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Supporting Information for Manuscript Entitled

Effects of Length and Hydrophilicity/Hydrophobicity of Diamines on Self-

assembly of Diamine/SDS Gemini-like Surfactants

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SANS Analysis Process for Micelle Core + Shell Model

The SANS data for the diamine/SDS mixtures are consistent with small globular interacting micelles which grow as the ratio of diamine/SDS increases. The data have been quantitatively analyzed on that basis. In SANS the scattering cross section, or scattered intensity, for colloidal aggregates or micelles in solution can be written by the general expression (1),

$$I(Q) = N \left| \int_{v} \left(\rho_{p}(r) - \rho_{s} \right) \exp iQ.rd^{3}r \right|^{2}$$
(1)

where ρ_p and ρ_s are the aggregate and solvent scattering length densities, and *N* is the number of aggregates per unit volume. In the micellar phase, the micelle structure is determined by analyzing the scattering data using a standard and well established model for globular micelles.¹ For a solution of globular polydisperse interacting particles (micelles) the scattered intensity can be written, in the "decoupling approximation"¹ as,

$$I(Q) = n \left[S(Q) \langle F(Q) \rangle_{Q} \right|^{2} + \left\langle \left| F(Q) \right\rangle_{Q}^{2} - \left| \langle F(Q) \rangle_{Q} \right|^{2} \right]$$
(2)

where the averages denoted by $\langle Q \rangle$ are averages over particles size and orientation, *n* is the micelle number density, *S*(*Q*) the structure factor, and *F*(*Q*) the form factor. The micelle structure (form factor) is modeled using a standard "core and shell" model (1), where the form factor is,

$$F(Q) = V_1(\rho_1 - \rho_2)F_0(QR_1) + V_2(\rho_2 - \rho_s)F_0(QR_2)$$
(3)

and R_1 , R_2 are the core and shell radii, $V_i = 4\pi R_i^3/3$,

 $F_0(QR_i) = 3j_1(QR_i)/(QR) = 3[\sin(QR) - QR\cos(QR)]/(QR)^3$, ρ_1 , ρ_2 and ρ_s are the scattering length densities of the micelle core and shell, and of the solvent, and $j_1(QR_i)$ is a first order spherical Bessel

function.

The micelle core + shell model¹ comprises an inner core made up of the alkyl chains only and constrained to space fill a volume limited by a radius, R_1 , the fully extended chain length of the surfactant, *l*. For larger aggregation numbers, ν , volumes greater than that defined by R_1 (as is found in this study) are accommodated by a prolate elliptical distortion with dimensions R_1 , R_1 , *eeR*₁ (where *ee* is the elliptical ratio). The outer shell, of dimensions R_2 , R_2 , *eeR*₂, contains headgroups and the corresponding hydration water. Representative hydration values for the anion and the bound counterions are included as fixed values¹ and the modeling is not particularly sensitive to variations in hydration. From the known molecular volumes and neutron scattering lengths the scattering length density (ρ) for the core, shell and solvent can be estimated.¹ The inter-particle interactions are included using the rescaled mean spherical approximation, RMSA, calculated for a repulsive screened coulombic potential,^{2,3} defined by the surface charge, *z*, the micelle number density, *n*, the micelle diameter, and the Debye-Huckel inverse screening length, κ .² The model parameters refined are then ν , *z*, and *ee*, and an acceptable model fit requires the shape of the scattering to be reproduced and the absolute value of the scattered intensity to be predicted to within $\pm 20\%$.

The Debye-Huckel inverse screening length, κ , (in Å⁻¹) is calculated from the estimated monomer concentration and (in the case of added electrolyte) the electrolyte concentration, such that,

$$\kappa = \sqrt{0.05Cee} \tag{4}$$

and *Cee* is the effective ionic concentration in moles, taking into account added electrolyte, free monomer anions and cations and macroions. In the calculations/modeling presented here κ is fixed at 0.05 (unless otherwise stated), and this corresponds to an effective ionic strength ~ 50 mM (this needs to be checked). Hydration/headgroup was fixed at 5.0 and unless stated otherwise no additional background subtraction was required other than that made during the data reduction. In the initial data analysis the solution concentration was fixed at 3 and 10 mM (unless otherwise stated) and the implications of this are discussed later. The effective concentration is in some cases much lower as the CMC can be a significant fraction of the overall concentration. This also has implications for the scale factors obtained and will be discussed in more detail later. The micelle number density, *n* (and micelle volume fraction, ϕ) are calculated from the known surfactant concentration, the CMC, and the solution concentration such that,

$$n = cN/\upsilon \tag{5}$$

where c is the micelle concentration, ($c = c_s - CMC$) and c_s is the solution concentration, and the volume fraction of micelles is,

$$\phi = NcV/\upsilon \tag{6}$$

The model has not at this stage specifically included the diamine in the structure and is accommodated for the longer hydrophobic diamines with the parameter ext. Ext is an additional parameter which allows the extent of the inner core to vary from *I*, to allow for packing variations. Ext typically varies from 0.8 to 1.2.

