Detachment of Oil Drops from Solid Surfaces in Surfactant Solutions: Molecular Mechanisms at a Moving Contact Line

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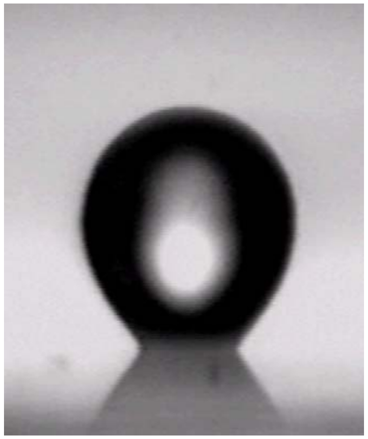
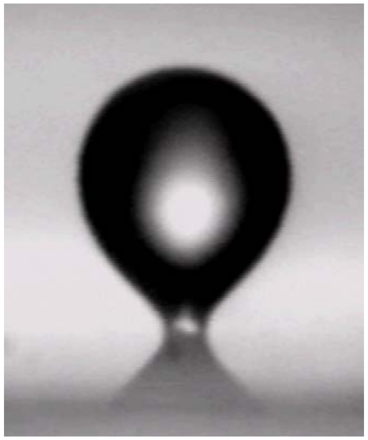


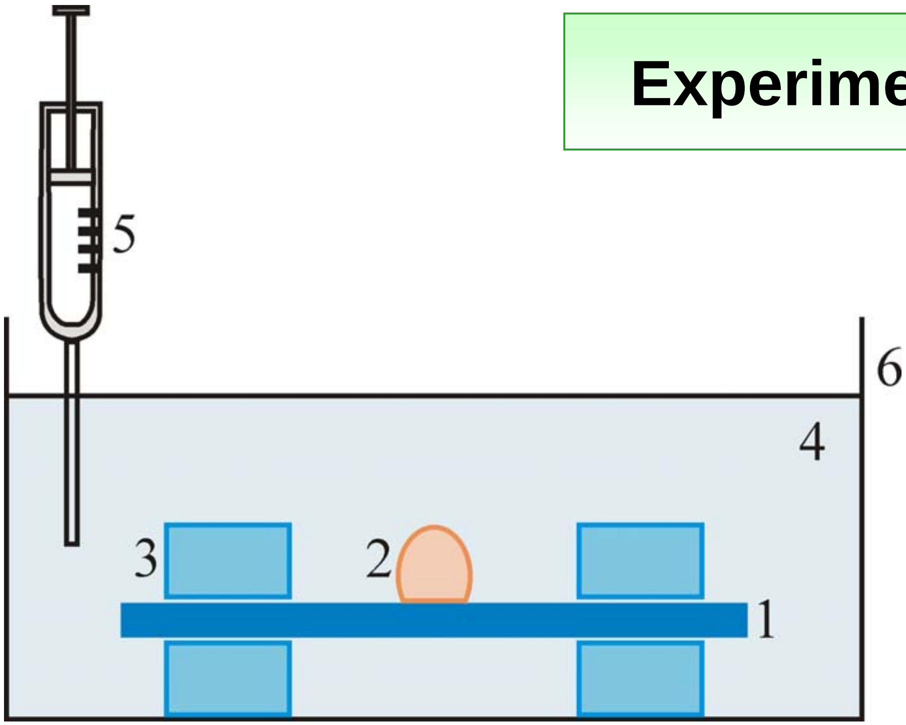


Drop detachment:
Moving contact line;
Importance for Detergency;
Membrane emulsification;
Other processes with moving three-phase contact line

Aim: (i) Examine the effect of temperature, surfactant and salt concentrations, on the dynamics of drop detachment.

(ii) Develop of a quantitative theoretical model; fit the experimental data; determine the values of the involved physicochemical parameters.

Experiment



Scheme of the experimental cell:
1 – glass plate;
2 – oil droplet ≈ 1 μl;
3 – glass holders;
4 – surfactant solution;
5 – syringe; 6 – cuvette.

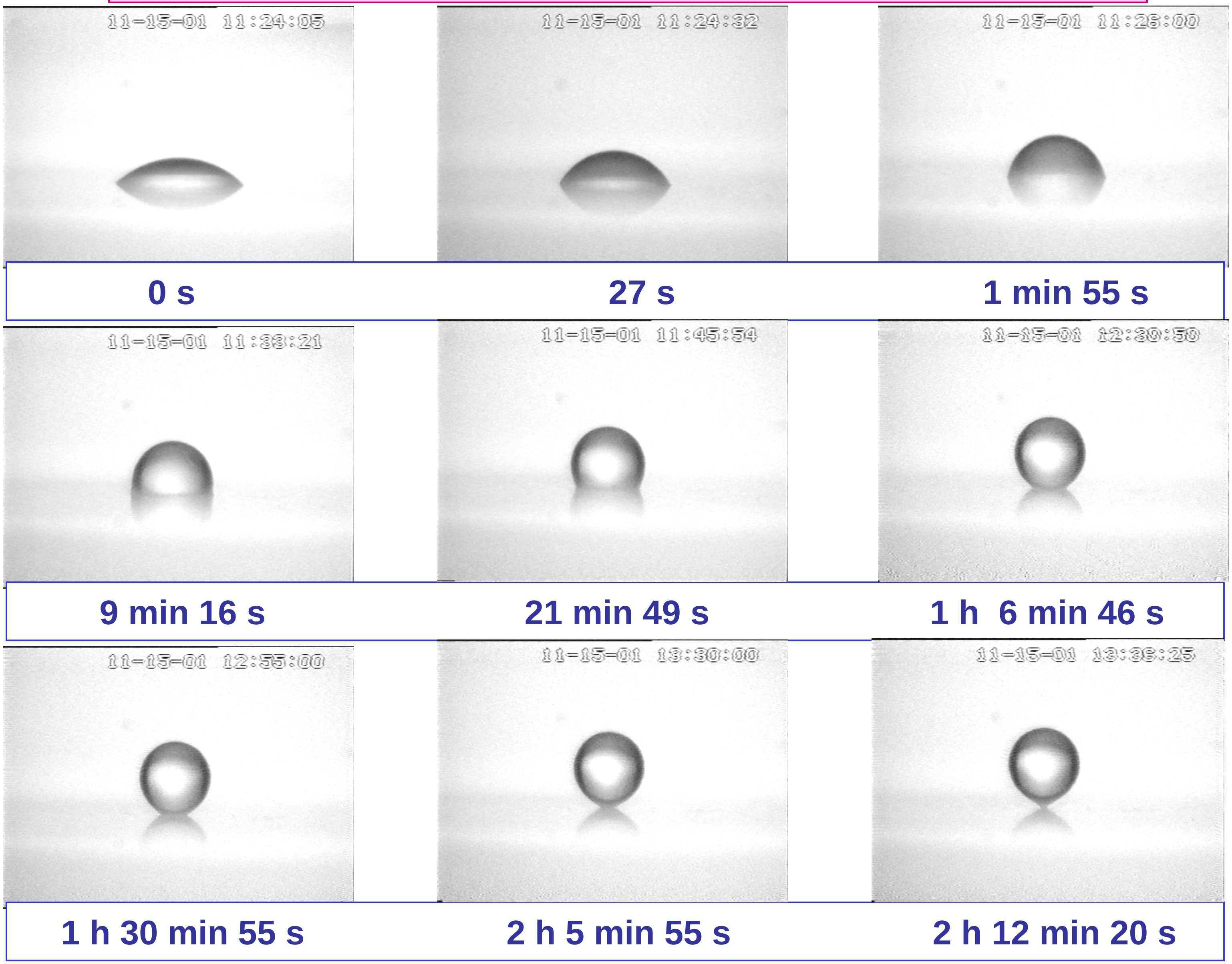
Procedure:

