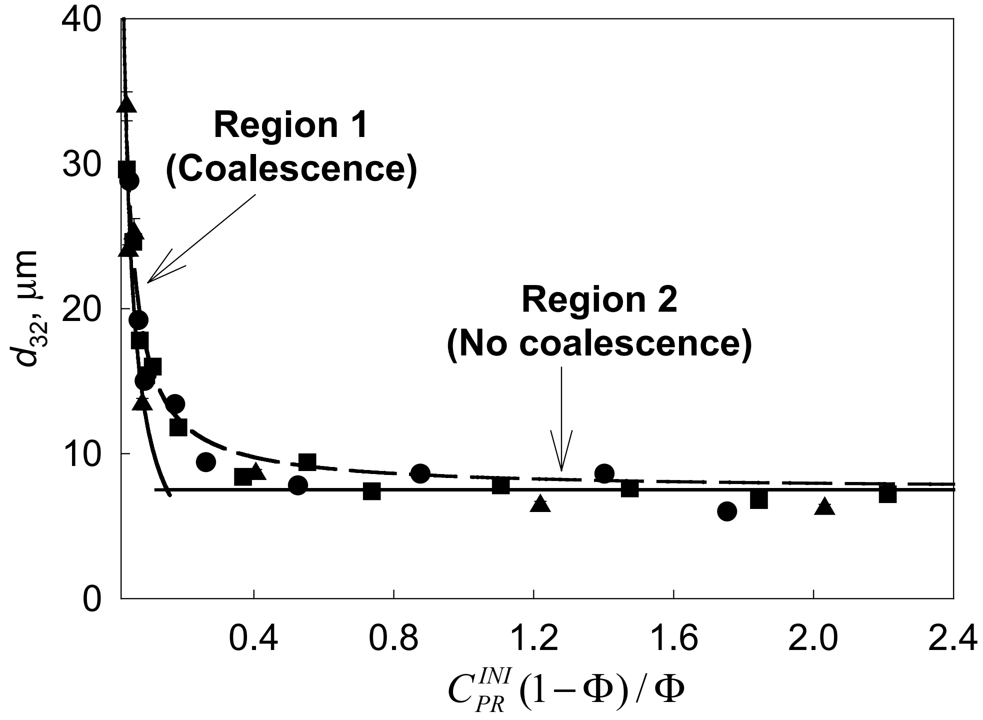
Experimental Results
Effect of surfactant concentration



For all studied emulsifiers

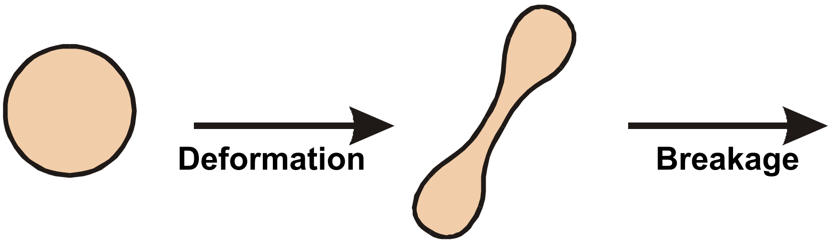
- **Region 1 – d_{32} strongly depends on the initial surfactant concentration when $C_S^{INI} < 0.1$ wt %.**
- **Region 2 – d_{32} does not depend on C_S^{INI}**

For SDS stabilized emulsions

- **Region 1 – d_{32} is much lower at C_{EL} = 10 mM than that at C_{EL} = 150 mM.**
- **Region 2 – d_{32} is almost the same for both C_{EL}.**

Drop Breakage Process
Kolmogorov-Hinze theory

1. Schematic presentation of the breakage process



2. **Necessary condition for drop breakage in inertial turbulent flow** - the amplitude of the spatial fluctuations of the turbulent pressure is equal to the capillary pressure of the drops

$\langle \Delta P_T(d) \rangle \sim P_C(d)$ **where** $\langle \Delta P_T(d) \rangle \sim \rho \overline{u^2} \sim \rho \varepsilon^{2/3} d^{2/3}$

Mean drop size

$$d \approx \varepsilon^{-0.4} \sigma^{0.6} \rho^{-0.6}$$

$$d > \lambda_0$$

3. Main factors affecting the breakage process

⇒ **Interfacial tension** – depends on the used emulsifier and its concentration

⇒ **Average power density** – depends on the hydrodynamic conditions during emulsification

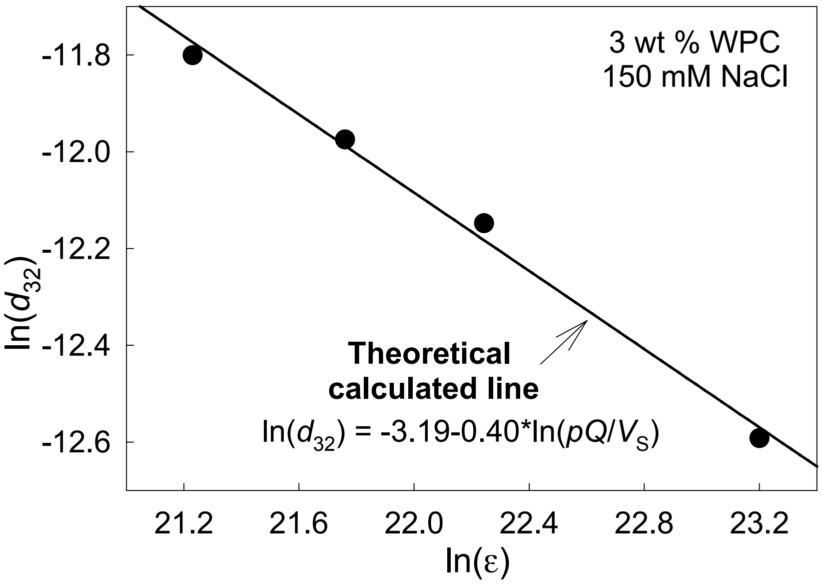
4. Consequences of the Kolmogorov-Hinze theory

