

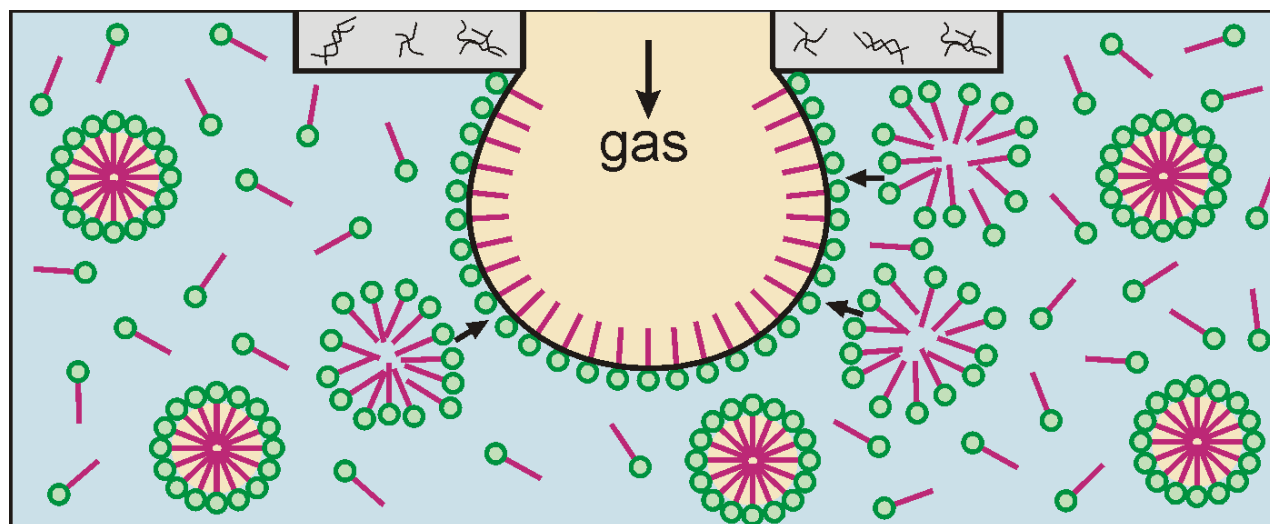
The Four Kinetic Regimes of Adsorption from Micellar Surfactant Solutions

P.A. Kralchevsky, K.D. Danov, N.D. Denkov, N.C. Christov,
K.P. Ananthapadmanabhan,* and Alex Lips*

Laboratory of Chemical Physics and Engineering, Faculty of Chemistry,
University of Sofia, Bulgaria, and *Unilever R&D, Trumbull, CT, USA

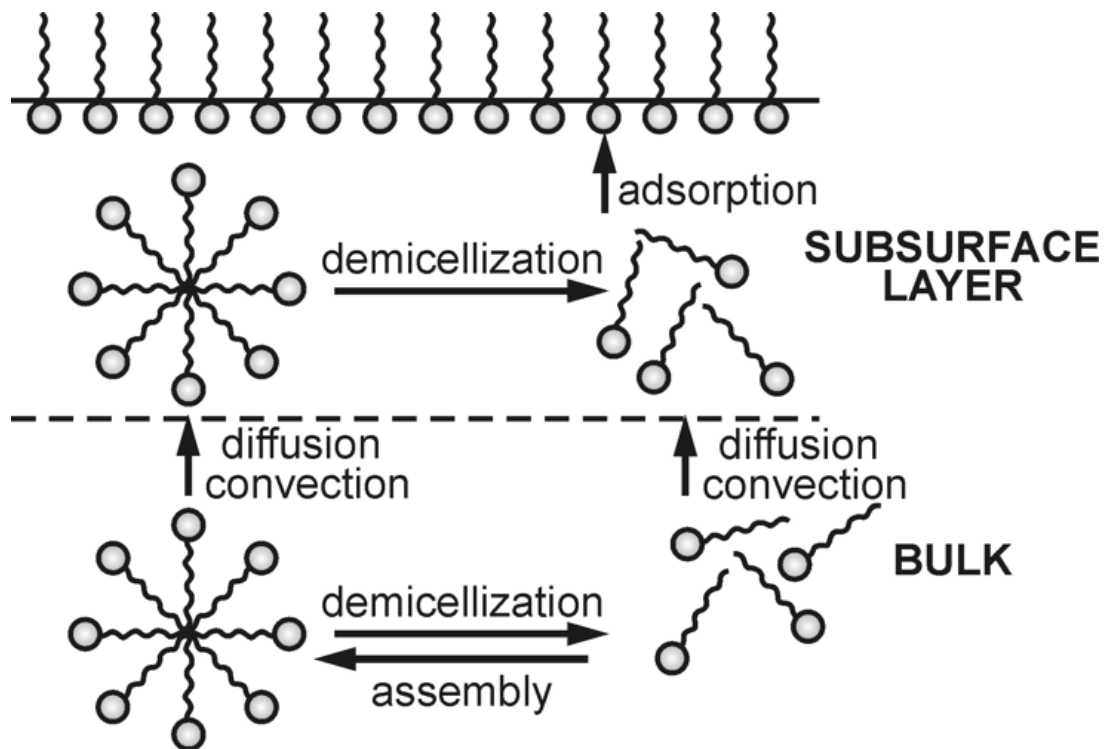
Plenary Lecture at the 59th Divisional Meeting on Colloid and Interface
Chemistry, The Chemical Society of Japan

Hokkaido University, Sapporo, Japan, September 13-15, 2006



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.

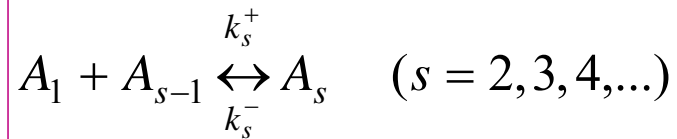


{**Fast micellar process**} =
 {**Exchange of monomers**
 between the micelles}
 (Rate constant k_m)

{**Slow micellar process**} =
 {**Decomposition of a**
 "critical-size micelle"
 to monomers}.
 (Rate constant k_s)

General Set of Equations (Aniansson & Wall, 1974)

Multi-Step Micellization:



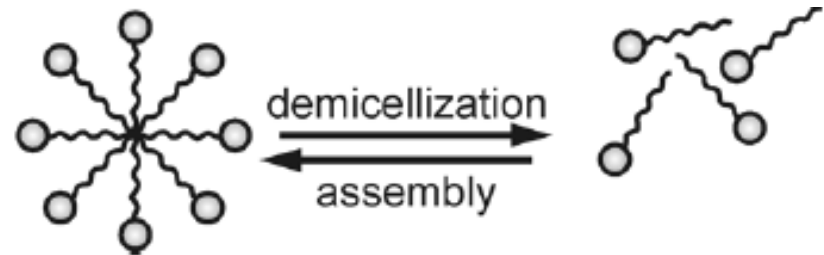
$$\frac{dc_1}{dt} + \nabla \cdot \mathbf{I}_1 = -2J_2 - \sum_{s=3}^{\infty} J_s$$

$$\frac{dc_s}{dt} + \nabla \cdot \mathbf{I}_s = J_s - J_{s+1} \quad (s = 2, 3, 4, \dots)$$

Diffusion and Reaction Fluxes:

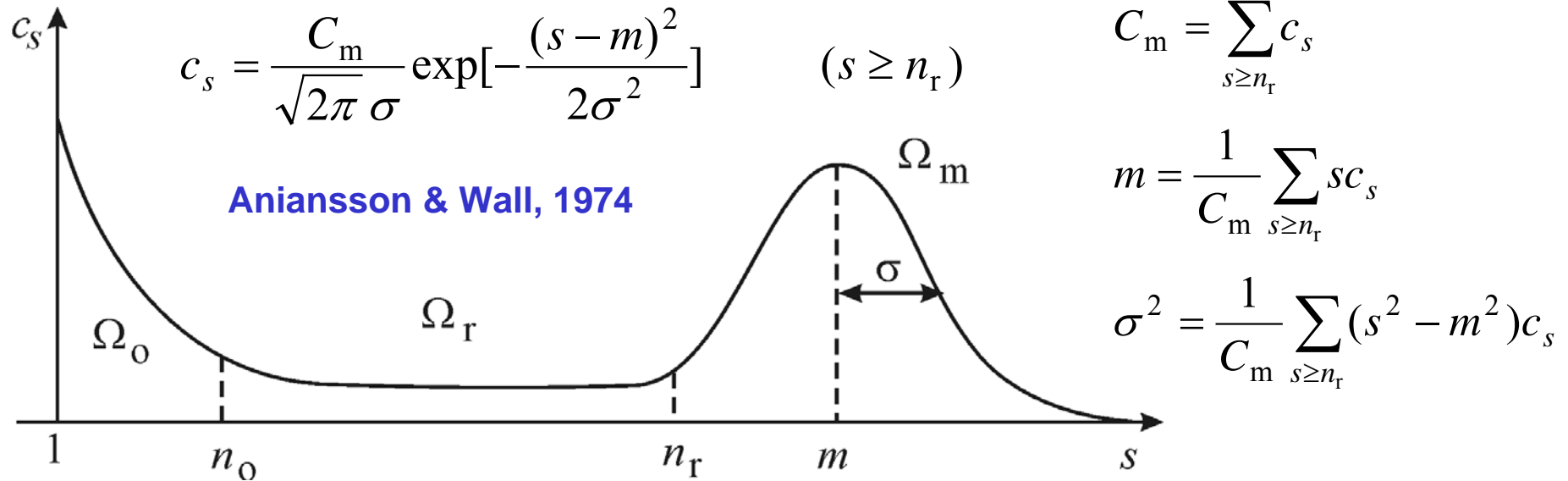
$$\mathbf{I}_s = -D_s \nabla c_s \quad (s = 1, 2, 3, \dots)$$

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



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



- (i) Region of the monomers and oligomers, Ω_o ($1 \leq s \leq n_o$)
- (ii) Region of the rare aggregates, Ω_r ($n_o < s < n_r$)
- (iii) Region of the abundant micelles, Ω_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**

$$c_1(\mathbf{r},t),$$

$$C_m(\mathbf{r},t),$$

$$m(\mathbf{r},t),$$

$$\sigma(\mathbf{r},t)$$

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

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

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

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

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

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

$$\mathbf{I}_{m,i} \equiv \sum_{s \geq n_r} s^i \mathbf{I}_s \quad (i = 0,1,2)$$

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 ξ_c , ξ_m , and ξ_σ

$$\xi_c \equiv \frac{C_{m,p}}{C_{m,eq}};$$

$$\xi_m \equiv \frac{m_p}{m_{eq}};$$

$$\xi_\sigma \equiv \frac{\sigma_p}{\sigma_{eq}}$$

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

⇒ characteristic equation

I_1, I_2, I_3 – invariants of the matrix (a_{ij});
three eigenvalues ⇒ three relaxation times:

$$\tau_c, \tau_m, \tau_\sigma$$

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

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

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

The Three **Micellar** Characteristic Relaxation Times

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

$$\beta \equiv \frac{C_{\text{tot}} - \text{CMC}}{\text{CMC}} \quad \text{Dimensionless micelle concentration}$$

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

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_σ is the **second** characteristic time of the **fast process**, related to the relaxation of the **micellar polydispersity**, σ ; (**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:

$$m_{\text{eq}} = 60; \quad \sigma_{\text{eq}} = 5; \quad k_S / k_m = 10^{-7}$$

| Dimensionless relax. time | Exact | Approximate expressions |
|---|-----------------------|-------------------------|
| Low micelle concentration: $\beta = 1$ | | |
| τ_c | 4.12×10^3 | 4.11×10^3 |
| τ_m | 1.87×10^1 | 1.87×10^1 |
| τ_σ | 1.21×10^1 | 1.21×10^1 |
| High micelle concentration: $\beta = 100$ | | |
| τ_c | 1.18×10^5 | 1.18×10^5 |
| τ_m | 6.43×10^{-1} | 6.43×10^{-1} |
| τ_σ | 1.25×10^1 | 1.25×10^1 |

Dimensionless micelle concentration:

$$\beta \equiv \frac{C_{\text{tot}} - \text{CMC}}{\text{CMC}}$$

Low micelle concentrations :

$$\tau_c > \tau_m > \tau_\sigma$$

High micelle concentrations :

$$\tau_c > \tau_\sigma > \tau_m$$

τ_c – relaxation time of **micelle concentration** (of the **slow** process, Aniansson & Wall)

τ_m – relaxation time of **mean aggreg. number** (of the **fast** process, Aniansson & Wall)

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

Asymptotic Expressions:

The three basic physical parameters, C_m , m and σ , are perturbed.

(1) The Relaxation of a Perturbation in **Micelle Concentration**, C_m , is Governed only by the **Slow Micellar Time**, t_c

$$\xi_c(t) \approx A_c \exp(-t/t_c) \quad (t_c \gg t_m, t_\sigma)$$

(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 σ !

The Relaxation of a Perturbation in Micelle **Mean Aggregation Number** is Governed by both the **Slow** and **Fast** Times, t_c and t_m

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

(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 σ , 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_σ

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

Hence, if the relaxation of micelle **polydispersity** is measured, then the **two fast** micellar times, t_m and t_σ , could be determined.

Note that a perturbation in polydispersity σ does not affect C_m and m .

Summary of Part 1: Micellar Relaxation Processes in the Bulk

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, σ , are characterized by three distinct relaxation times: t_c , t_m , and t_σ .
- (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_σ , 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 the relaxation of σ is affected by t_σ 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.

