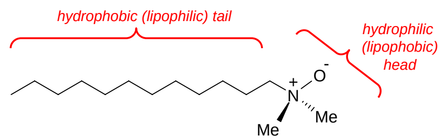
Surfactants:
Structure and Properties

Boris Zhmud, Ph.D., Assoc.Prof.

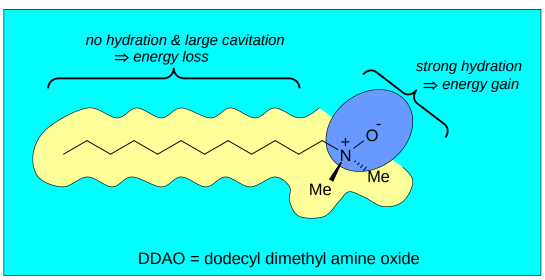
Sveacon® Consulting Company

Molecular Aspects of Surface Activity



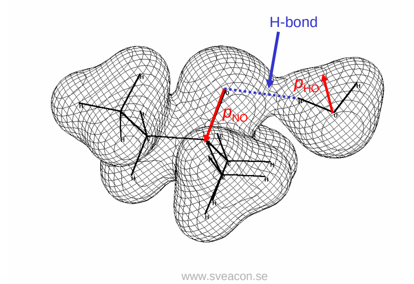
DDAO = dodecyl dimethyl amine oxide

Hydration Energy



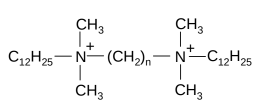
Hydration Energy Components

- Hydrogen bonding
- Static ion-dipole and higher multipole interactions
- Dispersion forces (a.k.a. van der Waals forces)

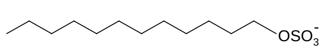


Classification of Surfactants Based on Charge

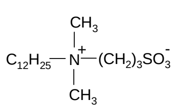
Cationic



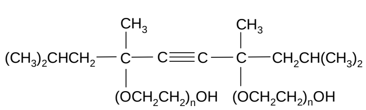
Anionic



Zwitter-ionic (amphoteric)

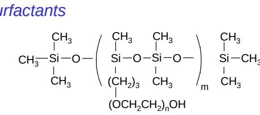


Nonionic



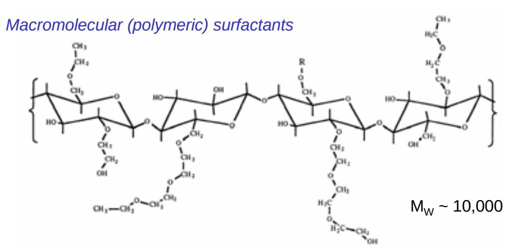
Classification of Surfactants Based on Molecular Size

Molecular surfactants



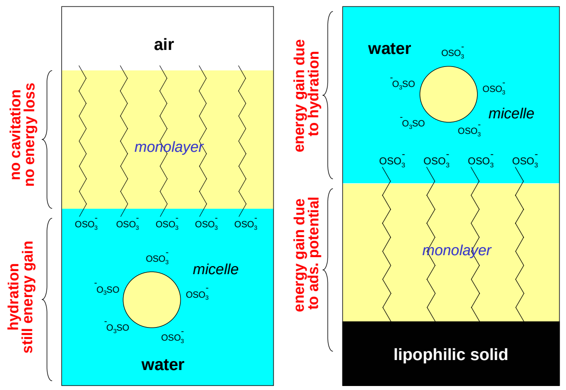
M_W ~ 100 - 1,000

Macromolecular (polymeric) surfactants



M_W ~ 10,000

Surfactant Adsorption and Energy Changes



The Gibbs Equation

$$\mathrm{d}U = \underbrace{-p\mathrm{d}V}_{\text{work done on the system}} + \underbrace{T\mathrm{d}S}_{\text{heat transferred to the system}} + \underbrace{\gamma\mathrm{d}A}_{\text{work done to stretch the surface}} + \underbrace{\sum_i \mu_i \mathrm{d}n_i}_{\text{changes in concentration of reagents}}$$

