Influence of emulsifiers on double emulsion stability

Muschiolik, G.[1], Knoth, A.[2], Bindrich U.[3]
[1] Food Innovation Consultant, Potsdam
[2] Gutena Nahrungsmittel GmbH, Apolda
[3] DIL e.V., Quakenbrück

www.muschiolik.de

Agenda

- **What are double (multiple) emulsions?**
- **Emulsion preparation, influence of homogenization method**
- **Influences of emulsifiers**

  - W/O emulsifier

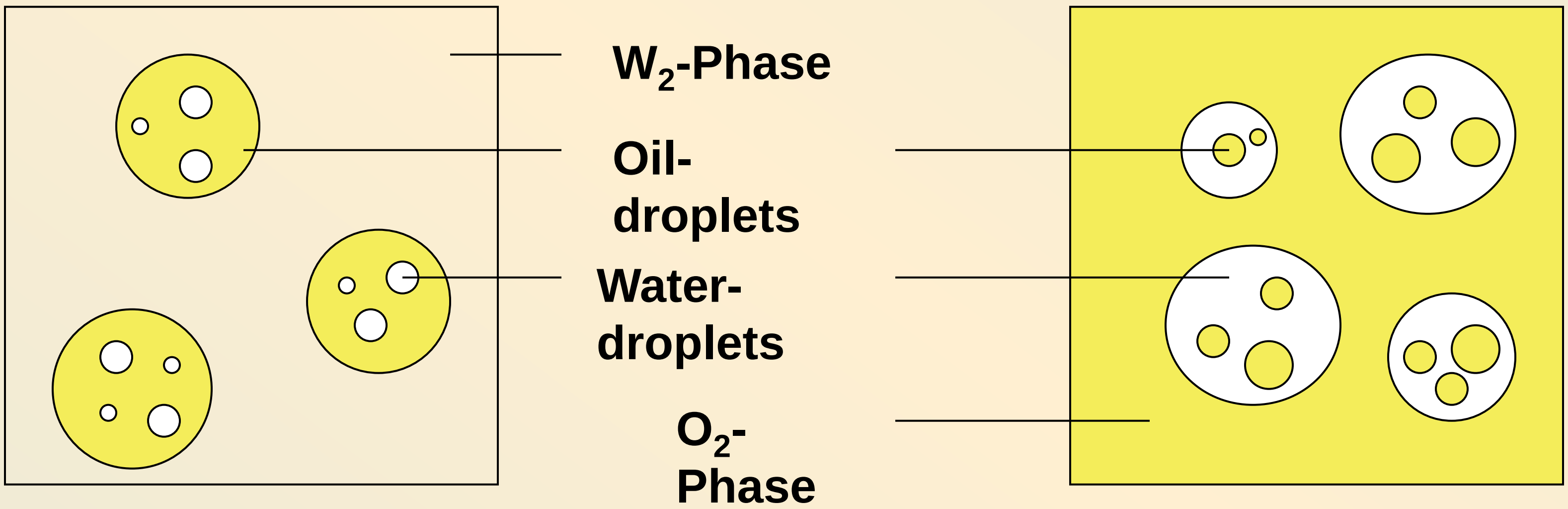
  - O/W emulsifier
- **Summary**

What are double (multiple) emulsions?

Double emulsions

Definition:

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



$W_1/O/W_2$ $O_1/W/O_2$

Special multiple types: O/W/O/W/O and W/O/W/O/W

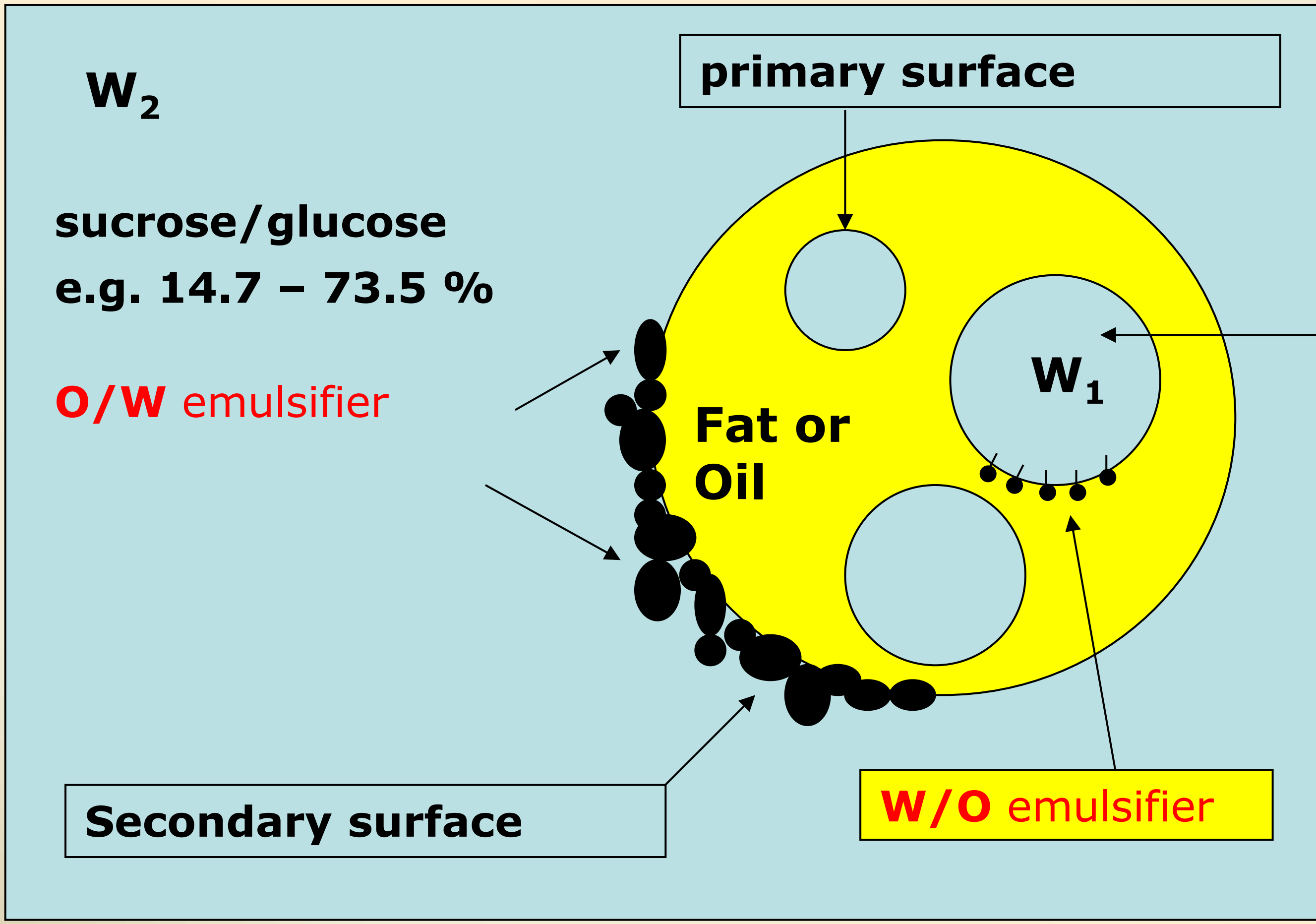
Advantages of double emulsions

– 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



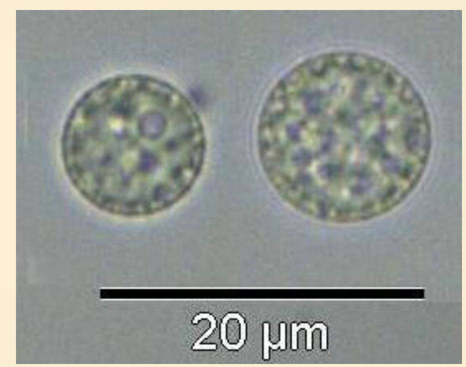
Sucrose/glucose

e.g.14.7 – 73.5%

Thickener

Osmotic agent

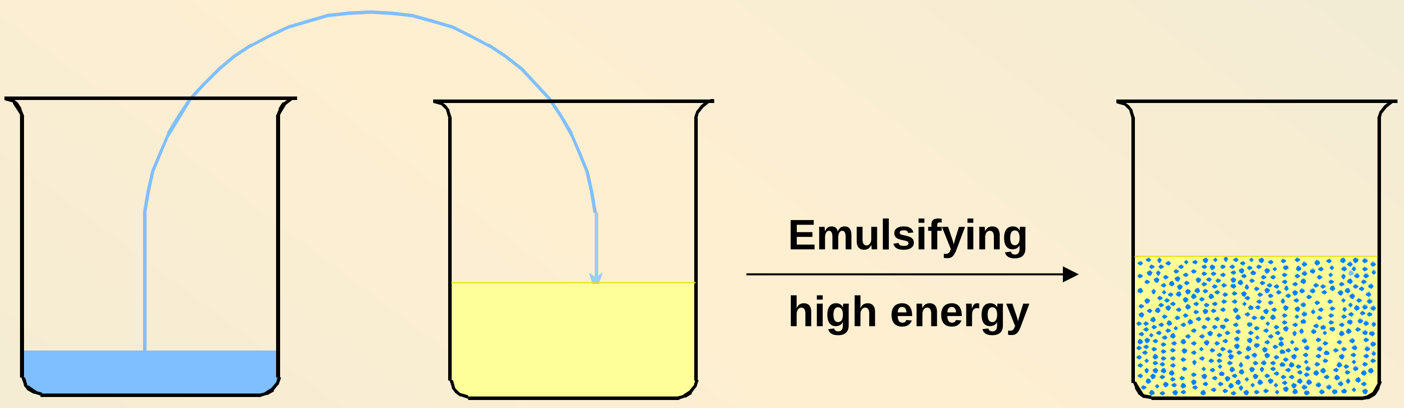
Healthy additives



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**

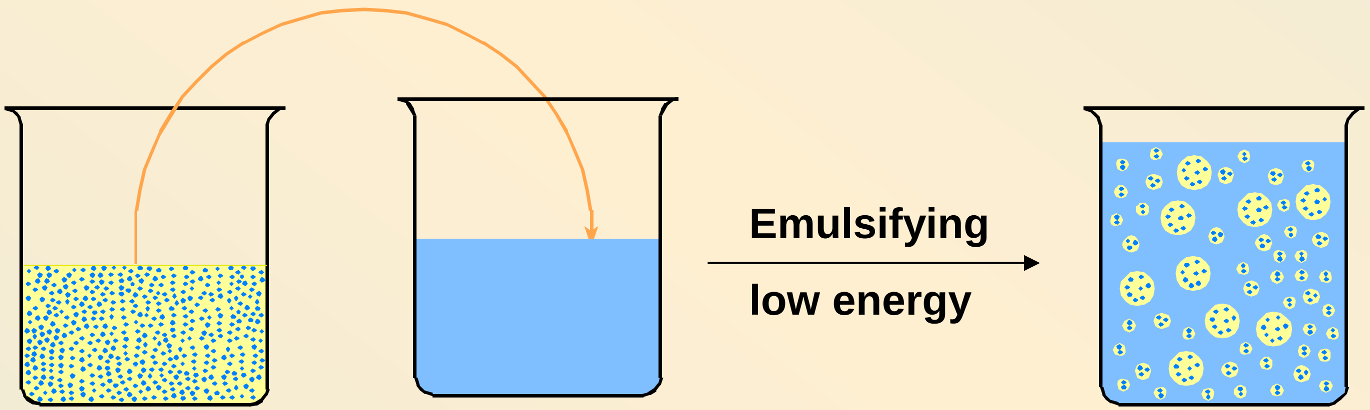
fat composition tailored

W_1/O- emulsion

particle size of primary water droplets ~ 1 µm

Principle of multiple emulsion preparation

2. $W_1/O/W_2$- Emulsion



W_1/O-Emulsion

W_2-phase +

water + sugar

O/W emulsifier

$W_1/O/W_2$- Emulsion

Particle size of filled oil droplets with W_1 ~ 5 – 7 µm

Methods for emulsion preparation
(emulsification of W_1/O in W_2)

Avoid:

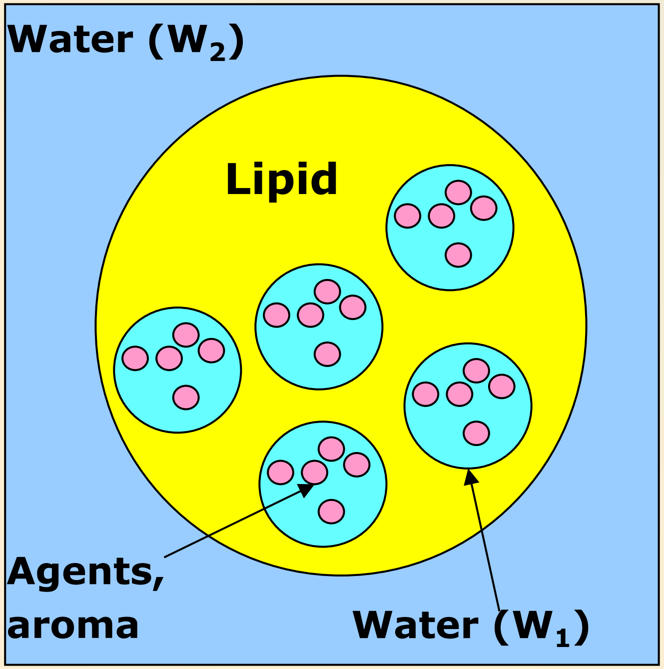
Disruption of internal emulsion droplets (W_1) and fusion with the external phase (W_2)

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!