[K.D. Danov, P.A. Kralchevsky, et al., *Adv. Colloid Interface Sci.* 119 (2006) 1-16]

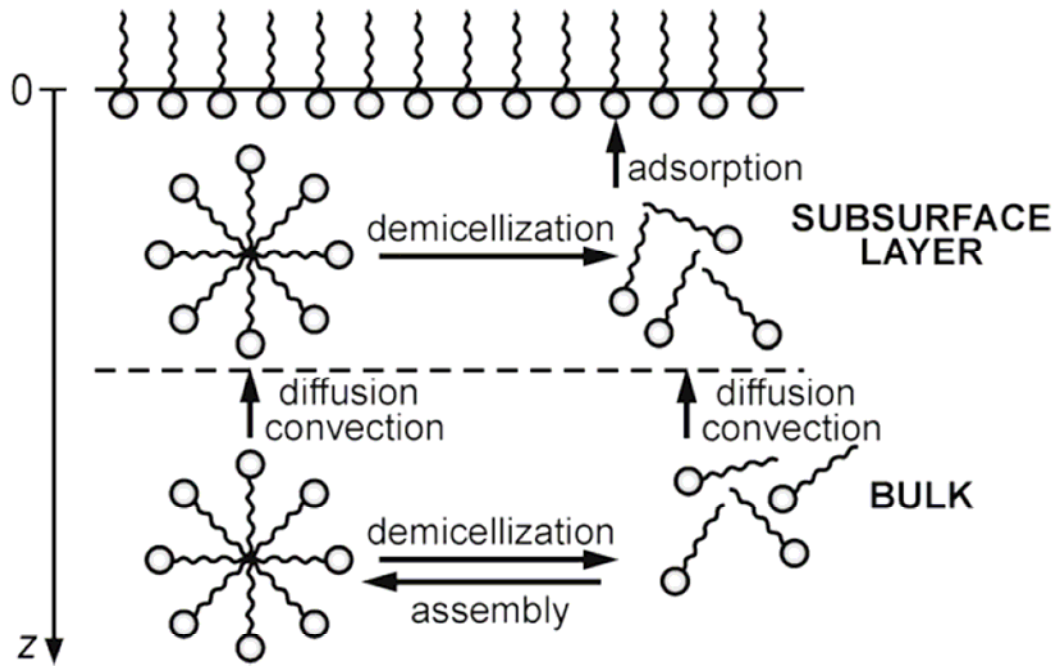
Next step: Investigation of the problem about the **kinetics of adsorption** from micellar solutions, and the respective **dynamic surface tension (Part 2)**.

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: $[\Delta\sigma \propto \exp(-t/\tau)]$.
- **Which** of the two **very different** theoretical expressions for the **effective diffusivity** of a micellar solution is correct ?
 - (a) by **J. Lucassen** (1975): $D_{\text{eff}} = D_1(1 + \beta m_{\text{eq}})(1 + \beta m_{\text{eq}} D_{\text{m}}/D_1)$
 - (b) by **Paul Joos** (1988): $D_{\text{eff}} = D_1(1 + \beta)(1 + \beta D_{\text{m}}/D_1)$

Parameters of the Adsorption Process



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

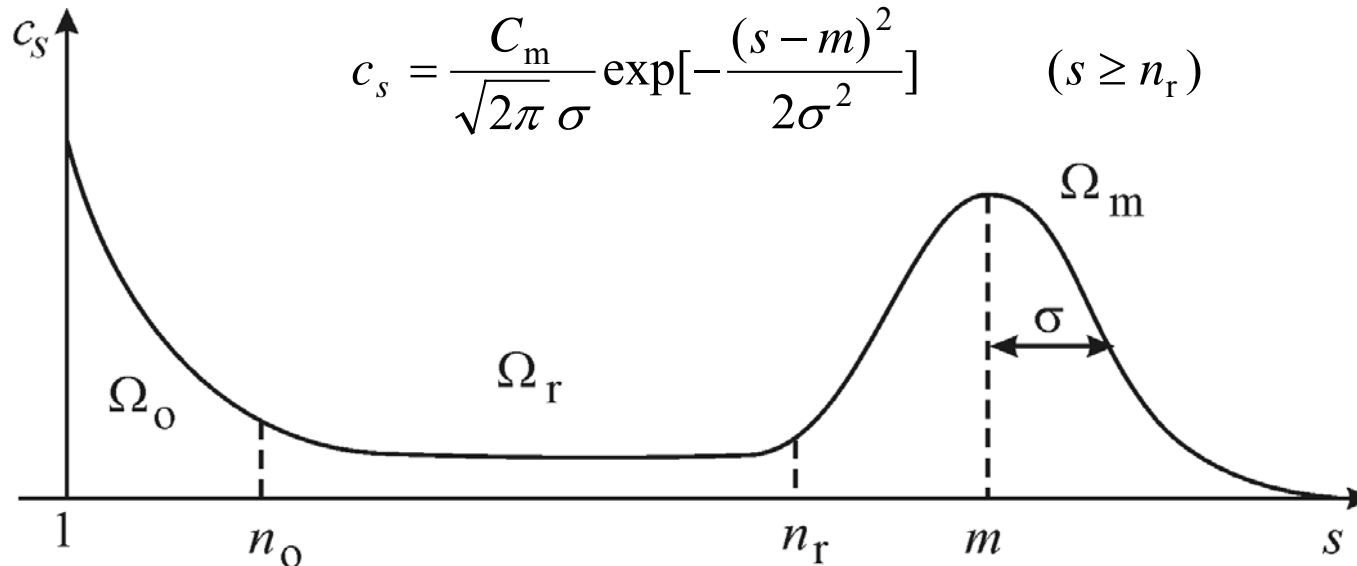
$$K_s \equiv \frac{h_a^2}{D_1} k_s^-; \quad K_m \equiv \frac{h_a^2}{D_1} k_m^-$$

$$h_a \equiv \left(\frac{\partial \Gamma}{\partial c_1} \right)_{\text{eq}}$$

(adsorption length)

ζ – dimensionless **distance**; τ – 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



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

ξ_1 – dimensionless perturbation in the concentration of monomers, c_1 ;

ξ_c – dimensionless perturbation in the **micelle concentration**, C_m ;

ξ_m – dimensionless perturbation in the **micelle mean aggregation number**, m ;

ξ_σ – dimensionless perturbation in the **micelle polydispersity**, σ .

General System of Kinetic Equations (from Part 1)

$$\frac{\partial \xi_1}{\partial \tau} = \frac{\partial^2 \xi_1}{\partial \zeta^2} - (m_{\text{eq}} - w\sigma_{\text{eq}}) \frac{K_s}{S} \varphi_s - \frac{\beta K_m}{m_{\text{eq}} S} \varphi_m \quad (\text{surfactant monomers})$$

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

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

$$\frac{\partial \xi_\sigma}{\partial \tau} = B_m \frac{\partial^2 \xi_\sigma}{\partial \zeta^2} + K_s (w^2 - 1) \frac{m_{\text{eq}}}{2\beta} \varphi_s - \frac{K_m}{2\sigma_{\text{eq}}^2} \varphi_m - \frac{2K_m}{\sigma_{\text{eq}}^2} \xi_\sigma \quad (\text{polydispersity})$$

$$\boxed{B_m = \frac{D_m}{D_1}}$$

φ_s – dimensionless reaction flux of the **slow** relaxation process;
 φ_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 $\varphi_m = 0$

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

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

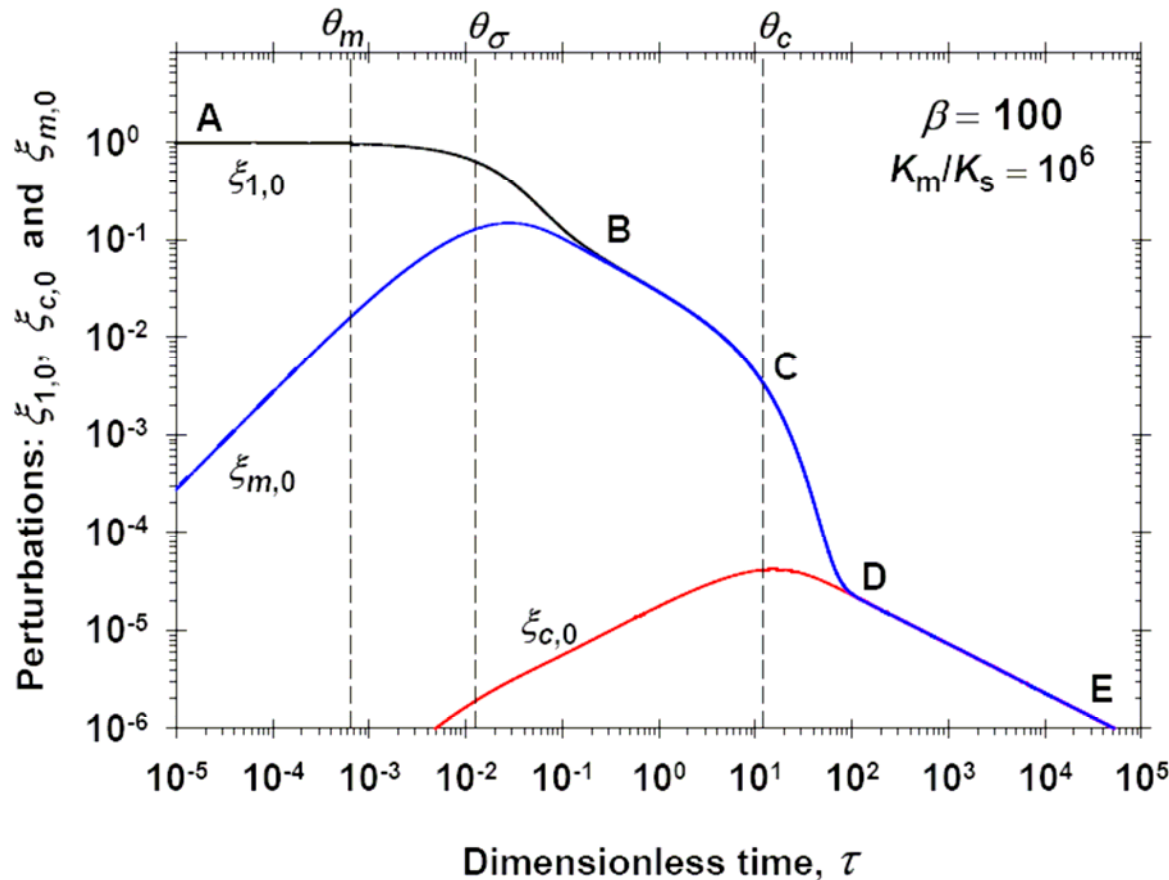
For $\xi_1 = \xi_c = \xi_m$, we obtain $\varphi_s = 0$

(**crit**erion 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)



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

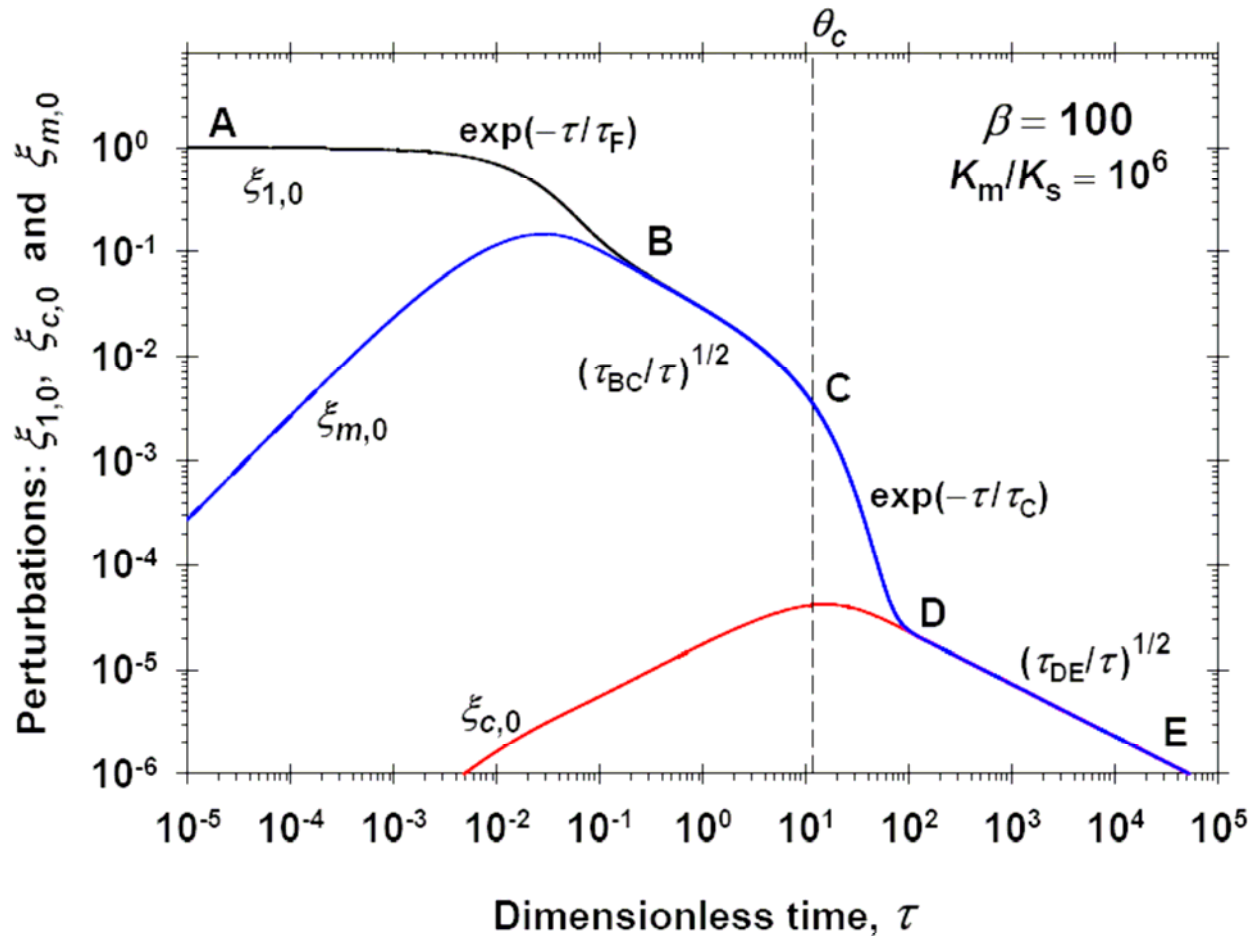
$\Rightarrow \xi_{1,0}$ describes the relaxation of the surface tension $\gamma(t)$.