$G \equiv U + pV - TS$
$(p,V = \text{const})$

$$\mathrm{d}G = \gamma\mathrm{d}A + \sum_i \mu_i \mathrm{d}n_i$$

by integration

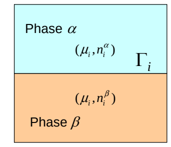
$$G = \gamma A + \sum_i \mu_i n_i$$

by differentiation

$$\mathrm{d}G = \gamma\mathrm{d}A + A\mathrm{d}\gamma + \sum_i \mu_i \mathrm{d}n_i + \sum_i n_i \mathrm{d}\mu_i$$

$$A\mathrm{d}\gamma + \sum_i n_i \mathrm{d}\mu_i = 0$$

$$\mathrm{d}\gamma = -\sum_i \Gamma_i \mathrm{d}\mu_i$$



since, by virtue of Gibbs-Duhem's equation $\sum_i n_i^\alpha \mathrm{d}\mu_i + \sum_i n_i^\beta \mathrm{d}\mu_i = 0$

www.sveacon.se

Adsorption Parameters from Surface Tension Titration

Assumptions:
- Uniform adsorption potential
- No lateral interactions
- Monolayer adsorption

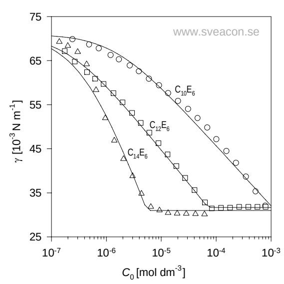
$$\mathrm{d}\gamma = -\sum_i \Gamma_i \mathrm{d}\mu_i$$

$$\Gamma(c) = \frac{\Gamma_m K c}{1 + Kc}$$

$$\gamma(c) = \gamma_0 - RT\Gamma_m \ln(1 + Kc)$$

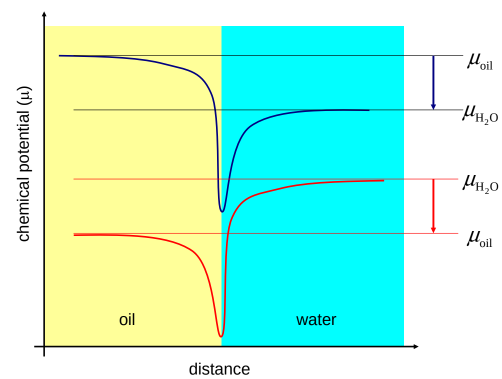
N.B. Surface tension can be negative only for solid/liquid interface.

$$\pi(c) = \gamma_0 - \gamma(c) > 0$$

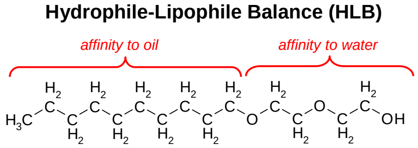


$C_{10}E_6$
$K = 7\cdot10^{5}$ dm³ mol⁻¹, $\Gamma_m = 2.4\cdot10^{-6}$ mol m⁻²
$C_{12}E_6$
$K = 5\cdot10^{6}$ dm³ mol⁻¹, $\Gamma_m = 2.7\cdot10^{-6}$ mol m⁻²
$C_{14}E_6$
$K = 3\cdot10^{6}$ dm³ mol⁻¹, $\Gamma_m = 6\cdot10^{-6}$ mol m⁻²

Adsorption Potential



Hydrophile-Lipophile Balance (HLB)



Functional Group	Contribution
Hydrophilic	
COO⁻	19.1
Ester	2.4
Hydroxyl (alcohols, glycols)	1.9
Hydroxyl (carbohydrates)	0.5
Lipophilic	
CH, CH_2, CH_3	0.475

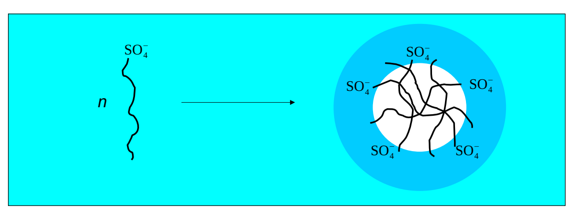
HLB = Σ (*hydrophilic group contributions*) - Σ (*lipophilic group contributions*) + 7

