## 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:

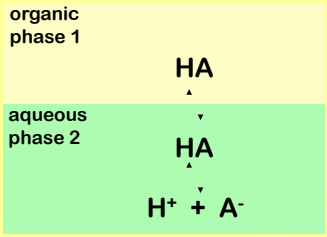
$$K_P = \frac{[Z]_1}{[Z]_2}$$

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

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

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

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.

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

(1)

(2)

log $D_c$

pH

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

1 - $[H^+] >> K_a$, $D_c \sim K_P$

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 x $10^{-2}$ M (in aq. phase)

## Solute extraction

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

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

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

$\%E = 100\ p = 75\%$

## Solute extraction

**Determining amounts**

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

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

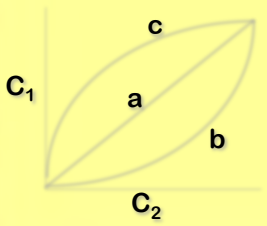
Solutions can vary from ideal behavior either from the start or during an extraction.

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.

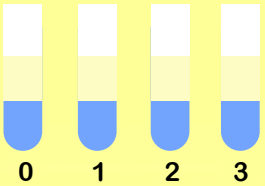
Multiple extractions can effectively remove a single species or a group of related species at the same time.

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.

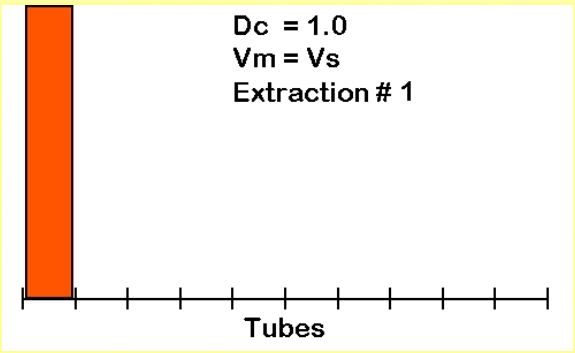
## Countercurrent extractions

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

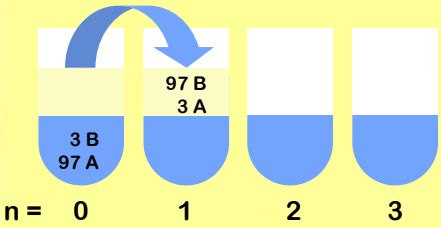
A single extraction with an organic phase removes 3% of A and 97% of B.

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

## First extraction

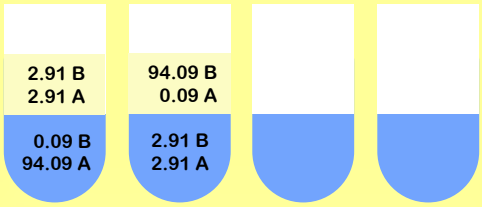
**Totals**
**A 100**
**B 100**

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



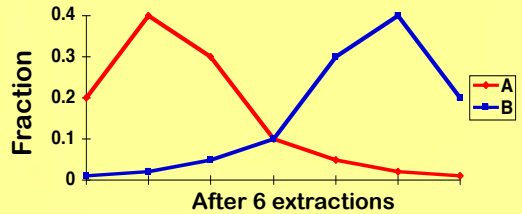

## Second extraction

**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


## 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.

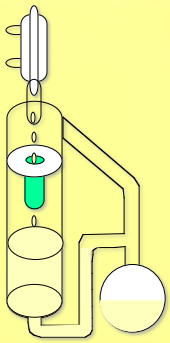
log t $t_{1/2}$

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.

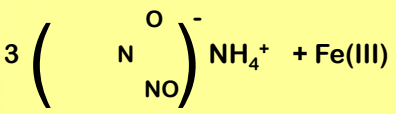
## Some extraction methods

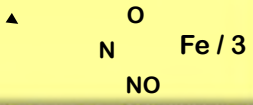
- Organic species
  "Like disolves like"
- Ionizing organic species
  Limit ionization by controlling pH
- Use of organic complexing reagents.
  Many reagents available to complex metal ions - more soluble in organic phase.
- Ion-association complexes
  Formation of neutral ion pairs.

## Complexing reagents

Cupferron

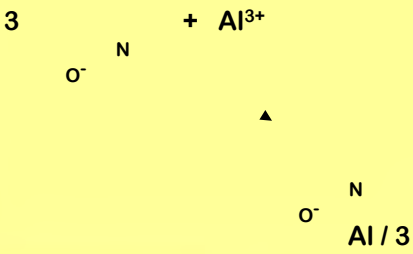
Will form a complex with iron that can then be extracted.



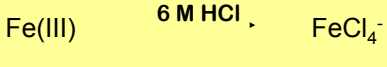

## Complexing reagents

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.




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.