Parametrization of Chain Molecules in Dissipative Particle Dynamics

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Supporting Information

ABSTRACT: This paper presents a consistent strategy for parametrization of coarse-grained models of chain molecules in dissipative particle dynamics (DPD), where the soft-core DPD interaction parameters are fitted to the activities in solutions of reference compounds that represent different fragments of target molecules. The intercomponent parameters are matched either to the infinite dilution activity coefficients in binary solutions or to the solvent activity in polymer solutions. The respective calibration relationships between activity and intercomponent interaction parameter are constructed from the results of Monte Carlo simulation of the coarse-grained solutions of reference compounds. The chain conformation is controlled by the near neighbor and second neighbor bond potentials, which are parametrized by fitting the intramolecular radial distribution functions of the coarse-grained chains to the respective atomistic molecular dynamics simulations. The consistency, accuracy, and transferability of the proposed parametrization strategy is demonstrated drawing on the example of nonionic surfactants of the poly(ethylene oxide) alkyl ether (CnEm) family. The lengths of tail and head sequences are varied ($n = 8$–$12$ and $m = 3$–$9$), so that the critical micelle concentration ranges from $10$ to $0.1$ mM. The surfactants are modeled at different coarse-graining levels using DPD beads of different diameters. We found consistent agreement with experimental data for the critical micelle concentration and aggregation number, especially for surfactants with relatively long hydrophilic segments. Depending on the system, we observed surfactant aggregation into spheroidal, elongated, or core–shell micelles, as well as into irregular agglomerates. Using the models at different coarse-graining levels for the same molecules, we found that the smaller the bead size the better is agreement with experimental data.

1. INTRODUCTION

Dissipative particle dynamics (DPD) has become a common tool for mesoscale modeling of self-assembly in surfactant and polymeric systems. In DPD, the system components are modeled by beads, each of which represents several atoms that are lumped together. The beads interact via short-range soft repulsion potentials that affords superb computational efficiency. Despite their simplicity, DPD models provide qualitative and sometimes quantitative description of the structure and thermodynamics of quite complex systems. Examples include micellization in surfactant solutions,$^1$–$^3$ morphology of cell membranes and lipid bilayers,$^4$–$^5$ and phase segregation in polyelectrolyte membranes,$^6$–$^8$ to name a few. However, quantitative predictions with DPD are hindered by apparent problems with customization and parametrization of coarse-grained models. Commonly, parametrization of DPD models is based on a top-down approach; the parameters of interbead potentials are fitted to reproduce certain physicochemical properties, like solubility or interfacial tension, which are known either from experiments or from established theoretical models, like Flory–Huggins (FH) theory$^9$ or COSMO-RS method.$^{10}$ A rigorous bottom-up approach to upscaling of atomistic potentials is hardy practical, because it involves expensive and case-specific atomistic simulations, and yet the coarse-grained models obtained often do not predict correctly the macroscopic properties.$^{1,11}$

The basic principles of top-down parametrization of DPD models were summarized and illustrated on several case study systems by Groot and Warren (GW).$^{12}$ Detailed analysis of the GW correlation and its applicability to parametrization of DPD models at different coarse-graining levels is given in Supporting Information, section S2. Due to its simplicity and computational efficiency, the GW model is widely used in the literature for modeling various systems.$^{1,2,4,6,8}$ Therefore, parametrization approaches, which are briefly reviewed in the following paragraph, are mostly developed with the GW model in mind. However, substantial attention is now being paid to modifications of GW model in order to widen the limit the applicability of DPD to quantitative description of self-assembly. In particular, the efforts have been directed to (1) using different effective bead diameters and force cutoff for different bead types, (2) introducing dependence of the intracomponent repulsion parameters on the bead type or coarse graining level, and (3) applying additional (that is beyond weak harmonic bonds between neighboring beads).
restraints in order to account for the actual conformations of the molecules.

Groot and Rabone\(^1\) scaled the intracomponent parameters based on the physical unit of bead diameter and linked intercomponent parameters to physical properties of surfactant and lipid molecules. The phospholipid model was parametrized to match the density and elasticity because these properties are critically influenced by the conformations of alkane tails.\(^14\) whose rigidity is ignored in the standard GW model. For this reason, the intracomponent repulsion between the lipid head heads in ref\(^4\) was made stronger than that for other bead types. Travis et al.\(^15\) suggested determining both intra- and intercomponent parameters from the cohesive energy density of individual components. Maiti and McGrother\(^16\) rederived GW theory by taking into account the bead size. They suggested that the intercomponent parameters should be scaled with coarse grained level, yet the intracomponent parameter should remain unaffected. Their DPD parameters are fitted to surface tension between liquid phases and the cohesive energy densities. Spaeth et al.\(^17\) introduced beads of different effective diameters. The mixtures of soft DPD spheres of different sizes were studied in depth by Kacar et al.\(^18\) The parameters for DPD models of individual components were designed to produce the same pressure in pure liquids; the bead densities in different phases were allowed to differ. The authors obtained an equation of state for mixtures of single-bead components and related the intercomponent DPD parameters to the FH parameters. Extending the Monte Carlo study for soft potential by Wijmans et al.\(^19\), Liyana-Arachchi et al.\(^20\) presented a detailed MC study of thermodynamic properties and liquid structure of single-component DPD fluids, as well as the phase diagrams of binary mixtures whose intracomponent is unified or various by bead type. They suggested an equation of state for single-bead DPD mixtures that allowed facile fitting of the parameters to experimental LLE data. The other target property for fitting DPD parameters is the surface tension between liquid phases. The correlations between the surface tension and DPD parameter first obtained by Groot and Warren are often used in DPD simulations of polymers.\(^21\)–\(^23\) Maiti and McGrother\(^16\) extended this approach to beads of different diameters. Extension of this parametrization to other systems is hindered by a limited availability of experimental data on the surface tension.

