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

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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?

non-ionic surfactant

Polysorbate 80
PEG-based surfactant

emulsification

solubilisation

prevent aggregation

wetting

etc.

Why alkylglycoside surfactant?

non-ionic 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?

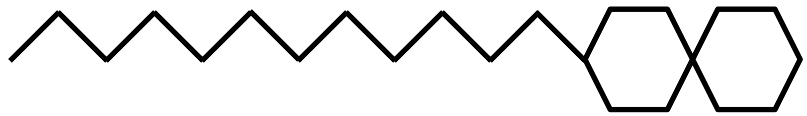
Why alkylglycoside surfactant?

Why oligomeric head-group?

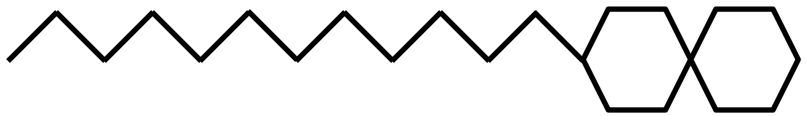
Conventional technology

Why alkylglycoside surfactant?
Why oligomeric head-group?

Conventional technology



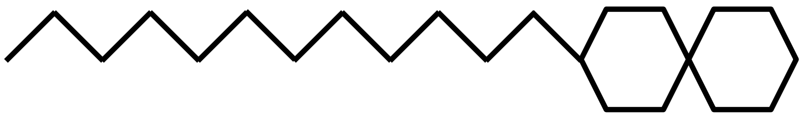
Enzimatic technology



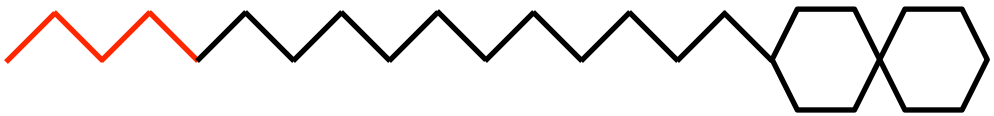
Svensson D. *et al.*, *Green Chem.*, 2009, **11**, 1222-1226

Why alkylglycoside surfactant?
Why oligomeric head-group?

Conventional technology



Enzimatic technology



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Why alkylglycoside surfactant?

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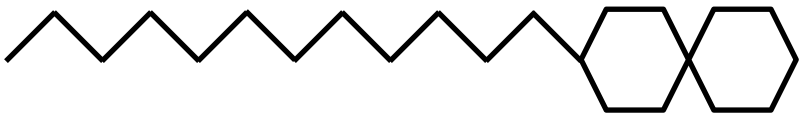
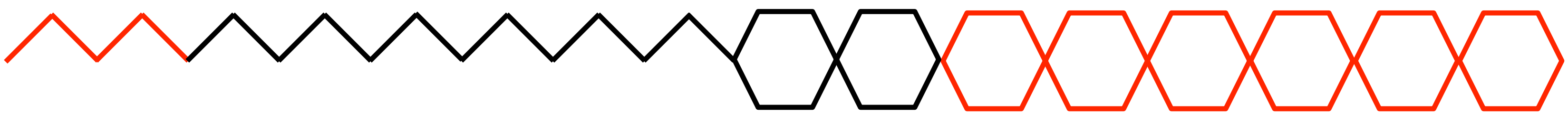
Conventional technology



Enzimatic technology



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Why alkylglycoside surfactant?
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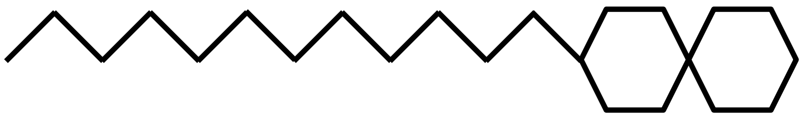
Conventional technology



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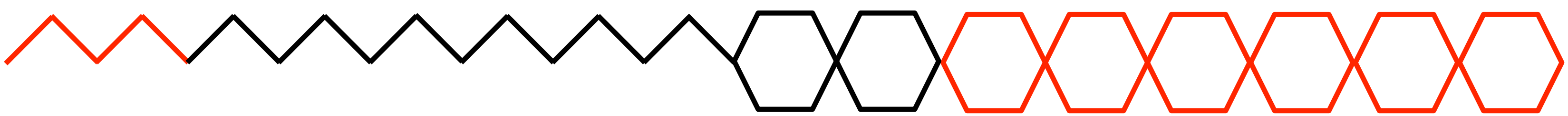
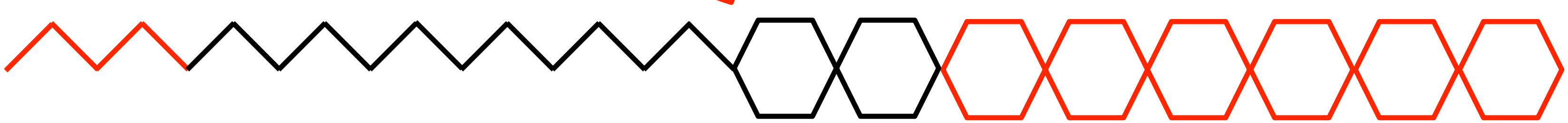


C16G8

Biocompatible
Biodegradable
From sustainable raw material
Soluble

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

Enzimatic technology



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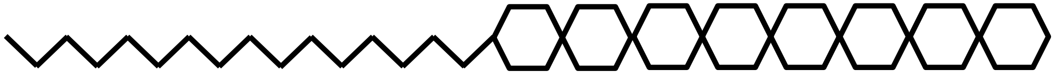
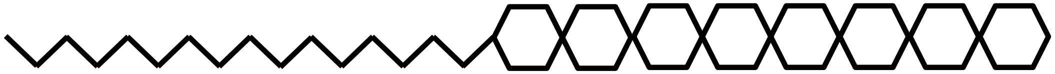
C16G8 

Self-assembly in water

C16G8-αβ

C16G8-β

C16G8 

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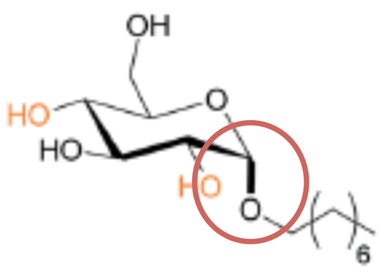
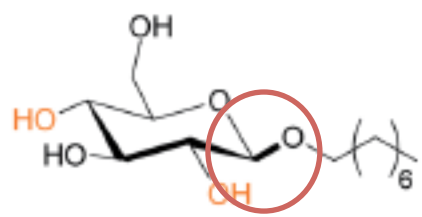
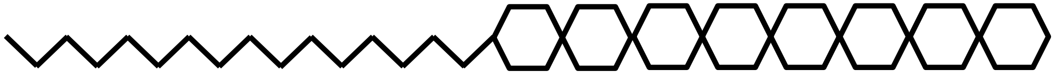


αOctylGlc **5**

C16G8-β



βOctylGlc **6**

C16G8 

Self-assembly in water

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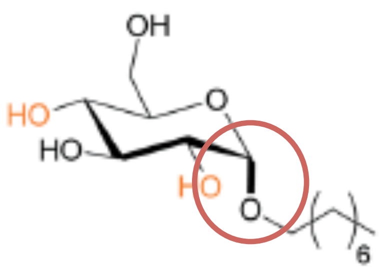
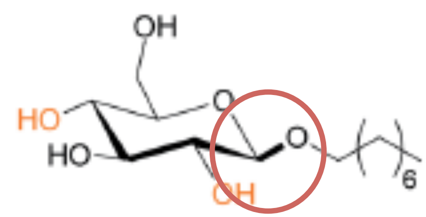


αOctylGlc **5**

C16G8-β



βOctylGlc **6**

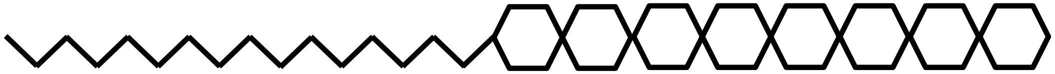
DLS

SLS

SAXS

SANS

2 temperatures and c = 1 mg ml^{-1}

C16G8 

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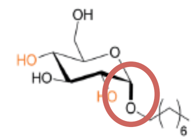

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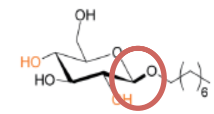


βOctylGlc **6**

C16G8-αβ

C16G8-β

DLS

hydrodynamic radius, R_H

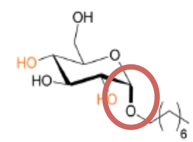
SLS

SAXS

SANS

C16G8

Self-assembly in water



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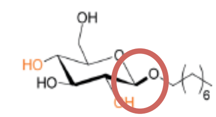


βOctylGlc **6**

C16G8-αβ

C16G8-β

DLS

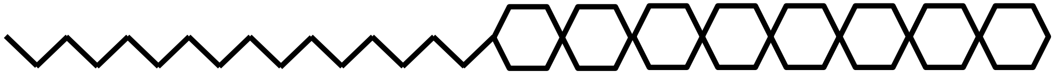
hydrodynamic radius, R_H

SLS

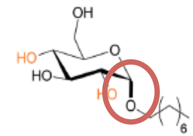
radius of gyration, R_G

SAXS

SANS

C16G8 

Self-assembly in water



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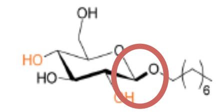


βOctylGlc **6**

C16G8-αβ

C16G8-β

DLS

hydrodynamic radius, R_H

SLS

radius of gyration, R_G

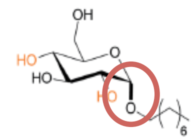
SAXS

SANS

shape and cross section

C16G8 

Self-assembly in water



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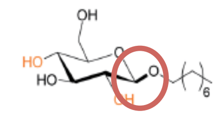


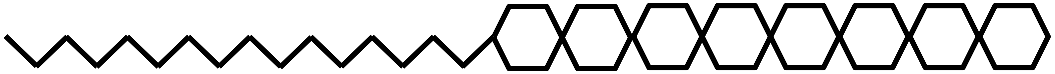
βOctylGlc **6**

C16G8-αβ

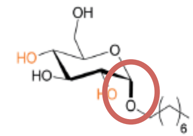
C16G8-β

What do we see?

particle motion	refractive index	electron density	nuclei and isotopes
DLS	SLS	SAXS	SANS
hydrodynamic radius, R_H	radius of gyration, R_G	shape and cross section	

C16G8 

Self-assembly in water



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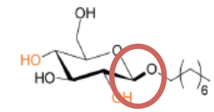


βOctylGlc **6**

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

	C16G8-αβ	C16G8-β
25°C		
45°C		

DLS

hydrodynamic radius, R_H

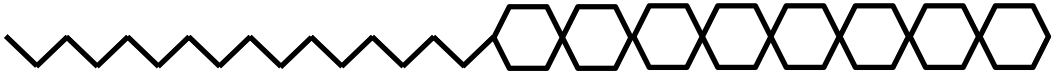
SLS

radius of gyration, R_G

SAXS

SANS

shape and cross section

C16G8 

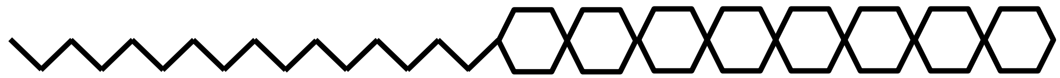
Self-assembly in water

αOctylGlc **5** βOctylGlc **6**

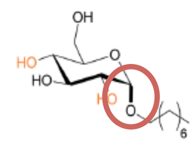
$c = 1\ \mathrm{mg\ ml^{-1}}$

	C16G8-αβ		C16G8-β	
25°C	83±3 nm		65±2 nm	
45°C	79±2 nm		59±1 nm	

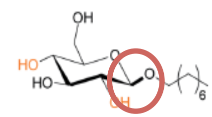
DLS	SLS	SAXS	SANS
hydrodynamic radius, R_H	radius of gyration, R_G	shape and cross section	

