

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

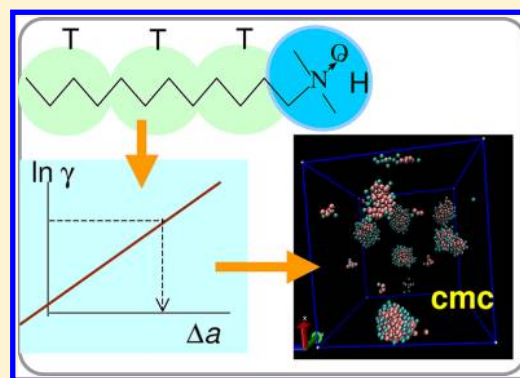
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S Supporting Information

ABSTRACT: Micellization of surfactant solutions is a ubiquitous phenomenon in natural systems and technological processes, and its theoretical description represents one of the cornerstone problems in the physical chemistry of colloidal systems. However, successful attempts of quantitative modeling confirmed by experimental data remains limited. We show, for the first time, that the dissipative particle dynamics with rigorously defined soft repulsion interaction and rigidity parameters is capable of predicting micellar self-assembly of nonionic surfactants. This is achieved due to a novel approach suggested for defining the interaction parameters by fitting to the infinite dilution activity coefficients of binary solutions formed by reference compounds that represent coarse-grained fragments of surfactant molecules. Using this new parametrization scheme, we obtained quantitative agreement with the experimental critical micelle concentration and aggregation number for several typical surfactants of different chemical structures. The proposed approach can be extended to various colloidal and polymeric systems beyond nonionic surfactant solutions.

SECTION: Glasses, Colloids, Polymers, and Soft Matter



Self-assembly in surfactant solutions is a ubiquitous phenomenon in natural systems and technological processes. Once the concentration of the surfactant exceeds the critical micelle concentration (CMC), the surfactant molecules aggregate into micelles, which may contain from scores to hundreds of molecules. Micelles may coalesce further and form various ordered and disordered mesophases. The problem of theoretical prediction of the CMC and micelle aggregation number (N_{ag} , the average number of surfactant molecules per micelle) has many important practical implications and constitutes one of the cornerstone problems in colloid science and engineering.

Micellization of ionic and nonionic surfactants has been extensively studied using molecular simulations starting from the early 1990s.^{1–3} However, the attempts to quantitatively predict experimental data remain limited. The most advanced simulation studies^{4–9} are based on the state-of-the-art coarse-grained molecular dynamics (CGMD) and Monte Carlo (MC) methods, including recent CGMD calculations using graphics processing units⁷ and atomistic implicit-solvent MD using the EEF1 solvation model¹⁰ designed for proteins.

Despite the recent progress in CGMD simulations of micellar systems, it is desirable to elaborate on a more computationally efficient method, which would be based on the use of soft repulsion potentials within the dissipative particle dynamics (DPD) framework. In DPD, individual atoms or molecules are lumped together into quasi-particles (beads), which interact via pairwise forces and obey the Newton

equations of motion. To reproduce the molecule chemical structure and rigidity, the beads are connected by harmonic bond potentials $F_{ij}^{(B)}$. Random $F_{ij}^{(R)}$ and drag $F_{ij}^{(D)}$ forces take into account fluctuation and dissipation of energy and serve as the Langevin thermostat.¹¹ Conservative force $F_{ij}^{(C)}$ accounts for nonbonded interactions; it is represented conventionally as a short-range harmonic repulsion.

$$F_{ij}^{(C)}(r_{ij}) = a_{IJ} \left(\frac{R_c - r_{ij}}{R_c} \right) \left(\frac{\mathbf{r}_{ij}}{r_{ij}} \right) \quad \text{at } r_{ij} \leq R_c$$

$$F_{ij}^{(C)}(r_{ij}) = 0 \quad \text{at } r_{ij} > R_c \quad (1)$$

R_c represents the effective bead diameter. The repulsion parameter a_{IJ} depends on the bead types I and J to which beads i and j belong. The short-range soft-core repulsion (eq 1) between the DPD particles provides exceptional computational efficiency compared to the models with attractive forces^{12,13} and hard-core potentials.¹⁴

