Protein-stabilised emulsions

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Emulsion - definition

- An emulsion consists of two immiscible liquids (generally oil and water) with one liquid forming the continuous phase while the other the dispersed phase.
  - Oil-in-water (O/W)
  - Water-in-oil (W/O)
  - Water-in-oil-in-water (double emulsion, W/O/W)
  - Oil-in-water-in-oil (double emulsion, O/W/O)
Examples

- O/W – milk, cream, mayonnaise, soups and sauces
- W/O – butter and margarine
Oil-in-water emulsions

Coarse
- Raw milk
- Salad dressing
- Mayonnaise
- Homogenised/Recombined milk

Fine
- UHT beverage
- Canned/Retorted beverage

Demanding more physical stability
O/W - Chocolate milk and infant formulae
O/W - Complete nutritional formula
O/W - Mayonnaise
W/O – butter and margarine
Two & three-phase emulsions

- Water in oil (W/O)
- Oil in water (O/W)

![Diagram of emulsions](image)
Emulsion formation

- Oil-soluble/dispersible ingredient
- Water-soluble/dispersible ingredients

Blend tank

- Homogenisation
- Packaging

Further heating

Additives
Emulsion formation

- Oil-soluble/dispersible ingredient
- Water-soluble/dispersible ingredients

Blend tank → Homogenisation → Packaging → Further heating

Important variables: Additives
Sequence of events

• During homogenisation, fat globules with sub-micron size are formed
• Milk proteins migrate to the newly formed fat globule surfaces
• Capability to form a stable emulsion is determined by the ability of the protein to unfold at the fat-water interface
• Protein load affects the stability of emulsion towards heating and storage
Setup for reconstitution of protein ingredient

- Agitator
- Recirculation line
- Water
- Reconstitution tank
- Powder
- Powder-water Blending unit
Homogenising devices

- High-speed blender
- Colloid mills
- High-pressure valve homogeniser
- Ultrasonic homogeniser
- Microfluidiser
- Membrane-based homogeniser
Homogenising devices

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Homogenisation efficiency

\[ E_H = \frac{\Delta E_{\text{min}}}{\Delta E_{\text{total}}} \times 100 \]

- \( E_H \) – homogenisation efficiency
- \( \Delta E_{\text{min}} \) – Minimum amount of energy theoretically required to form emulsion = \( \Delta A\gamma \) (interfacial area and interfacial tension)
- \( \Delta E_{\text{total}} \) – Actual amount of energy expended during homogenisation
Two-stage homogeniser

Unhomogenised product → Stage 1 → Stage 2 → Homogenised product
Effect of homogenisation on fat globules in milk

Natural milk

Homogenized milk
Casein micelles and whey proteins at oil-water interface

Sharma (1993)

200 nm
TEM of an oil-water emulsion

Sharma (1993)
Particle size distribution – A stable emulsion
Particle size distribution – unstable emulsion
Protein adsorption

Spherical interface (emulsion or foam)

Flat interface (solid surface, e.g. Stainless steel tank)

Homogenisation or Quiescent conditions
CASEIN

- Strong hydrophobic regions
- Low cysteine
- High ester phosphates
- Little or no secondary structure
- Unstable in acidic conditions
- Micelles in native form
- Random coil in dissociated form

WHEY PROTEIN

- Balance in hydrophobic and hydrophilic residues
- Contains cysteine and cystine
- Globular, much helical
- No ester phosphate
- Easily heat denatured
- Stable in mild acidic conditions
- Present as soluble aggregates (<10 nm)
### Selective Chemical Composition and Physico-Chemical Attributes of Milk Protein Products

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Milk protein concentrate</th>
<th>Sodium caseinate concentrate</th>
<th>Whey protein concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (%)</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Total protein (N*6.38, %)</td>
<td>82.5</td>
<td>92</td>
<td>83.5</td>
</tr>
<tr>
<td>Casein (%)</td>
<td>66.0</td>
<td>92.0</td>
<td>0</td>
</tr>
<tr>
<td>Whey protein (%)</td>
<td>16.5</td>
<td>0</td>
<td>83.5</td>
</tr>
<tr>
<td>Calcium (%)</td>
<td>2.20</td>
<td>0.01</td>
<td>0.06</td>
</tr>
<tr>
<td>Potassium (%)</td>
<td>0.01</td>
<td>0.005</td>
<td>0.05</td>
</tr>
<tr>
<td>Phosphorus (%)</td>
<td>1.40</td>
<td>0.80</td>
<td>0.18</td>
</tr>
<tr>
<td>Protein state</td>
<td>Casein micelles, Soluble aggregates Soluble whey soluble whey protein of casein proteins</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Kinetics of protein adsorption

Diffusion-controlled (Ward & Tordai, 1946)

\[
\frac{d\Gamma}{dt} = C_0 \left(\frac{D}{\Pi t}\right)^{1/2}
\]

\(\Gamma\) – surface protein concentration, \(t\) – time

\(D\) – diffusion coefficient
Kinetics of protein adsorption

Diffusion-controlled (Ward & Tordai, 1946)

Total adsorbed protein

\[ \Gamma = 2C_0 (Dt/\Pi)^{1/2} \]
Kinetics of protein adsorption

Convection-controlled (Walstra, 1983)

\[ \Gamma (t) = KC_0d_g (1+d_p/d_g)^3t \]

\( C_0 \) is the bulk protein concentration, \( d_g \) and \( d_p \) are the fat-globule and protein-particle sizes, respectively, and \( K \) is a constant.
Protein load

\[ \Gamma = \frac{\text{Protein at the oil droplet surface (mg)}}{\text{Total droplet surface area (m}^2\text{)}} \]
## Protein load at oil-water interface