(1) Oil drop is placed on the dry glass substrate;

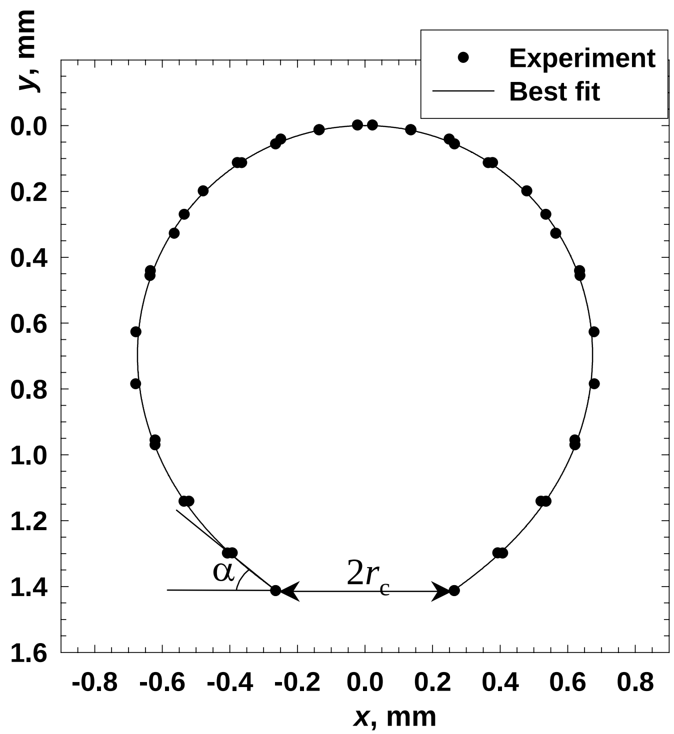
(2) Solution of surfactant + NaCl is poured in the cuvette;

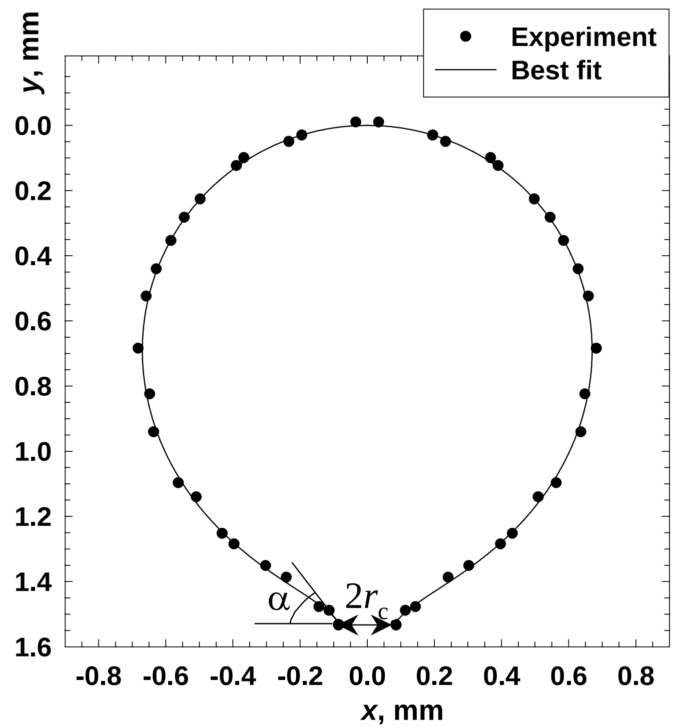
(3) The process of oil drop detachment is recorded by horizontal microscope and video-camera.

Dynamics of Spontaneous Drop Detachment



Drop Profile: Digitization and Fit by Laplace Equation

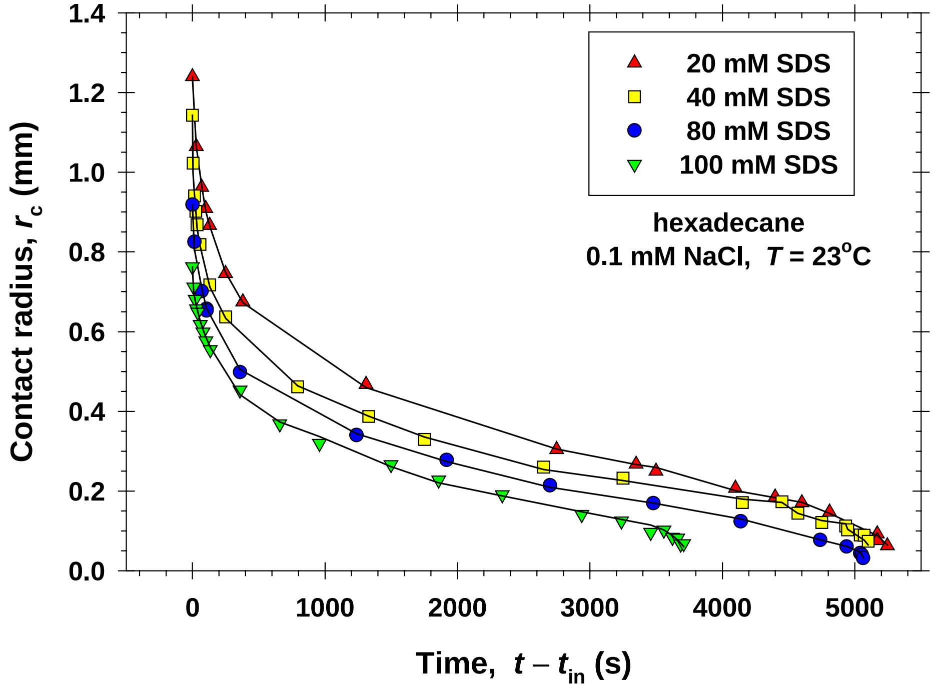




Results from the fit:

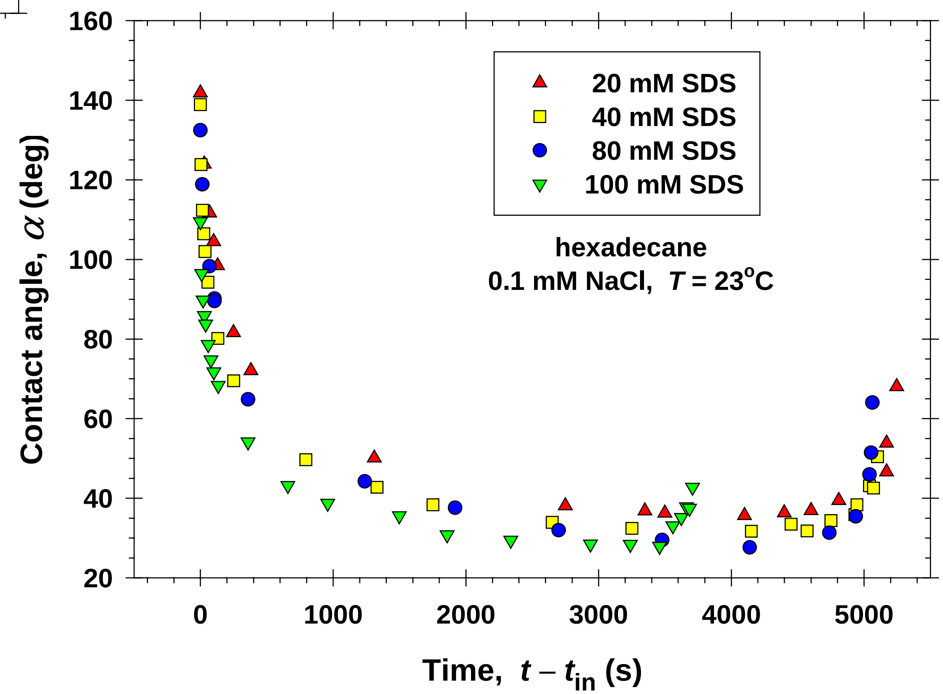
Determination of the contact radius, r_c, and contact angle, α, as functions of time, t.

Effect of SDS concentration on detachment of hexadecane drops from glass:

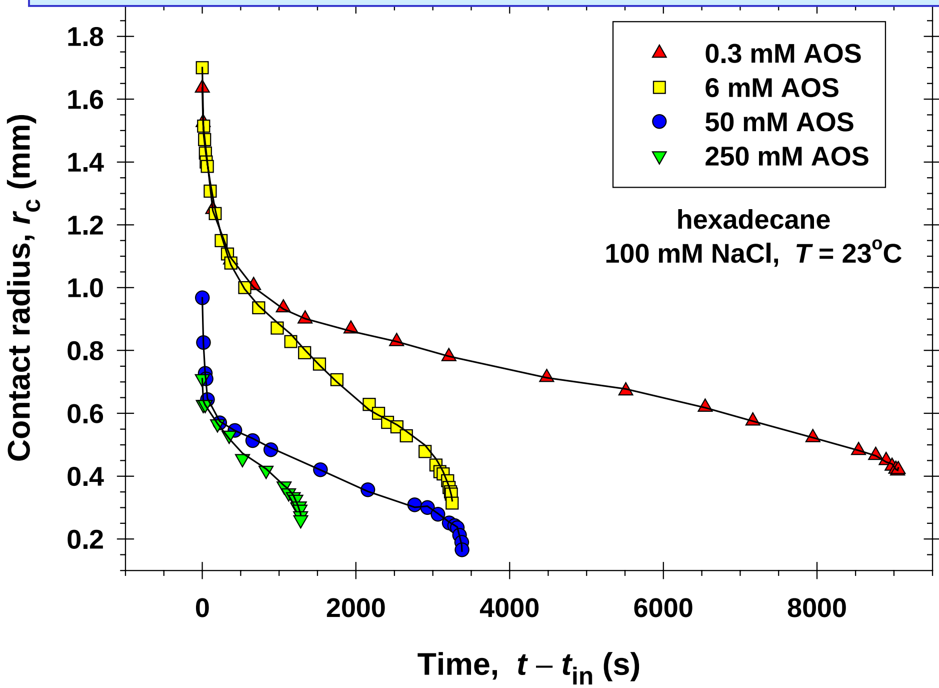


Data for the contact radius, r_c, and for the contact angle, α, plotted vs. time; the initial moment, t_{in}, corresponds to the first experimental point. The NaCl concentration is 0.1 mM and the temperature is 23 °C.

The increase of the SDS (sodium dodecyl sulfate) concentration accelerates the oil-drop detachment.

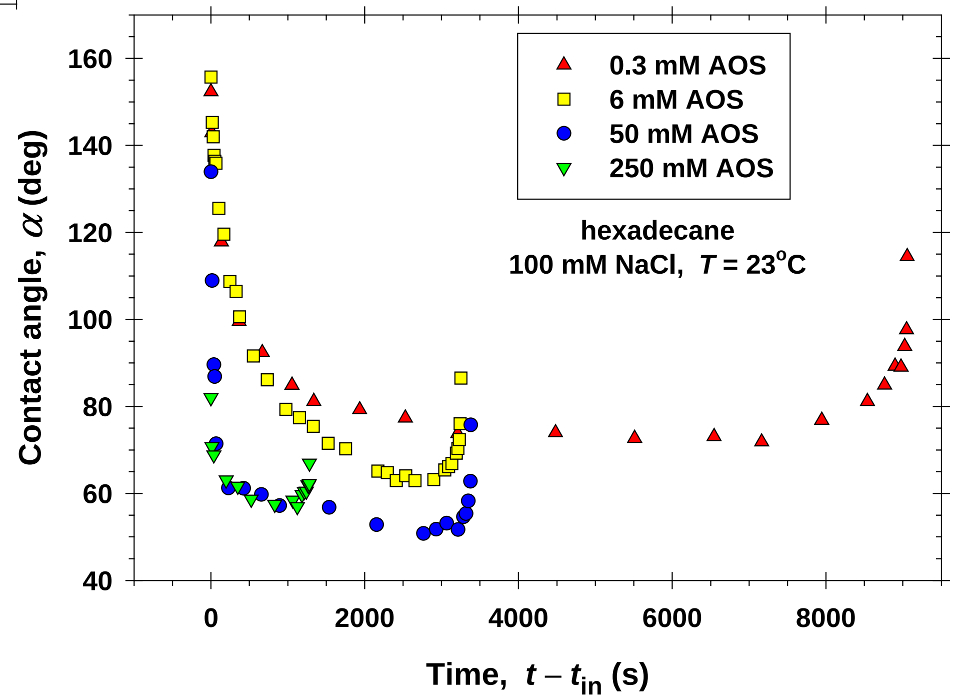


Effect of AOS concentration on detachment of hexadecane drops from glass:

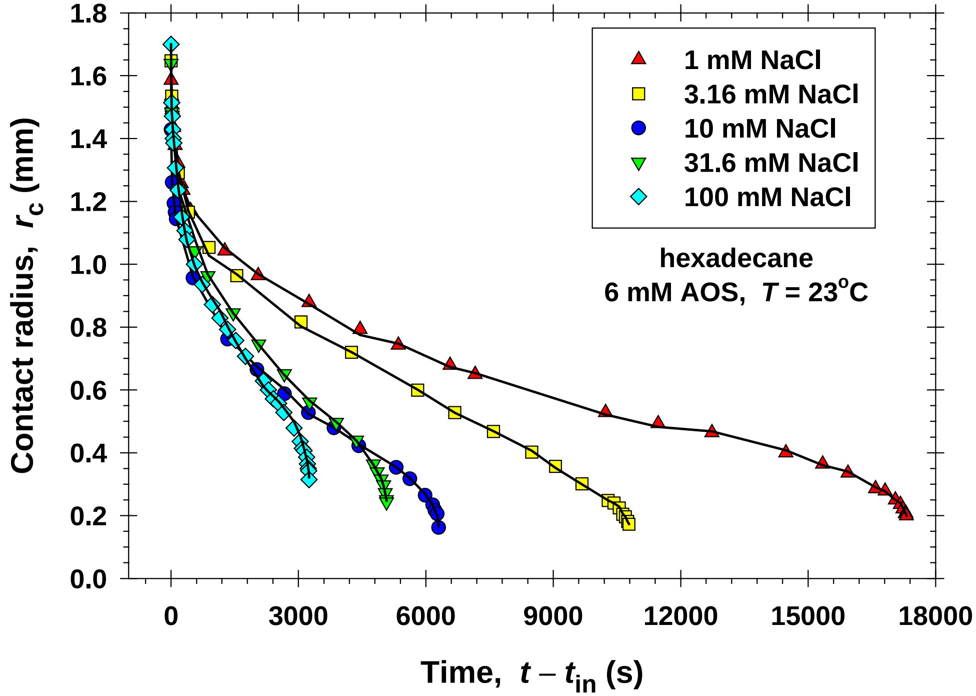


Data for the contact radius, r_c, and for the contact angle, α, plotted vs. time; the initial moment, t_{in}, corresponds to the first experimental point. The NaCl concentration is 100 mM and the temperature is 23 °C.

The increase of the AOS (sodium C_{16} alpha-olefin-sulfonate) concentration accelerates the oil-drop detachment.

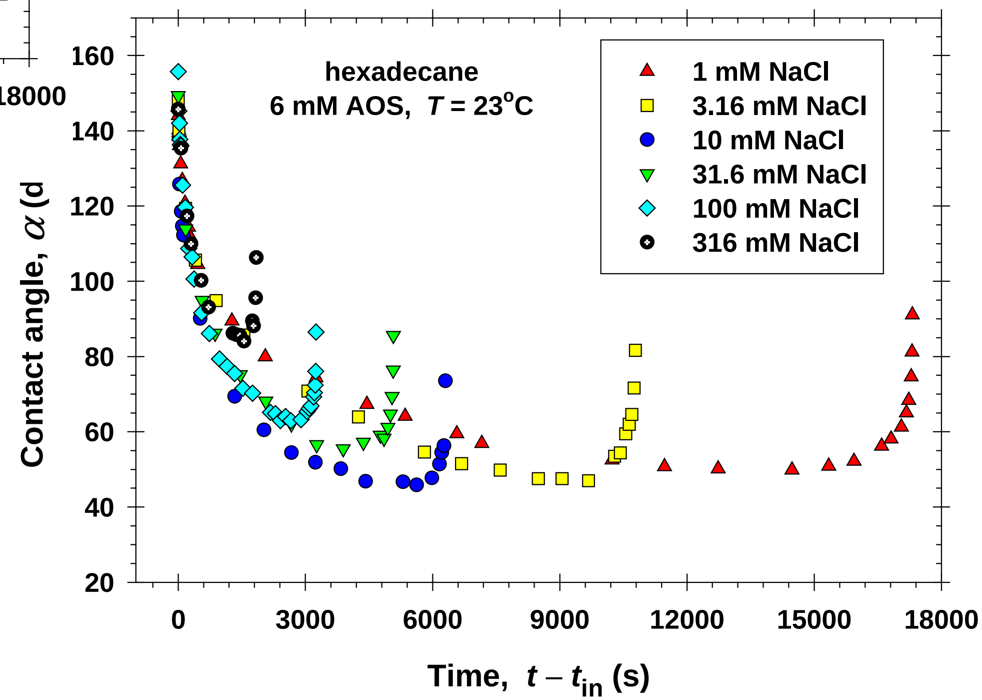


Effect of NaCl concentration on detachment of hexadecane drops from glass:

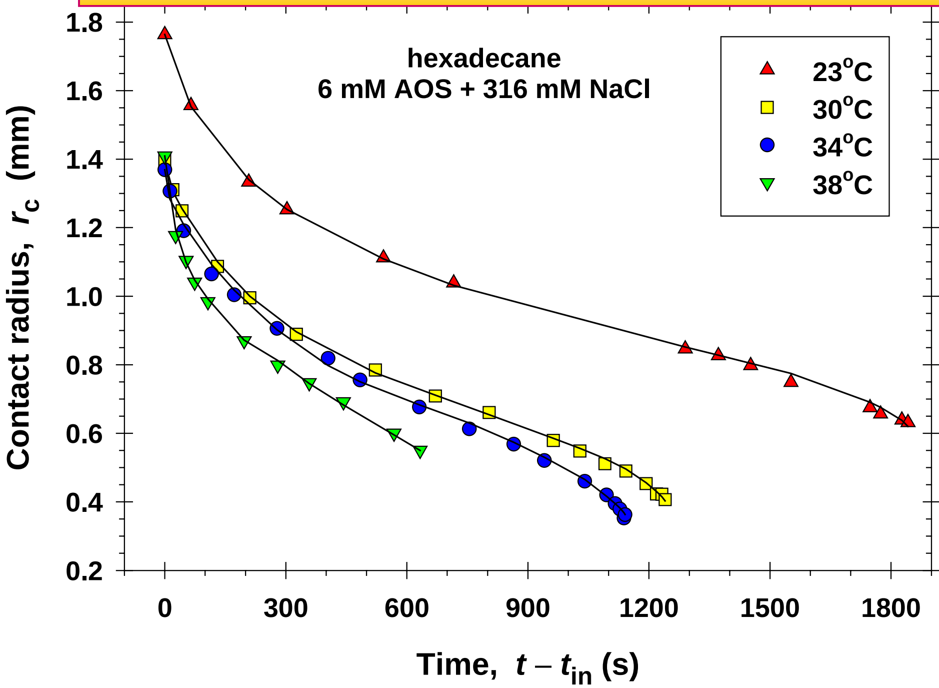


Data for the contact radius, r_c, and for the contact angle, α, plotted vs. time; the initial moment, t_{in}, corresponds to the first experimental point. The AOS concentration is 6 mM and the temperature is 23 °C.

