Solvent Extraction

A significant method based on relative solubility of an analyte in two immiscible liquids

Used to
- remove interference
- concentrate species prior analysis
- produce measurable form of a species

Theory is very applicable to chromatography.

Solvent extraction theory

For a solute, Z, in equilibrium exists between an aqueous and organic solvent:

$$Z_{(2)} \rightleftharpoons Z_{(1)}$$

At equilibrium, we have:

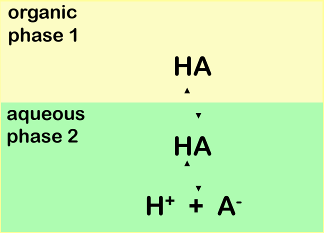
$$K_P = \frac{[Z]_1}{[Z]_2}$$

This assumes ideal behavior at low concentrations. It actually results in a ternary system.

Solvent extraction theory

When dealing with aqueous species, the solute may exist in equilibrium with several other forms.

Example
- a weak acid



Distribution ratio

Due to competing equilibria, we define an alternate form of the partition coefficient:

$$\text{distribution ratio} = D_c = \frac{[\text{ total } Z\ ]_1}{[\text{ total } Z\ ]_2} = \frac{C_1}{C_2}$$

Total Z represents the total of all equilibrium forms of species Z.

This ratio is based on specific solution conditions such as pH.

Distribution ratio

If $K_P = [HA]_1 / [HA]_2$

and $K_a = [H^+]_2\, [A^-]_2 / [HA]_2$

then $D_c = \dfrac{[HA]_1}{[HA]_2 + [A^-]_2}$

$$= \frac{[HA]_1}{\dfrac{[HA]_1}{K_P} + \dfrac{K_a\,[HA]_1}{K_P\,[H^+]_2}}$$

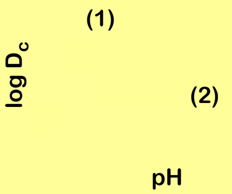
$$= \frac{K_P[H^+]_2}{[H^+]_2 + K_a}$$

Obligitory derivation designed to impress you with how much I know. Do you really care about this?

pH dependence of D_c

In the case of a weak acid, D_c is dependent on solution pH.

$$D_c = \frac{K_P[H^+]_2}{[H^+]_2 + K_a}$$



A plot of log D_c vs log pH shows two regions.

1 - $[H^+] \gg K_a$, $D_c \simeq K_P$

2 - D_c is pH dependent

Its best to hold pH and other factors constant.

Solute partitioning

The D_c can be defined based on total equilibrium concentrations as:

$$D_c = \frac{C_1}{C_2}$$

where:

1 is the phase being extracted into

2 is the phase being extracted from

All solution conditions are assumed constant. Total solute amounts are based on solution volume.

Solute partitioning

The initial moles of solute is C_0V_2 so at equilibrium:

$$n_{solute1} = C_1V_1$$

$$n_{solute2} = C_2V_2$$

In terms of fractional amounts:

$$p = \text{fraction in 1} = \frac{C_1V_1}{C_1V_1 + C_2V_2}$$

Amount extracted

$$q = \text{fraction in 2} = \frac{C_2V_2}{C_1V_1 + C_2V_2}$$

Amount remaining

Solute partitioning

If we define the volume ratio (V_R) as

$$V_R = \frac{V_1}{V_2}$$

then

Amount extracted

$$q = \frac{1}{D_cV_R + 1}$$

Amount remaining

$$p = \frac{D_cV_R}{D_cV_R + 1}$$

Single extractions

To help keep things straight, let's define some conditions for a single extraction or contact unit.

Most often, we are interested in extracting from an aqueous into an organic phase.

organic phase

density > or < 1.00 g/ml - call it phase 1

aqueous phase

density ~ 1.00 g/ml - call it phase 2

Single extractions

Single Extractions

If the aqueous phase is what we are extracting from, then:

V - volumes, all must be in same units

C - total concentrations

C_1 - organic concentration

C_2 - aqueous concentration

C_0 - initial concentration

Solute extraction

We can determine the percent extracted as:

%E = 100 p

Example

For a solute, X, determine [X] and total amounts in each phase if:

V_1 = 100.0 ml
V_2 = 100.0 ml
D_c = 3.0
$[X]_0$ = 1.00×10^{-2} M (in aq. phase)

Solute extraction

Since $V_1 = V_2$, $V_R = 1$,

Amount extracted $p = \frac{D_c V_R}{D_c V_R + 1} = \frac{3.0}{3.0 + 1} = \frac{3}{4}$

