SANS study of the self-aggregation of alkylglycoside surfactants with oligomeric head-groups

Dr Federica Sebastiani
Postdoc at CR competence AB – Physical Chemistry Department, Lund University

Neutrons and Food 2016
Why alkylglycoside surfactant?
Why alkylglycoside surfactant?
Why alkylglycoside surfactant?

non-ionic surfactant
Why alkylglycoside surfactant?

- Polysorbate 80
- PEG-based surfactant

- emulsification
- solubilisation
- prevent aggregation
- wetting
- etc.

non-ionic surfactant
Why alkylglycoside surfactant?

Polysorbate 80
PEG-based surfactant

BUT…
Why alkylglycoside surfactant?

non-ionic surfactant

Polysorbate 80
PEG-based surfactant

BUT...

oxidation

radicals

unfavourable biodegradation

phase separation at high temperature
Why alkylglycoside surfactant?

non-ionic surfactant

Polysorbate 80
PEG-based surfactant
Why alkylglycoside surfactant?

- non-ionic surfactant
- Polysorbate 80
- PEG-based surfactant

Why oligomeric head-group?
Why alkylglycoside surfactant?
Why oligomeric head-group?

Conventional technology
Why alkylglycoside surfactant?
Why oligomeric head-group?

Conventional technology

Enzymatic technology

Svensson D. et al., Green Chem., 2009, 11, 1222-1226
Why alkylglycoside surfactant?
Why oligomeric head-group?

Conventional technology

Enzimatic technology

Svensson D. et al., Green Chem., 2009, 11, 1222-1226
Why alkylglycoside surfactant?
Why oligomeric head-group?

Conventional technology

Enzimatic technology

Svensson D. et al., Green Chem., 2009, 11, 1222-1226
Why alkylglycoside surfactant?
Why oligomeric head-group?

Conventional technology

Enzymatic technology

C16G8

Biocompatible
Biodegradable
From sustainable raw material
Soluble

Svensson D. et al., Green Chem., 2009, 11, 1222-1226
Enzimatic technology

C16G8

Biocompatible
Biodegradable
From sustainable raw material
Soluble

Svensson D. et al., Green Chem., 2009, 11, 1222-1226
Self-assembly in water

C16G8-αβ  C16G8-β
Self-assembly in water

C16G8-αβ

C16G8-β
Self-assembly in water

C16G8-αβ  C16G8-β

DLS  SLS  SAXS  SANS

2 temperatures and c = 1 mg ml⁻¹
Self-assembly in water

C16G8-αβ  C16G8-β

DLS  SLS  SAXS  SANS

hydrodynamic radius, $R_H$
C16G8

Self-assembly in water

C16G8-αβ  C16G8-β

DLS  SLS  SAXS  SANS
hydrodynamic radius, $R_H$
radius of gyration, $R_G$
Self-assembly in water

C16G8-αβ  C16G8-β
Self-assembly in water

C16G8

What do we see?

- DLS: particle motion
- SLS: refractive index
- SAXS: electron density
- SANS: nuclei and isotopes

hydrodynamic radius, \( R_H \)

radius of gyration, \( R_G \)

shape and cross section
Self-assembly in water

c = 1 mg ml$^{-1}$

25°C

45°C

C16G8-αβ    C16G8-β

DLS     SLS     SAXS     SANS

hydrodynamic radius, $R_H$

radius of gyration, $R_G$

shape and cross section
C16G8

Self-assembly in water

c = 1 mg ml$^{-1}$

C16G8-αβ

25°C 83±3 nm

45°C 79±2 nm

C16G8-β

25°C 65±2 nm

45°C 59±1 nm

DLS  
SLS  
SAXS  
SANS

hydrodynamic radius, $R_H$

radius of gyration, $R_G$

shape and cross section
Self-assembly in water

\[ c = 1 \text{ mg ml}^{-1} \]

- C16G8-αβ
- C16G8-β

Temperature:
- 25°C
- 45°C

Techniques:
- DLS
- SLS
- SAXS
- SANS

Parameters:
- Hydrodynamic radius, \( R_H \)
- Radius of gyration, \( R_G \)

