Effect of Surfactants and Hydrodynamic Factors on the Drop-Size Distribution in Membrane Emulsification

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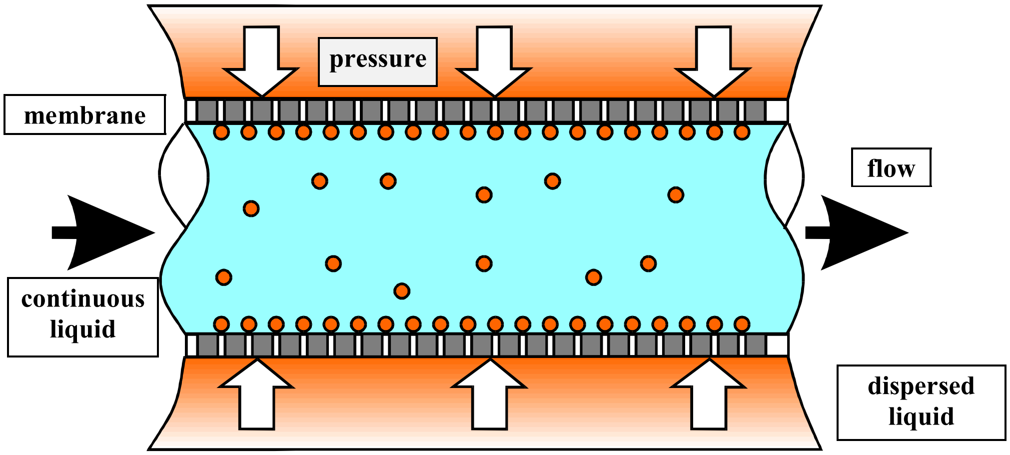
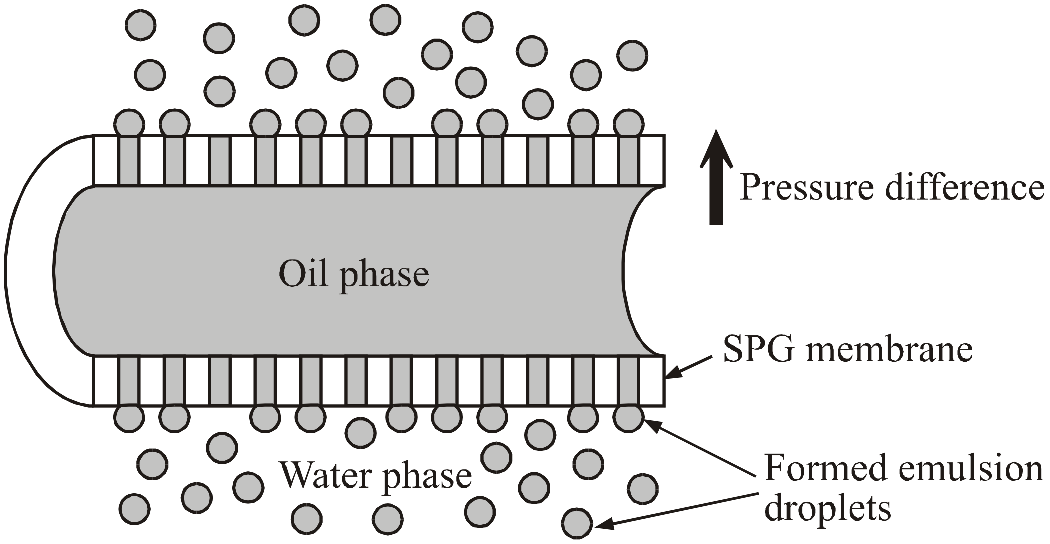
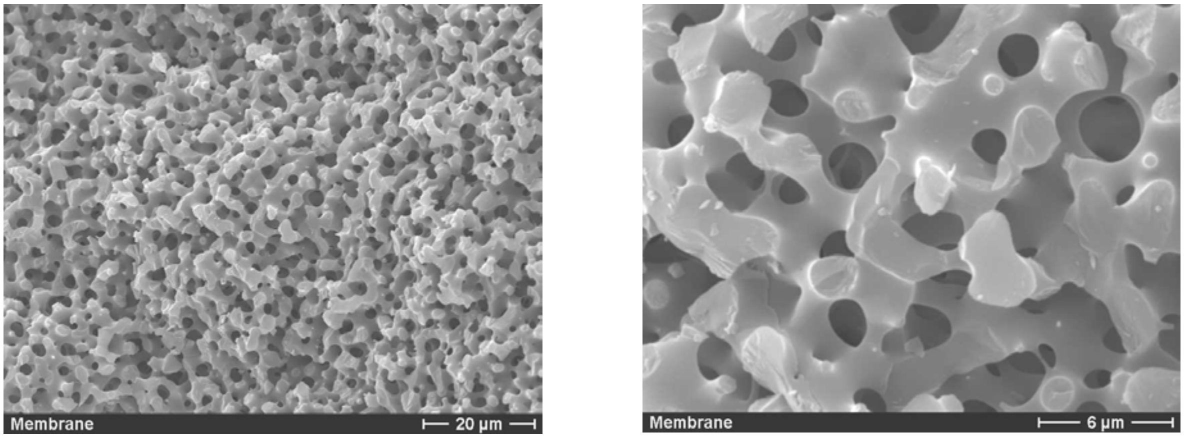


