

Chapter IV:

Extraction by an Immiscible Solvent



Introduction:

Phase transfer extraction is a separation process that involves transferring a solute from one phase to another. This method is widely used in chemistry, biochemistry, and the pharmaceutical industry to isolate or purify specific compounds. The general principle involves choosing two immiscible phases (often liquid-liquid or solid-liquid), allowing the solute to migrate into one phase based on its solubility.

V.1 Liquid-Liquid Extraction (Solvent Extraction):

Liquid-liquid extraction, or solvent extraction, is a technique where a solute is separated between two immiscible liquids. The goal is to transfer the desired compound (solute) from one liquid phase to another, typically from an aqueous phase to an organic phase or vice versa.

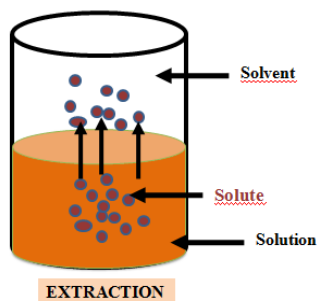


Fig. V.1: Extraction¹



Fig. V.2: Decanting funnel²

V.1.1 Principle:

- Two immiscible liquids are mixed: one containing the dissolved solute (usually water), and the other being the extraction solvent (an organic solvent).
- The solute migrates to the solvent in which it is more soluble, depending on its relative solubility in the two phases.
- After mixing, the two phases separate, allowing recovery of the solute in the extraction phase.

V.1.2 Applications:

¹ https://en.wikipedia.org/wiki/Separatory_funnel

² <https://vocal.media/education/solvent-extraction>

- Extraction of chemicals from aqueous solutions into organic solvents.
- Purification of pharmaceutical products.
- Recovery of heavy metals from industrial solutions.

V.1.2 Partition Coefficient (or Distribution Coefficient) :

The **partition coefficient (K)** measures how a solute distributes itself between two immiscible solvents. It is the ratio of the concentration of the solute in the organic phase to its concentration in the aqueous phase.

$$K = \frac{[\text{Solute}]_{\text{organic}}}{[\text{Solute}]_{\text{aqueous}}}$$

A high K value means the solute is more soluble in the organic phase, while a low K indicates a preference for the aqueous phase.

V.1.3 Factors affecting the partition coefficient:

- ✓ **Nature of the solute:** Hydrophobic solutes are more soluble in organic solvents.
- ✓ **pH:** The pH of the aqueous solution can affect solute ionization and solubility.
- ✓ **Temperature:** Temperature changes can alter the interactions between solute and solvents, affecting the coefficient.

V.1.4 Types of Solvents and Their Characteristics:

Choosing the right solvent is critical for efficient extraction, as it must be suitable for both the solute and the phases involved. Below is a classification of common solvents with their characteristics:

Solvent Type	Examples	Characteristics
Polar solvents	Water, Methanol, Ethanol	Used to dissolve polar or ionic compounds. Suitable for extracting hydrophilic substances.
Non-polar solvents	Hexane, Toluene, Benzene	Effective for extracting non-polar (hydrophobic) compounds. Immiscible with water.
Amphiphilic solvents	Acetone, Chloroform	Can dissolve both polar and non-polar substances. Versatile for different types of extractions.
Halogenated solvents	Dichloromethane (DCM), Chloroform	Dense solvents, often toxic, used for extracting molecules in the organic phase.
Green solvents	Ethanol, Ethyl Acetate	Environmentally friendly solvents used in more sustainable and ecological processes.

V.1.5 Key Solvent Characteristics:

- **Solubility:** The solvent's ability to dissolve a specific solute.
- **Toxicity:** Some solvents, like benzene and chloroform, are hazardous and must be handled with care.
- **Boiling Point:** Low boiling solvents (e.g., acetone) evaporate quickly, while high boiling solvents (e.g., toluene) are more stable at higher temperatures.
- **Density:** Some solvents, like dichloromethane, are denser than water, forming the bottom layer in liquid-liquid extractions.

Conclusion

Liquid-liquid extraction is a powerful technique to separate compounds based on their solubility in different solvents. The partition coefficient plays a crucial role in optimizing this process. Choosing the right solvent, considering its chemical and physical properties, is essential for successful extraction.