C16G8 

Self-assembly in water



αOctylGlc **5**



βOctylGlc **6**

c = 1 mg ml^{-1}

	C16G8-αβ	C16G8-β
25°C		
45°C		

DLS

hydrodynamic radius, R_H

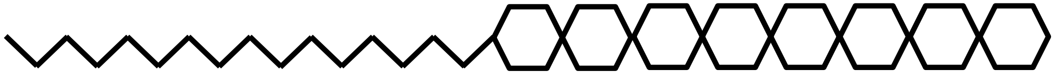
SLS

radius of gyration, R_G

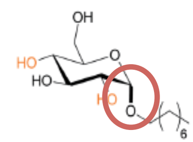
SAXS

SANS

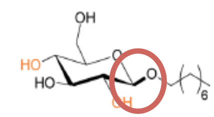
shape and cross section

C16G8 

Self-assembly in water



αOctylGlc 5



βOctylGlc 6

c = 1 mg ml^{-1}

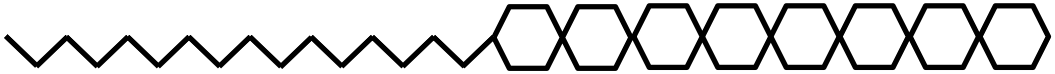
	C16G8-αβ	C16G8-β
25°C	Approximations not valid	51±2 nm
45°C		51±2 nm

q_{min} 6.8 × 10^{-4} Å^{-1}
$R_{g,max}$ 140 nm

DLS
hydrodynamic radius, R_H

SLS
radius of gyration, R_G

SAXS SANS
shape and cross section

C16G8 

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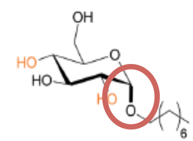

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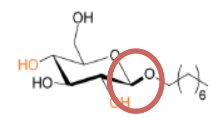