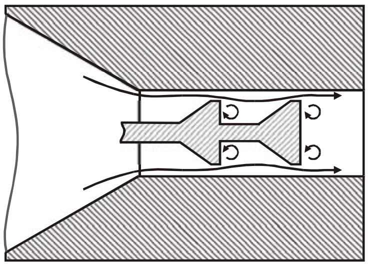
At σ = const $\Rightarrow \ln(d) = A - 0.4\ln(\varepsilon)$

At ε = const $\Rightarrow \ln(d) = B + 0.6\ln(\sigma)$

Comparison between the experimental data and the predictions of Kolmogorov-Hinze theory

1. Effect of hydrodynamic conditions on *d* at σ_{OW} = 10 mN/m.

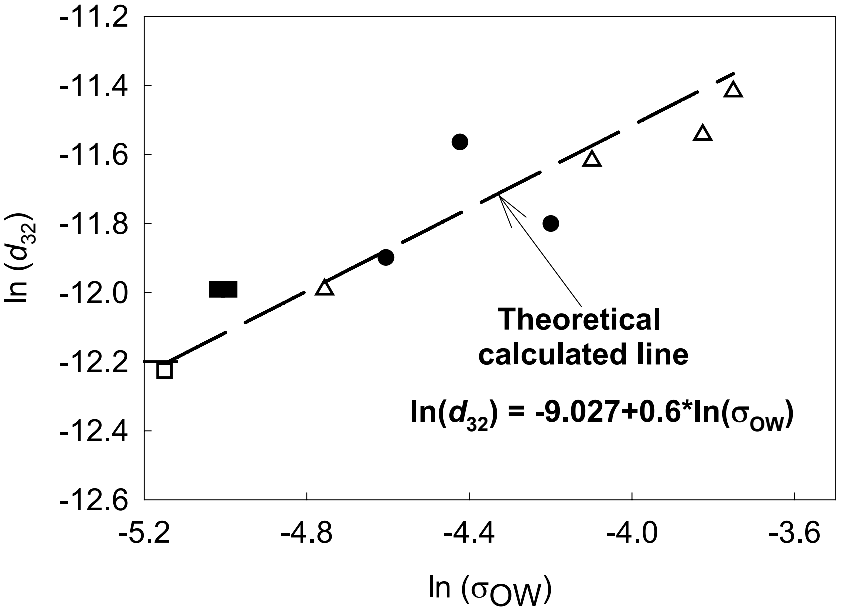




Average power density

$\varepsilon = pQ/V_S$

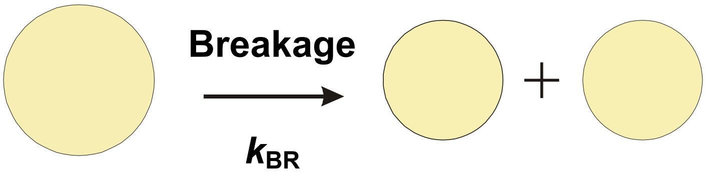
2. Effect of interfacial tension on *d* at $\varepsilon = 2 \times 10^5$ J/(s.kg)



The Kolmogorov-Hinze theory describes very well the data for:

- ⇒ **The surfactant-reach regime (Region 2) in all systems**
- ⇒ **At low surfactant concentration for SDS + 10 mM NaCl**

Estimate of Breakage Rate Constant from Experimental Results



❑ Main assumptions

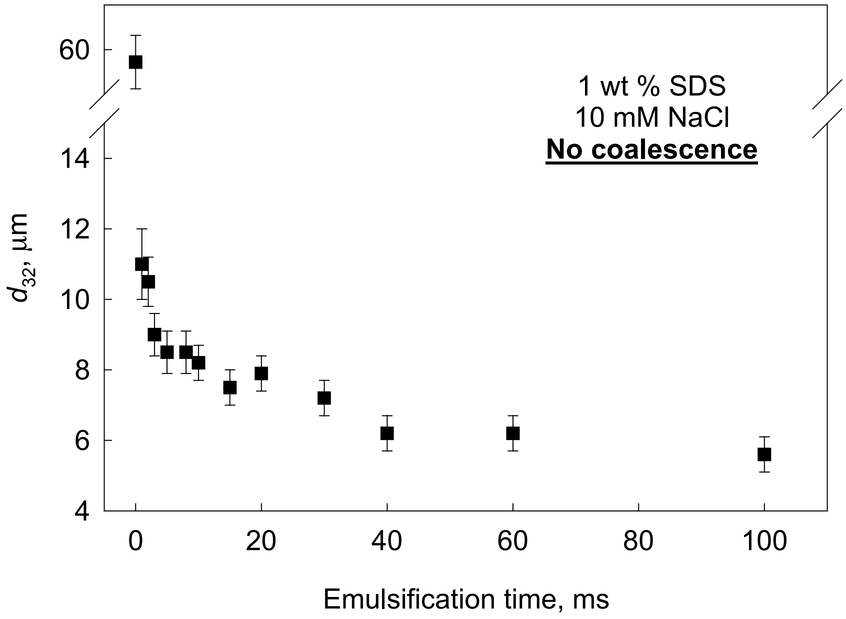
⇒ The coalescence between the drops is negligible

