Kinetics of Solubilization of Oils that are Soluble or Insoluble in Pure Water: Comparison of Theory and Experiment

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PLAN

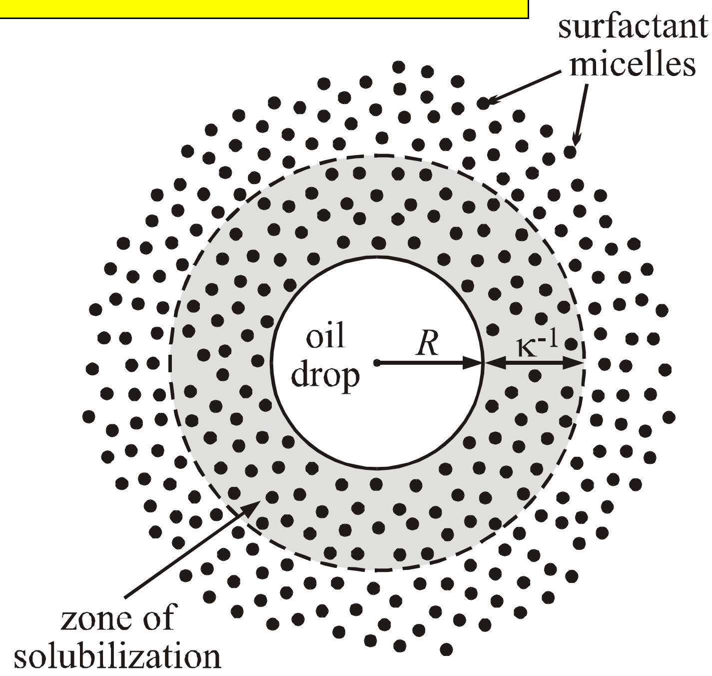
1. Mechanisms of solubilization: bulk and surface reaction;
2. Used experimental methods;
3. Solubilization of decane and benzene in solutions of SDS;
4. Triglycerides: ionic surfactants – inhibitors of solubilization;
5. Triglycerides: trb. copolymers – promoters of solubilization;

Two Major Mechanisms of Solubilization

(A) Bulk Reaction:

– the oil is soluble in pure water

– micelles capture oil molecules



Kinetic parameters:

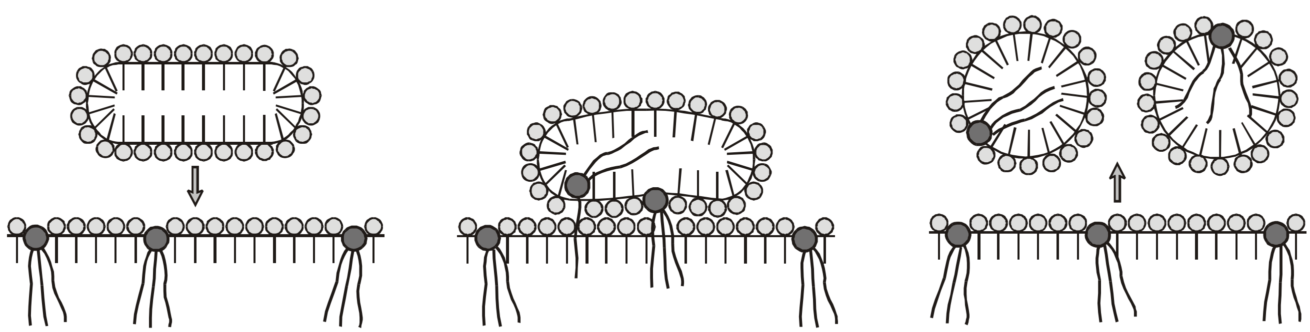
α – mass transfer coefficient

k_+ – rate constant of the reaction

{micelle} + {oil molecule}

= {swollen micelle}

(B) Surface Reaction:



(a) Micelle adsorption (b) Uptake of oil (c) Desorption

– the oil is insoluble in pure water (like the triglycerides)

– parameters of the model:

k_a – rate constant of adsorption (Stage 1)

k_s – rate constant of the surface reaction (Stage 2)

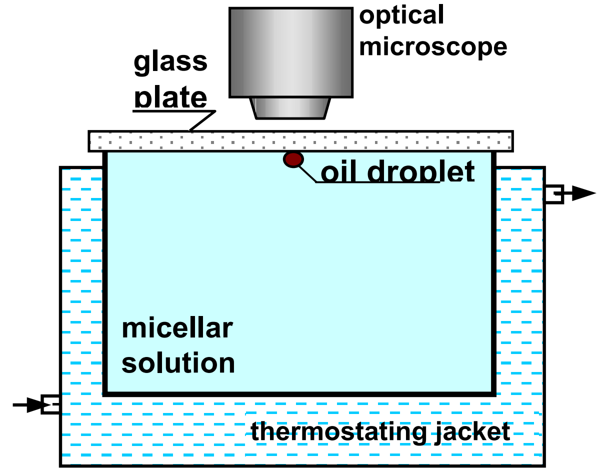
k_d – rate constant of desorption (Stage 3)