DPD simulations¹⁵ have become widespread in the theoretical studies of self-assembly of amphiphilic molecules. However, the first attempts to employ the soft repulsion potentials to study micellization in surfactant solutions were

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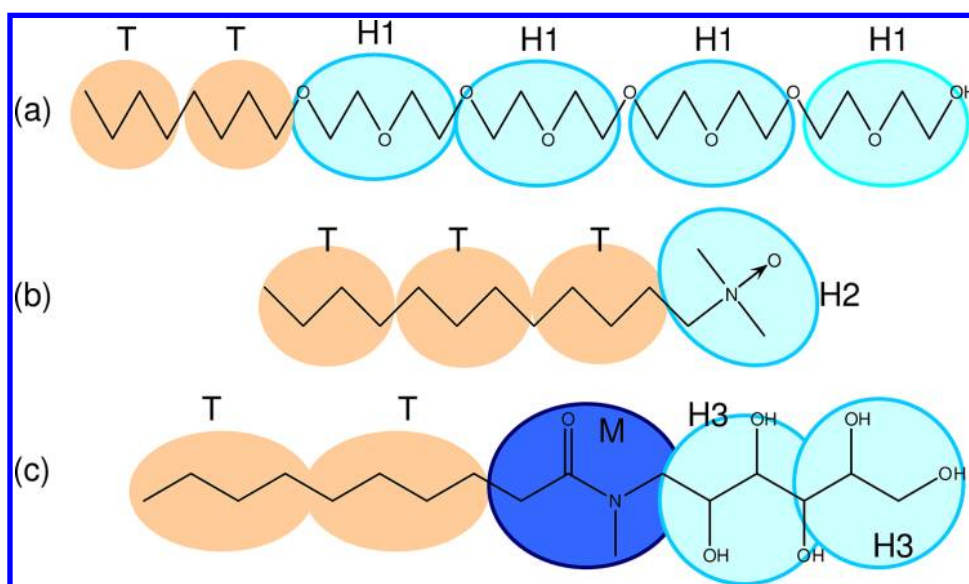


Figure 1. Schematics of coarse-graining. (a) C_8E_8 (octaethylene glycol monoethyl ether $nC_8H_{17}(OCH_2CH_2)_8OH$; coarse-grained model TT-H1H1H1H1); (b) DDAO (dodecyltrimethylamineoxide $nC_{12}H_{25}NO(CH_3)_3$, coarse-grained model TTT-H2); and (c) MEGA-10 (*N*-decanoyl-*N*-methyl-*D*-glucamine $nC_9H_{19}(NCH_3)(HCOH)_4CH_2OH$, coarse-grained model TT-MH3H3).

unsuccessful. Pool and Bolhuis¹⁶ performed MC simulations with the soft repulsion potentials from ref 17 and obtained extremely low values of CMC. The authors expressed doubts on the very applicability of coarse-grained models with soft repulsion potentials to qualitative predictions of such parameter-sensitive properties like CMC and suggested that hard-core solvent should be an essential feature of the coarse-grained model. DPD studies of micellization have been so far rather sparse. The authors of recent publications^{18,19} studied micellization of model nonionic surfactants of different structure and demonstrated the DPD ability of modeling the formation dynamics and equilibrium distribution of micellar aggregates, but they did not target particular experimental systems.