V.1.6 Parameters influencing the extraction operation:

- (a) **Polarity:** Polarity refers to a property of a molecule where there is an uneven distribution of electrical charges within the molecule. A molecule is said to be **polar** if it has opposite poles with partial positive and partial negative charges.
- (b) **Effect on Solubility:** Polar molecules interact well with other polar molecules through dipole-dipole interactions or hydrogen bonding. This is why polar substances, such as salt (NaCl), dissolve well in water (which is polar).
- (c) **Non-Polarity:** A molecule is said to be **non-polar** when the distribution of electrical charges is **even or nearly even** throughout the molecule, so there is no significant charge separation.
- (d) **Effect on Solubility:** Non-polar molecules are soluble in non-polar solvents (like hydrocarbons) because they cannot interact effectively with polar molecules like water. Hence, the saying "like dissolves like" applies.
- (e) **Affinity:** In chemistry, **affinity** refers to the tendency of a substance to interact, react, or bind with another substance. Specifically, it denotes the attraction one substance has for another, often based on chemical forces like polarity, hydrogen bonding, or ionic interactions.

Concept	Description	Examples
Polarity	Molecules with an unequal distribution of charges, creating positive and negative poles.	Water, Ammonia
Non-Polarity	Molecules where charges are evenly distributed, with no distinct poles.	Methane
Affinity	The tendency of a substance to bind, interact, or dissolve in another substance.	Salt in water, oil in gasoline

V.1.7 Solvent Selection in Liquid-Liquid Extraction:

- Liquid-liquid extraction is a separation method based on the distribution of a solute between two immiscible liquid phases. The choice of solvent is crucial for maximizing

the efficiency of this operation. Below are the main criteria to consider when selecting an appropriate solvent:

- **Solvent Affinity for the Solute:** The solvent must have a high affinity for the solute to be extracted, meaning the solute should be more soluble in the solvent than in the initial liquid. This allows for maximizing the transfer of the solute into the organic or aqueous phase.
- **Polarity Difference:** In general, solvents and starting liquids should have different polarities to avoid miscibility. For example, water (polar) and non-polar organic solvents like ether or dichloromethane are often used together. This polarity difference helps facilitate phase separation after extraction.
- **Solvent Density:** It is preferable that the chosen solvents have a density different from that of the aqueous phase to allow for a clear separation of the two phases after extraction. For instance, solvents like dichloromethane, which is denser than water, will settle at the bottom of the separatory funnel, while less dense solvents like ether will float on top of the aqueous phase.
- **Volatility:** A solvent with moderate volatility is desirable because it can be easily evaporated after extraction to recover the purified solute. For instance, ether and chloroform are frequently used volatile solvents because they can be easily removed under vacuum or by evaporation.
- **Chemical Inertness:** The solvent should be chemically inert toward the solute and other compounds present in the mixture. This ensures that only the physical extraction of the solute occurs without chemical reactions taking place between the solvent and the solute or phases in contact.
- **Safety and Environmental Impact:** The chosen solvent should have minimal toxicity and a limited environmental impact. Solvents like dichloromethane are effective but toxic, whereas green solvents like ethanol or terpene-based solvents are increasingly favored.
- **Partition Coefficient (K):** The partition coefficient between the two phases is a key factor in solvent selection. It measures the distribution of the solute between the aqueous and organic phases, the higher the coefficient, the more efficient the extraction.

✓ **Commonly Used Solvents:**

- ✓ **Hexane:** A non-polar solvent used for extracting non-polar compounds.
- ✓ **Ethanol:** A moderately polar solvent used for some organic extractions.
- ✓ **Dichloromethane (DCM):** A non-polar solvent used for rapid and efficient extractions.
- ✓ **Ethyl Acetate:** A non-polar solvent with moderate density used in large-scale extractions.

A good choice of solvent ensures effective separation, good solute recovery, and lower costs for the extraction process.

When a solute migrates from the aqueous phase to an organic phase (solvent) during liquid-liquid extraction, the equilibrium reached is a partition equilibrium or distribution equilibrium. This equilibrium is based on thermodynamic principles, where the solute is distributed between the two phases according to its affinity for each. The equilibrium does not

mean that all the solute has migrated to one phase, but rather that a certain proportion of the solute is present in each phase.

V.1.8 Thermodynamic Equilibrium:

When the system reaches thermodynamic equilibrium, the chemical potentials of the solute in both phases are equal. This means that the tendency of the solute to leave the aqueous phase and enter the organic phase (and vice versa) is the same. This process depends on temperature, the nature of the phases, and molecular interactions.

The main formula describing this equilibrium is the **partition coefficient** or **distribution coefficient** (K):

- **Interpreting the Equilibrium:**

- ✓ **If $K > 1$:** The solute is more soluble in the solvent (organic phase), meaning that a larger portion of the solute migrates to this phase.
- ✓ **If $K < 1$:** The solute is more soluble in the aqueous phase, so most of the solute remains in that phase.