Aim of the study: to determine the kinetic parameters

Experimental Methods

1. Simple Solubilization Cell (Cell # 1)

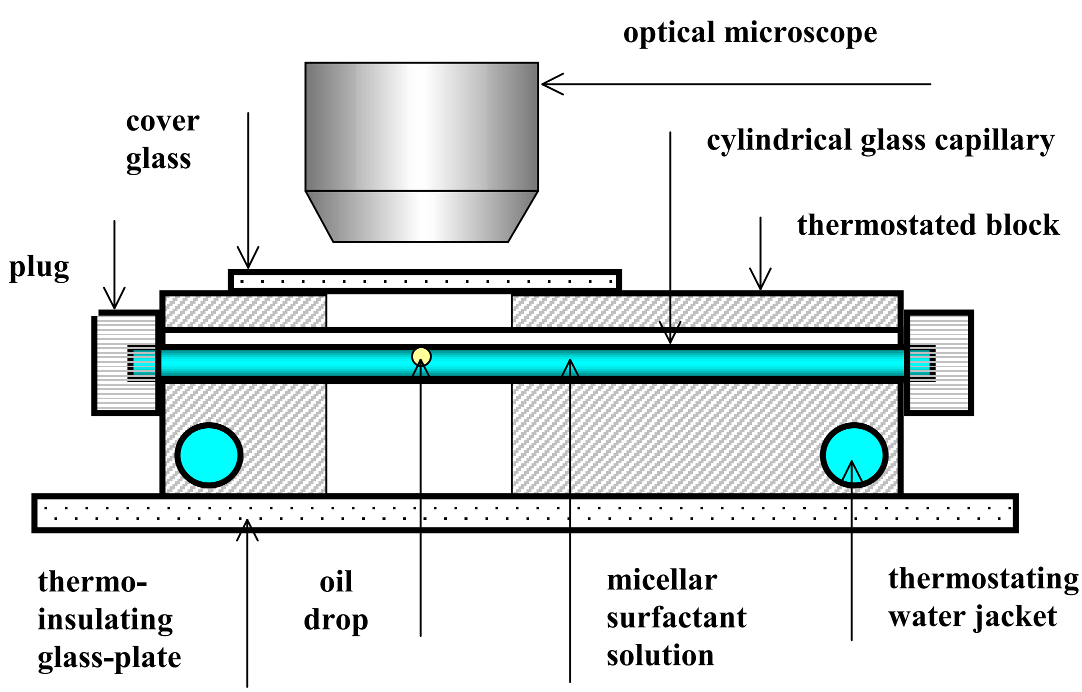
(2 × 2 × 1.5 cm)



Advantage: Easy to operate

Disadvantage: the kinetics is influenced by uncontrollable thermal convections

2. Capillary Cell (Cell # 2)



– horizontal capillary of inner diameter $2R = 0.06$ cm (= 600 μm);

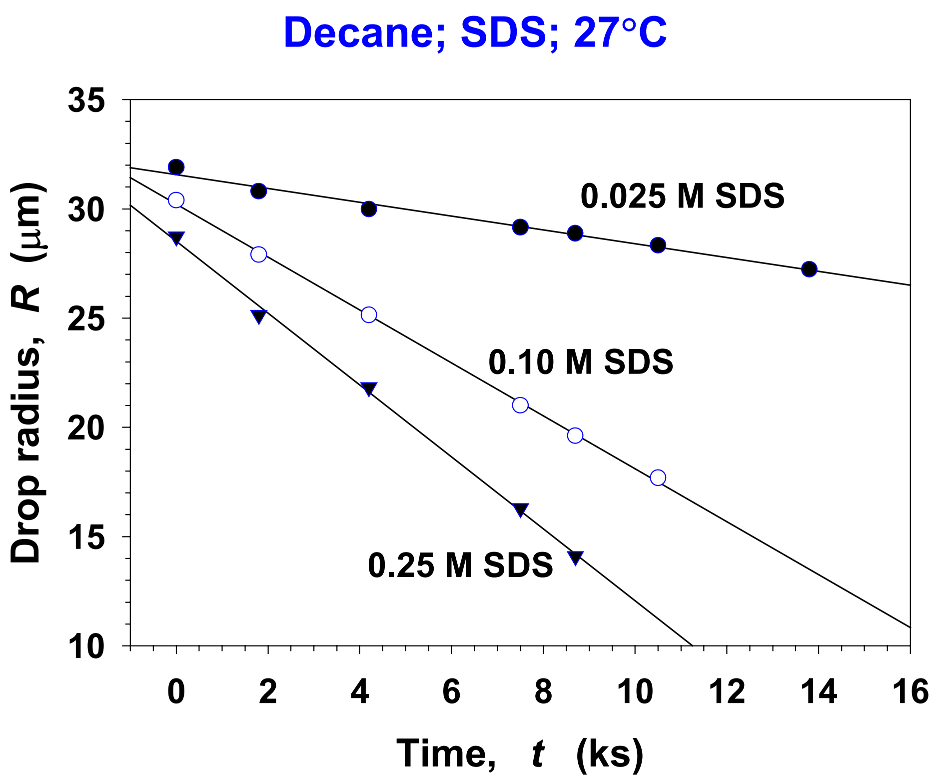
– a single oil drop is injected by syringe;