Here, we present a systematic parametrization methodology, some fragments of which were discussed in our recent papers.\(^5,24\)–\(^26\) In particular, we suggested determining the DPD repulsion parameters by matching the infinite dilution activity coefficients (IDAC) of reference solutions.\(^5\) The calibration relationships between intercomponent parameter and IDAC were obtained by MC simulation of respective binary mixtures of reference DPD fluids. Alternatively, the repulsion parameters were obtained from the concentration dependence of the solvent activity in respective polymer solutions. The proposed approach is systematically tested drawing on the example of a series of poly(ethylene oxide) alkyl ether C\(_n\)E\(_m\) surfactants of different composition with the spread of CMC over 3 decimal orders. A molecule of C\(_n\)E\(_m\) surfactant consists of \(n\) hydrophobic CH\(_3\) groups and \(m\) hydrophilic oxyethylenic units (\(\text{CH}_2\text{OCH}_2\text{−}\)). Quantitative prediction of micellar properties is a benchmark problem for testing parametrization algorithms in DPD and other coarse-grained simulation methods.\(^5,27,28\) By varying the chain composition and comparing the simulation results with experimental data on critical micelle concentration (CMC) and aggregation number \((N_{\text{ag}})\), we demonstrate and verify the robustness of the proposed methodology and its consistency through different coarse grained levels. The method is outlined as follows: (1) dissection of system compounds into equal size fragments, which correspond to reference compounds, and choice of the bead size that determines the level of coarse-graining, (2) determination of the intracomponent repulsion parameter from the density and compressibility of the solvent at given coarse-graining level, (3) determination of the bond potentials between the same type beads from the fitting to atomistic MD simulations of conformations of respective homo-oligomers, (4) determination of intercomponent (mismatch) parameters from the fitting of the infinite dilution activity coefficient (IDAC) in binary solutions of reference compounds to the results of MC simulations of respective DPD fluids, (5) if IDAC reference data is not available, determination of intercomponent (mismatch) parameters from the fitting of the activity in aqueous solution of respective reference compound oligomers, and (6) determination of head−tail bond parameters and verification of the overall set of parameters against atomistic MD simulations of the conformations of short molecules composed of a few head and tail groups. In this work, the parametrization strategy is applied to the simplest situation, where all bead types have the same \(R_b\) and same \(a_q\) in any particular simulation, but these restrictions are not inherent, and the same strategy can be extended to systems with differently sized beads.

The rest of the paper is structured as follows: Section 2 describes DPD models of C\(_n\)E\(_m\) surfactants with different coarse-graining levels and the force field used in DPD simulations. Section 3 discusses the choice of intracomponent repulsion parameters. In section 4, we describe how to define the rigidity on the head and tail segments on the basis of atomistic MD modeling of conformations of alkanes and PEO molecules in bulk phases. We fit the bond potentials of the DPD model to reproduce the conformations. In section 5, we choose reference compounds for the tail and head blocks at different coarse-graining levels; we also describe in detail the protocol of matching the intracomponent repulsion parameters to the activities in solution of reference compounds, including IDAC and the solvent activities in polymer solutions. In sections 6 and 7, the DPD models obtained in sections 2–5 are applied to modeling self-assembly and calculating the critical micelle concentration (CMC) and the aggregation number \((N_{\text{ag}})\) in aqueous solutions of C\(_n\)E\(_m\) surfactants. In addition, we compare the performance of different methods of bond rigidity calibration, using FENE and harmonic potentials parametrized either from the fitting to atomistic simulations or using an empirical correlation between the stiffness and the number of flexible torsions suggested in ref\(^7\). Conclusions are summarized in section 8.

2. SURFACANT MODELS

A C\(_n\)E\(_m\) surfactant molecule consists of \(n\) hydrophobic CH\(_3\) or CH\(_2\) groups and \(m\) hydrophilic oxyethylene units (\(−\text{CH}_2\text{OCH}_2−\)). We model several systems with alkyl tail length from \(n = 8\) to \(n = 12\) and PEO head from \(m = 3\) to \(m = 9\). In coarse-grained models, the surfactant molecule is dissected into fragments represented by beads. The first DPD model of C\(_n\)E\(_m\) was introduced by Groot and Rabone, who studied the effect of surfactants on the properties and rupture of lipid bilayers.\(^7\) Parametrization was based on FH model parameters.
Other coarse-grained simulation techniques were also applied to CE surfactants; for example, Jusufi et al.\textsuperscript{29} derived hard-core potentials from atomistic simulation of short PEO oligomers in the water. CMC and aggregation number for C\textsubscript{m}E\textsubscript{n} (n = 6–12, m = 3–9) near-quantitatively reproduced the experimental results.

Coarse-grained representations of C\textsubscript{m}E\textsubscript{n} surfactants are shown in Figure 1. The molecule is dissected into hydrophobic

![Figure 1](image)

and hydrophilic fragments represented by tail (T) and head (H) beads. The hydroxyl group terminating the E\textsubscript{n} block is also included in the end H bead to reduce the number of parameters.\textsuperscript{13,25} The coarse-grained model containing x tail beads and y head beads is denoted as T\textsubscript{x}H\textsubscript{y}. The tail and head fragments are to be of approximately equal volume to fulfill the requirement of the equal bead size in the basic DPD model.\textsuperscript{13} The size of the water (W) bead is chosen to match the volumes of T and H beads. Based on the neutron reflection data\textsuperscript{30} interpreted by Groot and Rabone,\textsuperscript{4} two ethyl groups are assumed to occupy the same volume as one oxyethylene or two water molecules. For example, the T bead representing (CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2})\textsubscript{6} (CH\textsubscript{2}OCH\textsubscript{2})\textsubscript{3} fragment of the hydrophobic alkyl block and H bead representing (CH\textsubscript{2}OCH\textsubscript{2}CH\textsubscript{2}OCH\textsubscript{2})\textsubscript{3} oxyethylene fragment have approximately the same volume as a W bead representing four water molecules. Noteworthy, the coarse-graining level and the bead size, R\textsubscript{c}, is determined by the chosen dissection of surfactant molecules. In order to explore the robustness of the proposed parametrization method, we explored several dissection schemes at different coarse-graining levels quantified by the number, N\textsubscript{w}, of water molecules in a W bead. From the liquid densities of octane (chosen as a reference alkane to estimate the tail bead volumes) and water at ambient conditions, we estimated using a standard procedure\textsuperscript{13} that at the bead density of ρ = 3, R\textsubscript{c} equals to 0.65, 0.71, 0.77, and 0.81 nm when W bead contains N\textsubscript{w} = 3, 4, 5, and 6 water molecules, respectively. Details of coarse graining are listed in the Table 1.

The important condition for the choice of the chain dissection is the availability of the data on activities for mixtures of the reference compounds, which may be represented by either single T and H beads or their dimers or oligomers. The activity data for reference compounds are used for parametrization of interaction potentials. The reference compounds must be liquid at given conditions, because standard DPD models cannot adequately represent vapor–liquid and solid–liquid equilibria. For example, at the coarse-graining level of N\textsubscript{w} = 4, n-octane is chosen as the reference compound and modeled as a dimer of T beads; at the coarse-graining level of N\textsubscript{w} = 6, the reference compound is n-hexane modeled as a single T bead. The reference compounds for the models considered are given in Table 1.