Amount remaining $q = \frac{1}{D_c V_R + 1} = \frac{1}{3.0 + 1} = \frac{1}{4}$

%E = 100 p = 75%

Solute extraction

Determining amounts

We started with 1.00×10^{-2} M in 100.0 ml of the aqueous phase so:

$n_T = (0.100\ \text{l})(1.00 \times 10^{-2}\ \text{M}) = 1.00 \times 10^{-3}$ mol

$n_1 = 7.5 \times 10^{-4}$ mol $\quad M_1 = 7.5 \times 10^{-3}$
$n_2 = 2.5 \times 10^{-4}$ mol $\quad M_2 = 2.5 \times 10^{-3}$

Deviations from ideal behavior

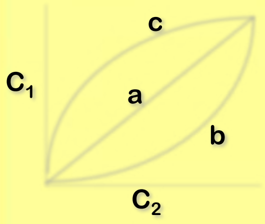
Solutions can vary from ideal behavior either from the start or during an extraction.

Possible causes include:

- dissolution of one phase into the other
- solute saturation of a phase
- reaction of solute with a phase
- alteration of conditions like pH during an extraction.

Deviations from ideal behavior

You can end up with three types of behavior - partition isotherms.



a - ideal behavior

b - solute association, dimerization, etc.

c - phase 1 is an absorbed phase. Approaching saturation

Deviations from ideal behavior

You must also remember that we assumed that activity and concentration were proportional.

We attempt to avoid problems by:

- Working at low concentrations
- Maintaining factors like pH as constants

We do our best to stay as close to ideal conditions as possible.

Multiple extractions

It is not always possible to quantitatively remove the solute using a single extraction.

Your options typically are to:

Increase the volume of the extracting solvent - not usually a good idea.

Use multiple extractions.

Multiple extractions

For n extractions, the amount of solute in each phase can be determined by:

organic phase $pq^{n-1} C_0V_2$

aqueous phase $q^n C_0V_2$

Solute concentrations can be found by:

organic $pq^{n-1} C_0V_2 / V_1 = pq^{n-1} C_0 / V_R$

aqueous $q^n C_0V_2 / V_2 = q^n C_0$

Multiple extractions

Total amounts extracted are the sum of all extractions so:

$$(p + pq + pq^2 \ldots + pq^{n-1})C_0V_2 = (1-q^n)C_0V_2$$

or

$$1 - q^n = E \quad , \quad \%E = 100\,(1-q^n)$$

Multiple extractions

In our earlier example, 75% of a solute was removed with one extraction. We can determine how much would be removed from 10 sequential extractions.

$n = 10$

$q = 0.25$

$E \cong 1 - 0.25^{10} = 1 - 9.6 \times 10^{-7}$

$\%E = 99.9999\%$

Countercurrent extractions

A precursor to chromatography.

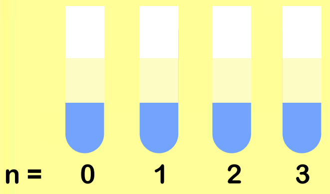
Multiple extractions can effectively remove a single species or a group of related species at the same time.

What do you do if the goal is to separate two or more species with similar D_c values?

Even if the D_c values for two species differ by 1000, you still can't get better than 97% purity.

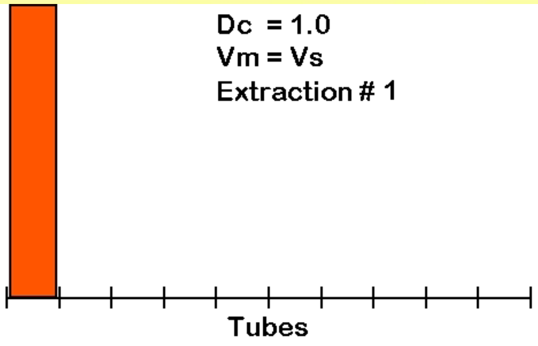
Countercurrent extractions

We can conduct a sequence of extractions to effect quantitative separation of multiple solutes - countercurrent extraction



We transfer the extracting phase to the next tube and add fresh phase to the first.

Countercurrent extraction



Countercurrent extractions

Assume

Equimolar amounts of solutes A and B.

Equal volumes of both phases

A single extraction with an organic phase removes 3% of A and 97% of B.