βOctylGlc 6

c = 1 mg ml^{-1}

	C16G8-αβ	C16G8-β
25°C		
45°C		

DLS

hydrodynamic radius, R_H

SLS

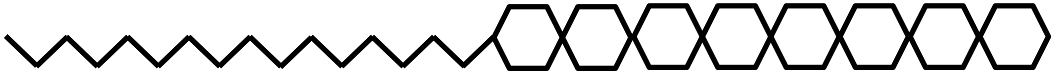
radius of gyration, R_G

SAXS

SANS

shape and cross section

C16G8

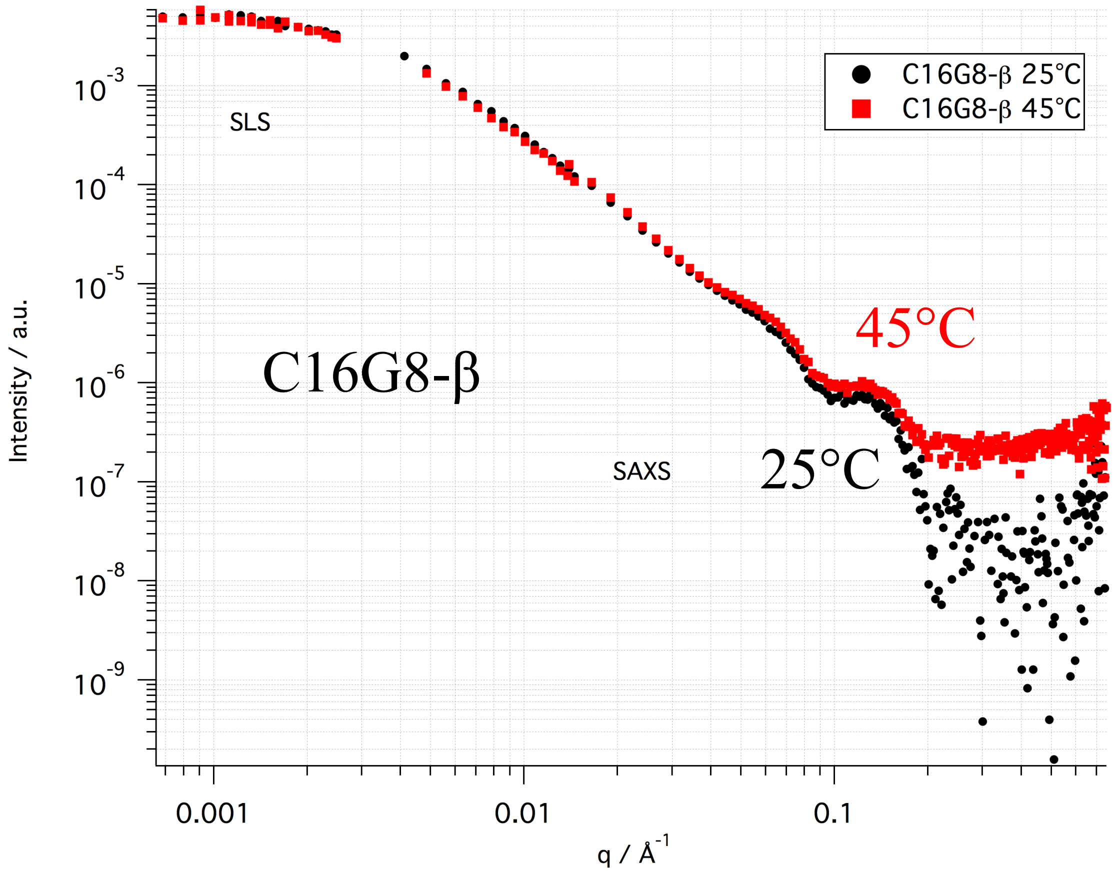


Self-assembly

c = 1 mg ml^{-1}

25°C

45°C



DLS

SLS

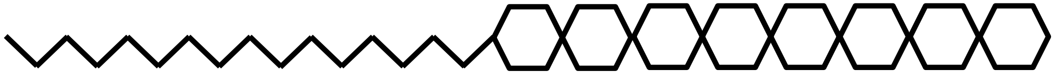
SAXS

SANS

hydrodynamic radius, R_H

radius of gyration, R_G

shape and cross section

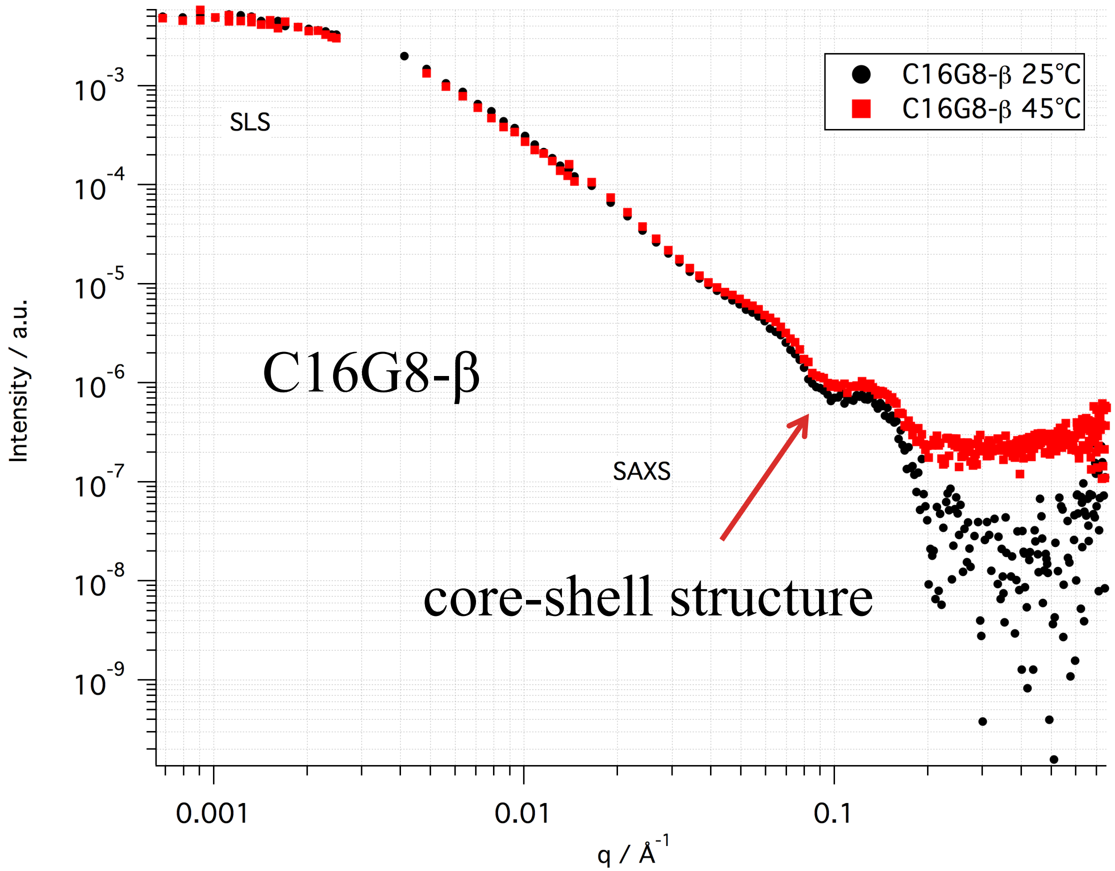
C16G8 

Self-assembly

c = 1 mg ml^{-1}

25°C

45°C



DLS

hydrodynamic radius, R_H

SLS

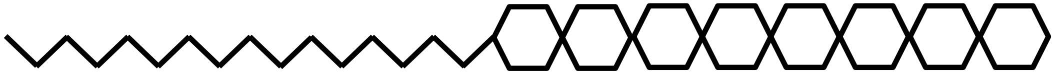
radius of gyration, R_G

SAXS

SANS

shape and cross section

C16G8

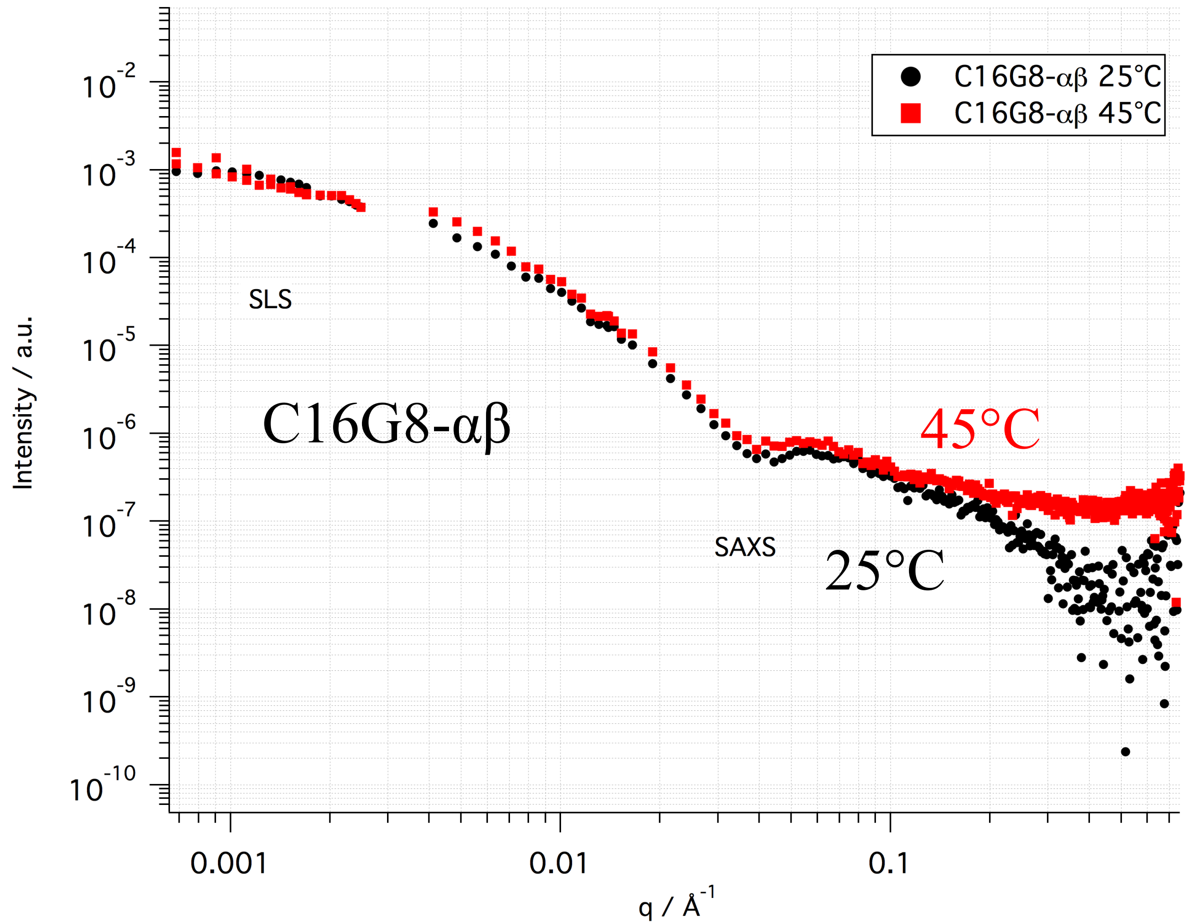


Self-assembly

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

25°C

45°C



DLS

SLS

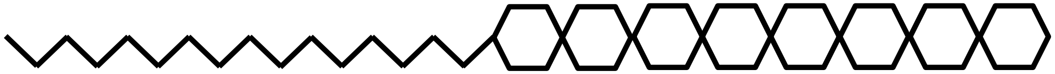
SAXS

SANS

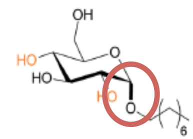
hydrodynamic radius, R_H

radius of gyration, R_G

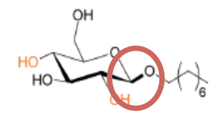
shape and cross section

C16G8 

Self-assembly in water



αOctylGlc **5**



βOctylGlc **6**

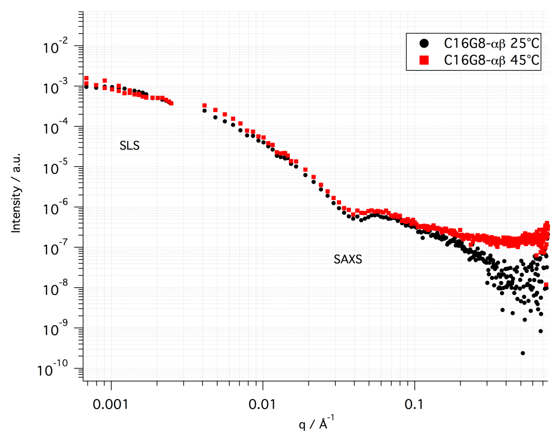
$c = 1\ \mathrm{mg\ ml^{-1}}$

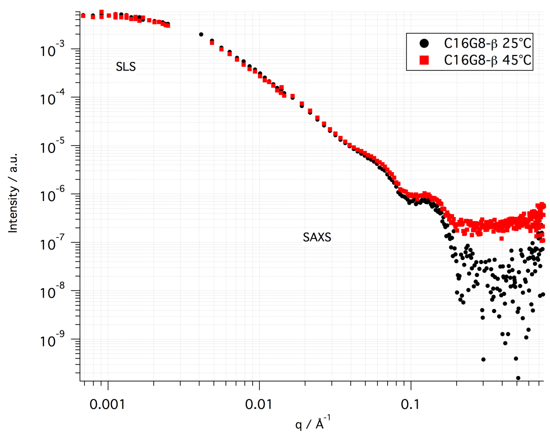
C16G8-αβ

C16G8-β

25°C

45°C





core-shell structure

DLS

hydrodynamic radius, R_H

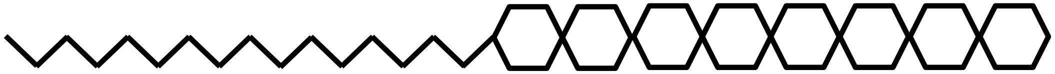
SLS

radius of gyration, R_G

SAXS

SANS

shape and cross section

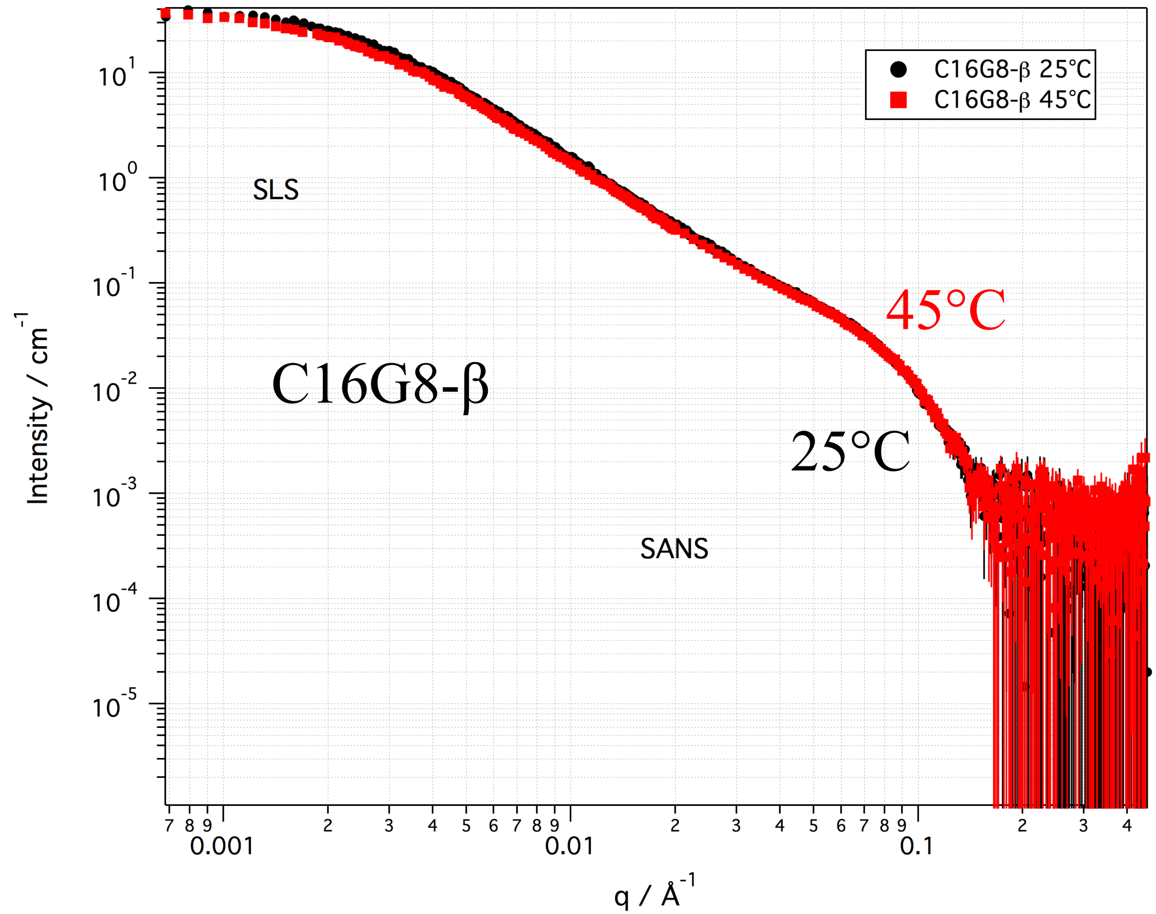
C16G8 

Self-assembly

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

25°C

45°C



DLS

hydrodynamic radius, R_H

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radius of gyration, R_G

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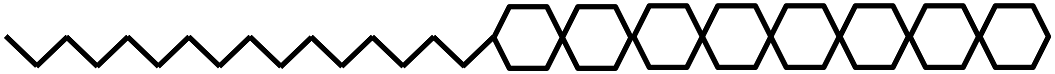
shape and cross section

C16G8 

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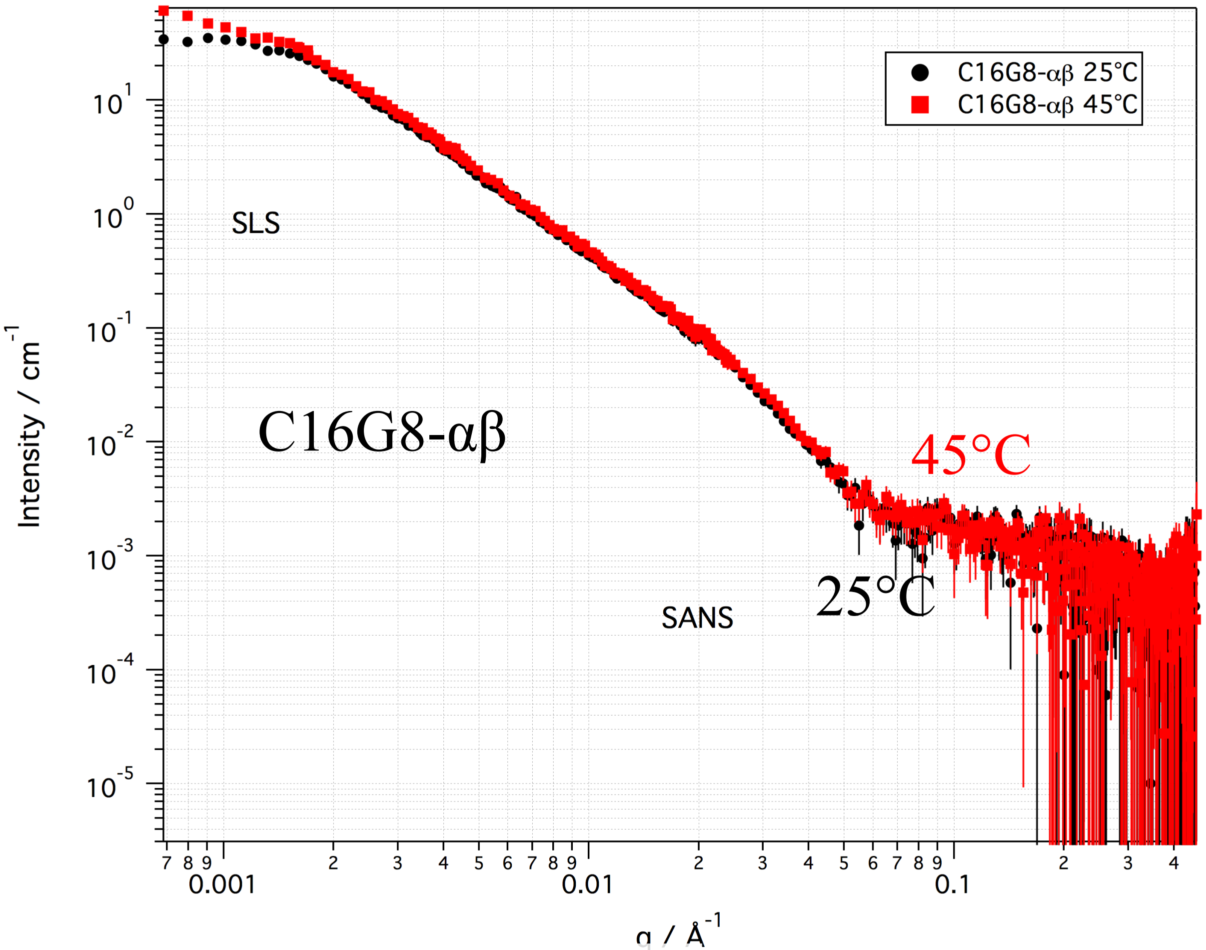

DLS

hydrodynamic radius, R_H

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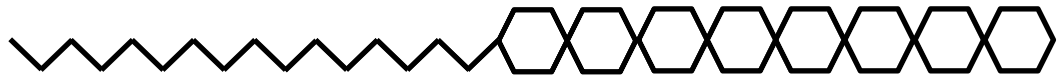
shape and cross section

C16G8 

Self-assembly

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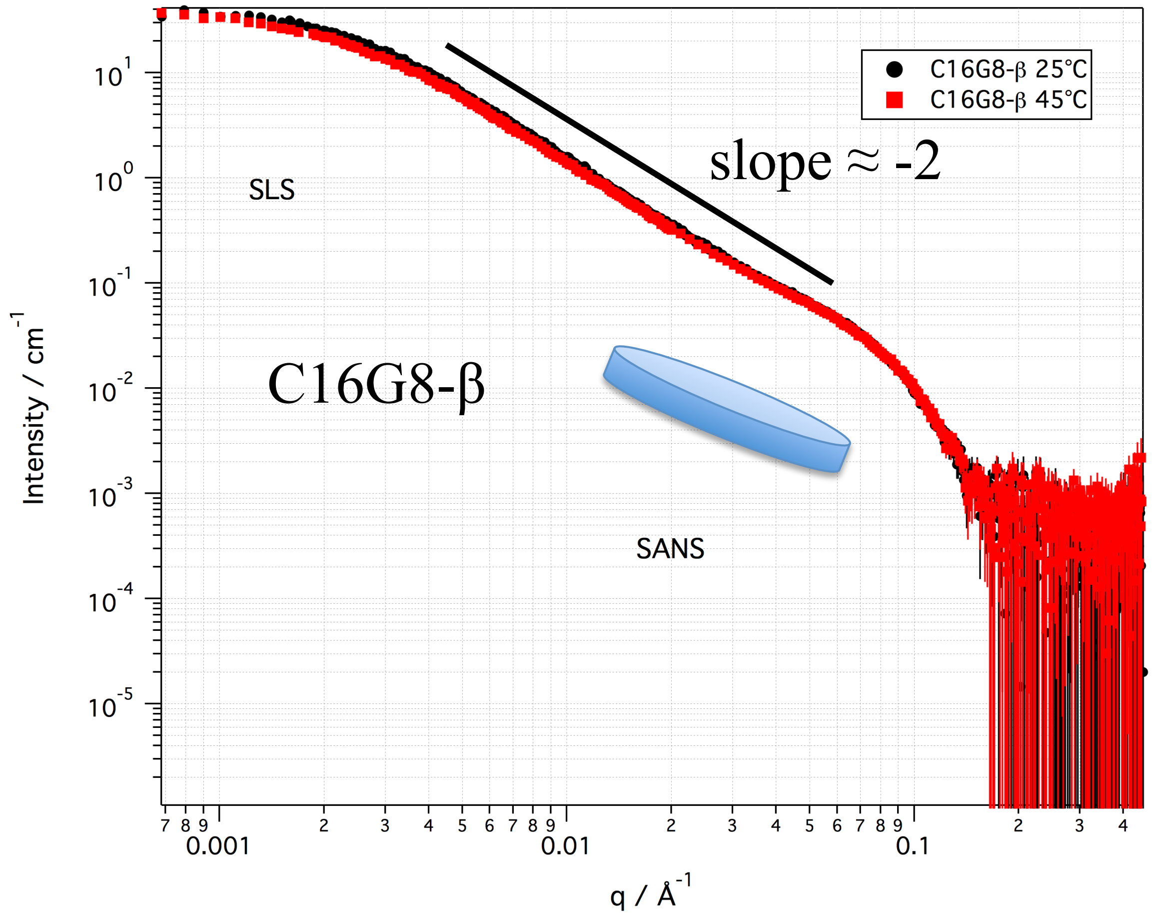
25°C