The main problem hindering such attempts is a lack of verified coarse-grained soft-core potentials. In general, the coarse-grained potentials should be fitted to the thermodynamic^{20–22} and/or structural^{7,14,22} properties of reference systems. For this purpose, one has to simulate the model fluid and to choose the potential parameters from the best fit of the calculated target properties to the properties of a reference fluid, obtained from atomistic simulations or experiments. Liquid–liquid equilibria and interfacial tensions between liquid phases are the most common target properties used for validating coarse-grained models. In their seminal paper,²⁰ Groot and Warren suggested a linear correlation between the DPD repulsion parameter a_{ij} and the Flory–Huggins (FH) mismatch parameter χ_{ij} . It was shown that the FH parametrization provides reasonable description of the interfacial tension between homopolymer melts. This method is convenient because the FH parameters are available in the literature for many systems. However, the FH model for DPD parametrization is merely a proxy; one has to take into account the particular method used for defining χ_{ij} parameters. In addition, it was shown that the LLE diagram predicted by the FH model qualitatively differs from the results of MC simulation of the DPD fluid.²¹

For immiscible components, the repulsion parameters can be determined directly from fitting the interfacial tension. For

example, Schillcock and Lipowsky in their DPD simulations of bilayer vesicles formed by polyethyleneglycol (PEG)–polybutene diblock copolymers²² used the tension of films formed by corresponding oligomers as target properties. Noteworthy, this method is not suitable for determining the repulsion parameters for hydrophilic beads and water because these compounds are mutually soluble. In this case, the authors used the radial distribution function as a target property. The structural properties, like radial distribution functions and end-to-end distances of polymer chains, are practical for fitting the bond potentials responsible for the chain rigidity²²

In this Letter, we suggest a new approach to parametrizing the soft-core interactions and demonstrate that the classical DPD scheme with repulsion potentials (eq 1) between the beads of the same size R_c is capable of quantitatively predicting micellization in nonionic surfactant solutions. We studied three typical examples of surfactant molecules of different chemical structures with experimentally known CMC and N_{ag} values. These examples were chosen to represent different classes of nonionic and zwitterionic surfactants of suitable molecule size and structure that could be handled with modest computational resources, (1) octaethylene glycol monoethyl ether C_8E_8 , made of a hydrophobic octyl tail and a hydrophilic oxyethylene head, (2) dodecyltrimethylamineoxide (DDAO), whose hydrophilic segment is a zwitterionic aminoxide group treated as nonionic for the short distance between the charged atoms, and (3) *N*-decanoyl-*N*-methyl-*D*-glucamine (MEGA-10), also composed of an alkyl tail and amide middle segments, and glycol hydrophilic segments.

The coarse-grained models of the surfactant molecules are presented in Figure 1 and Table 1. The surfactants were dissected into the tail, head, and middle beads of approximately the same size. The volumes of different fragments were estimated from the masses and densities of reference compounds *n*-octane, triglyme, *N*-methylacetamide, ethylene glycol, and water. For CE surfactant, we followed the dissection by Groot.²³ Because the tails in all three surfactants are alkyl chains of length in multiples of four, the tail T-bead contained four carbon atoms, approximately representing the

Table 1. Coarse-Grained Models of Surfactants, Reference Compounds, and DPD Repulsive Parameters (a_{ij})

bead type	reference compound	model compound	repulsion parameter, kT/R_c^2
W	4H ₂ O	monomer W	$a_{WW} = a_{II} = 106.5$
T	CH ₃ (CH ₂) ₆ CH ₃	dimer TT	$\Delta a_{TW} = 19.6$
H ₁ in C ₈ E ₈	CH ₃ OCH ₂ CH ₂ OCH ₃	dimer H ₁ H ₁	$\Delta a_{H1W} = 1.0$; $\Delta a_{TH1} = 6.5$
H ₂ in DDAO	CH ₃ N(O)(CH ₃) ₂	dimer H ₂	$\Delta a_{H2W} = -23.5$; $\Delta a_{TH2} = 6.2$
H ₃ in MEGA-10	OHCH ₂ (CHOH) ₃ CH ₂ OH	dimer H ₃ H ₃	$\Delta a_{H3W} = 1.0$; $\Delta a_{TH3} = 9.8$
M in MEGA-10	CH ₃ CON(CH ₃) ₂	monomer M	$\Delta a_{MW} = 3.0$; $\Delta a_{H3M} = 3.0$; $\Delta a_{TM} = 3.6$

butyl group, C₄H₉. The water W-bead was chosen to contain $n_W = 4$ water molecules. This choice is consistent with ref 24, where the T-bead volume was evaluated from experimental scattering volumes of water and dodecane;²⁵ roughly one CH₂ group in the T-bead corresponds to one water molecule in the W-bead.