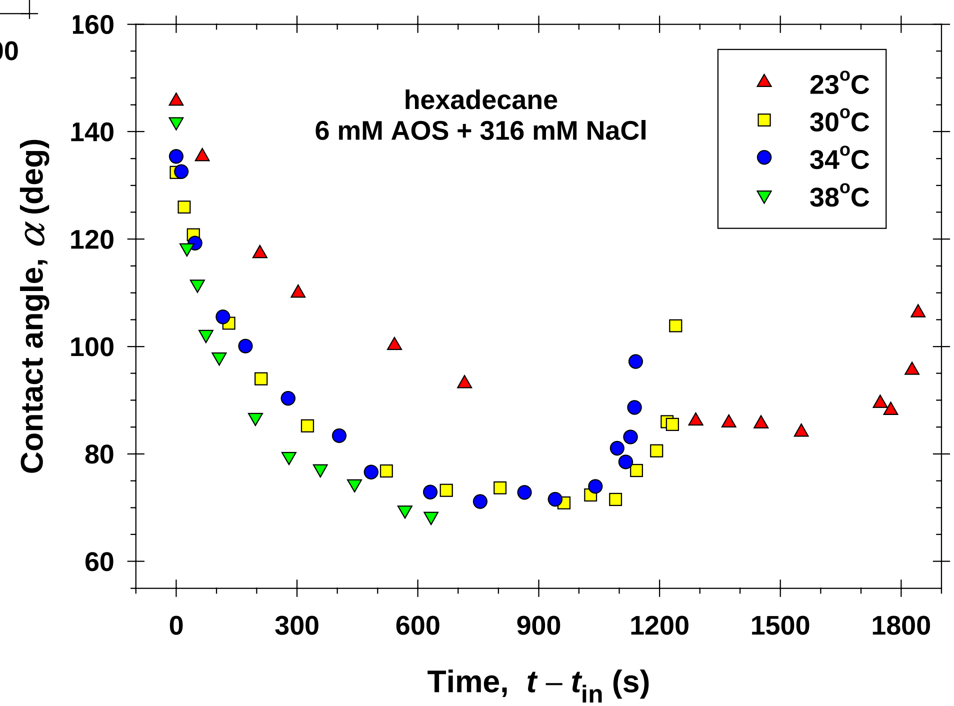
The increase of the NaCl concentration accelerates the oil-drop detachment.



Effect of temperature on detachment of hexadecane drops from glass:

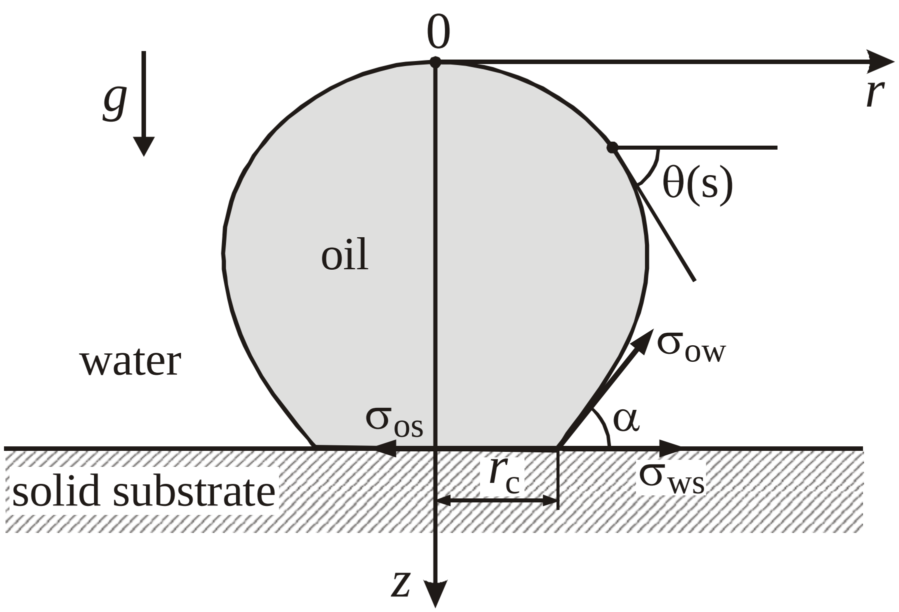


Data for the contact radius, r_c, and for the contact angle, α, plotted vs. time; the initial moment, t_{in}, corresponds to the first experimental point. The AOS concentration is 6 mM and the NaCl concentration is 316 mM.



The increase of the temperature accelerates the oil-drop detachment.

Theoretical Basis



At equilibrium:

the Young equation holds

$$\sigma_{os} = \sigma_{ws} + \sigma_{wo} \cos \alpha_{eq}$$

During relaxation:

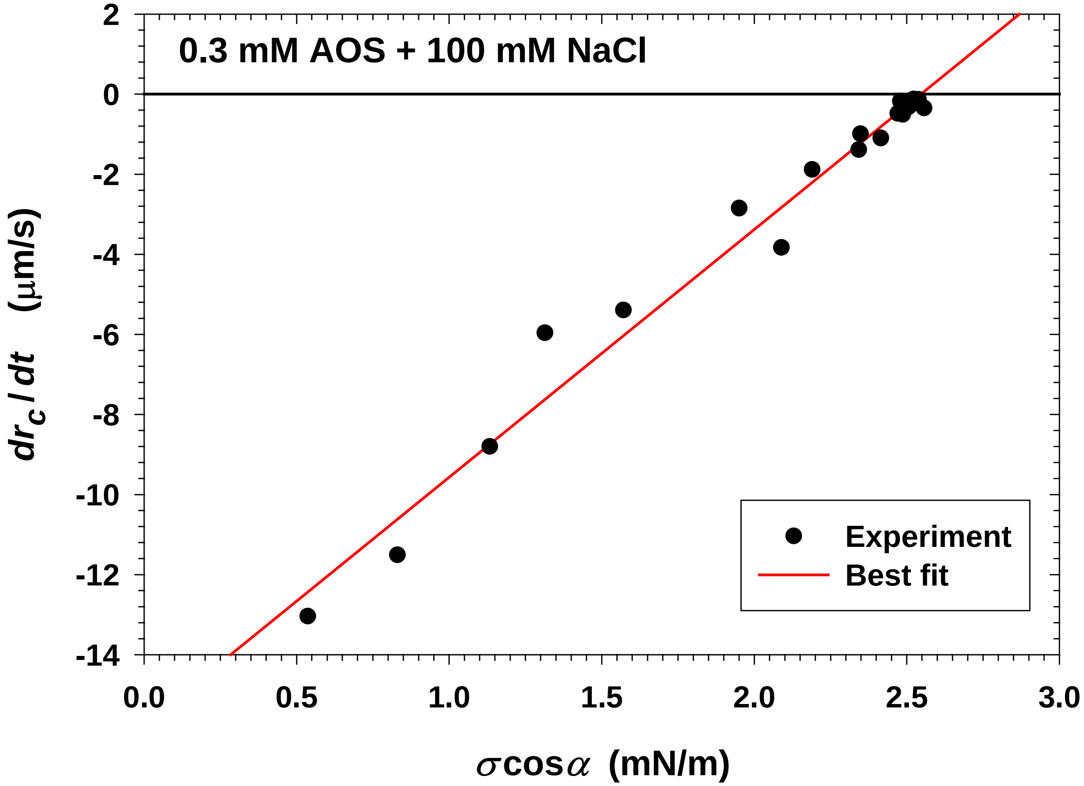
the Young equation contains an additional friction term, which compensates the imbalance of the tree interfacial tensions:

$$\beta \frac{d\, r_c}{d\, t} = \sigma_{ow} \cos \alpha + \sigma_{ws} - \sigma_{os}$$

β is the line friction coefficient

Determination of the Line Friction Coefficient

$$\frac{d r_c}{d t} = \frac{1}{\beta}\left(\sigma_{ow} \cos\alpha + \sigma_{ws} - \sigma_{os}\right)$$