Scheme of a typical membrane emulsification modulus ➡

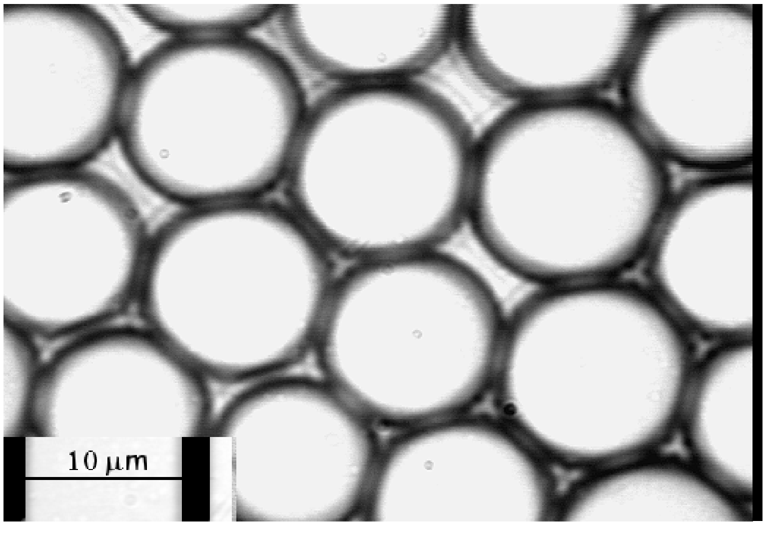
Tubular membrane of porous glass (Shirazu, Miyazaki, Japan)



Observation of the forming drops at the outer membrane surface

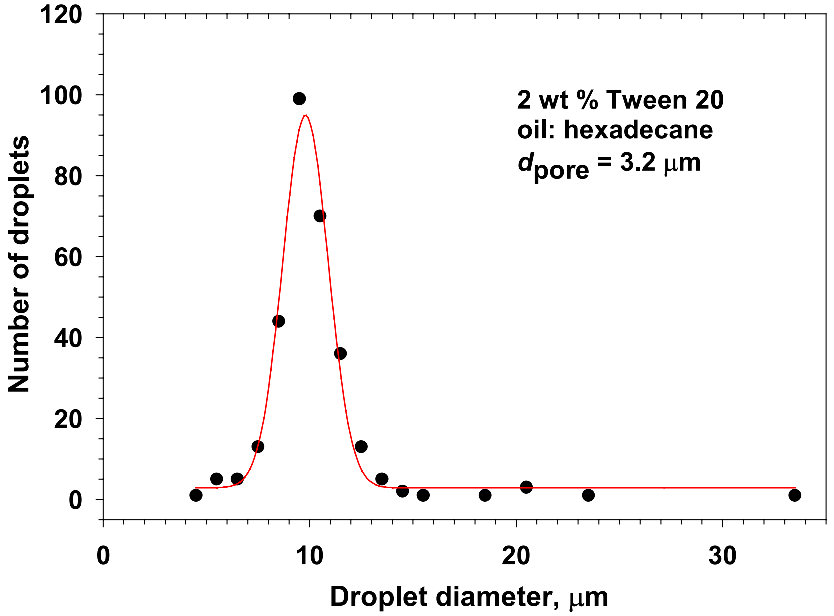


Surface of membrane with 2 µm pore size

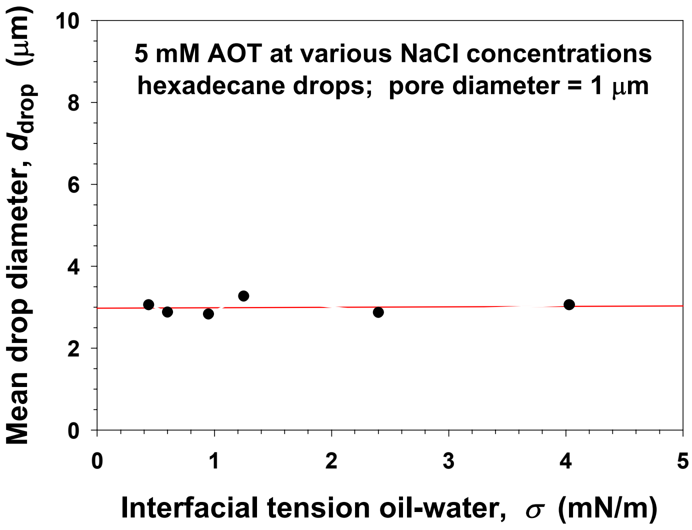


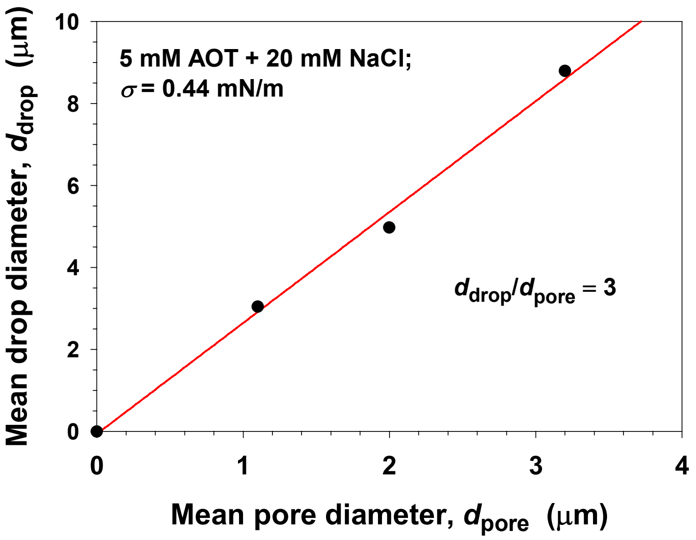
Produced monodisperse emulsion (pore diameter 3.2 µm) ➡

Oil-in Water Emulsions Obtained by Hydrophilic Membranes



Typically $d_{drop}/d_{pore} \approx 3$





d_{drop}/d_{pore} is independent of the interfacial tension

d_{drop}/d_{pore} is independent of the pore size

<u>Basic Question</u>:

Why $d_{\mathrm{drop}}/d_{\mathrm{pore}} \approx 3$?

(irrespective of pore size, interfacial tension and viscosity of the liquid phases?)