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

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

(D) $\xi_1 = \xi_c = \xi_m \Rightarrow \varphi_s = \varphi_m = 0 \Rightarrow$ equilibrated fast and slow micellar processes.

Analytical Expressions for the Relaxation in Different Regimes



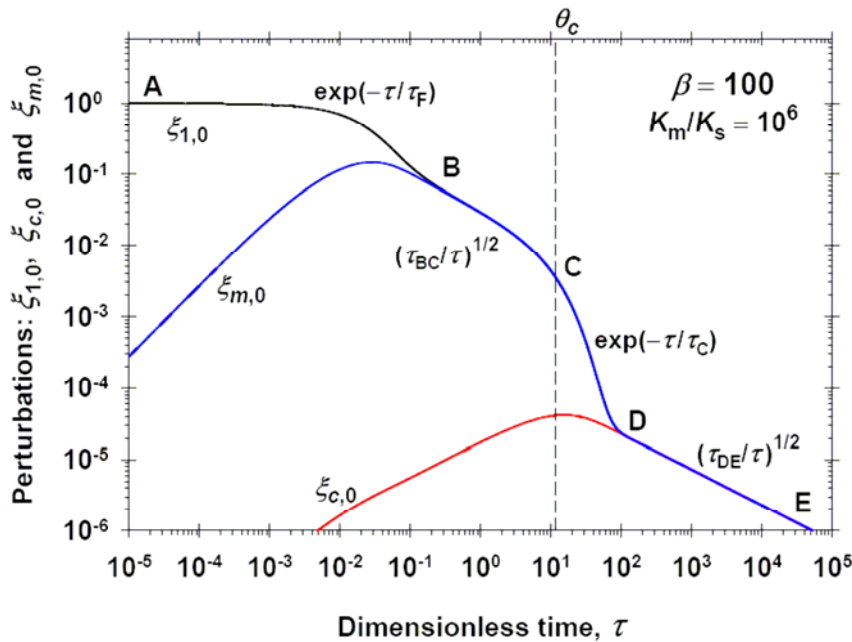
$$\frac{1}{\tau_F} = \frac{1}{\theta_m} - \frac{1}{2\theta_\sigma}$$

$$\tau_C = \theta_c$$

θ_c – dimensionless relaxation time of the **slow** process;
 θ_m and θ_σ – dm.less relaxation time of the **fast** process.

Two **exponential** regimes (AB and CD) with relaxation times τ_F and τ_C ;

Two **inverse-square-root** regimes (BC & DE) with relaxation times τ_{BC} and τ_{DE} .



(1) Kinetic Regime AB

The **fast** micellar process governs the adsorption kinetics [$\exp(t/\tau_F)$]

$$\tau_F \equiv \frac{m_{\text{eq}}}{\beta K_m} = \frac{1}{\theta_m} - \frac{1}{2\theta_\sigma}, \quad s_F \equiv \left(1 + \frac{4}{\tau_F}\right)^{1/2}$$

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

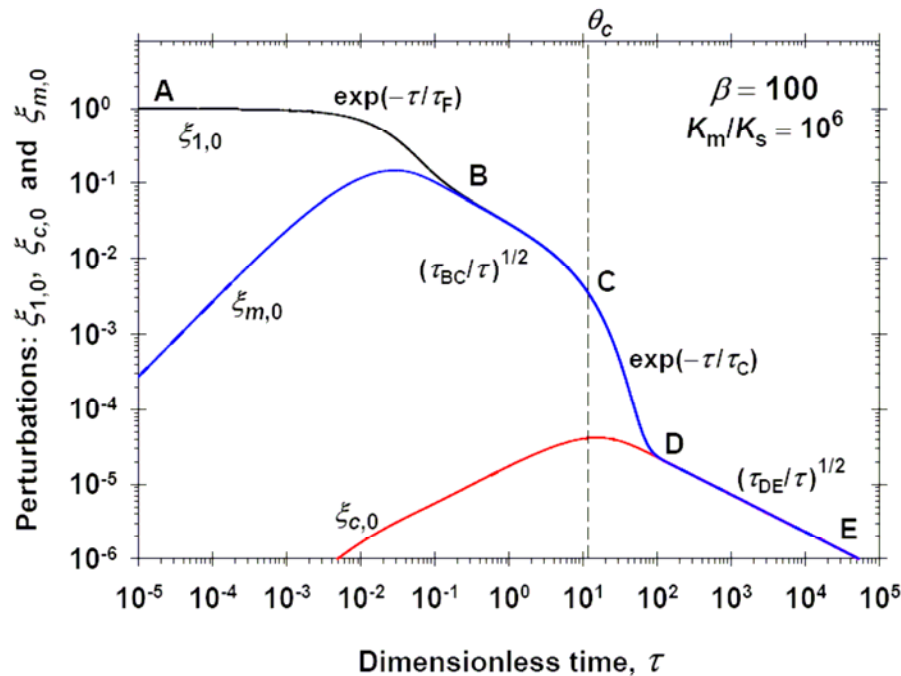
$$\xi_{1,0} = 1 - 2\left(\frac{\tau}{\pi}\right)^{1/2} + \tau + \dots \quad (\text{short-time asymptotics})$$

$$\xi_{1,0} = \frac{s_F - 1}{s_F} \exp\left(-\frac{s_F - 1}{2} \tau\right) + \dots \quad (\text{long-time asymptotics})$$

$$\frac{s_F - 1}{2} \approx \frac{1}{\tau_F}$$

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!)



(2) Kinetic Regime BC

$$\xi_{1,0} \approx \xi_{m,0}$$

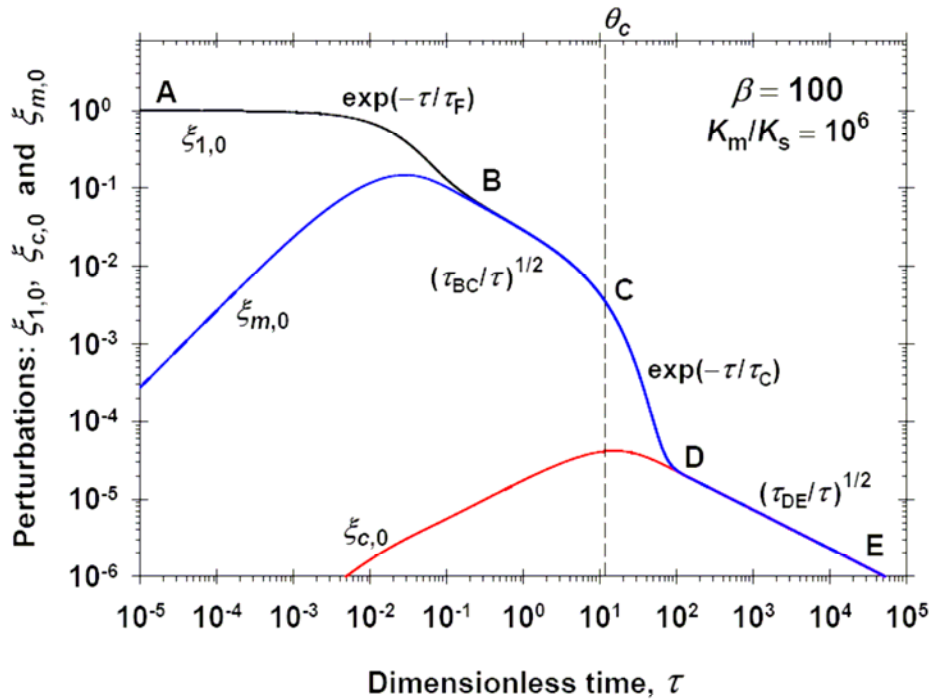
Diffusion control – the **fast** micellar process is **equilibrated**, whereas the effect of the **slow** process is **negligible** [$t^{-1/2}$]

$$\xi_{1,0} = \left(\frac{\tau_{BC}}{\pi \tau}\right)^{1/2} + \dots \quad (\text{inverse-square-root time dependence})$$

$$\frac{1}{\tau_{BC}} = \frac{D_{BC}}{D_1} = \left(1 + \frac{\beta \sigma_{eq}^2}{m_{eq}}\right) \left(1 + \frac{\beta \sigma_{eq}^2}{m_{eq}} \frac{D_m}{D_1}\right) \quad (\text{relaxation time } \tau_{BC}, \text{ \& effective diffusivity } D_{BC})$$

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)**.



(3) Kinetic Regime CD

The **slow** micellar process governs the adsorption kinetics

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

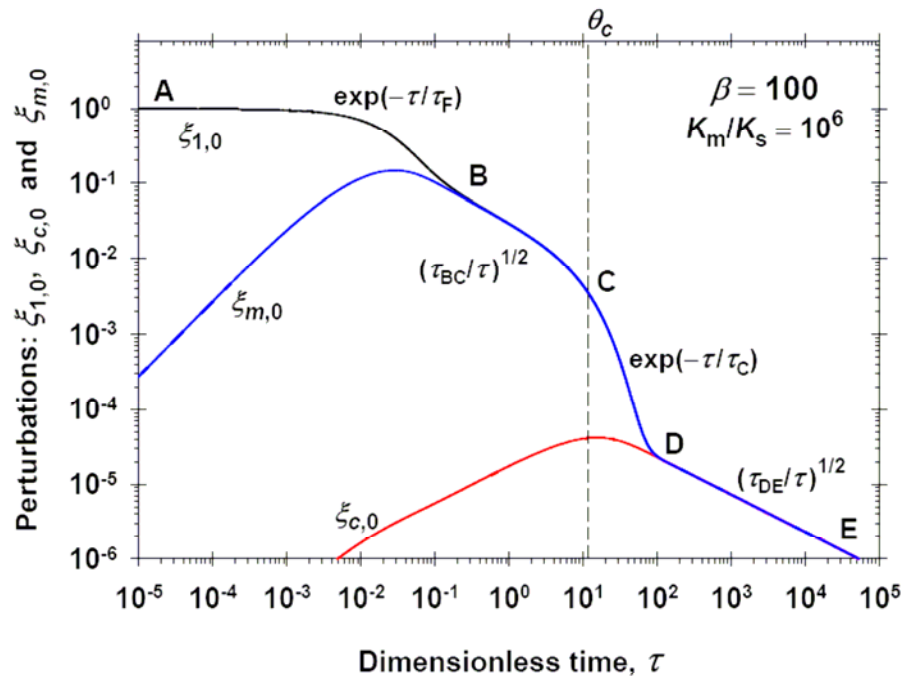
$$\frac{\gamma(t) - \gamma_{eq}}{\gamma(0) - \gamma_{eq}} = \xi_{1,0}(\tau)$$

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

(exponential relaxation)

$$\tau_C \equiv \theta_c \approx \frac{\beta \sigma_{eq}^2}{m_{eq}^3 K_s}$$

(the relaxation time, τ_C , coincides with the characteristic time of the **slow** micellar process)



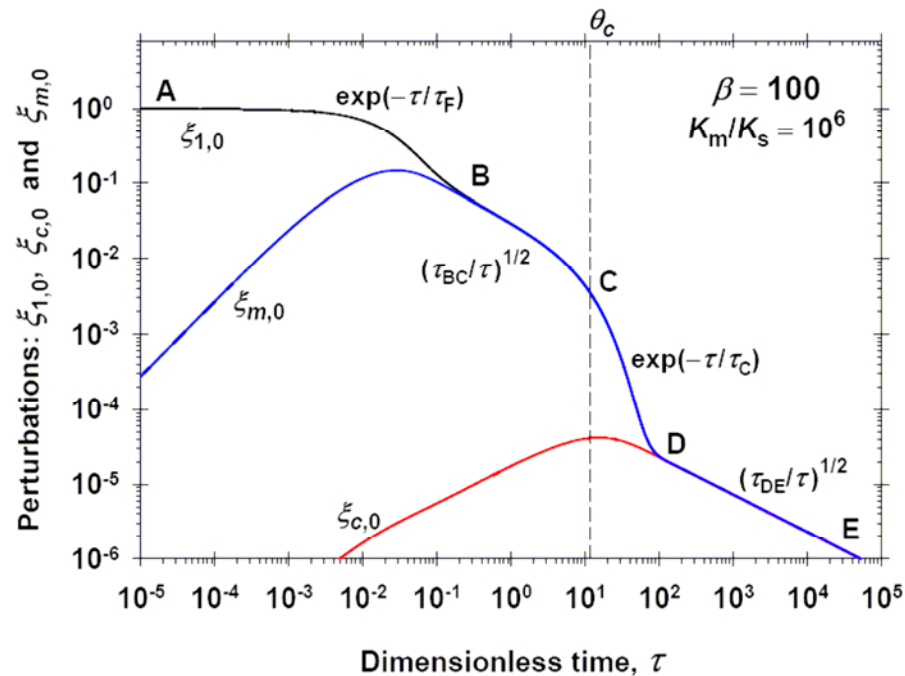
(4) Kinetic Regime DE

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

$$\xi_{1,0} = \left(\frac{\tau_{DE}}{\pi \tau}\right)^{1/2} + \dots \quad (\text{inverse-square-root-of-time dependence; Lucassen 1975})$$

$$\frac{1}{\tau_{DE}} = \frac{D_{DE}}{D_1} \equiv \left(1 + \beta \frac{\sigma_{eq}^2 + m_{eq}^2}{m_{eq}}\right) \left(1 + \beta \frac{\sigma_{eq}^2 + m_{eq}^2}{m_{eq}} \frac{D_m}{D_1}\right) \quad (\text{Expression for the Relaxation Time \& Diffusivity})$$

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.



