ESTIMATION OF THE INTERFACIAL HYDROPHILICITY IN pH-SENSITIVE SURFACTANT-OIL-WATER SYSTEMS FROM THE ATTAINMENT OF OPTIMUM FORMULATION By THE DUAL SCAN TECHNIQUE

Raquel E. Antón, Ricardo Torres, Jean-Louis Salager
Lab. FIRP, Ingeniería Química, Universidad de Los Andes, Mérida Venezuela
Phone: (58)-274-240-2954 Fax (58)-274-240-2957
Email firp@ula.ve Web site: www.firp.ula.ve

14th International symposium “Surfactants in Solution”, SIS2002, Barcelona Spain June 9-14
The relative amount of fatty acid and soap in an aqueous phase directly depends on the pH of the bulk phase and can be straightforwardly calculated from the dissociation equilibrium.

\[
\text{AcH} = \text{RCOOH} \quad \text{fatty acid: a low HLB lipophilic surfactant}
\]
\[
\text{Ac}^- = \text{RCOO}^- \quad \text{soap: a high HLB hydrophilic surfactant}
\]

\[
\text{AcH} \rightarrow \text{Ac}^- + \text{H}^+ \quad \text{Ka} = \frac{[\text{Ac}^-][\text{H}^+]}{[\text{AcH}]} \approx 10^{-6}
\]

In water: mixture of two surfactants

**HLB of surfactant mixture depends on pH**

\[
\frac{[\text{Ac}^-]}{[\text{AcH}]} = \text{pH} - \text{PKa}
\]
AcH is lipophilic, thus suffers a stronger hydrophobic effect to adsorb at interface.

bulk water-interface
equilbria
for both species

\[
\frac{[\text{AcH}]_{\text{int}}}{[\text{AcH}]_{\text{bulk}}} > \frac{[\text{Ac-}]_{\text{int}}}{[\text{Ac-}]_{\text{bulk}}} \quad \rightarrow \quad \frac{[\text{AcH}]_{\text{int}}}{[\text{Ac-}]_{\text{int}}} > \frac{[\text{AcH}]_{\text{bulk}}}{[\text{Ac-}]_{\text{bulk}}}
\]
Thus \( \left[ \frac{[H^+]}{K_a} \right]_{\text{int}} > \left[ \frac{[H^+]}{K_a} \right]_{\text{bulk}} \)

If pH is the same at interface and bulk then

\[ K_{a\text{int}} < K_{a\text{bulk}} \]

Less dissociation at air-water interfacial mixture

is more hydrophobic than bulk water mixture
Dissociation in water of AcH in Ac\(^{-}\) (depends on pH)

Partitioning between oil and water of AcH (depends on acid, oil and water nature)

in water / oil system = 2 equilibria

how dissociation at interface is affected?
Two Winsor III Systems containing same oil, same water, same alcohol at same temperature, but different surfactants

Winsor’s Ratio, Shinoda’s PIT Correlations for optimum formulations indicates that the two surfactants exhibit the same hydrophilic/hydrophobic characteristic parameter.
take two formulation scans

Two Winsor III systems with
Same oil
Same aqueous phase
Same alcohol content
Same temperature
But different surfactants

One with ethoxylated nonyl phenol surfactant (EON scan) $\rightarrow$ determine HLB$_{opt}$

One with carboxylic acid (pH scan) $\rightarrow$ determine pH$_{opt}$
(1) Ethoxylated nonyl phenol surfactant (EON scan) \(\rightarrow\) determine HLB \(_{\text{opt}}\) for both systems, i.e. the HLB of the AcH / Ac- mixture
Then the interfacial composition \(\text{“} x \text{”}\) is estimated from
HLB \(_{\text{opt}}\) = \(x\) HLB acid + \((1-x)\) HLB soap \((HLB \ of \ acid \ and \ soap \ are \ known)\)
Thus \([\text{AcH}] / [\text{Ac-}] \text{ at interface} = 1 / (1-x) \rightarrow \) interfacial mixture HLB

(2) Carboxylic acid (pH scan) \(\rightarrow\) determine pH \(_{\text{opt}}\) \(\rightarrow\) thus \([\text{AcH}] / [\text{Ac-}] \) in water
\(\rightarrow\) bulk water mixture HLB

(3) From \([\text{AcH}] / [\text{Ac-}] = [\text{H}^+] / \text{Ka}\) either at interface and in water
and assuming that pH is the same at interface and in water
The dissociation constant can be calculated at interface \(\text{Ka}_{\text{int}}\)

**EXPERIMENTAL**

4 combinations of oil/alcohol are used (containing decane, heptane, cyclohexane, sec-butanol and n-pentanol). The equivalent EACN term which ranges from 10 to 1.3 takes into account the alcohol effect (EACN-f(A)/k).
The water phase is a 4 wt% NaCl brine, Temp = 25°C, WOR = 1
Tested acids are capric (C10), lauric (C12) and myrystic (C14)
**RESULTS** for EON scan with ethoxylated nonyl phenol
EON interfacial is calculated from Graciaa et al. partitioning theory.