Theoretical Analysis:

Condition for Detachment of a Growing Drop from a Pore

<u>KEY</u>:

Analogy: detachment of a pendant drop

- **Steady state growth: $F_{\mathrm{tot}} = 0$;**
- **At a given size the drop profile becomes <u>unstable</u>;**
- **The critical value of the body (gravitational) force is:**

$$F_{\mathrm{cr}} = \sigma d_{\mathrm{drop}}\,\lambda(x); \qquad x = d_{\mathrm{drop}}/d_{\mathrm{pore}}$$

$\lambda(x)$ – known universal function

➡

$\lambda(x) \propto (\mathrm{V}_{\max})^{2/3}$; $\mathrm{V}_{\max}$ – dimensionless maximum drop volume [2]

In the case of membrane emulsification the deformation of drop profile is due to the hydrodynamic force (rather than to gravity)

At the moment of detachment:

$$\{\text{hydrodynamic force}\} = \{\text{critical body force}\}$$

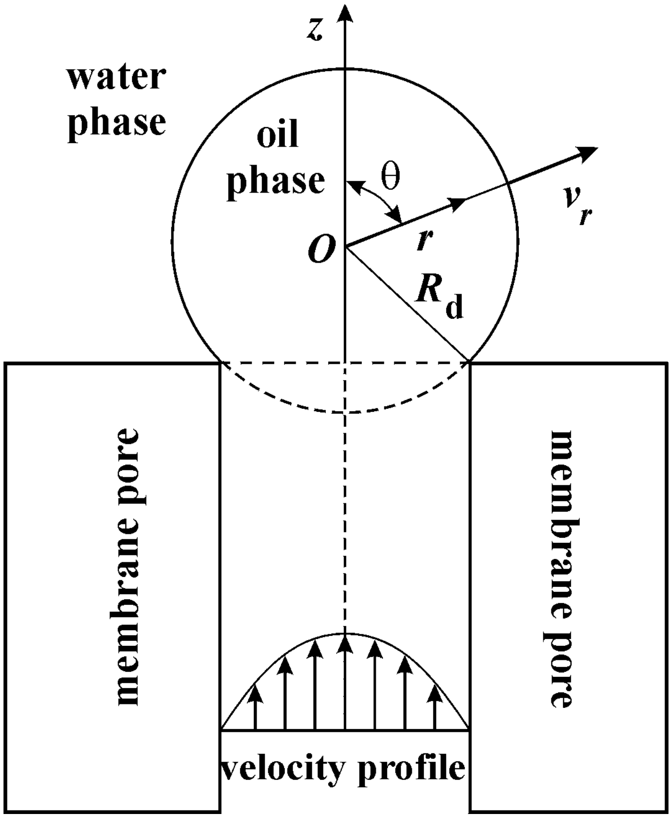
$$\Rightarrow \qquad f_{\mathrm{d}}\, \eta\, R_{\mathrm{drop}}\, \mathrm{v}_{\mathrm{av}}(\Delta P) = \sigma\, d_{\mathrm{drop}}\, \lambda(x)$$

f_{d} – hydrodynamic drag coefficient;

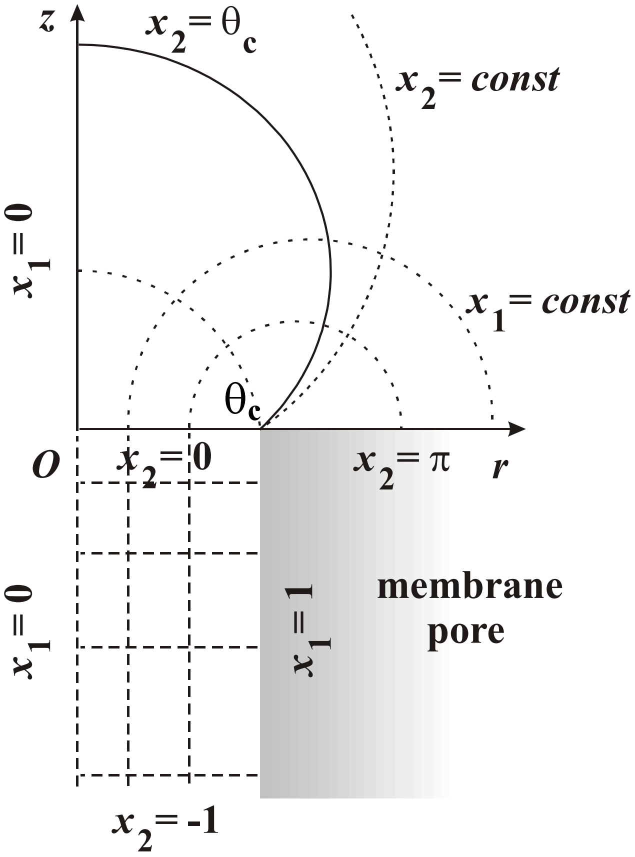
η – viscosity of the drop (oil) phase;

$\mathrm{v}_{\mathrm{av}}(\Delta P) = \dfrac{R_{\mathrm{pore}}^{2}}{8\eta L}\left(\Delta P - \dfrac{2\sigma}{R_{\mathrm{d}}}\right)$ – average velocity of oil supply