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:

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

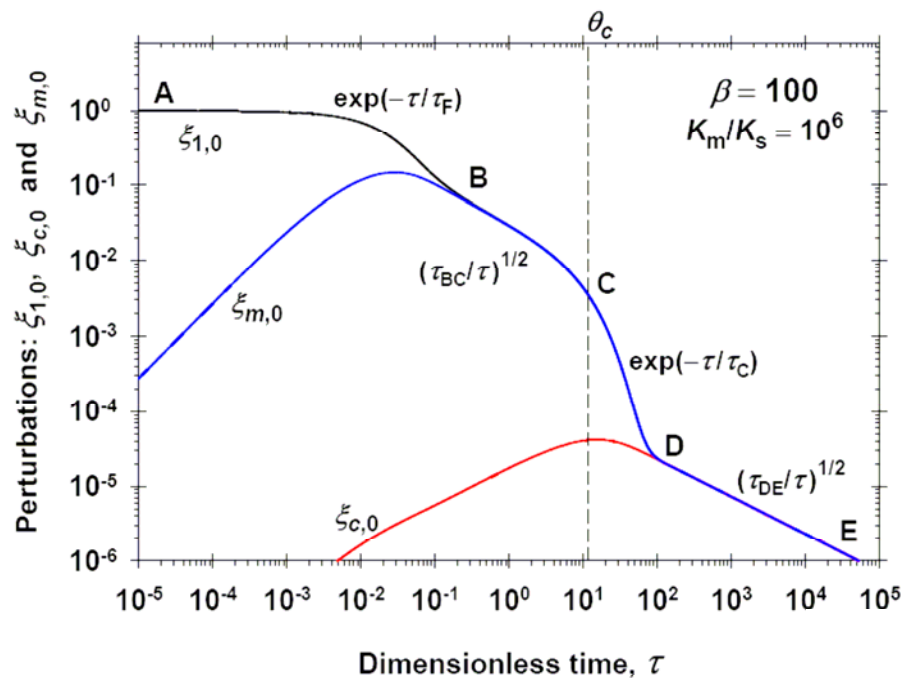
$$\frac{1}{\tau_{DE}} \equiv \left(1 + \beta \frac{\sigma_{eq}^2 + m_{eq}^2}{m_{eq}}\right) \left(1 + \beta \frac{\sigma_{eq}^2 + m_{eq}^2}{m_{eq}} \frac{D_m}{D_1}\right)$$

$$\frac{1}{\tau_{BC}} = \left(1 + \frac{\beta \sigma_{eq}^2}{m_{eq}}\right) \left(1 + \frac{\beta \sigma_{eq}^2}{m_{eq}} \frac{D_m}{D_1}\right)$$

$$m_{eq}^2 / \sigma_{eq}^2 \approx 100 \gg 1 \Rightarrow \tau_{DE} \ll \tau_{BC}$$

(easy to distinguish regime BC from DE)

[Details in: K.D. Danov, P.A. Kralchevsky, et al., *Adv. Colloid Interface Sci*, 119 (2006) 17-33.]



Difference between the exponential regimes AB and CD

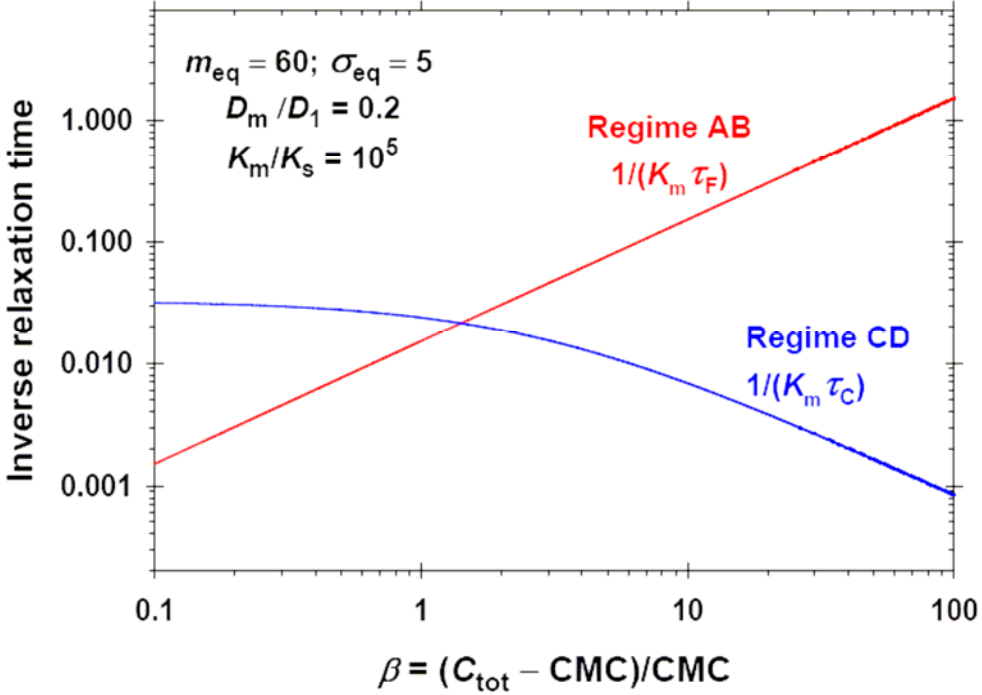
$1/\tau_F$ increases with micelle concentration;
 $1/\tau_C$ decreases with micelle concentration

Exponential regime AB:

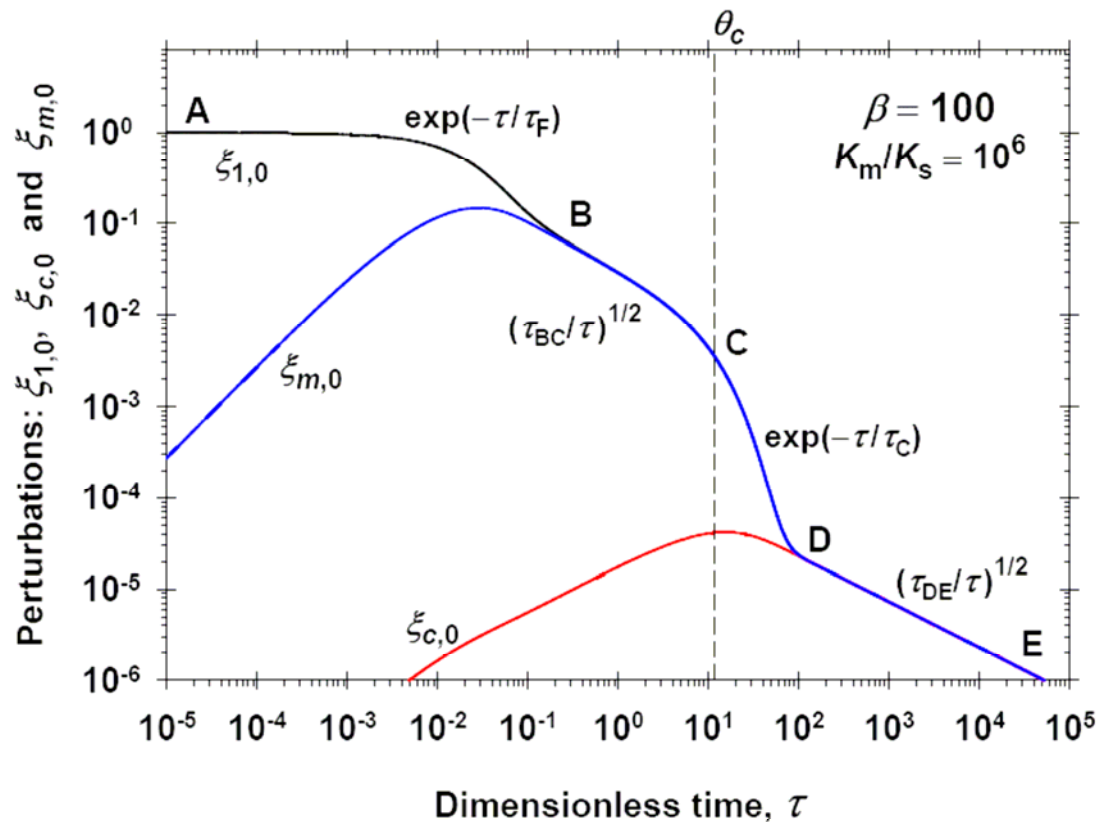
$$\xi_{1,0} = \frac{2}{\tau_F + 2} \exp\left(-\frac{\tau}{\tau_F}\right)$$

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}:

Fast method = {method that measures early surface age}:

Regime AB:

Can be detected for “**slow**” surfactants by “**fast**” methods.

Example: **Triton X-100** by **inclined plate** method.

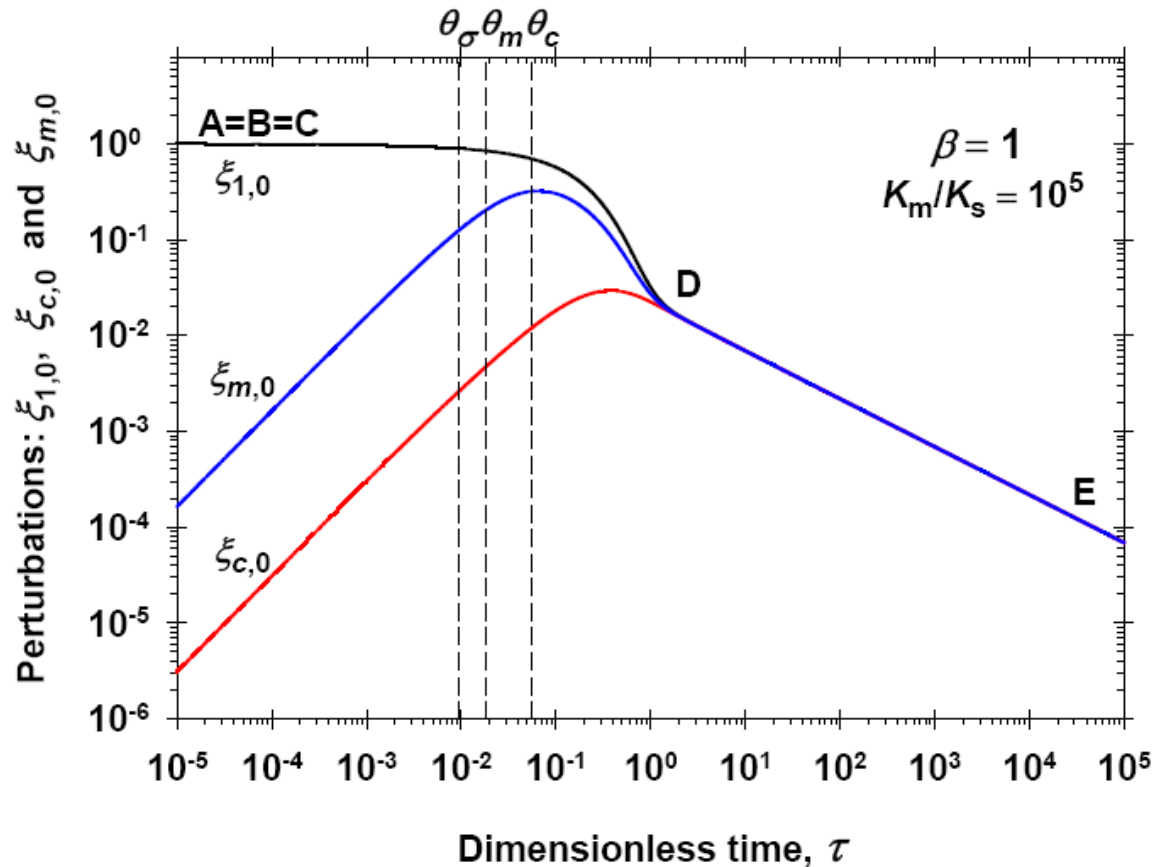
Regime BC:

Can be detected for “**fast**” surfactants by “**slow**” methods.

Example: **SDS** by **MBPM**.

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.

Rudimentary Kinetic Diagram at Low Micelle Concentration ($\beta \approx 1$) and/or at Smaller Difference between the Rates of the Fast and Slow Micellization Processes (smaller K_m/K_s)



The three micellar relaxation times, θ_c , θ_m and θ_σ , are close to each other.