Following ref 24, the reduced density ρ^* of DPD beads (the average number of bead centers in $1R_c^3$) was set to $\rho^* = 3$, which corresponds to the bead size of $R_c = 7.1$ Å. For the sake of simplicity, we followed the conventional implementation²⁴ and assumed that the self-repulsion parameter a_{II} and size $R_{c,I}$ for all types of beads are the same and equal to those of W-beads; $a_{II} = a_{WW}$ and $R_{c,I} = R_c$. The self-repulsion conservative parameter $a_{WW} = 106.5kT/R_c$ was determined from the water compressibility, as in ref 26. This value is in reasonable agreement with published data.²³ Note that the W-bead self-repulsion parameter a_{WW} represents the starting point for parameterization of other coarse-grained components.

Assigning the binary repulsion parameters a_{ij} for beads of different types is the most critical step in the parameterization procedure. Here, we suggest defining a_{ij} values from the best match of the infinite dilution activity coefficients γ_∞ of binary solutions of A and B model particles composed of I and J type beads calculated within the adopted DPD model to the experimental or ab initio computed γ_∞ values of the solutions formed by the reference compounds, which correspond to the coarse-grained beads. The A and B components of these binary solutions may represent either monomers or dimers of coarse-grained beads. In particular, a convenient choice is to select A = I or A = I₂ and B = J or B = J₂, depending on the availability of reference data needed for the parameter fitting. Infinite dilution activity coefficients are standard properties of binary solutions, with the vast body of data available in the literature, as they are measured with well-established methods such as head space technology.

For model binary solutions, γ_∞ are calculated with the Widom insertion MC technique,²⁷ which is especially efficient for soft particle systems

$$\ln(\gamma_\infty) = \ln \left\langle \exp \left(\frac{-E_{AB}^{\text{ins}}}{kT} \right) \right\rangle_{NVT} - \ln \left\langle \exp \left(\frac{-E_{AA}^{\text{ins}}}{kT} \right) \right\rangle_{NVT} - \ln \frac{n_B b_A}{n_A b_B} \quad (2)$$

Here, E_{AB}^{ins} is the energy of random insertion of A molecule into a bath of B molecules simulated in the canonical ensemble, E_{AA}^{ins} is the energy of insertion of A particle into the bath of A particles, and $b_{A/B}$ is the number of beads in A or B particles ($b = 1$ for monomers and $b = 2$ for dimers). Equation 2 is derived in the Supporting Information. Note that in eq 2, only the E_{AB}^{ins} term depends on a_{ij} .

The strategy of assigning of a_{ij} is the following. First, we construct in MC simulations for the calibration $\gamma_\infty(a_{ij})$ dependencies, which are unique for monomer–monomer, monomer–dimer, and dimer–dimer solutions. The respective calibration curves are presented in Figure 2. Because γ_∞ has a

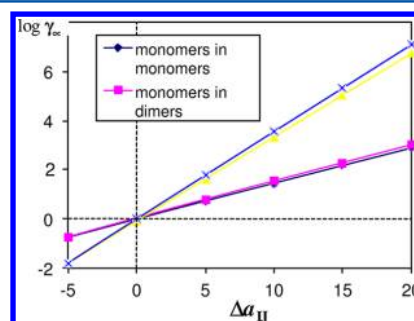


Figure 2. Calibration correlations between infinite dilution activity coefficient γ_∞ and mismatch DPD parameter Δa_{ij} for binary solutions formed by monomeric coarse-grained compound and their dimers at $R_c = 7.1$ (note decimal logarithms).

relatively weak dependence on the self-repulsion parameter, it is determined by the mismatch parameter $\Delta a_{ij} = a_{ij} - a_{II}$, which is correlated almost linearly with $\log(\gamma_\infty)$, which is convenient for fitting (see the Supporting Information). Then, interpolating experimental γ_∞ onto the respective reference curve, a_{ij} is obtained for the particular bead pair.