⇒ The breakage process is considered as a reaction of first order

$$\frac{dN(d)}{dt} = k_{BR}(d)N(d)$$

$$N(d,t) = N(d,0)\exp\left(-k_{BR}(d)t\right)$$

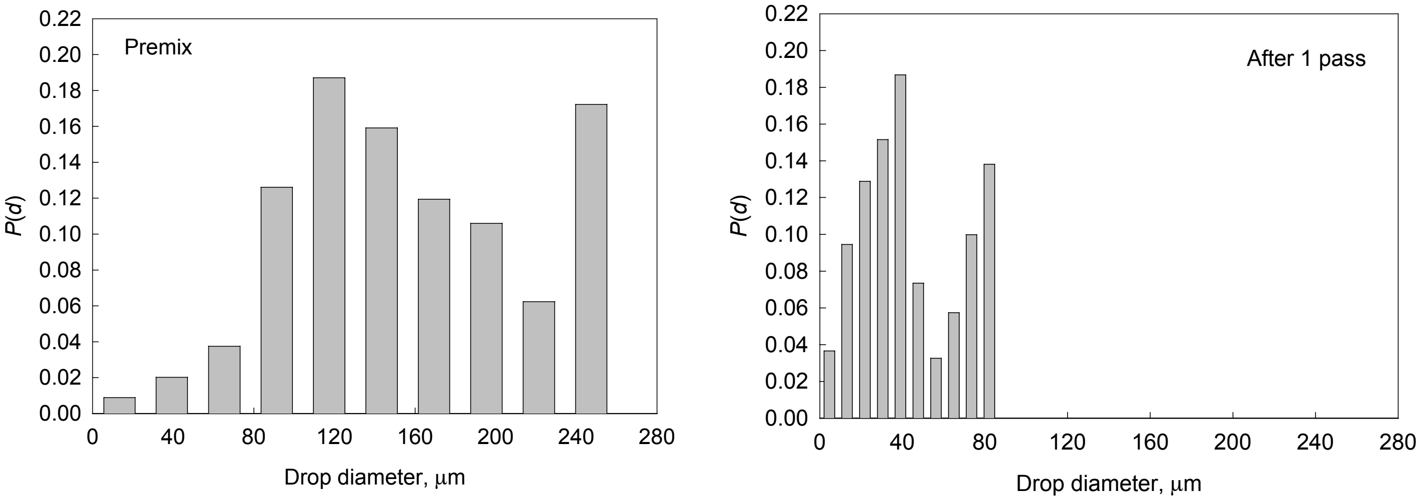
❑ Experimental results



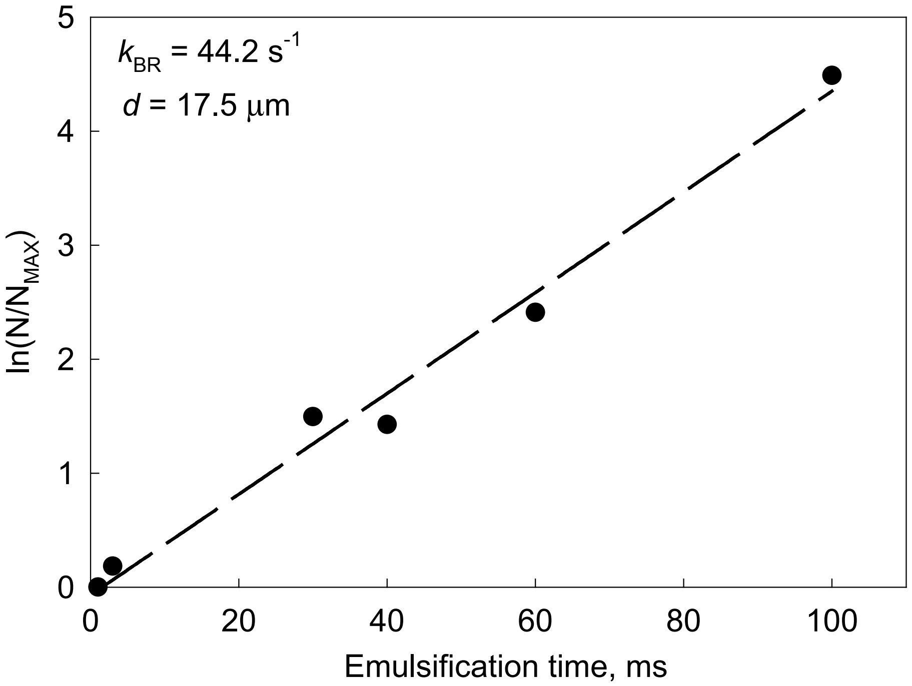
⇒ **The mean drop size decreases with emulsification time.**

⇒ **The number concentration of drops increases with time.**

❑ Evolution of drop size distribution during emulsification



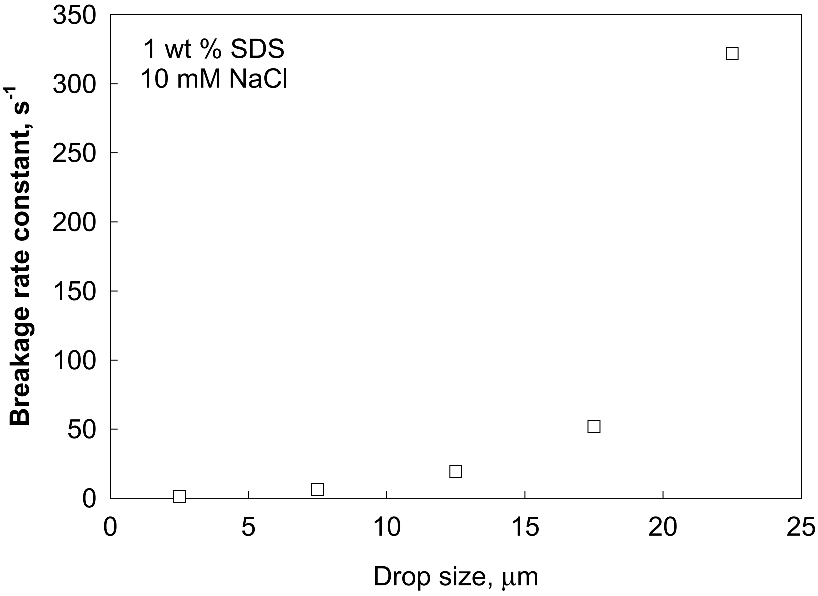
❑ Determination of breakage rate from drop-size histograms



$$\ln\left(\frac{N(d,t)}{N(d,0)}\right) = -k_{BR}(d)\,t$$

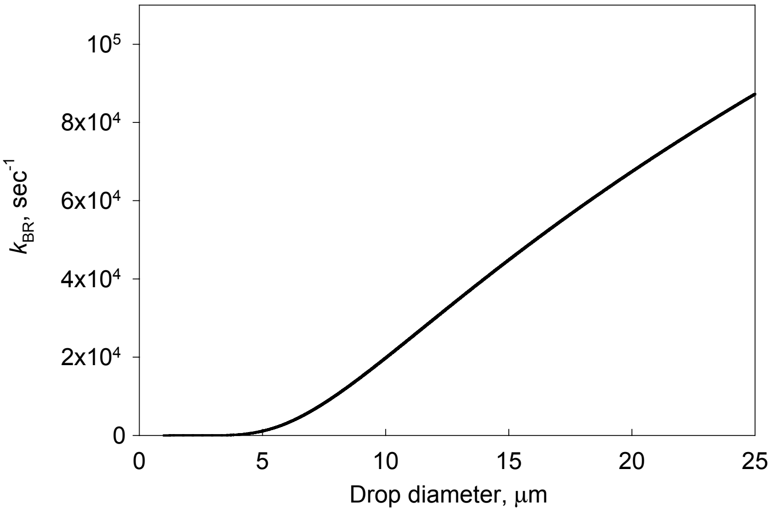
Comparison between experimentally estimated and theoretically calculated $k_{BR}(d)$