Points A, B, and C coincide.

$$\xi_{1,0} = 1 - 2\left(\frac{\tau}{\pi}\right)^{1/2} + \tau + \dots$$

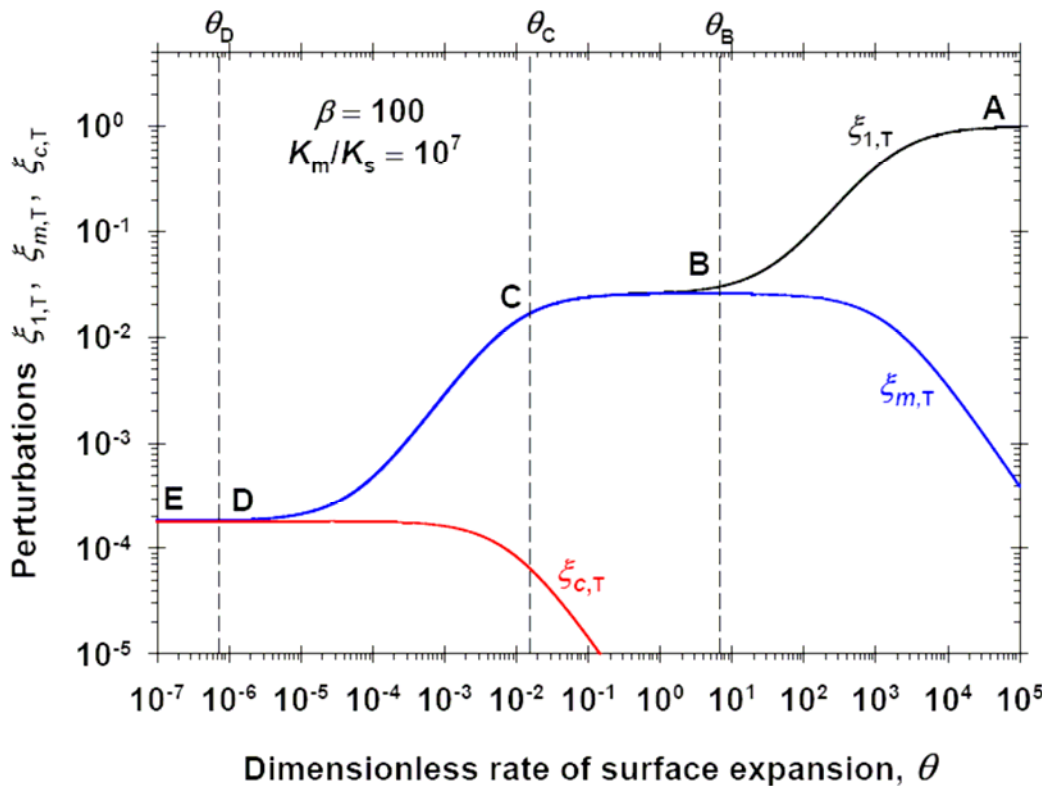
(short – time asymptotics)
(the same as in regime AB)

$$\xi_{1,0} = \frac{2}{\tau_C + 2} \exp\left(-\frac{\tau}{\tau_C}\right)$$

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 $\tau_F \rightarrow \tau_C$

**Methods with Stationary
Interfacial Expansion:
Micellar Kinetics**



$$\theta \equiv \frac{h_a^2}{D_1} \dot{\alpha}$$

θ – dimensionless
expansion rate

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

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**;

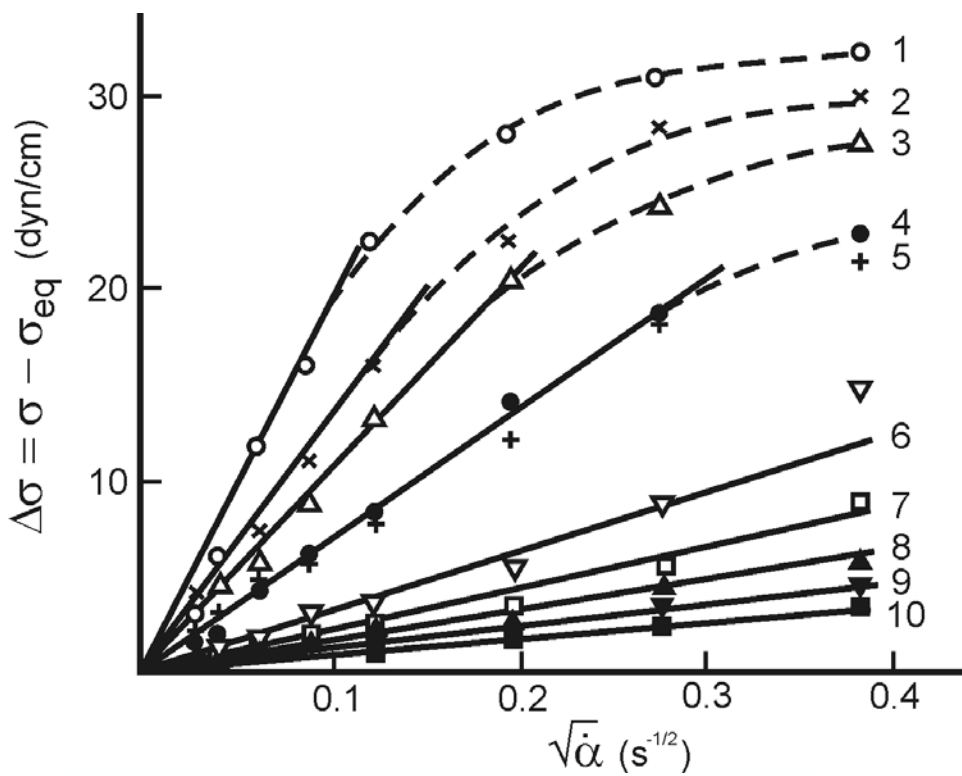
(DE) $\theta^{1/2}$ – **diffusion-limited** regime at equilibrated **both** the fast and slow micellization processes.

[Details in: K.D. Danov, P.A. Kralchevsky, et al., *Colloids & Surfaces A*, 282-283 (2006) 143-161]

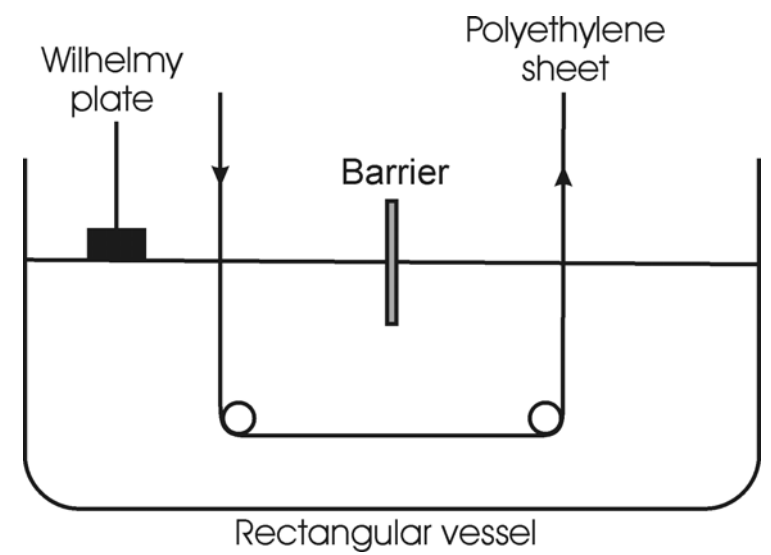
Comparison of Theory and Experiment

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

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



Different curves correspond to different micelle concentrations, β

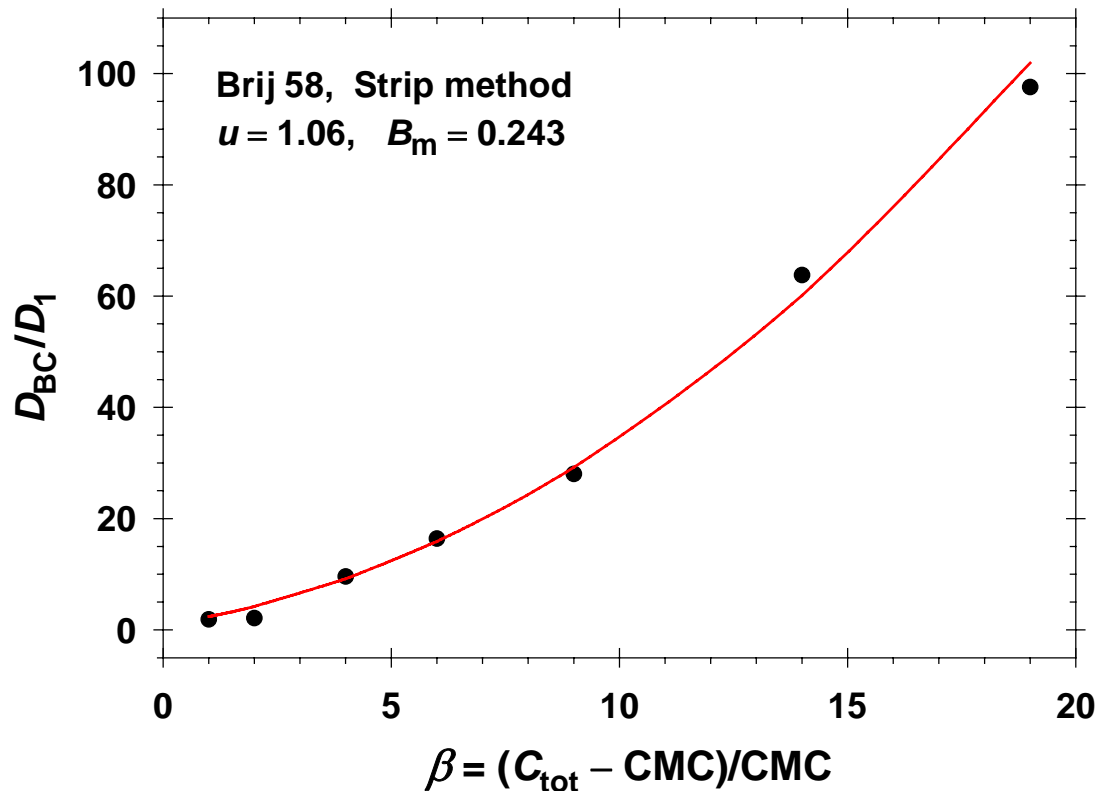


$CMC = 1.0 \times 10^{-8} \text{ mol/cm}^3$
 $\Gamma_{eq} = 2.70 \times 10^{-10} \text{ mol/cm}^2 \text{ (at CMC)}$

From the slope of the plot
 $\sigma - \sigma_{eq}$ vs. $\dot{\alpha}^{1/2}$ at fixed β , one determines the apparent diffusivity $D_{BC}(\beta)$.

Comparison of Theory and Experiment (Continued)

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



$$D_{\text{BC}} \equiv D_1(1 + u\beta)(1 + u\beta B_m)$$

$$B_m = D_m / D_1 = 0.243$$

(reasonable value)

From the fit of the data, one determines: $u \equiv \sigma_{\text{eq}}^2 / m_{\text{eq}} = 1.06$

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

The obtained reasonable values confirm that the kinetic regime is BC

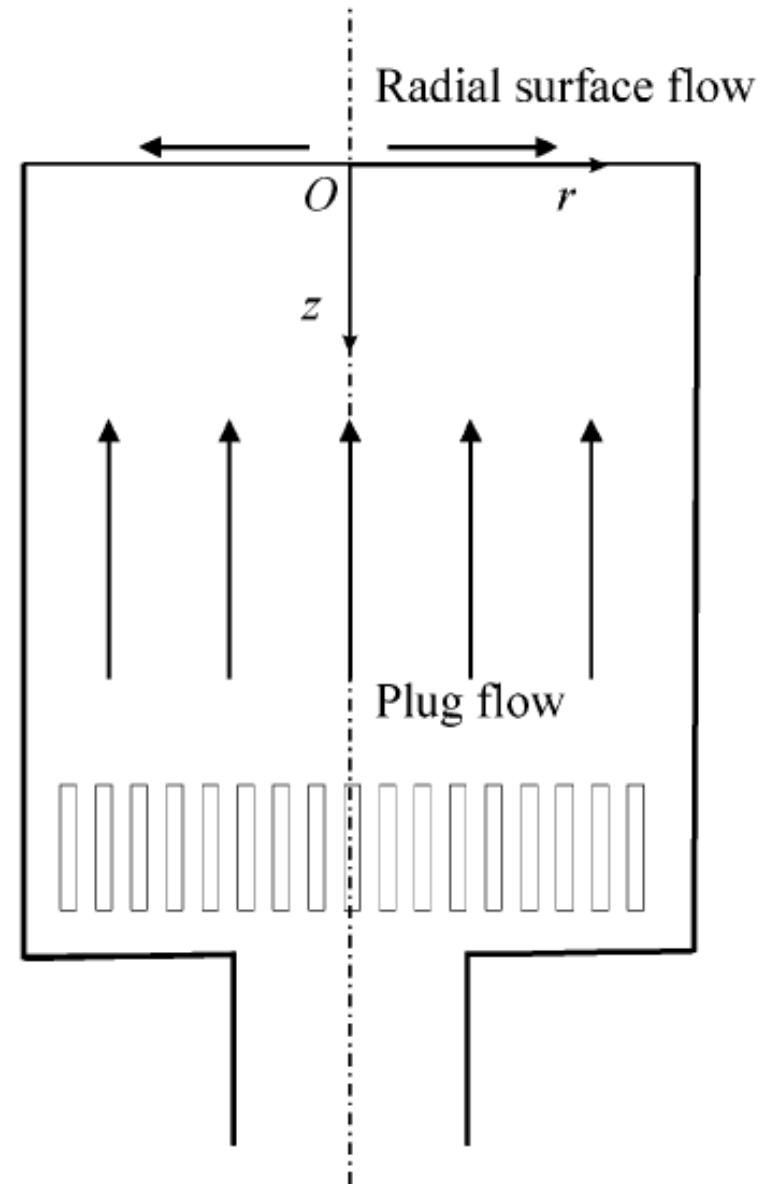
The Overflowing Cylinder Method

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.
Langmuir **2004**, *20*, 4436-4445



**Example 2: Dynamic surface tension of C₁₄TAB by the Overflowing Cylinder Method
(Colin Bain et al.; the adsorption Γ is directly measured by ellipsometry)**

The data points are not for the same β !