The equilibrium is influenced by several factors, including:

- **Temperature** (which affects solubility).
- The **nature of the solvent and solute** (polar or nonpolar).
- The **interactions** between the solute and the solvent and water molecules (hydrogen bonding, dipole-dipole interactions, etc.).
- ✓ **Thermodynamic Formula of the Equilibrium**

The equilibrium can also be expressed in terms of the **Gibbs free energy** (ΔG):

$$\Delta G = \Delta H - T\Delta S$$

For a process to be favorable and reach equilibrium, the change in free energy ΔG must be negative ($\Delta G < 0$).

Problem:

A substance is extracted from a mixture using 100 mL of solvent S2 (ether) from 500 mL of solvent S1 (water). The initial concentration of the substance in S1 is 0.2 mol/L. After extraction, the concentration of the substance in S1 is 0.05 mol/L. Calculate the extraction yield.

V.2 Solid-Liquid Extraction:

Solid-liquid extraction is a method used to separate soluble components from a solid using a solvent. It is commonly used to extract substances such as essential oils, pigments, or active ingredients from plants. Here is a detailed explanation of the two main categories of this method: immersion and percolation.

V.2.1 Immersion:

V.2.1.1 Definition: Immersion is a solid-liquid extraction process where the solvent is brought into direct contact with the solid to be extracted. The solid remains immersed in the solvent for a specified period, allowing soluble compounds to dissolve into the solvent. This process is often used to extract active substances from plants, essential oils, or pigments. The extraction is done at room temperature or with mild heating.

V.2.1.2 Principles:

- The solid, containing the substances to be extracted, is immersed in a solvent.
- The soluble compounds of the solid gradually migrate into the solvent through diffusion.
- The mixture is filtered to separate the residual solid and the solution containing the extracted substances.

V.2.1.3 Types of Immersion and Pharmaceutical Examples:

✓ **Maceration:**

- **Principle:** The solid is left to rest in a solvent at room temperature. The process can last from several hours to several days to allow for maximum extraction.
- **Pharmaceutical Example:** Used to prepare mother tinctures or medicinal plant extracts. For example, macerating chamomile leaves in alcohol to obtain an extract used in the preparation of calming teas.

✓ **Infusion:**

- **Principle:** The solid is immersed in a hot solvent (usually water), and the mixture is left to rest to release the active compounds.
- **Pharmaceutical Example:** Infusion of mint leaves to extract active ingredients with digestive properties, often used to prepare medicinal teas.

✓ **Decoction:**

- **Principle:** The solid is boiled in a solvent (often water), promoting a more complete extraction of compounds that are difficult to dissolve at lower temperatures.
- **Pharmaceutical Example:** Extraction of active ingredients from roots or stems like licorice root, which is boiled to prepare syrups used for treating coughs.

V.2.2 Percolation:

Definition: Percolation is an extraction process where the solvent continuously flows through the solid, ensuring a more efficient extraction of soluble substances. Unlike immersion, where the solid remains static in the solvent, percolation involves the movement of the solvent, allowing constant renewal of the solvent around the solid. This increases the extraction yield.

V.2.2.1 Principles:

- The solid is placed in a device (such as a column or percolator).
- The solvent is introduced at the top of the device, and it flows through the solid, carrying away the soluble substances.
- The solution containing the extracts is collected at the outlet of the device.
- The process continues until most of the soluble compounds are extracted.

V.2.2.2 Types of Percolation and Pharmaceutical Examples:

a) **Simple Percolation:**

- **Principle:** The solvent is poured over the solid placed in a percolator, and the solvent slowly flows through the solid to extract the active ingredients.

- **Pharmaceutical Example:** Extraction of alkaloids from plants like poppy (*Papaver somniferum*) to prepare concentrated extracts of morphine. This type of percolation allows the recovery of active substances present in low concentrations in plants.

b) **Soxhlet Extraction:**

- **Principle:** The solvent is heated to evaporate, then condensed and dripped onto the solid to be extracted, ensuring continuous and renewed extraction. The solvent loaded with active ingredients is siphoned off periodically, which allows for an increasing concentration of the extracted compounds.



Fig V. 3 : Soxhlet³

- **Pharmaceutical Example:** Extraction of lipid compounds from seeds like soybeans to isolate essential fatty acids, or extraction of active substances from quinine bark for the production of ant-malarial drugs.

³ <https://www.dutscher.com/article/724269>