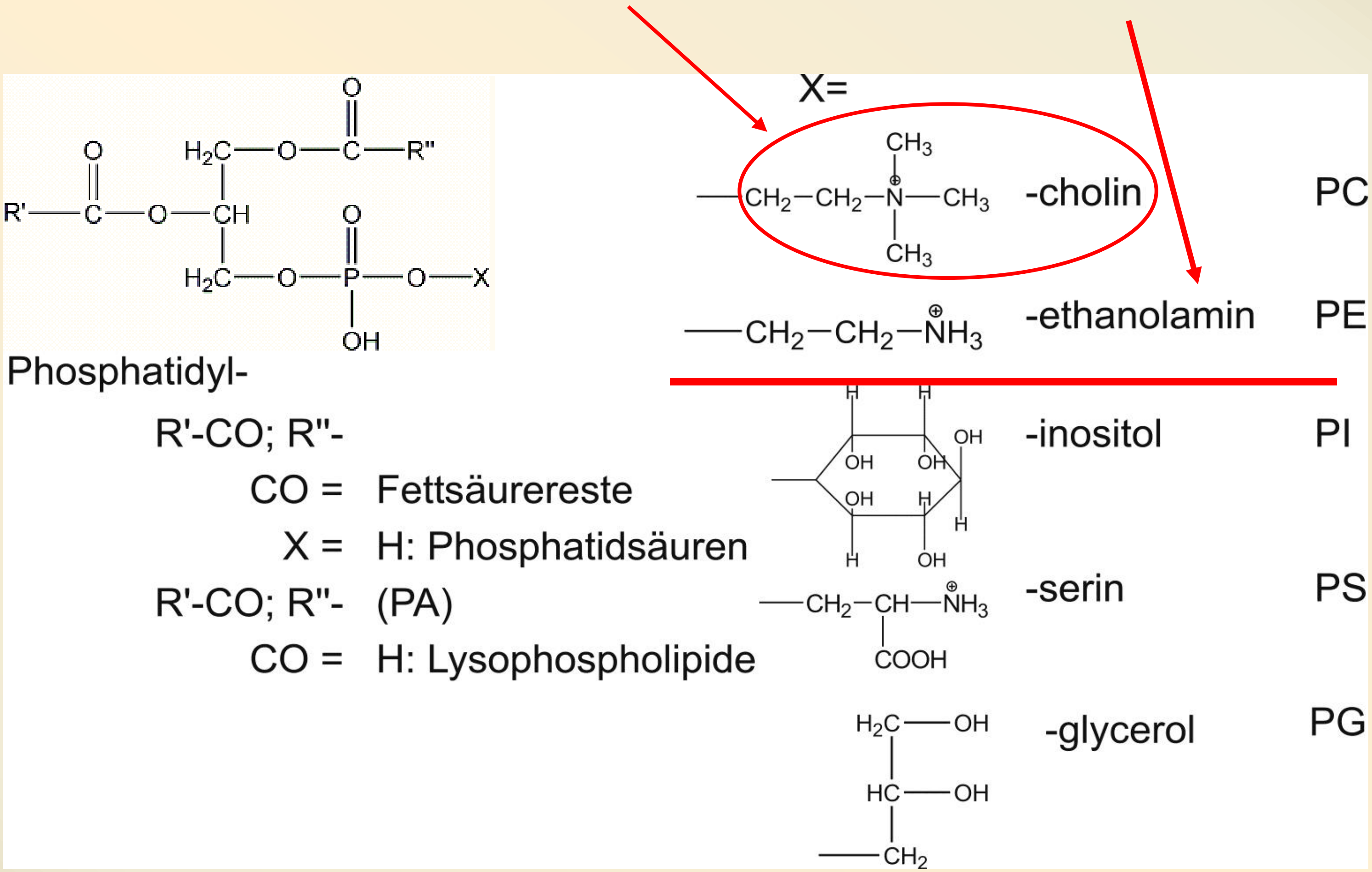
Influence of emulsifiers

W/O emulsifier lecithin

PC depleted and PE enriched

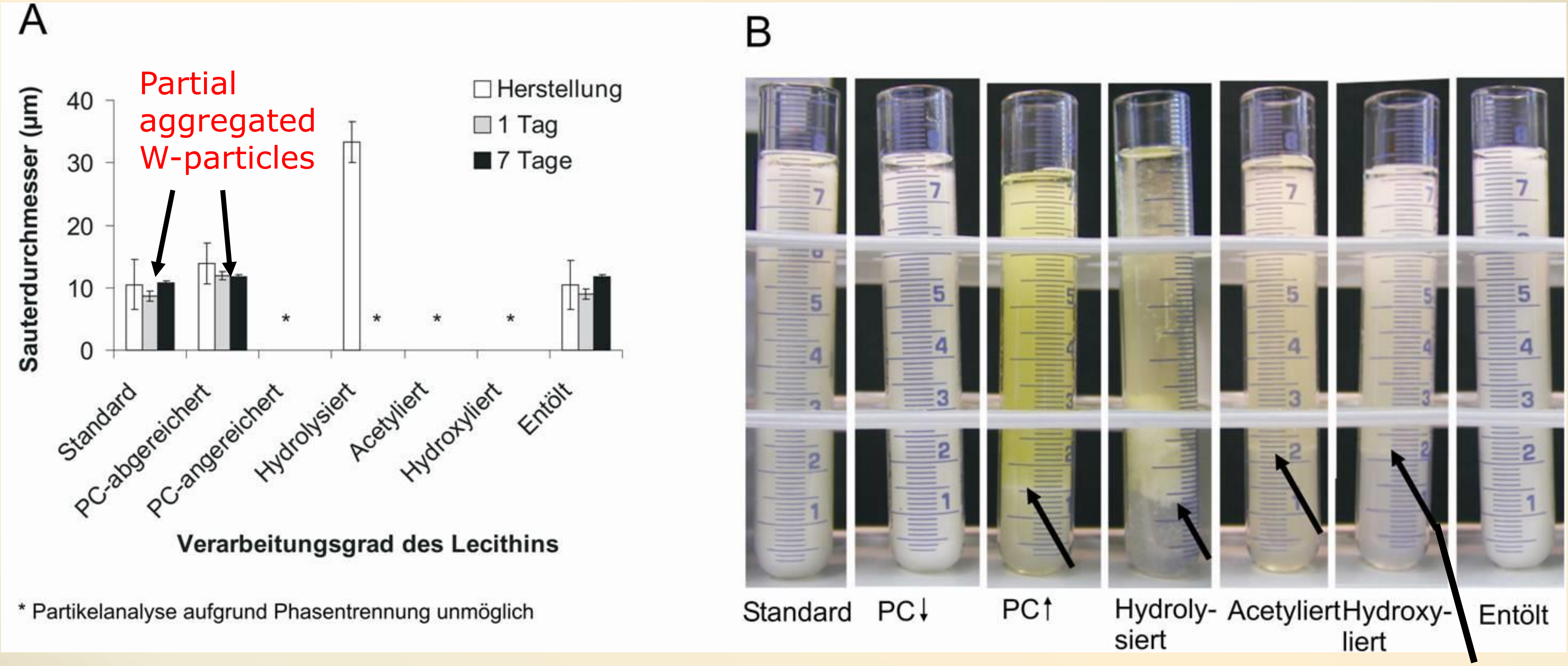
< 5% > 11 %

low molecular



Hydrophobic lecithin with higher PE content as W/O emulsifier

W/O-Premix prepared with different lecithins



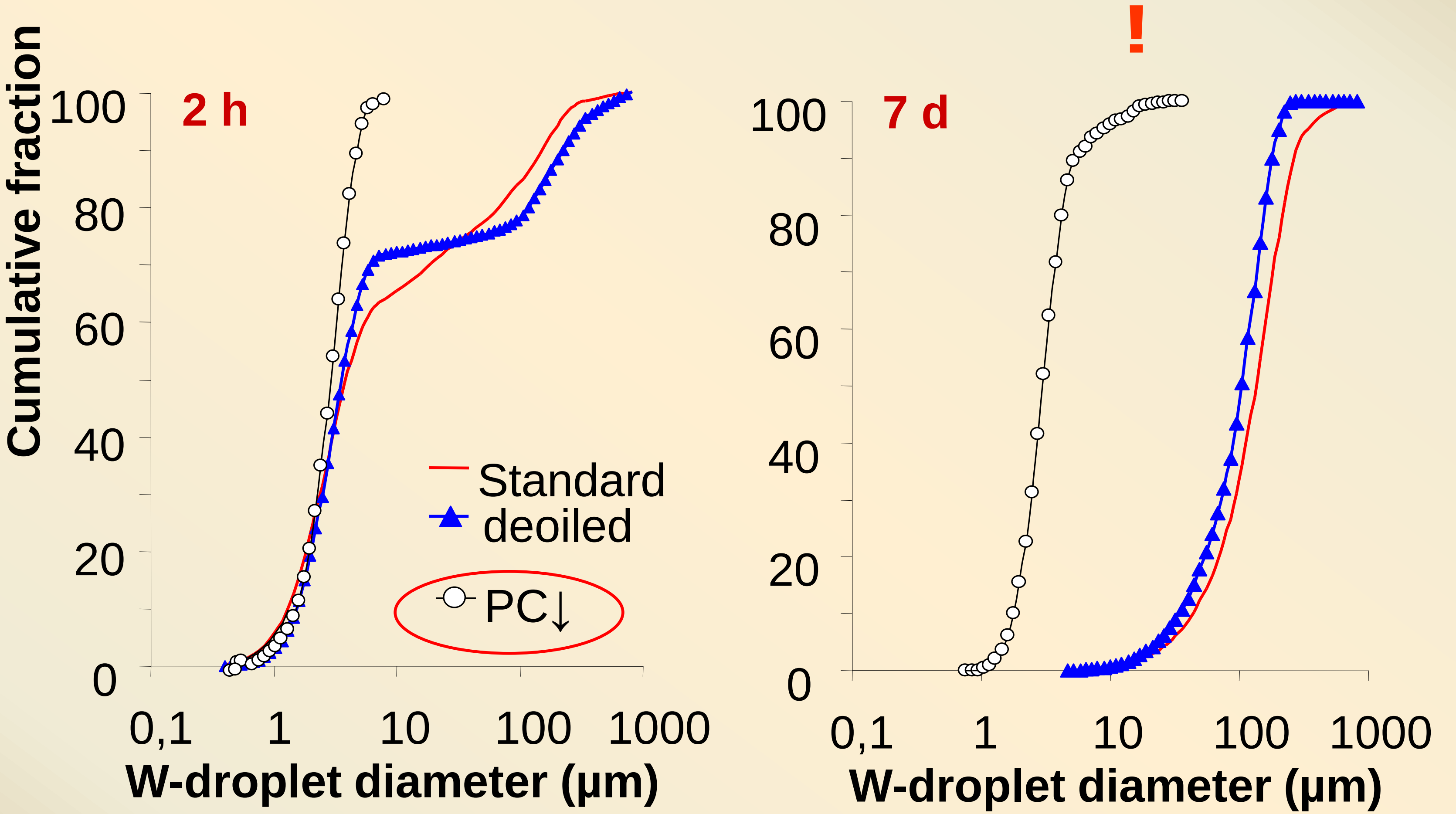
*Phase separation