Set of preliminary data:

glass plates cleaned by sulfo-chromic acid

From the slope of the best fit we determine the line friction coefficient:

$$\beta = 1.6 \text{ Pa.s}$$

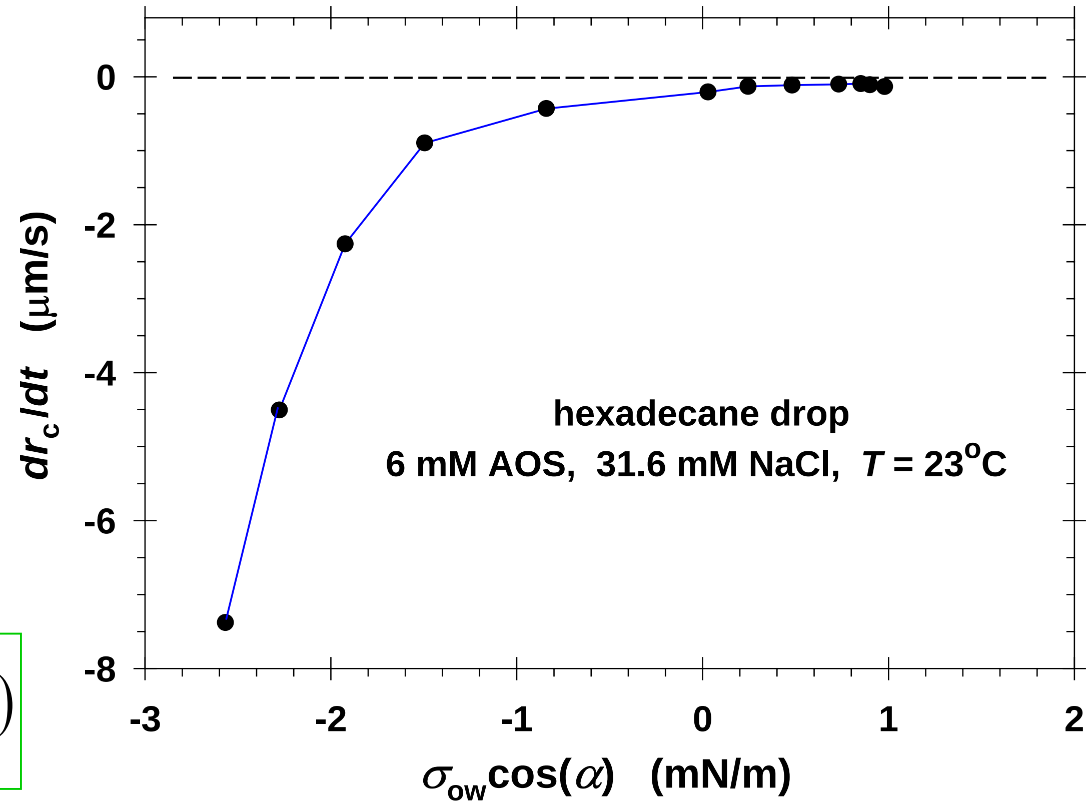
Basic question:

How does β depend on surfactant and salt concentrations and on the temperature?

New Set of Data

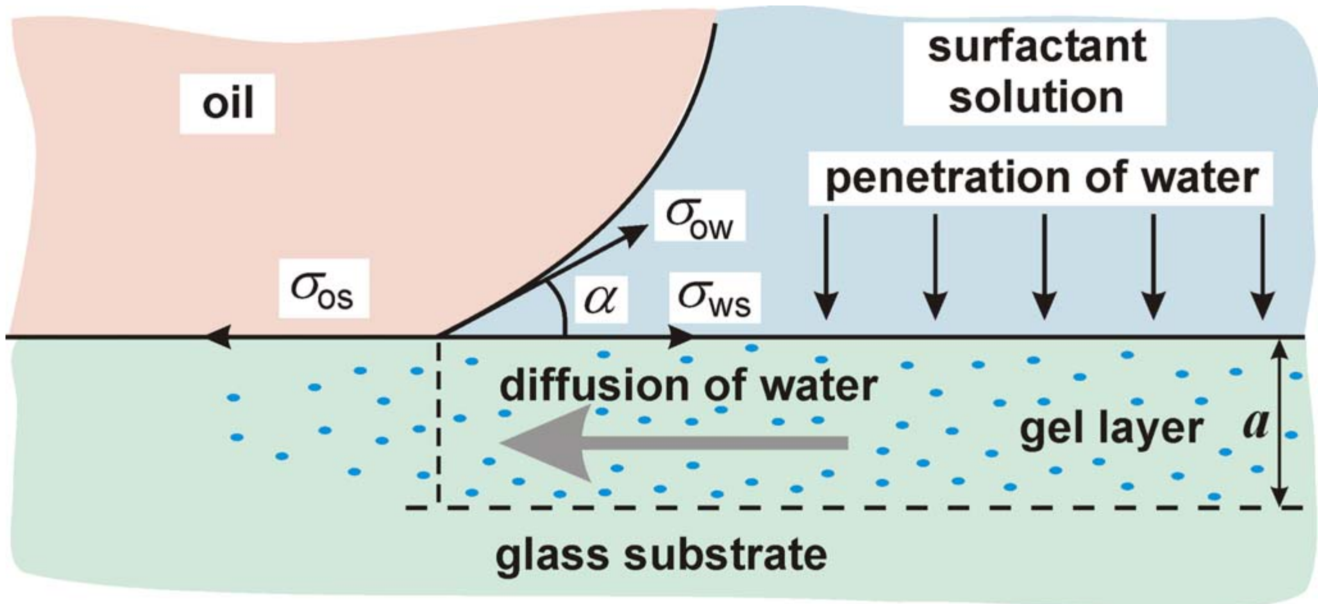
The **glass plates** are used as provided by the producer; **no** cleaning by **sulfo-chromic acid**

$$\frac{d\,r_c}{d\,t} = \frac{1}{\beta}\left(\sigma_{ow}\cos\alpha + \sigma_{ws} - \sigma_{os}\right)$$



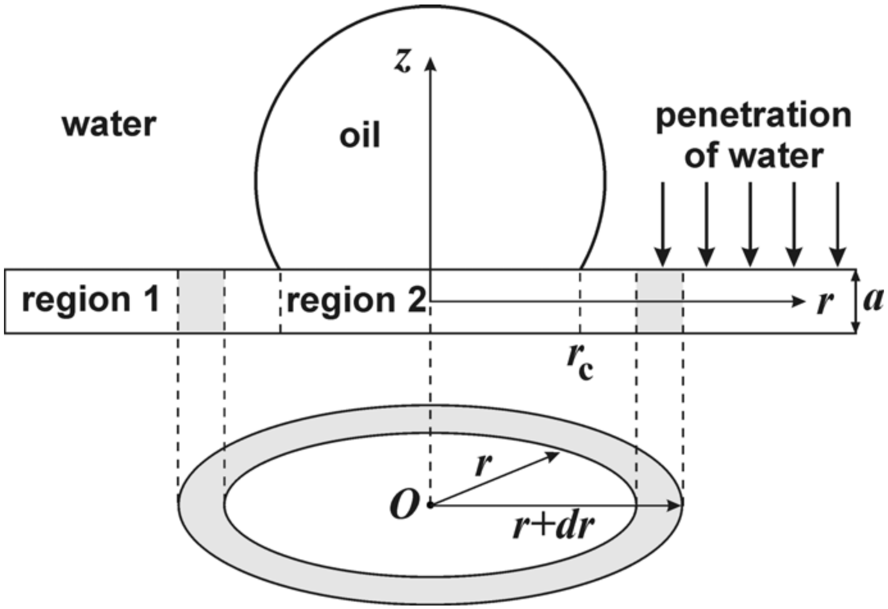
The difference $\sigma_{os} - \sigma_{ws}$ is not constant, but varies with time: Consequence of the formation of a gel layer on the glass surface in contact with water.