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

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

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

The best fit Γ vs. Y corresponds to

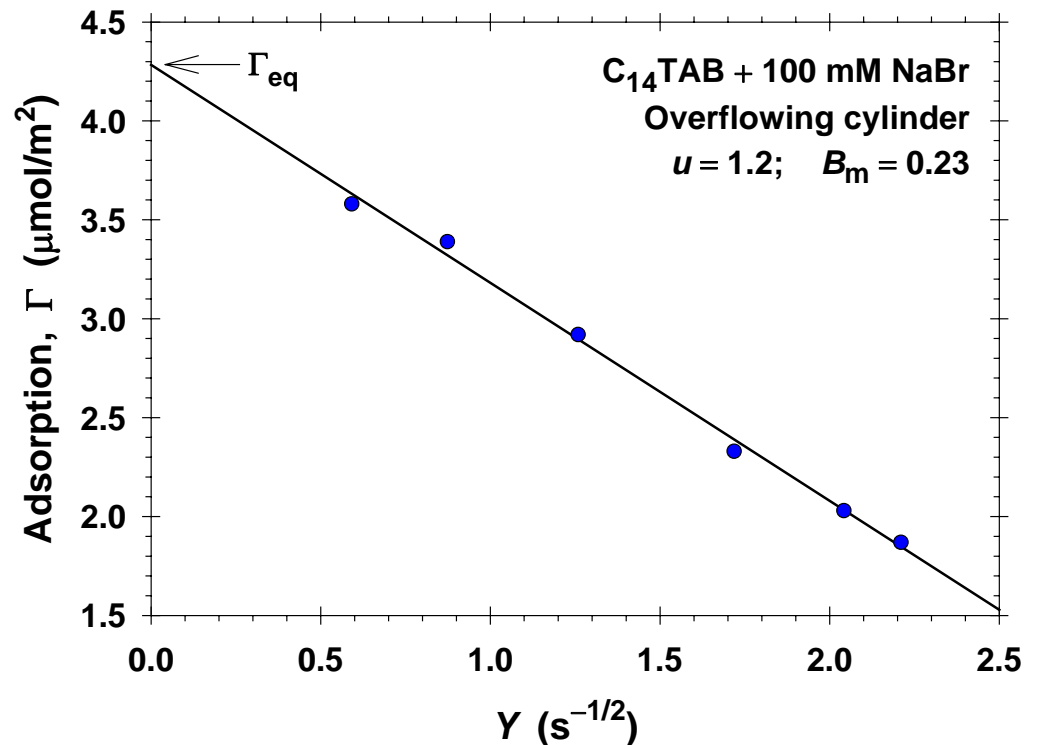
$$B_m = D_m/D_1 = 0.23 \text{ and } u = \sigma_{\text{eq}}^2/m_{\text{eq}} = 1.2$$

$m_{\text{eq}} = 80$; from $u = 1.2$ we determine that the polydispersity of the C₁₄TAB micelles is

$\sigma_{\text{eq}} = 9.8$. The obtained values of Γ_{eq} , B_m and σ_{eq} are reasonable.

This confirms that the kinetic regime is BC.

$[\tau_{\text{dif}} = h_a^2/D_1 \text{ is the characteristic diffusion time}]$

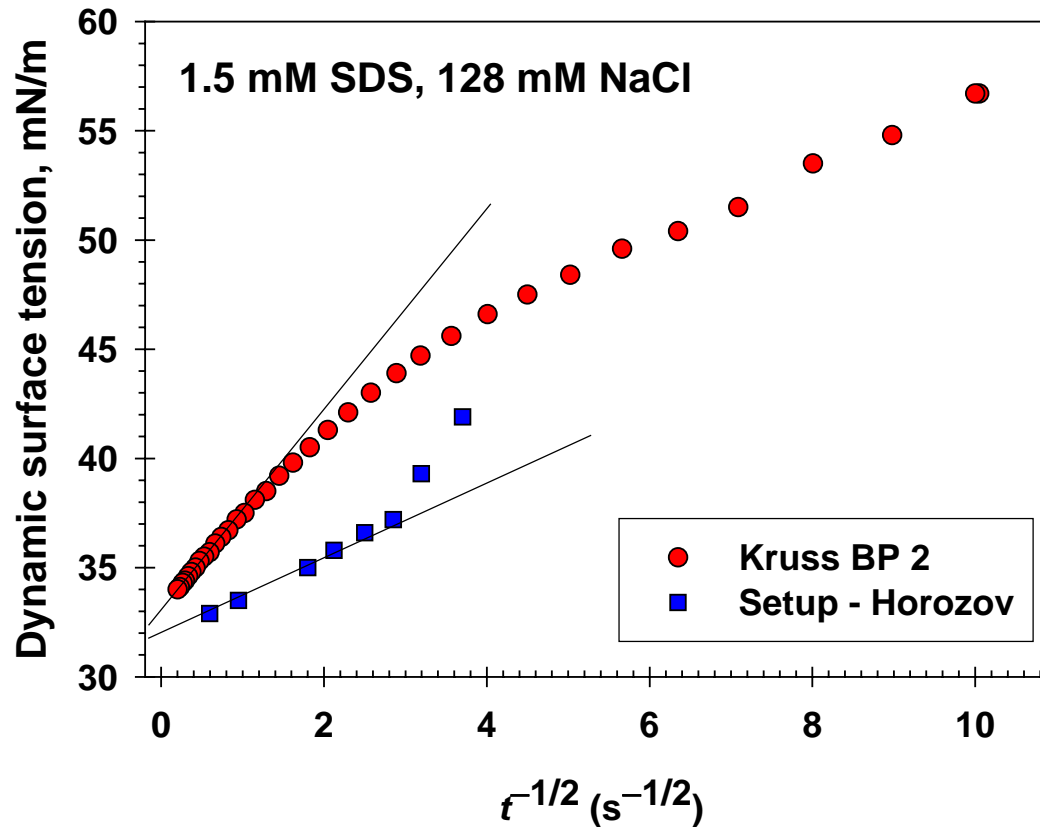


Part 3: Application of the Maximum Bubble Pressure Method

Problem: **Different** tensiometers - **different** results for the dynamic surface tension.

This difference is demonstrated with our data for two apparatuses.

The data are plotted as **DST** vs. $t^{-1/2}$:



Explanation:

Different **time-dependence, $A(t)$** , of the **bubble surface area** for different apparatuses.

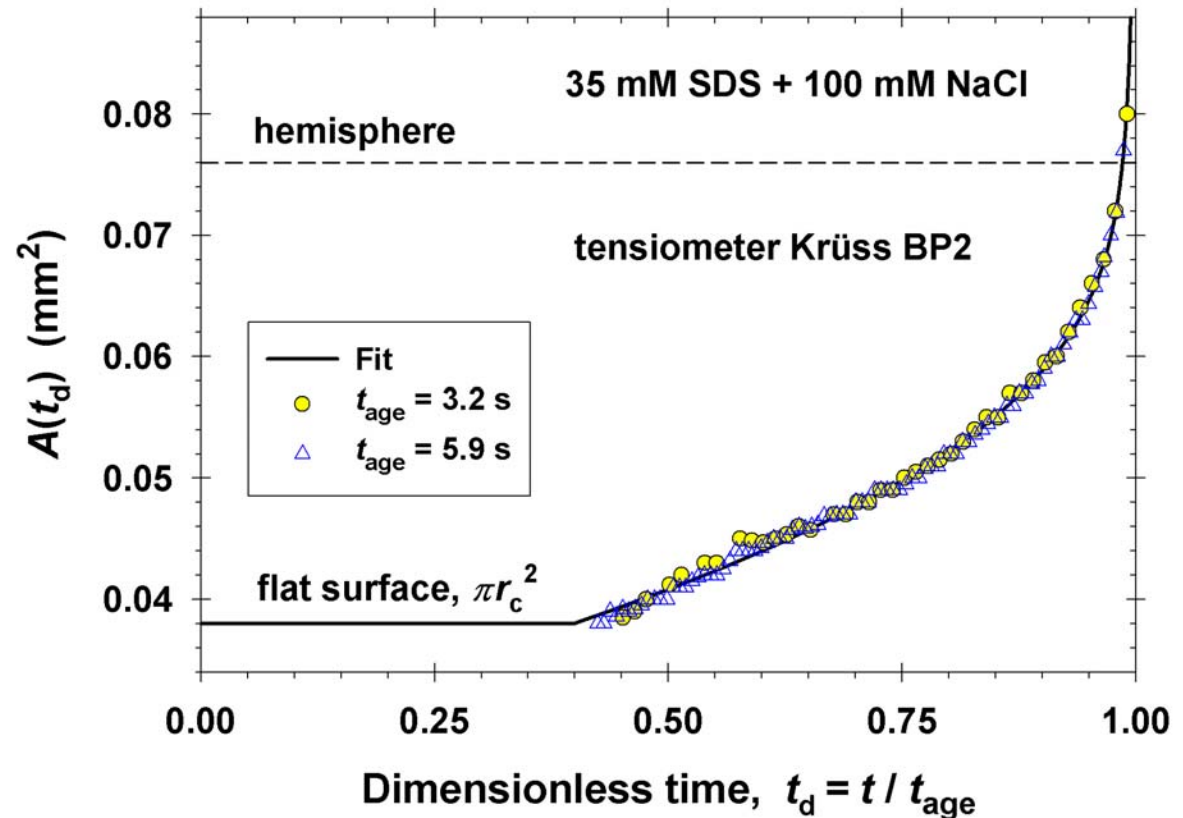
Solution of the Problem Suggested by the Experiment



The **experiment** indicates that $A(t_d)$ is independent of:

1. Bubbling period, t_{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;

λ (the apparatus **constant**) can be determined also by MBPM (**much easier!**)

Below we check whether λ is independent of t_{age} , **surfactant type** and **concentration**.

Expanding Surface vs. Immobile Surface

$$\gamma = \gamma_{\text{eq}} + \frac{s_{\gamma}}{(t_{\text{age}})^{1/2}} = \gamma_{\text{eq}} + \frac{s_{\gamma,0}\lambda}{(t_{\text{age}})^{1/2}} = \gamma_{\text{eq}} + \frac{s_{\gamma,0}}{(t_{\text{u}})^{1/2}}$$

$$s_{\gamma} = \lambda s_{\gamma,0} = \lambda \frac{kT \Gamma_{\text{eq}}^2}{(\pi D)^{1/2} c_{\infty}}, \quad t_{\text{u}} = t_{\text{age}} / \lambda^2$$

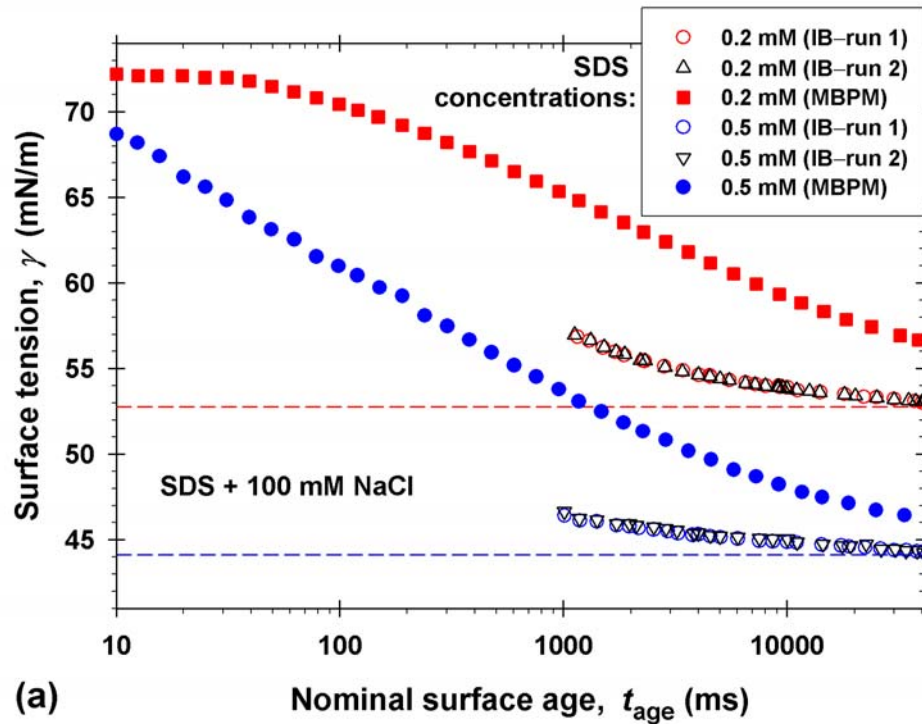
$$\lambda \equiv \int_0^1 \frac{1}{(\tau_1 - \tau)^{1/2}} \frac{d}{dt_d} \left[\frac{A(t_d)}{A_0} \right] dt_d$$

$$\tau \equiv \int_0^{t_d} \frac{A^2(\hat{t}_d)}{A_0^2} d\hat{t}_d, \quad \tau_1 = \tau(t_d = 1)$$

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

(2) t_{u} (universal surface age), is the age of an (initially clean) immobile surface with the **same** γ as that registered by the MBPM tensiometer.

c_{∞} – bulk surfactant concentration; Γ_{eq} – equilibrium adsorption;
 γ_{eq} – equilibrium surface tension; D – surfactant diffusivity;
 $s_{\gamma,0}$ – the value of s_{γ} for an immobile interface.