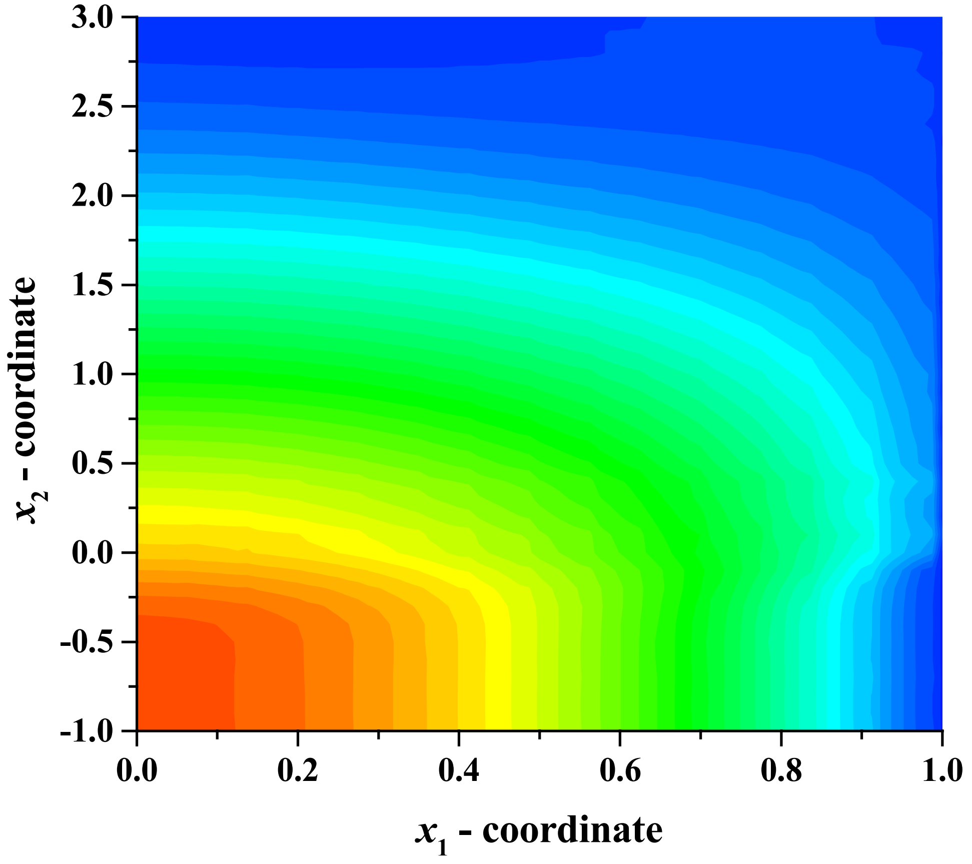
ΔP – pressure difference between the oil and water phases.



Determination of the hydrodynamic drag coefficient f_d

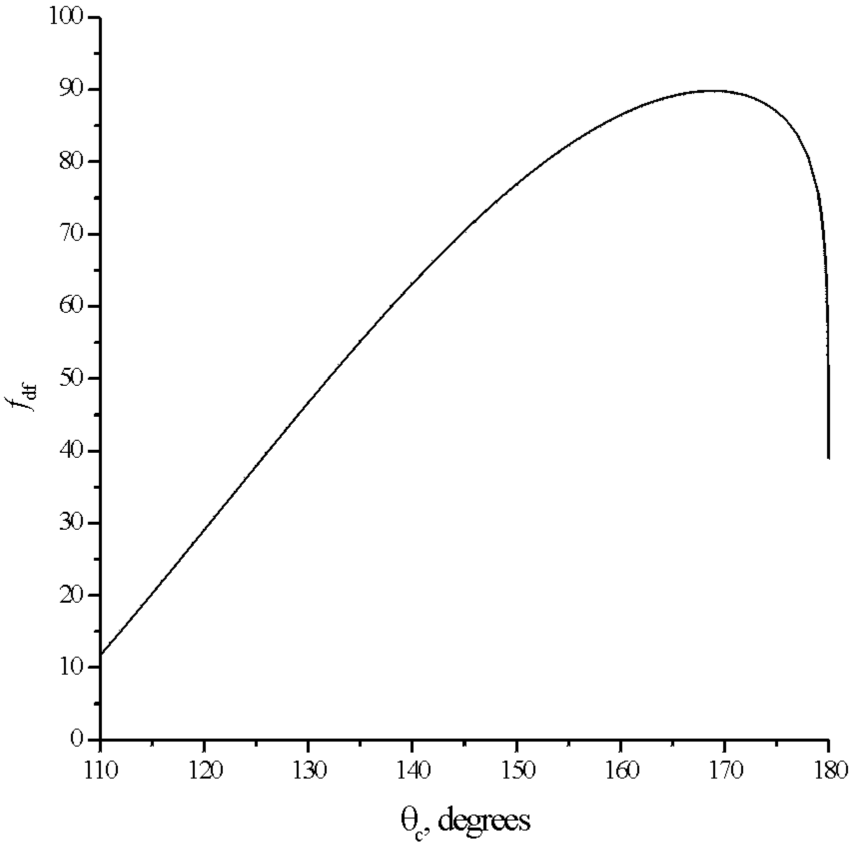


- **The Navier-Stokes equation is integrated numerically**
- **The fields of *velocity* and *pressure* are computed for the *interior* and *exterior* of an oil drop growing at the orifice of a membrane pore**