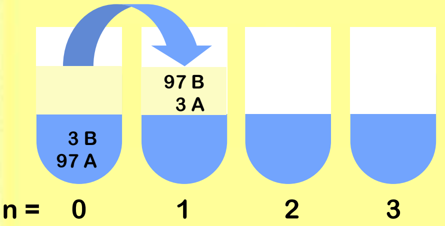
After each extraction, you transfer the organic phase to the next tube and add fresh organic phase to the original one.

First extraction

Totals

A	**100**
B	**100**

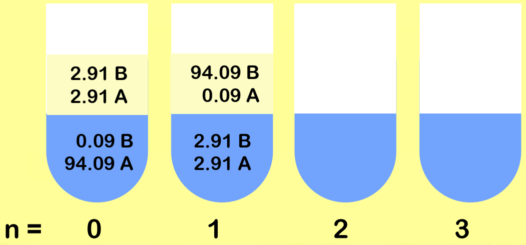
Next, the organic phase is transferred to the second tube. A new equilibrium is established.



Second extraction

Totals

A	**97**	**3**
B	**3**	**97**



Movement of solutes

Materials with larger D_c values tend to move along with the organic (mobile) phase more rapidly.

Peak shape

As the number of tubes are increased, the distribution of solutes appears more Gaussian. Ultimately, you can resolve them.

n=6 **n=25** **n=100**

The peaks also become broader and shorter - they are distributed over a larger range of tubes.

Continuous extraction

In some cases, it is difficult to efficiently remove a solute unless a large number of extractions are conducted.

An alternate approach is a continuous extraction.

With an appropriate setup, an efficient extraction can be conducted with a minimum of extracting solvent.

Continuous extraction

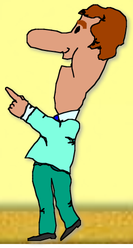
Advantages

Only uses a small amount of solvent
Can remove a high percent of a solute
Can work unattended for long periods

Setup

Dependent on relative density of liquids or if solids are to be extracted.

Continuous extraction



Setup when the extracting fluid is more dense.

Continuous extraction

Setup when the extracting solvent is less dense.

Continuous extraction

For these systems to work

- Density difference must be high
- Solute being collected must be less volatile than the extracting solvent
- Solute being collected must be thermally stable under conditions used.

Continuous extraction

Extraction times follow first order kinetics and are ranked based on halflife.

log t

$t_{1/2}$

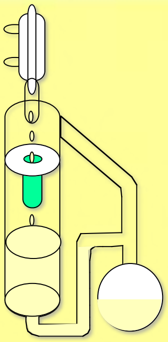
50

% E

Continuous extraction

Continuous extraction can also be applied to solids.

Major limitation is a loss in efficiency during extraction due to channels developing in the solid



Soxhlet extraction

An alternate approach to extracting solids.

Repeated soaking of the solid prevents formation of channels

Rapid return of cool fluid can represent a hazard. Solvent should not be flammable.

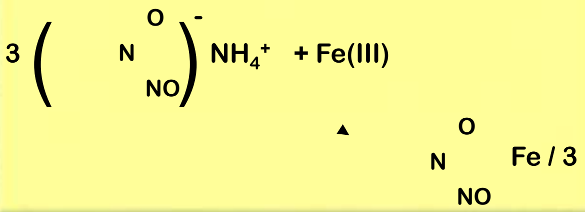
Some extraction methods

- Organic species
  "Like disolves like"
- Ionizing organic species
  Limit ionization by controlling pH
- Use of organic complexing reagents.
  Many reagents available to complex metal ions - more soluble in organic phase.
- Ion-association complexes
  Formation of neutral ion pairs.

Complexing reagents

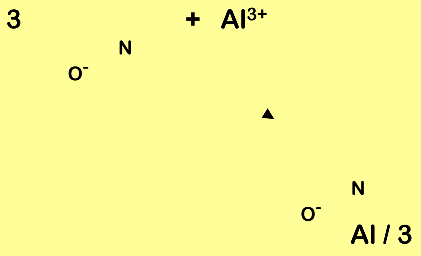
Cupferron

Will form a complex with iron that can then be extracted.



Complexing reagents

Oxine - formation of an aluminum complex



Ion association complexes

At high levels of a complexing acid, it is possible to form a neutral species that is extractable.

$$Fe(III) \xrightarrow{6\ M\ HCl} FeCl_4^-$$

This can be extracted as $HFeCl_4$.

To work: Conditions must favor formation of a large ion and the solvent must strongly solvate the ion pair.