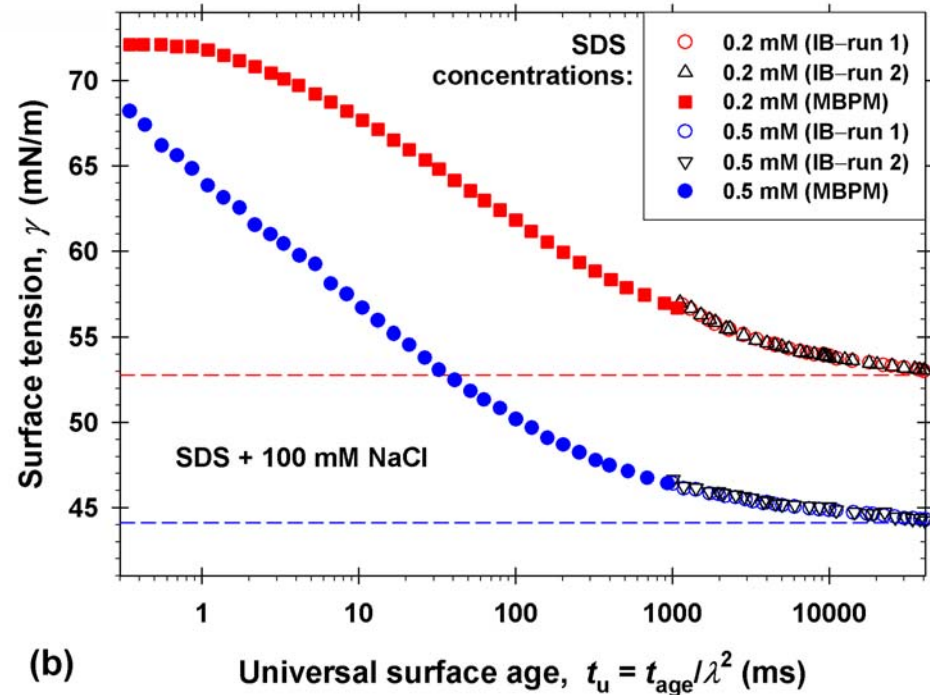


(a)

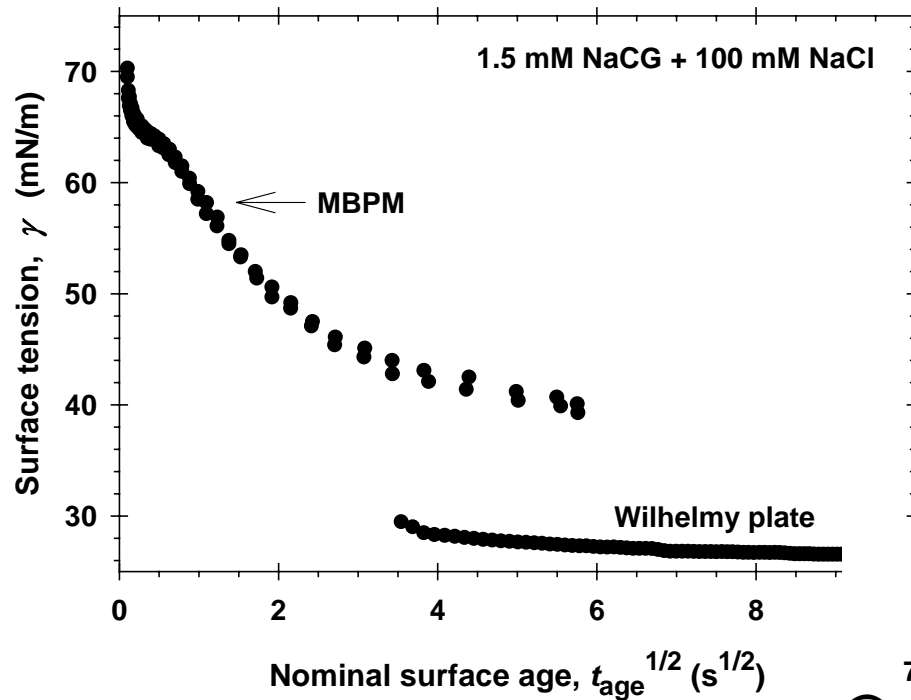
For MBPM $\lambda = 6.074$ is determined by integration of the experimental $A(t)$ curve (for our apparatus);
 For IB we have $\lambda = 1$ (no expansion)
 $t_u = t_{age} / \lambda^2$ is used to plot the MBPM data in (b) ($\lambda^2 \approx 37$)

Example 1:

Comparison of data obtained by MBPM (expanding bubbles) with data for immobile bubbles (IB) for SDS + 100 mM NaCl.



(b)



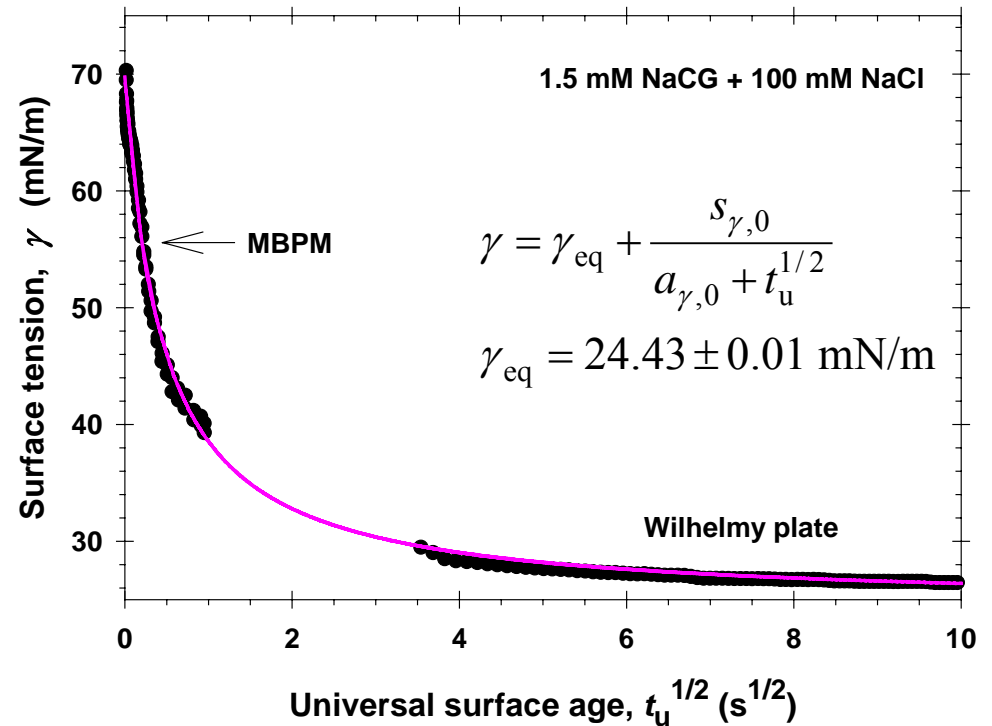
Example 2:

Comparison of data obtained by MBPM (expanding bubbles) with data from Wilhelmy plate method for Na N-Cocoylglycinate.

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

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

The excellent fit with the theoretical dependence evidences diffusion-limited adsorption kinetics.



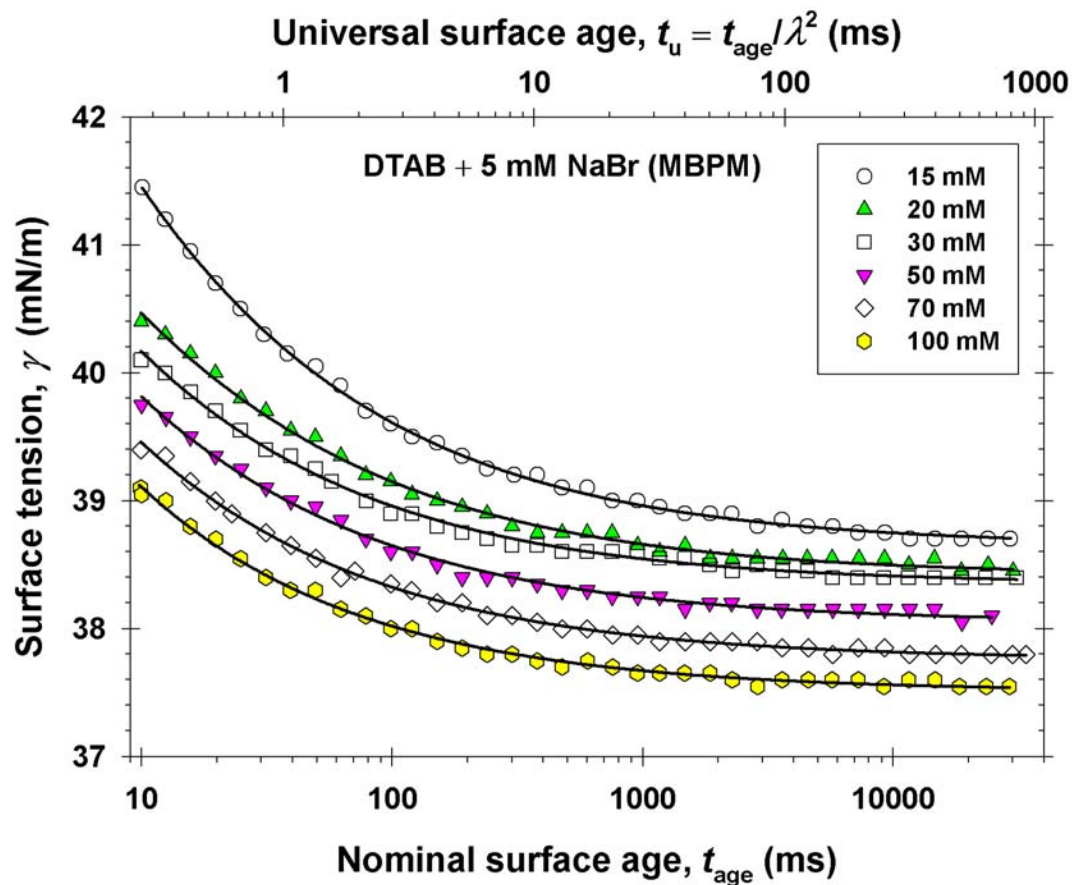
Two ways to determine the apparatus constant, λ :

(1) By integration of the experimental $A(t)$ curve;

(2) By MBPM experiments, $\lambda = s_\gamma / s_{\gamma,0}$.

(Compare the values of λ obtained in the two ways!)

$$s_{\gamma,0} = \frac{kT \Gamma_{\text{eq}}^2}{(\pi D)^{1/2} c_\infty}$$



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_γ is determined.

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

(3) $\lambda = s_\gamma / s_{\gamma,0}$

| C_{SDS} (mM) | Γ_{eq} ($\mu\text{mol}/\text{m}^2$) | $s_{\gamma,0}$ ($\text{mN}\cdot\text{m}^{-1}\cdot\text{s}^{1/2}$) | s_{γ} ($\text{mN}\cdot\text{m}^{-1}\cdot\text{s}^{1/2}$) | $\lambda = s_{\gamma}/s_{\gamma,0}$ |
|--------------------------|--|--|--|-------------------------------------|
| SDS + 10 mM NaCl | | | | |
| 0.1 | 0.91 | 0.553 | 3.36 | 6.077 |
| 0.5 | 2.65 | 0.979 | 5.95 | 6.078 |
| 1 | 3.32 | 0.796 | 4.83 | 6.066 |
| 2 | 3.76 | 0.545 | 3.31 | 6.073 |
| 3 | 3.96 | 0.423 | 2.57 | 6.075 |
| SDS + 100 mM NaCl | | | | |
| 0.2 | 3.43 | 4.560 | 27.7 | 6.074 |
| 0.5 | 3.86 | 2.316 | 14.0 | 6.046 |
| 0.75 | 4.00 | 1.658 | 10.1 | 6.091 |
| 1 | 4.08 | 1.299 | 7.89 | 6.075 |

