The Four Kinetic Regimes of Adsorption from Micellar Surfactant Solutions

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Effect of *micelle diffusion and disassembly* on the dynamic surface tension
(1) The interfacial expansion gives rise to surfactant adsorption and to decrease in the monomer concentration near the interface;
(2) This leads to micelle decomposition and to diffusion of micelles.

\[
\begin{align*}
\{\text{Fast micellar process}\} &= \{\text{Exchange of monomers between the micelles}\} \\
&= (\text{Rate constant } k_m) \\
\{\text{Slow micellar process}\} &= \{\text{Decomposition of a “critical-size micelle” to monomers}\} \\
&= (\text{Rate constant } k_S)
\end{align*}
\]
Multi-Step Micellization:

\[ A_1 + A_{s-1} \leftrightarrow A_s \quad (s = 2, 3, 4, \ldots) \]

\[ \frac{d c_1}{d t} + \nabla \cdot I_1 = -2J_2 - \sum_{s=3}^{\infty} J_s \]

\[ \frac{d c_s}{d t} + \nabla \cdot I_s = J_s - J_{s+1} \quad (s = 2, 3, 4, \ldots) \]

Diffusion and Reaction Fluxes:

\[ I_s = -D_s \nabla c_s \quad (s = 1, 2, 3, \ldots) \]

\[ J_s \equiv k_s^+ c_1 c_{s-1} - k_s^- c_s \quad (s = 2, 3, 4, \ldots) \]

The process is theoretically described by a system containing tens of kinetic equations, which is inconvenient for applications. For this reason, one of the basic problems of micellar kinetics is how to simplify the general set of equations without losing the adequacy and correctness of the theoretical description.
Introduction of a Model (Gaussian) Micelle Size Distribution

\[ c_s = \frac{C_m}{\sqrt{2\pi} \sigma} \exp\left[-\frac{(s - m)^2}{2\sigma^2}\right] \quad (s \geq n_r) \]

\[ C_m = \sum_{s \geq n_r} c_s \]

\[ m = \frac{1}{C_m} \sum_{s \geq n_r} sc_s \]

\[ \sigma^2 = \frac{1}{C_m} \sum_{s \geq n_r} (s^2 - m^2)c_s \]

(i) Region of the monomers and oligomers, \( \Omega_o \) \((1 \leq s \leq n_o)\)

(ii) Region of the rare aggregates, \( \Omega_r \) \((n_o < s < n_r)\)

(iii) Region of the abundant micelles, \( \Omega_m \) \((s \geq n_r)\)

New: (1) We do not assume \( \sigma = \text{const.} \)

(2) We do not use of the quasi-equilibrium approximation: local chemical equilibrium between micelles and monomers.

(3) The derived general equations are nonlinear: applicable to both large and small perturbations.
Reduction of the Problem to 4 Equations for 4 Unknown Functions

Monomer concentr.; Total micelle conc.; Mean aggreg. number; Polydispersity

\[ c_1(r,t), \quad C_m(r,t), \quad m(r,t), \quad \sigma(r,t) \]

\[ \frac{dc_1}{dt} + \nabla \cdot \mathbf{I}_1 = -n_r J - J_{m,0} \]

\[ \frac{dC_m}{dt} + \nabla \cdot \mathbf{I}_{m,0} = J \]

\[ \frac{d}{dt}(mC_m) + \nabla \cdot \mathbf{I}_{m,1} = n_r J + J_{m,0} \]

\[ \frac{d}{dt}[(m^2 + \sigma^2)C_m] + \nabla \cdot \mathbf{I}_{m,2} = n_r^2 J - J_{m,0} + 2J_{m,1} \]

Nonlinear expressions for the fluxes \(J, J_{m,0},\) and \(J_{m,1}\) are derived.

\[ J \equiv J_{n_r}, \quad J_{m,i} \equiv \sum_{s > n_r} s^i J_s \quad (i = 0, 1) \]

\[ \mathbf{I}_{m,i} \equiv \sum_{s \geq n_r} s^i \mathbf{I}_s \quad (i = 0, 1, 2) \]
Relaxation of a Spatially Uniform Perturbation

(C – jump;  
T – jump;  
P – jump:  bulk relaxation methods)

Our purpose is to see what are the predictions of the model for this type of perturbations.

