EXTRACTION

The partition of a solute between two immiscible phases is an equilibrium process that is governed by the distribution law.

If the solute species A is allowed to distribute itself between water and an organic phase, the resulting equilibrium may be written as

$$A_{aq} \rightleftarrows A_{org}$$

$$K = \frac{a_{A,org}}{a_{A,aq}} \approx \frac{[A]_{org}}{[A]_{aq}}$$
 Distribution constant



Distribution constant:

- Permit to calculate the concentration of an analyte remaining in a solution after a certain number of extractions.
- Provide guidance as to the most efficient way to perform an extractive separation.
- The concentration of A remaining in an aqueous solution after i extractions with an organic solvent ([A]i) is given by

$$[A]_{i} = \left(\frac{V_{aq}}{V_{org}K + V_{aq}}\right)^{i} [A]_{0}$$

 $[A]_i$ = the concentration of A remaining in the aqueous solution after extracting

 $V_{aq} = mL$ of the solution

 $[A]_0$ = an original concentration of A

i = portions of the organic solvent

 V_{org} = a volume of organic solvent



The improved efficiency of multiple extractions falls off rapidly as a total fixed volume is subdivided into smaller and smaller portions.

Liquid-Liquid Extraction

- The principal is that a sample is distributed or partitioned between two immiscible liquids or phases in which the compound and matrix have different solubilities. Normally, one phase is aqueous (often the denser or heavier phase) and the other phase is an organic solvent (the lighter phase).
- The basis of the extraction process is that the more polar hydrophilic compounds prefer the aqueous (polar) phase and the more nonpolar hydrophobic compounds prefer the organic solvent.
- The main advantages of LLE are its wide applicability, availability of high purity organic solvents and the use of low-cost apparatus.



$$E = \frac{C_0 V_0}{(C_0 V_0 + C_{aq} V_{aq})}$$

$$E = \frac{K_d V}{(1 + K_d V)}$$

E = the fraction of compound extracted

 C_0 = the concentrations of the compound in the organic phase

 C_{aq} = the concentrations of the compound in the aqueous phase

 V_0 = the volume of the organic phase

 V_{aq} = the volume of the aqueous phase

V = the phase ratio

$$E = 1 - \left[\frac{1}{(1 + K_d V)} \right]^n$$

n = the number of extraction



Selection of Solvents

Organic solvent for LLE is chosen because of its:

- Low solubility in the aqueous phase (typically <10%)
- High volatility for solvent evaporation in the concentration stage
- High purity which could pre-concentrate any impurities within the solvent
- Compatibility with the choice of chromatographic analysis
- Polarity and hydrogen-bonding properties that can enhance compound recovery in the organic phase, i.e. increase the value of Kd



Discontinuous LLE

- Equilibrium is established between two immiscible liquids.
- The most common approach uses a separating funnel.

Continuous LLE

- Equilibrium may not be reached
- The kinetics of the extraction process are slow, such that the equilibrium of the compound between the aqueous and organic phases is poor.