<u>Data Interpretation</u>: Diffusion of water into the surface layer of glass and development of a gel layer



Theoretical model is developed, which accounts for the penetration and diffusion of water in the surface of glass, and for the dependence of σ_{os} and σ_{ws} on the concentration of water in the gel layer at the contact line.

Theoretical Model



$$\frac{\partial c_1}{\partial t} = \frac{D}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_1}{\partial r}\right) + \frac{1}{t_p}(c_{eq} - c_1) \qquad (r > r_c)$$

Diffusion equation for region 1 (the last term accounts for the influx from the water phase);
D – diffusivity of water in the gel layer;
c – concentration of water in the gel layer;
t_p – characteristic penetration time.

Diffusion equation for region 2

$$\frac{\partial c_2}{\partial t} = \frac{D}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_2}{\partial r}\right) \qquad (0 < r < r_c)$$

Concentrations and fluxes equal at the boundary region 1 / region 2

Limiting case of fast diffusion:

$$c_b(t) = \frac{c_{eq}}{2}\left[1 - \exp\left(-\frac{t}{t_p}\right)\right]$$

c_b – concentration of water at the boundary between regions 1 and 2 (at $r = r_c$);
c_{eq} – equilibrium value of *c*.

Comparison of Theory and Experiment

We assume a simple Henry law for the interfacial tensions:

$$\sigma_{\rm ws} = \sigma_{\rm ws}(0) - \lambda_{\rm ws} c_{\rm b}$$

$$\sigma_{\rm os} = \sigma_{\rm os}(0) + \lambda_{\rm os} c_{\rm b}$$

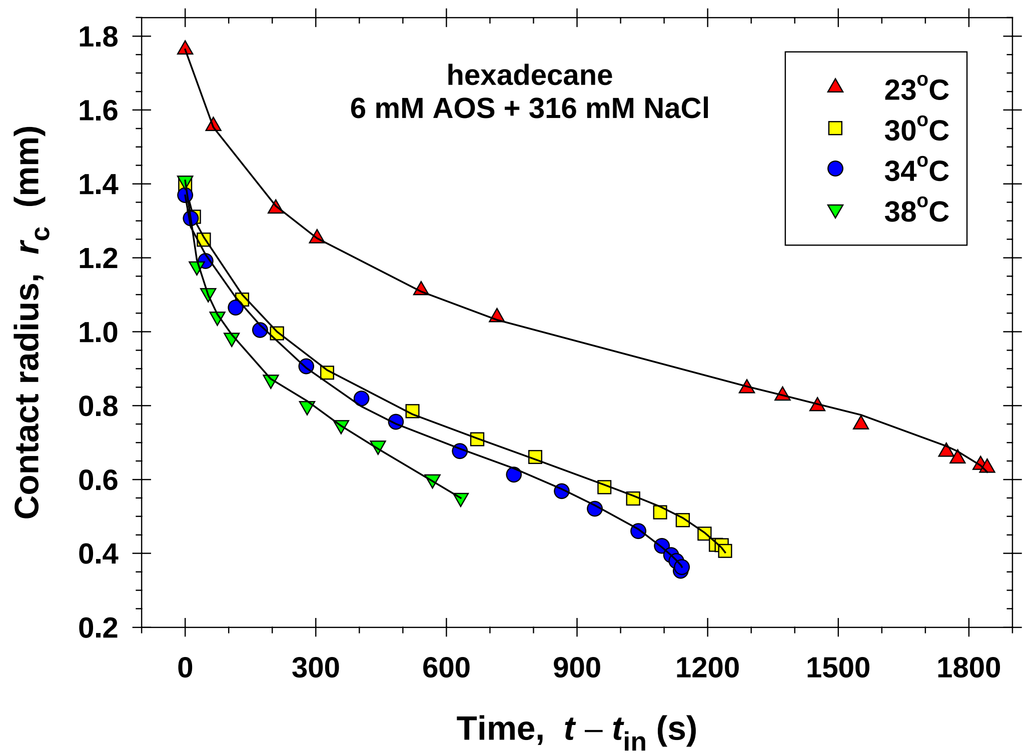
Integrated equation of contact-line motion:

$$r_{\rm c}(t) = r_{\rm c}(0) + \frac{\sigma_{\rm ow}}{\beta}\int_0^t \cos\alpha(\hat{t})\,d\hat{t} - \frac{\Delta\sigma}{\beta}t + \frac{\gamma t_{\rm p}}{\beta}[1-\exp(-\frac{t}{t_{\rm p}})]$$

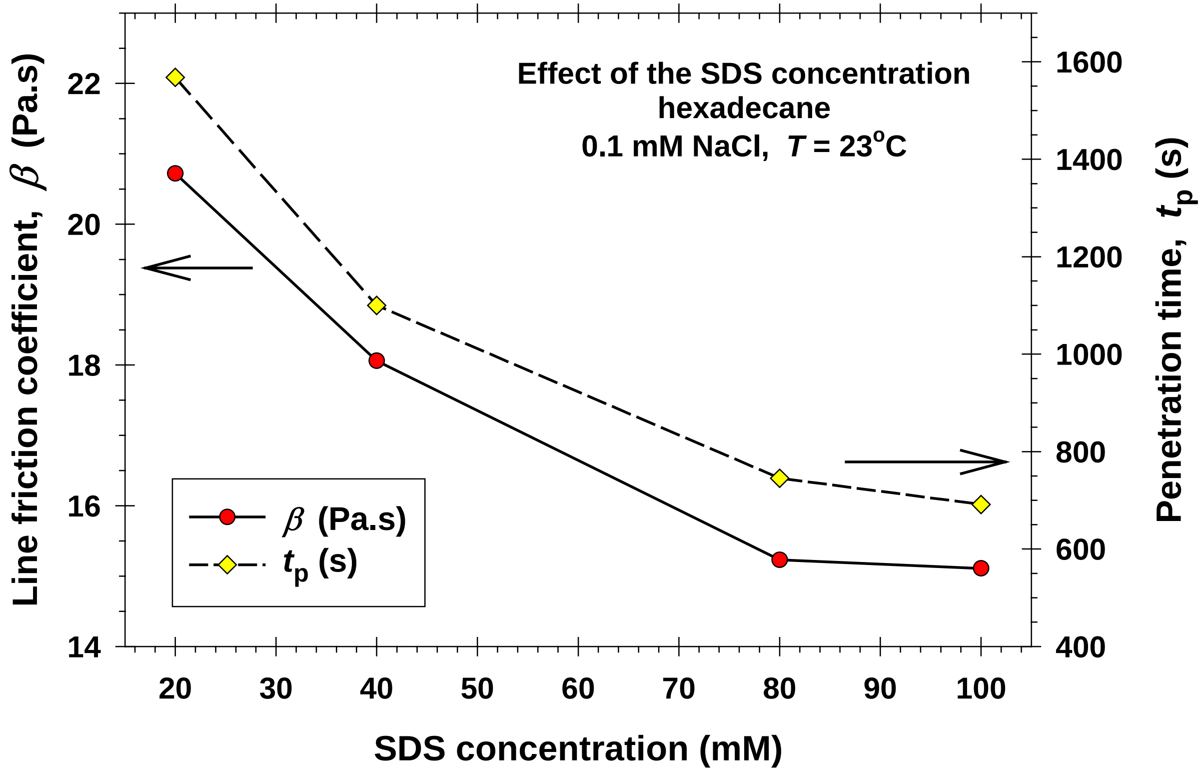
$$\Delta\sigma \equiv \sigma_{\rm os}(c_{\rm eq}/2) - \sigma_{\rm ws}(c_{\rm eq}/2)$$