Dimensionless perturb. in: Total mic. conc.;  Mean aggreg. number;  Polydispersity

### Linearization of the problem:
System of three linear equations for \( \xi_c, \xi_m, \) and \( \xi_\sigma \)

\[
\xi_c \equiv \frac{C_{m,p}}{C_{m,eq}}; \quad \xi_m \equiv \frac{m_p}{m_{eq}}; \quad \xi_\sigma \equiv \frac{\sigma_p}{\sigma_{eq}}
\]

A homogeneous system has a nontrivial solution only if its determinant is equal to zero
⇒ characteristic equation

\( l_1, l_2, l_3 \) – invariants of the matrix \( (a_{ij}) \);
three eigenvalues ⇒ three relaxation times:

\[
\tau_c, \quad \tau_m, \quad \tau_\sigma.
\]

\[
\sum_{j=c,m,\sigma} (a_{ij} - \lambda \delta_{ij}) \xi_j = 0, \quad i = c, m, \sigma
\]

\[
\lambda^3 - I_1 \lambda^2 + I_2 \lambda - I_3 = 0
\]

\[
\lambda_j \equiv -\frac{1}{\tau_j} \equiv -\frac{1}{k_m t_j}; \quad j = c, m, \sigma
\]
The Three Micellar Characteristic Relaxation Times

\[ \lambda_j \equiv -\frac{1}{\tau_j} \equiv -\frac{1}{k_m t_j} ; \quad j = c, m, \sigma \]

\[ \beta \equiv \frac{C_{\text{tot}} - \text{CMC}}{\text{CMC}} \]

Dimensionless micelle concentration

\[ \frac{1}{t_c} \approx k_S \frac{m_{\text{eq}}}{\beta} \left( 1 + \frac{m_{\text{eq}} \beta}{1 + \sigma_{\text{eq}}^2 \beta / m_{\text{eq}}} \right) \]

\( t_c \) is the characteristic time of the slow process, that is the relaxation of the total micellar concentration \( C_m \);

\( k_S \) – rate constant of the slow process (Aniansson-Wall)

\[ \frac{1}{t_m} \approx k_m \frac{m_{\text{eq}} + \beta \sigma_{\text{eq}}^2}{m_{\text{eq}} \sigma_{\text{eq}}^2} \]

\( t_m \) is the first characteristic time of the fast process, related to the relaxation of the mean micellar aggregation number, \( m \);

\( k_m \) – rate constant of the fast process (Aniansson-Wall)

\[ \frac{1}{t_\sigma} \approx k_m \frac{2}{\sigma_{\text{eq}}^2} \]

\( t_\sigma \) is the second characteristic time of the fast process, related to the relaxation of the micellar polydispersity, \( \sigma \); (new!)

\( k_m \) – rate constant of the fast process.

The expressions for \( t_c \) and \( t_m \) by Aniansson & Wall are confirmed!
Numerical Results for **Typical** Parameter Values:

\[ m_{eq} = 60; \quad \sigma_{eq} = 5; \quad k_s / k_m = 10^{-7} \]

<table>
<thead>
<tr>
<th>Dimensionless relax. time</th>
<th>Exact</th>
<th>Approximate expressions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low micelle concentration:</strong> ( \beta = 1 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \tau_c )</td>
<td>( 4.12 \times 10^3 )</td>
<td>( 4.11 \times 10^3 )</td>
</tr>
<tr>
<td>( \tau_m )</td>
<td>( 1.87 \times 10^1 )</td>
<td>( 1.87 \times 10^1 )</td>
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<tr>
<td>( \tau_\sigma )</td>
<td>( 1.21 \times 10^1 )</td>
<td>( 1.21 \times 10^1 )</td>
</tr>
<tr>
<td><strong>High micelle concentration:</strong> ( \beta = 100 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \tau_c )</td>
<td>( 1.18 \times 10^5 )</td>
<td>( 1.18 \times 10^5 )</td>
</tr>
<tr>
<td>( \tau_m )</td>
<td>( 6.43 \times 10^{-1} )</td>
<td>( 6.43 \times 10^{-1} )</td>
</tr>
<tr>
<td>( \tau_\sigma )</td>
<td>( 1.25 \times 10^1 )</td>
<td>( 1.25 \times 10^1 )</td>
</tr>
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</table>

\( \tau_c \) – relaxation time of *micelle concentration* (of the **slow** process, Anianssson & Wall)

\( \tau_m \) – relaxation time of *mean aggreg. number* (of the **fast** process, Anianssson & Wall)

\( \tau_\sigma \) – relaxation time of *micelle polydispersity* (**new** effect, predicted by present theory)

**Dimensionless micelle concentration:**

\[ \beta \equiv \frac{C_{tot} - CMC}{CMC} \]

**Low micelle concentrations:**

\[ \tau_c > \tau_m > \tau_\sigma \]

**High micelle concentrations:**

\[ \tau_c > \tau_\sigma > \tau_m \]
The Relaxation of a Perturbation in Micelle Concentration, $C_m$, is Governed only by the Slow Micellar Time, $t_c$.

\[
\xi_c(t) \approx A_c \exp\left(-t/t_c\right) \quad (t_c \gg t_m, t_\sigma)
\]

($A_c$ – amplitude of the perturbation in $C_m$)

Hence, if the relaxation of micelle concentration is measured, only the Slow Micellar Time, $t_c$, could be determined.

