Influence of emulsifiers on double emulsion stability

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Agenda

- What are double (multiple) emulsions?
- Emulsion preparation, influence of homogenization method
- Influences of emulsifiers
  - W/O emulsifier
  - O/W emulsifier
- Summary
What are double (multiple) emulsions?
Double emulsions

Definition:
Droplets of a dispersed phase (Oil or Water) contain small droplets of another phase

Special multiple types: O/W/O/W/O and W/O/W/O/W
Advantages of double emulsions

- Controlled aroma release
- Encapsulation of bioactive components
- Reduction of fat content without changing the mouthfeeling

Problem:
- Finding the optimal ingredient composition to
- realize a long time stability

Important:
Selection of emulsifier type and emulsifier combination
Structure of confectionery W/O/W

$W_2$

sucrose/glucose

e.g. 14.7 – 73.5 %

O/W emulsifier

$W_1$

Fat or Oil

primary surface

Secondary surface

W/O emulsifier

Sucrose/glucose
e.g. 14.7 – 73.5%

Thickener

Osmotic agent

Healthy additives

20 μm
Emulsion preparation, influence of homogenization method
Principle of formation multiple emulsions

1. $W_1/O$-Emulsion

$W_1$-phase:
- Water + sugar
- And hydrocolloid,
- Osmotic pressure regulated

Oil-phase + W/O emulsifier:
- Fat composition tailored

$W_1/O$-emulsion:
- Particle size of primary water droplets
  - $\sim 1 \mu m$
Principle of multiple emulsion preparation

2. $W_1/O/W_2$-Emulsion

- $W_1/O$-Emulsion
- $W_2$-phase + water + sugar
- $O/W$ emulsifier

Emulsifying low energy

$W_1/O/W_2$-Emulsion

Particle size of filled oil droplets with $W_1 \sim 5 – 7 \mu m$
Methods for emulsion preparation
(emulsification of $W_1/O$ in $W_2$)

Avoid:
Disruption of internal emulsion droplets ($W_1$) and fusion with the external phase ($W_2$)

Emulsification methods for multiple systems are described by:

Muschiolik and Bunjes, 2007 (Behr’s Verlag, 2007)
Stability of W/O/W is influenced by:

- Size of inner water droplets ($W_1$)
- Oil droplet size
- Osmotic gradient between $W_1$ and $W_2$
- Laplace curvature pressure
- Water flow between $W_1$ and $W_2$ (influenced by osmotic gradient)
- Viscosity of the emulsion phases
- **Interaction between W/O and O/W-emulsifier**

Hindrance between different emulsifiers should be prevented!
Influence of emulsifiers
W/O emulsifier lecithin
PC depleted and PE enriched
< 5% > 11%

Hydrophobic lecithin with higher PE content as W/O emulsifier
**W/O-Premix prepared with different lecithins**

**Improved W/O stability with higher PE content**

W/O : 30/70; O-phase: sunflower oil, emulsion preparation at 3000 rpm, 2 min; \( \geq 50 ^{\circ}C \); Homogenizer MPW-302 (Metronex, Poland)
Lecithin-screening
- W/O emulsions with 0.75 % Lecithin (2.5 % in O)

Cumulative particle-size distribution for W-droplets
Flow behaviour of W/O-Emulsionen prepared with lecithin

Due to aggregation of water particles W/O emulsions with lecithin are higher viscous
Influences of emulsification methods
- W/O with lecithin -

A: 10 ml, 240 s ultrasonic, 60 % amplitude; B: 30 ml, 240 s ultrasonic, 60 % amplitude

0.2 % XPS and 1.5 % whey protein in W; 2.5 % PC↓ in O; 50 °C
W/O with lecithin

W/O phases prepared with lecithin

- are more viscous than w/o phases with PGPR

and

- the stability depends strongly on the emulsifying methods
W/O emulsifier PGPR

Polyglycerol-Polycinoleate E476

ZZuIV, 29.01.98, appendix 7

- max. 4 g/kg in spreads with less than 41 % fat, spreads with < 10 % fat and salat dressings
- max. 5 g/kg in sweets with cacao
Lecithin or PGPR in O
- Influence of NaCl and WPI in W₁-phase -

2.5 % PC + 3.0% Gelatine + 0.2% Xanthan

4.0 % PGPR + 3 % Gelatine
Influence of other emulsion components:

- Electrolytes (NaCl) are essential to achieve coalescence-stable emulsions prepared with PGPR.