The repulsion parameter a_{TW} between T- and W-beads was determined as following. The most natural choice of the reference compound for the T-bead would be butane. However, butane is a vapor at ambient conditions, and the DPD model is not suitable for simulating the vapor–liquid equilibrium. Therefore, we chose octane as the reference compound for the T-beads. We present octane, which has the volume of approximately eight water molecules or two T-beads, as the T₂ dimer. The T–T bond length is chosen at $0.8R_c$, which is consistent with both the octane molecular structure and the DPD fluid density of $\rho^* = 3$ because the distance between neighboring beads in the BCC lattice at this density is close to $0.8R_c$. The value of $a_{TW} = a_{WW} + \Delta a_{TW}$ is estimated from the experimental value of γ_∞ using the monomer–monomer and dimer–monomer reference curves from Figure 2. Because water and octane are almost completely immiscible, γ_∞ is obtained from the solubility of octane in water as $\gamma_\infty = 1/x_{LLE}$, where x_{LLE} is the octane molar fraction at the liquid–liquid equilibrium. Using experimental data from ref 28, we obtained $\Delta a_{TW} = 18.7kT/R_c^2$ or $a_{TW} = 125.2kT/R_c^2$. Similarly, from water solubility in octane, we obtained $\Delta a_{TW} = 20.6kT/R_c^2$, which is close to the first value as well as to the parameter obtained from FH using the $\Delta a = \chi/0.293$ correlation suggested by Wijmans et al.²¹

In a similar fashion, we chose the reference compounds for the other coarse-grained fragments of the surfactants given in Table 1 and calculated a_{ij} for all bead pairs using the similar algorithm from monomer–monomer or dimer–dimer refer-

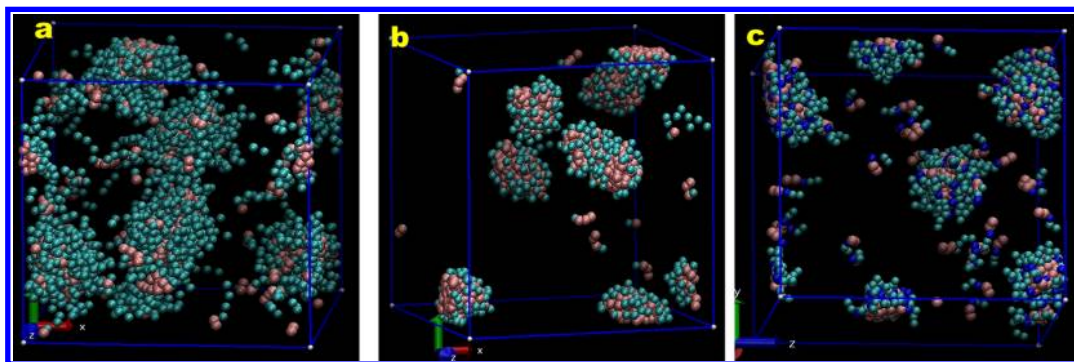


Figure 3. Snapshots of equilibrated DPD configurations for surfactant (a) C_8E_8 (model: TTHHH) at $\varphi_S = 0.04$, (b) DDAO (model: TTH) at $\varphi_S = 0.02$, and (c) MEGA-10 (model: TTMHH) at $\varphi_S = 0.04$ in water. Bead colors: cyan head, H-bead; pink tail, T-bead; and blue middle M-bead (in MEGA-10).

ence curves from Figure 2, in accord with the respective reference compounds. The experimental data for the reference compounds of some bead pairs was not found. In this case, we calculated γ_∞ using the COSMO-RS model²⁹ with COSMOtherm software.³⁰ However, these calculations did not always lead to plausible results. For example, diglyme, the reference head bead of C_8E_8 , modeled as the H1H1 dimer, is miscible with water,³¹ which means that a_{HIW} should be close to a_{WW} . Unable to find the experimental value of γ_∞ , we performed COSMO-RS calculations and found that the calculated value of γ_∞ depended heavily on the conformer and showed relatively hydrophobic solvation, with $\log(\gamma_\infty)$ varying from 0.95 to 2.6. This implies, in conflict with experiments, that diglyme would be miscible with octane rather than with water. As a reasonable compromise, we assigned a_{HIW} from the Flory mismatch parameter $\chi_{HIW} = 0.3$ reported by Saeki et al.³²