45°C



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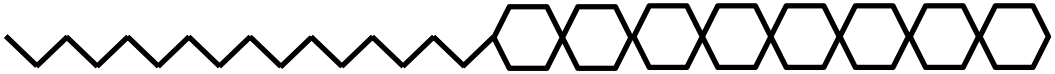
SANS

shape and cross section

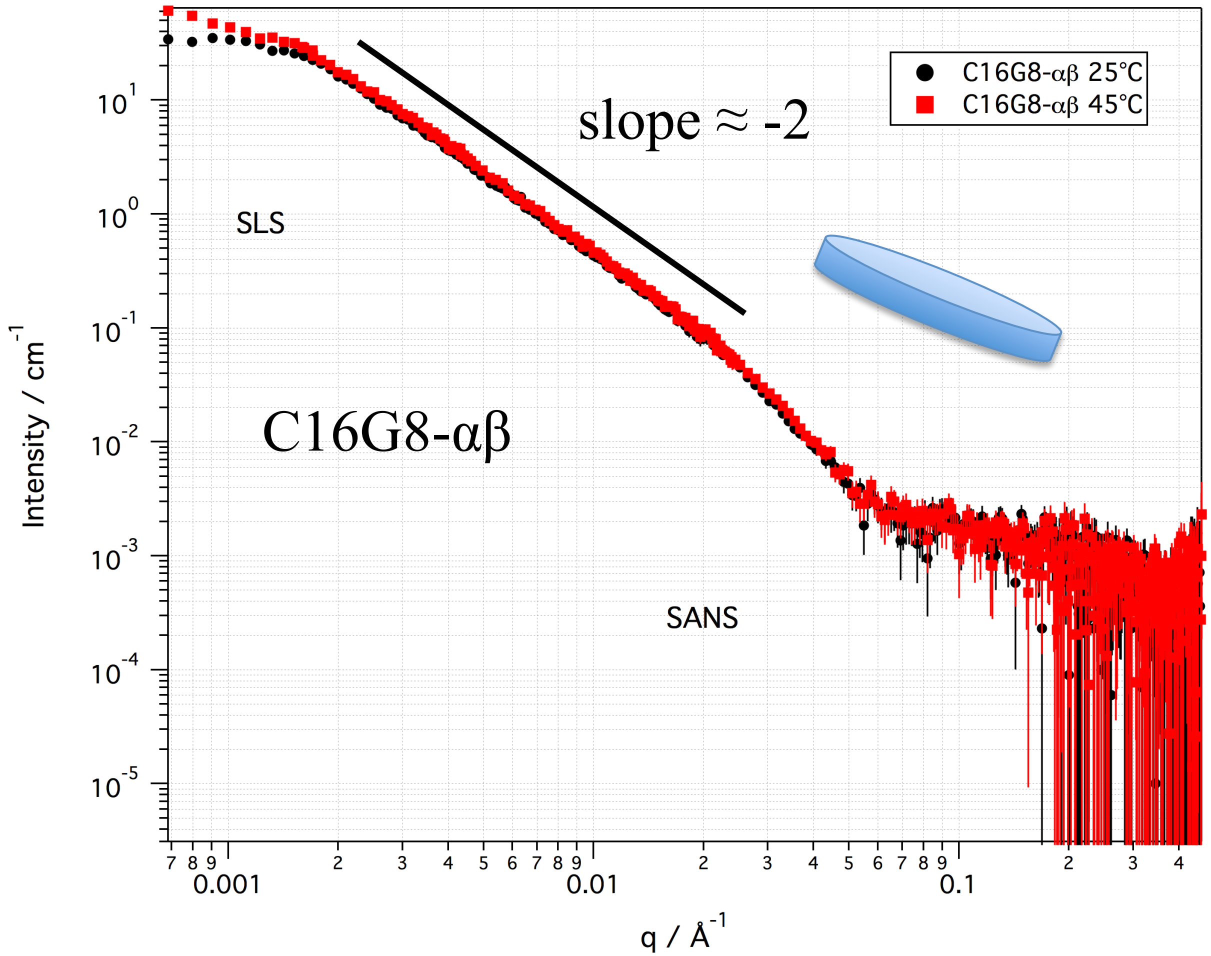
C16G8 

Self-assembly

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

25°C

45°C



DLS

hydrodynamic radius, R_H

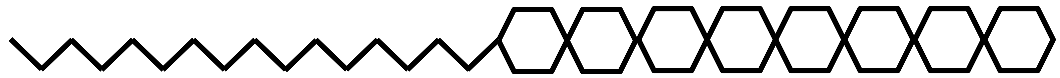
SLS

radius of gyration, R_G

SAXS

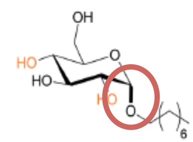
SANS

shape and cross section

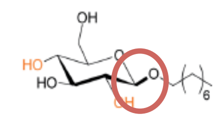
C16G8 

SUMMARY

Self-assembly in water



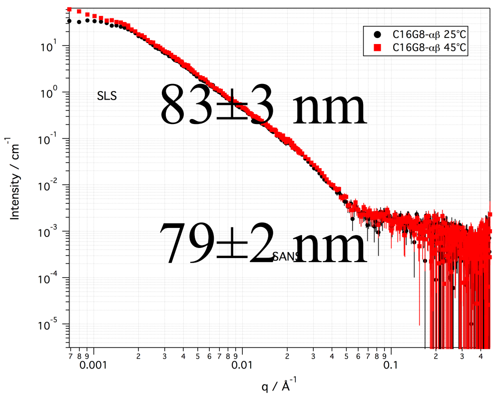
αOctylGlc **5**

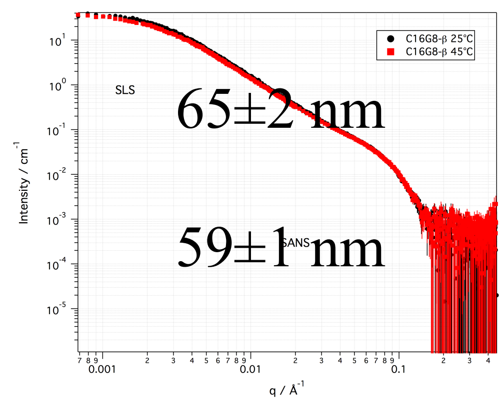


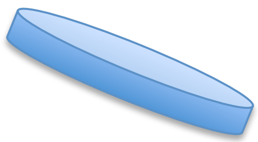
βOctylGlc **6**

c = 1 mg ml^{-1}

	C16G8-αβ	C16G8-β
25°C	83±3 nm	65±2 nm
45°C	79±2 nm	59±1 nm





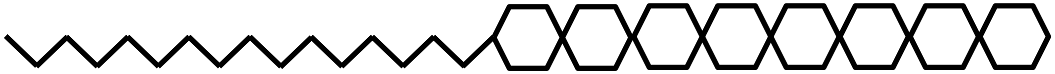


core-shell

DLS — hydrodynamic radius, R_H

SLS — radius of gyration, R_G

SAXS, SANS — shape and cross section

C16G8 

Self-assembly in water C16G8-β 25°C

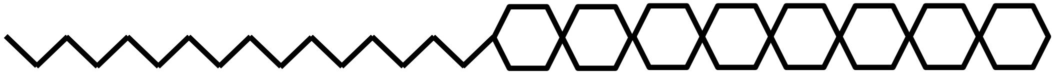
11 concentrations from 2.5 μM to 250 μM (cmc = 25 μM = 0.034 mg ml^{-1})

DLS

hydrodynamic radius, R_H

NMR Diffusion

self-diffusion coefficient, D

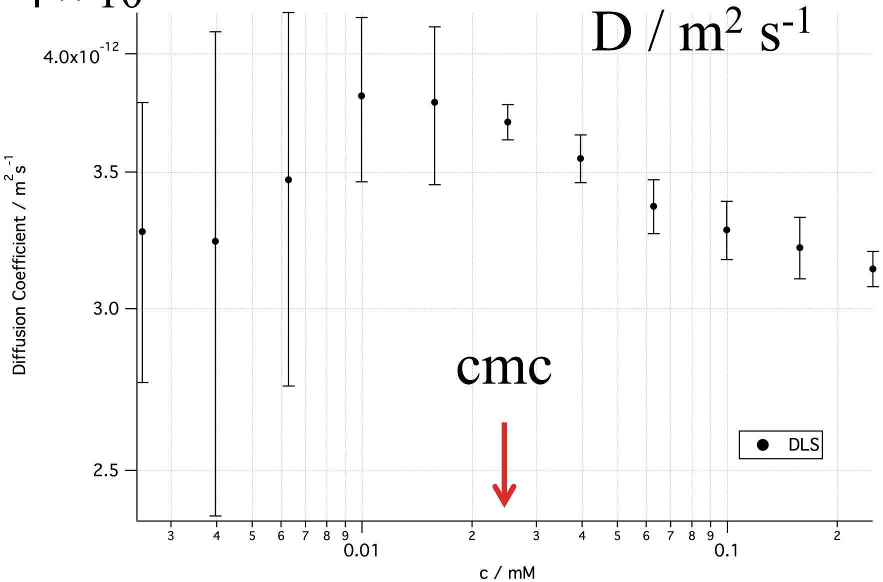
C16G8 

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 / m^2 s^{-1}



cmc

DLS

NMR Diffusion

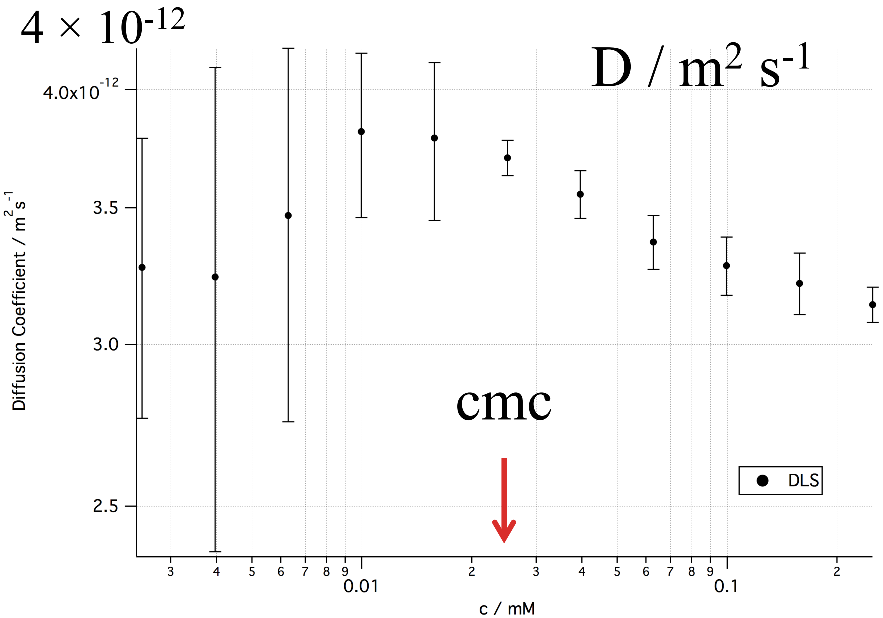
hydrodynamic radius, R_H

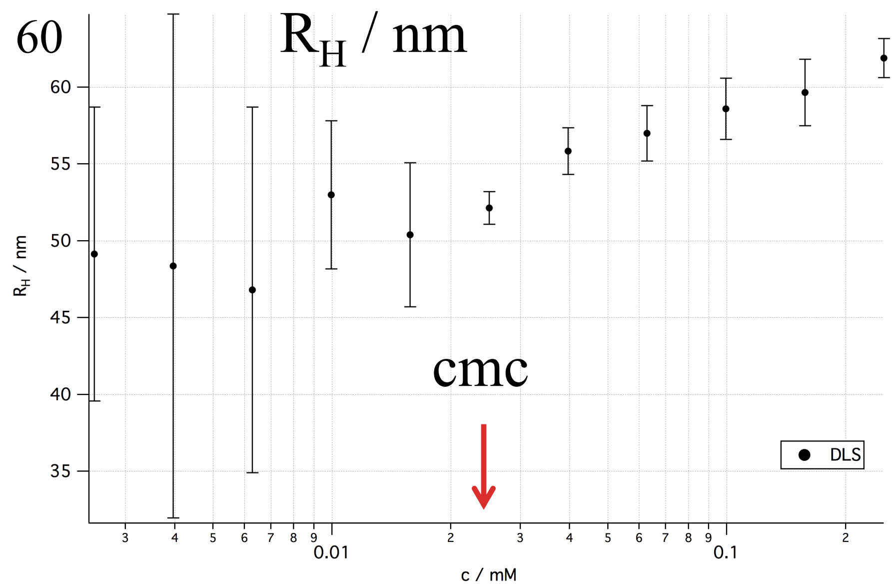
self-diffusion coefficient, D

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})





