Supporting Information:

"Prediction of Critical Micelle Concentration of Nonionic Surfactants by Dissipative Particle Dynamics Simulations"

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S1 Description of DPD simulations,

All surfactants in this work were modeled by linear sequences of beads, connected by harmonic bonds; water solvent was composed of single beads by lumping several water molecules. One-third harmonic bonds are applied to account the rigidity of the molecules.

Bead density $\rho \ast R_c^{3}$ in the system was set to 3, a common choice for aqueous solutions. The random force, which accounts for thermal fluctuations, is taken proportional to the conservative force that is also acting along the vector between the bead centers: $F_{ij}^{(R)}(r_{ij}) = \sigma w^R r_{ij} \theta_j(t) \mathbf{r}_{ij}$, where $\theta_j(t)$ is a randomly fluctuating in time variable with Gaussian statistics. The drag force is velocity-dependent: $F_{ij}^{(D)}(\mathbf{r}_{ij}, \mathbf{v}_{ij}) = -\gamma w^D(r_{ij}) (\mathbf{r}_{ij\ast}\mathbf{v}_{ij})$, where, $\mathbf{v}_{ij} = \mathbf{v}_j - \mathbf{v}_i$, \mathbf{v}_i and \mathbf{v}_j are the current velocities of the particles. We assume the common relationship between the drag and random force parameters $w^D(r) = [w^R(r)]^2$. σ and γ are parameters that determine the level of energy fluctuation and dissipation; they are related as and $\sigma^2 = 2\gamma kT$ that allows to maintain constant temperature in the course of simulation and fitted to the diffusion coefficient of pure water here depends on whether we include anything with 4 water molecules per bead. random positions were assigned to all beads, and the energy was minimized by steepest descent algorithm. Then the DPD simulation was started with the temperature controlled by simple velocity scaling over the starting 100000 steps. After that, the temperature was controlled naturally for over 400000 steps. The time step was sufficiently short to keep the temperature deviation within 0.01% of the designated value of 298.2K. The integration of the Langevin equations of motion was performed according to the algorithm by Pagonabarraga et al[1]. Inhouse DPD program was used. Every 1000 steps the locations of surfactant molecules were saved to disk for analysis.

S2. Details of MC simulation of activity coefficients

Consider coarse-grained models of molecules A and B. Each model molecule consists of b_A and b_B beads, correspondingly (b = 1 for monomers and b = 2 for dimers) and represent n_A and n_B actual molecules of their corresponding components. By definition, activity coefficient γ satisfies the following equation

$$\mu(x) - \mu_0 = kT \ln x + kT \ln \gamma(x) \tag{S1}$$

where *x* is the molar fraction and μ_0 is the chemical potential of the same component in pure liquid (*x* = 1). In diluted solutions, the solute interacts only with the solvent, $\gamma = \gamma \mu(x) - \mu_0$ of actual molecular solution by a coarse-grained model. μ and μ_0 of the model coarse-grained systems can be calculated using the Widom insertion method:

$$\mu_{\rm A} = kT \ln \left(\Lambda_{\rm A}^{\rm o}\right) + kT \ln \rho_{\rm A} + kT \ln \left(\langle \exp(-E^{\rm ins}/kT) \rangle\right) \tag{S2}$$

where Λ is thermal de Broglie wavelength and ρ_A is the density of A molecules, and <exp($-E_{ins}/kT$)> is the average exponent of random insertion of A molecule into the solution. Now we need to express ρ_A via molar volume fraction *x* of the actual molecular solution. Since the density of beads ρ^* is fixed, $\rho_A(x) = \rho^*/b_A$ in a bath of model A molecules. In dilute solutions of A in B, $\rho_A(x) = x(n_B/n_A) \times \rho^*/b_B$. Feeding these expressions and eq. S2 into eq. S1,

we obtain
$$\ln \gamma_{\infty} = \ln \left\langle \exp \left(-\frac{E_{AB}^{\text{ins}}}{kT} \right) \right\rangle_{NVT} - \ln \left\langle \exp \left(-\frac{E_{AA}^{\text{ins}}}{kT} \right) \right\rangle_{NVT} - \ln \frac{n_{B}b_{A}}{n_{A}b_{B}}$$
 (S3)

that is equivalent to eq. 2.

S3. Linear approximations of calibration curves in Figure 2.