### 3. INTRACOMPONENT REPULSION PARAMETERS

Nonbond interaction between coarse-grained beads i and j in DPD is described by a linear, repulsive force,

\[
F^{(C)}_{ij}(r_{ij}) = \mathbf{a}_{ij} \left(1 - \frac{r_{ij}}{R_{c}}\right) \frac{r_{ij}}{r_{ij}} \quad \text{for} \quad r_{ij} < R_{c}
\]

This force decays to zero at the effective bead diameter, R\textsubscript{c}, and is characterized by the repulsion parameter a\textsubscript{ij}. The intracomponent repulsion parameter, a\textsubscript{ii}, is set equal for all bead types and fitted to the isothermal compressibility of water.\textsuperscript{13} This approximation is reasonable for dilute surfactant solutions

### Table 1. C\textsubscript{m}E\textsubscript{n} Surfactant Molecules and the Corresponding DPD Models T\textsubscript{x}H\textsubscript{y} at Different Coarse-Graining Levels Determined by the Bead Size, R\textsubscript{c} (diameter in nm)\textsuperscript{a}

<table>
<thead>
<tr>
<th>C\textsubscript{m}E\textsubscript{n}</th>
<th>T\textsubscript{x}H\textsubscript{y}</th>
<th>R\textsubscript{c} (nm)</th>
<th>T bead fragment</th>
<th>H bead fragment</th>
<th>box size (R\textsubscript{c})</th>
<th>reference compound for tail</th>
<th>model for reference compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 4 2 2 0.71 (CH\textsubscript{2}H\textsubscript{4})  (CH\textsubscript{2}OCH\textsubscript{2})\textsubscript{3}</td>
<td>30 octane</td>
<td>dimer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 6 2 3 0.71 (CH\textsubscript{2}H\textsubscript{4})  (CH\textsubscript{2}OCH\textsubscript{2})\textsubscript{3}</td>
<td>30 octane</td>
<td>dimer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 8 2 4 0.71 (CH\textsubscript{2}H\textsubscript{4})  (CH\textsubscript{2}OCH\textsubscript{2})\textsubscript{3}</td>
<td>30 octane</td>
<td>dimer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 5 2 2 0.77 (CH\textsubscript{2}H\textsubscript{4})  (CH\textsubscript{2}OCH\textsubscript{2})\textsubscript{3}</td>
<td>45 decane</td>
<td>dimer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 3 4 2 0.65 (CH\textsubscript{2}H\textsubscript{4})  (CH\textsubscript{2}OCH\textsubscript{2})\textsubscript{3}</td>
<td>60 hexane</td>
<td>dimer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 6 4 4 0.65 (CH\textsubscript{2}H\textsubscript{4})  (CH\textsubscript{2}OCH\textsubscript{2})\textsubscript{3}</td>
<td>60 hexane</td>
<td>dimer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 9 4 6 0.65 (CH\textsubscript{2}H\textsubscript{4})  (CH\textsubscript{2}OCH\textsubscript{2})\textsubscript{3}</td>
<td>60 hexane</td>
<td>dimer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 8 3 4 0.71 (CH\textsubscript{2}H\textsubscript{4})  (CH\textsubscript{2}OCH\textsubscript{2})\textsubscript{3}</td>
<td>64 octane</td>
<td>dimer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 3 2 1 0.81 (CH\textsubscript{2}H\textsubscript{4})  (CH\textsubscript{2}OCH\textsubscript{2})\textsubscript{3}</td>
<td>60 hexane</td>
<td>monomer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 6 2 2 0.81 (CH\textsubscript{2}H\textsubscript{4})  (CH\textsubscript{2}OCH\textsubscript{2})\textsubscript{3}</td>
<td>60 hexane</td>
<td>monomer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 9 2 3 0.81 (CH\textsubscript{2}H\textsubscript{4})  (CH\textsubscript{2}OCH\textsubscript{2})\textsubscript{3}</td>
<td>60 hexane</td>
<td>monomer</td>
<td></td>
<td></td>
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</tbody>
</table>

\textsuperscript{a}Subscript n and m are the numbers of methylene and ethyleneoxide groups, and x and y are the numbers of tail and head beads. System size (simulation box length in R\textsubscript{c}) is chosen with respect to the experimental CMC (the smaller CMC, the bigger the box). Last two columns show the reference compounds and their DPD models used for the calibration for intercomponent parameters (details discussed in section 5).
(volume fraction of surfactant in this work is around 2% to 4%), where water occupies most of the volume. Because of a difference in opinions in the literature (for example, different intracomponent parameters were used in similar simulations of Naion<sup>2,31</sup>) on the scaling of the intracomponent repulsion parameter with the bead size, we performed MC simulations on the dependence of the compressibility κ on a<sub>B</sub> for a given R<sub>c</sub>. The simulation results are shown in Supporting Information, section S2. The dependence of the inverse reduced isothermal compressibility, κ<sub>1</sub> in, on a<sub>B</sub> can be approximated by a correlation, according to which a<sub>B</sub> increases linearly with R<sub>c</sub>.<sup>2,3,13</sup> The intracomponent parameters for different R<sub>c</sub> are shown in Table 2. They are in reasonable agreement with the values used in the literature.<sup>4,13</sup>

### Table 2. Intracomponent Repulsion Parameters<sup>a</sup> and 1–2 and 1–3 Bond Parameters<sup>b</sup> of DPD Surfactant Model at Different Coarse Grained Bead Size, R<sub>c</sub>

<table>
<thead>
<tr>
<th>R&lt;sub&gt;c&lt;/sub&gt; (nm)</th>
<th>a&lt;sub&gt;B&lt;/sub&gt;</th>
<th>bond type</th>
<th>K&lt;sub&gt;0&lt;/sub&gt;</th>
<th>r&lt;sub&gt;0&lt;/sub&gt;</th>
<th>r&lt;sub&gt;m&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>78.5</td>
<td>1–2</td>
<td>280.0</td>
<td>0.50</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1–3</td>
<td>80.0</td>
<td>1.11</td>
<td>4</td>
</tr>
<tr>
<td>0.71</td>
<td>106.1</td>
<td>1–2</td>
<td>280.0</td>
<td>0.61</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1–3</td>
<td>20.0</td>
<td>1.50</td>
<td>4</td>
</tr>
<tr>
<td>0.77</td>
<td>133.7</td>
<td>1–2</td>
<td>180.0</td>
<td>0.70</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1–3</td>
<td>8.0</td>
<td>1.85</td>
<td>4</td>
</tr>
<tr>
<td>0.81</td>
<td>161.2</td>
<td>1–2</td>
<td>190.0</td>
<td>0.81</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1–3</td>
<td>8.0</td>
<td>1.75</td>
<td>4</td>
</tr>
</tbody>
</table>

### 4. PARAMETRIZATION OF BOND POTENTIALS

To maintain the chain integrity, the neighboring beads are connected by nearest neighbor bonds (1–2 bond). Additional bonds are applied between the second neighbor beads (1–3 bond) in order to describe the chain rigidity, which significantly influences the mechanism of surfactant micellization.<sup>2,5</sup> We use both harmonic (eq 2) and FENE (eq 3) potential:

\[
\mathbf{F}_{ij}^{(h)}(r_{ij}) = -\frac{r_{ij}}{r_0}K_0(r_{ij} - r_0) \quad (2)
\]

\[
\mathbf{F}_{ij}^{(f)}(r_{ij}) = \frac{-2K_0r_{ij} + r_0}{1 - \left(\frac{r_{ij}}{r_m}\right)^2} \quad \text{for } r_{ij} < r_0 + r_m
\]

\[
\mathbf{F}_{ij}^{(f)} = \infty \quad \text{for } r_{ij} \geq r_0 + r_m
\]

where r<sub>0</sub> is the equilibrium bond length, r<sub>m</sub> is the maximum bond length (if applicable), and K<sub>0</sub> is the bond stiffness.

