Liquid-liquid extraction principles

A liquid–liquid extraction is an important separation technique for environmental, clinical, and industrial laboratories. A standard environmental analytical method illustrates the importance of liquid–liquid extractions.

Feed phase contains a component, **i**, which is to be removed. addition of a second phase (solvent phase) which is immiscible with feed phase but component i is soluble in both phases. Some of component i (solute) is transferred from the feed phase to the solvent phase. After extraction the feed and solvent phases are called the raffinate (R) and extract (E) phases respectively.
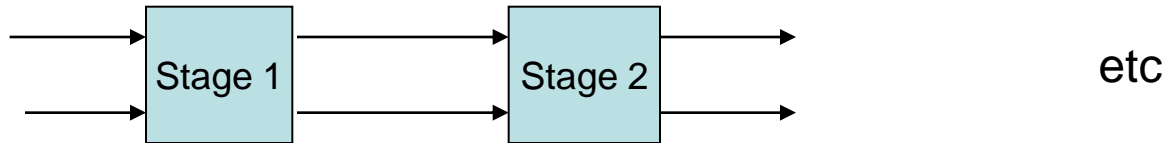
Methods of operation

- Non steady state – concentration changes with time e.g. batch processes
- Steady state
- Stage
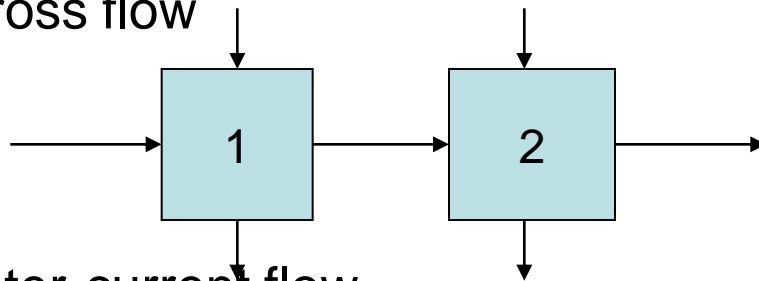- Differential contact (continuous contact)

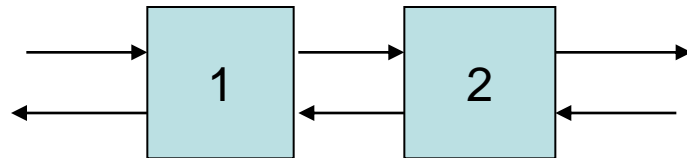# Methods of operation

When both phases are flowing:

- Co-current contact

Stage 1   Stage 2   etc
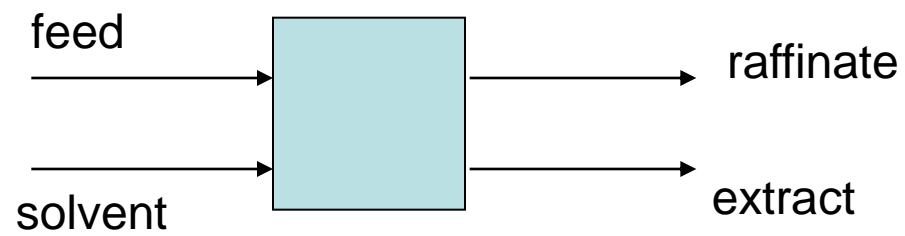
- Cross flow

1   2

Counter-current flow

1   2

Choice of separation process

Factors to be considered:

- Feasibility
- Product value
- Cost
- Product quality
- selectivity

feed → | | → raffinate

solvent → | | → extract

Liquid-liquid extraction principles

Normally one of the two phases is an organic phase while the other is an aqueous phase. Under equilibrium conditions the distribution of solute i over the two phases is determined by the distribution law. After the extraction the two phases can be separated because of their immiscibility. Component i is then separated from the extract phase by a technique such as distillation and the solvent is regenerated.Further extractions may be carried out to remove more component i.Liquid liquid extraction can also be used to remove a component from an organic phase by adding an aqueous phase.