$\alpha(t)$ is known from the experiment; adjustable parameters: β, $\Delta\sigma$, $t_{\rm p}$ and $t_{\rm in}$.

Excellent agreement between theory and experiment is obtained!



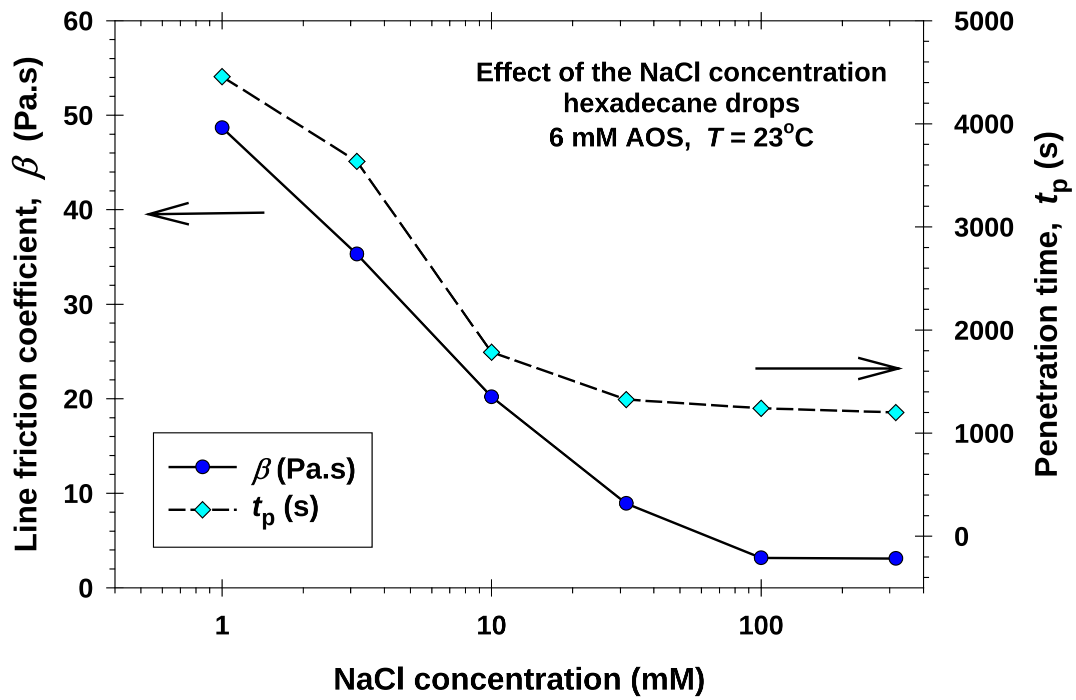
Effect of Surfactant on Line Friction Coefficient and Penetration Time

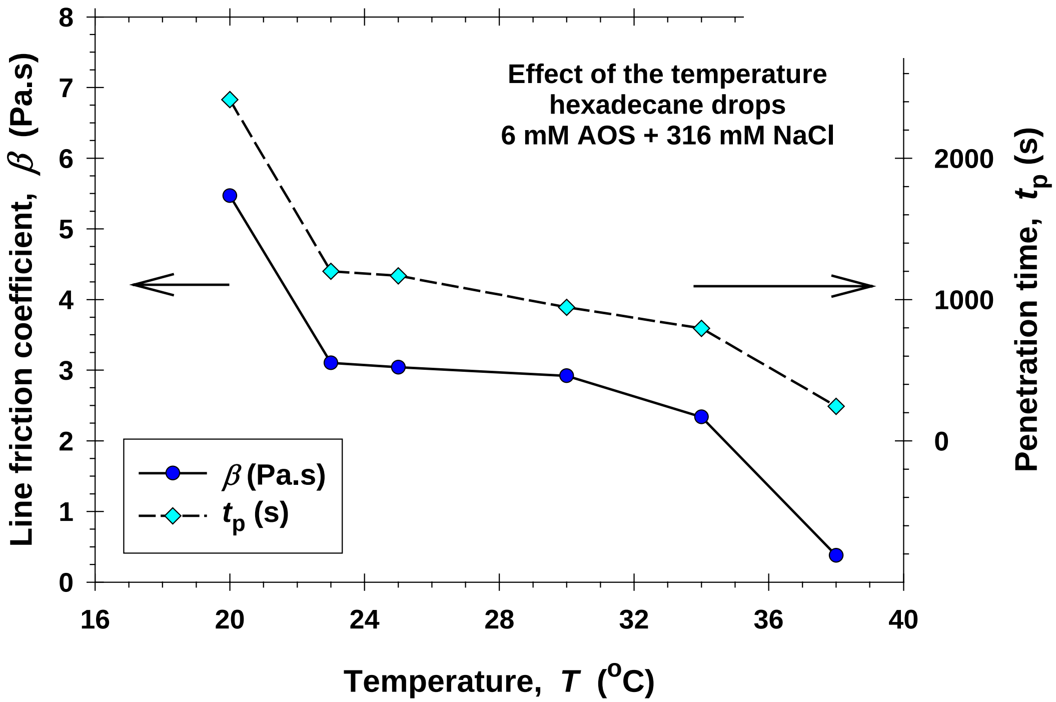


The detected effect of surfactant on β and t_p is most probably related to its role for hydrophilization and/or removal of the hydrophobic coverage (gloss) of the glass surface.

Effects of Salt and Temperature

The salt facilitates the surfactant adsorption.





The temperature is known to reduce the viscous effects and accelerate the diffusion processes.

Conclusions

1. The increase of temperature, surfactant and salt concentrations accelerate the oil-drop detachment.

2. The spontaneous drop detachment is due to penetration of water in a thin (gel) layer at the surface of glass.

3. The data are excellently fitted by the dynamic Young equation, and the line friction coefficient, β, is determined.