

1. Phase equilibria

1.a. Determination of the partition coefficient in the extraction system



In the extraction systems the three components are the most important: the solvent (mostly water), the solute, and the extractant (frequently organic solvent). If the extraction is to be successful, the system must have appropriate phase behaviour. The miscibility of the solvents and extractant must be negligible and the solubility of the solute in the extractant as large as possible.

After the addition of the extractant to the solution, two liquid phases are formed: a phase rich in the solvent (aqueous phase) and the extractant phase rich in the solute (organic phase). The rate of the equilibrium reaching is proportional to the size of the interfacial surface, which can be increased by intensive stirring. The extraction yield depends on the composition of coexisting phases in the extraction equilibrium. The phase compositions can be predicted from the phase diagram of the extraction system. In practice, the solute contents are more simply described in both extractant and solvent liquid phases by the partition coefficient of extraction:

$$K_{Ex} = \frac{c_{Ex}}{c_V} = \frac{\frac{m_0 - m_1}{V_{Ex}}}{\frac{m_1}{V_V}} = \frac{x_{Ex}}{x_V} \cdot \frac{V_V}{V_{Ex}} \quad (4.1.)$$

where symbol c_{Ex} in g/l unit and x_{Ex} (molar ratio) means the equilibrium concentration of the solute in the extractant phase, which has the volume V_{Ex} . Symbol c_V and x_V means the equilibrium concentration of the solute in the solvent phase, which has the volume V_V . The m_0 mass is equal to the amount of the solute that was originally in solution (in the aqueous phase) before extraction. Concurrently, the m_0 represents the total mass of the solute in the extraction system. The m_1 is the mass of the solute in the solvent after extraction. The amount of the extracted solute substance transferred to the organic phase is therefore consistent with the law of preservation of matter $m_0 - m_1$.

The partition coefficient is dependent on the temperature, pressure, and overall composition of the extraction system. The dependence of the coefficient on the overall composition of the system is neglected in practice for low contents of the solute substance. However, this simplification does not apply to systems where components are involved in the reaction equilibria (association, dissociation, dimerization, ...).

It follows from the expression (4.1.) that after extraction, the mass of the solute in the separated solvent (in aqueous phase) is:

$$m_1 = \frac{m_0 V_V}{(V_V + K_{Ex} V_{Ex})} \quad (4.2.)$$

The separated solute-depleted aqueous phase may be subjected to further extraction. The separated extractant phase rich in the solute can be used for another purpose.

If the mutual miscibility of the aqueous and organic phases and the partial molar volume of the solute in the phases mentioned are negligible, we can deduce the relation for the n -stage extraction with the same amount V_{Ex} of organic solvent:

$$m_n = \frac{m_{n-1} V_V}{(V_V + K_{Ex} V_{Ex})} = m_0 \left[\frac{V_V}{(V_V + K_{Ex} V_{Ex})} \right]^n \quad (4.3.)$$

Yield after n -stage extraction is as follow:

$$\pi_n = \frac{m_0 - m_n}{m_0} = 1 - \left[\frac{V_V}{(V_V + K_{Ex} V_{Ex})} \right]^n \quad (4.4.)$$

Among other it follows that if the partition coefficient of extraction K_{Ex} is a constant, then the n -stage extraction with addition of extractor volume V_{Ex} leads to a greater yield than a 1-stage extraction using extractor in an undivided amount $n \cdot V_{Ex}$. The extraction yield is usually given as a percentage: $\pi_{\%} = 100 \cdot \pi_n$.



TASK: Determine the partition coefficient of extraction K_{Ex} of the methylene blue in extraction system water – methylene blue – amyl alcohol. Verify the relationship (4.3.) for 2-stage extraction. Compare the yield (in %) of 1-stage extraction with 2-stage extraction using the same total amount of extractor.



LABORATORY AIDS AND CHEMICALS: the stock solution $4 \cdot 10^2 \text{ g/dm}^3$ of the solute – methylene blue (CAS No 122965-43-9) dye in water, extractor – amyl alcohol (CAS No 71-41-0), laboratory test tube rack, 9 teflon tubes with plugs, 4 scale pipettes (1, 2, 5, and 10 ml), syringe with long needle or thin hosepipe, 1 volumetric flask (100 ml), 5 volumetric flasks (25 ml), spectrophotometer, wash bottle with ethanol, at least 3 pcs of conventional rod stirrers, or one stirrer with rotary disc on at least 10 test tubes.