Theory: $\lambda = 6.074$

Average: $\lambda = 6.07 \pm 0.01$

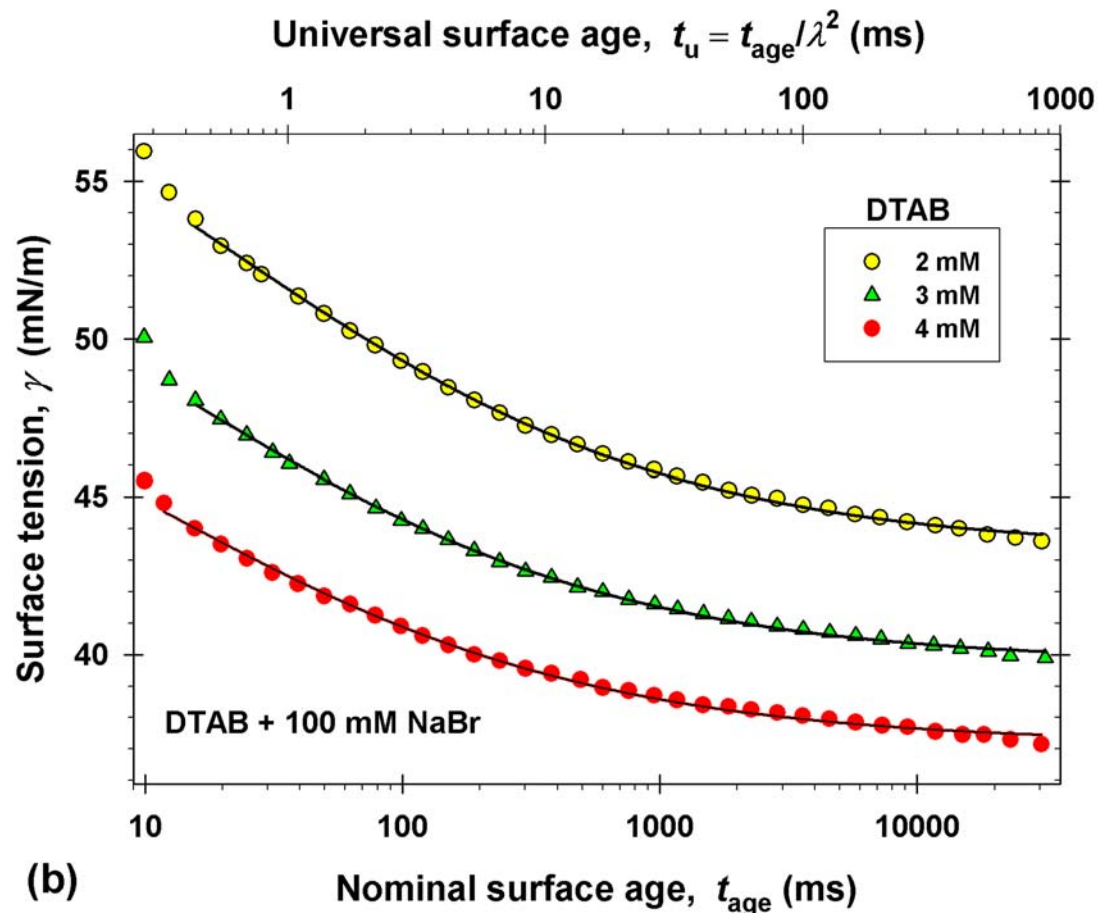
| C_{DTAB} (mM) | Γ_{eq} ($\mu\text{mol}/\text{m}^2$) | $s_{\gamma 0}$ ($\text{mN}\cdot\text{m}^{-1}\cdot\text{s}^{1/2}$) | s_{γ} ($\text{mN}\cdot\text{m}^{-1}\cdot\text{s}^{1/2}$) | $\lambda = s_{\gamma}/s_{\gamma 0}$ |
|---------------------------|--|--|--|-------------------------------------|
| DTAB + 5 mM NaBr | | | | |
| 1 | 1.69 | 0.222 | 1.35 | 6.083 |
| 2 | 2.36 | 0.236 | 1.43 | 6.057 |
| 3 | 2.68 | 0.217 | 1.32 | 6.079 |
| 5 | 3.01 | 0.178 | 1.08 | 6.060 |
| 7 | 3.18 | 0.150 | 0.912 | 6.075 |
| 10 | 3.33 | 0.122 | 0.738 | 6.066 |
| 12 | 3.40 | 0.108 | 0.657 | 6.069 |
| DTAB + 100 mM NaBr | | | | |
| 2 | 3.26 | 0.438 | 2.66 | 6.068 |
| 3 | 3.35 | 0.312 | 1.89 | 6.068 |
| 4 | 3.41 | 0.244 | 1.48 | 6.075 |

Theory: $\lambda = 6.074$

Average: $\lambda = 6.07 \pm 0.01$

Conclusions: The results confirm the concept about the apparatus constant:

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



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

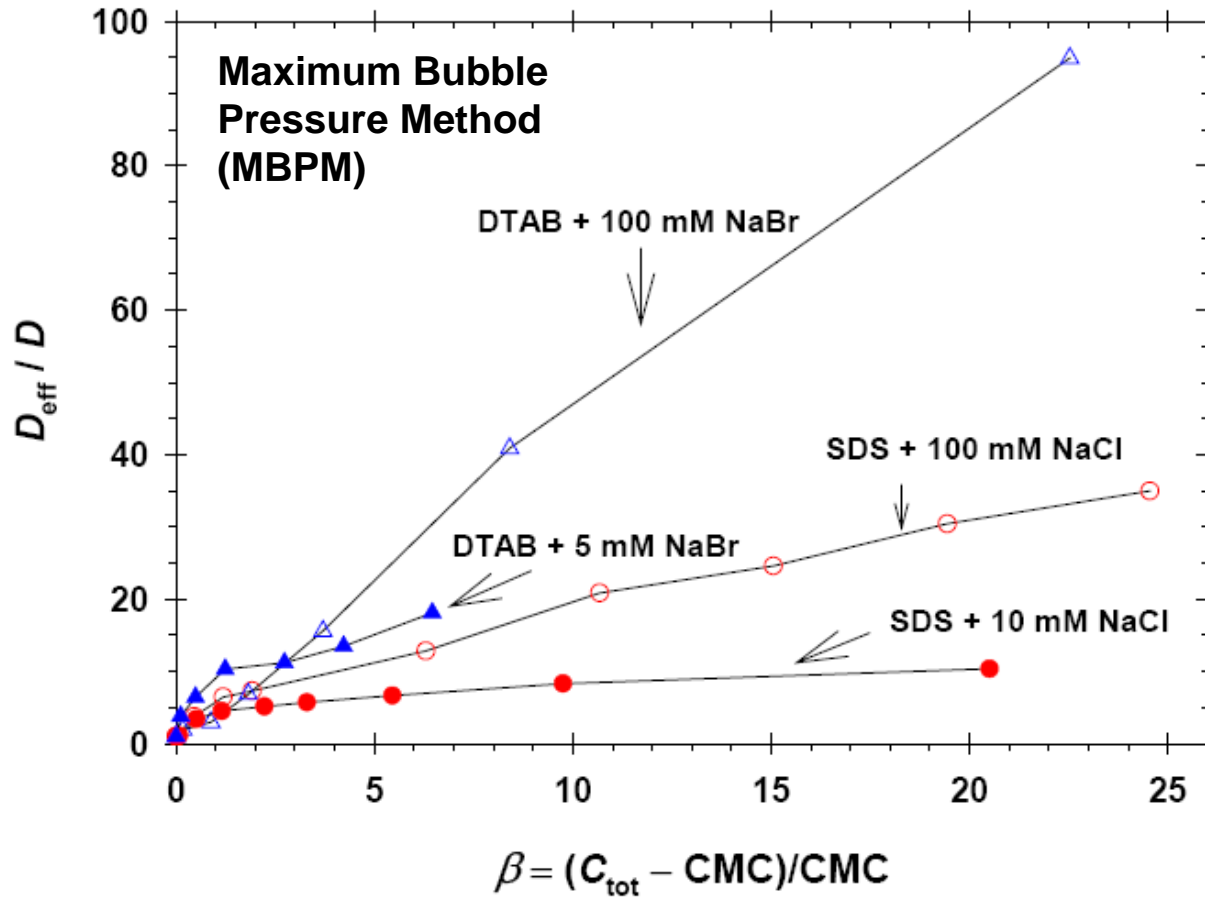
$$\lambda^2 = (6.07)^2 \approx 37$$

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

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

Details in: Christov et al., *Langmuir* 22 (2006) 7528.

Plot of the dimensionless effective diffusivity of micellar solutions, D_{eff}/D , vs. β



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

D – diffusivity of surfactant monomers.

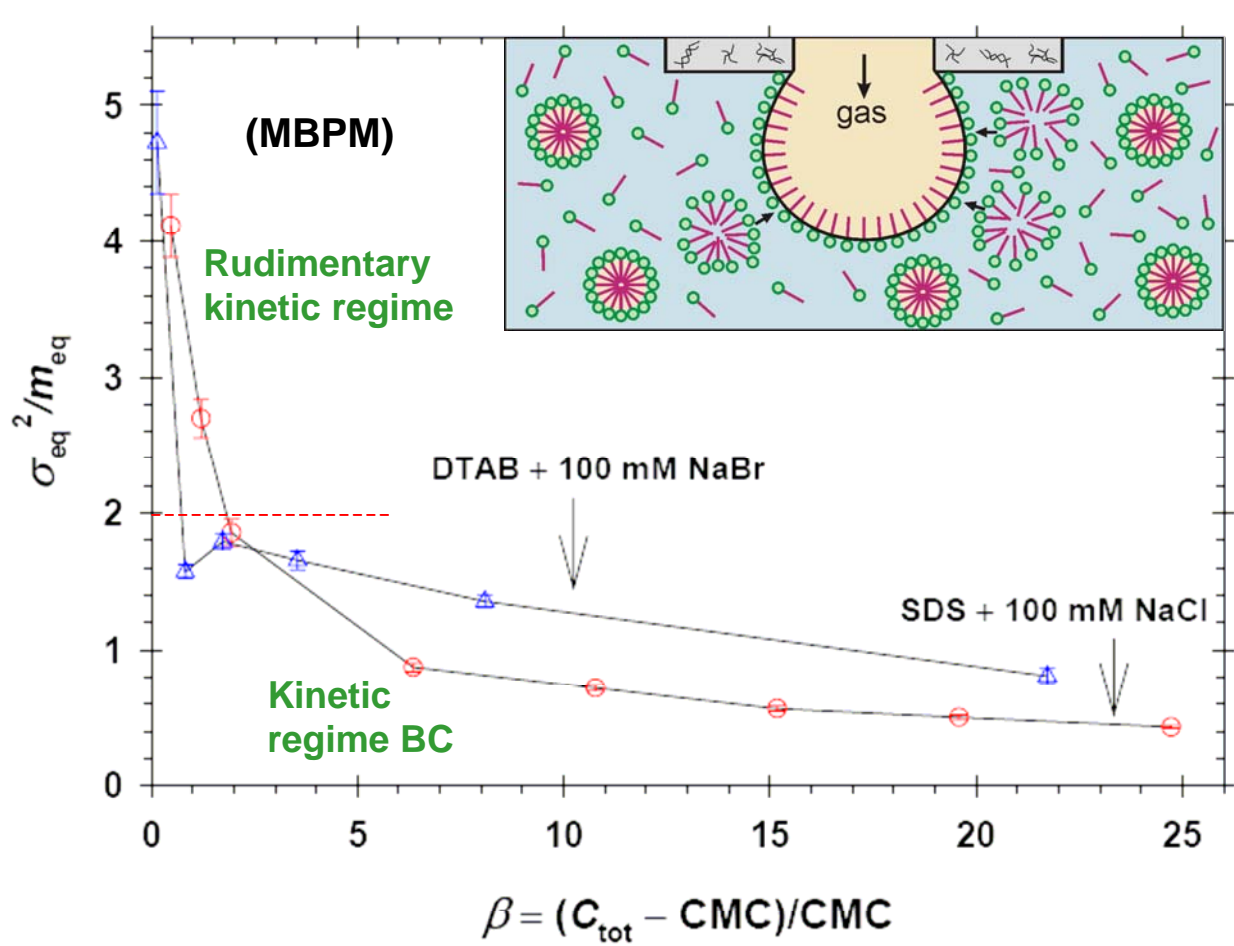
The data for $\gamma(t)$ are fitted well with the expression for diffusion-limited adsorption:

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

$$\frac{D_{\text{eff}}}{D} = \frac{D_{\text{BC}}}{D} = \left(1 + \frac{\sigma_{\text{eq}}^2}{m_{\text{eq}}} \beta\right) \left(1 + \frac{\sigma_{\text{eq}}^2}{m_{\text{eq}}} \frac{D_{\text{m}}}{D} \beta\right)$$

Hence, the kinetic regime is either BC or DE. The data complies with BC!

Plot of Plot of σ_{eq}^2 vs. β calculated from the data for D_{eff}/D



m_{eq} – micelle mean aggregation number;

σ_{eq} – micelle polydispersity

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)

Reasonable parameter values \Rightarrow the kinetic regime is BC

Summary and Conclusions

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**, λ , 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:

1. K.D. Danov, P.A. Kralchevsky, N.D. Denkov, K.P. Ananthapadmanabhan, and A. Lips, “**Mass Transport in Micellar Surfactant Solutions: 1. Relaxation of Micelle Concentration, Aggregation Number and Polydispersity**”, *Adv. Colloid Interface Sci.* 119 (2006) 1-16.
2. K.D. Danov, P.A. Kralchevsky, N.D. Denkov, K.P. Ananthapadmanabhan, and A. Lips, “**Mass Transport in Micellar Surfactant Solutions: 2. Theoretical Modeling of Adsorption at a Quiescent Interface**”, *Adv. Colloid Interface Sci.* 119 (2006) 17-33.
3. K.D. Danov, P.A. Kralchevsky, K.P. Ananthapadmanabhan, and A. Lips, “**Micellar Surfactant Solutions: Dynamics of Adsorption at Fluid Interfaces Subjected to Stationary Expansion**”, *Colloids & Surfaces A*, 282-283 (2006) 143-161.
4. N.C. Christov, K.D. Danov, P.A. Kralchevsky, K.P. Ananthapadmanabhan, and A. Lips, “**The Maximum Bubble Pressure Method: Universal Surface Age and Transport Mechanisms in Surfactant Solutions**”, *Langmuir* 22 (2006) 7528-7542.
5. K.D. Danov, P.A. Kralchevsky, K.P. Ananthapadmanabhan, and A. Lips, “**Influence of Electrolytes on the Dynamic Surface Tension of Ionic Surfactant Solutions: Expanding and Immobile Interfaces**”, *J. Colloid Interface Sci.* (2006) in press.