Improved W/O stability with higher PE content

W/O : 30/70; O-phase: sunflower oil, emulsion preparation at 3000 rpm, 2 min;
ϑ 50 °C; Homogenizer MPW-302 (Metronex, Poland)

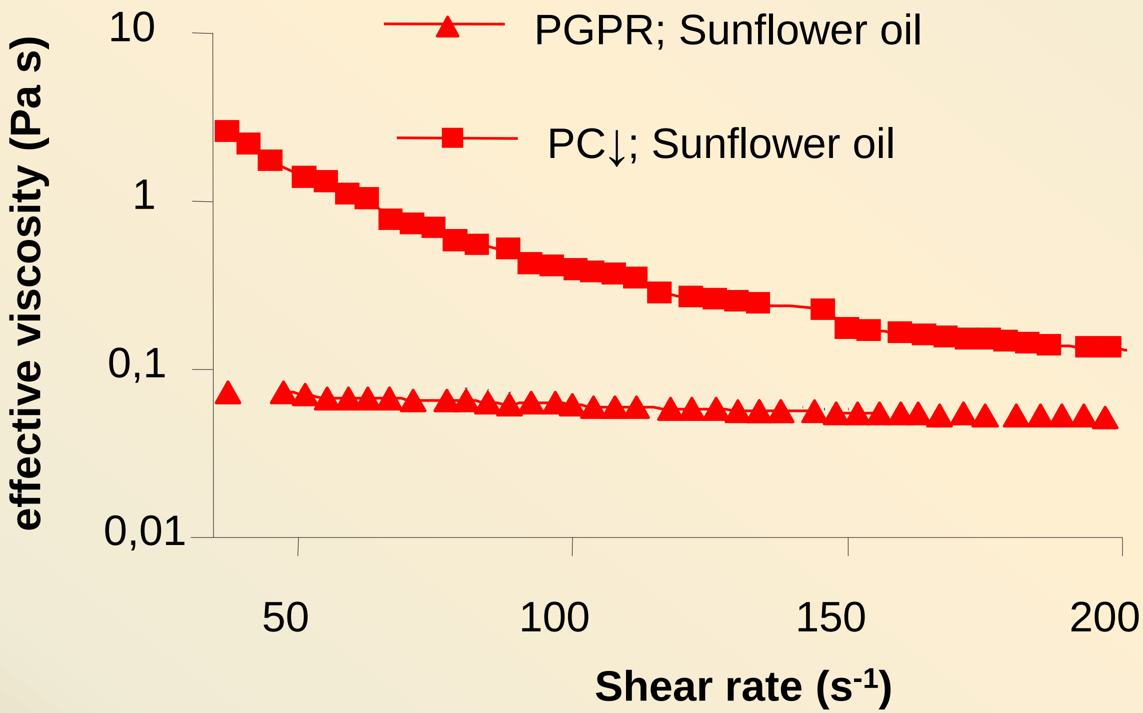
Lecithin-screening

- W/O emulsions with 0.75 % Lecithin (2.5 % in O)



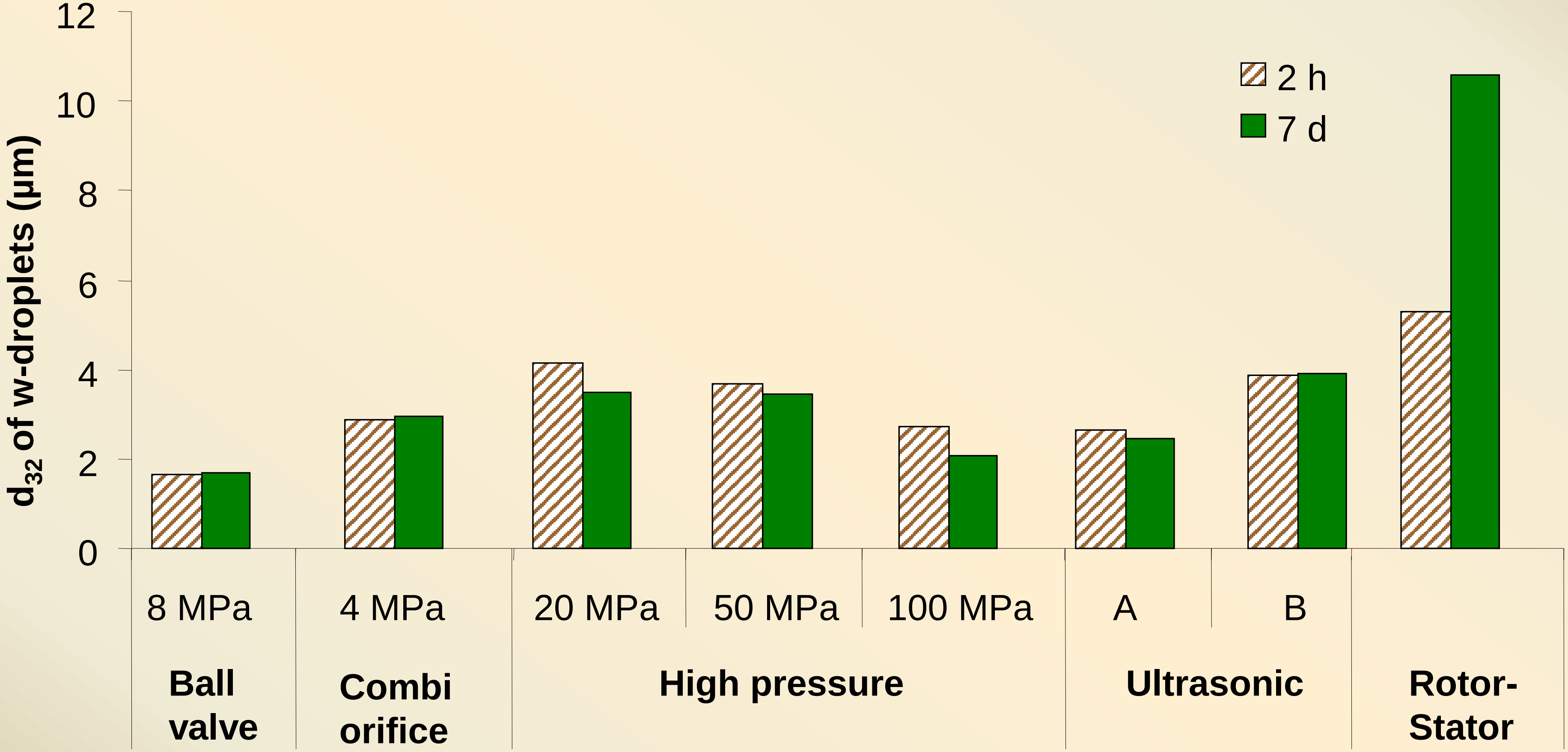
Cumulative particle-size distribution for W-droplets