(very hydrophobic) 0 < HLB < 20 (very hydrophilic)

solubility in oil *solubility in water*

www.sveacon.se

Micellisation



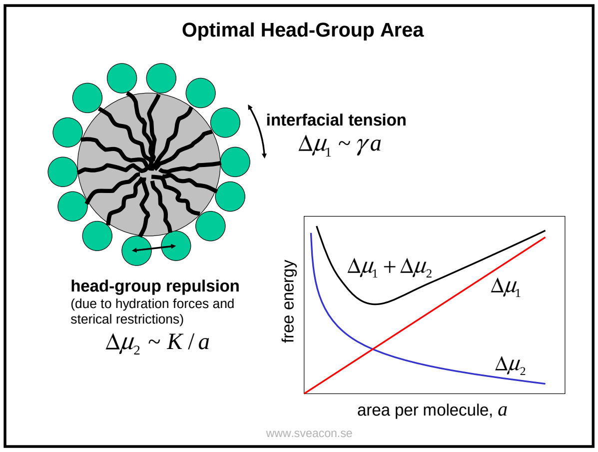
Oil-water transfer free energy:

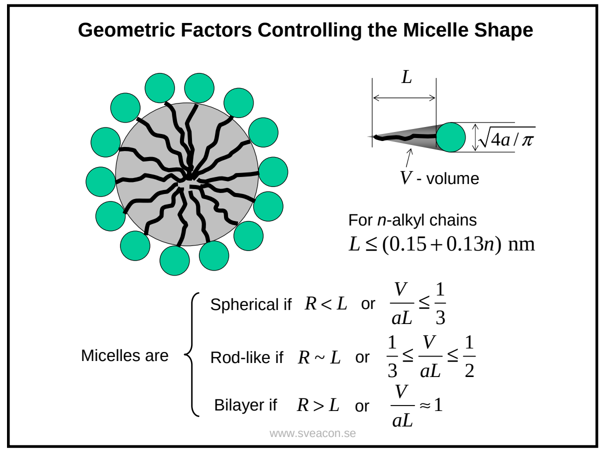
large negative for non-polar tail

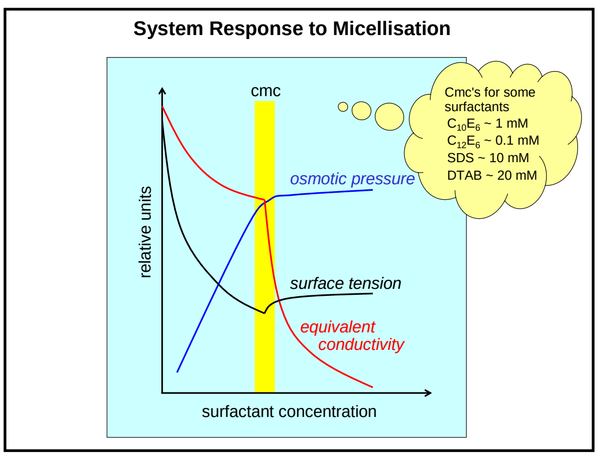
$$\Delta G = n(\mu_{H_2O} - \mu_{oil})$$

