Trimethylsilyl Hedgehogs - A novel class of super-efficient hydrocarbon surfactants

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Supporting Information

The experimental details which outline the various instruments and techniques used are included in the article. The supporting information provides the data and analysis used to help characterise the various TMS-hedgehogs synthesised, in the following order:

Pg. 2-8) Chemical structures, ¹H NMR profiles, peak assignment and elemental analysis.

Pg. 9-10) Determining the cmc of AOTSiC from surface tension data.

Pg. 11-13) Details of the scattering models used.

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Chemical Structures



NMR + Elemental analysis







4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.: f1 (ppm)

Table 1: Data from ¹H NMR spectra shown above for AOTA and corresponding elemental analysis where experimentally obtained values are shown in blue.

Chemica shift	ıl	Integration		Identified proton - Multiplicity			
AOTA - Diester							
0.95		18.0			a - s		
3.89		4.	4.0		b - s		
6.86		2.	2.0 c - s				
AOTA - Surfactant							
0.85-0.83		18.	18.02 a - s		a - s		
2.79-2.98		1.0			c - dd		
3.58-3.73		2.01		b - m			
3.58-3.73		2.01 d - m		d - m			
	Theoretical - Experimental						
AOTA	С		Η		S		
Diester	65.	5 - 65.6	9.36 - 9.35		-		
Surfactant	46.66 - 46.76		6.99 - 7.19		8.90 - 8.78		

AOTB



Table 2: Data from ¹H NMR spectra shown above for AOTB and corresponding elemental analysis where experimentally obtained values are shown in blue.

Chemical shift		Integ	gration	Identified proton - Multiplicity				
AOTB - Surfactant								
0.84-0.87		18	3.0 a - s		a - s			
1.41-1.46		4.01		b - m				
2.70-2.86		2.0		d - dd				
3.58-3.62		1.0		e - dd				
3.94-4.04		4.0 c -		c - m				
	Theoretical - Experimental							
AOTB	С		Η		S			
Surfactant	49.4 - 49.89		7.47 - 7.3	34	8.24 - 8.17			

AOTSiA



Table 3: Data from ¹H NMR spectra shown above for AOTSiA and corresponding elemental analysis where experimentally obtained values are shown in blue.

Chemical shift		Integ	ration	Identified proton - Multiplicity			
AOTSiA - Surfactant							
0		18	0.0	a - s			
2.73-2.92	2.73-2.92		1.98		c - dd		
3.67-3.74		4.98		b - m			
3.67-3.94		4.98			d - m		
	Theoretical - Experimental						
AOTSiA	С		Η		S		
Surfactant	36.72 - 37.98		6.42 - 6 .	.48	8.17 - 8.01		

AOTSiB



Table 4: Data from ¹H NMR spectra shown above for AOTSiB and corresponding elemental analysis where experimentally obtained values are shown in blue.

Chemical shift		Integ	ration	Identified proton - Multiplicity				
AOTSiB - Surfactant								
0		18	.0) a - s				
0.82-0.91		4.01		b - m				
2.69-2.90		2.0		d - dd				
3.58-3.64		1.0		e - dd				
3.96-4.09		4.03 c - 1		c - mm				
	Theoretical - Experimental							
AOTSiB	С		Н		S			
Surfactant	39.98 - 40.12		6.95 - <mark>6</mark> .	.98	7.62 - 7.48			

AOTSiC



Table 5: Data from ¹H NMR spectra shown above for AOTSiC and corresponding elemental analysis where experimentally obtained values are shown in blue.

Chemical shift		Integration		Identified proton - Multiplicity			
AOTSiC - Surfactant							
-0.06		18	18.0		a - s		
0.39-0.48		4.01		b - m			
1.44-1.53		4.02		c - m			
2.73-2.92		2.02		e - dd			
3.62-3.67		1.0		f - dd			
3.86-3.93		4.0	02 d - m		d - m		
	Theoretical - Experimental						
AOTSiC	С		Η		S		
Surfactant	42.83 - 42.88		7.41 - 7.48		7.15 - 7.07		

Determining the cmc of AOTSiC

The same procedure was used to determine the cmc of each surfactant discussed in the article (AOTA, B, SiA, SiB and SiC). Here, the procedure is outlined for AOTSiC. From the surface tension data shown in Figure 1 below, the double differential is taken to show points of inflection along the curve, see Figure 2. A Gaussian function is then applied over the double differential to accurately assign the point at which the surfactants begin to micellise, shown in Figure 3. Based on the following method: Hait, S.K. and Moulik, S.P., 2001. *Journal of Surfactants and Detergents*, 4, **3**, 303-309.



