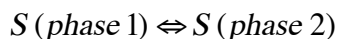


INTRODUCTION TO ANALYTICAL SEPARATIONS

Extraction is a separation technique, based on different solubility of solute(s) in two immiscible solvents. This technique is used for the separation and isolation of different solutes, concentrating of solute.

Since solvents used for the extraction are immiscible, they form a two-phase system (phase 1 and phase 2). Solute is partitioned between these phases:



and this partition is governed by the corresponding equilibrium constant:

$$K = \frac{[S]_2}{[S]_1}$$

If total amount of the solute in the system is m , then q is the fraction of it in phase 1 at equilibrium and $(1-q)$ is the fraction of the same solute at equilibrium in phase 2. Therefore, concentration of the solute in the phase 1 is:

$$S_1 = \frac{qm}{V_1}$$

and concentration of the solute in phase 2 is:

$$S_2 = \frac{(1-q)m}{V_2}$$

Thus, the expression for the equilibrium is:

$$K = \frac{[S]_2}{[S]_1} = \frac{\frac{(1-q)m}{V_2}}{\frac{qm}{V_1}} = \frac{(1-q)V_1}{qV_2}$$

If we solve this equation for q :

$$q = \frac{V_1}{V_1 + KV_2}$$

When n extractions are performed:

$$q = \left(\frac{V_1}{V_1 + KV_2} \right)^n$$

Sample 1. Solute A is extracted by toluene (V_2) from water ($V_1 = 100$ mL). In this system K value for the solute is equal 3. We can add 500 mL of toluene in one time, or 100 mL of toluene 5 times to perform the extraction. What is the best scenario?

$$1. \quad q = \frac{V_1}{V_1 + KV_2} = \frac{100}{100 + 3 \times 500} = 0.062$$

The fraction remaining in the aqueous phase is 6.2%.

$$2. \quad q = \left(\frac{V_1}{V_1 + KV_2} \right)^n = \left(\frac{100}{100 + 3 \times 100} \right)^5 = 0.00098$$

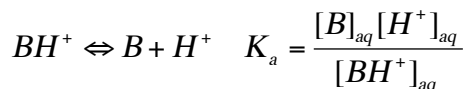
The fraction remaining in the aqueous phase is 0.098%.

The conclusion is, it is better to do few small extractions than one big extraction.

Effect of the pH

If solute is acid or base, its charge changes as pH is changed. Usually charged species are more soluble in aqueous phase and non-charged – in organic phase.

Base in aqueous solution undergoes the following equilibria:



The fraction of the neutral form present in aqueous phase is:

$$\alpha_B = \frac{[B]_{aq}}{[B]_{aq} + [BH^+]_{aq}} = \frac{[B]_{aq}}{[B]_{aq} + \frac{[B]_{aq}[H^+]_{aq}}{K_a}} = \frac{K_a}{K_a + [H^+]}$$

Neutral form is soluble in organic phase. And its distribution is governed by distribution coefficient D :

$$D = \frac{\text{concentration in organic phase}}{\text{concentration in aqueous phase}} = \frac{[B]_{org}}{[B]_{aq} + [BH^+]_{aq}}$$

It is similar to partition coefficient, but used instead when dealing with species present in **more than one chemical form**.

When $[BH^+]$ is expressed as function of the K_a and placed into the expression for D , we can end up with the following equation:

$$D = K \left(\frac{K_a}{K_a + [H^+]} \right) = K\alpha_B$$

If acid has to be extracted then equation for the D is:

$$D = K \left(\frac{[H^+]}{K_a + [H^+]} \right) = K\alpha_{HA}$$

Sample 2. Partition coefficient (K) for the base, B , is 3. This base dissolved in water ($pK_a = 9$), its concentration is 0.01M. 50 mL of this base is extracted with 100 mL of solvent. What would be the **formal** concentration of the base in aqueous phase at: (a) pH 10 and (b) pH 8?