- **Experimentally determined**



- **Theoretically calculated (Coulaloglou and Tavlarides, 1977)**

$$k_{BR} = \frac{1}{\tau_{BREAKAGE}} \exp\left(-\frac{E_\sigma}{\bar{E}}\right) = \frac{\rho_C d^{2/3} \varepsilon^{2/3}}{\eta_D} \exp\left(-\frac{\sigma_{OW}}{\rho\, \varepsilon^{2/3} d^{5/3}}\right)$$



The experimentally estimated constant is about 2-3 orders of magnitude lower than the theoretically predicted ones

Possible explanations for the observed difference

❑ Problems with the interpretation of the experimental data

⇒ Influence of Kolmogorov radius – three step model

⇒ The residence time should be taken into account

❑ Problems with the theoretical expression

⇒ Large uncertainty about the expressions for the breakage efficiency and for the breakage time.

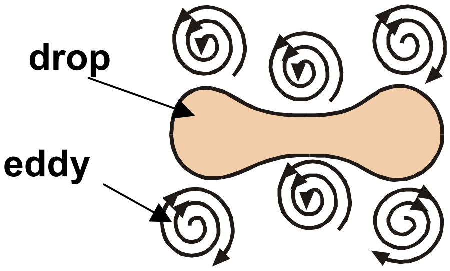
❑ Possible effects, which could be taken into account in the theoretical model

⇒ Comparison between the drop deformation time and the lifetime of the eddies

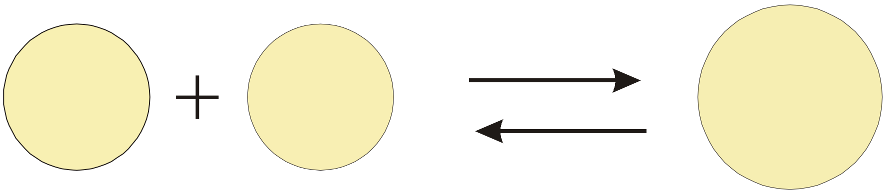
If the lifetime of the eddies is shorter than the drop deformation time, the eddy kinetic energy will dissipate in the eddies instead of deforming the drops.

⇒ The drop breaking efficiency could be significantly reduced by dissipating part of the eddy kinetic energy inside the drops (instead of using it for drop deformation)

⇒ The frequency of drop-eddy collision should be included in the pre-exponential factor (like the frequency of drop-drop collisions in the coalescence modelling).



Coalescence Process



$$v_C(d) = k_C(d)\left[n(d)\right]^2$$

1. Necessary condition for drop-drop coalescence – the hydrodynamic force, which pushes the drops against each other, should be larger than the barrier created by the repulsive forces between the drop surfaces.

$$F_T \sim d^{8/3}\rho\varepsilon^{2/3} \qquad\qquad F_{SF} \sim f\left(\Gamma, C_{EL}, \Psi_S, A_H\right)$$

2. Main factors affecting the coalescence process

⇒ **Surfactant adsorption** – depends on the used emulsifier and its concentration.

⇒ **Electrolyte concentration** – determines the height of the electrostatic barrier.

⇒ **Radius of the film**

⇒ **Drop size**

Phenomenological model for the mean drop size with coalescence (no electrostatic repulsion)

