

Extraction

- Liquid-liquid extraction is a useful method to separate components of a mixture.

Liquid-liquid extraction is based on the transfer of a solute substance from one liquid phase into another liquid phase according to the solubility.

The success of this method depends upon the difference in solubility of a compound in various solvents. For a given compound, solubility differences between solvents is quantified as the "distribution coefficient"

- Example, suppose that you have a mixture of sugar in vegetable oil (it tastes sweet!) and you want to separate the sugar from the oil. You suspect that the sugar is partially dissolved in the vegetable oil.

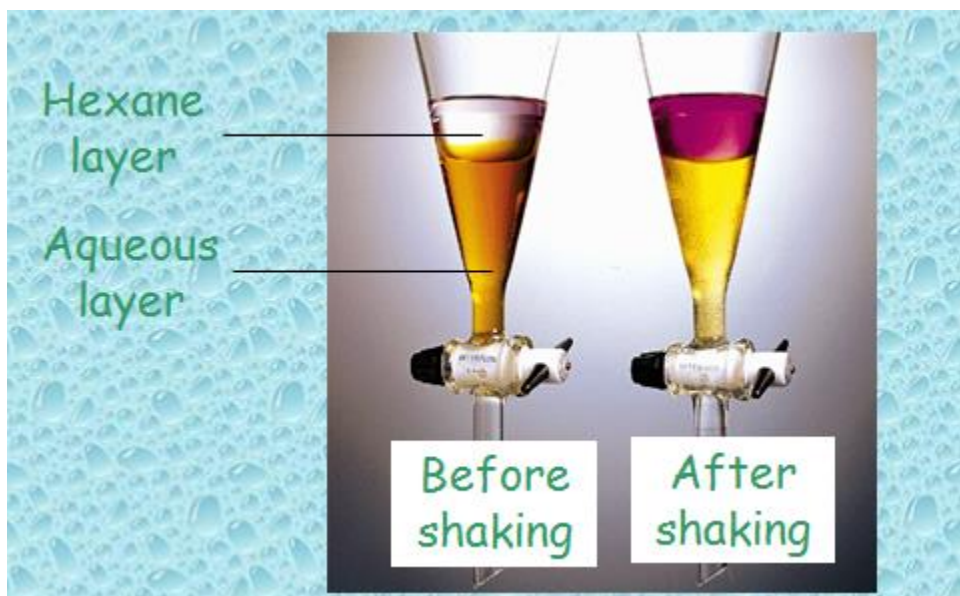
To separate the sugar from the oil we add water to the mixture with shaking.

Sugar is much more soluble in water than in vegetable oil, and water is *immiscible* (=not soluble) with oil.

By shaking the **sugar will move to the phase in which it is most soluble: the water layer**

At the end, the water phase tastes sweet, because the sugar is moved to the water phase upon shaking. ****You extracted sugar from the oil with water.****

- Example, Iodine can be extracted from water by adding hexane, shaking and separating the two layers in a separating funnel.



- To determine the efficiency with which one solvent can extract a compound from a second solvent we use the following equations:

The distribution coefficient is

$$K = \frac{W_1/V_1}{(W - W_1)/V_2}$$

By rearrangement, weight of solute extracted can be calculated using this equation:

$$W_n = W \left(\frac{KV_1}{KV_1 + V_2} \right)^n$$

w = weight in grams of a solute is extracted repeatedly

V_1 = volume in mL of original solvent

V_2 = volume in mL of a second solvent (extraction solvent)

w_1 = weight of the solute remaining in the original solvent after extraction

n = number of extraction repeating

Note: It can be shown from the equation that a most efficient extraction result when n is large and V_2 is small.

Example 9-7

The **distribution coefficient** for iodine between water and carbon tetrachloride at 25°C is $K = C_{\text{H}_2\text{O}}/C_{\text{CCl}_4} = 0.012$. How many grams of iodine are extracted from a solution in water containing 0.1 g in 50 mL by one extraction with 10 mL of CCl_4 ? How many grams are extracted by two 5-mL portions of CCl_4 ? We have

$$W_1 = 0.10 \times \frac{0.012 \times 50}{(0.012 \times 50) + 10}$$

= 0.0057 g remains or 0.0943 g is extracted

$$W_2 = 0.10 \times \left(\frac{0.012 \times 50}{(0.012 \times 50) + 5} \right)^2$$

= 0.0011 g of iodine

Thus, 0.0011 g of iodine remains in the water phase, and the two portions of CCl_4 have extracted 0.0989 g.

Preservative Action of Weak Acids in Oil-Water Systems

- Solutions of foods, drugs, and cosmetics are subject to deterioration by microorganisms. Sterilization and the addition of chemical preservatives are common methods used in pharmacy to preserve drug solutions.
- Benzoic acid in the form of its soluble salt, sodium benzoate, is often used for this purpose.
- The preservative action of benzoic acid and similar acids is due almost entirely to the undissociated acid and not to the ionic form and this due to the relative ease with which the un-ionized molecule penetrates living membranes, and, conversely, the difficulty with which the ion does so.

The undissociated molecule, consisting of a large nonpolar portion, is soluble in the lipoidal membrane of the microorganism and penetrates rapidly.

- Bacteria in oil-water systems are generally located in the aqueous phase and at the oil-water interface. Therefore, the efficacy of a weak acid, such as benzoic acid, as a preservative for these systems is largely a result of the concentration of the undissociated acid in the aqueous phase.
- The distribution of total benzoic acid among the various species in this system depends upon the distribution coefficient, K , the dissociation constant, K_a , of the acid in the aqueous phase, the phase volume ratio, and the hydrogen ion concentration of the aqueous phase.
- To calculate the total concentration of benzoic acid that must be added to preserve an oil-water mixture, we can use the following equations:

$$C = (Kq + 1 + K_a/[H_3O^+])[HA]_w$$

where,

C = total concentration of acid that must be added to the two-phase system to obtain a final specified concentration $[HA]_w$ of undissociated acid in the aqueous phase buffered at a definite pH or hydrogen ion concentration

K = the distribution coefficient = $[HA]_o / [HA]_w$

q = the volume ratio of the two phases, is needed when the volumes are not equal = V_o/V_w

K_a = the dissociation constant of the acid in the aqueous phase

By rearrangement the equation we can calculate the $[HA]_w$

$$[HA]_w = \frac{C}{Kq + 1 + K_a/[H_3O^+]}$$

EXAMPLE 10-25

If benzoic acid is distributed between equal volumes of peanut oil and water, what must be the original concentration in the water phase in order that 0.25 mg/mL of undissociated acid remains in the aqueous phase buffered at a pH of 4.0? The partition coefficient,

$K = [HA]_o/[HA]_w$, is 5.33 and the dissociation constant of the acid in water is 6.4×10^{-5} . Because the two phases are present in equal amounts, $q = V_o/V_w = 1$.

$$C = (Kq + 1 + K_a/[H_3O^+])[HA]_w$$

$$\begin{aligned} C &= (5.33 + 1 + (6.4 \times 10^{-5}/10^{-4}))0.25 \\ &= 1.74 \text{ mg/ml} \end{aligned}$$