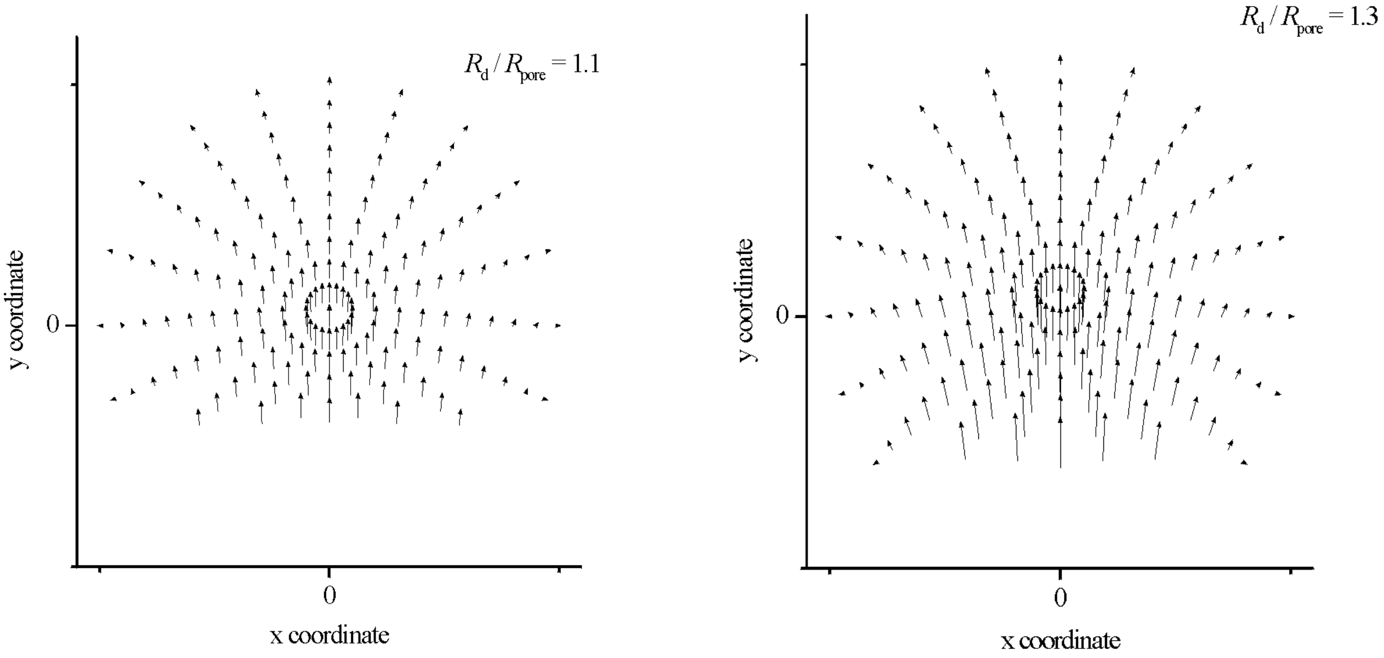


Vertical velocity component (domains A and B)

Contour plot of the vertical velocity component for $\theta_c = 160°$.



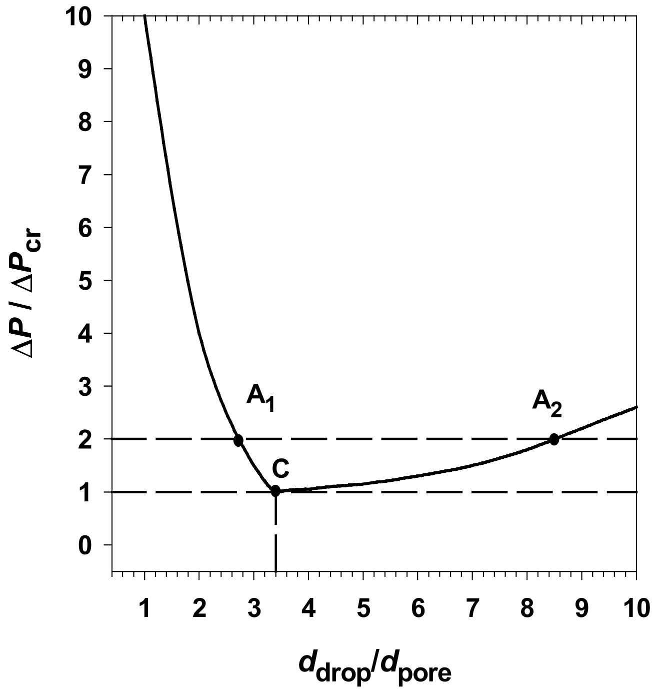
θ_c **– central angle of a spherical drop**

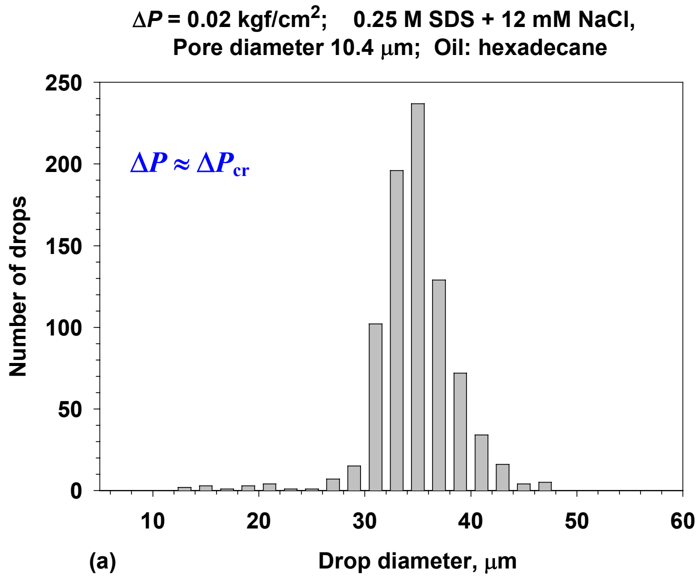


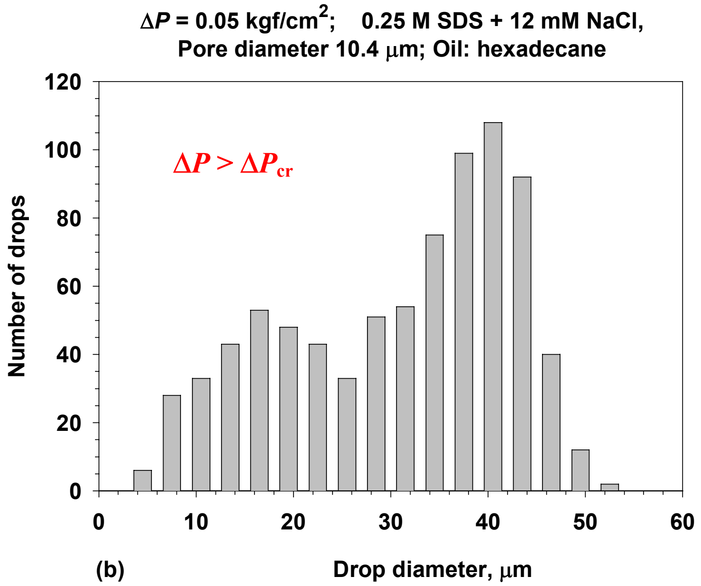
Distribution of the velocity field in the drop at different values of the ratio R_d/R_{pore}: a) 1.1 and b) 1.3. (No vortices!)