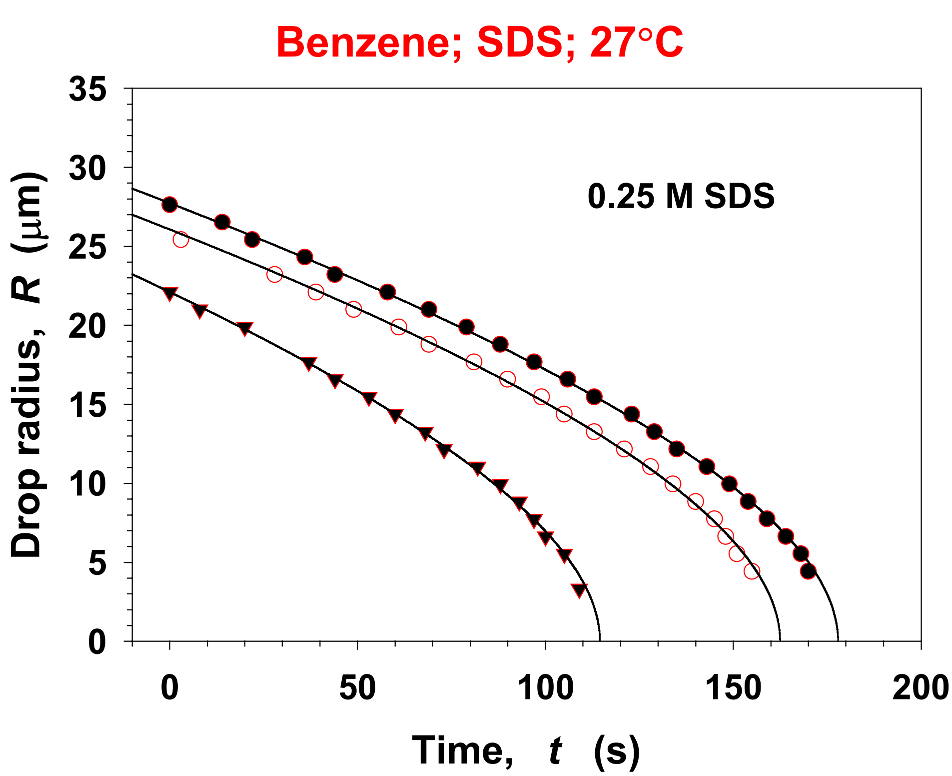
– the solubilization occurs under a purely diffusion regime (no thermal convections) ⇒ quantitative interpretation is possible.

n-Decane and Benzene in Water Solutions of SDS

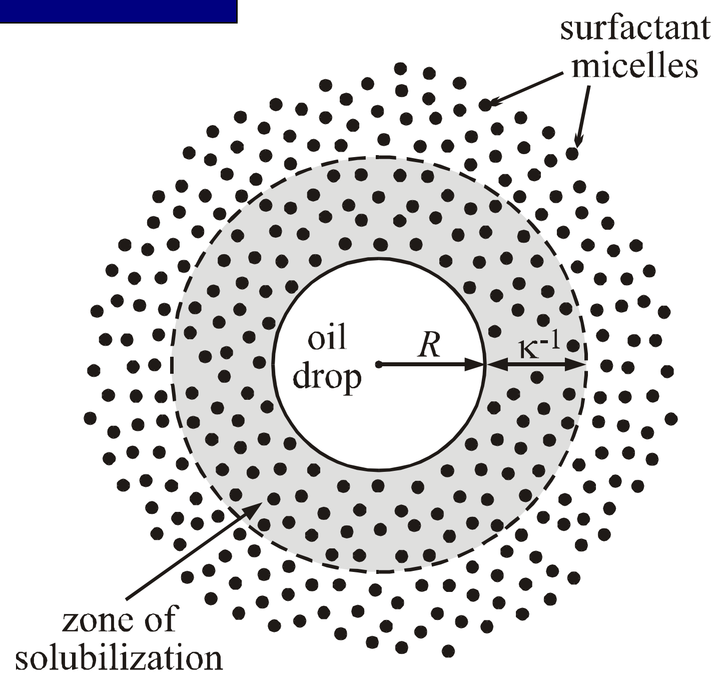
[P. D. Todorov et al. *J. Colloid Interface Sci*. **245** (2002) 371–382]

Dependence of the solubilization rate on the SDS concentration





Theoretical Model



Stationary Diffusion

+ Reaction of Solubilization:

$$D_{\mathrm{oil}} \nabla^2 c_{\mathrm{oil}} = k_+ c_{\mathrm{tot}} c_{\mathrm{oil}}$$

Boundary Condition:

$$-\left.\frac{\partial c_{\mathrm{oil}}}{\partial r}\right|_{r=R} = \alpha [c_{\mathrm{eq}} - c_{\mathrm{oil}}(R)]$$

α – **mass transfer coefficient**

$$c_{\mathrm{oil}}(r) = \frac{c_{\mathrm{eq}} R}{1 + (\kappa + R^{-1})/\alpha} \frac{\exp[\kappa(R-r)]}{r} \qquad \kappa^2 = k_+ c_{\mathrm{tot}} / D_{\mathrm{oil}}$$