<table>
<thead>
<tr>
<th>Protein</th>
<th>Protein load (mg/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_s$-Casein</td>
<td>3-4.2</td>
</tr>
<tr>
<td>$\beta$-Casein</td>
<td>1-1.75</td>
</tr>
<tr>
<td>$\kappa$-Casein</td>
<td>4.2</td>
</tr>
<tr>
<td>Casein micelle</td>
<td>20</td>
</tr>
<tr>
<td>Sodium caseinate</td>
<td>2.2-2.6</td>
</tr>
<tr>
<td>Skim milk powder</td>
<td>10-23</td>
</tr>
<tr>
<td>$\beta$-Lactoglobulin</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Factors affecting protein load

- Volume of oil
- Protein concentration
- Homogenisation temperature
- Homogenisation pressure
- Aggregation state of protein
- Pre-treatment of protein, i.e. Hydrolysis or cross-linking
Types of protein adsorption

- Reversible and irreversible adsorption
- Competitive adsorption
Basic emulsion characteristics

- Thermodynamically unstable
- Possible to make kinetically stable
Emulsion instability

- Emulsion
- Creaming
- Flocculation
- Coalescence
- Inversion
- Oil separation
Colloidal interactions

- Van der Waals Interactions
- Electrostatic interactions
- Polymeric steric interactions
- Depletion interactions
- Hydrophobic interactions
- Hydration interactions
- Thermal fluctuation interactions
- Total interaction potential
van der Waals interactions

Induction

Rotation

Dispersion
Electrostatic double-layer forces
Polymeric steric interactions
Depletion interactions

Particle excluded
From distance $r_c$
Hydrophobic interactions

- Oil
- Non-polar group
- Adsorbed protein
- Clathrate-like structure
- Water
Other interactions

- Hydration interactions
- Thermal fluctuation interaction
- Bridging flocculation
- Hydrodynamic interactions
DLVO Theory for colloidal stability

- Interaction energy
- Distance of separation (nm)

Electrostatic repulsion
van der Waals’ attraction
Total interaction
## Colloidal forces important for emulsion stability

<table>
<thead>
<tr>
<th>Type of force</th>
<th>Character</th>
<th>Origin</th>
<th>Influenced by</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals</td>
<td>Attraction</td>
<td>Permanent &amp; fluctuating dipoles</td>
<td>Refractive index, Dielectric constant, Ionic strength, pH</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>Repulsion</td>
<td>Surface charge</td>
<td>Polymer coverage &amp; solubility</td>
</tr>
<tr>
<td>Steric</td>
<td>Repulsion</td>
<td>Adsorbed polymers</td>
<td>Polymer coverage</td>
</tr>
<tr>
<td>Bridging</td>
<td>Attraction</td>
<td>Adsorbed polymers</td>
<td>Molecular weight, Polymer polydispersity, Ionic strength, polyelectrolyte coverage</td>
</tr>
<tr>
<td>Depletion</td>
<td>Attraction</td>
<td>Non-adsorbed polymers</td>
<td></td>
</tr>
<tr>
<td>Polyelectrolytes</td>
<td>Repulsion or attraction</td>
<td>Adsorbed polyelectrolytes</td>
<td></td>
</tr>
</tbody>
</table>
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<th>Type of force</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Hydrophobic</td>
<td>Attraction</td>
<td>Water-water affinity</td>
<td>Solvent properties, surface hydrophobicity</td>
</tr>
<tr>
<td>Hydration</td>
<td>Repulsion</td>
<td>Dehydration of polar group</td>
<td>Emulsifier head group, crystallinity</td>
</tr>
<tr>
<td>Protrusion</td>
<td>Repulsion</td>
<td>Reduction in movement of emulsifiers normal to the interface</td>
<td>Fluidity of the layer, head-group size, Oil/water interfacial tension</td>
</tr>
</tbody>
</table>

Structural organisation of molecules in liquids

- Thermodynamics of mixing
- Potential energy change on mixing
- Entropy change on mixing
- Free energy change on mixing
Structural organisation of molecules in liquids

- Thermodynamics of mixing

Immiscible liquid

Miscible liquid
Overall interactions

Dispersed phase

Continuous phase

h

r
Overall interaction

- Attractive interactions dominate at all separations
- Repulsive interactions dominate at all separations
- Attractive interactions dominate at larger separations, but repulsive interactions dominate at short separations
- Repulsive interactions dominate at large separations, but attractive interactions dominate at short separation
Inter-particle pair potential

Energy required to bring two emulsion droplets from an infinite distance apart

\[ w(h) = w_{\text{attractive}}(h) + w_{\text{repulsive}}(h) \]
Inter-particle pair potential

- Energy required to bring two emulsion droplets from an infinite distance apart to a surface-to-surface separation of ’h’
Attractive interactions dominate at all separations.
Repulsive interactions dominate at all separations.
Attractive interactions dominate at large separations, but repulsive interactions dominate at short separations.
Repulsive interactions dominate at large separations, but attractive interactions dominate at short separations.
Characterisation of emulsions

■ Emulsifying properties of proteins
  ■ Emulsifying activity
  ■ Emulsion capacity
  ■ Surface hydrophobicity

■ Emulsion stability
  ■ Emulsion droplet size
  ■ Protein load
  ■ Creaming and oil separation
  ■ Heat stability

■ Emulsion rheology
■ Emulsion microstructure
Recommeded reading

- Food Emulsions: Principles, practice and techniques by D.J. McClements, CRC Press, Boca Raton, USA, 1999
- Food Emulsions edited by Friberg, S.E. And Larsson, L, Marvel Dekker, Inc, New York, 1997
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