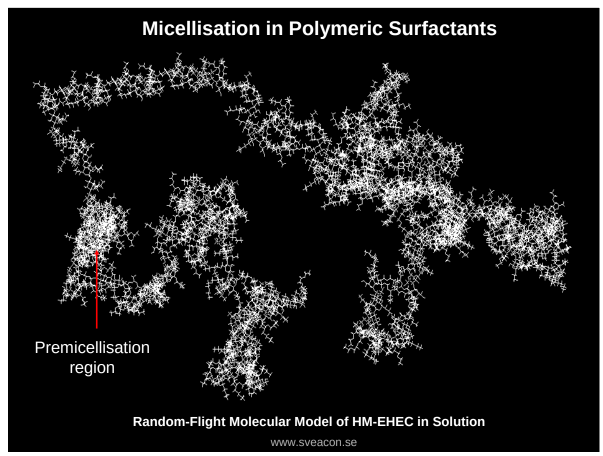
large negative for polar head

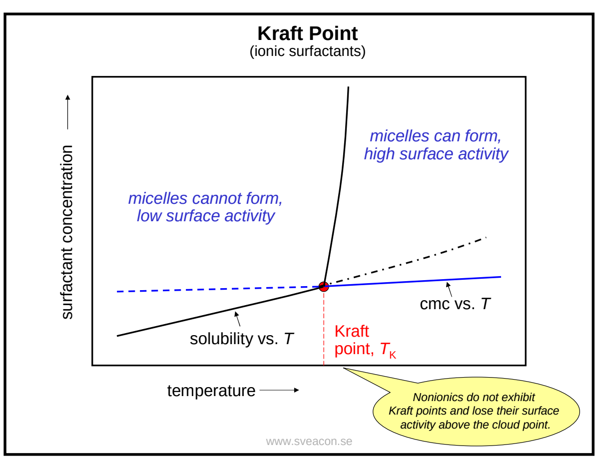
www.sveacon.se

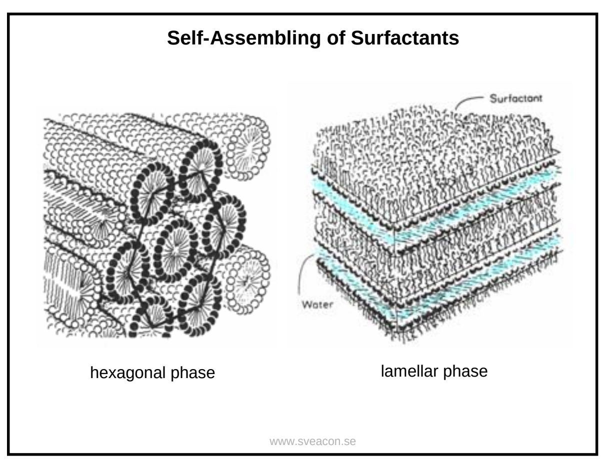

Optimal Head-Group Area
interfacial tension
$\Delta\mu_1 \sim \gamma a$
head-group repulsion
(due to hydration forces and sterical restrictions)
$\Delta\mu_2 \sim K / a$
free energy
$\Delta\mu_1 + \Delta\mu_2$
$\Delta\mu_1$
$\Delta\mu_2$
area per molecule, a
www.sveacon.se


Geometric Factors Controlling the Micelle Shape
L
$\sqrt{4a/\pi}$
V - volume
For n-alkyl chains
$L \le (0.15 + 0.13n)$ nm
Micelles are
Spherical if $R < L$ or $\frac{V}{aL} \le \frac{1}{3}$
Rod-like if $R \sim L$ or $\frac{1}{3} \le \frac{V}{aL} \le \frac{1}{2}$
Bilayer if $R > L$ or $\frac{V}{aL} \approx 1$
www.sveacon.se

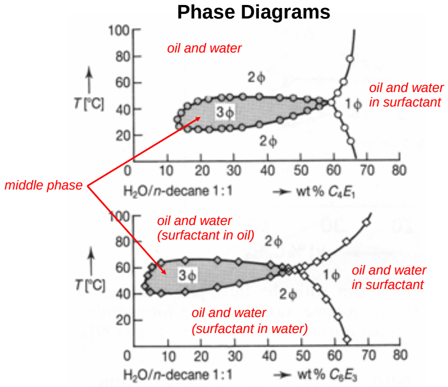

System Response to Micellisation
cmc
Cmc's for some surfactants
$C_{10}E_6$ ~ 1 mM
$C_{12}E_6$ ~ 0.1 mM
SDS ~ 10 mM
DTAB ~ 20 mM
osmotic pressure
relative units
surface tension
equivalent conductivity
surfactant concentration


Micellisation in Polymeric Surfactants
Premicellisation region
Random-Flight Molecular Model of HM-EHEC in Solution
www.sveacon.se


