THE USE OF MOLAR REFRACTION IN PHYSICO-CHEMICAL STUDIES

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Task 12a

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I. Aim of the experiment

The purpose of this task is to use molar refraction to determine the molecular structure of 1,4-dioxane and the concentration of 1,4-dioxane in aqueous solution.

II. Introduction

1. The laws of reflection and refraction of the light.
2. The index of refraction.
3. Molar refraction.
4. Additivity of molar refraction of the compound and mixtures.

References:

1. A. Goel, *Surface Chemistry*, Discovery Publishing Pvt. Ltd., 2006.
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3. K. Rębilas, Refraktometr Abbego. Pomiar współczynnika załamania światła i wyznaczanie stężenia roztworów. W: Materiały dydaktyczne (ćwiczenia laboratoryjne) [on-line]. krzysztofrebilas.republika.pl.
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III. Theory

III.1. Refraction of light

The light, or other waves, when passing through a boundary between two different isotropic media, is refracted (Fig. 1).

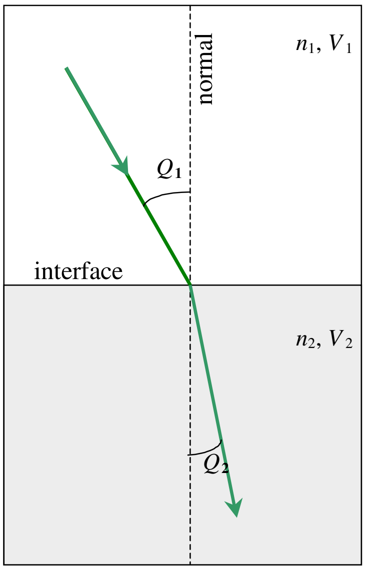

Fig. 1. Refraction of light.

According **the Snell's law** the ratio of the sines of the angles of incidence (Q_1) and refraction (Q_2) is equivalent to the ratio of light velocities in the two media, equal to the index of refraction (n):

$$n = \frac{n_1}{n_2} = \frac{V_1}{V_2} = \frac{\sin Q_1}{\sin Q_2} \quad (1)$$

where n_1, n_2 are the refractions indices in the media relative to the vacuum, and V_1, V_2 are the light velocities in these two media. **The index of refraction** is the unitless value and it depends on temperature and pressure.

According **the Lorentz-Lorenz equation**, the substance is characterized by **specific (*r*)** and **molar (*R*) refractions**, which are given as follows:

$$r = \frac{n^2 - 1}{n^2 + 2}\frac{1}{d} \quad (2)$$

$$R = \frac{n^2 - 1}{n^2 + 2}\frac{M}{d} \quad (3)$$

where d is the density and M is the molecular weight of the substance.

The molar refraction is expressed in m^3/mol and is constant for a given substance and independent of temperature and pressure, but depends on the light wavelength for which it is determined. Molar refraction, as the additive property depends upon both the number and arrangement of atoms in the molecule:

$$R = \sum n_i R_i \tag{4}$$

where n_i is the number of elements or groups in the molecule and R_i is the value of molar refraction of a given element or group.

Refraction gives the idea about geometry and structure of molecule. It can be used to determine the structure of unknown compound whose molecular formula is known. In **Tables 1** and **2** the values of molar refractions of elements or groups of elements and bonds measured with the D-line of sodium are presented.

The molar refraction can be calculated using **equation (4)** or **(3)** when the refractivity index and density of the substance are determined experimentally of a given temperature.

Table 1. Molar refraction contributions of atoms and groups measured with the D-line of sodium.

Name	Symbol	$R_D \cdot 10^6$ [m^3/mol]
carbon	C	2.418
hydrogen	–H	1.100
oxygen in carbonyl group	=O	2.211
oxygen in hydroxyl group	–O–	1.525
oxygen in ethers	>O	1.643
nitrogen in primary aliphatic amines	$–NH_2$	2.322
nitrogen in secondary aliphatic amines	–NH–	2.502
nitrogen in tertiary aliphatic amines	≡N	2.840
sulfur in mercaptans	–SH	7.690
single bond		1.733
triple bond		2.336
benzene ring		5.200

Table 2. Molar refraction contributions of bonds measured with the D-line of sodium.