Solubilization Flux:

$$Q_{\mathrm{oil}} = -D_{\mathrm{oil}} \left.\frac{\partial c_{\mathrm{oil}}}{\partial r}\right|_{r=R}$$

Diminishing of the Drop Volume:

$$-\frac{dV}{dt} = \mathrm{v}_{\mathrm{oil}} (4\pi R^2) \lambda Q_{\mathrm{oil}}$$

$\mathrm{v}_{\mathrm{oil}}$ – **volume per oil molecule;** **Wall:**

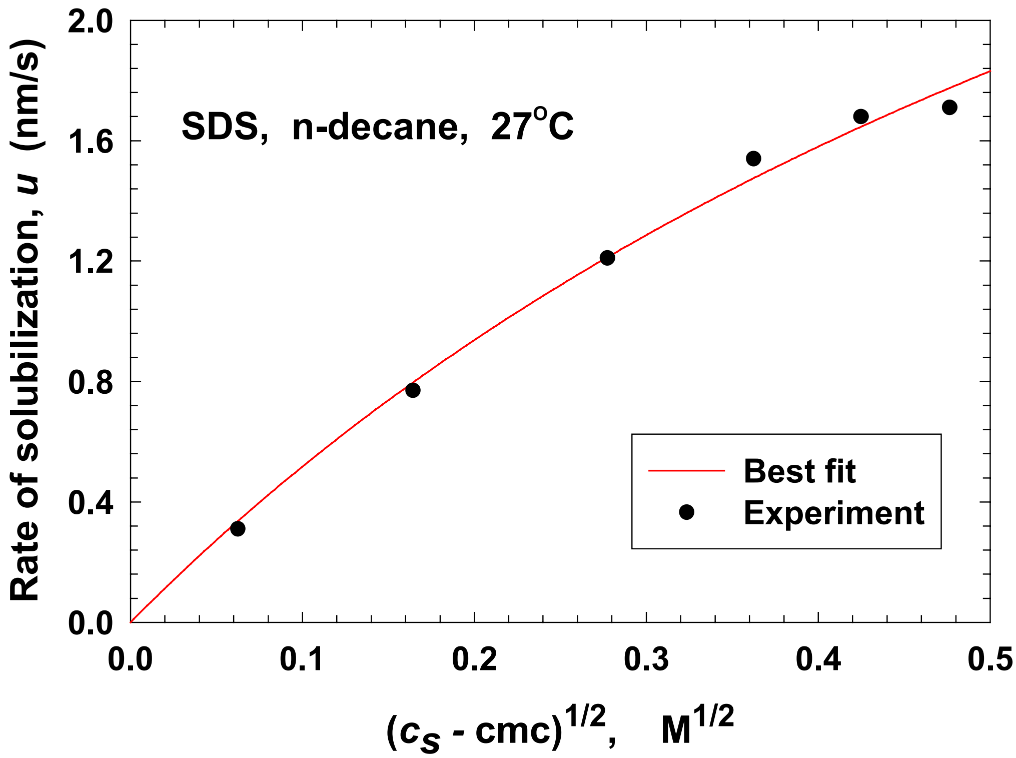
$$\lambda \approx \frac{0.9 + 4.725\,\kappa R + 2.1(\kappa R)^2}{1 + 5.25\,\kappa R + 2.1(\kappa R)^2}$$

$$\frac{dR}{dt} = -\frac{\alpha\beta(1+\kappa R)}{1 + (\alpha + \kappa)R} \lambda(\kappa R), \qquad \beta = \mathrm{v}_{\mathrm{oil}} D_{\mathrm{oil}} c_{\mathrm{eq}}$$

Results for n-Decane

In the limit $\kappa R >> 1$ $\Rightarrow$ $-\frac{dR}{dt} \approx \text{const.} \equiv u = \frac{a(c_s - \text{cmc})^{1/2}}{b + (c_s - \text{cmc})^{1/2}}$

(narrow solubilization zone)



From the fit we determine:

$\alpha = 29.8 \pm 5.8$ (μm^{-1})

(mass transfer coefficient)

$k_+ = (1.02 \pm 0.34) \times 10^{-13}$ (cm^3/s)

(rate constant: oil uptake by micelles)

SDS concentration c_s (M)	Solubilization rate u (nm/s)	Width of solubilization zone: κ^{-1} (nm)
0.025	0.31	267
0.25	1.71	61