Rigidity of surfactant molecules substantially influences the CMC, especially for long molecules. In this work, we maintained molecule rigidity by using 1–3 secondary harmonic bonds that connected beads separated by two primary bonds, and the length equals to the sums of the length of the beads. From MD simulations of hexadecane at 298 K and 1 atm performed with TraPPE force field,³³ we assumed a bond length proportional to the number of covalent bonds between the neighboring beads of the chain and a rigidity inverse proportional to the number of flexible angles. As a result, the rigidity K_{1-2} of 1–2 and 1–3 bonds was calculated as $320/n_f$, where n_f is the number of flexible torsion angles between the bead centers. In a homopolymer chain, 1–2 bonds are twice as rigid as 1–3 bonds. The validity of this assumption is confirmed by the distributions of the interbead distances calculated using the atomistic MD and DPD simulations. The effects of rigidity on the CMC and other experimentally verifiable quantitative characteristics of surfactants have, to our knowledge, never been systematically studied and call for a detailed separate work that is beyond the scope of this Letter.

Using the models and techniques described above and the model parameters from Table 1, CMC and N_{ag} were calculated and compared with available experimental data. DPD simulations were performed with the original algorithm based on the work of Pagonabarraga et al.¹³ and are described in the Supporting Information. The CMC was obtained from the recorded simulation trajectories as follows. Two surfactant molecules were assumed to belong to the same aggregate if any two of their tail or middle beads overlapped. If an aggregate

contained more than a certain threshold n_{mic} of surfactant molecules, it was counted as a micelle; if a surfactant molecule belonged to a cluster containing less than n_{mono} surfactant molecules, it was assumed to belong to the aqueous solution of monomers in equilibrium with the micelles. The concentration of “monomeric” surfactant in water was treated as CMC. Aggregation was considered as complete and equilibrium reached when CMC and micelle numbers stabilized and became practically insensitive to the choice of n_{mono} and n_{mic} within reasonable limits. In the “production” calculations, we used $n_{mic} = 15$ and $n_{mono} = 5$. In Figure 3, we present typical snapshots of the equilibrated micellar systems. CMC was calculated from the ratio of the number of “free” monomers n_{free} (that included surfactants in all aggregates smaller than n_{mono}) to the number of water beads and converted into mmol/L as $M_{CMC} = n_{free} / (N_A n_W n_{H_2O} R_c^3)$, where n_{H_2O} is the number of water beads in the box. In the Supporting Information, we present the dependence of the aggregation number on the values of n_{mono} and n_{mic} used for the micelle and cluster definitions for MEGA-10 system.

The possible dependence of M_{CMC} on the system size and the total surfactant load was carefully checked. For the C_8E_8 system, we performed a series of simulations at three surfactant volume fractions $\varphi_S = 0.02, 0.04$, and 0.06 . Even though the aggregation number increased drastically because of micelle merging (see Table 1 and snapshots in the Supporting Information), we observed very low fluctuations and no evident trend for the calculated M_{CMC} . The evolution of the number of micelles in the C_8E_8 system at $\varphi_S = 0.04$ is shown in Figure 4. The averaged CMC of 11.8 ± 0.4 mmol/L is in quantitative agreement with the experimental value of 10 .³⁴ The aggregation numbers 63 at $\varphi_S = 0.04$ and 83 at $\varphi_S = 0.06$ also agree with the experimental value of 72 ³⁵ at $\varphi_S = 0.05$ and the same temperature. Good agreement with the experiment was also obtained for DDAO, where the calculated CMC of 1.3 mmol/L fell within the experimental range of 1 – 2 mmol/L,³⁶ and the N_{ag} coincided with the experiment nearly exactly (77 versus 76). For MEGA-10, the calculated CMC was 7.5 mmol/L, which is close to the experimental value of 6 – 7 mmol/L.³⁷