Note, however, that a perturbation in $C_m$ perturbs also $m$ and $\sigma$!
The Relaxation of a Perturbation in Micelle Mean Aggregation Number is Governed by both the Slow and Fast Times, $t_c$ and $t_m$

\[ \xi_m(t) \approx -A_c \frac{\tau_m \beta}{m_{eq}} \exp(-t/t_c) + (A_m + A_c \frac{\tau_m \beta}{m_{eq}}) \exp(-t/t_m) \]

($A_c$ and $A_m$ – amplitudes of the perturbation in $C_m$ and $m$)

Hence, if the relaxation of micelle mean aggregation number is measured, then both the slow and fast micellar times, $t_c$ and $t_m$, could be determined.

Note that a perturbation in $m$ perturbs $\sigma$, but does not affect $C_m$. 

The Relaxation of a Perturbation in Micelle Polydispersity is Governed by the two Fast Relaxation Times, $t_m$ and $t_\sigma$

$$\xi_\sigma(t) \approx A_\sigma \exp\left(-\frac{t}{t_\sigma}\right)$$

$$+ \left(A_m + A_c \frac{\tau_m \beta}{m_{eq}}\right) \frac{m_{eq}}{2\sigma_{eq}^2} \frac{t_\sigma}{t_m - t_\sigma} \left[\exp\left(-\frac{t}{t_m}\right) - \exp\left(-\frac{t}{t_\sigma}\right)\right]$$

Hence, if the relaxation of micelle polydispersity is measured, then the two fast micellar times, $t_m$ and $t_\sigma$, could be determined.

Note that a perturbation in polydispersity $\sigma$ does not affect $C_m$ and $m$. 
The theoretical analysis implies:

(A) The relaxation of the three basic parameters, the micelle concentration, $C_m$, the mean aggregation number, $m$, and the polydispersity, $\sigma$, are characterized by three distinct relaxation times: $t_c$, $t_m$, and $t_\sigma$.

(B) The first two of them, $t_c$ and $t_m$, coincide with the conventional slow and fast micellar relaxation times.

(C) The third relaxation time, $t_\sigma$, is close to $t_m$ for low micelle concentrations, but at high micelle concentrations we have $t_c > t_\sigma > t_m$. 
(D) The relaxation of $C_m$ is affected by $t_c$ alone.

(E) The relaxation of $m$ is affected by both $t_m$ and $t_c$.

(F) The relaxation of $\sigma$ is affected by $t_\sigma$ and $t_m$.

Simple, but accurate analytical expressions are available:

(1) For calculation of the three relaxation times;

(2) For describing the evolution of a micellar system.


**Next step:** Investigation of the problem about the kinetics of adsorption from micellar solutions, and the respective dynamic surface tension (Part 2).
Part 2: Theoretical modeling of adsorption from micellar solutions at quiescent and expanding surfaces

Main questions to be answered:

• Why in different cases different kinetic regimes are observed?
  
  (a) diffusion – limited kinetics: \[ \Delta \sigma \propto t^{-1/2} \];
  
  (b) reaction – limited kinetics: \[ \Delta \sigma \propto \exp\left( -\frac{t}{\tau} \right) \].

• Which of the two very different theoretical expressions for the effective diffusivity of a micellar solution is correct?
  
  (a) by J. Lucassen (1975): \[ D_{\text{eff}} = D_1(1 + \beta m_{\text{eq}})(1 + \beta m_{\text{eq}}D_m/D_1) \]
  
  (b) by Paul Joos (1988): \[ D_{\text{eff}} = D_1(1 + \beta)(1 + \beta D_m/D_1) \]
Parameters of the Adsorption Process

\[ \zeta \equiv \frac{1}{h_a} z; \quad \tau \equiv \frac{D_1 t}{h_a^2}; \]

\[ K_s \equiv \frac{h_a^2}{D_1} k_s^-; \quad K_m \equiv \frac{h_a^2}{D_1} k_m^- \]

\[ h_a \equiv \left( \frac{\partial \Gamma}{\partial c_1} \right)_{eq} \]

(adsorption length)