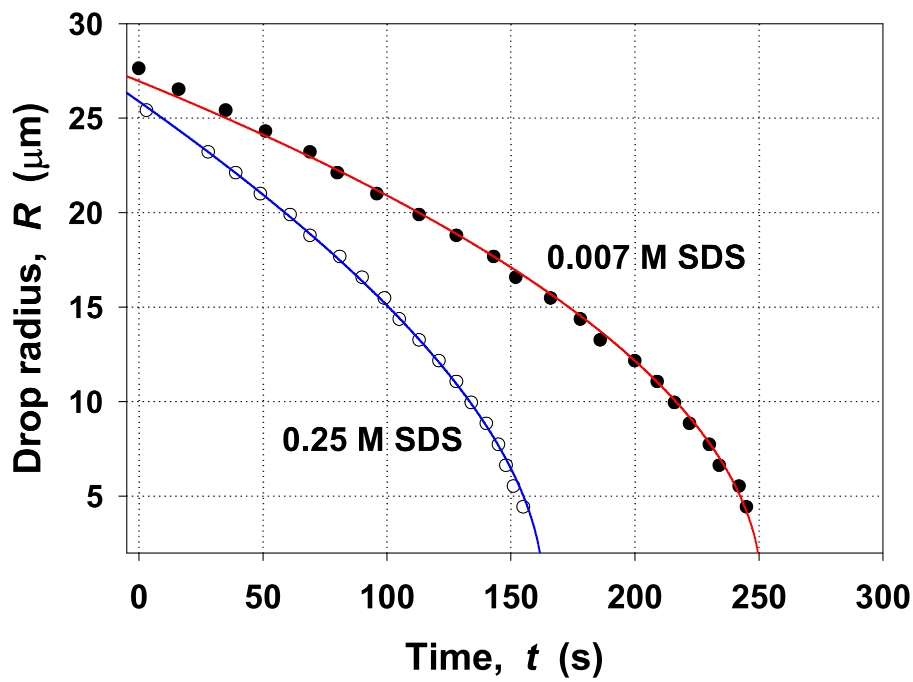
Results for Benzene

Fast dissolution of benzene in water $\Rightarrow \quad \alpha \to \infty, \qquad c_{\text{oil}}\big|_{r=R} = c_{\text{eq}}$

$$\Rightarrow \qquad \frac{dR}{dt} = -\frac{\beta}{R}(1+\kappa R)\lambda(\kappa R)$$

(1) Purely molecular dissolution of oil: no micellar solubilization, $\kappa = 0$**)**

$$R(t) = \sqrt{1.8\,\beta(t_0 - t)}\,, \qquad R(t_0) = 0$$ **(No adjustable parameters!)**



(2) Simultaneous molecular dissolution and micellar solubilization:

κ – adjustable parameter; $\qquad k_+ = \kappa^2 D_{\text{oil}}/c_{\text{tot}}$

Benzene: $k_+ = 2.3 \times 10^{-19}$ (cm^3/s), $\qquad \kappa^{-1} = 40.1$ μm, $\qquad$ **(0.25 M SDS)**

n-Decane: $k_+ = 1.0 \times 10^{-13}$ (cm^3/s)

Under diffusional control: $k_+ = 4\pi D_{\text{oil}}\, r_{\text{mic}} \approx 2.4 \times 10^{-11}$ (cm^3/s)

$\Rightarrow$ **Barrier control of the uptake of oil molecules by the micelles**

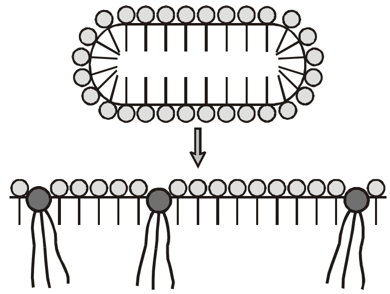
Insoluble Oils: Surface Reaction

Triglyceride solubilization by nonionic surfactant $C_{12}EO_n$ (n = 5 or 6)

A necessary step:

Micelle adsorption

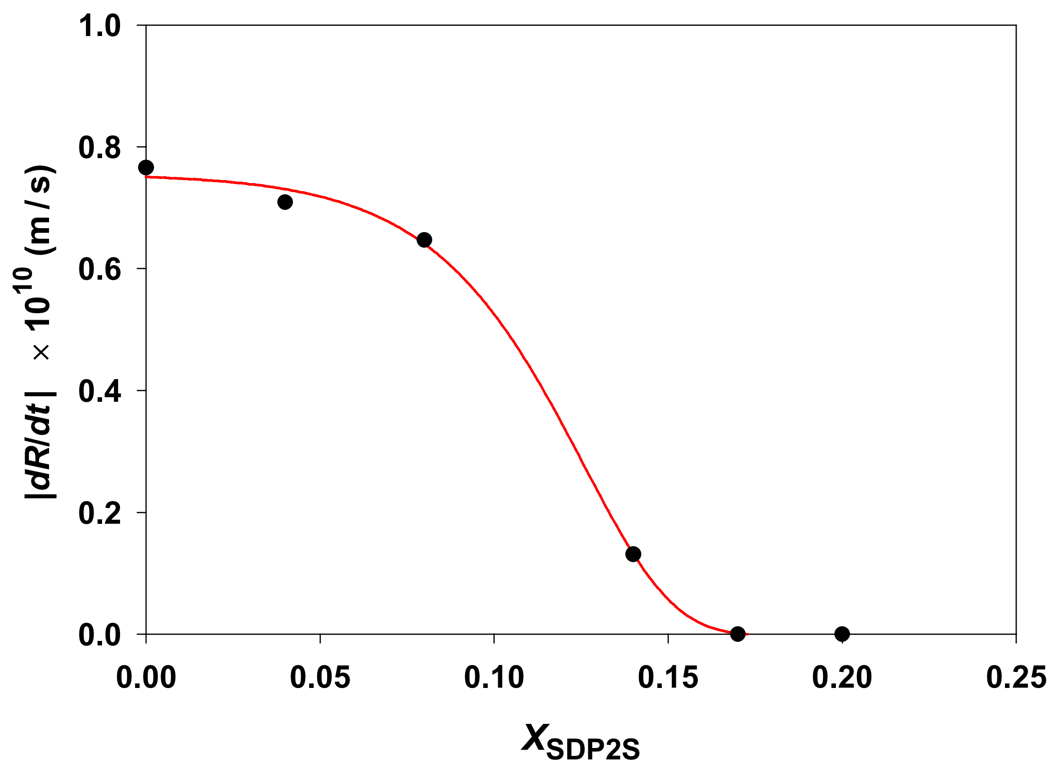
at oil/water interface



KEY: **Repulsion due to the surface electric charge suppresses the micelle adsorption and the solubilization.**

EXAMPLE: **(Added ionic surfactant inhibits the solubilization)**

12 mM $C_{12}E_6$ (nonionic) + SDP2S (ionic) + 0.2 M Na_2SO_4



$X_{SDP2S} = C_{SDP2S}/(C_{C12EO6} + C_{SDP2S})$

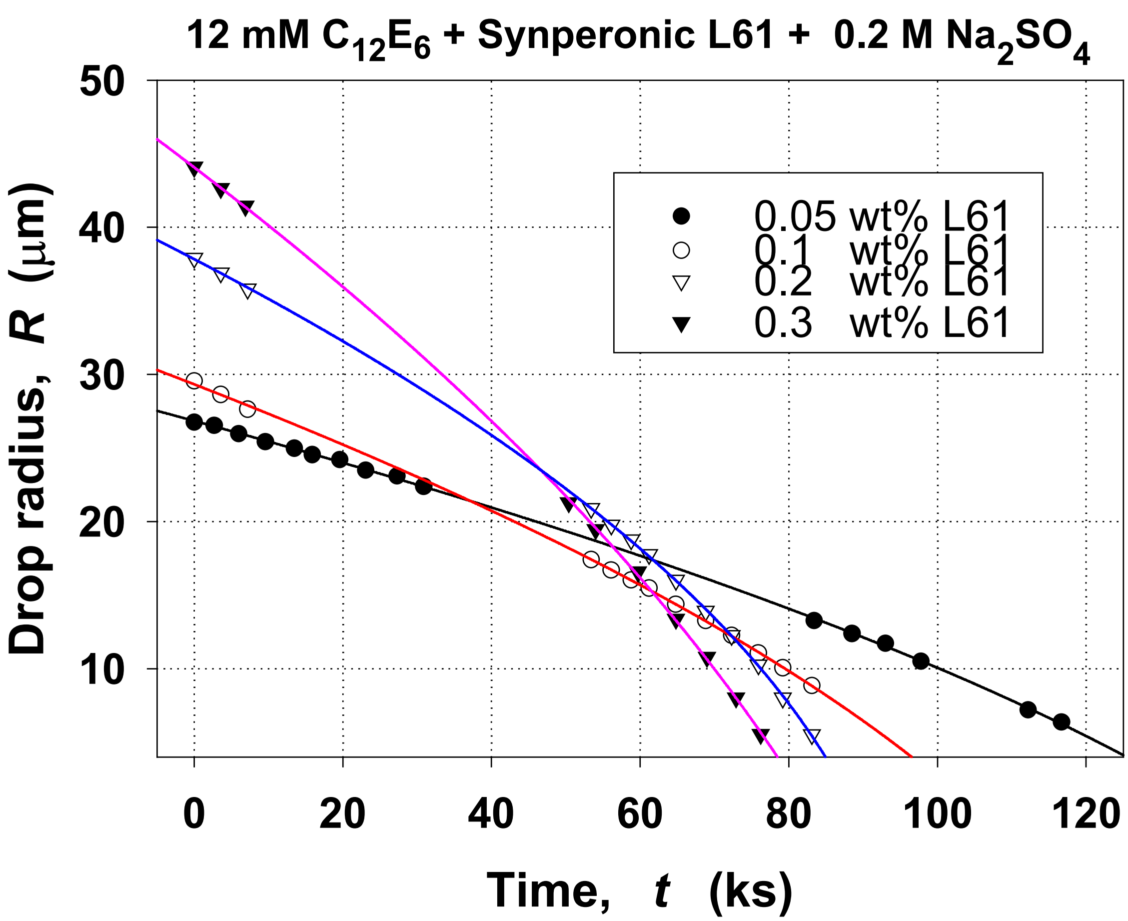
EO_n–PO_m–EO_n Triblock Copolymers as **Promoters** of Solubilization

Materials:

$C_{12}H_{25}(C_2H_4O)_5$, [$C_{12}E_5$] + 0.01 M NaCl

$C_{12}H_{25}(C_2H_4O)_6$, [$C_{12}E_6$] + 0.2 M Na_2SO_4

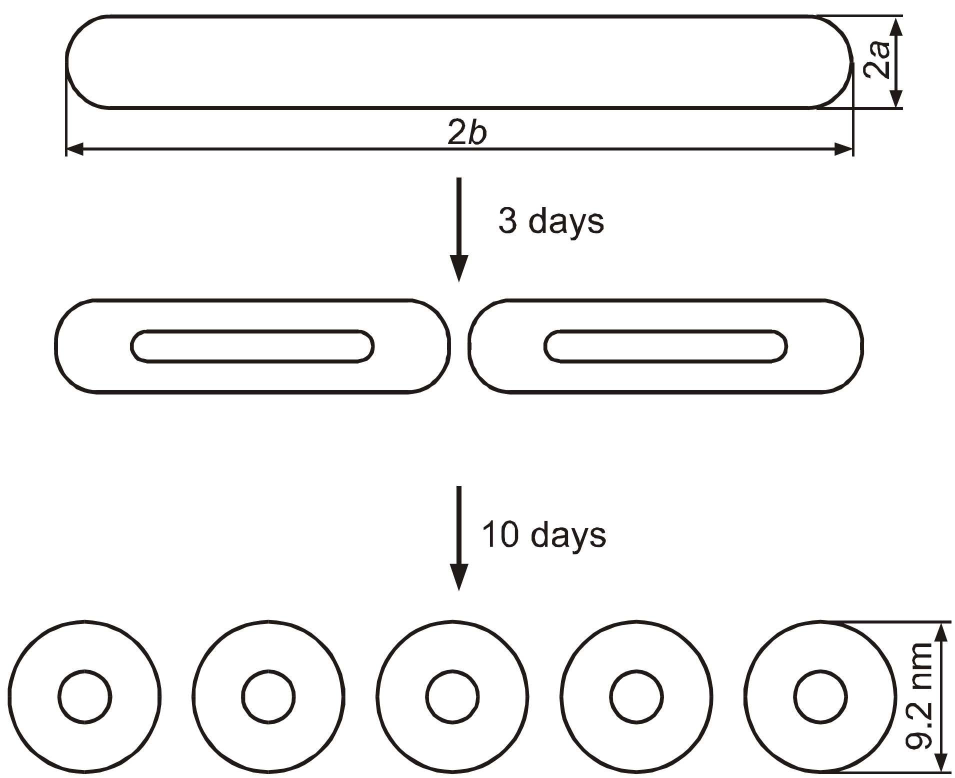
Synperonic L61: [$EO_{2.5}PO_{34}EO_{2.5}$] (molecular weight: 2100)

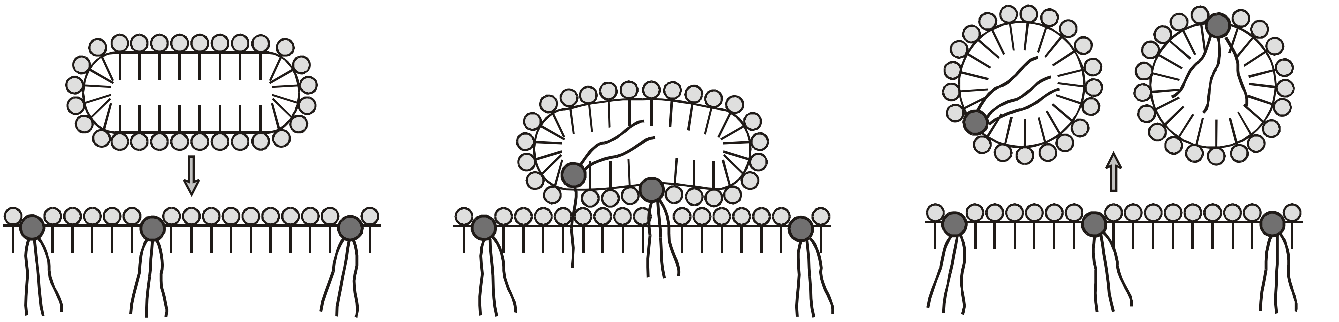


Mixed Micelles of $C_{12}E_5$ + Synperonic L61

SL61 (wt%)	$N_{surfact.}$	N_{SL61}	$N_{triolein}$	eccentricity p	a (nm)
Empty Micelles					
0.1	1841	77	0	24	2.8
0.2	895	74	0	21	2.4
0.3	726	90	0	17	2.5
10 days contact with oil					
0.1	341	13	20	1	4.6
0.2	261	22	15	1.3	4.1
0.3	235	29	12	3.3	3.0

12 mM $C_{12}E_5$ + 0.1 wt % SL61 + 0.01 M NaCl





Equation provided by the model for diminishing of the drop radius R:

$$R(t) = \alpha\{[1 + 2\beta(t_0 - t)]^{1/2} - 1\}/\beta$$

$$(\alpha, \beta) \rightarrow (\chi, n_s); \qquad \chi = k_s k_a/(k_s + k_d) \approx k_a \qquad (k_s >> k_d);$$