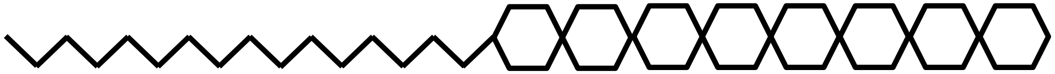
DLS

hydrodynamic radius, R_H

NMR Diffusion

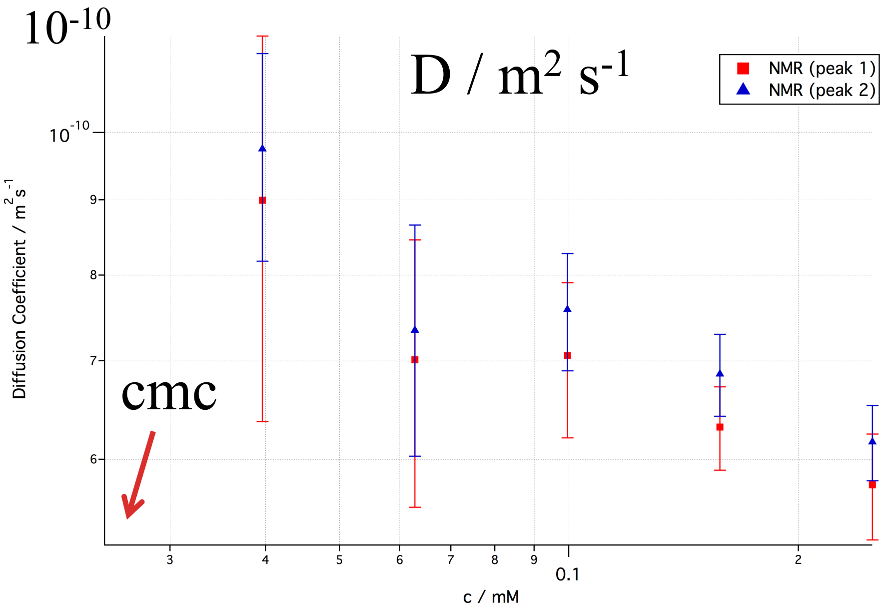
self-diffusion coefficient, D

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})

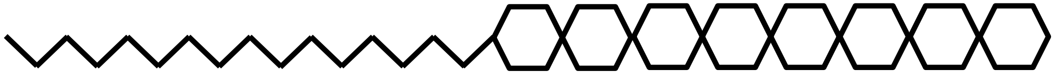


DLS

NMR Diffusion

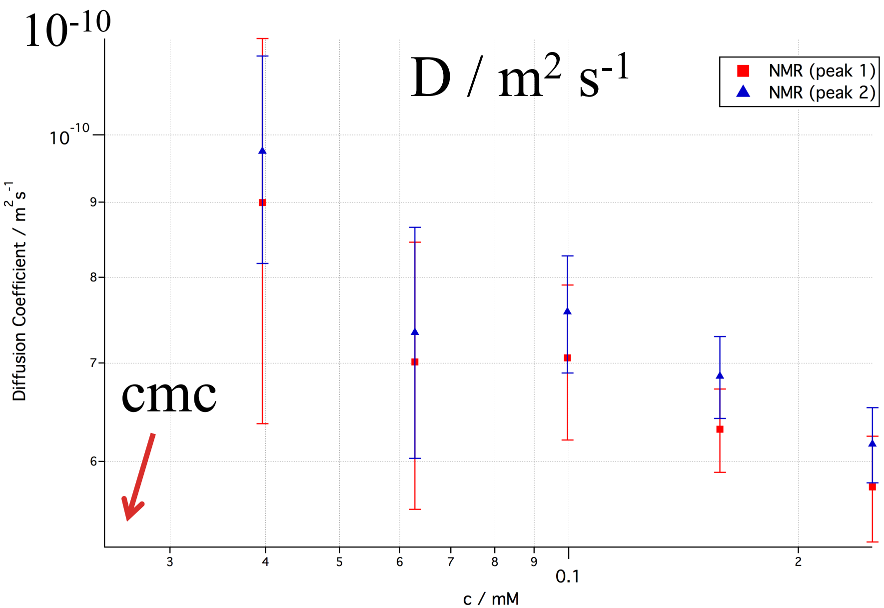
hydrodynamic radius, R_H

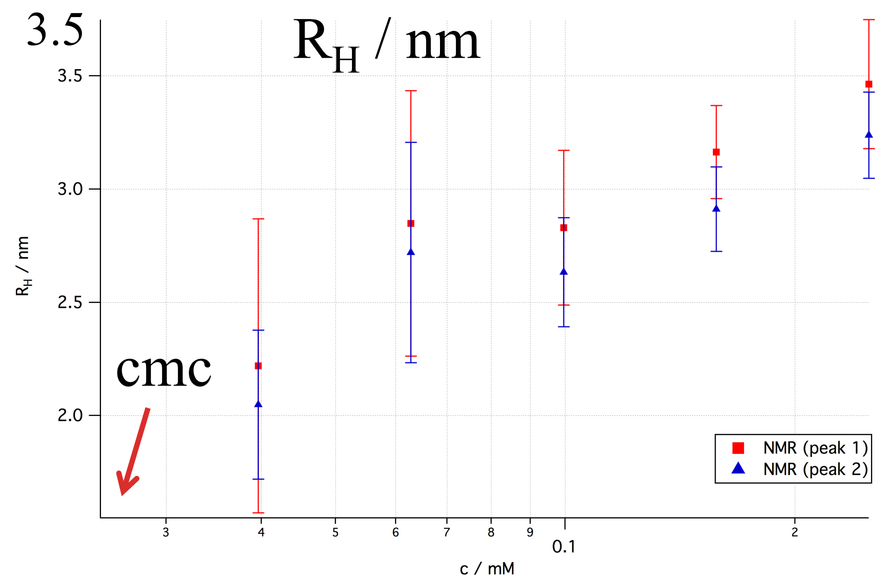
self-diffusion coefficient, D

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})





DLS

hydrodynamic radius, R_H

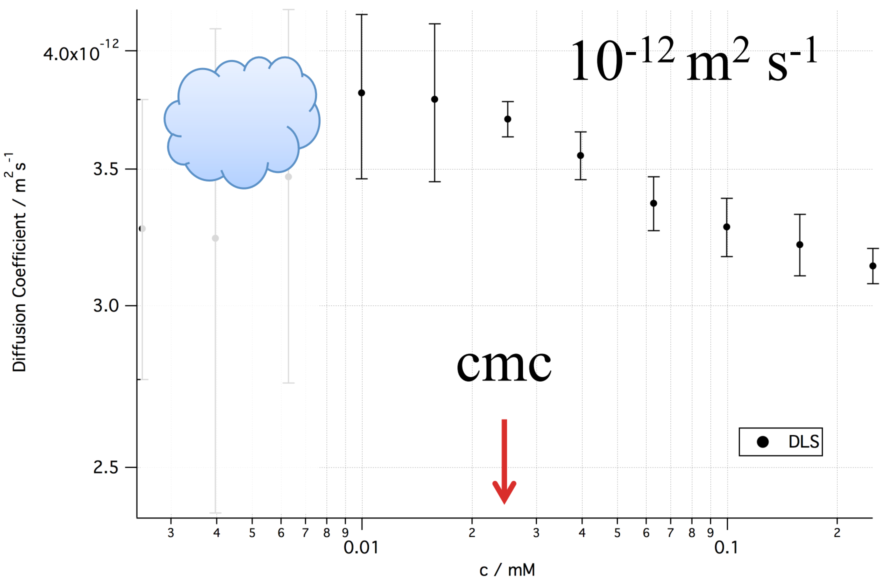
NMR Diffusion

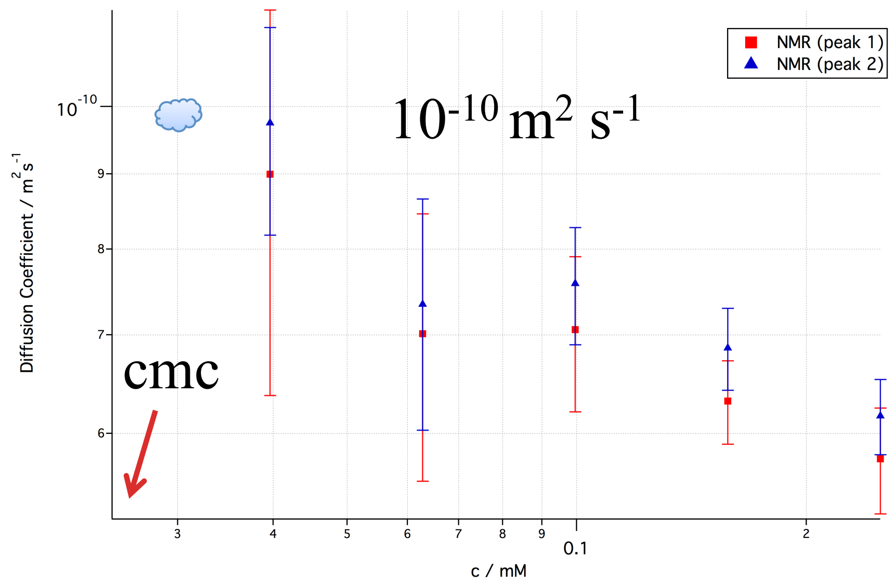
self-diffusion coefficient, D

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})





DLS

hydrodynamic radius, R_H

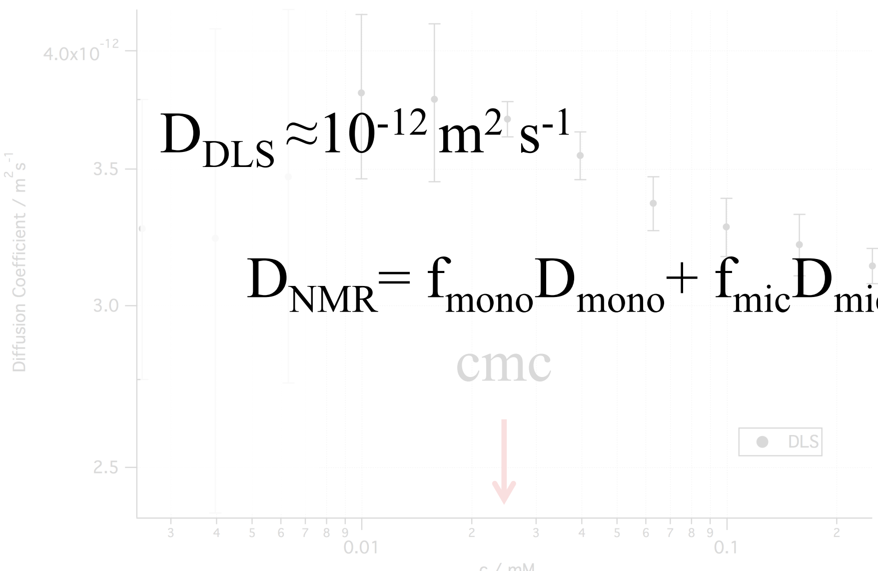
NMR Diffusion

self-diffusion coefficient, D

C16G8

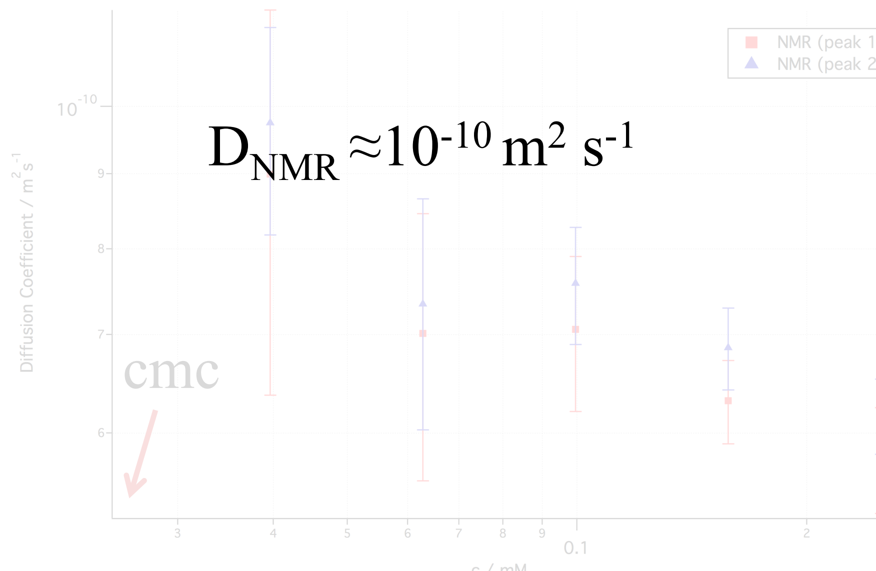
Self-assembly in water C16G8-β 25°C

11 concentrations from 2.5 μM to 250 μM (cmc = 25 μM = 0.034 mg ml^{-1})