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; <u>2.5 % PC</u>↓ in O; 50 °C

W/O with lecithin

W/O phases prepared with lecithin

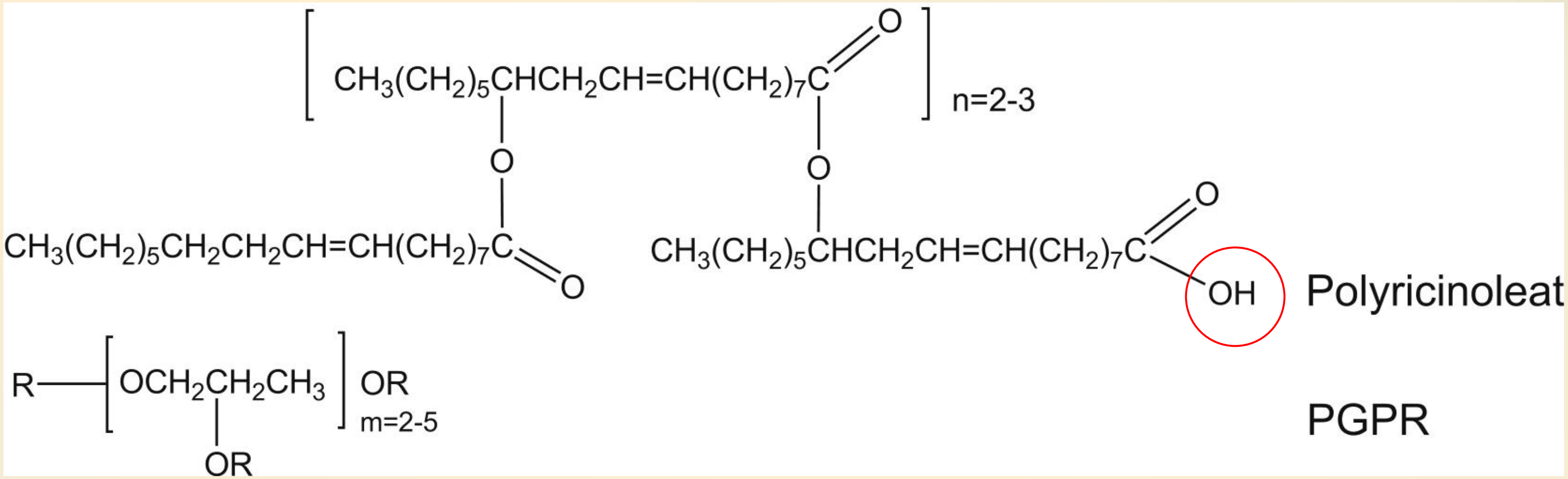
- are more viscous than w/o phases with PGPR

and

- the stability depends strongly on the emulsifying methods

W/O emulsifier PGPR

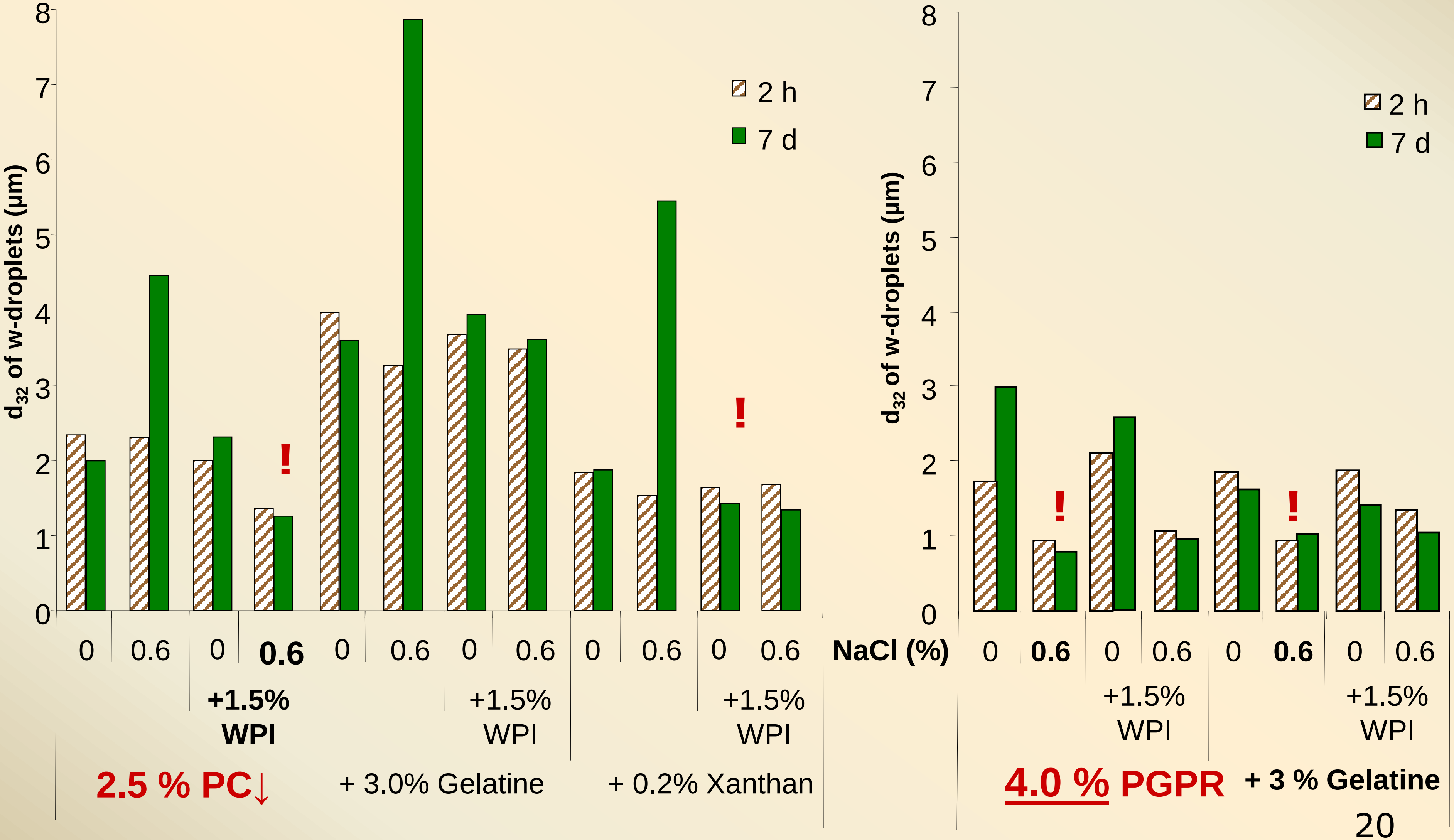
Polyglycerol-Polyricinoleate E476



ZZulV, 29.01.98, appendix 7

- max. 4 g/kg in spreads with less than 41 % fat, spreads with < 10 % fat and salat dressings
- **<u>max. 5 g/kg in sweets with cacao</u>**