The Calculation Procedure for the Relationship between Ideal Mixed CMC Values (CMC_{mix}) and Binding Efficiency (k).

The formation of gemini-like surfactants can be expressed as $2S + C = S_2C$, where S is single-chain surfactant, C is connecting molecule, and S_2C is gemini-like surfactant. If the initial concentration of S and C are s and c, the molar ratio Y is equal to c/s. Supposing the binding efficiency is k ($0 \le k \le 1$), the concentrations of S, C and S_2C are respectively s-2sYk, sY-sYk, and sYk when $Y \le 0.5$, and are s-sk, sY-1/2sk, and 1/2sk when Y > 0.5. The ideal mixed CMC values (CMC_{mix}) can be determined by Clint's model for binary mixed micellar systems.⁴ Clint's equation, which assumes non-interaction between the individual components, is given by:

$$\frac{1}{\text{CMC}_{mix}} = \frac{\alpha_1}{\text{CMC}_1} + \frac{\alpha_2}{\text{CMC}_2}$$
(7)

where α_1 and α_2 are the mole fractions of *S* and S_2C in solution, and CMC₁ and CMC₂ are the CMC of *S* and S_2C under the similar experimental conditions. Furthermore, the presence of excessive connecting molecules is also ignored and CMC₁ is supposed to be equal to *f*CMC₂. In this case, the CMC_{mix} can be calculated by equation 7, and is consequently expressed as:

for
$$Y \le 0.5$$
, $CMC_{mix} = \frac{CMC_1(1 - Yk)}{1 + (f - 2)Yk}$ (8)

for Y > 0.5,
$$CMC_{mix} = \frac{CMC_1(2-k)}{2+(f-2)k}$$
 (9)

Here CMC_1 and f are constant, so CMC_{mix} is dependent on Yk when $Y \le 0.5$, and CMC_{mix} is only linearly relevant to k when Y > 0.5. The schematic curves of CMC_{mix} as a function of binding efficiency at the various molar ratios and as a function of molar ratio at the various binding efficiencies are shown in Figure S1.



Figure S1. The illustrated curves of mixed critical micelle concentration (CMC_{mix}) for the binary mixtures of single-chain surfactant and constructed gemini-like surfactant as a function of (a) binding efficiency (k) at various diamine/SDS molar ratio (Y), and (b) the diamine/SDS molar ratio (Y) at various binding efficiency (k).



Figure S2. Scattering intensity for the N₂C_n/SDS mixtures at $C_{SDS} = 3 \text{ mM}$ (a) and 10 mM (b) and the N₂C_mO_x/SDS mixtures at $C_{SDS} = 3 \text{ mM}$ (c) with different molar ratios (Y = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) and the SDS concentration of 10, 12, 15, 18 and 20 mM. The solid lines are model calculations as described in the text.



Figure S3. The variations of ellipticity (*ee*) for the micelles in the mixtures of 3 mM SDS and diamine $(N_2C_5, N_2C_7, N_2C_9; N_2C_4O, N_2C_6O, N_2C_6O_2, N_2C_8O_3)$ in D₂O at different molar ratios (*Y* = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) derived from fitting SANS results.

