2. Optical and electrical properties of molecules

2.a. Refraction measurement of methanol-ethanol mixtures

The measurement of the refractive index by immersion refractometer is based on the determination of the limiting angle β_{lim} of refraction to which the Snell law applies:

$$\sin\beta_{lim} = \frac{n}{n_g} \qquad (1.1.)$$

where n is the refractive index of the measured environment and n_g the refractive index of the glass used for the refractometer prism. The limiting angle is given by the position of the interface between the illuminated and the dark part of the field of view read on the empirical scale of the instrument. The corresponding refractive index we find a from the calibration table. The refractive index of the sample is dependent on the wavelength of the passing light, and less on temperature and pressure.

The specific refraction is given by formula:

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{\rho} \qquad (1.2.)$$

where ρ is density of the environment. At given temperature and pressure, the specific refraction depends on the wavelength only.

The dependence of the specific refraction of the mixture on volume fractions of components ϕ_i has an additive character. This dependence may be linear for similar substances (Lorentz brothers' equations). For example, for a binary mixture:

$$\mathrm{R} = \mathrm{R}_1\phi_1 + \mathrm{R}_2\phi_2 \qquad (1.3.)$$

where R_1 and R_2 are specific refractions of pure components *1* and *2*.

For pure substances, we define so-called molar refraction R_M, which is given by the product of the specific refraction R and the molar mass of the substance M.

The molar refraction is a constitutive property and it can be calculated theoretically as the sum of the molar refractions of the atoms that we find in the molecule. Of course, the atom refraction R_A^i has to be corrected for different binding types (see **TABLE I**).

$$R_M = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} = \sum \nu_i \cdot R_A^i \qquad (1.4.)$$

where ν_i is number of atoms with the same *i*-bond neighbourhood in the molecule. This equation applies to both non-polar and polar substances, since the behaviour of their atoms varies very little in the electromagnetic field or light.

The specific refraction *n* of the binary mixtures is often used in the practice of refractometry for the determination of the composition of the minority component x_1 if

TABLE I: The atom refractions of the elements in alcohols.

Atom *i*:	C	H	O (v OH)
R_A^i / cm^3 mol^{-1}	*2,4*	*1,1*	*1,5*

the calibration function $n = f(x_1)$ is known. The calibration function is generally non-linear and temperature dependent.

Density measuring using glass pycnometer. First we weight an empty, clean and dry pycnometer. We then fill it with a measured liquid at the temperature slightly lower than the temperature of the thermostat bath into which the pycnometer will be consequently inserted. After the temperature has stabilized and according to the pycnometer design, the excess liquid either overflows spontaneously or we remove a liquid to the volume marker level using the syringe. Dry the pycnometer externally and weigh it. Thus we determine the weight of the pycnometer with all the investigated liquids or their mixtures and finally with the water. We use the distilled water to calibrate the actual volume of the pycnometer.

Next, we will find the tabulated water density for the bath temperature, and then calculate the actual volume of the pycnometer occupied by the water at the temperature inside the thermostat bath. Weighing can be further refined by correcting the buoyancy of the pycnometer by air so that the density of the fluid under investigation at temperature is calculated as follows:

$$\rho_t = \frac{m}{m_0}\left(\rho_0 - \rho^*\right) + \rho^* \qquad (1.5.)$$

where ρ_0 is the specific mass of pure water at the temperature of the thermostat bath (we found it in tables), *m* is the mass of the fluid under investigation, and m_o is the mass of water, ρ^* is specific mass of dry air (*1,168 kg/m^3* at 25°C and *100.0 kPa)*.

TASK: Find out the specific refraction of methanol and ethanol and their mixtures at 25.0°C, test linear dependence of the specific refraction on the composition, and verify the molar atom refraction additivity for pure alcohols.

LABORATORY AIDS AND CHEMICALS: Immersion refractometer, thermostatic bath, *7* refractometer cuvette, glass pycnometer (*25 ml*) for volatile liquids, methanol, ethanol, and its binary mixtures with volume ratios (ϕ_1): *0.80; 0.60: 0; 40; and 0.20.*

Methanol is a flammable toxic substance in ingestion, in contact with skin and in inhalation. Same smelling and taste as ethanol. If swallowed, seek medical advice immediately.

INSTRUCTIONS: Pour distilled water, ethanol, methanol, and alcohol mixtures into refractometer cuvettes. Place the liquid samples in a thermostatic bath. Clean the immerse refractometer with distilled water and place it in the cuvette involving water.

After equilibration, we perform the calibration of the refractometer by measuring the refractive index of the distilled water at bath temperature. Next, we proceed to measure the refractive indexes of the samples. When transferring the refractometer from one liquid to the other, carefully dry prism by filter paper.

The specific density of the monitored liquids can be measured by glass pycnometer for example.

REPORT: Start and end temperature of measurement. **Table 1:** the masses of the pycnometer with air, water, and with each mixture of alcohols, the masses of the filling only; the specific masses of the samples according to the relationship (1.5.). **Table 2:** for all measured liquids: composition (volume fraction of ethanol and methanol), refractive index, specific mass, specific refraction calculated by eqn (1.2.). Add also the value of the specific refractions of the mixtures obtained using the relationship (1.3.) (use specific refraction of methanol R_1 and ethanol R_2 from the experiment as input), the differences between the experimental and calculated specific refractions. **Graph 1**: the composition dependence of the refractive index. **Common graph 1**: dependences of both experimental and calculated specific refractions of alcohol mixtures on its compositions. **Table 3:** for pure methanol and ethanol: comparing experimental values of molar refraction R_M with values calculated using atomic refractions R_A^i (use **TABLE I** and eqn (1.4.)).