- Electrolytes (NaCl) in emulsions containing lecithin contribute more to coalescence of water droplets and phase separation (other components are necessary to regulate the osmotic pressure, e.g. glucose).

- Combination of lower surface active whey protein with xanthan in W-phase (1.5 % protein + 0.2 % XPS in W) reduces the W-droplets additionally when W/O emulsions are prepared with PC depleted lecithin (2.5 % in O).
Influence of emulsification method
- W/O with PGPR -

4 % PGPR
Rotor-stator-system is effective!
W/O emulsifier sucrose esters

- Sucrose erucate ER-190, HLB 1
- Sucrose erucate ER-290, HLB 2

- Sucrose esters, which are allowed in the European Union have to contain at least 80 % mono-, di-, and tri-esters

- At the present time the tested sucrose esters with HLB 1 and 2 are not permitted

RYOTO® SUGAR ESTER Technical Information
Particle size of W/O
Sugar esters with HLB 1 and HLB 2
(2, 4 and 6 % emulsifier in O; 0.6 % NaCl in W)

MCT: Medium-chain triglyceride (Miglyol 812), Oil: Vegetable oil (BISKIN)
Particle size of W/O
Sugar ester with HLB 1 and HLB 2
(2, 4 and 6 % emulsifier in O)

MCT: Medium-chain triglyceride (Miglyol 812), Oil: Vegetable oil (BISKIN)
Surface area of O-droplets (W/O in W) depending on storage
(Particle size between 26 – 29 µm)

$W_2$: 25 % dry matter (sugar, milk protein, starch, maltodextrin)
4 % sugar ester (ER 290, HLB 2); PGPR: 4 %;
BF: butter fat; MCT: Miglyol 812; Oil: vegetable oil
$W_1/O = 20:80, (W_1/O) : W_2 = 20:80$
Summarised effects of sugar esters

- Esters with HLB 2 are more effective in forming small $W_1$ particles than esters with HLB 1
- Application of NaCl in $W_1$ supports the formation of small water droplets
- W/O are stable with 4 % sugar ester in O (HLB 2) and 0.6 % NaCl in $W_1$
- The size of O-droplets (surface area) in W/O/W is comparable to emulsions with PGPR
Emulsifiers for $W_1/O$ in $W_2$
Emphasized O/W emulsifiers for double emulsions

- Native proteins (whey, vegetable)
- Protein-ionic polysaccharide mixtures
  (a high zeta-potential is advantageous)
- Protein-polysaccharide conjugates

Combination of proteins with ionic polysaccharides in $W_2$ increases the barrier function!

Structural compatibility between W/O- and O/W-emulsifiers is of importance!
Protein-polysaccharide conjugate at O/W-surfaces

Available space for adsorbing at oil surfaces depends on the polysaccharides molecule weight

according to Dunlap u. Côté, 2005
Milk protein and protein-pectin-conjugate as O/W-emulsifier in W/O/W

W/OW were heated for 10 min at 90 °C, and stored for 6 weeks

Milk protein concentrate in $W_2$
Conjugate in $W_2$

Double emulsions with conjugate in $W_2$ are heat stable! No aggregation of O-droplets!
Influence of O-phase on W/O/W stability

The **stability** can be improved by using O-phases with a high degree of saturated fatty acids, i.e. by fat phases with a low polarity

(promotion of a close packed condensed interfacial film)
Conclusions

**Stable W/O/W can be prepared by using**

**W/O emulsifiers in O:**
- 4 % PGPR (0.6 % NaCl in \(W_1\)) or
- 2.5 - 6 % PE enriched lecithin (without NaCl) or
- (4 % sucrose ester; HLB 2; 0.6 % NaCl)

**O/W emulsifiers in \(W_2\):**
- Whey or vegetable protein or
- Protein-ionic polysaccharide conjugates

Low molecular weight **W/O emulsifier**
+ high molecular weight **O/W emulsifier**
= better compatibility and no negative interactions!
Conclusions

The stability of multiple systems depends on:

- osmotic balance, electrolyte and ionic status and
- fat phase composition (saturation degree, polarity)

The selection of emulsifiers for double emulsions has to consider the electrolyte and ionic status.
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