\( \zeta \) – dimensionless distance; \( \tau \) – dimensionless time; \( D_1 \) – diffusivity of the monomers; \( k_s \) – rate constant of the slow micellar process; \( k_m \) – rate constant of the fast process.
Dimensionless Perturbations

\[ c_s = \frac{C_m}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(s - m)^2}{2\sigma^2}\right] \quad (s \geq n_r) \]

\[ \xi_1 \equiv \frac{h_a}{\Gamma_p(0)} c_{1,p} ; \quad \xi_c \equiv \frac{h_a}{\beta \Gamma_p(0)} C_{m,p} ; \quad \xi_m \equiv \frac{h_a c_{1,eq}}{\sigma_{eq}^2 \Gamma_p(0)} m_p ; \quad \xi_\sigma \equiv \frac{h_a c_{1,eq}}{\sigma_{eq} \Gamma_p(0)} \sigma_p \]

\( \xi_1 \) – dimensionless perturbation in the concentration of monomers, \( c_1 \);
\( \xi_c \) – dimensionless perturbation in the micelle concentration, \( C_m \);
\( \xi_m \) – dimensionless perturbation in the micelle mean aggregation number, \( m \);
\( \xi_\sigma \) – dimensionless perturbation in the micelle polydispersity, \( \sigma \).
General System of Kinetic Equations (from Part 1)

\[
\frac{\partial \xi_1}{\partial \tau} = \frac{\partial^2 \xi_1}{\partial \zeta^2} - \left( m_{eq} - w \sigma_{eq} \right) \frac{K_s}{S} \phi_s - \frac{\beta K_m}{m_{eq} S} \phi_m \quad \text{(surfactant monomers)}
\]

\[
\frac{\partial \xi_c}{\partial \tau} = B_m \frac{\partial^2 \xi_c}{\partial \zeta^2} + \frac{K_s}{\beta} \phi_s \quad \text{(concentration of micelles)} \quad \beta = (C_{tot} - \text{CMC}) / \text{CMC}
\]

\[
\frac{\partial \xi_m}{\partial \tau} = B_m \frac{\partial^2 \xi_m}{\partial \zeta^2} - K_s \frac{w m_{eq}}{\beta \sigma_{eq}} \phi_s + \frac{K_m}{\sigma_{eq}^2} \phi_m \quad \text{(micelle mean aggregation number)}
\]

\[
\frac{\partial \xi_\sigma}{\partial \tau} = B_m \frac{\partial^2 \xi_\sigma}{\partial \zeta^2} + K_s \left( w^2 - 1 \right) \frac{m_{eq}}{2 \beta} \phi_s - \frac{K_m}{2 \sigma_{eq}^2} \phi_m - \frac{2 K_m}{\sigma_{eq}^2} \xi_\sigma \quad \text{(polydispersity)}
\]

\[
B_m = \frac{D_m}{D_1}
\]

\( \phi_s \) – dimensionless reaction flux of the slow relaxation process;

\( \phi_m \) – dimensionless reaction flux of the fast relaxation process.
Reaction fluxes from the **slow** and **fast** relaxation processes

\[ \varphi_m \approx \xi_1 - \xi_m \]

For \( \xi_1 = \xi_m \), we obtain \( \varphi_m = 0 \)

*(criterion for equilibrium with respect to the fast micellization process)*

\[ \varphi_s \approx (m_{eq} - w \sigma_{eq})\xi_1 - m_{eq} \xi_c + \sigma_{eq} w \xi_m \]

For \( \xi_1 = \xi_c = \xi_m \), we obtain \( \varphi_s = 0 \)

*(criterion for equilibrium with respect to the slow micellization process)*

**Method of solution** of the general system of **linear partial differential equations**: Laplace transform, solving the equations, and **numerical** reverse Laplace transform
Numerical Results: Typical Relaxation Curves

(Four kinetic regimes of adsorption: AB, BC, CD, and DE)

\[
\frac{\gamma(t) - \gamma_{eq}}{\gamma(0) - \gamma_{eq}} = \xi_{1,0}(\tau)
\]

⇒ \( \xi_{1,0} \) describes the relaxation of the surface tension \( \gamma(t) \).