Distribution curve

Plot of y (kgsoluteB/kgsolventS) in E phase
v x (kgsoluteB/kgA) in R phase

Choice of solvent

Factors to be considered:

- Selectivity
- Distribution coefficient
- Insolubility of solvent
- Recoverability of solute from solvent
- Density difference between liquid phases
- Interfacial tension
- Chemical reactivity
- Cost
- Viscosity, vapour pressure
- Flammability, toxicity

Distribution coefficient
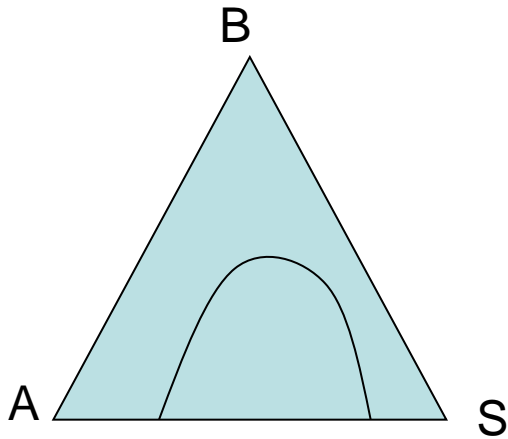
K = y/x

Large values are desirable since less solvent is required for a given degree of extraction

Insolubility of solvent
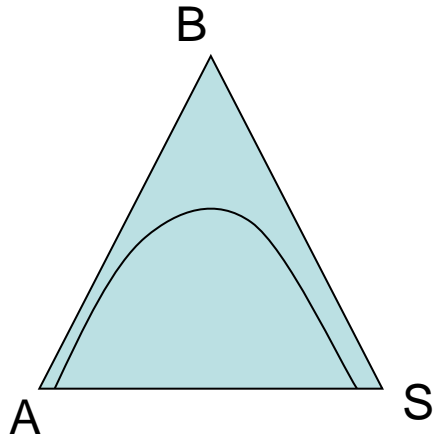
Preferred solvent – A and S have limited solubility

S very soluble in A and A very soluble in S

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Recoverability of solvent and solute

- No azeotrope formed between solvent and solute

- Mixtures should have a high relative volatility

- Solvent should have a small latent heat of vapourisation

Density

A density difference is required between the two phases.

Interfacial tension

The larger the interfacial tension between the two phases the more readily coalescence of emulsions will occur to give two distinct liquid phases but the more difficult will be the dispersion of one liquid in the other to give efficient solute extraction.

Chemical reactivity

Solvent should be stable and inert

Physical properties

For material handling:

- Low viscosity

- Low vapour pressure

- Non-flammable (high flash point)

- Non-toxic

A graphical procedure may be used to analyse these systems. The number of theoretical stages (n) required to pass from x_F to xn is found by drawing in 'steps' between the operating line and the equilibrium curve (yn, xn).

In practice equilibrium conditions may not be attained and extraction efficiency will be less than 100% thus requiring more stages in practice than the above analysis would suggest.

Also partial miscibility of the solvents has to be considered in the separation process.

Example - Penicillin G

6-aminopenicillanic acid (6-APA) is manufactured by GSK in Irvine. It is used to manufacture amoxicillin and 'Augmentin'.

Fermentation products (penicillin G broth) are filtered (microfiltration) and extracted at low pH with amyl acetate or methyl isobutyl ketone. The penicillin G is then extracted further at a higher pH into an aqueous phosphate buffer.

Extractants

The efficiency of a liquid liquid extraction can be enhanced by adding one or more extractants to the solvent phase. The extractant interacts with component i increasing the capacity of the solvent for i.To recover the solute from the extract phase the extractant-solute complex has to be degraded.

Distribution coefficient

K = <u>mass fraction solute in E phase</u>

     mass fraction solute in R phase

Immiscible liquids

e.g. water – chloroform

Consider a feed of water/acetone(solute).

K = <u>mass fraction acetone in chloroform phase</u>

       mass fraction acetone in water phase

K = <u>kg acetone/kg chloroform</u> = y/x

    kg acetone/kg water

K = 1.72

i.e. acetone is preferentially soluble in the chloroform phase

Partition Coefficients and Distribution Ratios

As we learned earlier in this chapter, a solute's partitioning between two phases is described by a partition coefficient, KD. If we extract a solute from an aqueous phase into an organic phase

$$S_{aq} \rightleftharpoons S_{org}$$
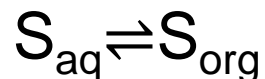
then the partition coefficient is

$$KD=[S_{org}] /[S_{aq}]$$

A large value for KD indicates that extraction of solute into the organic phase is favorable.