Point C:

$\Delta P = \Delta P_{\mathrm{cr}}$



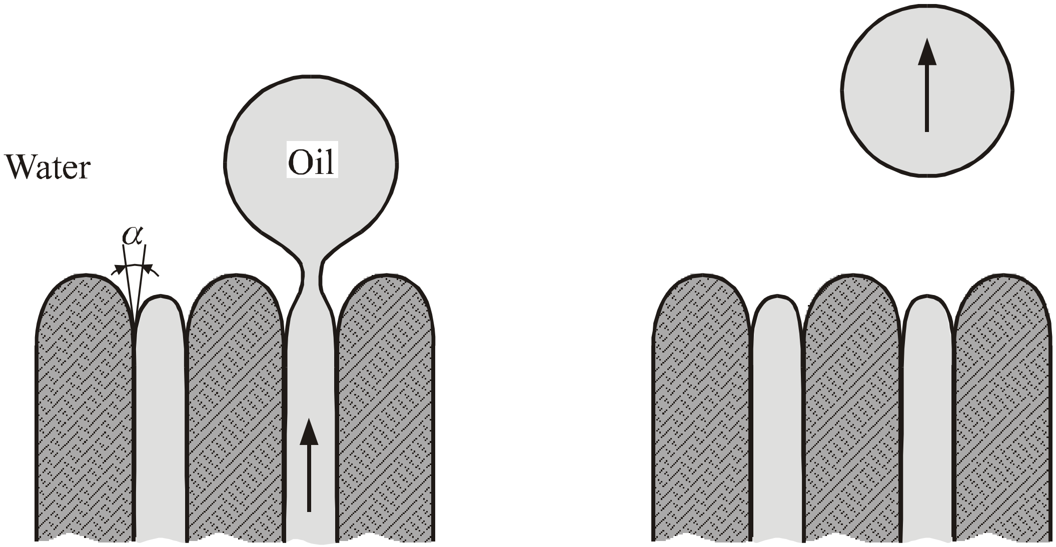




- **For $\Delta P < \Delta P_{\mathrm{cr}}$ emulsion drops are not released from the membrane.**
- **For $\Delta P > \Delta P_{\mathrm{cr}}$ drops with two different sizes, corresponding to the points A_1 and A_2, $\Rightarrow$ two-peak drop-size distribution;**
- **For $\Delta P = \Delta P_{\mathrm{cr}}$ (point C) monodisperse drops are produced with $d_{\mathrm{drop}}/d_{\mathrm{pore}} \approx 3$.**

This explains why if monodisperse drops are produced by means of a microporous membrane, one has $d_{\mathrm{drop}}/d_{\mathrm{pore}} \approx 3$, irrespective of the type of the oily and aqueous phases, of the interfacial tension, bulk viscosities, surfactant adsorption kinetics, etc.