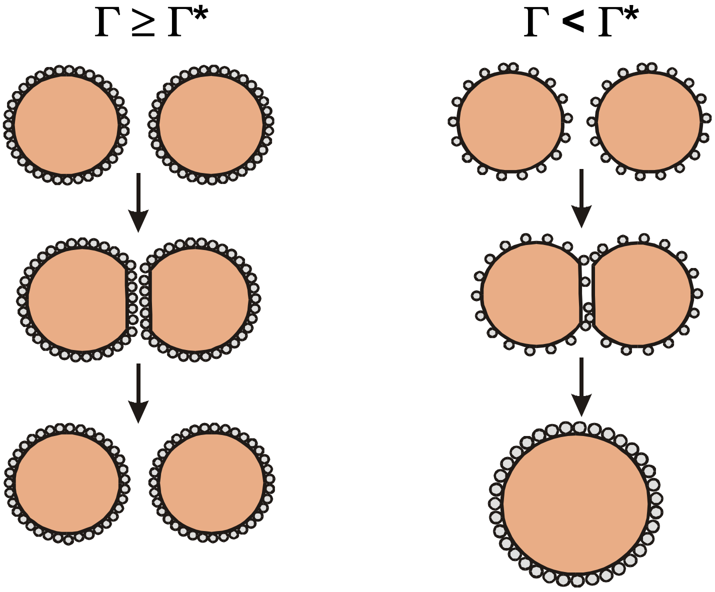
❑ Assumptions

⇒ **Threshold value of adsorption, Γ^***

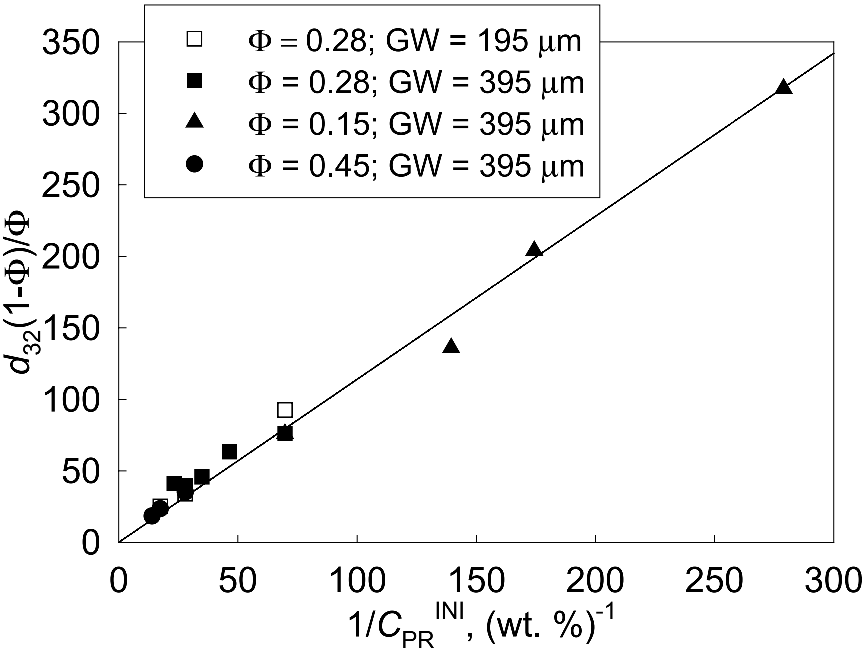
⇒ **All surfactant is adsorbed on the drop surface, $C_{SER} \approx 0$**

Threshold Adsorption

$$\frac{d_{32}(1-\Phi)}{\Phi} \approx \frac{1}{C_{SUR}^{INI}}\Gamma^*$$



❑ Experimental results

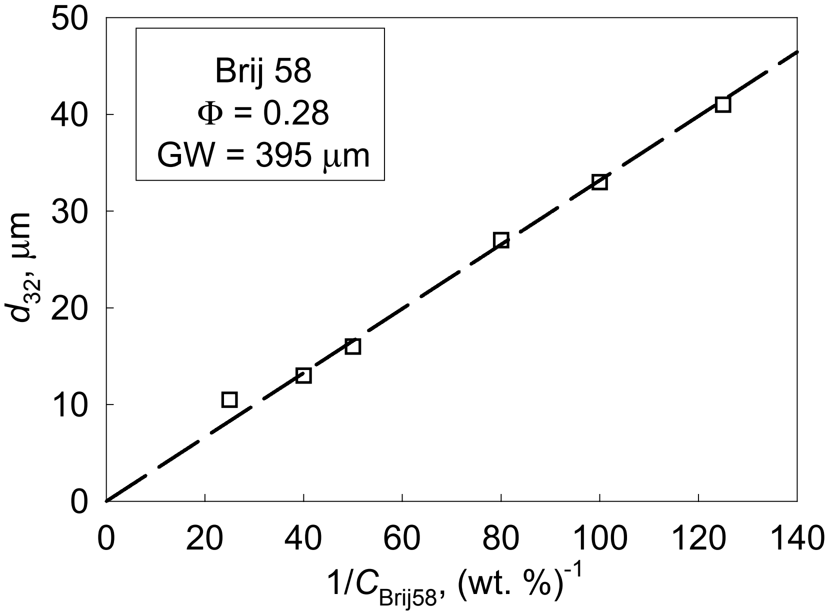


WPC + 150 mM NaCl

$\Gamma^* = 1.9$ mg/m^2

$\theta^* = \Gamma^*/\Gamma_M = 0.9$

- **Nonionic surfactant in presence of 150 mM NaCl**



Brij 58 + 150 mM NaCl

$\Gamma^* = 1.4$ mg/m^2

$\theta^* = 0.9$

- **The model is applicable for systems, in which the steric repulsion governs the emulsion stability**

Brij 58 + 150 mM NaCl

WPC + 150 mM NaCl

- **The model is inapplicable to emulsions stabilized by anionic surfactants and at low electrolyte concentration.**

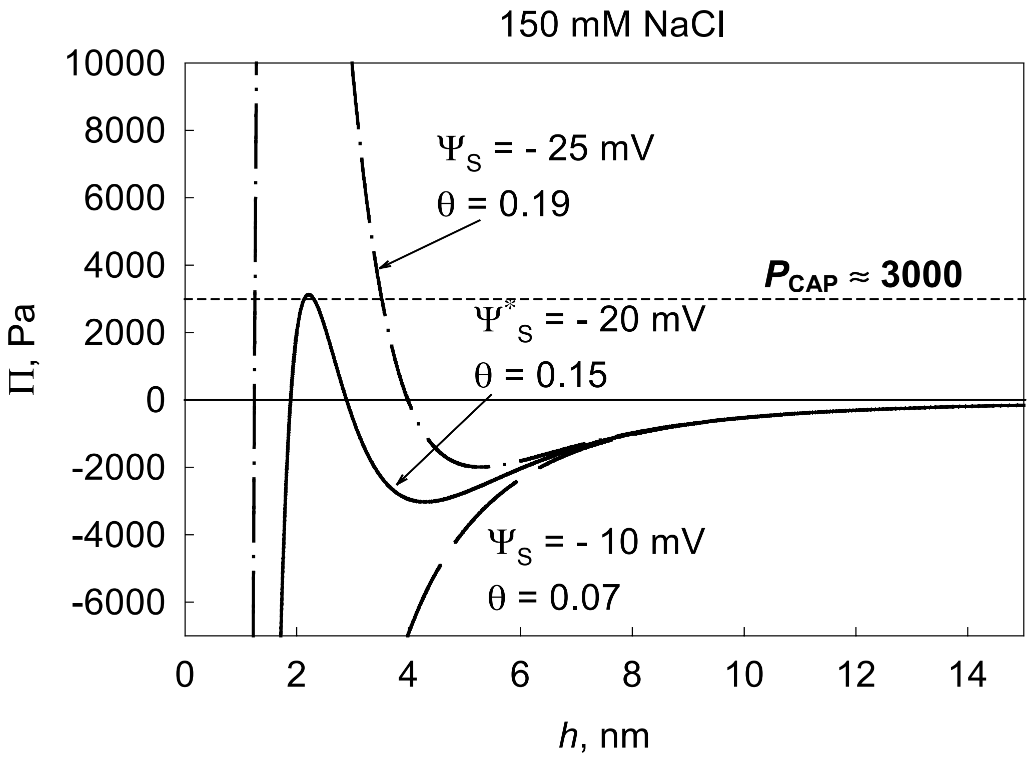
SDS + 150 mM NaCl

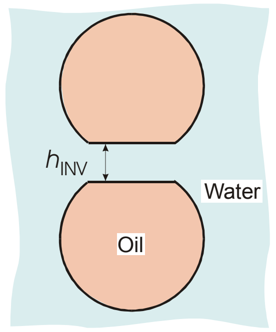
SDS + 10 mM NaCl

The electrostatic repulsion is the main factor, determining the stability of these emulsions.