Shape and cross section
Self-assembly in water

c = 1 mg ml\(^{-1}\)

$C_{16}G_8$-$\alpha\beta$

25°C

Approximations not valid

45°C

$q_{\text{min}} \sim 6.8 \times 10^{-4}$ Å\(^{-1}\)

$R_{g,\text{max}}$ 140 nm

$C_{16}G_8$-$\beta$

51±2 nm

51±2 nm

DLS

SLS

SAXS

SANS

Hydrodynamic radius, $R_H$

Radius of gyration, $R_G$

Shape and cross section
Self-assembly in water

\[ c = 1 \text{ mg ml}^{-1} \]

25°C

C16G8-αβ

45°C

C16G8-β

DLS

SLS

SAXS

SANS

hydrodynamic radius, \( R_H \)

radius of gyration, \( R_G \)

shape and cross section
Self-assembly

c = 1 mg ml\(^{-1}\)

25°C

45°C

C16G8-β

25°C

45°C

DLS

SLS

SAXS

SANS

hydrodynamic radius, \(R_H\)

radius of gyration, \(R_G\)

shape and cross section
Self-assembly

\[ c = 1 \text{ mg ml}^{-1} \]

25°C

45°C

C16G8-β

Core-shell structure

Hydrodynamic radius, \( R_H \)

Radius of gyration, \( R_G \)

DLS

SLS

SAXS

SANS

Shape and cross section
Self-assembly

c = 1 mg ml\(^{-1}\)

25\(^\circ\)C

45\(^\circ\)C

C16G8

DLS
hydrodynamic radius, \(R_H\)

SLS
radius of gyration, \(R_G\)

SAXS
shape and cross section

SANS
C16G8

Self-assembly in water

c = 1 mg ml\(^{-1}\)

\[ \text{C16G8-} \alpha \beta \quad \text{C16G8-} \beta \]

\[ \text{25°C} \quad \text{45°C} \]

\begin{align*}
\text{DLS} & \quad \text{SLS} \\
\text{hydrodynamic radius, } R_H & \quad \text{radius of gyration, } R_G \\
\text{SAXS} & \quad \text{SANS} \\
\text{core-shell structure} & \quad \text{shape and cross section}
\end{align*}
Self-assembly

c = 1 mg ml$^{-1}$

25°C

45°C

DLS: hydrodynamic radius, $R_H$
SLS: radius of gyration, $R_G$
SAXS: shape and cross section
SANS: SANS
C16G8

Self-assembly

c = 1 mg ml\(^{-1}\)

25°C

45°C

hydrodynamic radius, \(R_H\)

radius of gyration, \(R_G\)

shape and cross section
Self-assembly

$c = 1 \text{ mg ml}^{-1}$

$25^\circ\text{C}$

$45^\circ\text{C}$

C16G8-

C16G8-

radius of gyration, $R_G$

hydrodynamic radius, $R_H$

SLS

SAXS

SANS

shape and cross section
C16G8

Self-assembly

$c = 1 \text{ mg ml}^{-1}$

25°C

45°C

SLS

DLS

hydrodynamic radius, $R_H$

radius of gyration, $R_G$

shape and cross section

SAXS

SLS

SANS

SANS

slope $\approx -2$
C16G8

SUMMARY

Self-assembly in water

c = 1 mg ml\(^{-1}\)

25°C

C16G8-αβ

83±3 nm

45°C

C16G8-β

65±2 nm

79±2 nm

59±1 nm

DLS
SLS
SAXS
SANS

hydrodynamic radius, \(R_H\)
radius of gyration, \(R_G\)
shape and cross section
Self-assembly in water

C16G8-β

25°C

11 concentrations from 2.5 μM to 250 μM (cmc = 25 μM = 0.034 mg ml⁻¹)

DLS
hydrodynamic radius, \( R_H \)

NMR Diffusion
self-diffusion coefficient, \( D \)
C16G8

Self-assembly in water

C16G8-β  25°C

11 concentrations from 2.5 µM to 250 µM (cmc = 25 µM = 0.034 mg ml⁻¹)