For comparison purposes, we follow our original parameterization algorithm, where the harmonic potential is used for both 1–2 and 1–3 bonds of the surfactant model. Bond parameters are fitted by comparing the conformation of united atom MD simulation for a fluorocarbon melt with its DPD representative at coarse grained size R<sub>c</sub> = 0.71 nm.<sup>3</sup> We adopt the same approximation of this simplistic model that the equilibrium bond length and stiffness are scaled by the number of flexible torsions, n<sub>flex</sub>, of the connected DPD bead centers:

\[
K_0(r_{ij} - r_0) = \frac{320}{n_{\text{flex}}} 
\]

The simplistic model was not fitted to the atomistic MD conformations. The parameters at all coarse grained levels are given in Table 2c.

Compared with harmonic potential, FENE potential was found<sup>2</sup> to be better in describing the atomistic conformation of the surfactant molecule. In particular, the finite possible bond extension in FENE model allowed reproduction of the asymmetry of 1–4 and 1–5 distance distributions, while distributions obtained with the harmonic potential were more or less symmetric.<sup>7</sup> The parameters of 1–2 and 1–3 bonds are obtained by a bottom-up approach, where the conformations of coarse-grained chains are fitted to the results of atomistic MD simulation for the reference compounds. The reference compound for the tail of C<sub>16</sub>E<sub>m</sub> surfactant is hexadecane, and it is poly(ethylene oxide) (PEO, MW = 400) for surfactant head. Based on the molecule dissection rule described in section 2, a hexadecane molecule was dissected into equal fragments of 3, 4, 5, or 6 carbons at R<sub>c</sub> equals 0.65, 0.71, 0.77, and 0.81 nm. We calculated intramolecular distance distributions between the centers of mass of the fragments. These distributions were matched to the distributions of the distances between corresponding beads of the coarse-grained model of hexadecane melt by adjusting the 1–2 and 1–3 FENE bond parameters (coarse-grained C<sub>16</sub>H<sub>32</sub> was modeled for R<sub>c</sub> = 0.65 nm and R<sub>c</sub> = 0.77 nm, C<sub>14</sub>H<sub>30</sub> was modeled for R<sub>c</sub> = 0.71 nm and R<sub>c</sub> = 0.77 nm, C<sub>18</sub>H<sub>36</sub> was modeled for R<sub>c</sub> = 0.81 nm).

Figure 2a shows the beads and corresponding fragments for R<sub>c</sub> = 0.71 nm. The obtained bead-to-bead distance distributions are presented in Figure 2b. The comparison of atomistic MD and DPD results shows that by using 1–2 and 1–3 FENE bonds, we are able to mimic the flexibility of the alkane tail in DPD simulations fairly well. The FENE bonds turn out to be superior to the harmonic bonds in reproducing the rigidity of surfactant molecules. The detailed description of the simulations and fitting of DPD bonded parameters to the atomistic MD conformations is given in Supporting Information, section S3. In order to obtain bond parameters for the hydrophilic PEO head beads, we simulated PEO fragments of nine monomers using a similar procedure. The shapes of intramolecular bead–bead distance distributions in PEO melts are much more complex compared with alkanes. In general, PEO chains are more flexible with a shorter persistent length.
Correspondingly, hexane in this case is modeled as a single alkane. For alkanes are presented as dimers of tail beads TT. For atomistic MD simulations is obtained with 1^-ff-hexane. Hexane serves as a natural reference compound for T at the simulation conditions, the smallest suitable alkane is octane and decane, respectively. The reference compounds for compounds and models are listed in Table 1.

Panels b and c show the distribution of r_{12}, r_{13}, and r_{14} from MD (solid lines) and from DPD simulations (dashed lines) of the reference system n-alkane (b) and PEO (c).

Small peaks on MD distributions correspond to particular preferential conformations of PEO chains. However, the overall rigidity of the PEO chains is reproduced within reasonable accuracy as shown in Figure 2c. The bonding parameters obtained with this procedure are given in Table 2 ab.

It is worth mentioning that the equilibrium distances for the second neighbor bonds are in several systems longer than twice the equilibrium length of the corresponding nearest neighbor bonds. In this paper, 1^-2 bonds are short (r_{e} < r_{c}), nearest neighbors experience conservative repulsion from each other, and the actual distances between them exceed r_{e}. The best fit to MD simulations is obtained with 1^-3 bonds with equilibrium length close to the sum of average nearest neighbor distances (see Supporting Information, section S7).

5. INTERCOMPONENT REPULSION PARAMETERS

Intercomponent repulsion parameters (a_{ij} in eq 1) for tail (T), head (H), and water (W) beads are obtained from the activities in reference binary solutions. For hydrophobic beads T, we choose different linear alkanes as reference compounds; the choice depends on the bead size R_{c}. Since the reference compound has to be a liquid well below its boiling temperature at the simulation conditions, the smallest suitable alkane is hexane. Hexane serves as a natural reference compound for T bead with the coarsest dissection of R_{c} = 0.81 nm, where one T bead effectively represents six methyl/methylene groups. Correspondingly, hexane in this case is modeled as a single bead T molecule. At finer coarse-graining levels, reference alkanes are presented as dimers of tail beads TT. For R_{c} = 0.65 nm, T bead comprised of three CH_{2} groups, hexane is modeled as a TT dimer. The reference compounds for R_{c} = 0.71 nm and R_{c} = 0.77 nm are octane and decane, respectively. The reference compounds and models are listed in Table 1.

The intercomponent parameters between T and W beads are fitted to the experimental IDAC for reference compounds. Since the reference compounds are represented either by single beads or by bead dimers, we considered the respective binary systems and constructed the calibration relationships for the IDAC ln γ^∞(Δa_{ij}) as functions of the mismatch parameter Δa_{ij} = a_{ij} - a_{ii}. The chemical potential of solute was calculated by equilibrating the bath of pure reference compounds of component I (modeled by monomer I or dimer I–I) in a series of canonical Monte Carlo simulations augmented by Widom insertion of a test molecule of the reference compound of component J (monomer J or dimer J–J).