$D_{DLS} \approx 10^{-12}\ m^2\ s^{-1}$

$D_{NMR} = f_{mono}D_{mono} + f_{mic}D_{mic}$



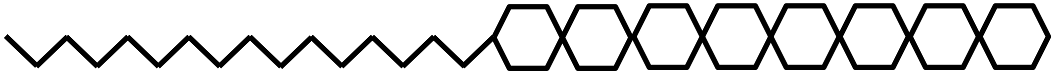
$D_{NMR} \approx 10^{-10}\ m^2\ s^{-1}$

DLS

hydrodynamic radius, R_H

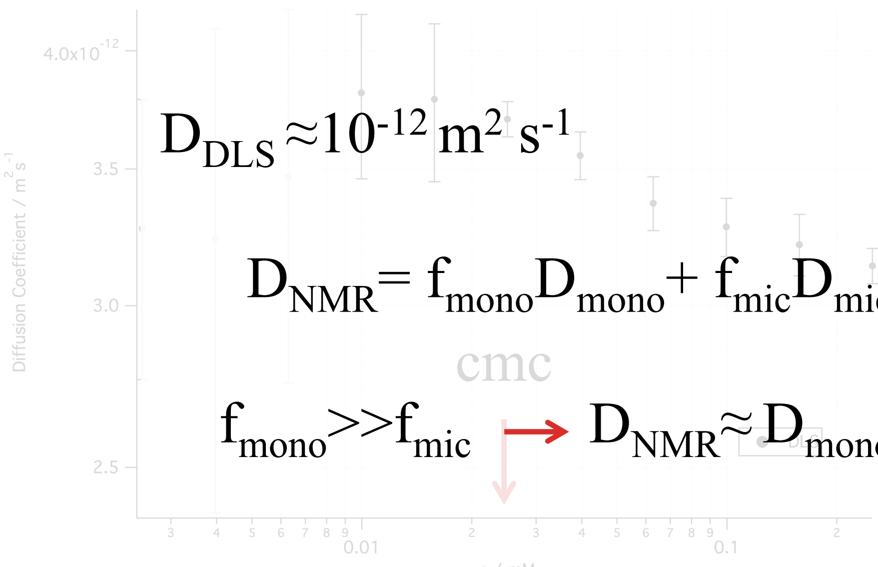
NMR Diffusion

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})

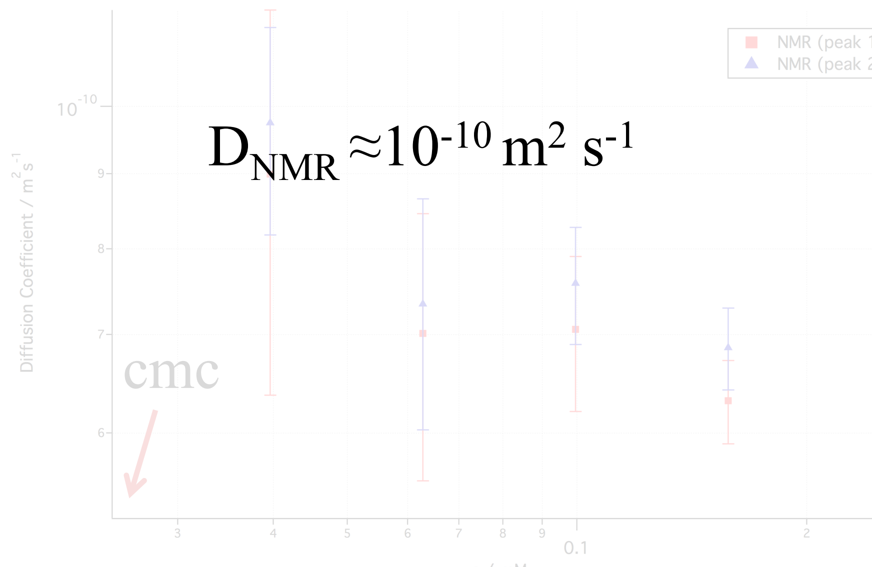


$D_{DLS} \approx 10^{-12}\ m^2\ s^{-1}$

$D_{NMR} = f_{mono}D_{mono} + f_{mic}D_{mic}$

cmc

$f_{mono} >> f_{mic} \rightarrow D_{NMR} \approx D_{mono}$



$D_{NMR} \approx 10^{-10}\ m^2\ s^{-1}$

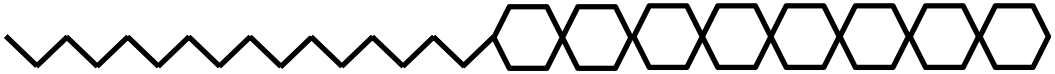
cmc

DLS

hydrodynamic radius, R_H

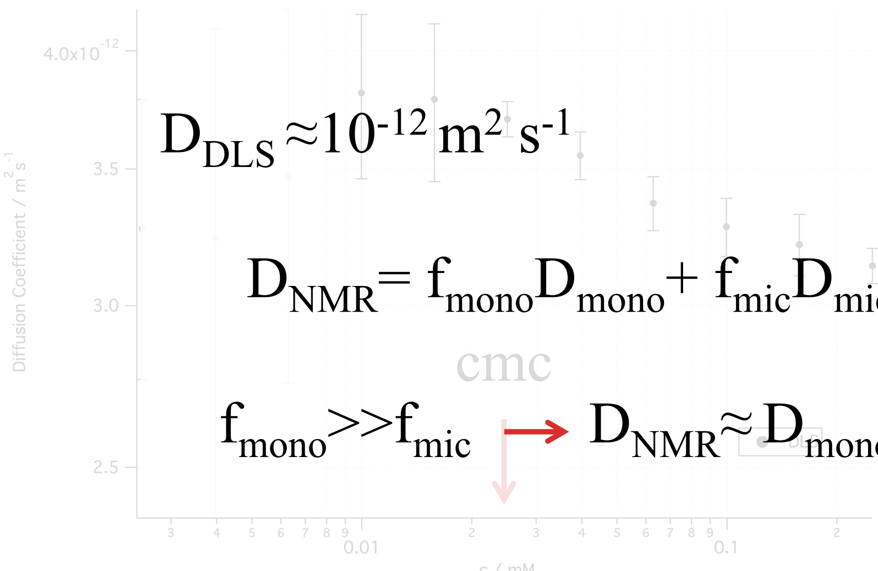
NMR Diffusion

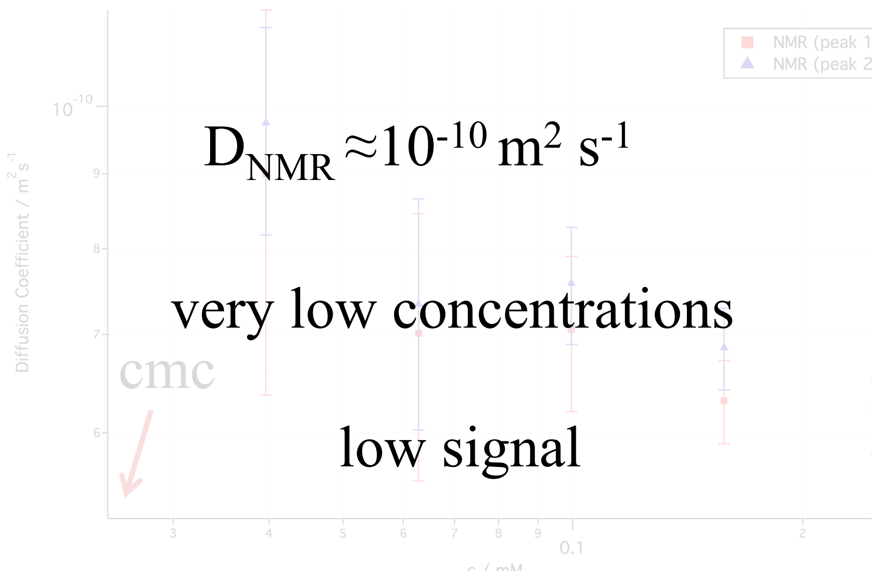
self-diffusion coefficient, D

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})





$D_{DLS} \approx 10^{-12}$ m^2 s^{-1}

$D_{NMR} = f_{mono} D_{mono} + f_{mic} D_{mic}$

$f_{mono} >> f_{mic} \rightarrow D_{NMR} \approx D_{mono}$

$D_{NMR} \approx 10^{-10}$ m^2 s^{-1}

very low concentrations

low signal

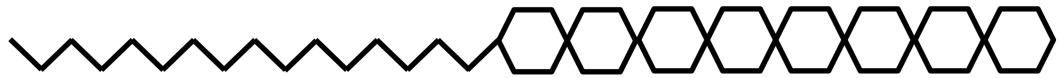
DLS

hydrodynamic radius, R_H

NMR Diffusion

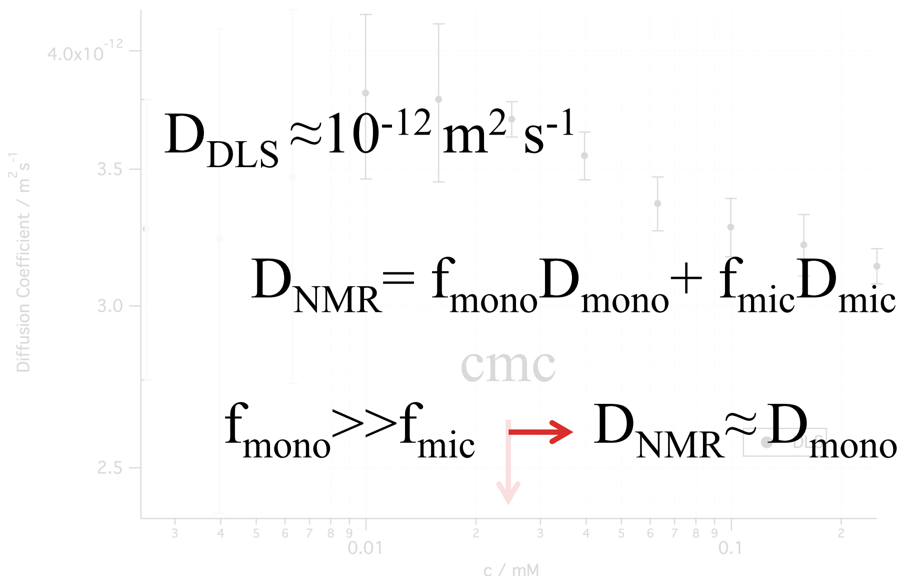
self-diffusion coefficient, D

C16G8



Self-assembly in water C16G8-β 25°C

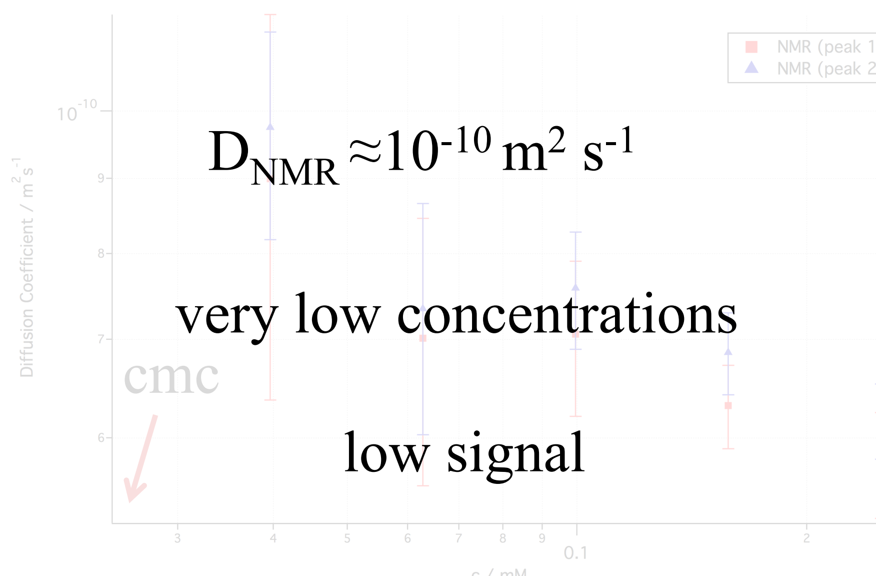
11 concentrations from 2.5 µM to 250 µM (cmc = 25 µM = 0.034 mg ml^{-1})