Monomers in monomers	$\log_{10}(\gamma_{\infty}) = 0.144 \ \Delta a_{\rm IJ}$
Monomers in dimers	$\log_{10}(\gamma_{\infty}) = 0.149 \ \Delta a_{\rm IJ} - 0.043$
Dimers in monomers	$\log_{10}(\gamma_{\infty}) = 0.370 \Delta a_{\rm IJ} + 0.081$
Dimers in dimers	$\log_{10}\left(\gamma_{\infty}\right) = 0.354 \Delta a_{\rm IJ}$

S4. Snapshots of final structures of C8E8 surfactants at different volume fraction



Figure S1. Snapshots of final configuration in simulations of micellization of non-ionic surfactants C₈E₈ surfactants (modeled as TTHHHH) at $\varphi_S =$ (a) 0.01, (b) 0.02, (c) 0.04 and (d) 0.06 in water. Bead colors: cyan-head bead, pink-tail bead.

S5 Sensitivity of CMC to DPD parameters.

In order to determine how sensitive the resulting CMC is to repulsive parameters between different beads, we performed a number of DPD simulations with C_8E_8 surfactant. As expected, a_{TW} that reflects the degree of hydrophobicity of the tail is the most important. Increase Δa_{HT} by 3.6 leads CMC changed by 7.7. However, changing Δa_{TW} by 0.9 will lead 5.4 differences in CMC. Three methods are compared for the calculated Δa_{TW} : (1) 20.5 from Flory-Huggins parameters used in Groot and Rabone's work [2], (2) 19.6 from experimental mutual solubilities of octane and water, and (3) +18.7 from COSMOtherm calculations. With Δa_{HW} equals to 1 and equals to 1/3 of Δa_{TW} [2], the simulation CMC are found as 17.2, 11.8 and 9.5, and all are in acceptable agreements with experimental values 10. Finally, we verified that the results obtained with the proposed parameterization for CE surfactants are consistent with those obtained with the model of Groot and Rabone [2]

S6 Summary of results

surfactant	φs	model		Exp. CMC	Aggregation number	
Sunaciani				[mM]	DPD	explt
C ₈ E ₈	0.02		11.1		36	-
$CH_3(CH_2)_7(OCH_2CH_2)OH$	0.04	$TT-H_1H_1H_1H_1$	12.3	10	63	72 at
Octaethylene glycol monooctyl ether	0.06		11.9		83	<i>φ</i> _S =0.05
DDAO Dodecyldimethylamineoxide CH ₃ (CH ₂) ₁₁ N(O)(CH ₃) ₂	0.02	TTT-H ₂	1.3	1~2	77	76
MEGA-10						
$C_{17}H_{35}NO_{6}$	0.03	$TTM-H_3H_3$	7.5	6~7	50	-
N-Decanoyl-N-methylglucamine						

Table S1. Calculated and experimental CMC and aggregation numbers.

S7. Sensetivity of the resulting CMC and micelle size to n_{mono} and n_{mic} parameters

Calculation of micelle size and CMC involved two parameters n_{mono} and n_{mic} that had to be assigned in arbitrary fashion, as we could find no clear criterion for them. All surfactant molecules found in aggregates containing fewer then n_{mono} molecules were treated as free monomers, and the resulting CMC was proportional to the average number thereof. All aggregates bigger than n_{mic} monomers were considered as micelles and thus affected the calculated aggregation number. The aggregates whose size fell between n_{mono} and n_{mic} were accounted for in nether of these quantities.

I all our systems micelles were relatively large and well-defined. Majority of nonmicellized surfactant was in monomer form. Small clusters were rarely observed. That is why the results of aggregation analysis barely depend on n_{mono} and n_{mic} when they are reasonably chosen. For example, for MEGA-10 surfactant, only when minimum micelle size increased beyong 30 molecules n_{mic} would affect the average micelle size, and only when surfactant molecules found in clusters of 10 molecules were considered as belonging to the non-aggregated homogeneous solution, n_{mono} started influencing CMC. Certainly, surfactants with poorely defined aggregation or ionic surfactants require more sophisticated methods of aggregation analysis.

n _{mic}	n _{mono}	CMC	N _{agg}	Median number	Median number
		[mM]		of free	of micelles
				monomers	
43	3	7.6	109	44	2
40	3	7.6	90	44	4
33	3	7.6	82	44	5
27	3	7.6	75	44	6
20	3	7.6	75	44	6
20	6	7.7	75	45	6
13	3	7.7	75	44	6
13	6	7.7	75	45	6
13	10	7.8	75	48	6

Table S2. Dependence of the results of aggregation analysis on arbitrary parameters n_{mono} and n_{mic}

[1] Pagonabarraga, I.; Hagen, M.H.J.; Frenkel, D. Europhys. Lett., 1998 42, 377-382.

[2] Groot, R. D.; Rabone, K. L. *Biophys. J.* **2001**, *81*, 725-736.