For a given a_{ij}, γ^∞ is calculated using eq 4 (see derivation in Supporting Information section S5):

\[
\ln r_{ij}^∞ + \ln \left( \frac{b_1 \rho_1}{b_1 \rho_2} \right) = \ln(\exp(-E_{ins}^∞/(kT))) - \ln(\exp(-E_{ins}^∞/(kT)))
\]

γ^∞ values obtained experimentally or by thermodynamic modeling are interpolated onto the reference curves. For type J, b_{ij} is the number of physical molecules that a bead of type J represents. For example, if the octane molecule is presented as a dimer with R_{c} = 0.71 nm, one T bead is 1/2 of the molecule. The W bead in this case represents four water molecules; thus b_{W} = 4. It should be noted that the pressure of a DPD fluid of dimers is different from that of monomers. In order to maintain the equal pressure in the fluids of monomers and fluids of dimer, one has to adjust the dimer fluid density to match the pressure of the monomer fluid. Such adjustment is similar to that of Kacar et al. and contributes to the correction term \rho_{i}/\rho_{j} in eq 4 compared with the original formula.\rho_{j} is the bead density for component I at the pressure of solvent bulk. As illustrated by the schematic in Figure 3, the density \rho_{j} for dimers or polymers differs from that of the solvent, which is set to 3.

Although the term ln(\rho_{j}/\rho_{i}) is rather small (ρ = 3 for monomer solvent, ρ = 3.11, 3.05, and 3.01 for TT dimer at R_{c} = 0.65, 0.71, and 0.81 nm), the density difference between the single-bead fluid and the fluid of dimers substantially affects the insertion energies and therefore dramatically changes the calibration curves γ^∞(Δa_{ij}). This is because the short and stiff bonds, which reproduce the conformations of the molecules (Table 2), affect the structure of the dimer fluid, which becomes quite different from the structure of the single-bead fluid with the same R_{c}. In the simulation of surfactant solution, water constitutes the bulk (96% in volume) of the system and alone determines the pressure in the NVT ensemble. The hydrophobic cores of the micelles are effectively under constant pressure conditions created by the solvent, even though the DPD simulations are carried out in the canonical ensemble. For this reason, the reference γ^∞(Δa_{ij}) curves for the systems with dimers were calculated at the pressure

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corresponding to the solvent (a single-bead fluid) at the reduced density of $\rho = 3$. Note that the issue is not essential when the dimer has relatively soft bond$^{4,13}$ or the 1–2 bond equilibrium length equals 0.88$^{3}$. In such cases, the structure and the pressure of a dimer fluid differ insignificantly from a monomer solvent.

With the aforementioned procedure, we obtained the reference correlations between $\gamma^\infty$ and $\Delta a_{II}$ for different combinations of monomer and dimer fluids. The correlations are given in Table 3. All reference relationships are monotonic, but we have to note that the slope depends on the bead size, as shown in Figure 4. Even for the same physical solution of two molecules of similar sizes (say, hexane and water), different values of $\Delta a$ are needed to achieve the same solubility for different coarse-grained levels, especially when these liquids are very dissimilar and strongly separate. This is related to the dependence of the DPD fluid structure on $a_{II}$ and should be taken into account when $a_I$ is calculated from the thermodynamic properties of reference solutions, including the calculations of $\Delta a$ from FH parameters $\chi$. For alkane–water mixtures, $\gamma^\infty$ are estimated from the experimental solubilities and interpolated onto the corresponding reference curves. Following ref 3, we averaged the $a_{IW}$ parameters obtained from water solubilities in alkanes and alkane solubilities in water. We have to mention that the experimental errors for such insoluble compounds as octane and decane are very substantial, but several sources give values that are reasonably consistent, and they are used in the present work. We took the values recommended by the IUPAC series$^{32–34}$ which collect and examine different resources. The resulting parameters are given in Table 4.

5.1. Tail–Water Repulsion Parameter. The tail–water mismatch parameters depend on the bead size. Generally, the larger the bead size, the higher the $\Delta a_{TW}$. The reason that $\Delta a_{TW}$ for $R_c = 0.65$ nm is higher than that for $R_c = 0.71$ nm is due to the shorter bond enforced on the tail–tail link, and it needs to be compensated somehow to reach the correct overall hydrophobicity. Such effects are not considered if $\Delta a$ is mapped to the FH parameters, for the FH theory assumes flexible molecules. In the simplistic model, equilibrium bond length is scaled with $R_c$; therefore $a_{TW}$ monotonically increases with $R_c$. It is difficult to tell what extent the linearity ($\Delta a \propto R_c$) suggested in ref 16 holds, but the increase of $\Delta a$ with $R_c$ is significant.

5.2. Head–Water and Head–Tail Repulsion Parameter. For the H beads, ethers (such as CH$_3$OCH$_2$CH$_2$OCH$_3$) appear to be the most suitable reference compounds. However, we face a shortage of reliable data on activities for the appropriate reference solutions. Groot and Rabone$^{4,27}$ fitted H–W parameters to LLE data for water–PEO solutions at higher temperatures, where the PEO–water system undergoes a liquid–liquid separation. They obtained $\chi = 0.3$ and $\Delta a_{HW} = 1.3$ $kT/R_c$. Here we opted to take short PEO oligomers with molecular weight of 400 Da for reference compounds, because the data on water activity in PEO–water solutions was reported for a wide range of concentrations$^{35,36}$. The procedure of $a_{HW}$ parameter fitting is essentially the same as that in ref 24. We perform MC simulations with DPD models for PEO–water mixtures, where the overall bead densities are adjusted to yield the bulk water pressures similarly to the dimer simulations described above.
Figure 5 shows the activity of water in the PEO–water solution as a function of PEO mass fraction at 298.15 K for \( R_c = 0.65 \) nm. The activity of water, \( a_W(x) \), is calculated for different values of \( \Delta a_{HW} \) and compared with experimental data.\(^2\) The DPD model cannot describe the water activity in PEO over the entire range of concentrations (which is not surprising taking in account the DPD phase diagrams for polymers\(^3\)). The best overall agreement for \( R_c = 0.65 \) and 0.71 nm is achieved with \( \Delta a = 1.5kT/R_c \), although activities of water in polymer-rich solutions are underestimated with this parameter. The resulting \( \Delta a \) agrees well with the estimates of Groot and Rabone.\(^4\) For \( R_c = 0.77 \) and 0.81 nm, MC statistics was very poor, and we used the same \( \Delta a_{HW} \) for all coarse-grained levels. For soluble fluids, \( \gamma(\Delta a) \) reference correlations generally show very weak dependence on the coarse-graining size. For tail and head interaction, the only available data also requires the extrapolation from a higher temperature.\(^5\) We employed in this case the mixing rule proposed by Groot and Rabone based on the chemical structure of ethylene oxide, and set \( \Delta a_{TH} \) equaled to one-third of \( \Delta a_{TW} \) (given in Table 4). Head–tail interactions for \( R_c = 0.71 \) nm were estimated from the IDAC for diglyme–octane system. Diglyme, \( \text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3 \), and octane are presented as symmetric dimers HH and TT, and a calibration curve \( \gamma(\Delta a_{TH}) \) was constructed in ref 3. Because \( a_{TH} \) showed only a weak dependence on \( R_c \), H–T mismatch is relatively low, and this