Kraft Point
(ionic surfactants)
surfactant concentration
micelles can form, high surface activity
micelles cannot form, low surface activity
cmc vs. T
solubility vs. T
Kraft point, T_K
temperature
Nonionics do not exhibit Kraft points and lose their surface activity above the cloud point.
www.sveacon.se

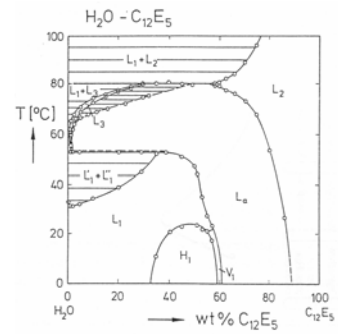

Self-Assembling of Surfactants
Surfactant
Water
hexagonal phase
lamellar phase
www.sveacon.se

Phase Diagrams



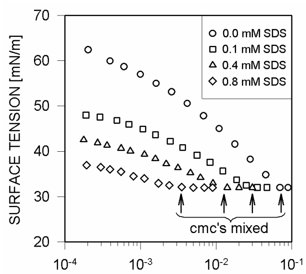
Phase diagram for decane/water/C_nE_m surfactant system (decane/water 1:1)

Phase Diagrams (cont'd)



Phase diagram of the water/$C_{12}E_5$ system: L_1, L_2, L_3 - isotropic liquid phases, H_1 - the hexagonal phase, V_1 - cubic liquid crystalline phase, L_α - lamellar phase.

Micellisation in Mixed Surfactants



Use of surface tension titration for the determination of cmc values in $C_{12}E_6$/SDS mixed surfactant solutions in 0.1 M NaCl. The cmc's of pure $C_{12}E_6$ and SDS are 0.08 mM and 1.0 mM, respectively. The interaction parameter β = -3.4 indicating attractive interaction between $C_{12}E_6$ and SDS molecules.

$$\frac{1}{\text{cmc}} = \frac{\phi_1}{\text{cmc}_1}\exp(-\beta x_2^2) + \frac{\phi_2}{\text{cmc}_2}\exp(-\beta x_1^2)$$

$$\phi_i = \frac{c_i}{c_1 + c_2} \quad (i = 1, 2)$$

$$x_1 + x_2 = 1$$

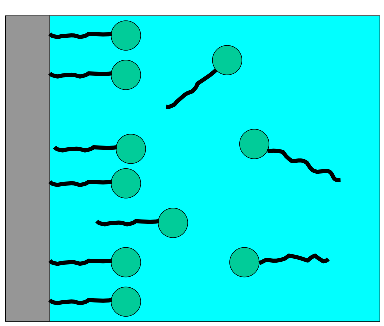
c_i - the monomer concentration for the *i*th surfactant in solution at cmc;
x_i - the mole fraction of the *i*th surfactant in the micelles;
β - the interaction parameter.

Surface Tension in Mixed Surfactants

$$\gamma(x_1, x_2, ..., x_N) - \gamma_0 = \Gamma_m \left[\underbrace{k_B T \ln\left(1 - \sum_i x_i^S\right)}_{\text{Langmuir-Szyszkowski equation}} + \underbrace{\tfrac{1}{2}\sum_i \beta_i (x_i^S)^2 + \sum_{i<j} \varepsilon_{ij} x_i^S x_j^S}_{\text{additional interaction terms}} \right]$$

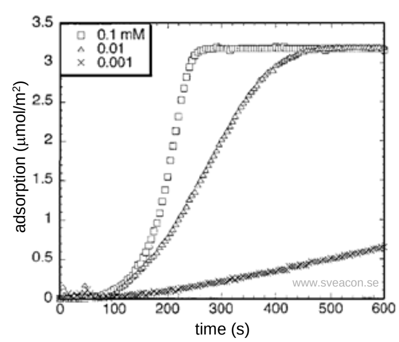
x_i - molar (weight, volume, etc.) fraction of the its surfactant in the bulk
x_i^S - the same at the surface

Adsorption Dynamics



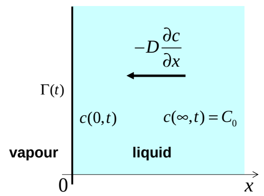
- Transport to the surface (“logistics problem”)
- Orientation at the surface (“fitting problem”)

Adsorption Dynamics (cont’d)



Adsorption of $C_{14}E_6$ surfactant to silylated silica substrate measured by ellipsometry.