Analysis of the possibility for drop-drop coalescence during emulsification in electrostatically stabilized emulsions

$$\Pi = 64 C_{EL} k_B T \left[\tanh\left(\frac{e\Psi_0}{4k_BT}\right)\right]^2 \exp(-\kappa h) - \frac{A_H}{6\pi h^3}$$





SDS+150 mM NaCl

There is a critical value of Ψ_S

$\Psi_S < \Psi^* \Rightarrow \Pi_{MAX} < P_{CAP}$ Coalescence

$\Psi_S > \Psi^* \Rightarrow \Pi_{MAX} > P_{CAP}$ Electrostatic barrier preventing the drop-drop coalescence

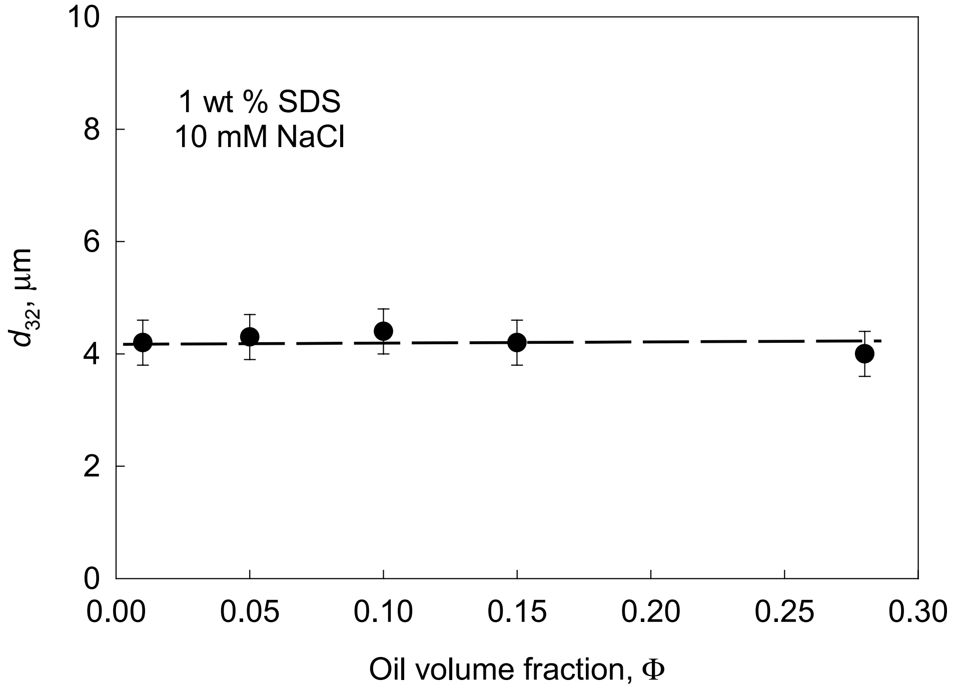
SDS+10 mM NaCl

At all $\Psi_S \Rightarrow \Pi_{MAX} > P_{CAP} \Rightarrow$ Electrostatic barrier for drop-drop coalescence at any adsorption.

Comparison of the experimental results with the predictions of the theoretical model

$$k_{BR}\left(\sqrt[3]{2}d\right)=k_C\left(d\right)n\left(d\right),\quad n\left(d\right)=\frac{2\Phi}{\pi d^3}$$

Effect of Oil Volume Fraction at high surfactant concentrations

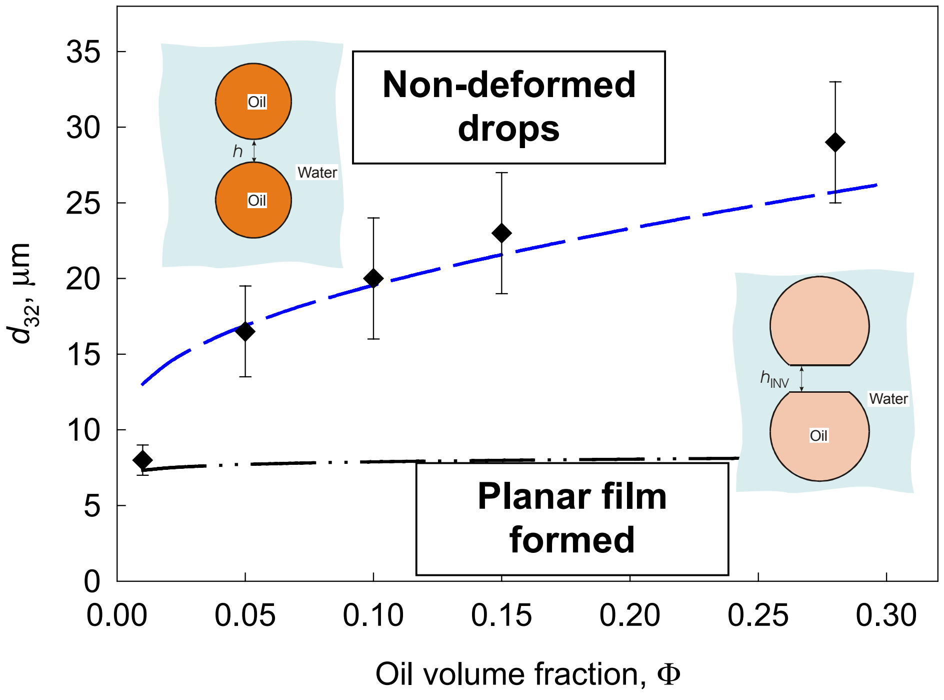


Emulsions stabilized by 1 wt % SDS (+10 mM NaCl)