System	Diamine molar	Aggregation	Charge, z	Ext	ee
	ratio, Y	number, v			
SDS	0.0	58±5	16±2	1.0	1.00±0.05
N_2C_3/SDS	0.10	/1±/	32±4	1.0	1.20±0.05
	0.20	82±8	28		1.37
	0.30	84±8	22		1.41
	0.40	95±9	20		1.59
	0.50	82±8	26	_	1.39
N ₂ C ₅ /SDS	0.10	93±9	18±2	1.0	1.56±0.05
	0.20	118±12	18±2		1.97
	0.30	170±15	10±2		2.85±0.10
	0.40	1050±100	1		17.6±0.50
	0.50	1572±150	1		26.3±0.50
N ₂ C ₇ /SDS	0.10	118±10	24±2	1.0	2.00±0.05
	0.20	135±10	20±2		2.27
	0.30	242±20	9±2		4.06±0.1
	0.40	1286±100	1	1.05±0.02	18.6±0.5
N ₂ C ₉ /SDS	0.10	118±10	16±2	1.0	2.00±0.05
	0.20	147±14	22±2	1.0	2.46
	0.30	667±50	1	1.0	9.70±0.10
	0.40	1532±150	1	1.05±0.02	19.5±0.50
	0.50	2246±200	1	1.1±0.02	24.8±0.50
N ₂ C ₄ O/SDS	0.10	103±10	18±2	1.0	1.73±0.05
	0.20	138±12	16±2	1.0	2.32
	0.30	354±30	1	1.0	5.93±0.1
	0.40	1346±100	1	1.0	22.6±0.5
	0.50	1477±120	1	1.0	24.8±0.5
N ₂ C ₆ O/SDS	0.10	103±10	25±2	1.0	1.73±0.05
	0.20	128±12	20±2	1.0	2.14
	0.30	179±15	1	1.0	3.00±0.10
	0.40	918±100	1	1.0	15.4±0.50
$N_2C_6O_2/SDS$	0.10	104±10	16±2	1.0	1.73±0.05
	0.20	119	16	1.0	1.99
	0.30	141	14	1.0	2.37
	0.40	293±20	1	1.0	4.91±0.10
	0.50	687±50	1	1.0	11.2±0.50
N ₂ C ₈ O ₃ /SDS	0.10	106±10	17±2	1.0	1.78±0.05
	0.20	117	18	1.0	1.95
	0.30	130	17	1.0	2.18
	0.40	143	14	1.0	2.40
	0.50	100	7	1.0	2.70

Table S1. Key micelle model parameters for diamine/SDS systems in D_2O at the fixed 10 mM SDS and different molar ratios.

Note: For ext = 1.0, R_1 = 16.7, R_2 = 19.7; ext = 1.05, R_1 = 17.5, R_2 = 20.7; ext = 1.1, R_1 = 18,4, R_2 = 21.7; and ext = 1.15, R_1 = 19.2, R_2 = 22.7.

SDS concentration (mM)	Aggregation Number, v	Charge, z	ее	δ
10	58±5	16±2	1.00±0.05	0.28±0.03
12	59±5	14±2	1.00±0.05	0.24±0.03
15	73±7	18±2	1.23±0.05	0.25±0.03
18	68±7	17±2	1.14±0.05	0.25±0.03
20	74±7	18±2	1.25±0.05	0.25±0.03

Table S2. Key model parameters for the SDS micelles in D_2O .

 $R_1 \!=\!$ 16,7, $R_2 \!=\!$ 19.7, ext = 1.0, $<\!\!v\!\!>$ = 66, $<\!\!\delta\!\!>$ = 0.25

System	Diamine mole ratio, Y	Aggregation number, v	Charge, z	ext	ee
N ₂ C ₅ /SDS	0.1	213±20	1	1.0	3.57±0.10
	0.2	310±30	1	1.0	5.19
	0.3	581±50	1	1.0	9.74
	0.4	1354±100	1	1.0	22.7±0.50
	0.5	1700±150	1	1.0	28.5
N ₂ C ₇ /SDS	0.1	138±10	1	1.0	2.3±0.10
	0.2	194±20	1	1.0	3.24
	0.3	541±50	1	1.0	9.07
	0.4	1625±100	1	1.05	23.5±0.50
	0.5	1992±150	1	1.1	25.1
N ₂ C ₉ /SDS	0.1	138±10	1	1.0	2.31±0.10
	0.2	353±30	1	1.0	5.91
	0.3	816±80	1	1.05	11.8±0.20
	0.4	1943±150	1	1.1	24.5±0.50
	0.5	2133±200	1	1.15	26.9
N ₂ C ₄ O/SDS	0.1	217±20	1	1.0	2.30±0.10
	0.2	1256±120	1	1.0	21.0±0.50
	0.3	1859±150	1	1.0	32.1
	0.4	1967±150	1	1.0	32.0
	0.5	1951	1	1.0	32.7
N ₂ C ₆ O/SDS	0.1	137±10	1	1.0	2.30±0.10
	0.2	232±20	1	1.0	3.90
	0.3	454±30	1	1.0	7.60±0.20
	0.4	466	1	1.0	7.80
	0.5	1823±150	1	1.0	30.6±0.50
$N_2C_6O_2/SDS$	0.1	130±10	1	1.0	2.17±0.05
	0.2	138	1	1.0	2.30
	0.3	159±15	1	1.0	2.66
	0.4	242±20	1	1.0	4.05±0.1
	0.5	392	1	1.0	6.58
N ₂ C ₈ O ₃ /SDS	0.2	131±10	1	1.0	2.21±0.05
	0.3	140	18±2	1.0	2.34
	0.4	142	13±2	1.0	2.38
	0.5	148	1	1.0	2.43

Table S3. Key model parameters for diamine/SDS in D_2O at the fixed 3 mM and different diamine/SDS molarratios in the diamine/SDS mixtures.

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