DISTRIBUTION LAW

1. PURPOSE OF THE WORK

Determination of the distribution coefficient of acetic acid between water and ethyl acetate.

2. THEORETICAL NOTIONS

If in a system of two immiscible or partially miscible liquids a third substance soluble in the two liquids is added, this substance is distributed between the two liquids in a certain proportion.

The variance of the system results from the law of phases

$$v = c - f + 2 \tag{1}$$

where v - the number of degrees of freedom (variable), c - the number of components and f - the number of phases.

In the case of a three-component system in which two phases occur, the number of variables that must be known to define the system is

$$v = c - f + 2 = 3 - 2 + 2 = 3 \tag{1'}$$

it follows that, at fixed temperature and pressure, a single variable determines the composition of the entire system. Thus, if at one temperature the concentration in one phase is known, the concentration in the other phase can be determined.

Also considering the equilibrium activities a_A^I and a_A^{II} in the two liquid phases noted I and II, at constant temperature the ratio of these activities is constant and independent of the amount of dissolved substance, respectively:

$$\frac{a_A^I}{a_A^{II}} = K \tag{2}$$

Relationship (1) is Nernst's *law of distribution* or distribution. The constant K is called the *distribution coefficient* and does not depend on the presence of other dissolved substances.

In the case of diluted solutions, the distribution law becomes:

$$\frac{c_A^I}{c_A^{II}} = K \tag{3}$$

If the two phases are in permanent contact with a solid substance, saturated solutions are obtained at equilibrium. If the solubilities of the two layers are $s_{\mathrm{A}}^{\mathrm{I}}$ and $s_{\mathrm{A}}^{\mathrm{II}}$, the distribution law is expressed by solubilities, as follows:

$$\frac{s_A^I}{s_A^{II}} = K \tag{4}$$

The distribution law, as expressed in relations (2) and (3), represents an approximation based on the assumption of an ideal behavior of the solutions and on the hypothesis that the dissolved substance does not change the miscibility of the two liquids.

But the dissolved substance may have associations or dissociations in one or both layers. If the dissolved substance A is presented in layer I as the associated molecules A_m (aggregates containing as many m monomer molecules A), and in layer II as the associated molecules A_n, the distribution corresponds to equilibrium

$$nA_m \rightleftarrows \tag{5}$$

from where

$$\frac{\left(c_A^I\right)^n}{\left(c_A^{II}\right)^m} = K_c^0 \tag{6}$$

or

$$\frac{c_A^I}{\left(c_A^{II}\right)^{m/n}} = K \quad , \quad K = \sqrt[n]{K_c^0} \tag{7}$$

The logarithm of the last expression is obtained

$$\ln c_A^I - p \cdot \ln c_A^{II} = \ln K \tag{8}$$

with notation $p = m/n$.

Using this equation it is possible to calculate the distribution coefficient if the dependence is known $\ln c_A^I$ as function of $\ln c_A^{II}$.

3. EXPERIMENTAL PART

3.1. APPARATUS AND SUBSTANCES

- 4 vials of 200 mL with stopper, 100 mL Erlenmayer vessel, 2 x 50 mL graduated cylinders, a 5 mL pipette and two 1 mL pipettes, acetic acid solutions of varying concentrations.

3.2. PROCEDURE

In the four Erlenmayer flasks, pour 12.5 mL of ethyl acetate (measured with the cylinder), 12.5 mL of distilled water (measured with the cylinder) and then add 5 mL of acetic acid solution (measured with the appropriate pipette), as follows:

- vial 1: 5 mL sol. acetic acid 1 N;
- vial 2: 5 mL sol. acetic acid 3 N;
- vial 3: 5 mL sol. acetic acid 4 N;
- vial 4: 5 mL sol. acetic acid 5 N;

Stopper the bottles and after vigorously shaking for 15 minutes, leave to stand until the two liquid phases are completely separated. The organic and aqueous layers are then analyzed in order to determine the concentration of acetic acid in the two phases.

To better see the layers, the contents of the vial are poured into a graduated cylinder with the smallest diameter, so that 1 ml of each layer can be easily extracted, which is then titrated with 0.1 N NaOH in the presence of phenolphthalein. Previously dilute this volume of 1 mL with about 10 or 20 mL of distilled water.

Thus, the aqueous and organic layers are analyzed successively for the four vials, resulting in the concentrations of acetic acid in the two phases, noted with $c_{\mathrm{A}}^{\mathrm{I}}$ (aqueous layer) and $c_{\mathrm{A}}^{\mathrm{II}}$ (organic layer).

4. EXPERIMENTAL DATA PROCESSING

4.1. The experimental results are presented in a form table:

No. vial	aqueous layer (bottom)		organic layer (top)		$\ln c_{\mathrm{A}}^{\mathrm{I}}$	$\ln c_{\mathrm{A}}^{\mathrm{II}}$	***K***
	V_{NaOH}, mL	**$c_{\mathrm{A}}^{\mathrm{I}}$, mol/L**	**V_{NaOH},mL**	**$c_{\mathrm{A}}^{\mathrm{II}}$, mol/L**			
1							
2							
3							
4							

4.2. Dependence $\ln c_A^I$ is represented graphically as function of $\ln c_A^{II}$; from the slope of the regression line is obtained $p = \frac{m}{n}$, and from the ordinate at the origin it is obtained ln *K*, from which the distribution coefficient *K* is determined;

4.3. *K* is calculated by the analytical method: based on the relation (4.7), *K* is calculated for each of the four data and the obtained values are averaged. For this the p value determined in point 4.2 is used;

4.4. The values obtained by the two methods are compared: graphical and analytical, calculating percentage errors.

Data from the literature

$M_{H_2O} = 18,03$ g/mol ; $\rho_{H_2O} = 0,9982$ g/cm^3

$M_{CH_3COOC_2H_5} = 88,11$ g/mol ; $\rho_{CH_3COOC_2H_5} = 0,8970$ g/cm^3

$M_{CH_3COOH} = 60,05$ g/mol ; $\rho_{CH_3COOH} = 1,049$ g/cm^3

5. QUESTIONS

5.1. How is the partition coefficient used in the pharmaceutical field? Give examples.

5.2. But in the process of purifying the products of a reaction (chemical engineering extraction)? Give examples and imagine an experimental protocol using a separation funnel.