Supporting Information for:

Many-body Dissipative Particle Dynamics Simulations of Micellization of Sodium Alkyl Sulfates

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1 Derivation of relationship between $\ln(\gamma)$ and μ.

In the main article, we stated that it is possible to define the infinite dilution activity coefficient γ^∞ in terms of the chemical potentials for substance A in solution (μ_A) and for a pure liquid ($\mu_A^\ominus$). In this section we derive this expression in full.

It is possible to express the nonideal chemical potential μ_i of substance i in terms of the activity a_i as

$$\mu_i = \mu_i^o + k_B T \ln a_i, \tag{1}$$

where for each component i we choose a standard reference state μ_i^o. In an ideal solution $a_i = x_i$, where x_i is the mole fraction. The difference, therefore, between a real-solution chemical potential μ_i and an ideal solution μ_i^{ideal} is

$$\mu_i - \mu_i^{\text{ideal}} = k_B T \ln \frac{a_i}{x_i}. \tag{2}$$

Therefore, we define the activity coefficient $\gamma_i = a_i/x_i$ as the means for characterising the deviation from ideal behaviour. Substituting this into Eq. 1 allows us to express the chemical potential as

$$\mu_i = \mu_i^o + k_B T \ln \gamma_i x_i. \tag{3}$$

If we take the convention that the standard state of each component i is taken as the pure liquid i, we set

$$\mu_i^o = \mu_i^\ominus \tag{4}$$

where $\ominus$ indicates pure substance. In other words, we say that the activity coefficient of any species in the solution tends to the unity when its mole fraction tends to unity. i.e. $\gamma_i \to 1$ when $x_i \to 1$, for all i. Note that this is a particular type of convention referred to as the symmetrical convention, other choices for reference state can be made if the pure compound isn't a liquid (further details of which can be found in Levigne [1]).

We can now combine Eqs. 3 and 4 to write the chemical potential as

$$\mu_i - \mu_i^\ominus = k_B T \ln \gamma_i x_i. \tag{5}$$

We can define the chemical potential in terms of the excess chemical potential and its ideal component

$$\mu = \mu^{\text{excess}} + \mu^{\text{ideal}} \tag{6}$$

where the ideal part is calculated using $\mu^{\text{ideal}} = k_B T \ln \rho \Lambda^3$ where Λ is the thermal de Broglie wavelength and ρ is the number density.

Supposing our solution consists of substance A at infinite dilution in a solvent of B, the density of A in B is $x_A \rho_B$, while the density of pure a is ρ_A. This means we can say that

$$\mu_A = \mu_A^{\text{excess}} + k_B T \ln x_A \rho_B \Lambda_A^3. \tag{7}$$

$$\mu_A^\ominus = \mu_\ominus^{\text{excess}} + k_B T \ln \rho_A \Lambda_A^3. \tag{8}$$

Substituting Eqs 7 and 8 into Eq. 6

$$\mu_A^{\text{excess}} + k_B T \ln x_A \rho_B \Lambda_A^3 = \mu_\ominus^{\text{excess}} + k_B T \ln \rho_A \Lambda_A^3 + k_B T \ln \gamma^\infty x_A. \tag{9}$$

Rearranging and simplifying yields

$$\mu_A^{\text{excess}} - \mu_\ominus^{\text{excess}} + k_B T \ln \left(\frac{\rho_B}{\rho_A} \right) = k_B T \ln \gamma^\infty. \tag{10}$$

2 Intial parameter estimates for our system

We noted in the main article that our choice to set a bond length of $l_0 = 0.6$ was based on the results of some of our previous work. Here we explain this reasoning.

We showed in the main article that, when converted into real units, the choice of $l_0 = 0.6r_C$ translates to a bond length which is realistic for octane. However, this conversion requires knowledge of what r_C is going to be, which is only defined in our approach after one has already calculated MDPD parameters for the octane molecule. Therefore, we made some initial estimates for what r_C was likely to be before performing our Widom insertions of octane.

In our previous work [2] we performed various calculations and Widom insertions for single beads in MDPD. One can approximate that the excess chemical potential μ_{excess} of two bonded beads is approximately double μ_{excess} for single beads. This isn't absolutely correct, due to the fact that bonding beads together causes them to overlap, thus altering their chemical potential. A fact which has already been discussed in literature for standard DPD [3]. However, this assumption coupled with our previous work allows us to estimate that the interaction value for the tail beads will be somewhere around $a_{TT} \approx -21$. Using equations which relate a_{ii} to the density from our previous work [2], we can estimate that this generates a DPD bead density of around $\rho = 4.67$, and therefore $r_C \approx 8.6$ Å, suggesting a bond length in DPD units of around $l_0 = 0.6r_C$ would be appropriate.

The calculations for octane presented in our main article determine the actual values we use for a_{TT} and r_C in this work, though the small change that we find in r_C means that $l_0 = 0.6r_C$ is still a good choice for the bond length.