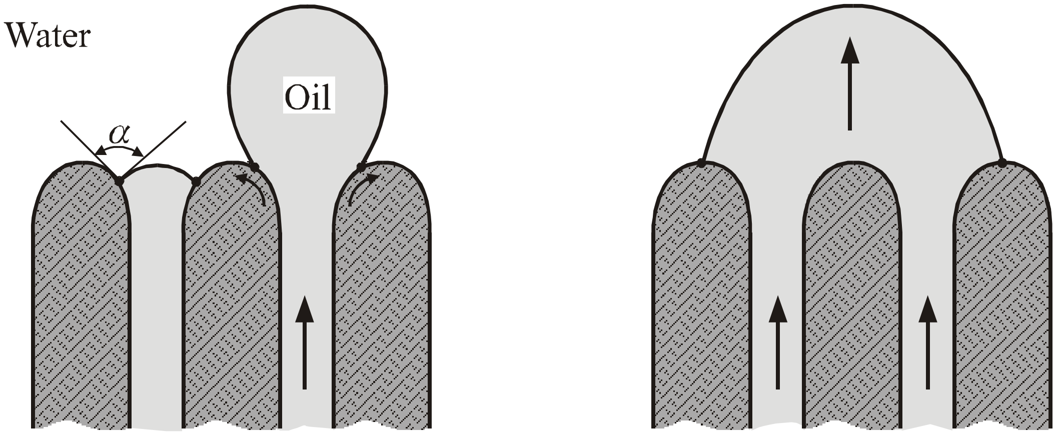
Role of the Membrane Wettability



$(t = t_0)$ $(t = t_0 + \Delta t)$

(a) small dynamic contact angle α

$$\cos\alpha = (\sigma_{so} - \sigma_{sw})/\sigma_{ow}$$



$(t = t_0)$ $(t = t_0 + \Delta t)$

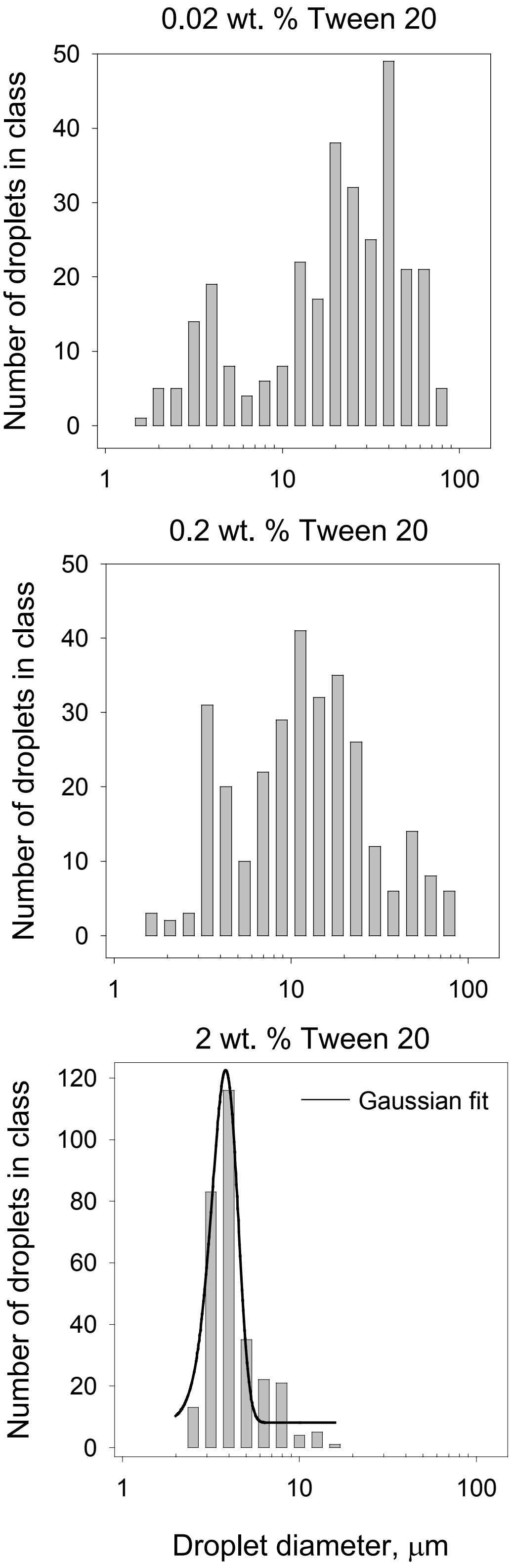
(b) larger dynamic contact angle α

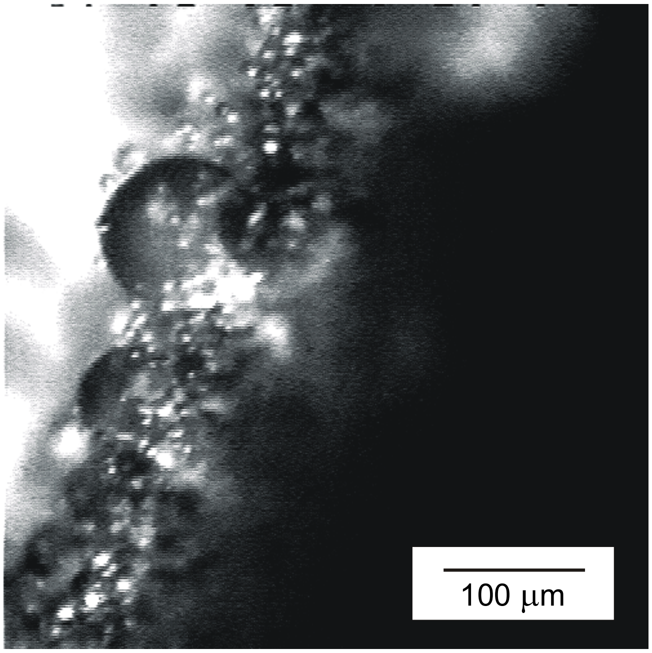
- **(a) Small dynamic contact angle α: the contact line solid-water-oil is fixed at the pore diameter: ⇒ $d_{drop}/d_{pore} \approx 3$.**
- **(b) Larger angle α facilitates contact-line expansion; the latter may span two or more pores: $d_{drop}/d_{pore} > 3$ (exclusions from the rule) [3].**

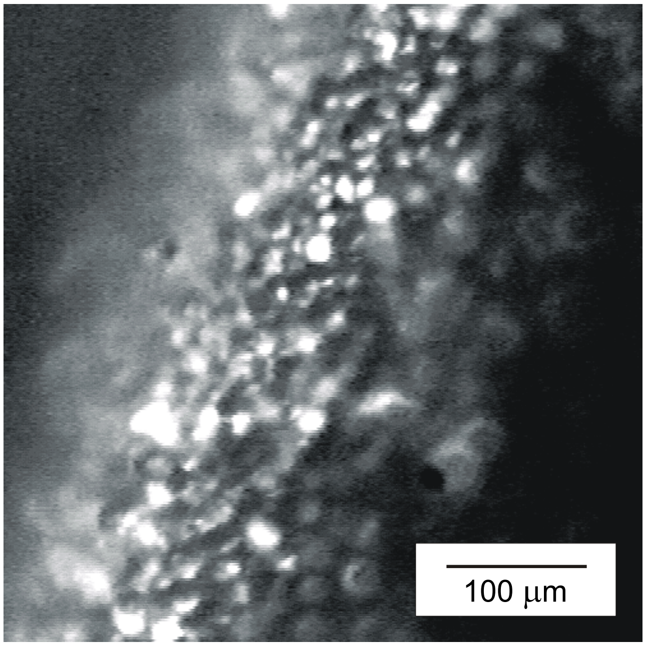
Exclusions from the Rule $d_{\text{drop}}/d_{\text{pore}} \approx 3$