Lecithin or PGPR in O
- Influence of NaCl and WPI in W_1-phase -



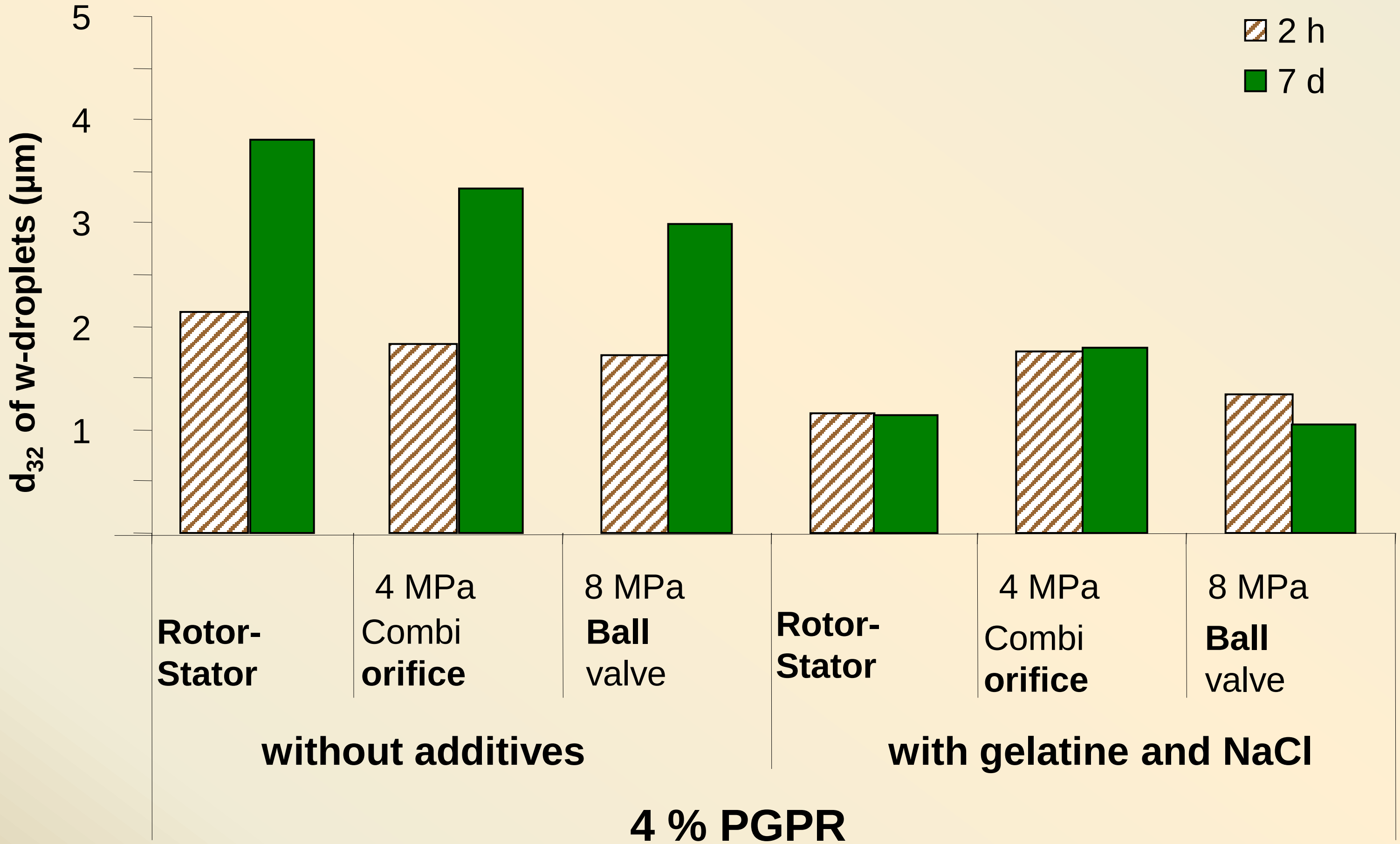
Influence of other emulsion components:

- 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).

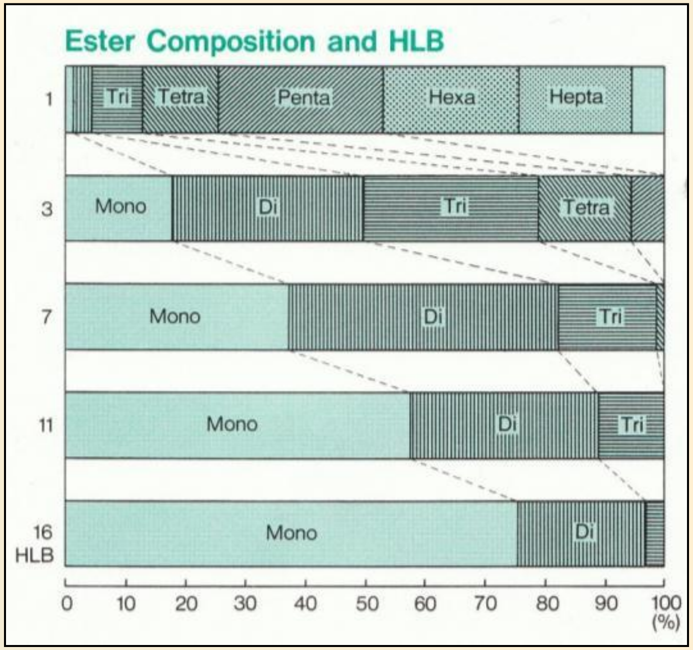
- Combination of lower surface active whey protein with xanthan in W-phase (1.5 % protein + 0.2 % XPS in W) reduces the W-droplets additionally when W/O emulsions are prepared with PC depleted lecithin (2.5 % in O).

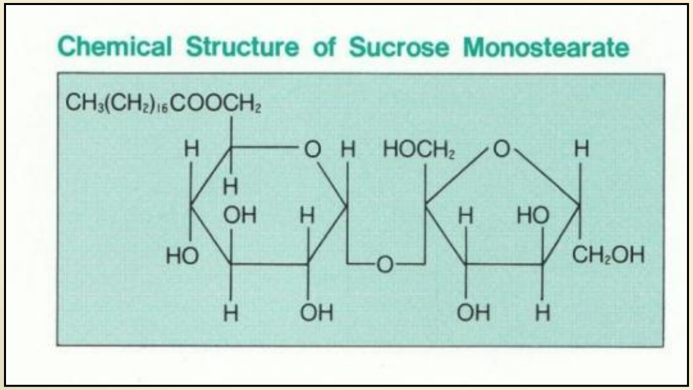
Influence of emulsification method
- W/O with PGPR -



Rotor-stator-system is effective!

W/O emulsifier sucrose esters





- **Sucrose erucate ER-190, <u>HLB 1</u>**
- **Sucrose erucate ER-290, <u>HLB 2</u>**

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

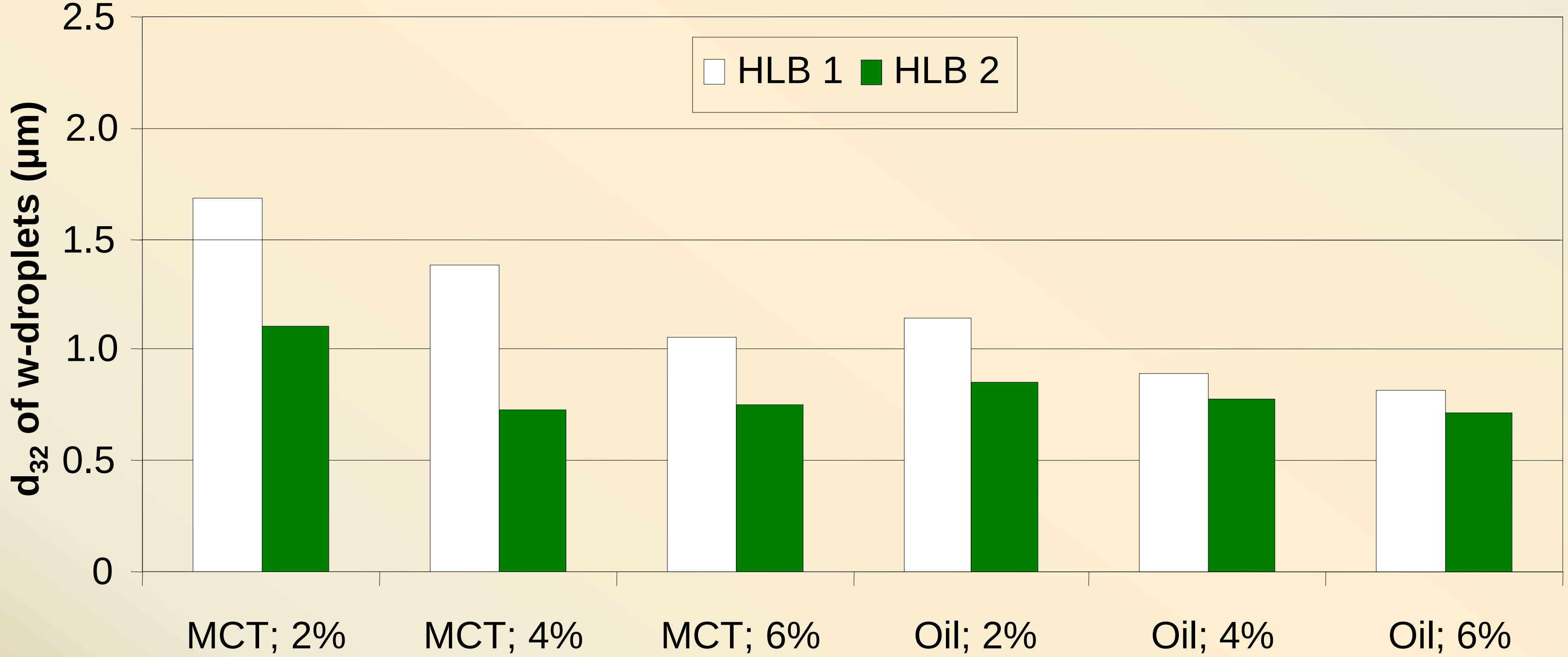
- **At the present time the tested sucrose esters with HLB 1 and 2 are not permitted**