3 Pressure in MDPD simulations

The equation of state for MDPD systems was extensively discussed by Warren [4], where the mean-field EOS was predicted to take the form

$$p_{MP} = \rho k_B T + \frac{\pi}{30}(A + 2Br_d^4\rho)\rho^2. \tag{11}$$

However, Warren [4] showed that the actual EOS differs from this expression, and fit an EOS of the form

$$p = \rho + \alpha A\rho^2 + 2\alpha B r_d^4(\rho^3 - c\rho^2 + d) \tag{12}$$

where the fitted constants $\alpha = 0.101$, $c = 4.16$ and $d = 18$. From Eq. 12 one can observe that a Van der Waals loop is possible, and hence vapor-liquid coexistence. It can also be observed from this EOS that, unlike in a real fluid, it is possible to generate negative pressure in MDPD. We state in our main article that when the liquid phase is in coexistence with a very low-density vapour (as in our simulations), the pressure which generates liquid phase density ρ_L can be estimated as being at the point the pressure vanishes. To illustrate the relationship between pressure and density around the expected density of the liquid phase, and verify the EOS in Eq. 12, we calculate the density for an MDPD system in various NPT simulations of different pressures. We show in Fig. S1 how the pressure in the system relates to the density, and we can see that extremely small changes in the density correspond to fairly large fluctuations in the pressure (in our units system). Looking at it from the other point of view, relatively large changes in P are required to alter the density.

4 Critical micelle concentration for S12S

Here we illustrate the sensitivity of the CMC to the value of the tail-water interaction. We calculate the CMC using an alternative value of a_{TW}, increasing it from the original value of $|a_{TW}| = 36.576$ to $|a_{TW}| = 37.076$. This has the effect of increasing the attraction between the surfactant tail and water, thereby increasing the CMC. Fig. S2 shows the relationship between the solution concentration and the fraction of surfactants in micelles. By calculating the concentration at which half of the surfactant molecules are in micelles, we determine a CMC value of 9.1 mM, which is almost double the value calculated using the original interaction value (5.04 mM).

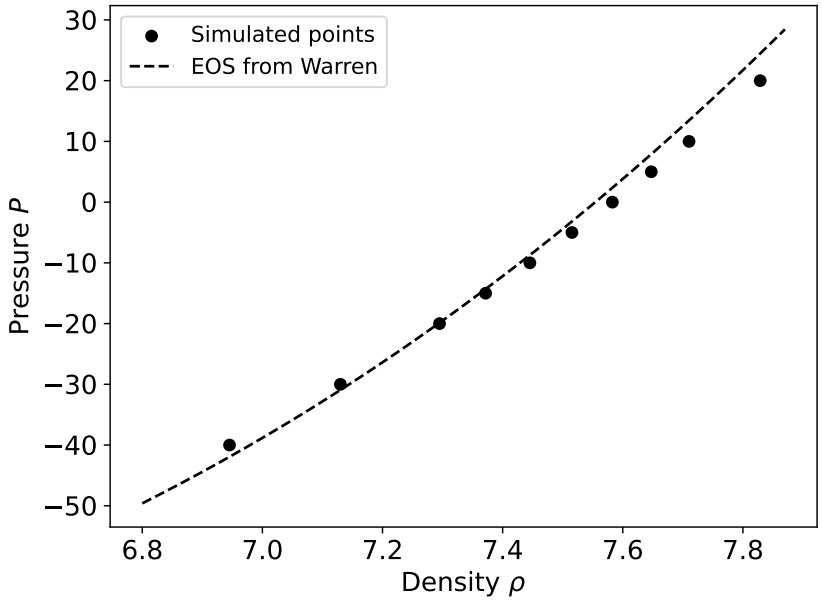

Fig. S1: Relationship between the pressure and number density in an MDPD system with $A = -60$ and $B = 25$. Cutoffs are the same as described in the main article. The EOS given is Eq. 12, fitted by Warren [4].

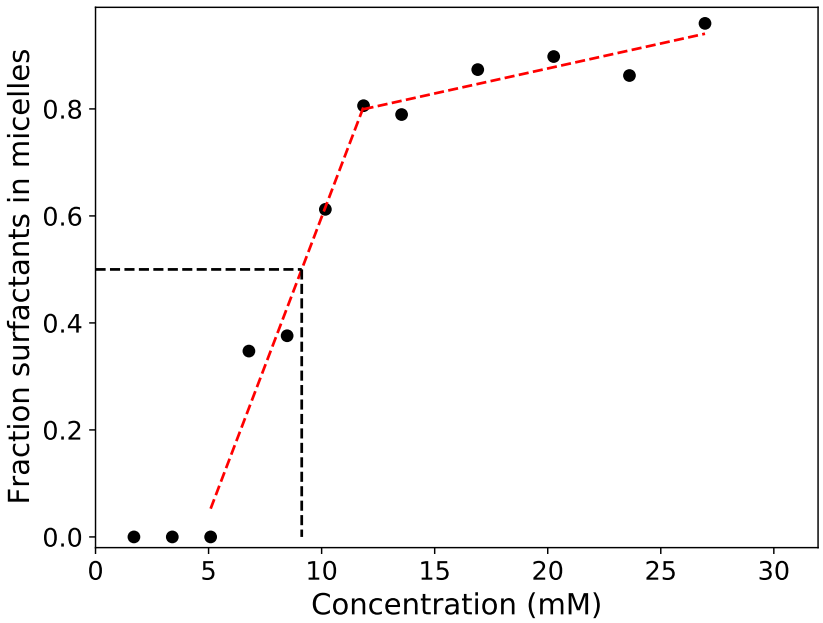

Fig. S2: The fraction of S12S surfactant molecules existing in micelles at different concentrations. Red linear fits are shown and CMC values are highlighted by black lines.

References

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[4] P. B. Warren. Vapor-liquid coexistence in many-body dissipative particle dynamics. *Phys. Rev. E*, 68:066702, Dec 2003.