{Lowering of surfactant concentration} ⇒ {Slowdown of adsorption}

⇒ {Worsening of the membrane wetting by water}

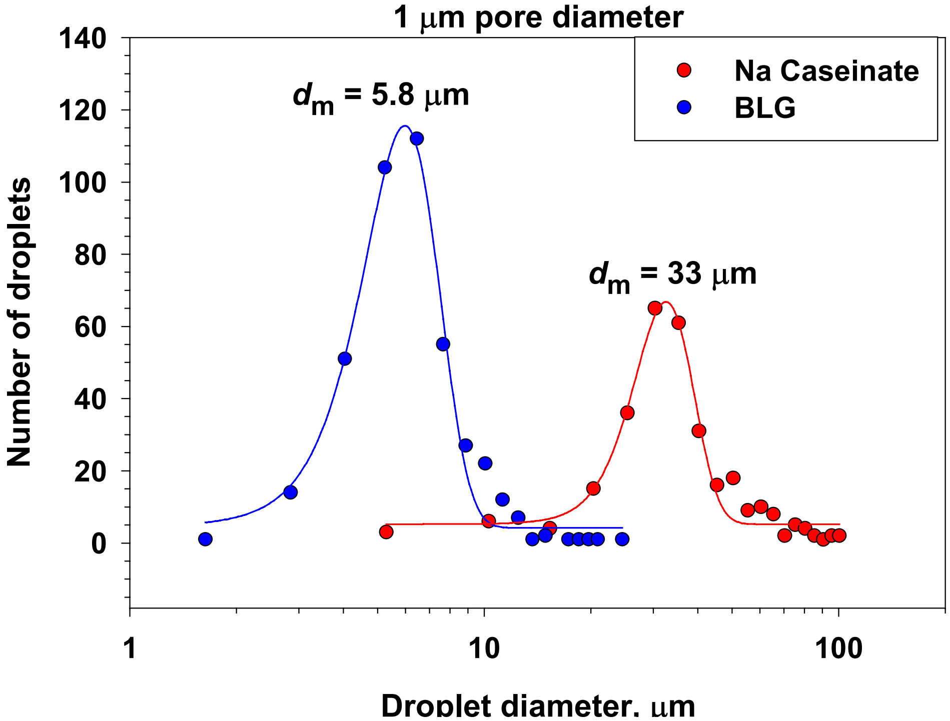






Emulsification in Protein Solutions

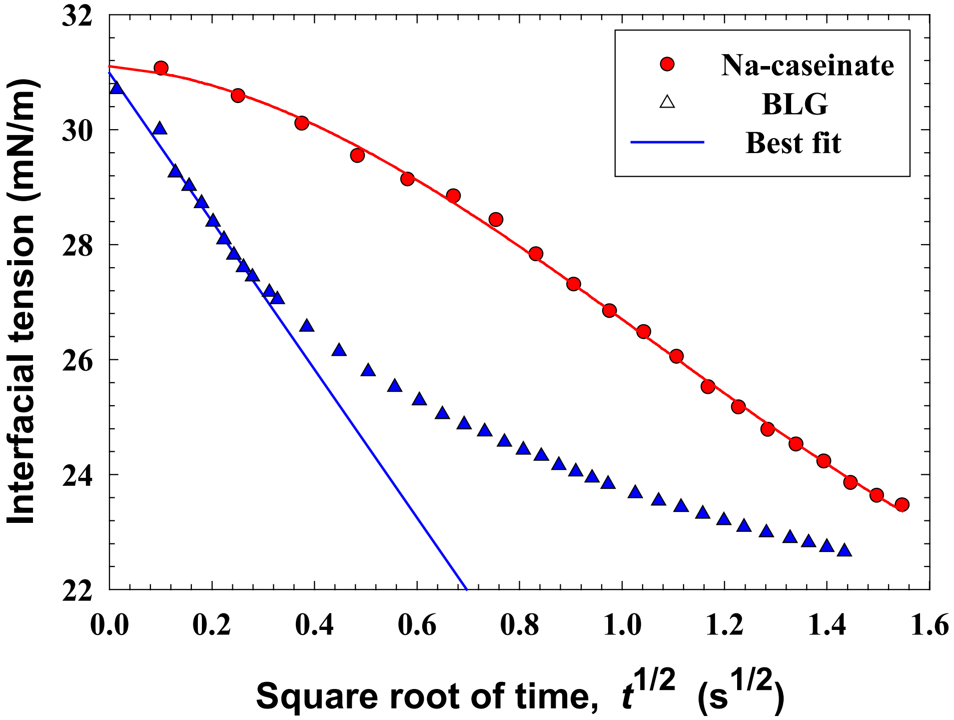
Beta Lactoglobulin (BLG) and Na-Caseinate [3]



Regime of adsorption:

BLG: diffusional

Na-Caseinate: barrier [4]



{Lower interfacial tension σ_{ow}} ⇒ {smaller angle α}

SUMMARY AND CONCLUSIONS

Condition for producing small and monodisperse drops:

1. **The applied pressure difference should be slightly greater than the critical pressure: $\Delta P \approx \Delta P_{\mathrm{cr}}$;**
2. **The dynamic contact angle α should be as small as possible $\cos\alpha = (\sigma_{\mathrm{so}} - \sigma_{\mathrm{sw}})/\sigma_{\mathrm{ow}}$;**
3. **The surfactant should adsorb fast at the expanding oil-water interface.**

References

[1] T. Nakashima, M. Shimizu, M. Kukizaki (Eds.) "*Membrane emulsification operational manual,*" 1st Edition, Dept. of Chemistry, Industrial Research Institute of Miyazaki Prefecture, Miyazaki, 1991.

[2] Pu, B., Chen, D. "*A study of the measurement of surface and interfacial tension by the maximum liquid drop volume method. I. Using a back-suction syringe technique*," J. Colloid Interface Sci. 235 (2001) 265.

[3] N. C. Christov, D. N. Ganchev, N. D. Vassileva, N. D. Denkov, K. D. Danov, and P. A. Kralchevsky, *"Capillary Mechanisms in Membrane Emulsification: Oil-in-Water Emulsions Stabilized by Tween 20 and Milk Proteins"*, Colloids and Surfaces A (2002) – in press.

[4] K. D. Danov, D. S. Valkovska, and P. A. Kralchevsky, *"Adsorption Relaxation for Nonionic Surfactants under Mixed Barrier-Diffusion and Micellization-Diffusion Control"*, J. Colloid Interface Sci. 251 (2002) 18–25.