<table>
<thead>
<tr>
<th>Oil EACN</th>
<th>1.3</th>
<th>5.3</th>
<th>7</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>EON global</td>
<td>6.3</td>
<td>5.7</td>
<td>5.4</td>
<td>5.0</td>
</tr>
<tr>
<td>EON\textsubscript{int}</td>
<td>7.2</td>
<td>6.4</td>
<td>6.4</td>
<td>6.0</td>
</tr>
<tr>
<td>HLB\textsubscript{g}</td>
<td>11.2</td>
<td>10.6</td>
<td>10.3</td>
<td>10.1</td>
</tr>
<tr>
<td>HLB\textsubscript{int}</td>
<td>11.8</td>
<td>11.3</td>
<td>11.2</td>
<td>10.9</td>
</tr>
</tbody>
</table>

**RESULTS** for pH scans with fatty acids

optimum pH* depends on acid and oil phase
### Non-dissociated Acid molar faction in water at pH*

<table>
<thead>
<tr>
<th>Oil EACN</th>
<th>1.3</th>
<th>5.3</th>
<th>7</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10 acid</td>
<td>0.032</td>
<td>0.039</td>
<td>0.048</td>
<td>0.065</td>
</tr>
<tr>
<td>C12 acid</td>
<td>0.018</td>
<td>0.025</td>
<td>0.026</td>
<td>0.043</td>
</tr>
<tr>
<td>C14 acid</td>
<td>0.010</td>
<td>0.016</td>
<td>0.017</td>
<td></td>
</tr>
</tbody>
</table>

### Non-dissociated Acid molar faction at interface at pH*

<table>
<thead>
<tr>
<th>Oil EACN</th>
<th>1.3</th>
<th>5.3</th>
<th>7</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>HLB int</td>
<td>11.8</td>
<td>11.3</td>
<td>11.2</td>
<td>10.9</td>
</tr>
<tr>
<td>C10 acid</td>
<td>0.59</td>
<td>0.62</td>
<td>0.62</td>
<td>0.64</td>
</tr>
<tr>
<td>C12 acid</td>
<td>0.53</td>
<td>0.57</td>
<td>0.57</td>
<td>0.59</td>
</tr>
<tr>
<td>C14 acid</td>
<td>0.48</td>
<td>0.51</td>
<td>0.51</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Interface contains much more undissociated acid than water phase.
Interfacial Ka values (compare with 1 E-06 in water)

<table>
<thead>
<tr>
<th>Oil EACN</th>
<th>1.3</th>
<th>5.3</th>
<th>7</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10 acid</td>
<td>2.4 E-08</td>
<td>2.5 E-08</td>
<td>3.0E-08</td>
<td>3.9 E-08</td>
</tr>
<tr>
<td>C12 acid</td>
<td>1.6 E-08</td>
<td>2.0 E-08</td>
<td>2.1 E-08</td>
<td>3.1 E-08</td>
</tr>
<tr>
<td>C14 acid</td>
<td>6.6 E-09</td>
<td>1.5 E-08</td>
<td>1.7 E-08</td>
<td></td>
</tr>
</tbody>
</table>

However, a lot of undissociated acid can partition into oil (low EACN)

\[ \text{HLB global} = y_{\text{water}} \cdot \text{HLB}_{Ac} - (1-y)_{\text{oil}} \cdot \text{HLB}_{AcH} \]

50 times lower

interface is more hydrophilic or more lipophilic than overall system depending on oil EACN and acid
CONCLUSION

Interfacial acid/soap mixture composition is in general much less dissociated (i.e. more lipophilic) than bulk water acid/soap mixture.

Ka interfacial values depend on the acid type and oil EACN. Ka int value increases when EACN diminishes (because AcH goes into oil) Ka int value increases when acid length diminishes (ionic dissociation)

Interfacial HLB does not change much with EACN and acid length.

Contrariwise global HLB strongly depends on these physicochemical variables. Global HLB is higher for lower EACN and longer chain acid.

Consequently

Interface is more hydrophobic than overall system for long acids and low EACN

Interface is more hydrophilic than overall system for short acid and high EACN