Symbol	$R_D \cdot 10^6$ [m^3/mol]	Symbol	$R_D \cdot 10^6$ [m^3/mol]
C–H	1.68	C=S	11.91
C–N	1.57	N–H	1.76
C=N	3.76	O–H	1.80
C–F	1.44	Si–C	2.52
C–Cl	6.51	Si–H	3.17
C–Br	9.39	P–C	3.58

C–I	14.61	P–H	4.01
C–C	1.296	P–O	3.10
C=C	4.17	S–H	4.80
C≡C	6.24	S–O	4.94
C–O	1.54	S→O	0.20
C=O	3.32	N–N	1.99

The molar refraction of mixture (*R_{mix}*) is the additive property as well. It means that this is a sum of molar contributions of particular components molar refractivity:

$$R_{mix} = \sum x_i R_i \tag{5}$$

where x_i and R_i are the values of molar fraction and refraction of component "*i*" in the mixture. For a two-component mixture this equation has he following form:

$$R_{mix} = x_1 R_1 + x_2 R_2 \tag{6}$$

The molar refraction of mixture can be calculated from the refractivity index (n_{mix}), and in the case of a two-component mixture the following equation is applied:

$$R_{mix} = \frac{n_{mix}^2 - 1}{n_{mix}^2 + 2} \frac{x_1 M_1 + x_2 M_2}{d_{mix}} \tag{7}$$

where M_1 and M_2 are the molecular weights of mixture components and d_{mix} is the density of a mixture.

The measurement of refractivity index can be used to determine the concentration of unknown solution.

III.2. Abbe refractometer – the principle of operation and optical scheme

Let us assume that a beam of light passes from the medium with a higher optical density to a lower density medium. In this case, only beams falling at an angle of less or equal to critical value pass through the border between these media. In the reverse situation, i.e., when the beam falls from the medium of a less optical density, it passes the border regardless of the angle of incidence. In this case, the largest value of refraction angle is equal to the critical angle. This feature is used in the Abbe refractometer to measure the refractive index.

The principle of refractometer is shown in **Figure 2**. The essential elements of refractometer are two glass prisms (P1 and P2) of high refractive index. Between the prisms a sample, i.e., a few drops of liquid, is introduced. The surface of prism P1 is rough and disperses the light that falls on it in all possible directions. This dispersed light refracts at the border between liquid and prism P2. The light limited by the critical beam enters the prism P2, as the optically denser medium. The border between the light and dark regions corresponds to the critical beam in the prism P2, which depends on the refractive index of liquid.

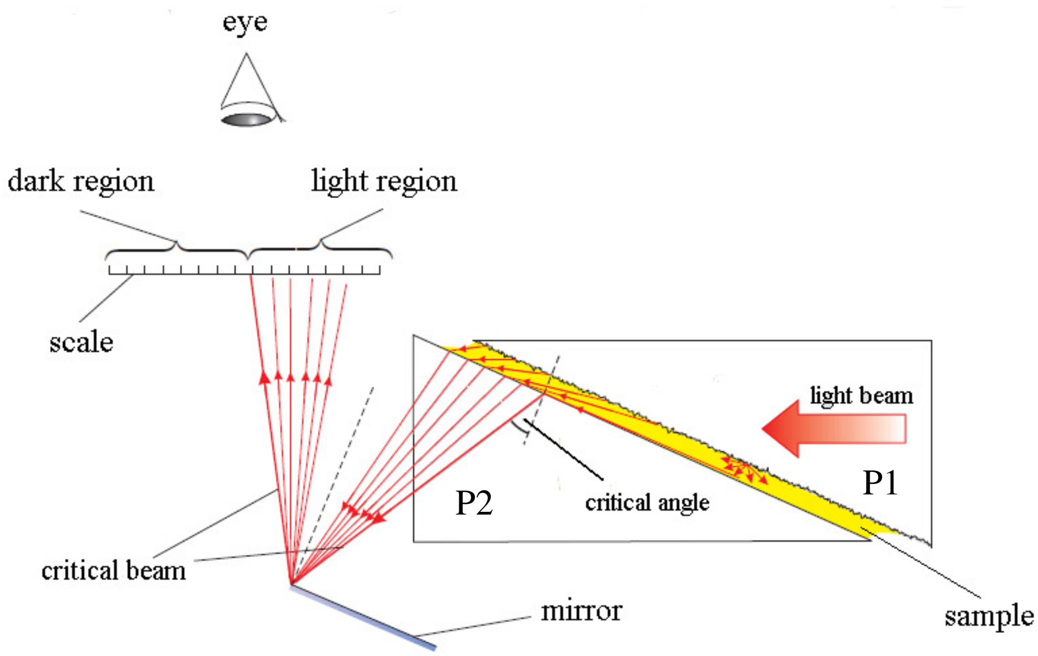

Fig. 2. Abbe refractometer - the principle of operation [3].