Four different relaxation regimes: AB, BC, CD, DE

(B) \( \xi_1 = \xi_m \), then \( \varphi_m = 0 \) ⇒ equilibrated fast micellar process;

(D) \( \xi_1 = \xi_c = \xi_m \) ⇒ \( \varphi_s = \varphi_m = 0 \) ⇒ equilibrated fast and slow micellar processes.
Analytical Expressions for the Relaxation in Different Regimes

Two exponential regimes (AB and CD) with relaxation times $\tau_F$ and $\tau_C$;

Two inverse-square-root regimes (BC & DE) with relaxation times $\tau_{BC}$ and $\tau_{DE}$.

$$\frac{1}{\tau_F} = \frac{1}{\theta_m} - \frac{1}{2\theta_\sigma}$$

$\tau_C = \theta_c$

$\theta_c$ – dimensionless relaxation time of the slow process;
$\theta_m$ and $\theta_\sigma$ – dm.less relaxation time of the fast process.
The regime AB(exp) was observed by P. Joos for Triton X-100, inclined plate method. (Depending on the surfactant and experiment. method, different regimes are observed!)

\[ \tau_F \equiv \frac{m_{cq}}{\beta K_m} = \frac{1}{\theta_m} - \frac{1}{2\theta_\sigma}, \quad s_F \equiv (1 + \frac{4}{\tau_F})^{1/2} \]

\[ \dot{\xi}_{1,0} = \frac{s_F - 1}{s_F} \exp\left(-\frac{s_F - 1}{2}\tau\right) + \frac{2}{\pi} \int_0^\infty \exp\left[-\left(\frac{\tau}{\tau_F} + \tau^2\right)\right] \frac{\tau^2}{(\tau^2 + 1/\tau_F)^2 + \tau^2} d\tau \]

\[ \dot{\xi}_{1,0} = 1 - 2\left(\frac{\tau}{\pi}\right)^{1/2} + \tau + \ldots \quad \text{(short – time asymptotics)} \]

\[ \dot{\xi}_{1,0} = \frac{s_F - 1}{s_F} \exp\left(-\frac{s_F - 1}{2}\tau\right) + \ldots \quad \text{(long – time asymptotics)} \]

\[ \frac{s_F - 1}{2} \approx \frac{1}{\tau_F} \]
The regime BC was observed by us for SDS with the maximum bubble pressure method (MBPM), and by Makievski et al. for Triton X-100, MBPM again. For $\sigma_{eq}^2/m_{eq} \approx 1$, the expression for $D_{BC}$ reduces to that proposed by Joos (1988).
The slow micellar process governs the adsorption kinetics

\[ [\exp(t/\tau_s)] \]

\[
\frac{\gamma(t) - \gamma_{eq}}{\gamma(0) - \gamma_{eq}} = \xi_{1,0}(\tau)
\]

\[
\xi_{1,0} = \left(\frac{\tau_{BC}}{\pi \tau}\right)^{1/2} \exp\left(-\frac{\tau}{\tau_C}\right)
\]

(exponential relaxation)

\[
\tau_C \equiv \theta_C \approx \frac{\beta \sigma_{eq}^2}{m_{eq}^3 K_s}
\]

(the relaxation time, \( \tau_C \), coincides with the characteristic time of the slow micellar process)
The Lucassen equation was unsuccessfully tried by Joos et al. to fit data for Brij 58 (strip method). It turns out that the data by Joos et al. (1988) correspond to the regime BC, which has not been identified at that time.

**Diffusion control** – both the fast and slow micellar processes are equilibrated $[t^{-1/2}]$
Combined Expression for the whole BCDE region

Analyzing the basic system of equations we arrived at the following combined formula for the whole region BCDE:

\[
\xi_{1,0} = \left(\frac{\tau_{DE}}{\pi \tau}\right)^{1/2} + \left(\frac{\tau_{BC}}{\pi \tau}\right)^{1/2} \exp\left(-\frac{\tau}{\tau_C}\right)
\]

\[
\frac{1}{\tau_{DE}} = \left(1 + \beta \frac{\sigma^2_{eq} + m^2_{eq}}{m_{eq}}\right)\left(1 + \beta \frac{\sigma^2_{eq} + m^2_{eq}}{m_{eq}} \frac{D_m}{D_1}\right)
\]

\[
\frac{1}{\tau_{BC}} = \left(1 + \frac{\beta \sigma^2_{eq}}{m_{eq}}\right)\left(1 + \frac{\beta \sigma^2_{eq}}{m_{eq}} \frac{D_m}{D_1}\right)
\]

\[m^2_{eq} / \sigma^2_{eq} \approx 100 >> 1 \Rightarrow \tau_{DE} << \tau_{BC}\]

(easy to distinguish regime BC from DE)

Difference between the exponential regimes AB and CD

1/\(\tau_F\) increases with micelle concentration;  
1/\(\tau_C\) decreases with micelle concentration

Exponential regime AB:
\[ \xi_{1,0} = \frac{2}{\tau_F} \exp\left(-\frac{\tau}{\tau_F}\right) \]

Exponential regime CD:
\[ \xi_{1,0} = \left(\frac{\tau_{BC}}{\pi \tau}\right)^{1/2} \exp\left(-\frac{\tau}{\tau_C}\right) \]
Surfactant vs. Methods in Relation to the Relaxation Regime

Fast surfactant = \{surfactant that adsorbs quickly\}:

Regimes CD and DE: Difficult for detection because \(\xi_{1,0}\) has become very small for these regimes; in principle, these regimes could be detected for very fast surfactants by very slow and sensitive methods.