Figure 1: Equilibrium surface tension data for AOTSiC at 25° C in water at an EDTA : surfactant ratio of 250 : 1.



Figure 2: Double differential of surface tension data shown in Figure 1 showing the greatest points of inflection along the curve.



Figure 3: Gaussian distribution applied over the double differential to accurately highlight the cmc which can be calculated from the exponential of the value xc.

Scattering models

SANS data were fitted to form factors describing either an ellipsoidal model, lamella paracrystal model, or spherical model using the fitting program SansView, which uses an iterative, least-squares fitting process. Known model parameters can be set to constant values (e.g. scattering length densities, dielectric constants, volume fractions) and unknown fit parameters set to 'float' allowing the program to refine them to obtain an optimized fit. The equations describing the different forms factors used are as follows:

Ellipsoids

The form factor (f(Q)) can be multiplied by a Hayter-Penfold charge repulsion (S(Q)) for charged particles. When $R_a < R_b$ the ellipsoid is said to be oblate (disc-like), when $R_a =$ R_b the equations effectively tend to that of the sphere form factor above and when $R_a > R_b$ the ellipsoid is said to be prolate (rod-like). The ellipsoid form factor is best employed for ellipticities (given by R_a , R_b , and X) that do not deviate from unity a great deal. When X $< \approx 0.2$ the scattering particle can said to be disc-like and a disc form factor would better describe the data. When X $> \approx 5$ the particle is rod-like and a cylinder form factor is more suitable.

$$p(q,\alpha) = \frac{Scale}{V}f^2(q) + bkg$$
(1)

$$f(q) = \frac{3(\Delta p)V(sin[qr(R_a, R_b, \alpha)] - qrcos[qr(R_a, R_b, \alpha)])}{qr(R_a, R_b, \alpha)}$$
(2)

$$r(R_a, R_b, \alpha) = [R_b^2 sin^2 \alpha + R_a^2 cos^2 \alpha]^{\frac{1}{2}}$$
(3)

where α is the angle between the axis of the ellipsoid and the Q-vector, V is the volume of the ellipsoid, R_a is the polar radius of the ellipsoid, R_b is the equatorial radius of the ellipsoid and $\Delta \rho$, the contrast, is the scattering length density difference between the scattering ellipsoid and the solvent.

Lamella paracrystal

The paracrystal model calculates the scattering from a stack of repeating lamellar structures with the stacks of laterally infinite lamellae treated as a paracrystal to account for the repeating spacing. The repeat distance is further characterized by a Gaussian polydispersity. The scattering intensity I(Q) is calculated as:

$$I(Q) = 2\pi (\Delta \rho)^2 \Gamma_m \frac{P_{bil}(Q)}{Q^2} Z_N(Q)$$
(4)

The form factor of the bilayer is approximated as the cross section of an infinite, planar bilayer of thickness D.

$$P_{bil}(Q) = \left(\frac{\sin(\frac{QD}{2})}{QD/2}\right)^2 \tag{5}$$

Here, the scale factor is used instead of the mass per area of the bilayer. The scale factor is the volume fraction of the material in the bilayer, not the total excluded volume of the paracrystal. $Z_N(Q)$ describes the interference effects for aggregates consisting of more than one bilayer. The parameters for this model are: bilayer thickness D, average distance between two adjacent layers L, distribution of layer distance P, and the number of layers N_{layer} .

Spheres

The form factor for a sphere is described below:

$$P(q) = \frac{Scale}{V} \left[\frac{3V(\Delta\rho)[sin(QR) - QRcos(QR)]}{(QR)^3}\right]^2 + bkg$$
(6)

Where scale is a factor used to put the intensity on an absolute scale, V is the scattering particle volume, R the scattering particle radius and bkg the background incoherent scattering. In the case of polydisperse spheres R is 148 further defined by a Gaussian distribution of homogeneous spheres given by the following equation:

$$f(R) = \frac{1}{\sigma\sqrt{2\pi}} exp[-\frac{1}{2\sigma^2}(R - R_{avg})^2]$$
(7)

Here σ is the standard deviation, R_{avg} is the average radius, and the polydispersity, $\mathbf{P} = \sigma/R_{avg}$.