4 × 10⁻¹²

D / m² s⁻¹

hydrodynamic radius, R_H

self-diffusion coefficient, D

DLS

NMR Diffusion

cmc
Self-assembly in water  

C16G8-β  25°C

11 concentrations from 2.5 μM to 250 μM (cmc = 25 μM = 0.034 mg ml⁻¹)

\[ 4 \times 10^{-12} \]

D / m² s⁻¹

60

R_H / nm

cmc

diffusion coefficient, D

hydrodynamic radius, R_H

DLS

NMR Diffusion
Self-assembly in water \(\text{C16G8-}\beta\text{ at } 25^\circ\text{C}\)

11 concentrations from 2.5 \(\mu\text{M}\) to 250 \(\mu\text{M}\) (\(\text{cmc} = 25 \mu\text{M} = 0.034 \text{ mg ml}^{-1}\))

DLS

NMR Diffusion

hydrodynamic radius, \(R_H\)  self-diffusion coefficient, \(D\)
C16G8

Self-assembly in water

C16G8-β  25°C

11 concentrations from 2.5 µM to 250 µM (cmc = 25 µM = 0.034 mg ml⁻¹)

hydrodynamic radius, \( R_H \)

self-diffusion coefficient, \( D \)

NMR Diffusion

DLS
Self-assembly in water

C16G8-β  25°C

11 concentrations from 2.5 µM to 250 µM (cmc = 25 µM = 0.034 mg ml⁻¹)

DLS

hydrodynamic radius, $R_H$

NMR Diffusion

self-diffusion coefficient, $D$

$10^{-12}$ m² s⁻¹

$10^{-10}$ m² s⁻¹
Self-assembly in water

C16G8-β  25°C

11 concentrations from 2.5 µM to 250 µM (cmc = 25 µM = 0.034 mg ml⁻¹)

\[ D_{\text{DLS}} \approx 10^{-12} \text{m}^2\text{s}^{-1} \]

\[ D_{\text{NMR}} = f_{\text{mono}}D_{\text{mono}} + f_{\text{mic}}D_{\text{mic}} \]

\[ D_{\text{NMR}} \approx 10^{-10} \text{m}^2\text{s}^{-1} \]
Self-assembly in water

C16G8-β 25°C

11 concentrations from 2.5 µM to 250 µM (cmc = 25 µM = 0.034 mg ml⁻¹)

\[ D_{\text{DLS}} \approx 10^{-12} \text{ m}^2 \text{s}^{-1} \]
\[ D_{\text{NMR}} = f_{\text{mono}} D_{\text{mono}} + f_{\text{mic}} D_{\text{mic}} \]
\[ f_{\text{mono}} >> f_{\text{mic}} \rightarrow D_{\text{NMR}} \approx D_{\text{mono}} \]

DLS

NMR Diffusion

hydrodynamic radius, \( R_H \)

self-diffusion coefficient, \( D \)
Self-assembly in water

C16G8-β  25°C

11 concentrations from 2.5 µM to 250 µM  (cmc = 25 µM = 0.034 mg ml⁻¹)

\[ D_{\text{DLS}} \approx 10^{-12} \text{ m}^2 \text{ s}^{-1} \]

\[ D_{\text{NMR}} = f_{\text{mono}} D_{\text{mono}} + f_{\text{mic}} D_{\text{mic}} \]

\[ f_{\text{mono}} >> f_{\text{mic}} \quad \rightarrow \quad D_{\text{NMR}} \approx D_{\text{mono}} \]

\[ D_{\text{NMR}} \approx 10^{-10} \text{ m}^2 \text{ s}^{-1} \]

very low concentrations

low signal

DLS

NMR Diffusion

hydrodynamic radius, \( R_H \)

self-diffusion coefficient, \( D \)
Self-assembly in water

C16G8-β 25°C

11 concentrations from 2.5 µM to 250 µM (cmc = 25 µM = 0.034 mg ml⁻¹)