Regime AB:
Can be detected for “slow” surfactants by “fast” methods. 
Example: Triton X-100 by inclined plate method.

Regime BC:
Can be detected for “fast” surfactants by “slow” methods. 
Example: SDS by MBPM.
The three micellar relaxation times, \( \theta_c \), \( \theta_m \), and \( \theta_\sigma \), are close to each other.

Points A, B, and C coincide.

The effect of the fast relaxation process disappears at low surfactant concentrations (\( \beta \approx 1 \)).

The long-time asymptotics is the same as in regime AB but \( \tau_F \to \tau_C \).
Methods with **Stationary Interfacial Expansion: Micellar Kinetics**

\[
\dot{\alpha}(t) \equiv \frac{1}{A} \frac{dA}{dt} = \frac{d\alpha(t)}{dt} = \text{const.}
\]

The **kinetic regimes** are:

**(AB)** \( \theta/(K_{AB} + \theta)^{1/2} \) kinetic regime governed by the fast micellization process;

**(BC)** \( \theta^{1/2} \) diffusion-limited regime at equilibrated fast process but negligible slow process;

**(CD)** \( \theta/(K_{CD} + \theta)^{1/2} \) kinetic regime governed by the slow micellization process;

**(DE)** \( \theta^{1/2} \) diffusion-limited regime at equilibrated both the fast and slow micellization processes.

\[
\theta \equiv \frac{h_a^2}{D_1} \dot{\alpha} \quad \theta \text{ – dimensionless expansion rate}
\]

Example 1: Dynamic surface tension of Brij 58 measured by the strip method (Paul Joos)

Theory: \[ \sigma - \sigma_{eq} = \frac{\Gamma_{eq}^2 kT}{CMC} \left( \frac{\pi \alpha}{2 D_{BC}} \right)^{1/2} \]

From the slope of the plot \( \sigma - \sigma_{eq} \) vs. \( \sqrt{\alpha} \) at fixed \( \beta \), one determines the apparent diffusivity \( D_{BC}(\beta) \).

CMC = \( 1.0 \times 10^{-8} \) mol/cm³
\( \Gamma_{eq} = 2.70 \times 10^{-10} \) mol/cm² (at CMC)

Different curves correspond to different micelle concentrations, \( \beta \).
Example 1: Dynamic surface tension of Brij 58 measured by the strip method (Paul Joos)

From the fit of the data, one determines:

\[ u = 1.06, \quad B_m = 0.243 \]

\[ D_{BC} \equiv D_1 (1 + u\beta)(1 + u\beta B_m) \]

\[ B_m = \frac{D_m}{D_1} = 0.243 \]

(reasonable value)

For Brij 58, \( m_{eq} = 70 \); hence the polydispersity of the micelles is \( \sigma_{eq} = 8.6 \)

The obtained reasonable values confirm that the kinetic regime is BC.
Another method with stationary interfacial expansion

\[ \dot{\alpha}(t) \equiv \frac{1}{A} \frac{dA}{dt} = \text{const.} \]

Adsorption (rather than surface tension) is detected by ellipsometry or neutron reflection.

The Overflowing Cylinder Method (OFC)
C.D. Bain et al.
Example 2: Dynamic surface tension of C$_{14}$TAB by the Overflowing Cylinder Method
(Colin Bain et al.; the adsorption $\Gamma$ is directly measured by ellipsometry)

The data points are not for the same $\beta$!

Theory: $\Gamma = \Gamma_{eq} - (\tau_{dif})^{1/2} \Gamma_{eq} Y$

$Y \equiv \{\pi \dot{\alpha} / [2(1 + u \beta)(1 + u \beta B_m)]\}^{1/2}$

$Y = 0$ (i.e. $\dot{\alpha} = 0$), gives the equilibrium adsorption at CMC, $\Gamma_{eq}$.

The best fit $\Gamma$ vs. $Y$ corresponds to

$B_m = D_m/D_1 = 0.23$ and $u = \sigma_{eq}^2/m_{eq} = 1.2$

$m_{eq} = 80$; from $u = 1.2$ we determine that the polydispersity of the C$_{14}$TAB micelles is $\sigma_{eq} = 9.8$. The obtained values of $\Gamma_{eq}$, $B_m$ and $\sigma_{eq}$ are reasonable.