To evaluate an extraction's efficiency we must consider the solute's total concentration in each phase, which we define as a distribution ratio, D.

$$D=[S_{org}]_{total} /[S_{aq}]_{total}$$

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The partition coefficient and the distribution ratio are identical if the solute has only one chemical form in each phase; however, if the solute exists in more than one chemical form in either phase, then KD and D usually have different values. For example, if the solute exists in two forms in the aqueous phase, A and B, only one of which, A, partitions between the two phases, then

$$D=[S_{org}]_A/[S_{aq}]_A+[S_{aq}]_B \quad \leq KD=[S_{org}]_A/[S_{aq}]_A$$

This distinction between KD and D is important. The partition coefficient is a thermodynamic equilibrium constant and has a fixed value for the solute's partitioning between the two phases. The distribution ratio's value, however, changes with solution conditions if the relative amounts of A and B change. If we know the solute's equilibrium reactions within each phase and between the two phases, we can derive an algebraic relationship between KD and D.

In a simple liquid–liquid extraction, the only reaction that affects the extraction efficiency is the solute's partitioning between the two phases (Figure 1)
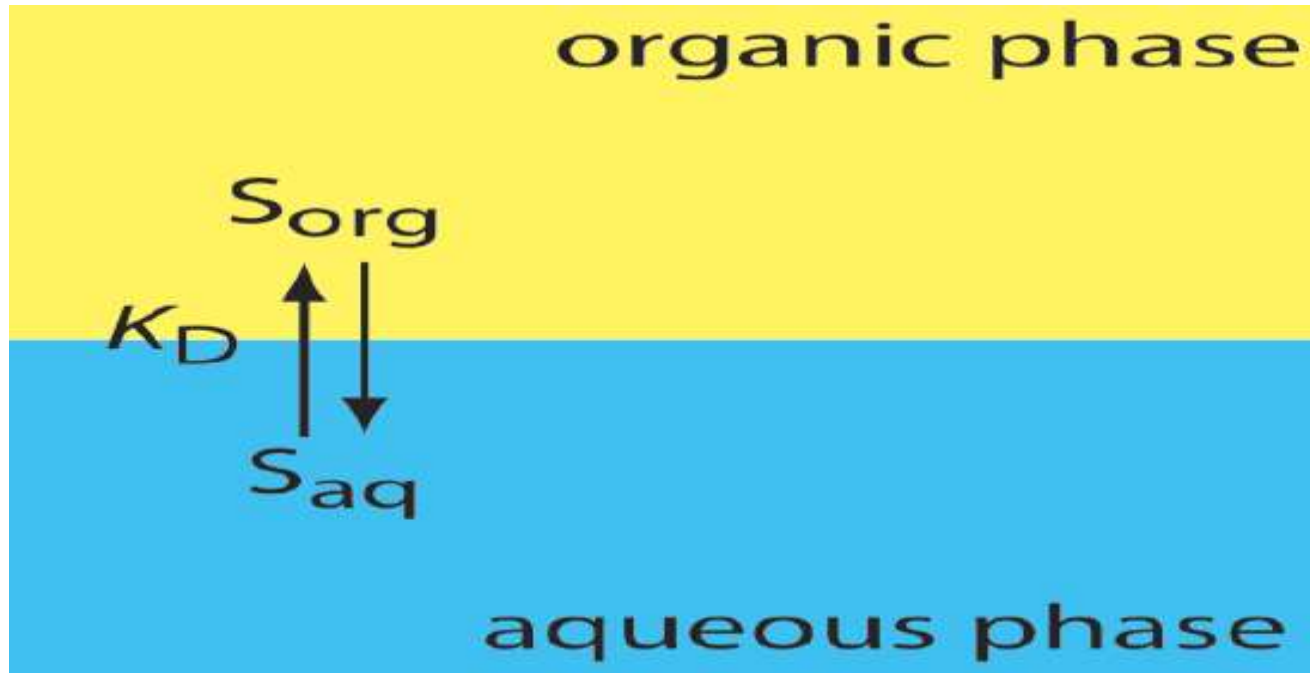

Fig 1 Scheme for a simple liquid–liquid extraction in which the solute's partitioning depends only on the K_D equilibrium

In this case the distribution ratio and the partition coefficient are equal.

$$D=[S_{org}]_{total}/[S_{aq}]_{total} = KD=[S_{org}]/[S_{aq}] \qquad (1)$$

Let's assume the solute initially is present in the aqueous phase and that we wish to extract it into the organic phase. A conservation of mass requires that the moles of solute initially present in the aqueous phase equal the combined moles of solute in the aqueous phase and the organic phase after the extraction.