The optical scheme of Abbe refractometer is presented in Figure 3.

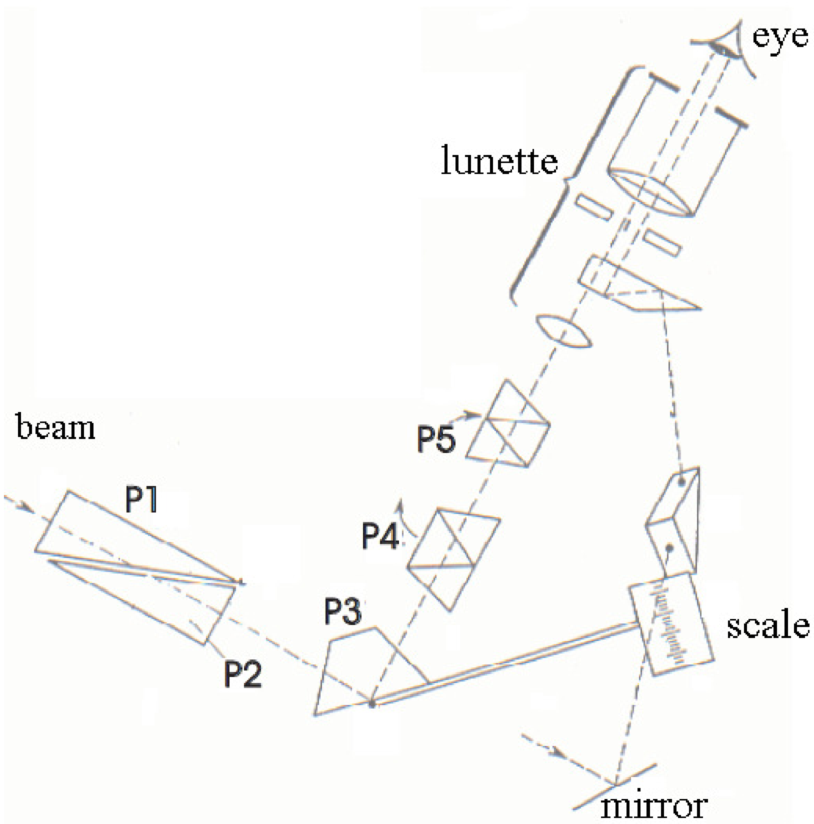

Fig. 3. Abbe refractometer – the optical scheme [3].

IV. Experimental

A. Devices and materials

1. **Device:**
   – Abbe refractometer,
   – temperature control system.
2. **Equipment:**
   – measuring flask – 25 cm^3 – 5 u,
   – graduated pipette: 2.5 and 10 cm^3.
3. **Materials:**
   – distilled water,
   – 1,4-dioxane (pure).

B. Program

1. Preparation of the temperature control system for the measurements:
   – turn on the temperature control system;
   – set a slight flow of water;
   – set the correct temperature, i.e. 20°C.
2. Determination of 1,4-dioxane structure.
3. Determination of unknown concentration of 1,4-dioxane in aqueous solution.

C. Use of devices

Abbe refractometer (Fig. 4) is used to measure the refractivity index of liquid.

Fig. 4. Abbe refractometer.

To conduct measurements:

– apply the liquid sample (typically 3 to 4 drops) to the prism,
– close the prism assembly,
– open the window in the moving part of prism assembly,
– if you do not see a light and a dark region, adjust the lower handwheel (on the right side of the instrument) (Fig. 4) until you do,

