Double emulsions: Fundamentals and opportunities

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Food emulsions
Covered in this lecture

- Emulsion structures
- Double emulsions
  - Applications
  - Issues
  - Formulation
- Textbook references

Mixing oil and water

www.simscience.org/membranes/advanced/page3.html
Stabilised droplets

Emulsion microstructures

- Single emulsions
- Double emulsions (multiple emulsions, duplex emulsions)
- Submicron emulsions
- Biliquid foams / high internal phase emulsions (HIPE)
Single emulsions

(o/w) emulsion or simple emulsion
- thermodynamically unstable, but...
- kinetic stable system
- droplet sizes (0.1) 1...100 µm

mini emulsion or submicron emulsion:
- droplet sizes 100 nm ...1 µm
- nano emulsion: droplet sizes < 100 nm

micro emulsion
- thermodynamically stable system through very low interfacial tension < 10^{-3} mN/m
- self forming upon mixing of ingredients
- droplet sizes well < 100 nm
- up to 30 % of surfactants & co-surfactants required

Double emulsions

(o/w)-in-oil (o/w/o)

(w/o)-in-water (w/o/w)

water-in-oil (w/o)

(w/o)-in-water (w/o/w)
**Micrographs**


Monodisperse emulsions

Advanced manufacture: microfluidics


Pictures from the Webpage of the Experimental Soft Condensed Matter Group at Harvard University, Prof DA Weitz
Monodisperse emulsions
Advanced manufacture: membrane emulsification.

Sketch and data courtesy of F. Spyropoulos, University of Birmingham, UK.

Sintered porous glass membranes. Left: 2.8 µm membrane. Right: 7 µm membrane.

Microstructure & flow characteristics


Emulsion stability

**flocculation/aggregation**

\[ \text{w} \rightarrow \text{o} \]

**phase inversion**

\[ \text{w} \rightarrow \text{o} \]

**Ostwald ripening**

\[ P_{\text{cap}} \propto x^{-1} \]

**Breaking - phase separation**

\[ \text{w} \rightarrow \text{o} \]

**sedimentation/creaming**

\[ v \propto x_{\text{droplet}}^2 \]

**coalescence**

Emulsifiers

- **molecular (surfactant)**
  - hydrophilic
  - lipophilic

- **small molecular**

- **polymeric**

- **microbial**

- **particulate**

**Oil soluble:**
- monoglycerides, lecithins, glycolipids, fatty alcohols, fatty acids...

**Water soluble:**
- proteins, polysaccharides (gum arabic, methylcellulose)

Particulate emulsifiers

<table>
<thead>
<tr>
<th>Size Range</th>
<th>Water</th>
<th>Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;90 μm</td>
<td>Contact angles &gt; 90 degrees</td>
<td></td>
</tr>
<tr>
<td>0–90 μm</td>
<td>Contact angles ~ 90 degrees</td>
<td></td>
</tr>
<tr>
<td>&gt;90 μm</td>
<td>No preferential formation.</td>
<td></td>
</tr>
</tbody>
</table>

Particles at interfaces

Oil-in-water emulsion stabilised with 200nm silica particles.

Oil-in-water emulsion stabilised with partially hydrophobised 500nm silica particles. Scarce surface coverage as also observed by others\textsuperscript{1,2}.

Food examples

Fat globule stabilised air bubble of a whipped cream

Water (30%) in cocoa butter emulsion

Cellulose micro-rods for foam stabilisation.

Double emulsion with inner interface fat crystal stabilised

\textsuperscript{1} Binks BP et al (2005) Langmuir 21, 8161.

Applications for double emulsions

• Encapsulation
  – Flavour
  – High value ingredients/nutrients
  – Masking
• Partial fat reduction
• Salt reduction

Partial fat reduction

• Savoury sauces and dressings
• Spreads
• Chocolate and confectionary

See contribution by Philip Cox (TP2)
Salt reduction

Hypothesis:
Concentrating salt in external product phase increases salt perception\(^2\).

\[\text{o/w} \quad \text{o/w+} \quad \text{w/o/w} \quad \text{w/o/w+}\]

\(100\ \mu\text{m}\)

+ indicates presence of pea purée

‘more texture’ enabling sensory analysis for salt perception\(^2\)

\(^2\)Lad et al (unpublished data)

Salt reduction

<table>
<thead>
<tr>
<th>Test</th>
<th>Emulsion type</th>
<th>NaCl content per 100 g of water/ emulsion</th>
<th>NaCl concentration in aqueous phase</th>
<th>Answers</th>
<th>Significance</th>
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</thead>
<tbody>
<tr>
<td>water</td>
<td>--</td>
<td>0.94 g</td>
<td>[0.160 M]</td>
<td>4</td>
<td>&lt;0.0001***</td>
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<tr>
<td></td>
<td>--</td>
<td>1.21 g</td>
<td>[0.207 M]</td>
<td>37</td>
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<tr>
<td>fluid</td>
<td>single</td>
<td>0.63 g</td>
<td>[0.160 M]</td>
<td>14</td>
<td>0.0596</td>
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<tr>
<td>samples</td>
<td>duplex</td>
<td>0.63 g</td>
<td>[0.207 M]</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>thickened</td>
<td>single</td>
<td>0.63 g</td>
<td>[0.160 M]</td>
<td>9</td>
<td>0.0004***</td>
</tr>
<tr>
<td>samples</td>
<td>duplex</td>
<td>0.63 g</td>
<td>[0.207 M]</td>
<td>32</td>
<td></td>
</tr>
</tbody>
</table>

→ Hypothesis was successfully tested.

Lad et al (unpublished data)
Issues with double emulsions

“To date, there are no products on the market that contain double emulsions, because they are difficult to keep stable and also to manufacture in volume. Part of the problem is that when a double emulsion containing water has sugar or salt in one of the other phases, the combination creates osmotic pressure. This means that the water migrates towards the more salty or sugary side of any interface, and so the emulsion breaks down.”


Difference in chemical potential between water compartments rather than unbalanced osmotic pressures can be reason for instability.

Pawluk et al (unpublished data)

Stable double emulsions

• Particle stabilisation.
• Gelation of the internal phase.
• Strong elastic external interface through appropriate structuring based on PGPR.
Textbooks

- Encyclopedic Handbook of Emulsion Technology by Johan Sjoblom
- Emulsions and Emulsion Stability: 132 (Surfactant Science) by Johan Sjoblom
- Encyclopedia of Emulsion Technology: Basic Theory: 001 by Paul Becher