$$(mol\ S_{aq})_0=(mol\ S_{aq})_1+(mol\ S_{org})_1 \qquad (2)$$

where the subscripts indicate the extraction number with 0 representing the system before the extraction and 1 the system following the first extraction. After the extraction, the solute's concentration in the aqueous phase is

$$[S_{aq}]_1=(mol\ S_{aq})_1/V_{aq} \qquad (3)$$

and its concentration in the organic phase is

$$[S_{org}]_1 = (mol\ S_{org})_1 / V_{org} \qquad (4)$$

where Vaq and Vorg are the volumes of the aqueous phase and the organic phase.
Solving equation 2 for $(mol\ S_{org})_1$ and substituting into equation 4 leave us with

$$[S_{org}]_1 = (mol\ Saq)_0 - (mol\ S_{aq})_1 / V_{org} \qquad (5)$$

Substituting equation.3 and equation 5 into equation 1 gives

$$D = (mol\ S_{aq})_0 - (mol\ S_{aq})_1 / V_{org}\ /\ (mol\ S_{aq})_1 / Vaq = (mol\ S_{aq})_0 \times V_{aq} - (mol\ S_{aq})_1 \times Vaq\ / (mol\ S_{aq})_1 \times V_{org}$$

Rearranging and solving for the fraction of solute that remains in the aqueous
phase after one extraction, $(q_{aq})_1$, gives

$$(q_{aq})_1 = (mol\ S_{aq})_1 / (mol\ S_{aq})_0 = Vaq\ /\ DV_{org} + V_{aq} \qquad (6)$$

The fraction present in the organic phase after one extraction, $(q_{org})_1$, is

$$(q_{org})_1 = (molS_{org})_1 / (molS_{aq})_0 = 1 - (q_{aq})_1 = Dv_{org}\ /\ DV_{org} + V_{aq}$$

A solute has a KD between water and chloroform of 5.00. Suppose we extract a 50.00-mL sample of a 0.050 M aqueous solution of the solute using 15.00 mL of chloroform. (a) What is the separation's extraction efficiency? (b) What volume of chloroform do we need if we wish to extract 99.9% of the solute?

Solution

For a simple liquid–liquid extraction the distribution ratio, D, and the partition coefficient, KD, are identical.

(a) The fraction of solute that remains in the aqueous phase after the extraction is given by equation   6 .

$$(q_{aq})_1 = V_{aq}/DV_{org}+V_{aq}=50.00 \text{ mL} / (5.00)(15.00 \text{ mL})+50.00 \text{ mL}=0.400$$

The fraction of solute in the organic phase is 1–0.400, or 0.600. Extraction efficiency is the percentage of solute that moves into the extracting phase; thus, the extraction efficiency is 60.0%.

b) To extract 99.9% of the solute $(q_{aq})_1$ must be 0.001. Solving equation 6 for V_{org}, and making appropriate substitutions for $(q_{aq})_1$ and V_{aq} gives

$V_{org}=V_{aq}-(q_{aq})_1/V_{aq}/(q_{aq})_1 D = 50.00 \text{ mL}-(0.001)(50.00 \text{ mL})/(0.001)(5.00 \text{ mL})=999 \text{ mL}$
This is large volume of chloroform. Clearly, a single extraction is not reasonable under these conditions

In Example 1, a single extraction provides an extraction efficiency of only 60%. If we carry out a second extraction, the fraction of solute remaining in the aqueous phase, $(q_{aq})_2$, is

$$(q_{aq})_2 = (mol\ S_{aq})_2 / (mol\ S_{aq})_1 = V_{aq} / DV_{org} + V_{aq}$$

If V_{aq} and V_{org} are the same for both extractions, then the cumulative fraction of solute that remains in the aqueous layer after two extractions, $(Q_{aq})_2$, is the product of $(q_{aq})_1$ and $(q_{aq})_2$, or

$$(Q_{aq})_2 = (mol\ S_{aq})_2 / (mol\ S_{aq})_0 = (q_{aq})_1 \times (q_{aq})_2 = (V_{aq}/DV_{org} + V_{aq})^2$$

In general, for a series of n identical extractions, the fraction of analyte that remains in the aqueous phase after the last extraction is

$$(Q_{aq})n = (V_{aq} / DV_{org} + V_{aq})^n$$

(7)