This confirms that the kinetic regime is BC. $[\tau_{dif} = h_\alpha^2/D_1$ is the characteristic diffusion time]
Part 3: Application of the Maximum Bubble Pressure Method

Problem: Different tensiometers - different results for the dynamic surface tension. This is difference is demonstrated with our data for two apparatuses. The data are plotted as DST vs. $t^{-1/2}$:

![Graph showing DST vs. $t^{-1/2}$ for 1.5 mM SDS, 128 mM NaCl]

Explanation:
Different time-dependence, $A(t)$, of the bubble surface area for different apparatuses.
The **experiment** indicates that $A(t_d)$ is independent of:

1. Bubbling period, $t_{\text{age}}$
2. Surfactant concentration
3. Surfactant type

(General validity?)

The **theory** indicates that in most cases $\gamma(t)$ depends on a constant parameter, $\lambda = \text{integral of } A(t)$, rather than on the function $A(t)$.

$A(t)$ (the apparatus function) can be determined only by cinematography;

$\lambda$ (the apparatus constant) can be determined also by MBPM (much easier!)

Below we check whether $\lambda$ is independent of $t_{\text{age}}$, surfactant type and concentration.
Expanding Surface vs. Immobile Surface

\[ \gamma = \gamma_{eq} + \frac{s_\gamma}{(t_{age})^{1/2}} = \gamma_{eq} + \frac{s_{\gamma,0}\lambda}{(t_{age})^{1/2}} = \gamma_{eq} + \frac{s_{\gamma,0}}{(t_u)^{1/2}} \]

\[ s_\gamma = \lambda s_{\gamma,0} = \lambda \frac{kT\Gamma_{eq}^{2}}{\pi D} c_\infty^{1/2}, \quad t_u = t_{age} / \lambda^2 \]

(1) The whole effect of the interfacial expansion is incorporated in \( \lambda \);

(2) \( t_u \) (universal surface age), is the age of an (initially clean) immobile surface with the same \( \gamma \) as that registered by the MBPM tensiometer.

\[ \lambda \equiv \int_{0}^{1} \frac{1}{(\tau_1 - \tau)^{1/2}} d\left[ \frac{A(t_d)}{A_0} \right] dt_d \]

\[ \tau \equiv \int_{0}^{t_d} \frac{A^2(t_d)}{A_0^2} dt_d, \quad \tau_1 = \tau(t_d = 1) \]

\( c_\infty \) – bulk surfactant concentration; \( \Gamma_{eq} \) – equilibrium adsorption; 
\( \gamma_{eq} \) – equilibrium surface tension; \( D \) – surfactant diffusivity; 
\( s_{\gamma,0} \) – the value of \( s_\gamma \) for an immobile interface.
Example 1:
Comparison of data obtained by MBPM (expanding bubbles) with data for immobile bubbles (IB) for SDS + 100 mM NaCl.

For MBPM $\lambda = 6.074$ is determined by integration of the experimental $A(t)$ curve (for our apparatus);
For IB we have $\lambda = 1$ (no expansion)
$t_u = \frac{t_{age}}{\lambda^2}$ is used to plot the MBPM data in (b) \hspace{1cm} (\lambda^2 \approx 37)$
Example 2:
Comparison of data obtained by MBPM (expanding bubbles) with data from Wilhelmy plate method for Na N-Cocoylglycinate.

For Wilhelmy plate (immobile surface): $t_u = t_{age} \ (\lambda = 1)$

For MBPM (expanding surface): $t_u = t_{age}/\lambda^2 \ (\lambda = 6.07)$.

The excellent fit with the theoretical dependence evidences diffusion-limited adsorption kinetics.
Two ways to determine the apparatus constant, $\lambda$:

1. By integration of the experimental $A(t)$ curve;
2. By MBPM experiments, $\lambda = s_\gamma / s_{\gamma,0}$.

(Compare the values of $\lambda$ obtained in the two ways!)

Procedure:

1. $\gamma(t_{\text{age}})$ curves are obtained by MBPM and fitted with the dependence:

$$\gamma = \gamma_{\text{eq}} + \frac{s_\gamma}{a + (t_{\text{age}})^{1/2}}$$

Thus $s_\gamma$ is determined.