\[
\begin{array}{cccccc}
\text{compound} & \text{model} & \text{solubility [ref]} & \Delta a_{HW} & \Delta a_{TW} & \Delta a_{HT} \\
\hline
\text{hexane} & \text{dimer} & 2.4 \times 10^{-4} \text{[32]} & \text{average} & 25.9 & 23.4 \\
3\text{H}_2\text{O} & \text{monomer} & 6.1 \times 10^{-4} \text{[32]} & \Delta a_{HW} & 30.5 & 15.2 \\
\text{octane} & \text{dimer} & 1.1 \times 10^{-7} \text{[34]} & \text{average} & 20.4 & 13.6 \\
4\text{H}_2\text{O} & \text{monomer} & 6.1 \times 10^{-7} \text{[34]} & \Delta a_{HW} & 26.4 & 19.1 \\
\text{decane} & \text{dimer} & 3.3 \times 10^{-7} \text{[33]} & \text{average} & 23.6 & 15.4 \\
5\text{H}_2\text{O} & \text{monomer} & 6.3 \times 10^{-7} \text{[33]} & \Delta a_{HW} & 28.7 & 26.1 \\
\text{hexane} & \text{monomer} & 2.4 \times 10^{-6} \text{[32]} & \text{average} & 31.5 & 41.6 \\
6\text{H}_2\text{O} & \text{monomer} & 6.1 \times 10^{-6} \text{[32]} & \Delta a_{HW} & 26.0 & 15.8 \\
\end{array}
\]

Table 4. Mismatch Parameters for T–W Interactions Obtained with Eq 4\(^a\)

\(^a\)MD-fitted model uses the calibration relationships in Table 3. The simplistic model uses the approximate bond length from Table 2c. Solubilities are given in mole fractions.

Table 5. Experimental and Simulation CMC (in log\(10\) scale) for \( C_{6}E_{m} \) Surfactant at Different Tail \((n)\) and Head Length \((m)\) at Different Coarse Grained Level, \( R_c \)\(^d\)

\[
\begin{array}{cccccc}
C_{6}E_{m} \text{ surfactant} & n & m & R_c \text{ [nm]} & \text{expt}\(^{\text{18}}\) log\(\alpha\) [CMC] & \text{simplicistic log\(\alpha\)} [CMC] & \text{MD-fitted log\(\alpha\)} [CMC] & \text{relative error} & N_{ag} & \text{aggregation morphology} \\
\hline
& 8 & 4 & 0.71 & -2.1 & -2.3 & -2.0 & 0.1 & 905 & irregular \\
& 8 & 6 & 0.71 & -2.0 & -2.2 & -1.8 & 0.1 & 539 & irregular \\
& 8 & 8 & 0.71 & -2.0 & -2.2 & -1.7 & 0.1 & 83 & irregular and spherical \\
& 10 & 5 & 0.77 & -3.1 & -4.0 & -2.8 & 0.2 & 251 & irregular \\
& 12 & 3 & 0.65 & -4.0 & -4.2 & -4.4 & 0.2 & 728 & globular \\
& 12 & 6 & 0.65 & -4.0 & -4.2 & -4.2 & 0.5 & 258 & vesicular \\
& 12 & 9 & 0.65 & -4.1 & -4.3 & -4.0 & 0.1 & 111 & spherical and cylindrical \\
& 12 & 12 & 0.71 & -4.0 & -4.3 & -3.2 & 0.1 & 311 & vesicular \\
& 12 & 3 & 0.81 & -4.0 & -4.2 & -4.0 & 0.6 & 471 & globular \\
& 12 & 6 & 0.81 & -4.0 & -4.2 & -3.7 & 0.4 & 392 & globular \\
& 12 & 9 & 0.81 & -4.1 & -4.3 & -3.6 & 0.4 & 200 & spherical and cylindrical \\
\end{array}
\]

\(^d\)Simulation CMCs are calculated by two methods in determining bond parameter. Only a few characteristic systems are calculated by simplistic model for the purpose of comparison. \( N_{ag} \) is the average aggregation number, and the aggregation pattern is exemplified in Figure 8.
parameter is not crucial for the system behavior, we used the same mismatch $\Delta \text{diff} = 6.5kT$ for all bead sizes.

6. CALCULATIONS OF CMC OF C8E4, C8E6, SURFACANT

With the models and parameters described above, we calculate the CMC of select C8E4, surfactants. The DPD simulations are pretty standard and described in Supporting Information section S1. CMC is estimated from the average number of free surfactant molecules in the solution. Two surfactant molecules were assumed to belong to the same aggregate if any two of their tail or middle beads overlapped. The concentration of “monomeric” surfactant (that is, surfactant belonging to aggregates smaller than a certain critical size $n_{\text{mono}}$) in water was treated as the CMC. Reference 25 confirms that for nonionic surfactants this procedure is reasonably accurate, and CMC showed no significant dependence on the total surfactant loading or box size. The relative error is calculated from the mean square deviations of the free monomer concentrations from the average. The average aggregation numbers of all aggregates is reported as the aggregation number for the system, $N_{\text{ag}}$. The details of CMC and $N_{\text{ag}}$ calculations may be found in Supporting Information, section S4.

Table 5 summarizes the micellar properties obtained from the simulations compared with the available experimental data. CMC is mostly determined by the alkyl tail chain length $n$. Addition of one ethylene monomer decreases CMC by about 1 order of magnitude. The influence of $m$ on CMC is much weaker. Generally, CMC slowly increases with $m$. For the purpose of evaluation of the accuracy of the proposed parameterization method, we compared the results of the series of simulations for the chains with given tail length $n$ and different head lengths $m$, using, when possible, the models with different bead sizes. The results are shown in Figure 6. The upper panel presents data for $n = 8$, which was the shortest hydrophobic block considered; we modeled C8E4, C8E6, and C8E8 surfactants with the bead size $R_c = 0.71$ nm. Simulated CMC increases as the hydrophobic block becomes longer, which qualitatively agrees with experimental observation. The slight overestimation is visible but comparable to the statistical uncertainty of both simulations and experiments. Surprisingly, the simplistic model gives similar results but slightly underestimates the CMC. For $R_c = 0.77$ nm, decane is chosen as a reference compound for the tails and presented as a dimer. The DPD results for $n = 10$ showed the same tendencies as for $n = 8$: MD-fitted coarse-grained model slightly overestimated and the simplistic model slightly underestimated the CMC. Nevertheless, overall the decrease of CMC with $n$ is reproduced very reasonably with both models, confirming the consistency of our parametrization scheme.