- ❑ **The mean drop size does not depend on Φ.**
- ❑ **The coalescence between the drops is negligible due to significant electrostatic repulsion.**
- ❑ **The mean drop size is determined by Kolmogorov-Hinze equation.**

Effect of Oil Volume Fraction
No Surfactant Added

- 150 mM NaCl - Suppressed electrostatic repulsion, $\zeta \ll \Psi^*$

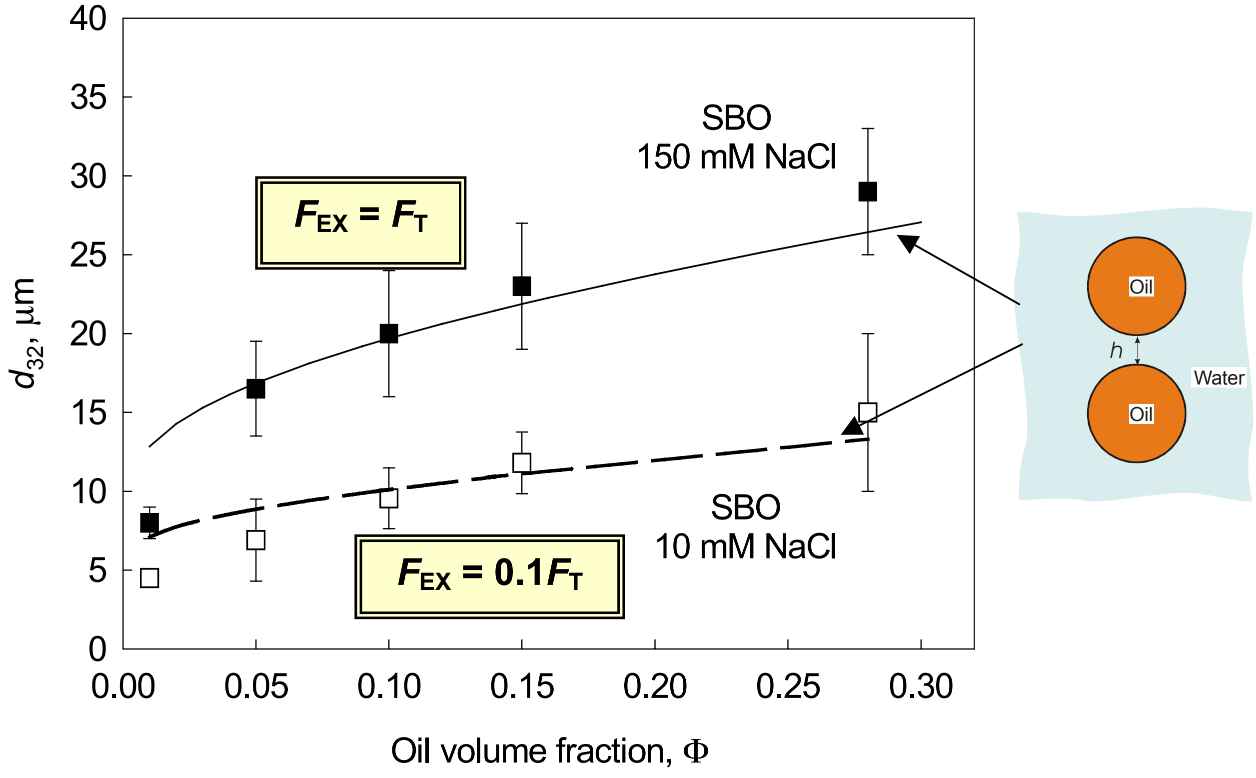


The comparison indicates that the Taylor regime describes more adequately the drop-drop approach.

The coalescence between the drops is determined primarily by the probability for drop-drop encounters.

The coalescence efficiency is almost 1 for Φ > 0.05.

- **10 mM NaCl, no surfactant added. There is a significant electrostatic barrier, which prevents the coalescence between the drops, $\zeta > \Psi^*$.**



In presence of 10 mM NaCl

The coalescence efficiency is significantly reduced by electrostatic repulsion between the drops

Effect of surfactant concentration

$$k_{BR}\left(\sqrt[3]{2}d\right)=k_C\left(d\right)n\left(d\right)$$

The presence of surfactant could affect:

⇒ **Breakage rate constant** – decreased interfacial tension, which leads to more efficient drop breakage.

⇒ **Coalescence rate constant** – suppressed coalescence due to slower film thinning and significant electrostatic repulsion.

Iterative procedure for determination of interfacial tension and mean drop size

- ❑ Interfacial tension vs. surfactant concentration

$$\sigma_{OW}=\sigma_0+B\ln C_S+D\left(\ln C_S\right)^2$$

- ❑ Determination of surfactant adsorption – from Gibbs adsorption isotherm and mass balance.

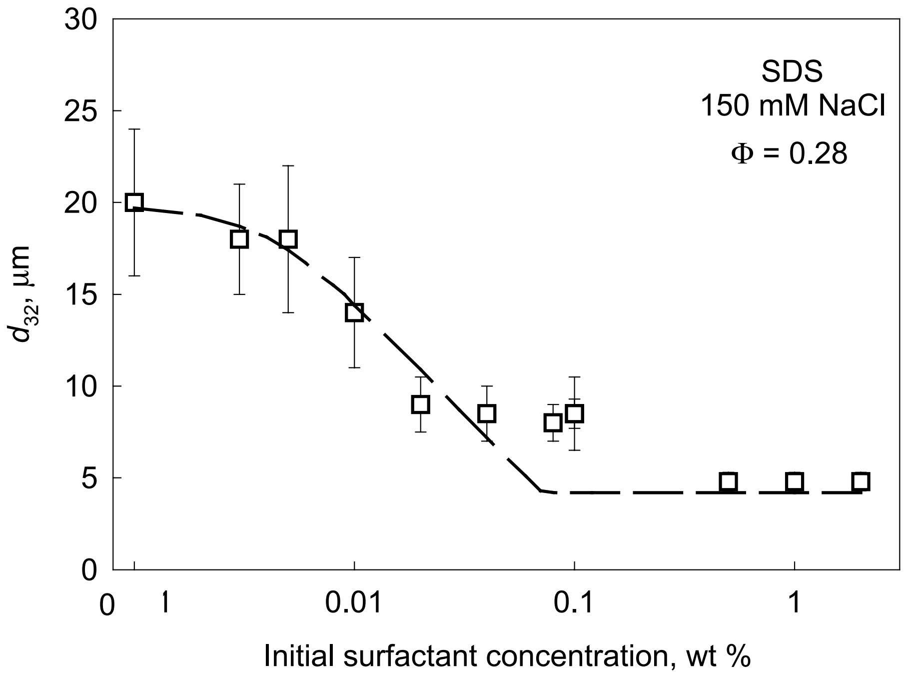
$$\Gamma=-\frac{1}{kT}\frac{d\sigma}{d\ln C_S} \qquad \Gamma=\frac{\left(C_S^{INI}-C_S\right)\left(1-\Phi\right)d}{6\Phi}$$

