Exercise 15

DETERMINATION OF THE PARTION COEFFICIENT IN A SYSTEM OF TWO IMMICSIBLE LIQUIDS

Topics: Matter on a macro scale, Thermodynamic description of mixtures, Activities, Ion activity

The basic condition for thermodynamic equilibrium in multiphase and multicomponent systems (at constant pressure and temperature) is the equality of chemical potentials of all components in all phases. Thus, if substance i dissolves in two adjacent immiscible liquids, equilibrium is established when the chemical potentials of this substance in both phases are equal:

$$\mu_i^{\alpha} = \mu_i^{\beta} \tag{1}$$

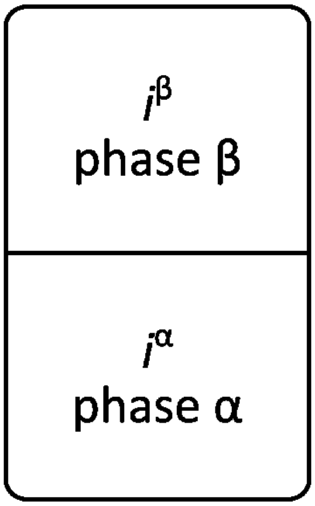

Fig. 1. Schematic representation of the partition of substance (*i*) between the α and β phase.

Since the chemical potential of substance *i* in each solution is a function of the corresponding activity α_i to equation (1) can be written as:

$$\mu_i^{\alpha,\ominus} + RT\ln\frac{a_i^{\alpha}}{a^{\ominus}} = \mu_i^{\beta,\ominus} + RT\ln\frac{a_i^{\beta}}{a^{\ominus}} \tag{2}$$

where $\mu_i^{\alpha,\ominus}, \mu_i^{\beta,\ominus}$- standard chemical potentials of the substance *i* in the phase α and β, respectively and $a_i^{\alpha}, a_i^{\beta}$- activities of substance *i* in the phase α and β related to the selected standard activity $a^{\ominus}$.

It is possible to use both the molar, molal, fractional and pressure activity systems.

The transformation of equation (2 shows that the equilibrium condition in a system of two phases exchanging one of the components comes down to the constant activity ratio of this component in both phases. Using molar activities (a_{c_i}), this condition is written as follows:

$$k_a = \exp\left(\frac{\mu_i^{\beta,\ominus} - \mu_i^{\alpha,\ominus}}{RT}\right) = \frac{a_{c_i}^{\alpha}}{a_{c_i}^{\beta}} = \frac{c_i^{\alpha} \cdot \gamma_i^{\alpha}}{c_i^{\beta} \cdot \gamma_i^{\beta}} = k_c \frac{\gamma_i^{\alpha}}{\gamma_i^{\beta}} \tag{3}$$

$$k_c = \frac{c_i^{\alpha}}{c_i^{\beta}} \tag{4}$$

where $c_i^{\alpha}, c_i^{\beta}$- molar concentration of the substance *i* in the α and β phase, respectively, in relation to the standard concentration $c^{\ominus}$=1M, $\gamma_i^{\alpha}, \gamma_i^{\beta}$- activity coefficients of substances *i* in the α and β phases, k_c- the Nernst coefficient (or approximate phase equilibrium constant) describes real (imperfect) systems

Constant k_a is called the thermodynamic phase equilibrium constant. As can be seen from equation (3, , its value depends on the difference in the standard chemical potentials of the component and in the adjacent phases.

It is worth remembering that the value of the k_c constant for real systems may change with the change in the amount of substance introduced into the two-phase system. Hence, for dilute solutions ($c_i \to 0$, $\gamma_i \to 1$), the values of the Nernst partition coefficient (k_c) and the thermodynamic phase equilibrium constant (k_a) are similar:

$$k_a \cong k_c \tag{5}$$

If you want to carefully analyze the process of dividing a given substance between individual phases, you must consider the possibility of its dissociation, formation of associations or complexes in the solvents used. The law of division applies separately to each type of chemical entity. Therefore, it is necessary to determine the partition coefficients for all types of molecules, ions and associates occurring in the α and β phase.

We will consider this problem using the example of the process of dividing benzoic acid between the water and benzene phases. In the aqueous phase, benzoic acid occurs mainly in the form of single molecules (monomers) and ions formed as a result of electrolytic dissociation. The concentration of monomer c_m^w depends on the degree of dissociation (α) and is:

$$c_m^w = c^w(1-\alpha) \tag{6}$$

where c^{w}– total concentration of benzoic acid in the aqueous phase.

