.

Average the frequency readings for each determination, and calculate the 95 percent confidence limit for each mean (see Chapter IIB).

Dichlorobenzene. Measurements should be made on pure benzene and on dilute solutions of *o*- and *m*-dichlorobenzene. Make up 50 or 100 mL of each solution as follows. Weigh a dry, clean volumetric flask; add an appropriate amount of solute using a Mohr pipette; and weigh again. Now carefully make up to the mark with benzene and reweigh. Suggested concentrations are 1, 2, 3, and 4 mole percent of solute. The densities can be calculated from these weighings. If desired, the refractive index of each solution can also be measured with an Abbe refractometer so that Guggenheim's method of calculation can be used.

Succinonitrile. Measurements should be made on pure benzene and on dilute solutions of succinonitrile and propionitrile (or acetonitrile). Make up 50 or 100 mL of each solution in the same manner as described above. Densities can be calculated and/or refractive indexes can be measured.

CALCULATIONS

For each solution studied, calculate κ from Eq. (30) as well as ρ and X_2. Plot κ and ρ versus the mole fraction of solute X_2, and draw the best straight lines through your points; see Eqs. (18) and (19). Obtain the slopes a and b; the intercepts should agree with the pure solvent results. Using Eq. (20), calculate P_{2M}^0, the molar polarization at infinite dilution. Estimate P_{2d}^0 from Eq. (21) using the literature value of the refractive index of the solute n_2, and obtain $P_{2\mu}^0$.

Alternatively, Guggenheim's method can be used if the indexes of refraction were measured for each solution. Plot κ and n^2 versus X_2 and draw the best straight lines through your points; see Eqs. (18) and (24). Using Eq. (25) and the appropriate slopes a and c, calculate $P_{2\mu}^0$. It would be instructive to follow both of these procedures and see what difference (if any) the method of extrapolation to infinite dilution has on the $P_{2\mu}^0$ values.

Finally, calculate the dipole moment from Eq. (23) in units of 10^{-30} C m, and report it also in debye units (D).

DISCUSSION

Dichlorobenzene. Compare your experimental results with the values computed from a vector addition of carbon–chlorine bond moments obtained from the dipole moment of monochlorobenzene (5.17×10^{-30} C m, or 1.55 D). If they do not agree, suggest possible physical reasons for the disagreement.

Succinonitrile. An excellent discussion of this system has been presented by Braun, Stockmayer, and Orwoll,[11] who were the first to propose studying the dipole moment of succinonitrile. They show that the average square of the dipole moment is given by

$$\langle \mu^2 \rangle = \tfrac{8}{3}(1 - X_t)\mu_1^2 \tag{31}$$

where X_t is the mole fraction in the trans form and μ_1 is the C—C≡N bond moment as determined from the dipole moment of either propionitrile or acetonitrile. Thus a measurement of μ^2 for succinonitrile will determine the distribution of molecules among the three "rotational isomeric" states at the given temperature. [Note that $X_+ = X_- = \frac{1}{2}(1 - X_t)$, since the gauche plus and gauche minus states are equivalent.] It can also be shown from the appropriate Boltzmann populations that

$$X_t = (1 + 2e^{-\Delta E/RT})^{-1} \tag{32}$$

where $\Delta E = E(\text{gauche}) - E(\text{trans})$. Thus the value of X_t obtained from Eq. (31) will determine the value of ΔE and one can predict the temperature dependence of μ. Calculate a value of X_t and ΔE from your results and predict the value of μ at 280 and 350 K.

Theoretical Calculations. As a project exercise for the class, dipole moments of the molecules studied might be calculated using an ab initio program such as Gaussian (see discussion of this program in Chapter III). Calculations at the Hartree–Fock level using the STO-3G basis set will be reasonably fast but will generally yield low values for the dipole moments of substituted benzenes.[12] Use of a 6-31G* or higher basis set would give better results, and this might be explored if computer time permits. Do the calculation also for chlorobenzene and use the calculated dipole moments of the three compounds to test the idea of bond dipole addition. A similar test could be done for succinonitrile using the dipole calculated for propionitrile or acetonitrile. It would also be interesting to calculate the energies of the trans and gauche forms of succinonitrile for comparison of the difference with your experimental ΔE value.

SAFETY ISSUES

Benzene can have both chronic and acute toxic effects. The risk of acute effects is low, since acute symptoms occur only at 1000 ppm or higher. *Chronic* vapor inhalation at the level of 25 to 50 ppm can cause changes in blood chemistry, and *continual* exposure at 100 ppm can cause severe blood disorders. The OSHA exposure limits for benzene vapor are 1 ppm as an 8-hour time-weighted average and a ceiling of 50 ppm for no more than 10 min. In order to reach the level of 10 ppm in a laboratory of 750 m^3 volume, 23 g of liquid benzene would have to evaporate into a closed atmosphere. Thus the hazards associated with the infrequent use of liquid benzene in a well-ventilated laboratory are very low.

Chlorobenzenes are also toxic substances that must be handled with care. Both benzene and solutions containing benzene or chlorobenzenes must be disposed of properly in a designated waste container.

APPARATUS

Capacitance cell as shown in Fig. 1; oscillator as described in the text and Fig. 2; frequency counter (range at least 0.5 to 5 MHz); shielded coaxial cables with connectors; five 50- or 100-mL volumetric flasks; a 5-mL Mohr pipette; acetone wash bottle; rubber pipette bulb.

Benzene (analytical grade, 500 to 1000 mL; *o*- and *p*-dichlorobenzene (10 to 20 mL each), or succinonitrile and propionitrile (10 to 20 mL each); constant-temperature bath set at 25°C.

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EXPERIMENT 31

Dipole Moment of HCl Molecules in the Gas Phase

The permanent dipole moment μ of a polar molecule is determined in Exp. 30 from measurements of the dielectric constant of a solution containing such molecules as solute. In the present experiment, the permanent dipole moment of a gas molecule is determined. The orientation polarization can be separated from the distortion polarization by means of measurements at more than one temperature, making use of the fact that the former is temperature dependent while the latter is not. An alternative method, which is recommended for this experiment, is to obtain the orientation polarization by subtracting from the molar polarization the distortion polarization as determined separately from the refractive index of the gas, which is determined by means of a laser interferometer.[1] Thus the molar polarization needs to be determined at only one temperature.

The gas recommended is hydrogen chloride, HCl, because it has a large permanent dipole moment and because it has a boiling point low enough (−83.7°C) to permit measurements of dielectric constant to be made down to Dry Ice temperature (−78.5°C) if the option of measuring the dielectric constant at more than one temperature is chosen.

Thus the experiment consists of two parts: the measurement of the dielectric constant of the gas by a method similar in principle to that of Exp. 30, and the measurement of the refractive index with an interferometer. The measurement of a dielectric constant at more than one temperature constitutes a complete stand-alone experiment, independent of the refractive index measurement; the measurement of refractive index can be used as a stand-alone experiment if a value for the low-frequency dielectric constant is supplied to permit the calculation of the dipole moment.

THEORY

The concepts of permanent dipole moment, induced dipole moment, and molar polarization are discussed in Exp. 30; this material should be reviewed. We assume further that deviations from the perfect-gas law are small in comparison with the experimental uncertainties.