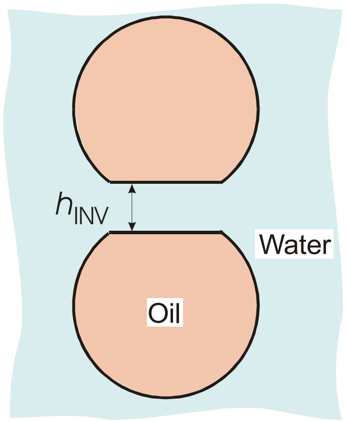
- ❑ Mean drop size.

$$k_{BR}\left(\sqrt[3]{2}d\right)=k_C\left(d\right)n\left(d\right)$$

We obtain - σ_{OW}, d and C_S at different initial surfactant concentrations.

❑ SDS + 150 mM NaCl.



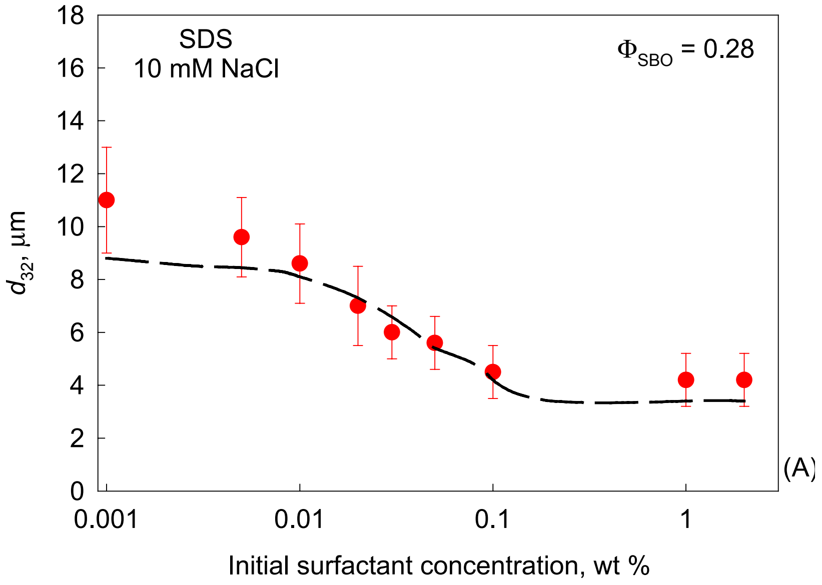


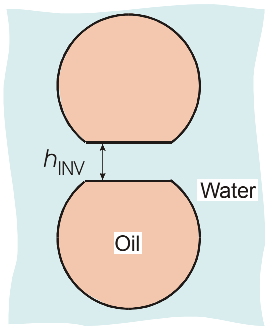
$R_F \sim \lambda_0$

SDS + 150 mM NaCl

The addition of surfactant affects both the coalescence and breakage processes.

❑ SDS + 10 mM NaCl .





$R_F \sim \lambda_0$

SDS + 10 mM NaCl

The addition of surfactant leads primarily to higher breakage rate due to lower σ_{OW} (except for very low C_S).

Conclusions

1. For all studied emulsifiers two regions (surfactant-rich and surfactant-poor) are found in the dependence d_{32} vs. C_S.

2. The results for d_{32} in the surfactant-rich regime are very well described by Kolmogorov theory of emulsification.

3. Breakage rate constant was experimentally determined and compared to literature models.

   A large discrepancy between theory and experiment is observed – ideas are suggested how to improve both.

4. The coalescence in the surfactant-poor regime is analyzed and the following different cases are distinguished:

☐ Nonionic or protein type of emulsifier with suppressed electrostatic repulsion (150 mM NaCl):

⇒ Threshold value of adsorption, Γ^*; simple model describes very well the results.

☐ Ionic surfactant at high electrolyte concentration

(SDS + 150 mM NaCl).

⇒ Critical surface potential, $\Psi^* = -20$ mV, ensuring electrostatic stabilization during emulsification.

☐ Ionic surfactant at low electrolyte concentration

(SDS + 10 mM NaCl).

⇒ The drop-drop coalescence is negligible except for extremely low SDS concentrations (well below CMC).

☐ Pure oil and water phases at 150 mM NaCl

⇒ **The drop-drop coalescence is determined primarily by the probability for drop-drop encounters. The coalescence efficiency is almost 1 for $\Phi > 0.05$.**

- ❑ **Pure oil and water phases at 10 mM NaCl**

  ⇒ **The coalescence efficiency is significantly reduced by electrostatic repulsion between the drops.**

Unclear points in data interpretation

- ❑ **The dynamic pressure in the gap between the drops is much larger than the capillary pressure ⇒ planar film is expected to form.**
- ❑ **The theoretically predicted values of *d*, assuming formation of a large planar film, are much lower than the experimentally obtained ones.**
- ❑ **The electrostatic barrier between the drops should affect the value of the surface force, which opposes the drop-drop approach (not the value of the external force).**
- ❑ **No adequate expressions are available for the coalescence efficiency, as well as for the radius and critical thickness of the film, formed between two colliding droplets.**

Significant experimental and theoretical efforts should be undertaken to match convincingly the theory and experiment.