Efficient control of the bulk and surface rheological properties by using C8-C18 fatty acids as co-surfactants

Zlatina Mitrinova,1* Zhulieta Popova,1 Slavka Tcholakova,1 Nikolai Denkov,1 Bivash R. Dasgupta2 and K.P. Ananthapadmanabhan2

1Department of Chemical and Pharmaceutical Engineering, Faculty of Chemistry and Pharmacy, Sofia University, Bulgaria
2UNILEVER R&D, Trumbull, USA
1. Introduction.

2. Aim of the study

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Introduction
Surfactant adsorption and surface modulus

\begin{align*}
A_0, \Gamma_0, \sigma_0 & & A_0 + \delta A_0 & & A_0 & & A_0 - \delta A_0 \\
\Gamma < \Gamma_0 & & \Gamma > \Gamma_0 & & \Gamma > \Gamma_0 & & \Gamma > \Gamma_0
\end{align*}

\begin{align*}
A(t) &= A_0 + \delta A \sin(\omega t) \\
\sigma(t) &= \sigma_0 + \delta \sigma \sin(\varphi + \omega t) \\
|G^*| &= \left| \frac{\delta \sigma}{\delta \ln A} \right|
\end{align*}
Surface properties

Oscillating drop

\[ G_D = \left( G_{ST}^2 + G_{LS}^2 \right)^{1/2} \]


Significant effect of FAc on SLES+CAPB surface rheological properties
Surface condensed layer formation
Foam rheology

\[ \tau(\gamma) = \tau_0 + k\gamma \]

- \( \tau_0 \) – yield stress
- \( k \) – consistency
- \( n \) – power law index

- \( n < 1 \) (concentrated foams)

\[ Ca = \left( \frac{\mu R}{\sigma} \right) \]

\[ \phi = \frac{\tau_V}{\sigma/R} \]

Value of \( n \) \( \leftrightarrow \) Viscous friction mechanism

Denkov et al., 2008; Tcholakova et al., 2008; Denkov et al., 2009.
Mechanism of energy dissipation in sheared foam

Inside film friction

\[ \dot{\rho}_F \propto Ca^{0.5} \]

Surface dissipation

\[ \dot{\rho}_S \propto G_{LS}Ca^{0.2} \]

Denkov et al., 2008; Tcholakova et al., 2008
Bubble break-up during inside foam friction

Golemanov et al., 2008

\[ R_{32} \approx 700 \, \mu m \]

\[ \tau \sim \frac{1}{R^n} \]

\[ BS+LAc, \ R_{32} \approx 150 \, \mu m \]

\[ BS, \ R_{32} \approx 300 \, \mu m \]

Much smaller bubbles are formed in presence of **long-chain FAc** as co-surfactant
Aim of the study

To clarify the effect of fatty acid on foam and bulk rheological properties

Studied factors:

- Fatty acid chain length
- Fatty acid concentration
- pH
Materials

Sodium laureth sulfate-SLES-1EO

Cocoamidopropyl betaine-CAPB

Fatty acids (FAc):
C8Ac - C18Ac

Concentrated solution:
(300 mM = 10 wt %)
SLES + CAPB = 2:1 + FAc

Basic solution (BS):
(300 mM = 10 wt %)
SLES + CAPB

Diluted solution:
(15 mM = 0.5 wt %)
SLES + CAPB = 2:1 + FAc
Methods for systems characterization

Oscillating drop

\[ G_D = \left( G_{ST}^2 + G_{LS}^2 \right)^{1/2} \]

P. Garrett et al., 1993

Tensiometer

Rheometer
Effect of fatty acids on solution rheology

Formation of wormlike micelles in presence of C8Ac and C10Ac, while longer FAc lead to formation of cylindrical micelles.

(Mitrinova et al. *Langmuir*, 2013)
Oscillatory measurements

2 % deformation

$G'$, $G''$, Pa

$t_R = \frac{1}{\omega_R}$

$t_R$ relaxation time of network restructuring:
5 s for C8Ac and 0.7 s for C10Ac

Full: $G'$
Empty: $G''$

$10 \text{ wt } % \text{ BS} + 1 \text{ wt } % \text{ C8Ac}$

$10 \text{ wt } % \text{ BS} + 1 \text{ wt } % \text{ C10Ac}$

Frequency of oscillation, s$^{-1}$
Cole-Cole plot

\[ \frac{G'}{G_{osc}} \]

\[ \xi = \left( \frac{t_{br}}{t_{rep}} \right)^{1/2} \approx 1.23 \text{ for } C8Ac \]

\[ \xi = \left( \frac{t_{br}}{t_{rep}} \right)^{1/2} \approx 10.2 \text{ for } C10Ac \]

Kern et al., 1992

\[ T_R = \frac{1}{\eta} \]

Combined relaxation time

reptation relaxation

\[ T_R = \frac{t_{rep}}{C_e} \]

reaction model

Systems:

<table>
<thead>
<tr>
<th>Systems</th>
<th>( T_R, ) sec</th>
<th>EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS+ C_8Ac</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>BS+ C_10Ac</td>
<td>0.14</td>
<td></td>
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</tbody>
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\( t_{br} \) – breaking time;
Effect of FAc on surface rheological properties

Oscillating drop

\[ G_D = \left( G_{ST}^2 + G_{LS}^2 \right)^{1/2} \]

C8Ac and C10Ac are unable to increase surface modulus of BS
C12Ac-C18Ac increase surface modulus above 100 mN/m

(Mitrinova et al. *Langmuir*, 2013)
Foams with $G_D > 100$ mN/m exhibit much higher foam friction, compared to solutions with lower surface modulus.

(Mitrinova et al. *Langmuir*, 2013)
C8Ac and C10Ac do not change $R_{32}$ for BS system. C12Ac-C18Ac lead to much smaller bubbles due to the high $G_D$.

(Mitrinova et al. Langmuir, 2013)
Equilibrium surface tension of diluted solutions

Significant decrease of equilibrium surface tension for all FAc
Most effective - C16 and C14Ac, followed by C12Ac

(Mitrinova et al. *Langmuir*, 2013)
At pH between 3 and 8 surface modulus are high (above 100 mN/m) and there is significant foam friction.

At pH = 11 $G_D$ reaches values for BS and foam friction decrease.
Effect of pH on BS+C14Ac surface tension

(Mitrinova et al. Colloid and surfaces A, 2013)

At natural pH $\sigma_{\text{EQ}}$ is low at pH between 3 and 8. At high pH significant molar fraction of FAc molecules are protonated and reach values for BS at pH=11.
Conclusions

- In presence of C8Ac and C10Ac:
  - Apparent viscosity of concentrated solutions significantly increase due to the formation of entangled wormlike micelles;
  - Foam rheological properties are not affected;

- In presence of C14Ac, C16Ac, C18Ac:
  - Apparent viscosity of concentrated solutions is slightly higher than those for BS system due to the presence of cylindrical micelles;
  - Surface modulus of diluted solution significantly increase;
  - Foam viscous friction is higher due to additional dissipation in adsorption layer.

- In presence of C12Ac:
  - In presence of C12Ac intermediate properties are observed.
Thank you for your attention!