2. Optical and electrical properties of molecules

2.b. Permittivity measurement of liquid substances

Permittivity as well as refractive index are important macroscopic constants that characterize the properties of the investigated substances in terms of their behaviour in the external electric field.

Experimentally, we usually measure relative permittivity.

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \qquad (2.1.)$$

where ε_o is permittivity of the vacuum $8{,}854.10^{-12} C.m^{-1}V^{-1}$. ε is absolute permittivity (formerly dielectric constant), which is a measure of substance polarity.

The relative permittivity can also be determined as the ratio of the capacitance C of the capacitor whose dielectric is the substance under investigation and the capacitance of the same capacitor C_o whose dielectric is the vacuum:

$$\varepsilon_r = \frac{C}{C_0} \cong \frac{C}{C_{air}} \qquad (2.2.)$$

Here the capacity C_o can be replaced by the air capacity C_{air}, because relative permittivity of dry air is approximately equal to one (exactly *1,000536* at *25°C* and *101,33 kPa*).

The capacity measurement, which is realized by a two-shell capacitance vessel, is used for the determination of the relative permittivity. The capacitance plates are two concentric cylinders from non-corrosive metal, which are insulated with a quartz or teflon ring. The measured liquid is poured into the space between the two cylinders. The capacitance vessel is connected to the dielectric resonance circuit of the dielectrometer, which works on the electro-compensation principle. Without connecting the capacitance vessel to device, the resonant circuit can be tuned to the auxiliary capacitance so that the external capacity is "zero". When the capacitance vessel is connected to device, the resonance is broken and the deflection appears on the device indicator. We repeat the compensation of the circuit and measure the external capacity C_m.

The external capacitance is composed of the container's own capacity, which is equal to $\varepsilon_{rel}.C_o$ and of the capacity of the connectors C_p :

$$C_m = \varepsilon_{rel} C_0 + C_p \qquad (2.3.)$$

To determine the relative permittivity of the liquid ε_{rel}, it is therefore necessary to know the parameters C_o and C_p from the measurement of at least two liquids with known ε_{rel} values.

An increase in the capacity of the capacitor by inserting a measured dielectric between its plates is due to the polarization of this dielectric. Polarization also occurs in nonpolar molecules. We therefore recognize induced polarization for nonpolar molecules and orientation polarization for polar molecules. In the electric field $\vec{E}$, both types of molecules are oriented in the opposite direction to the electric line forces and weaken the intensity of the electric field by theirs own polarization effect $\overleftarrow{P}$:

$$\overleftarrow{P} = (\varepsilon_r - 1)\varepsilon_0 \vec{E} \qquad (2.4.)$$

By multiplying the polarization P by the molar mass M of the monitored substance we obtain the value of the molar polarization P_M. Each polar molecule contributes to the total molar polarization with its molar induced polarization P_{in} and with the molar orientation polarization of P_{or} . The relationship between relative permittivity ε_{rel} and P_M polarization is given by Debye's equation:

$$P_M = P_{in} + P_{or} = \frac{\varepsilon_{rel} - 1}{\varepsilon_{rel} + 2} \cdot \frac{M}{\rho} \qquad (2.5.)$$

where ρ is specific mass of the substance under view.

The eqn (2.5.) was derived assuming the molecules of the polar substance are sufficiently distant from each other, so they do not interact with each other. However, this assumption is not fully met when polar substances are measured in the condensed state. Therefore, the molar polarization value of the polar liquids is obtained from the experimental data of their solutions in nonpolar solvents depending on the concentration. The subsequent extrapolation to infinite dilution is used for an obtaining of the molar polarization.

In the case of a non-polar substance ($P_{or} = 0$), the molar induced polarization P_{in} consist of electron polarization P_e and atomic polarization P_a. At the same time, the atomic molar polarization P_a is equal to the difference between the molar polarization P_M and the molar refraction R_M (also called optical polarization):

$$P_a = P_{in} - P_e = P_M - R_M \qquad (2.6.)$$

Refraction of R_M is obtained by measuring refractive index n using refractometer (see relationship

$$R_M = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} = \sum \nu_i \cdot R_A^i \qquad (2.7.)$$

Molar polarization of P_M is obtained by measuring relative permittivity (see relation (2.5.)).