For surfactants with longer hydrophobic tail, $n = 12$, the bottom panel in Figure 6 presents CMCs using different coarse-graining levels. The statistical errors for these surfactants are much higher both in simulations and experiments, because of lower free surfactant concentrations and large micelle size fluctuations. The finest coarse-graining with $R_c = 0.65$ nm gives very good agreement with the experiments. The $R_c = 0.81$ nm model slightly overestimates CMC, but the difference with experiment is still comparable to the statistical uncertainty of both simulations and experiments (almost exact agreement was obtained for C12E3). Noteworthy, the reference compound for the hydrophobic tail is hexane in both cases (Table 1), but it is presented as a monomer for $R_c = 0.81$ nm and as a dimer for $R_c = 0.65$ nm. The only system with a serious discrepancy with the experiment is C12E6, the $R_c = 0.71$ nm model overestimates CMC by the factor of 6.5. Overall, we find semiquantitative to quantitative agreement with the experiment. A selected system C12E5 modeled using the simplistic model at $R_c = 0.65$ and 0.81 nm also has good agreement with the experimental CMC. This indicates that although the representation of the molecule structure in the simplistic model is not as accurate as the MD-fitted model, it can still be applied to surfactants with alkyl tails and yield a reasonable CMC at low overall concentrations.

It should be stressed that the presented data confirm the robustness of the proposed parametrization strategy. The models at different coarse-graining levels, parametrized using experimental data on different reference compounds and atomistic MD simulations provide consistent results and predict CMC for the surfactants considered with reasonable accuracy.

7. MICELLE SIZES AND SHAPES AND AGGLOMERATION OF MICELLES

To analyze the role of the coarse-grained level on the structure of micellar aggregates beyond CMC, we used the asphericity factor, which quantifies the shape of the micelle, namely, the departure from spherical symmetry. The asphericity factor ($A$) is calculated as

$$ A = \frac{1}{2R_c^4} \left[ (R_1^2 - R_2^2) + (R_2^2 - R_3^2) + (R_3^2 - R_1^2) \right] $$

where $R_1^2$, $R_2^2$, and $R_3^2$ are eigenvalues of the gyration tensor $S_{ij} = 1/N \sum_{n=1}^{N} (\delta_{ij} - S_{ij}^{\text{CM}}) (S_{ij} - S_{ij}^{\text{CM}})$. $S_{ij}^{\text{CM}}$ stands for the center of mass of the micelle in coordinate $i$ ($i$ denotes $x$, $y$, or $z$). The asphericity factor is 0 for perfectly spherical micelles and reaches 1 for perfect cylinders.

Figure 7 shows the distribution of asphericity factors of micelles in 2 vol % solution of C12E6 generated with the T4H6 model ($R_c = 0.65$ nm) and T3H3 model ($R_c = 0.8$ nm). The fitter T4H6 model (that is, with smaller $R_c$) predicts two
pronounced peaks on the asphericity distribution corresponding to spherical and elongated micelle, see also Figure 8a for visualization. The average aggregation number is \( N_{ag} = 111 \), which agrees well with the experimental value reported by Zulauf et al. (about 100 for C12E8 at 303 K).\(^{40} \) The coarser T3H3 model produces mostly elongated micelles with no characteristic values for \( A \). The average aggregation number is about \( N'_{ag} = 200 \), exceeding the experimental value. This effect is related to the packing of the beads in the hydrophobic core: the bead size of the coarser model is comparable to the persistent length, and the chain therefore has no rigidity. It appears that despite the “softness” of DPD potentials, which are unable to reproduce the atomistic details, the finer T4H6 model with smaller and more tightly spaced beads gives a better representation of the hydrophilic tail packing in the micelle core compared with the coarser T3H3 model.

The tendency of micelles to agglomerate into bigger aggregates is overestimated by our models, especially for surfactants with shorter head segment, and prediction capability generally worsens as \( R_c \) increases. In experiments, the aggregation number generally decreases as the hydrophilic block becomes longer, due to the entropic repulsion between the hydrophilic chains. For the same hydrophobic segment length \( n = 12 \), this tendency is qualitatively reproduced in simulations, but it is much more pronounced compared with the experiments (Table 5). Experimental \( N_{ag} \) increases from \( N_{ag} = 100 \) for C12E8 to \( N_{ag} = 150 \) for C13E6 in simulations with the T4H6 model (\( R_c = 0.65 \) nm), \( N_{ag} \) increases from 111 and 258. The analysis of DPD configurations for C13E6 reveals a mixture of regular spherical micelles, elongated micelles, and core–shell micelles (Figure 8b). Core–shell micelles are especially common in solutions of C13E3 (Figure 8c). Aggregation of micelles into bigger agglomerates is also observed for \( n = 8 \) with \( R_c = 0.71 \) nm. Although the micelles in the C8E8 system are not of a well-defined spherical shape, they have a single hydrophobic core, and the aggregation number (\( N_{ag} = 83 \)) agrees very reasonably with the experimental value (\( N_{ag} = 72 \)).\(^{41} \) For the shorter molecule C8E4, the volumetric concentration \( \phi = 0.04 \) at which the DPD simulations are performed is above the aggregation transition. The micelles are agglomerated via core-to-core contacts into larger agglomerates of complex irregular shapes with the formal \( N_{ag} \) reaching 905 (sic!). In experiment, \( \phi = 0.04 \) is below aggregation transition, with \( N_{ag} = 147 \).

Figure 9 shows the size distribution of the aggregates in the C8E8 system. To show the importance of carefully assigning the

![Figure 7](image7.png)

**Figure 7.** Normalized asphericity distribution of the micelles for model C11E9 surfactant. The finer model, T4H6 at \( R_c = 0.65 \) nm (black line), produces well-defined spherical micelles; the coarser model, T2H3 at \( R_c = 0.81 \) nm (red line), produces micelles of more irregular shape and agglomeration between small micelles.

![Figure 8](image8.png)

**Figure 8.** Characteristic aggregation patterns in solutions of 4 vol % CnEm surfactants simulated by the T4H6 model with \( R_c = 0.65 \) nm bead size. Surfactant tail beads are shown in red, and head beads are shown in cyan. Water beads are not shown. Zoomed snapshots present the internal structure of the aggregates: (a) C12E9, mixture of spherical and elongated micelles; (b) C13E6, mixture of spherical, elongated, and core–shell micelles; (c) C11E8, core–shell micelles.