In conclusion, we suggested a straightforward methodology for obtaining conservative soft repulsion parameters for DPD simulations of surfactant solutions formed by relatively small molecules. The main idea of the proposed parametrization method is fitting to the experimental data on infinite dilution coefficients of reference compounds composed of coarse-grained fragments of the molecule under consideration. In most

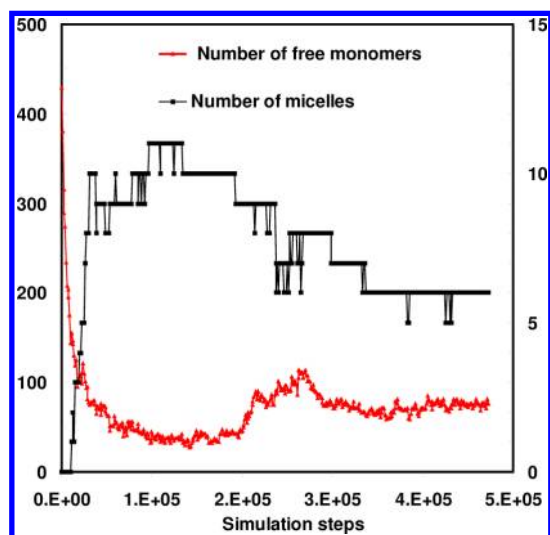


Figure 4. Evolution of the number of free monomers (left vertical axis) and the number of micelles (secondary vertical axis) in a solution of surfactant C_8E_8 at concentration $\phi_s = 0.04$. After 3.4×10^5 steps, the number of micelles is fluctuating from 5 to 6; the number of free monomers is fluctuating at an averaged 72, with an absolute variance equal to 5. Each dot represents one trajectory saved each 1000 simulation steps.

cases, such data are available from the literature or can be obtained in routine experiments. When experimental γ^∞ were unavailable, we used thermodynamic models (in this Letter, we selected COSMO-RS, but other approaches such as group contribution models are also available). These models have to be applied cautiously, as this Letter shows. Widening the scope of experimental data to which DPD parameters can be fitted is highly desirable. For example, water–octanol and water–hexane partitioning coefficients are widely used for environmental purposes, are available for many compounds, and characterize their relative hydrophobicity. However, utilization of this data is beyond the scope of this Letter.

We tested our approach against the CMC and mean aggregation number of several nonionic surfactants of different chemistry and obtained quantitative agreement with experiments. Although the methodology described here is limited by the assumptions of equal bead size and equal self-repulsion parameters, the presented examples show its potential for modeling complex micellar systems in a computationally efficient manner. Further development of the proposed parametrization method should involve the following: extension to multicomponent solutions of coarse-grained particles with the fractional numbers of groups per beads²² and beads of different sizes³⁸ in order to account for unequal volumes of reference compounds available from, for example, Bondi tables; extension to ionic surfactants by incorporation of electrostatic interactions with dissolvable counterions as was suggested in ref 39; and independent determination of self-repulsion parameters from the compressibility of reference pure liquids in a similar way as it is done for water. Also, the proposed method is not limited to surfactants; it can be adopted for coarse-grained modeling of self-assembly, rheological, and transport properties of other complex fluid and soft matter systems.

■ ASSOCIATED CONTENT

● Supporting Information

(1) Description of DPD simulations, (2) description of MC simulations of activity coefficients of coarse-grained fragments, (3) linear approximation of calibration dependences $\gamma_\infty(a_{ij})$, (4) snapshots of the evolution of the C_8E_8 self-assembly and micelle coalescence upon the increase of the surfactant volume fraction, (5) analysis of the sensitivity of CMC to DPD parameters, (6) cumulative table of results, and (7) results' dependence on n_{mono} and n_{mic} . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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