Logistics Problem: The Role of Diffusion



Diffusion equation:

$$\frac{\partial c(x,t)}{\partial t}=D\frac{\partial^2 c(x,t)}{\partial x^2}$$

Initial and boundary conditions:

$$c(x,0)=C_0$$

$$D\left.\frac{\partial c}{\partial x}\right|_{x=0}=\frac{\mathrm{d}\Gamma}{\mathrm{d}t};\quad c(\infty,t)=C_0$$

Mass conservation (removed from solution = adsorbed at the interface):

$$\underbrace{\Gamma(t)\equiv f[c(0,t)]}_{\text{adsorption isotherm}}=\int_0^\infty\{C_0-c(x,t)\}\mathrm{d}x$$

For the Henry adsorption isotherm:

$$\Gamma(t)=K_H c(0,t)=\underbrace{K_H C_0}_{\Gamma_{eq}}[1-\exp(at)\mathrm{erfc}(\sqrt{at})];\quad a=\frac{D}{K_H^2}$$

www.sveacon.se

Effect of Molecular Size on Diffusivity

Einstein-Stokes equation:

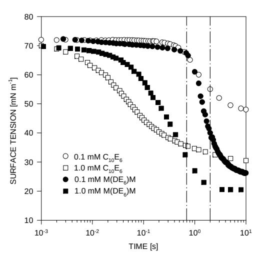
$$D\simeq\frac{k_BT}{6\pi\eta r_g}\approx\frac{k_BT}{6\pi\eta}\left(\frac{\rho N_A}{M_W}\right)^{1/3}\propto\frac{1}{M_W^{1/3}}$$

The actual effect is bigger because large molecules accept a random coil conformation in solution.

Surfactant	Mol. weight	cmc (g/L)	r_g (Å)	D (m²/s)
$C_{12}E_4$	362	0.002	10	10^{-9}
HM-HEC	400,000	1.9	690	10^{-11}
HM-PAA	5,000,000	0.37	3600	10^{-12}

www.sveacon.se

Surface Tension Relaxation

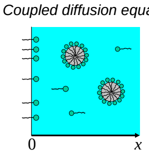


Surface tension relaxation dynamics for $C_{10}E_6$ and $((CH_3)_3SiO)_2Si(CH_3)(CH_2)_3(OCH_2CH_2)_6OH$ surfactant solutions.

www.sveacon.se

Effect of Micellisation on the Relaxation Rate

Coupled diffusion equations:



$$\begin{cases}\dfrac{\partial c_1}{\partial t}=D_1\dfrac{\partial^2 c_1}{\partial x^2}+Q(x,t)\\[2mm]\dfrac{\partial c_N}{\partial t}=D_N\dfrac{\partial^2 c_N}{\partial x^2}-Q(x,t)\end{cases}$$

due to monomers

due to micelles

c_1 - concentration of monomers (1-mers)
c_N - concentration of miceller (N-mers)

Initial conditions:

$$c_1(x,0)=\mathrm{cmc};\quad c_N(x,0)=C_0-\mathrm{cmc}$$

Boundary conditions:

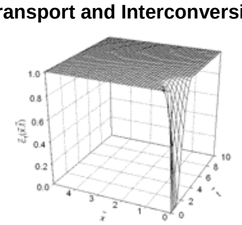
$$D_1\left.\frac{\partial c_1}{\partial x}\right|_{x=0}=\frac{\mathrm{d}\Gamma}{\mathrm{d}t};\quad D_N\left.\frac{\partial c_N}{\partial x}\right|_{x=0}=0;\quad c_1(\infty,t)=\mathrm{cmc};\quad c_N(\infty,t)=C_0-\mathrm{cmc}$$

