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

Peter A. Kralchevsky, N. D. Denkov, N. C. Christov, P. D. Todorov, G. Broze, P. Durbut and A. Mehreteab

Laboratory of Chemical Physics & Engineering
Faculty of Chemistry, University of Sofia, BULGARIA

Colgate-Palmolive R&D, Inc., Milmort (Herstal), Belgium

Colgate-Palmolive Technology Center, Piscataway, New Jersey, USA

**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:**

\( \alpha \) – mass transfer coefficient

\( k_+ \) – rate constant of the reaction

\( \{\text{micelle}\} + \{\text{oil molecule}\} = \{\text{swollen micelle}\} \)

(B) **Surface Reaction:**

– 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
1. **Simple Solubilization Cell** (Cell # 1)

   \[(2 \times 2 \times 1.5 \text{ cm})\]

   **Advantage**: Easy to operate

   **Disadvantage**: the kinetics is influenced by uncontrollable thermal convections

2. **Capillary Cell** (Cell # 2)

   - horizontal capillary of inner diameter \(2R = 0.06 \text{ cm} = 600 \mu\text{m}\);
   - a single oil drop is injected by syringe;
   - the solubilization occurs under a purely diffusion regime (no thermal convections) \(\Rightarrow\) quantitative interpretation is possible.
Dependence of the solubilization rate on the SDS concentration

**Decane; SDS; 27°C**

- 0.025 M SDS
- 0.10 M SDS
- 0.25 M SDS

**Benzene; SDS; 27°C**

- 0.25 M SDS
Theoretical Model

Stationary Diffusion
+ Reaction of Solubilization:

\[ D_{oil} \nabla^2 c_{oil} = k_+ c_{tot} c_{oil} \]

Boundary Condition:

\[ -\frac{\partial c_{oil}}{\partial r} \bigg|_{r=R} = \alpha [c_{eq} - c_{oil}(R)] \]

\( \alpha \) – mass transfer coefficient

\[ c_{oil}(r) = \frac{c_{eq}R}{1 + (\kappa + R^{-1})/\alpha} \frac{\exp[\kappa (R-r)]}{r} \]

\( \kappa^2 = k_+ c_{tot}/D_{oil} \)

Solubilization Flux:

\[ Q_{oil} = -D_{oil} \frac{\partial c_{oil}}{\partial r} \bigg|_{r=R} \]

Diminishing of the Drop Volume:

\[ -\frac{dV}{dt} = V_{oil} (4\pi R^2) \lambda Q_{oil} \]

\( V_{oil} \) – volume per oil molecule; \( \lambda \) – Wall:

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

\[ \frac{dR}{dt} = -\frac{\alpha \beta (1+\kappa R)}{1+(\alpha + \kappa)R} \lambda(\kappa R), \quad \beta = V_{oil} D_{oil} c_{eq} \]
Results for n-Decane

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

(narrow solubilization zone)

From the fit we determine:

\[ \alpha = 29.8 \pm 5.8 \ (\mu \text{m}^{-1}) \]

(mass transfer coefficient)

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

(rate constant: oil uptake by micelles)

<table>
<thead>
<tr>
<th>SDS concentration</th>
<th>Solubilization rate</th>
<th>Width of solubilization zone: ( \kappa^{-1} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c_s ) (M)</td>
<td>( u ) (nm/s)</td>
<td></td>
</tr>
<tr>
<td>0.025</td>
<td>0.31</td>
<td>267</td>
</tr>
<tr>
<td>0.25</td>
<td>1.71</td>
<td>61</td>
</tr>
</tbody>
</table>
Results for Benzene

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

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

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

\[ R(t) = \sqrt{1.8 \beta (t_0 - t)}, \quad R(t_0) = 0 \quad \text{(No adjustable parameters!)} \]

(2) Simultaneous molecular dissolution and micellar solubilization:

\( \kappa \) – adjustable parameter; \( k_+ = \kappa^2 D_{\text{oil}}/c_{\text{tot}} \)

Benzene: \( k_+ = 2.3 \times 10^{-19} \) (cm\(^3\)/s), \( \kappa^{-1} = 40.1 \) \( \mu \)m, \( (0.25 \text{ M SDS}) \)

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 \text{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)

$$12 \text{ mM } C_{12}E_6 \text{ (nonionic) } + \text{ SDP2S (ionic) } + 0.2 \text{ M } \text{Na}_2\text{SO}_4$$

$$X_{\text{SDP2S}} = \frac{C_{\text{SDP2S}}}{(C_{\text{C12EO6}} + C_{\text{SDP2S}})}$$

![Graph](image)
EO\textsubscript{n}–PO\textsubscript{m}–EO\textsubscript{n} Triblock Copolymers as Promoters of Solubilization

**Materials:**

\[ \text{C}_{12}\text{H}_{25}(\text{C}_{2}\text{H}_{4}\text{O})_{5}, \quad [\text{C}_{12}\text{E}_{5}] + 0.01 \text{ M NaCl} \]

\[ \text{C}_{12}\text{H}_{25}(\text{C}_{2}\text{H}_{4}\text{O})_{6}, \quad [\text{C}_{12}\text{E}_{6}] + 0.2 \text{ M Na}_{2}\text{SO}_{4} \]

Synperonic L61: \[ [\text{EO}_{2.5}\text{PO}_{34}\text{EO}_{2.5}] \] (molecular weight: 2100)
Mixed Micelles of $\text{C}_{12}\text{E}_5 + \text{Synperonic L61}$

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

$12 \text{mM C}_{12}\text{E}_5 + 0.1 \text{ wt }\% \text{SL61} + 0.01 \text{ M NaCl}$

![Diagram](image)
Equation provided by the model for diminishing of the drop radius $R$:

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

$(\alpha, \beta) \to (\chi, n_s)$; \quad $\chi = k_s k_a / (k_s + k_d) \approx k_a$ \quad $(k_s \gg k_d)$;

<table>
<thead>
<tr>
<th>$C_{SL61}$ (wt %)</th>
<th>rate constant $\chi$ (µm/s) [drop]</th>
<th>oil molecules per swollen micelle $n_s$ [drop]</th>
<th>oil molecules per swollen micelle $n_s$ [NMR]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solutions of 0.012 M C$_{12}$EO$_5$ + 0.01 M NaCl</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.20</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>0.1</td>
<td>0.34</td>
<td>20</td>
<td>20 ± 3</td>
</tr>
<tr>
<td>0.2</td>
<td>1.05</td>
<td>16</td>
<td>15 ± 2</td>
</tr>
<tr>
<td>0.3</td>
<td>1.74</td>
<td>13</td>
<td>12 ± 2</td>
</tr>
<tr>
<td><strong>Solutions of 0.012 M C$_{12}$EO$_6$ + 0.2 M Na$_2$SO$_4$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.22</td>
<td>5</td>
<td>12 ± 2</td>
</tr>
<tr>
<td>0.05</td>
<td>1.40</td>
<td>6</td>
<td>10 ± 2</td>
</tr>
<tr>
<td>0.1</td>
<td>1.44</td>
<td>7</td>
<td>8 ± 1</td>
</tr>
<tr>
<td>0.2</td>
<td>1.43</td>
<td>7</td>
<td>9 ± 1</td>
</tr>
</tbody>
</table>

Desorbing micelles: \quad EO5 – completely full; \quad 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;
\[ \alpha \] – 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;
\[ \text{SL61 promotes solubilization by decreasing the barrier to micelles adsorption at the oil-water interface.} \]
REFERENCES