\[ D_{\text{DLS}} \approx 10^{-12} \text{ m}^2 \text{ s}^{-1} \]

\[ D_{\text{NMR}} = f_{\text{mono}}D_{\text{mono}} + f_{\text{mic}}D_{\text{mic}} \]

\[ f_{\text{mono}} \gg f_{\text{mic}} \quad \rightarrow \quad D_{\text{NMR}} \approx D_{\text{mono}} \]

\[ D_{\text{NMR}} \approx 10^{-10} \text{ m}^2 \text{ s}^{-1} \]

very low concentrations

low signal

“unconventional” behaviour

NMR in concentrated samples needed
Self-assembly in water

\[
\begin{align*}
\text{C16G8-β} & \quad \{ \quad T = 25, 45, 65°C \\
\text{C16G8-αβ} & \quad c = 0.1, 0.5, 1, 5, 10, 20, 50 \text{ mg ml}^{-1}
\end{align*}
\]
Self-assembly in water

Intensity scales with concentration

\[ \text{C16G8-}\beta \quad \{ \begin{array}{l} T = 25, 45, 65 \degree C \\ c = 0.1, 0.5, 1, 5, 10, 20, 50 \text{ mg ml}^{-1} \end{array} \]
Self-assembly in water

C16G8-β

\[ T = 25, 45, 65^\circ C \]
\[ c = 0.1, 0.5, 1, 5, 10, 20, 50 \text{ mg ml}^{-1} \]

C16G8-αβ

\[ T = 25^\circ C \]
\[ c = 1 \text{ mg ml}^{-1} \]

**SANS**

shape and cross section

- \( a = 160 \text{ nm} \)
- \( b = 80 \text{ nm} \)
- \( c = 7.5 \text{ nm (3.5 nm core)} \)
Self-assembly in water

C16G8-β

\[ T = 25, 45, 65^\circ C \]

\[ c = 0.1, 0.5, 1, 5, 10, 20, 50 \text{ mg ml}^{-1} \]

C16G8-αβ

T = 45°C

T = 65°C

SANS

shape and cross section
C16G8

Self-assembly in water

C16G8-β

\[ T = 25, 45, 65°C \]
\[ c = 0.1, 0.5, 1, 5, 10, 20, 50 \text{ mg ml}^{-1} \]

SANS

shape and cross section
C16G8

Self-assembly in water

C16G8-β

C16G8-αβ

\{T = 25, 45, 65°C
\}
\{c = 0.1, 0.5, 1, 5, 10, 20, 50 \text{ mg ml}^{-1}\}

SANS

shape and
cross section

\text{T = 25°C}
Self-assembly in water

C16G8-β

\[ T = 25, 45, 65^\circ C \]
\[ c = 0.1, 0.5, 1, 5, 10, 20, 50 \text{ mg ml}^{-1} \]

C16G8-αβ

\[ T = 25^\circ C \]
\[ c = 1 \text{ mg ml}^{-1} \]

higher \( q_{\text{min}} \)
smaller \( h \)

SANS

shape and cross section

\( a = 220 \text{ nm} \)
\( b = 200 \text{ nm} \)
\( h = 20 \text{ nm (10 nm core)} \)
Self-assembly in water

C16G8-β

C16G8-αβ

\[ \begin{align*}
T &= 45°C \\
T &= 65°C \\
T &= 25, 45, 65°C \\
c &= 0.1, 0.5, 1, 5, 10, 20, 50 \text{ mg ml}^{-1} 
\end{align*} \]

C16G8

SANS

shape and cross section
Conclusions and Future plans

C16G8-αβ

C16G8-β

Temperature

Cross section
C16G8-β no change
C16G8-αβ change in shape

Concentration

“unconventional” cmc behaviour
C16G8-β no shape change over full c range
C16G8-αβ thinning at high concentration (T= 25°C)
Acknowledgements

Stefan Ulvenlund
CR Competence AB – Food Technology, Lund University

Karin Schillén
Physical Chemistry Department, Lund University

Göran Carlström
Department of Chemistry, Lund University

Lionel Porcar
Institut Laue Langevin, Grenoble, France