For the pH 10:

$$D = K \left(\frac{K_a}{K_a + [H^+]} \right) = 3 \left(\frac{10^{-9}}{10^{-9} + 10^{-10}} \right) = 2.73$$

Since charged species are involved, we have to use D in place of K to find q:

$$q = \frac{V_1}{V_1 + K V_2} = \frac{50}{50 + 2.73 \times 100} = 0.15$$

$$[B]_{aq} = 0.15 \times 0.01 = 0.0015M$$

For the pH 8:

$$D = K \left(\frac{K_a}{K_a + [H^+]} \right) = 3 \left(\frac{10^{-9}}{10^{-9} + 10^{-8}} \right) = 0.273$$

Since charged species are involved, we have to use D in place of K to find q:

$$q = \frac{V_1}{V_1 + K V_2} = \frac{50}{50 + 0.273 \times 100} = 0.65$$

$$[B]_{aq} = 0.65 \times 0.01 = 0.0065M$$

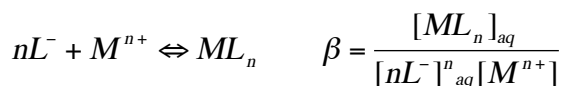
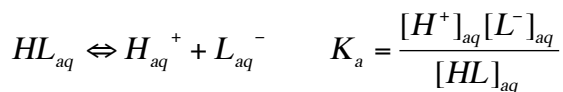
The conclusion is, to extract base with high efficiency one has to increase the pH of the aqueous phase.

Effect of the chelating agent

Selective chelating is a common practice to separate metal ions. However, charged chelated ions are better dissolved in aqueous phase, which makes extraction impossible. Therefore, special chelating agents are used for this purpose.

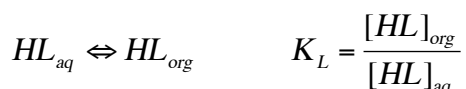
This time we should consider more equilibrium processes:

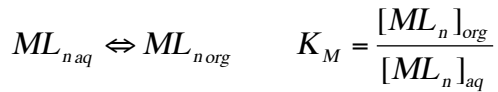
a. in aqueous phase



Each metal may complex with the ligand, but pH alters the selectivity.

b. between aqueous and organic phase





Assuming that M^{n+} is in aqueous phase and ML_n is in organic phase, the distribution coefficient is:

$$D = \frac{\text{total metal concentration in organic phase}}{\text{total metal concentration in aqueous phase}} = \frac{[ML_n]_{\text{org}}}{[M^{n+}]_{\text{aq}}}$$

$$[ML_n]_{\text{org}} = K_M [ML_n]_{\text{aq}} = K_M \beta [L^-]_{\text{aq}}^n [M^{n+}]_{\text{aq}}$$

Also,

$$[L^-]_{\text{aq}} = \frac{K_a [HL]_{\text{aq}}}{[H^+]_{\text{aq}}}$$

By substituting last equation into the previous:

$$[ML_n]_{\text{org}} = K_M \beta [L^-]_{\text{aq}}^n [M^{n+}]_{\text{aq}} = K_M \beta [M^{n+}]_{\text{aq}} \left(\frac{K_a [HL]_{\text{aq}}}{[H^+]_{\text{aq}}} \right)^n$$

If we put last equation into the expression for D:

$$D = \frac{[ML_n]_{\text{org}}}{[M^{n+}]_{\text{aq}}} = \frac{K_M \beta [M^{n+}]_{\text{aq}} \left(\frac{K_a [HL]_{\text{aq}}}{[H^+]_{\text{aq}}} \right)^n}{[M^{n+}]_{\text{aq}}} = K_M \beta \left(\frac{K_a [HL]_{\text{aq}}}{[H^+]_{\text{aq}}} \right)^n$$

Most of the HL is in organic phase, and therefore:

$$[HL]_{\text{aq}} = \frac{[HL]_{\text{org}}}{K_L}$$

By substitution we have final equation for D:

$$D = K_M \beta \left(\frac{K_a [HL]_{\text{aq}}}{[H^+]_{\text{aq}}} \right)^n = \frac{K_M \beta K_a^n}{K_L^n} \times \frac{[HL]_{\text{org}}^n}{[H^+]_{\text{aq}}^n}$$

The conclusion is, in order to extract metal ion with high efficiency one has to vary the pH and concentration of the chelating agent.