![Figure 9](image9.png)

**Figure 9.** Normalized distribution of the aggregate sizes for C4E8. The MD-fitted bond model produces well-defined mostly spherical micelles. The simplistic bond model leads to larger and irregular aggregates.
bond potentials, we present for comparison the results obtained with the simplistic bond model. The MD-fitted model predicts mostly spherical micelles with a well-defined peak and $N_{ag}$ = 83. Some elongated micelles containing up to 350 molecules are also detected, but overall a very reasonable agreement with the experimental $N_{ag}$ is observed. The simplistic model produces larger and irregular aggregates. The reason is that the simplistic model overestimates the end-to-end distances and the overall rigidity of CE surfactants compared with the MD-fitted model (Supporting Information S6). The rigidity decreases the chain entropy and promotes the formation of larger aggregates as discussed in our earlier work, resulting in the presence of several peaks in higher values of micelle size in Figure 9. The $N_{ag}$ is overestimated as 128.

Noteworthy, there were few attempts in the literature to quantitatively reproduce micellization in particular experimental systems in DPD simulations and to study the transformation from spherical micelles to ordered mesophases with increasing surfactant concentration. Therefore, it is not clear whether the observed disagreements between experimental and simulated morphologies indicate deficiencies of the proposed parametrization or the limitations of the DPD model in general. It is desirable yet perhaps impossible within the constraints of the DPD model to reproduce both the onset of micellization (CMC) and the consecutive morphological transformation in a wide concentration ranges above CMC with a single set of parameters. Observed underestimation of the concentration of the onset of micelle agglomeration may be related to the use of soft-core models for relatively small surfactant molecules like those considered in this work.

8. CONCLUSION

We presented a systematic strategy for parametrization of chain molecules in DPD simulations, which is based on a combination of top-down and bottom-up approaches. The key components of the proposed approach are the choice of the coarse-graining level (size of beads) and the dissection of molecules into head and tail beads with regard to the given molecular chemical structure, determination of interbead repulsion interaction parameters from the fitting of the experimental infinite dilution activity coefficients or solubilities of reference compounds to the results of the MC simulation of the respective coarse-grained solutions, and control of chain rigidity by introduction of the first (1–2) and second (1–3) neighbor bond potentials with parameters fitted to the results of atomistic MD simulations. The proposed approach was illustrated and its robustness discussed drawing on the example of poly(ethylene oxide) alkyl ether $C_nE_m$ surfactants of different composition with the DPD models constructed at different coarse-graining levels and parametrized based on the data for different reference compounds.

In this work, we have thoroughly examined the techniques of parametrization of DPD models based on fitting the mismatch parameters to the infinite dilution activity coefficients of the reference compounds. A reference compound is chosen to closely resemble a fragment of a target molecule represented as a bead or a dimer of beads. A reliable parametrization technique should, in general, produce similar results independent of the choice of coarse-graining level (that is the bead diameter) or the choice of reference compounds. In order to check the consistency of our parametrization strategy, we modeled aqueous solutions of $C_nE_m$ surfactants, which consist of hydrophobic alkane segment and hydrophilic PEO segment. We constructed DPD models of the $C_nE_m$ surfactants for different length of each segment. The parameters for the nearest neighbor and second neighbor bonds, which provide desired connectivity and rigidity, were matched to the results of atomistic simulations. We also employed a simplistic model for the bonds, with the bond length and stiffness calculated from the number of flexible torsions between the bead centers.3 The latter approach is not universally applicable, but it gave good agreement with experiments on CMC and $N_{ag}$ of several chemically different surfactants. We parametrized the repulsion parameters for DPD models of different coarse-graining level from the IDAC of n-alkanes (from $C_4$ to $C_{10}$) in water and of water in alkanes at room temperature. Water interactions with the hydrophilic segment were parametrized from the best match to experimental water activities in water—PEO mixtures of low molecular weight.

The models of $C_nE_m$ surfactant with different $R_e$ parameterized with different reference alkane show consistent results for CMC. We correctly reproduced the increase of CMC with the hydrophilic block length and most of the simulated CMC values agree (not without an exception) with the experimental data, for both MD-fitted and simplistic bond models. For $C_nE_m$ surfactants with longer hydrophilic segment, we also obtained reasonable agreement for the micelle size. The downside of the models is an apparent overprediction of a tendency to agglomeration of micelles into bigger aggregates. In several systems, we obtained various complex aggregates (such as cylindrical micelles, core–shell micelles, or irregular agglomerates), with the $N_{ag}$ values larger than those reported experimentally. The prediction of $N_{ag}$ generally worsens for short hydrophilic segments and larger bead sizes. The observed discrepancy in the onset of aggregation is most likely attributed to the limitations of the DPD model itself. Noteworthy, the CMC in the systems considered here is varied by 3 decimal decades, and the fact that we were able to reproduce the experimental data with reasonable (in most cases quantitative, accounting for the spread of experimental data) agreement testifies toward the robustness of the proposed approach.

Overall, the parametrization of DPD models from the activities appears to be a relatively straightforward and reliable technique, and the accuracy of the models derived with this procedure is very reasonable, considering inherent uncertainties in micellization experiments and approximations of the DPD method itself. The parametrization of bond potentials requires standard and inexpensive atomistic MD simulations of surfactant fragments. The calculation of the activity calibration relationships, $\gamma^\infty(\Delta a_{ij})$, are obtained very easily for smaller bead sizes using NVT simulations with Widom insertions. The accuracy of calculations of $\gamma^\infty(\Delta a_{ij})$ steeply declines with $a_i$ and advanced MC techniques may be needed when fluids of low compressibility are modeled with relatively large beads ($R_e > 0.7$ nm). Noteworthy, while the $\gamma^\infty(\Delta a_{ij})$ calibration for single bead reference compounds is universal for given bead size, in the case of dimer reference compounds, these correlations are specific to the bond parameters obtained by fitting to MD configurations.

The proposed parametrization strategy can be applied to other more complex aqueous and organic soft matter systems, like polymer—surfactant gels, polymer brushes, and polyelectrolytes. It should be noted that the self-assembled morphology of such irregular systems might be sensitive to the coarse-grained level, as shown above with example of $C_nE_m$ since the entropic repulsion between the hydrophilic blocks is difficult to
reproduce in soft-core models with large beads. Therefore, finer coarse-graining is recommended for chain molecules with small hydrophilic and hydrophobic blocks to provide at least 3–4 beads in each block, at the expense of increased computational costs. The latter could be lowered by extension of the proposed parametrization strategy to DPD models with beads of different diameters and using larger coarse-grained level for the solvent.

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.6b00031.

Section S1, DPD force field and simulation details, section S2, review of GW parametrization and the calculation of intracomponent repulsion parameters from solvent compressibility for different \( \phi \), section S3, details of MD simulations employed in section 4, section S4, details of calculations of CMC and \( N_\text{ag} \) section S5, derivation of eq 4, section S6, analysis of surfactant conformations in solution, and section S7, influence of 1–3 bond length on chain conformation (PDF)

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Notes

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