INSTRUCTIONS: For time reasons, select this work schedule:

- 1. Equilibration.** Pipette gradually 0.5; 0.75; 1.0; 1.25; 1.5; 1.75; 2.0; 2.5 and 5.0 cm^3 of methylene blue stock solution into 9 tubes (or separating funnels) and add water to make up total volume 5 cm^3 . Add 5.0 cm^3 of extractor (amyl alcohol) to each tube. I.e. each tube will involve a final volume of 10 cm^3 (resulting in the extraction systems No 1-9) Pipette 5.0 cm^3 of methylene blue stock solution and 2.5 cm^3 of extractor into 10th tube (extraction system No n2). Stir the contents of the tubes for at least 20 minutes. Ensure extraction takes place at a constant temperature.
- 2. Phase separation.** After stirring phases in the tubes, let both the clear organic and aqueous phases separate from the extraction mixtures. Use syringe with pipehose and suck the upper phase (rich in extractor). Discard the contents of the syringe into organic waste bottle despite upper phase contains most of the solute. Use the water rich phase (bottom phase) inside tubes No 1-9 for analysis.
- 3. Two-stage extraction.** Suck the upper organic phase through a syringe from the extraction system No n2 and pour it into the organic waste bottle. Add again 2.5 cm^3 of the extractor and repeat the extraction and phase separation under the same conditions as done before.

4. Measurement of calibration dependence. Pipette the volume 50 ml of the dye stock solution into 100 ml volumetric flask and make up with water. Use this new dye solution, pipette successively volumes 2.5 ; 5 ; 7.5 ; 10 ; 12.5 ; and 15 cm^3 into six 25 cm^3 volumetric flasks and fill them with water up to the marks. Measure the absorbance of the new stock solution and the prepared solutions by a spectrophotometer at a wavelength corresponding to the maximum absorbance value of the aqueous extract solution (methylene blue: 660 nm).

5. Measurement of the aqueous phase absorption after extraction. Dilute all water phases in the tubes after extraction (*No 1-9* and *n2*) with water in a 1:1 ratio (ie dilution factor = 2). The dilution should remove a possible turbidity in the water phase. Measure the absorbance of the solute in all samples with a spectrometer. Do the same for sample *No n2* after the second equilibration.

Wash the dishes after experiment with water and rinse them by ethanol.



DATA ANALYSIS: For all experiments *No 1-9*: Calculate the weights m_0 and m_1 of the solute from the concentrations of the dye c_0 and c_v in the water-rich phases before and after extractions. Use the calculated weights (m_0 , m_1), used volumes (V_{Ex} , V_v), and calculate the equilibrium concentrations of the solute c_{Ex} in the phases rich in the extractant. Evaluate the partition coefficients of the extractions K_{Ex} for all samples according to equation (4.1.).

Calculate the weight value m_2 using the average partition extraction coefficient obtained from experiments *No 1-9* and the volumes used in the extraction system *No n2* according to the relationship (4.3.). Use the calculated value m_2 to calculate the residual concentration of the solute c_2 in the water rich phase. Compare the calculated value c_2 with the experimentally measured value for extraction *No n2*.

Calculate the yield π_n of two-stage extraction ($n = 2$) according to the relationship (4.4.) using average partition coefficient of extraction and compare it with the extraction yield that we would get if we used the same amount of extractor for one-stage extraction ($n = 1$).



REPORT: Calibration table 1: for all dye solution: pipetted volume, concentration, absorption. **Calibration graph 1:** Dependence of the absorption on the solute concentration in water. **Table 2:** for each experiment *No 1-9* and *No n2*: the initial concentration of the extractant c_0 and its weight m_0 in the aqueous phase prior to the addition of the extractant, dilution factor of the aqueous phase after extraction, absorbance after extraction, concentration of the extractant in the water phase subtracted from the calibration graph, concentration c_v after extraction, weight of the solute in the water phase m_1 and in the organic phase ($m_0 - m_1$) after extraction, experimental yield π_1 , value of partition coefficient of extraction K_{Ex} , average of K_{Ex} from experiment *No 1-9*. **In addition**, for experiment *No n2* (use average of K_{Ex}): calculated mass m_2 and concentration c_2 . Theoretical yield calculation for one-stage extraction with 5 ml and for two-stage extraction with use of 2-times 2.5 ml of the extractor. Finally, compare the calculated yield of the 2-stage extraction with the yield of the experiment *No 9*.