However, in the benzene phase, benzoic acid is significantly associated with the formation of dimers:

$$2\ C_6H_5COOH \rightleftarrows (C_6H_5COOH)_2 \tag{7}$$

Hence, the total concentration of benzoic acid in the benzene phase (c^{b}) is the sum of the monomer concentrations (c_m^b) and twice the dimer concentration (c_d^b):

$$c^{b} = c_m^b + 2c_d^b \tag{8}$$

Because the equilibrium concentration constant of the association reaction (K_{as}) benzoic acid in the benzene phase, is described by the expression:

$$K_{as} = \frac{\frac{c_d^b}{c^{\ominus}}}{\left(\frac{c_m^b}{c^{\ominus}}\right)^2} \tag{9}$$

After rearranging equation(9, we get:

$$c_d^b = K_{as}\frac{\left(c_m^b\right)^2}{c^{\ominus}} \tag{10}$$

After substituting the right side of equation (10 into equation (8, we get:

$$c^{d} = c_m^b + 2K_{as}\frac{\left(c_m^b\right)^2}{c^{\ominus}} \tag{11}$$

The component that passes from the benzene phase to the water phase and vice versa is only the monomer, for which the partition coefficient is:

$$k_c = \frac{c_m^w}{c_m^b} \tag{12}$$

Using equations (6, (11 and (12, after transformations we obtain the following linear expression:

$$\frac{c_b}{c^{W}(1-\alpha)} = \frac{1}{k_c} + \frac{2K_{as}}{(k_c)^2}\frac{c^{w}}{c^{\ominus}}(1-\alpha) \tag{13}$$

Knowing the degree of dissociation of benzoic acid in the aqueous phase, it is possible to analyze the experimental data in coordinates $y = \frac{c_b}{c^{w}(1-\alpha)}, x = \frac{c^{W}}{c^{\ominus}}(1-\alpha)$ determine two dimensionless quantities:

the association constant K_{as} and the division coefficientk_c. Intercept of the equation of a straight line $b = \frac{1}{k_c}$, and the slope coefficient $a = \frac{2K_{as}}{(k_c)^2}$.

Nernst's division law is used to solve various theoretical and practical problems. The phenomenon of partitioning a substance between two phases is used between. including when performing extraction and in gas and liquid chromatography.

Performing the exercise

The aim of the exercise is to determine the partition coefficient of acetic acid between aqueous and butanol phases ($k_c = \frac{c_{HA}^{W}}{c_{HA}^{B}}$) assuming that there is no association phenomenon in both phases and dissociation in aqueous solution can be neglected ($K_{as} \approx 0$ i $\alpha \approx 0$).

Methodology and calculations

1. Before starting the exercise, pour one by one into five dry bottles 10 cm^3 of starting aqueous solutions of acetic acid with approximate concentrations: 0,025, 0,035, 0,05, 0,075 i 0,1 M.
2. Then we add 10 cm^3 of butanol to each bottle. Leave the tightly closed bottles for 60 minutes, shaking vigorously every 5 minutes. During this time, we determine the exact values of the initial c_{HA}^{P} concentration of starting CH_3COOH solutions by double titration with sodium hydroxide solution (C_{NaOH} = 0,010 M). After averaging the titration results for each sample, we calculate $\bar{c}_{HA}^{P}$.
3. After establishing the equilibrium state of the partition of acetic acid between the aqueous and butanol phases (about 60 minutes), we separate the aqueous phase using a separator. From each obtained aqueous acetic acid solution, we take 2 samples with a pipette and titrate them with sodium hydroxide solution (C_{NaOH} = 0,010 M). We again average the titration results for each sample and then calculate the average concentration of acetic acid in the aqueous layer after extraction($\bar{c}_{HA}^{W}$).
4. Since equal volumes of acetic acid in water and butanol were used to carry out the extraction process, the average concentration of the tested substance in the alcohol layer (c_{HA}^{B}) is equal to the difference in average concentrations in the aqueous layer before and after extraction:

$$\bar{c}_{HA}^{B} = \bar{c}_{HA}^{P} - \bar{c}_{HA}^{W} \tag{14}$$

5. For each of the tested systems we calculate $k_c = \frac{\bar{c}_{HA}^{W}}{\bar{c}_{HA}^{B}}$
6. From the obtained k_c values, we calculate the average valueą $\overline{k_c}$ from all measurements.