$D_{DLS} \approx 10^{-12}\ m^2\ s^{-1}$

$D_{NMR} = f_{mono} D_{mono} + f_{mic} D_{mic}$

$f_{mono} >> f_{mic} \rightarrow D_{NMR} \approx D_{mono}$



$D_{NMR} \approx 10^{-10}\ m^2\ s^{-1}$

very low concentrations

low signal

DLS

hydrodynamic radius, R_H

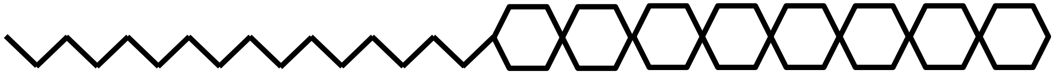
NMR Diffusion

self-diffusion coefficient, D

"unconventional" behaviour

NMR in concentrated samples needed

C16G8



Self-assembly in water

C16G8-β

C16G8-αβ

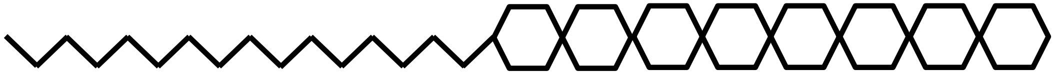
T = 25, 45, 65°C

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

SANS

shape and cross section

C16G8



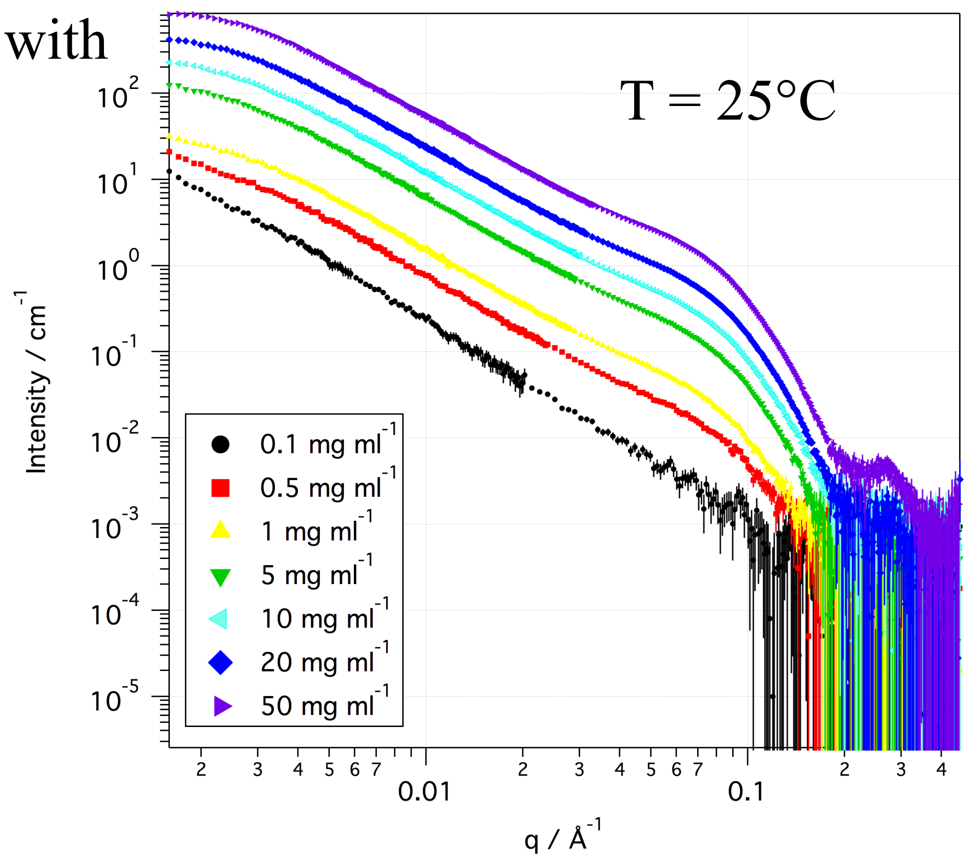
Self-assembly in water

C16G8-β

C16G8-αβ

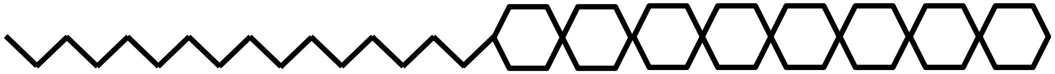
T = 25, 45, 65°C
c = 0.1, 0.5, 1, 5, 10, 20, 50 mg ml^{-1}

Intensity scales with concentration



SANS

shape and cross section

C16G8 

Self-assembly in water

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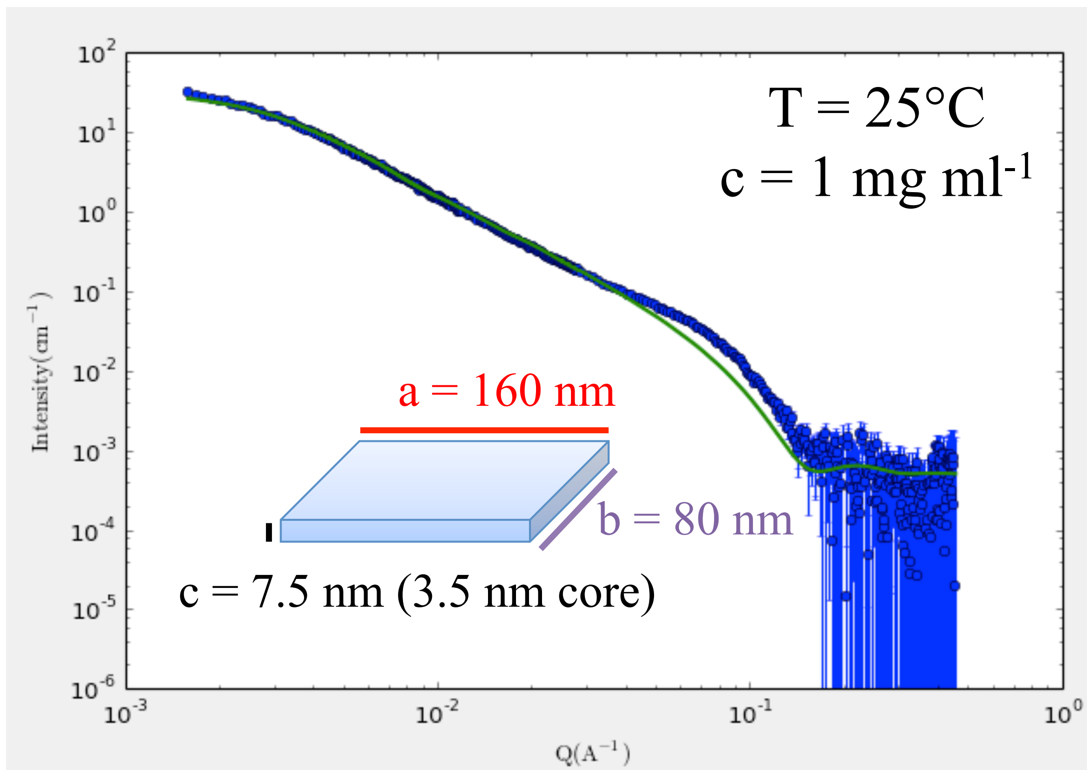
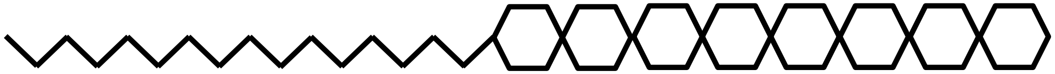


SANS

shape and cross section

C16G8

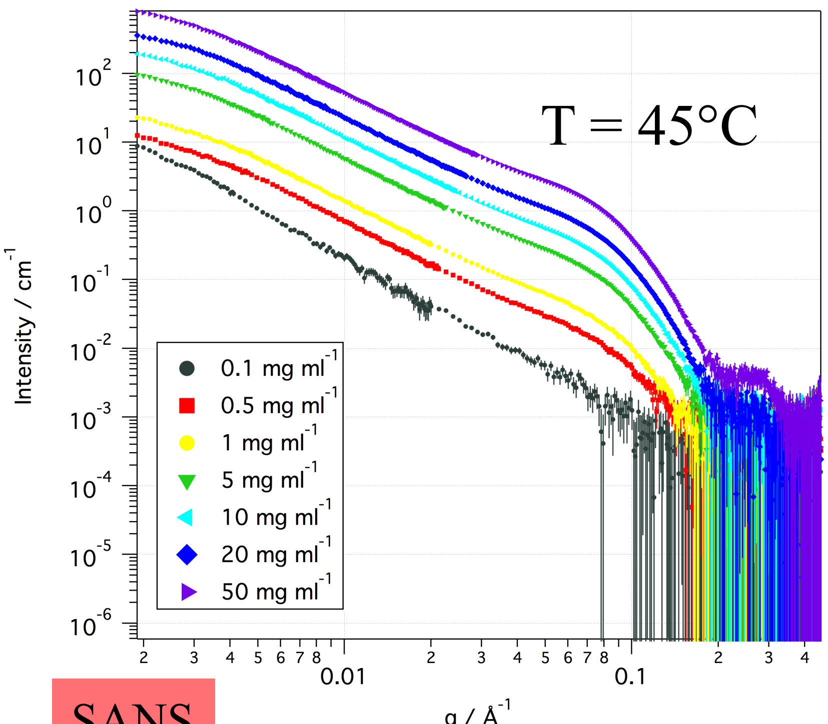


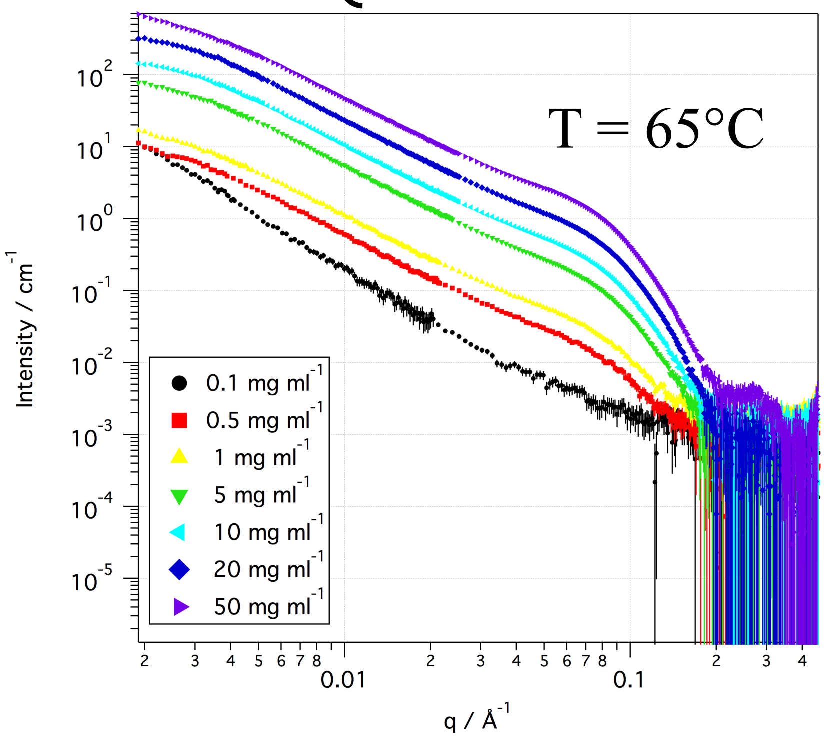
Self-assembly in water

C16G8-β

C16G8-αβ

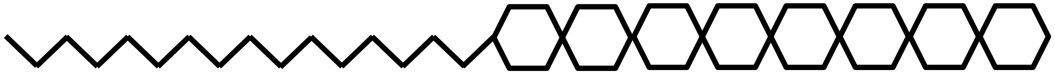
T = 25, 45, 65°C
c = 0.1, 0.5, 1, 5, 10, 20, 50 mg ml^{-1}