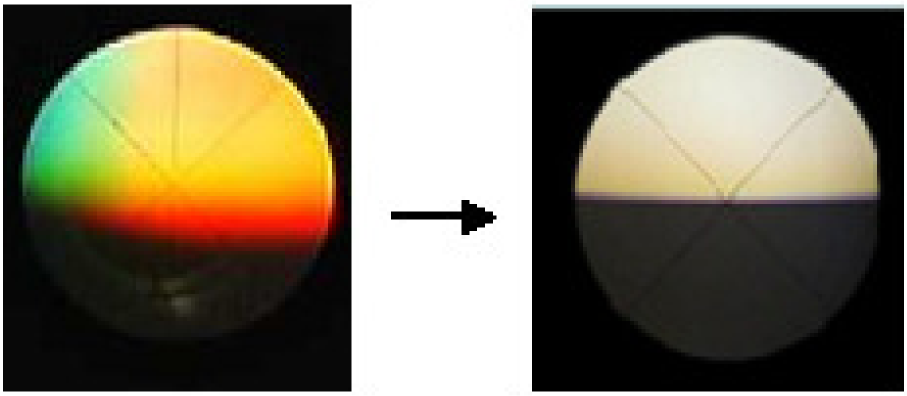

Fig. 5. How to sharpen the borderline between the dark and the light regions [4].

– to adjust the lamp position and to sharpen the borderline between the light and the dark regions use the upper handwheel (on the right side of the instrument) (Fig. 5),
– using the lower handwheel (on the right side of the instrument) set the borderline (between the light and dark regions) at the crossing of the lines (Fig. 6A),
– read the value of refraction index from the lower scale with the 4 decimal place accuracy (Fig. 6B),

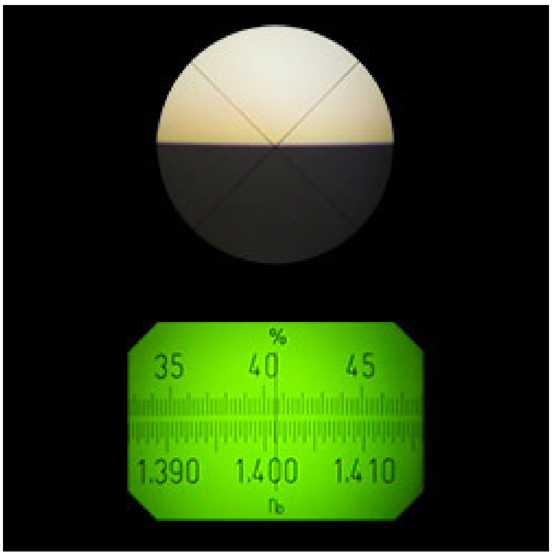

Fig. 6. Reading the value of refraction index.

– each measurement should be done three times,
– clean the refractometer with a tissue moistened with alcohol.

D. Methods

1. Determination of 1,4-dioxane structure:
   - measure three times the refractivity index of 1,4-dioxane.

2. Determination of unknown concentration of 1,4-dioxane in the aqueous solution:
   - prepare a series of 1,4-dioxane solutions in water with the following concentrations: 5, 10, 15 and 20 % (weight percent), no more than 10 g of each solution,
   - measure three times the refractivity index of water **(tabular value n_{water} = 1.33)** and each solution,
   - measure three times the refractivity index of unknown solution prepared by the teacher,
   - put the obtained values in Table 3.

Table 3.

C weight percent	$x_{dioxane}$ molar fraction	n	$n_{average}$
0 % (water)	0	1. 2. 3.	
5 %		1. 2. 3.	
10 %		1. 2. 3.	
15 %		1. 2. 3.	
20 %		1. 2. 3.	
$C_{unknown}$		1. 2. 3.	

E. Results and conclusions

1. Determination of 1,4-dioxane structure:
   - calculate the experimental molar refraction of 1,4-dioxane using the measured refractivity index and equation (3) (d = 1.03 g/cm^3, M = 88.11 g/cm^3),
   - knowing the formula of 1,4-dioxane ($C_4H_8O_2$), suggest its molecular structure, for example R-COOH, R_1-COO-R_2 etc.,

- calculate theoretical values of molar refraction for each structure using molar refraction contributions presented in Tables 2 and 3,
- comparing theoretical and experimental values of molar refraction of $C_4H_8O_2$, determine molecular structure of the compound.

2. Determination of unknown concentration of 1,4-dioxane in the aqueous solution:
   - express the concentrations of water-1,4-dioxane mixtures in molar fractions of 1,4-dioxane and put the values in Table 3,
   - draw the calibration line, i.e. $n = ax_{dioxane} + b$ relationship,
   - calculate regression parameters *a* and *b* of the calibration line,
   - knowing *a* and *b* parameters and refractivity index of unknown solution, calculate the molar fraction of 1,4-dioxane in an unknown mixture,
   - calculate weight percent of 1,4-dioxane in an unknown mixture.