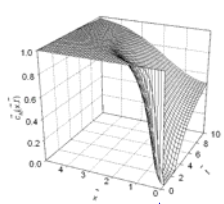
Source function:

$$\begin{aligned}Q(x,t)&=k_1(t)[\mathrm{cmc}-c_1(x,t)]c_N(x,t)-k_2(t)[(C_0-\mathrm{cmc})-c_N(x,t)]c_1(x,t)\\&=[\mathrm{cmc}-c_1(x,t)][k_1(t)c_N(x,t)+k_2(t)c_1(x,t)]\end{aligned}$$

www.sveacon.se

Transport and Interconversion of Monomers and Micelles

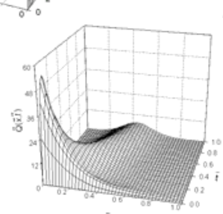




$$\tilde{c}_i=\frac{c_i}{\mathrm{cmc}}\quad(i=1,N);$$

$$\tilde{x}=\frac{x}{\sqrt{D_1\tau}};$$

$$\tilde{t}=\frac{t}{\tau}$$

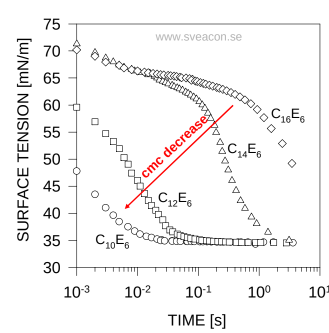


the adsorption rate is limited by slow transport of micelles

www.sveacon.se

www.sveacon.se

Effect of Micellisation on the Relaxation Rate:
Experimental Evidence



Surface tension relaxation for 10 mM aqueous solutions of hexa(ethylene glycol) monoalkyl ethers $C_nH_{2n+1}(OCH_2CH_2)_6OH$ (n = 10,12,14,16) with increasing aliphatic chain length.

Capillary Rise of Surfactant Solutions:
Diffusion-controlled dynamics

Let z-dimension of the diffusion zone be small as compared to $z(t)$.

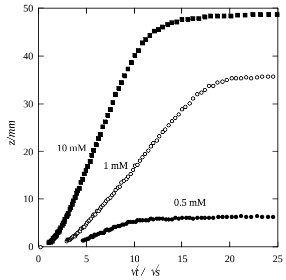
The concentration gradient,

$$\left.\frac{\partial c}{\partial \zeta}\right|_{\zeta=z} \approx -\frac{c_b}{\sqrt{Dt}}$$

Mass conservation,

$$\underbrace{2\pi r \Gamma_{ls}^{m} \mathrm{d}z}_{\text{amount adsorbed to the wall}} \approx \underbrace{\pi r^2 D \frac{c_b}{(Dt)^{1/2}} \mathrm{d}t}_{\text{amount transported to the lv interface}}$$

$$z(t) \approx \frac{r c_b}{\Gamma_{ls}^{m}} (Dt)^{1/2}$$



Recommended References

1. K.L. Mittal, E.J. Fendler, Solution Behavior of Surfactants: Theoretical and Applied Aspects, Plenum Press, New York, 1982.
2. M.J. Rosen, Surfactants and Interfacial Phenomena, Wiley, New York, 1978.
3. B. Zhmud and F. Tiberg, Interfacial Dynamics and Structure of Surfactant Layers. *Adv. Colloid Interface Sci.* 113 (2005) 21.
4. B. Zhmud, F. Tiberg, "Surfactants in Inkjet Inks" in "Surfactants in Polymers, Coatings, Inks and Adhesives" (D.R. Karsa, Ed.) Blackwell Publishing, England, 2003, chap.8.
5. F. Tiberg, B. Zhmud, K. Hallstensson, M. von Bahr, Capillary Rise of Surfactant Solutions. *Phys. Chem. Chem. Phys*. 2 (2000) 5189.
6. B. Zhmud, F. Tiberg, J. Kizling, Dynamic Surface Tension in Concentrated Solutions of C_nE_m Surfactants: A Comparison between the Theory and Experiment. *Langmuir* 16 (2000) 2557.

www.sveacon.se