Example 2

For the extraction described in Example 1 , determine (a) the extraction efficiency for two identical extractions and for three identical extractions; and (b) the number of extractions required to ensure that we extract 99.9% of the solute.
Solution
(a) The fraction of solute remaining in the aqueous phase after two extractions and three extractions is

$$(Q_{aq})_2 = (50.00 \text{ mL}/(5.00)(15.00 \text{ mL}) + 50.00 \text{ mL})^2 = 0.160$$
$$(Q_{aq})_3 = (50.0 \text{ mL}/(5.00)(15.00 \text{ mL}) + 50.00 \text{ mL})^3 = 0.0640$$

The extraction efficiencies are 84.0% for two extractions and 93.6% for three extractions.
(b) To determine the minimum number of extractions for an efficiency of 99.9%, we set $(Q_{aq})_n$ to 0.001 and solve for n using equation 7 .

$$0.001 = (50.00 \text{ mL}(5.00)(15.00 \text{ mL}) + 50.00 \text{ mL})^n = (0.400)^n$$

Taking the log of both sides and solving for n

$$\log(0.001)^n = n\log(0.400) = 7.54$$

we find that a minimum of eight extractions is necessary

he last two examples provide us with an important observation—for any extraction efficiency, we need less solvent if we complete several extractions using smaller portions of solvent instead of one extraction using a larger volume of solvent. For the conditions in Example 1 and Example.2 , an extraction efficiency of 99.9% requires one extraction with 9990 mL of chloroform, or 120 mL when using eight 15-mL portions of chloroform. Although extraction efficiency increases dramatically with the first few multiple, the effect diminishes quickly as we increase the number of extractions (Figure.2). In most cases there is little improvement in extraction efficiency after five or six extractions. For the conditions in Example 2 , we reach an extraction efficiency of 99% after five extractions and need three additional extractions to obtain the extra 0.9% increase in extraction efficiency.
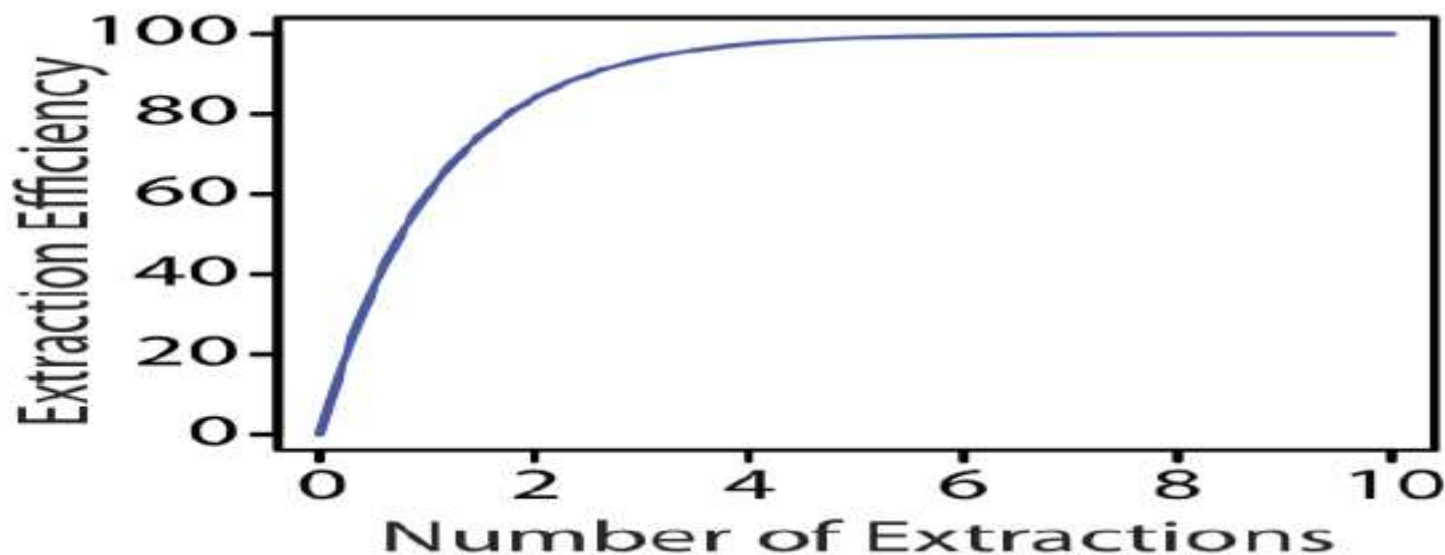

Figure 2 . Plot of extraction efficiency versus the number of extractions for the liquid–liquid extraction in Example 2 .