Principles of Extraction

Separatory Funnel

Separation of immiscible liquids
Extraction

- To pull out a compound from one layer into another
- A compound partitions more toward where it is more soluble (equilibrium)
- Partition coefficient
- Multiple extractions may be needed to completely extract a substance

Partition coefficient ($K$)

Any organic compound with $K > 1.5$ can be separated from water by an organic solvent.

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

$C_1$ = solubility of your compound in organic solvent

$C_2$ = solubility in water (aqueous)
Example: Benzoic Acid

Goal – extract benzoic acid from water into an organic solvent.
Which solvents can we cross out immediately?
Which solvent will give the most optimal partition coefficient?
What is the partition coefficient in this solvent?

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(M)</th>
<th>Mole Fraction (X)</th>
<th>pph (g/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>1.35</td>
<td>0.11</td>
<td>24.77</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>0.76</td>
<td>0.04</td>
<td>13.37</td>
</tr>
<tr>
<td>benzene</td>
<td>0.48</td>
<td>0.04</td>
<td>7.06</td>
</tr>
<tr>
<td>chloroform</td>
<td>1.8</td>
<td>0.15</td>
<td>17.95</td>
</tr>
<tr>
<td>ethanol</td>
<td>2.52</td>
<td>0.17</td>
<td>53.18</td>
</tr>
<tr>
<td>methanol</td>
<td>2.84</td>
<td>0.15</td>
<td>64.89</td>
</tr>
<tr>
<td>THF</td>
<td>3.37</td>
<td>0.29</td>
<td>69.27</td>
</tr>
<tr>
<td>toluene</td>
<td>0.65</td>
<td>0.07</td>
<td>9.81</td>
</tr>
<tr>
<td>water</td>
<td>0.03</td>
<td>0.00</td>
<td>0.37</td>
</tr>
</tbody>
</table>


Extraction Calculation

• If the partition coefficient between water and chloroform is about 49 for benzoic acid, how would 1.00 g of benzoic acid be distributed between 100 mL of water and 100 mL of chloroform?

• 49 = (X g/100mL)/(Y g/100mL) and X+Y = 1.00

• 49 = ((1.00-Y)/100)/(Y/100) = (1.00-Y)/Y

• Y = 0.020g in water and X = 0.980g in chloroform
Multiple Extractions

1 g of compound dissolved in 50 mL H₂O
Partition coefficient = 5
45 mL ether

Question: What is better, one 45 mL extraction, or three 15 mL extractions?

\[
\frac{(\text{Final mass of solute})_{\text{water}}}{(\text{Initial mass of solute})_{\text{water}}} = \left(\frac{V_2}{V_2 + V_1K}\right)^n
\]

Mohrig p. 145

\(V_1\) = volume of organic solvent used in each extraction
\(V_2\) = original volume of water
\(n\) = number of extractions
\(K\) = partition coefficient

Example Extraction Continued

\[
\frac{(\text{Final mass of solute})_{\text{water}}}{(\text{Initial mass of solute})_{\text{water}}} = \left(\frac{V_2}{V_2 + V_1K}\right)^n
\]

n = 1
K = 5
Initial mass = 1 g
Final mass = x
\(V_1\) = 45 mL ether
\(V_2\) = 50 mL water

n = 3
K = 5
Initial mass = 1 g
Final mass = x
\(V_1\) = 15 mL ether
\(V_2\) = 50 mL water

Final mass of compound in water =
Final mass of compound in water =

Takeaway message?
Separation Using Extraction

• What if our solid sample contains two substances?
• When the solids dissolve and partition, there are three possibilities—which would be effective for a purification technique?

Flowchart

Extract → Separate → Dry → Evaporate
Solubility

• To plan for an extraction, must be able to choose proper solvents to separate impurities from target
• Partitioning is based on relative solubility
• Is the compound more organic soluble or more aqueous soluble?

Solubility Rules of Thumb

• Water soluble
  – Ionic
  – Organic ions of < 7-8 carbons
  – Small polar molecules
  – Organic compounds with one H-bond donor per 3-4 carbons
**Water Insolubility Spectrum**

- Somewhat soluble
  - ![Chemical Structure](image)
- Insoluble
  - ![Chemical Structure](image)
- Detergents
  - ![Chemical Structure](image)

**Organic Solvent Solubility**

- **Organic Soluble**
  - Other organic molecules unless extremely different polarity
- **Organic insoluble**
  - Ionic
  - ![Chemical Structure](image)

These are not organic soluble:
Planning an Extraction

• You want to separate the following two impurities from your target with extraction. You dissolve the mixture in water/ether in a separatory funnel.
  – Will the purification work?
  – In which layer is your target (top or bottom)?

![target compound](image1)
![impurity 1](image2)
![impurity 2](image3)

Acid/Base Extractions

• Rather than neutral water, extract with aqueous acid or aqueous base
• What happens in our example case if we extract with aqueous NaOH instead of water? Where are the compounds? What about aqueous HCl?

![target compound](image1)
![impurity 1](image2)
![impurity 2](image3)
Flow charts are helpful for acid-case extractions. Example – separation of an acid (HA), base (B), and a neutral compound (N).