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)

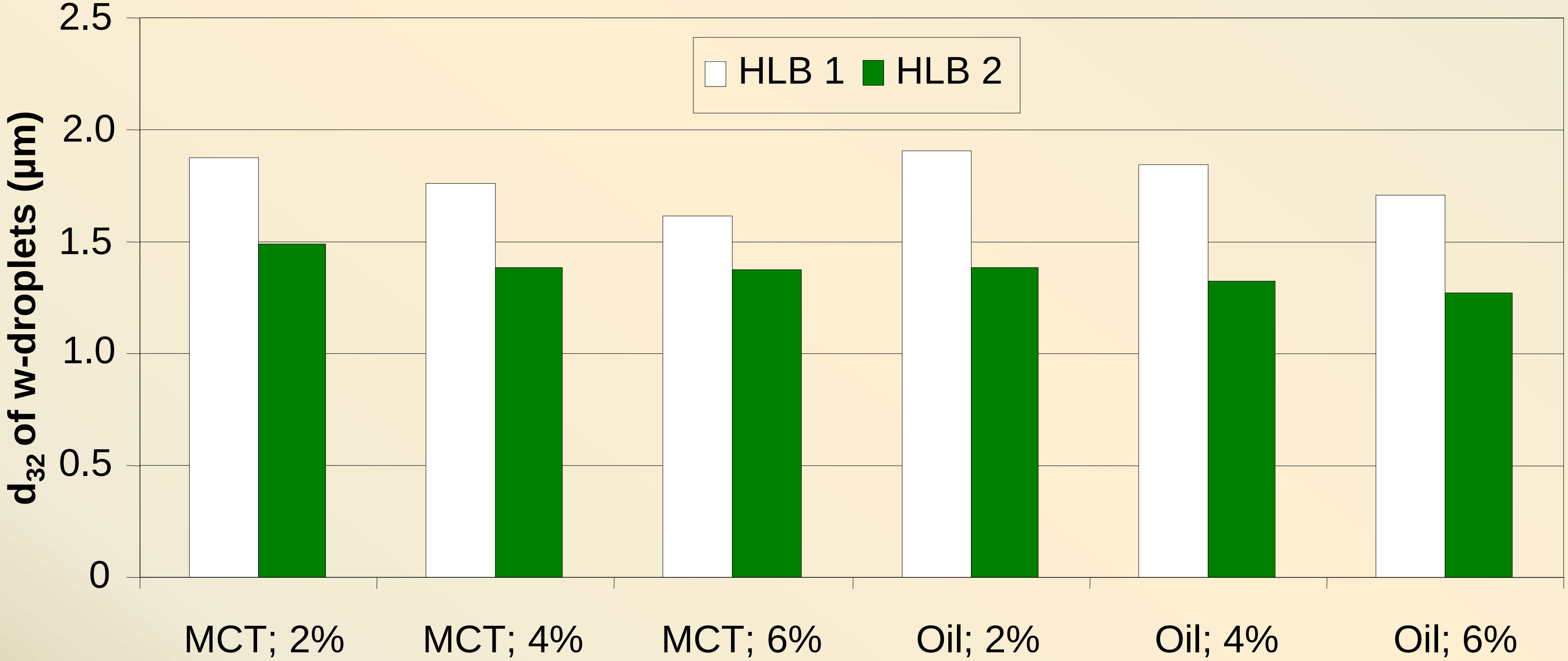


MCT: Medium-chain triglyceride (Miglyol 812), Oil: Vegetable oil (BISKIN)

Particle size of W/O

Sugar ester with HLB 1 and HLB 2

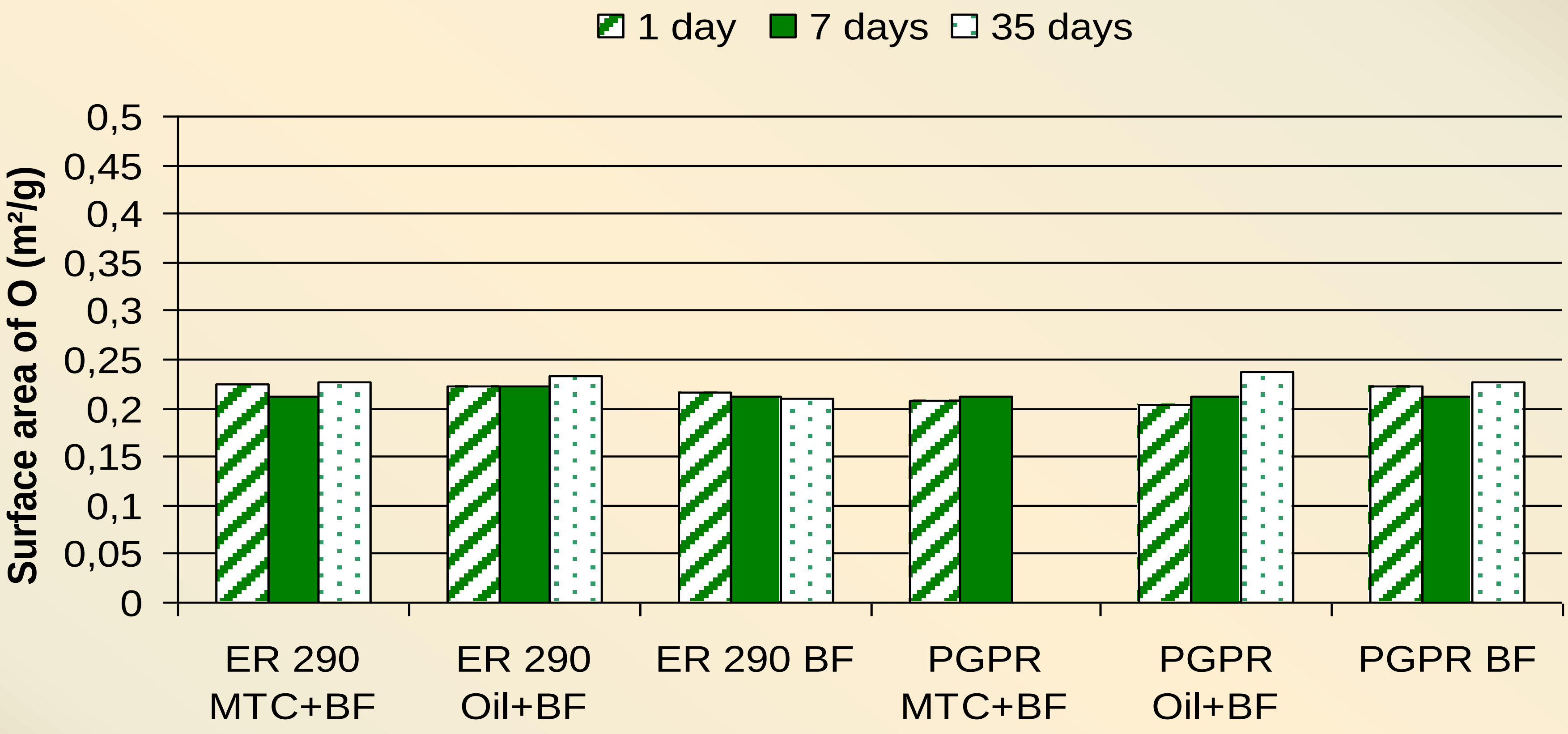
(2, 4 and 6 % emulsifier in O)