SANS

shape and
cross section

C16G8 

Self-assembly in water

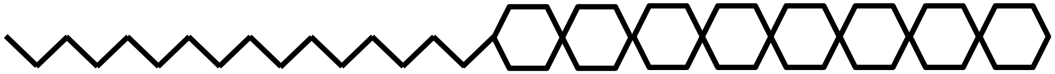
C16G8-β

C16G8-αβ

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

SANS

shape and cross section

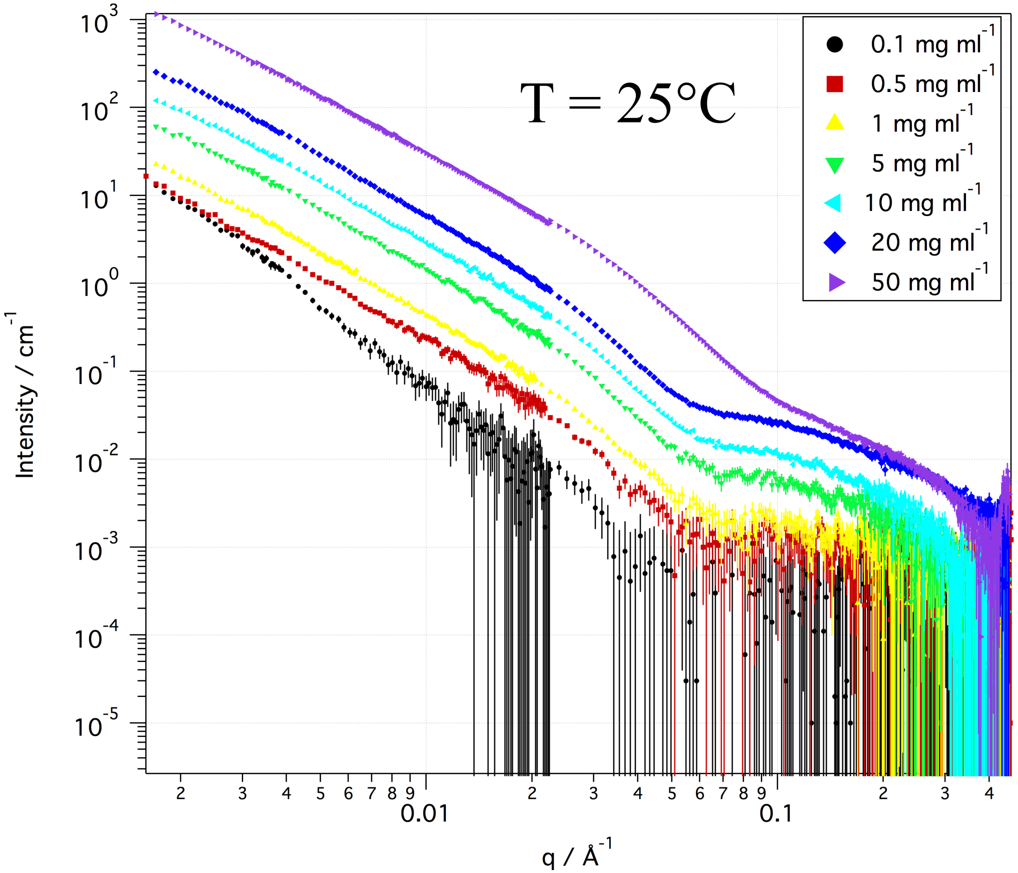
C16G8 

Self-assembly in water

C16G8-β

C16G8-αβ

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



SANS

shape and cross section

C16G8 

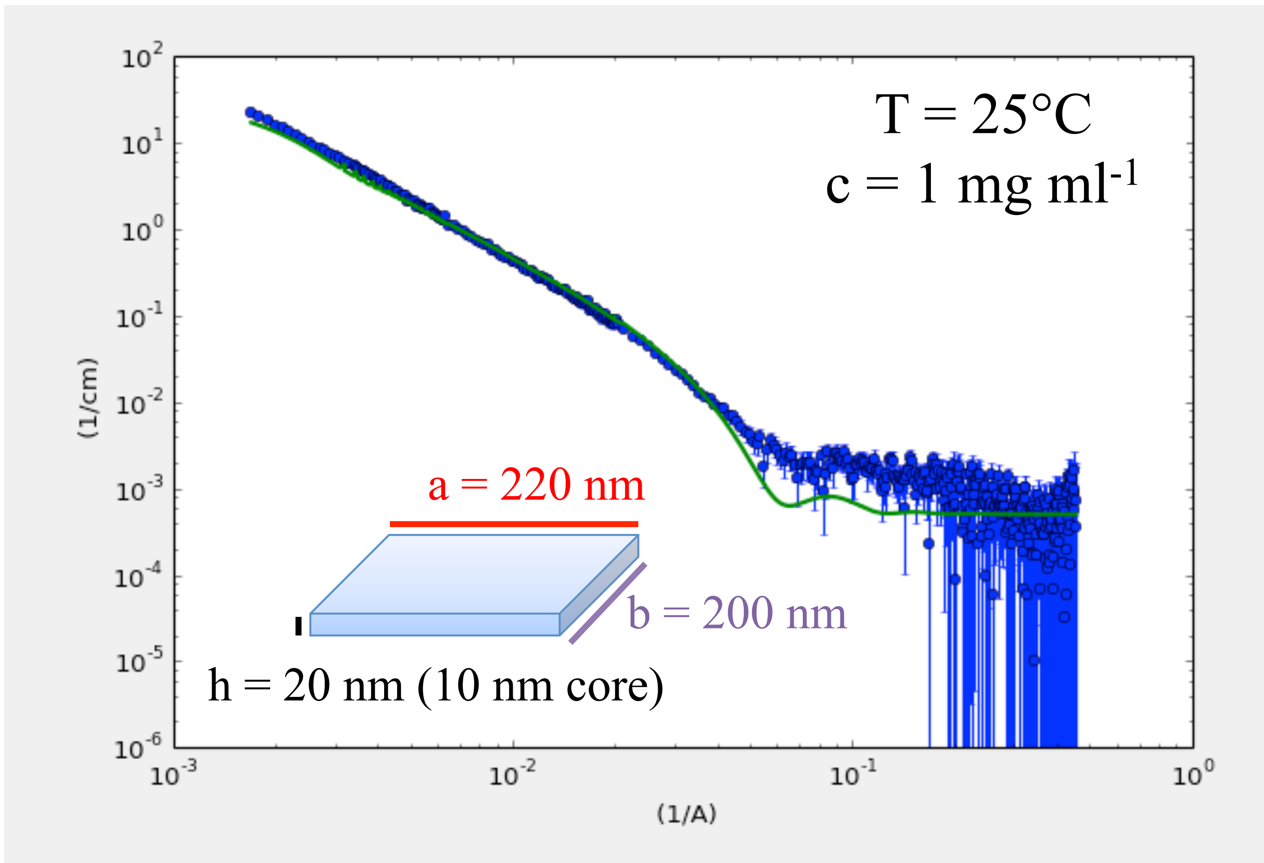
Self-assembly in water

C16G8-β

C16G8-αβ

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

higher q_{min}
smaller h



SANS

shape and cross section

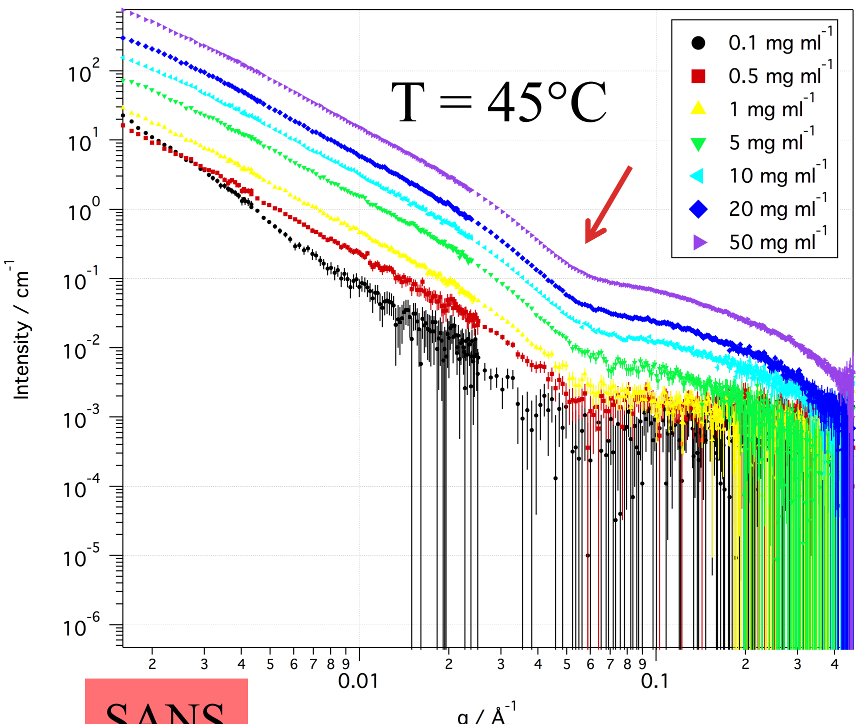
C16G8 

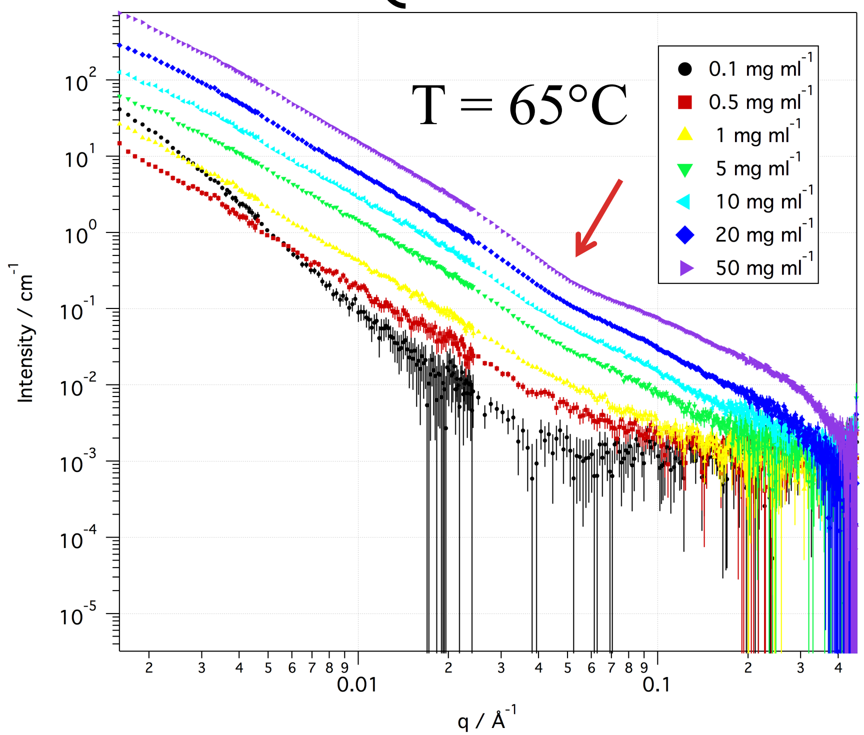
Self-assembly in water

C16G8-β

C16G8-αβ

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





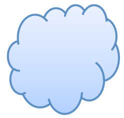
SANS

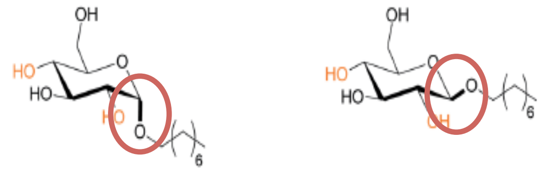
shape and cross section

Conclusions and Future plans

C16G8-αβ

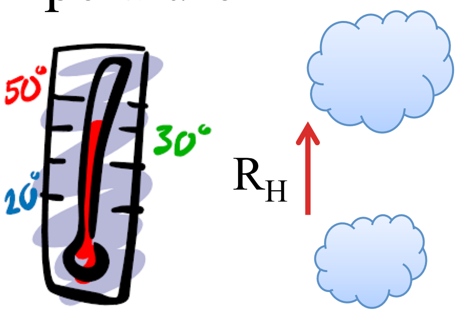
C16G8-β





αOctylGlc **5** βOctylGlc **6**

Temperature

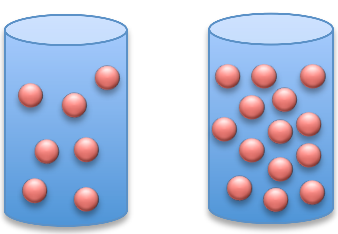


Cross section

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

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Göran Carlström

Department of Chemistry, Lund University

Lionel Porcar

Institut Laue Langevin, Grenoble, France