C_{SL61} (wt %)	rate constant χ (μm/s) [drop]	oil molecules per swollen micelle n_s [drop]	oil molecules per swollen micelle n_s [NMR]
Solutions of 0.012 M $C_{12}EO_5$ + 0.01 M NaCl			
0.0	0.20	–	–
0.1	0.34	20	20 ± 3
0.2	1.05	16	15 ± 2
0.3	1.74	13	12 ± 2
Solutions of 0.012 M $C_{12}EO_6$ + 0.2 M Na_2SO_4			
0.0	0.22	5	12 ± 2
0.05	1.40	6	10 ± 2
0.1	1.44	7	8 ± 1
0.2	1.43	7	9 ± 1

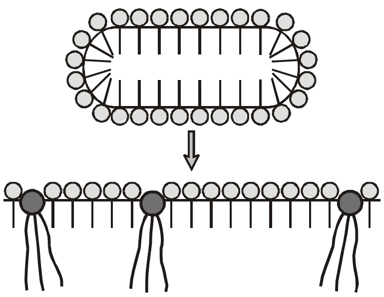
Desorbing micelles: EO5 – completely full; EO6: partially filled

Height of the Kinetic Barrier to Adsorption

For the solutions of $C_{12}E_5$ we have $\chi \approx k_{1,a} = P \exp(-E_a/kT)$,

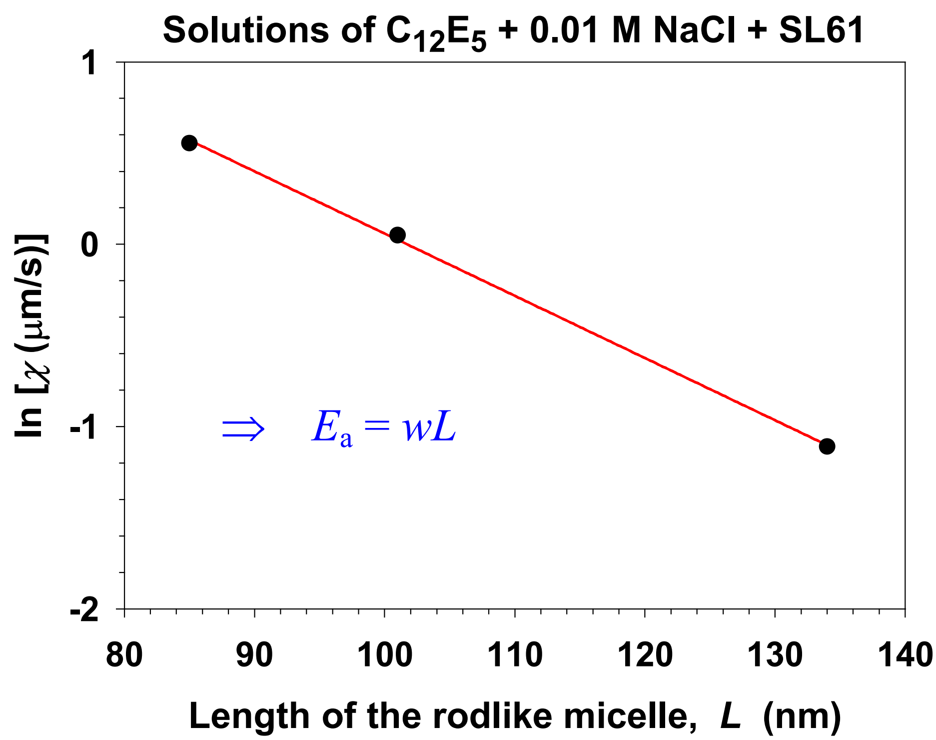
P **is a pre-exponential factor and** E_a **is the activation energy;**

L – **length of the rodlike micelles;** w – **activation energy per unit length.**



The slope yields:

$w = 0.034\ kT$ per nm



For: $L = 50,\ 100$ and 150 nm

$E_a = 1.7,\ 3.4$ and $5.1\ kT$, **respectively.**

⇒ **The addition of SL61 to the solution of nonionic surfactant decreases the length of the rodlike micelles, thus reducing the kinetic barrier to adsorption and accelerating the solubilization process.**

Summary and Conclusions

(A) Solubilization as a Bulk Reaction:

– **Water-Soluble Oil (decane, benzene)**

– **Ionic Surfactant (SDS)**

Theoretical model development and comparison with the experiment:

⇒ k_+ – **rate constant of solubilization;**

⇒ α – **mass transfer coefficient for oil.**

The act of catching of an oil molecule by a micelle occurs under a barrier (rather than diffusion) control.

(B) Solubilization as a Surface Reaction:

– **Water-Insoluble Oil (triglycerides: triolein, soybean oil)**

– **Nonionic Surfactant ($C_{12}EO_n$ + Synperonic L61 + Electrolyte)**

Investigation of the mixed micelles: giant aggregates containing

– **hundreds to thousand surfactant molecules;**

– **dozens of polymer (SL61) molecules**

Theoretical model development and comparison with the experiment

⇒ $\chi \approx k_a$ – **compound rate constant of solubilization;**

⇒ n_s – **number oil molecules in a swollen micelle;**

⇒ **SL61 promotes solubilization by decreasing the barrier to micelles adsorption at the oil-water interface.**

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