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

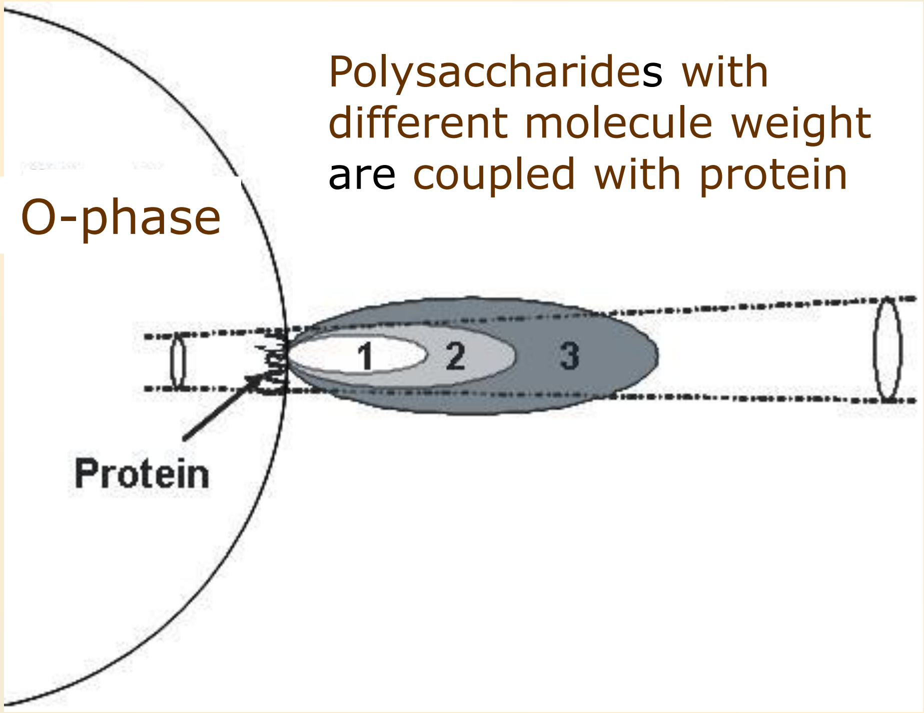
Emphasized O/W emulsifiers for double emulsions

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

Combination of proteins with ionic polysacharides 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

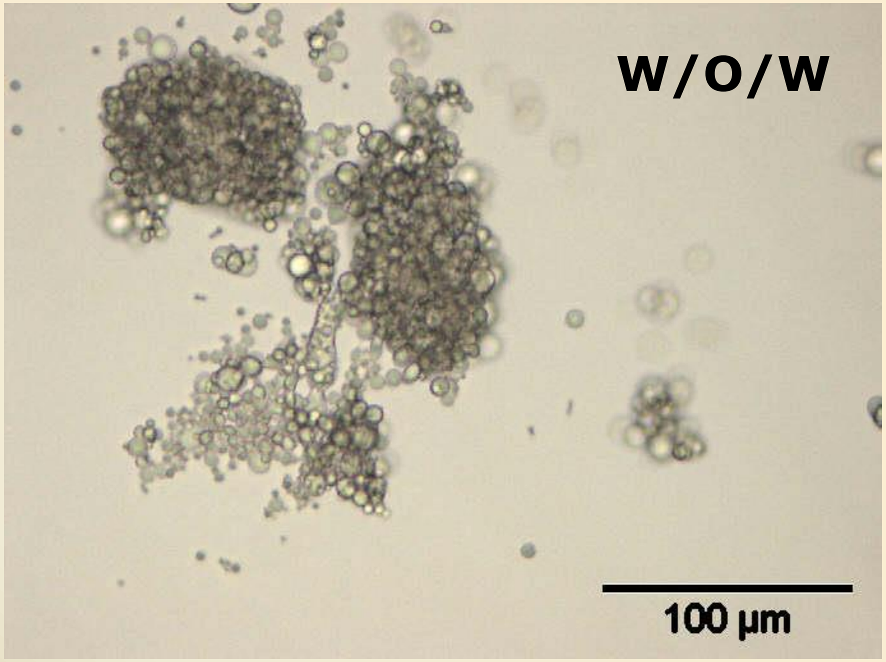


according to Dunlap u. Côté, 2005

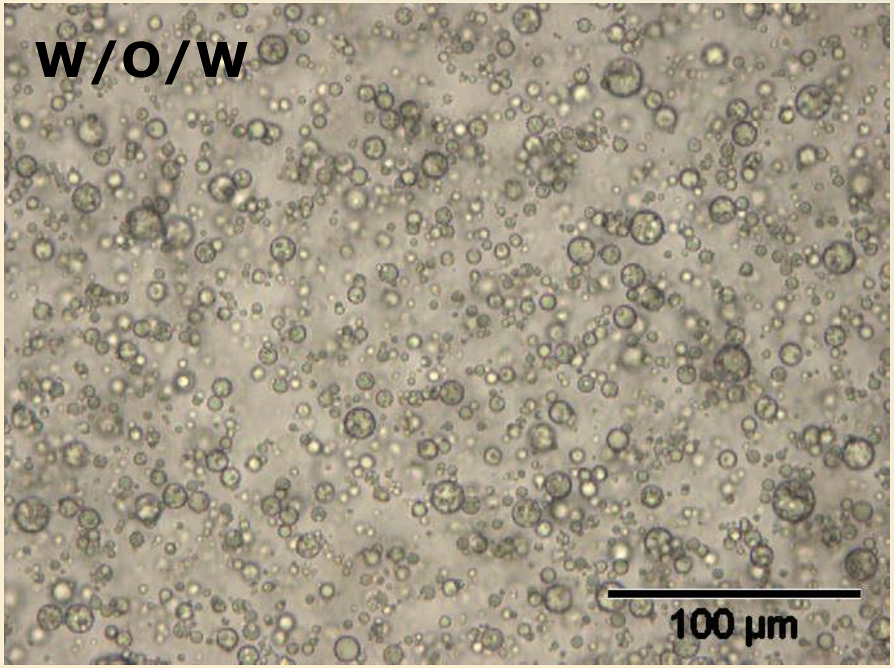
Available space for adsorbing at oil surfaces depends on the polysaccharides molecule weight

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.

Acknowledgement

This research project was supported by the German Ministry of Economics and Technology (via AiF) and the FEI (Forschungskreis der Ernährungsindustrie e.V., Bonn).

Project AiF 14087 BG

Main publications

- Muschiolik/Bunjes,
  Multiple Emulsionen
  Behr´s Verlag, 2007
- Muschiolik, G.
  Multiple emulsions for food use,
  Current Opinion in Colloid & Interface Science 12 (2007) 213-220
- Preissler, P.
  Süßwarenfüllmassen auf Emulsionsbasis
  Logos Verlag Berlin, 2006
- Weiss, J. and Muschiolik, G.
  Factors affecting the droplet size of water-in-oil emulsions (W/O) and the oil globule size in water-in-oil-in-water emulsions (W/O/W),
  J. Dispersion Sci. and Technol. 28 (2007) 703-716