? **TASK:** Measure relative permittivity of homological series of aliphatic alcohols. Measure the relative permittivity and refractive index of two non-polar liquids and calculate the difference between molar refraction and molecular polarization values. Estimate the ratio of the molar atom polarization to the molar polarization.

LABORATORY AIDS AND CHEMICALS: Dielectrometer equipped by capacity vessel, refractometer, pycnometer, automatic pipette, syringes; benzene, cyclohexane, trichloromethane, carbon tetrachloride, methanol, ethanol, propanol, butanol, pentanol, hexanol.

Certain substances used in this task are harmful to health. Therefore, we work in the fume hood and use the automatic pipettes or syringes.

Instructions:

1. **Calibration of the capacitance vessel.** At laboratory temperature, we measure the capacity C_m of the three selected dielectrics with a known ε_{rel} value (see **TABLE I**). When selecting air as a dielectric, it is sufficient to measure the capacity of an empty dry capacitance vessel. Then, continue with benzene and trichloromethane for example.

2. **Measurement of relative permittivity.** First, measure a homological series of aliphatic alcohols. Begin with the lowest homologue and move towards higher homologues. Do not wash the capacitance vessel, but let it dry out. Continue by measuring capacity C_m for non-polar substances (carbon tetrachloride and cyclohexane).
3. **Measurement of refractive index and density for non-polar substances.** Measure the refractive index n_D of tetrachloromethane and cyclohexane using refractometer with sodium lamp. The values should not differ noticeably from the n_D values given in **TABLE I**. Subsequently, measure the density of the substances. Use the glass pycnometer for example. Return the content of the pycnometer back to the original bottle with the liquid being examined only if you are sure about the substance.

DATA ANALYSIS: To calculate the relative permittivity of the examined alcohols from experimental C_m according to eqn (2.3.), the parameters C_o and C_p must be known. We evaluate the parameters from calibration of the capacitance vessel. Plot linear function C_m vs. ε_{rel} (2.3.) and find the slope (i.e. C_o) and intercept (i. e. C_p). The calibration has to be repeated if the coefficient of determination $R^2 > 0.95$.

REPORT: Table 1: the measured calibration values of the capacity C_m and their tabulated relative permittivity ε_{rel} .(**TABLE I**). **Graph 1:** calibration plot C_m vs. ε_{rel} . Parameters C_o and C_p . **Table 2:** for homological series of aliphatic alcohols: experimental capacity C_m, and relative permittivity ε_{rel} , tabulated permittivity from **TABLE II**. **Graph 2**: experimental dependence of relative permittivity on the number of carbons in the alcohol molecule. **Table 3:** the table according to the task for density determination using pycnometer. **Tabule 4:** for tetrachloromethane and cyclohexane: experimental and tabulated refractive index n and specific mass ρ, experimental values C_m and ε_{rel} , molar mass M_r, calculated value of molar polarization P_m using eqn (2.5.), molar refraction R_m ((2.7.), atomic polarization P_a and ratio P_a / P_m (in %).

TABLE I: Specific mass, relative permittivity and refraction index of some liquids. The refractive index is valid for 20°C and a wavelength of 589.3 nm (yellow sodium doublet).

substance	ρ_{20} / kg m^{-3}	ε_{rel}^{20}	n_D^{20}
water	*998.2*	*80.360*	*1.3330*
trichloromethane	*1498.5*	*4.810*	*1.4467*
benzene	*879.0*	*2.282*	*1.5015*
tetrachloromethane	*1595.0*	*2.236*	*1.4607*
cyclohexane	*779.0*	*2.020*	*1.4266*

TABLE II: Hodnoty relativních permitivit vybraných alkoholů.

látka	methanol	ethanol	n-propanol	n-butanol	n-pentanol	n-hexanol
ε_{rel}^{20}	*33,5*	*25,1*	*21,0*	*17,9*	*15,0*	*13,1*