2. Next, $s_{\gamma,0}$ is calculated from fits of equilibrium surface tension isotherms.

3. $\lambda = s_\gamma / s_{\gamma,0}$
<table>
<thead>
<tr>
<th>$C_{\text{SDS}}$ (mM)</th>
<th>$\Gamma_{\text{eq}}$ (μmol/m²)</th>
<th>$s_{\Gamma,0}$ (mN.m⁻¹.s¹/²)</th>
<th>$s_\gamma$ (mN.m⁻¹.s¹/²)</th>
<th>$\lambda = s_\gamma/s_{\Gamma,0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SDS + 10 mM NaCl</strong></td>
<td></td>
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<tr>
<td>0.1</td>
<td>0.91</td>
<td>0.553</td>
<td>3.36</td>
<td>6.077</td>
</tr>
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<td>5.95</td>
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<tr>
<td>2</td>
<td>3.76</td>
<td>0.545</td>
<td>3.31</td>
<td>6.073</td>
</tr>
<tr>
<td>3</td>
<td>3.96</td>
<td>0.423</td>
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<td>6.075</td>
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<td><strong>SDS + 100 mM NaCl</strong></td>
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<tr>
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<td>4.560</td>
<td>27.7</td>
<td>6.074</td>
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<td>1</td>
<td>4.08</td>
<td>1.299</td>
<td>7.89</td>
<td>6.075</td>
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</tbody>
</table>

Theory: $\lambda = 6.074$  
Average: $\lambda = 6.07 \pm 0.01$
<table>
<thead>
<tr>
<th>$C_{\text{DTAB}}$ (mM)</th>
<th>$\Gamma_{\text{eq}}$ (µmol/m²)</th>
<th>$s_{\gamma,0}$ (mN.m⁻¹.s¹/²)</th>
<th>$s_{\gamma}$ (mN.m⁻¹.s¹/²)</th>
<th>$\lambda = s_{\gamma}/s_{\gamma,0}$</th>
</tr>
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<tbody>
<tr>
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<tr>
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<td>0.657</td>
<td>6.069</td>
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<tr>
<td>DTAB + 100 mM NaBr</td>
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<td>4</td>
<td>3.41</td>
<td>0.244</td>
<td>1.48</td>
<td>6.075</td>
</tr>
</tbody>
</table>

Theory: $\lambda = 6.074$

Average: $\lambda = 6.07 \pm 0.01$
Conclusions: The results confirm the concept about the apparatus constant:

1. $\lambda$ is the same for all concentrations of a given surfactant and electrolyte;
2. $\lambda$ is the same for SDS and DTAB;
3. $\lambda$ is calculated from $s$ determined of the data fits for $10 \text{ ms} < t_{age} < 40 \text{ s}$

Universal surface age, $t_u = t_{age}/\lambda^2$ (ms)

$t_u = t_{age}/\lambda^2$

$\lambda^2 = (6.07)^2 \approx 37$

Hence, in terms of $t_u$ the MBP method is much (37 times) faster.

$t_u = t_{age}/\lambda^2$, accounts for the surface expansion, and for this reason $t_u$ gives the physically correct surface age.

Plot of the dimensionless effective diffusivity of micellar solutions, $D_{\text{eff}}/D$, vs. $\beta$

$D_{\text{eff}} = \frac{S_{\gamma, \text{CMC}}^2}{s_{\gamma}^2}$

$D$ – diffusivity of surfactant monomers.

The data for $\gamma(t)$ are fitted well with the expression for diffusion-limited adsorption:

$$\gamma = \gamma_{\text{eq}} + \frac{s_{\gamma}}{a + (t_{\text{age}})^{1/2}}$$

Hence, the kinetic regime is either BC or DE. The data complies with BC!
Plot of Plot of $\sigma_{eq}^2$ vs. $\beta$ calculated from the data for $D_{eff}/D$

$\sigma_{eq}$ – micelle polydispersity

$m_{eq}$ – micelle mean aggregation number;

Values $\sigma_{eq}^2/m_{eq} < 2$ are reasonable.

For example, for $\beta = 10$ and $m_{eq} = 70$ we obtain:

$\sigma_{eq} = 7.2$ (SDS)

$\sigma_{eq} = 9.5$ (DTAB)
The theory indicates the presence of four different kinetic regimes of adsorption from micellar surfactant solutions:

1. **Regime AB**: the fast micellar process governs the adsorption kinetics \([\exp(t/\tau_F)]\)

2. **Regime BC**: diffusion control – the fast micellar process is equilibrated, whereas the effect of the slow process is negligible \([t^{-1/2}]\).

3. **Regime CD**: the slow micellar process governs the adsorption kinetics \([\exp(t/\tau_S)]\)

4. **Regime DE**: diffusion control – both the fast and slow micellar processes are equilibrated \([t^{-1/2}]\).

5. **MBPM**: The determination of the apparatus constant, \(\lambda\), for a given tensiometer allows one to characterize a given surfactant solution with a universal dynamic surface tension curve, \(\gamma(t)\).
The results are published in the following papers:


