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Low Critical Micelle Concentration Discrepancy Between Theory and Experiment

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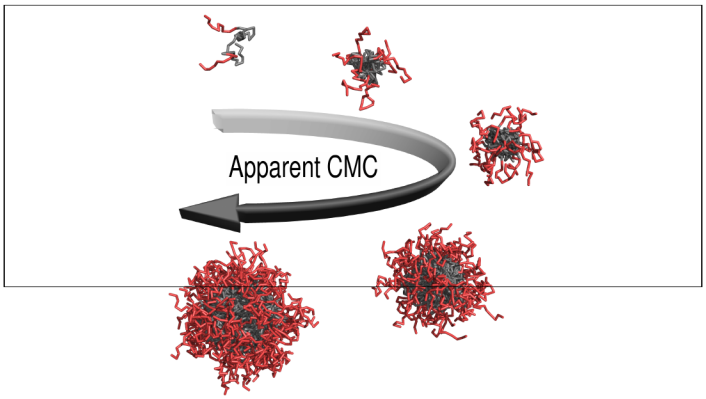
Abstract

Experimental measurements for a variety of surfactants unexpectedly show that the critical micelle concentration (CMC) becomes constant with respect to increasing the size of the hydrophobic tail. This observation disagrees with theoretical models where it is expected to continue to decrease exponentially. Due to the lack of a satisfactory explanation for such a discrepancy from theory, we have studied these systems using a coarse-grained model within the Single Chain Mean Field (SCMF) theory combined with relevant micellar kinetic effects. In particular, a microscopic model for polyethylene oxide alkyl ether was applied to describe a series of nonionic gemini surfactants. When kinetic effects are used to correct the equilibrium CMC values from the SCMF scheme together with the loss of surfactants due to adsorption on the experimental recipient, it is possible to reproduce the correct order of magnitude of the experimental CMC results. Hence it appears that the experimental values disagree with the theoretical predictions because they are not true equilibrium values due to the fact that the timescales for these low CMC values become astronomically large.

Graphical TOC Entry



Keywords

Critical micelle concentration, kinetic effects, coarse-grained, simulation, micelle, gemini surfactants

Surfactant molecules are of the utmost importance in a wide range of industries including the environmental, pharmaceutical, material synthesis and oil recovery, among others.[1–3] Key to their importance is their ability to associate into aggregates with well-defined geometrical shapes above a free surfactant concentration known as the critical micelle concentration (CMC). The ability to design surfactants to have specific properties can be expected to play a major role in various technological applications, for example, in the cleaning industry a lowering in surfactant CMC allows for a decrease in the concentration at which solubilization in the stain removal process occurs,[4] in emulsion polymerization the CMC and particle nucleation processes are related,[5] and in pharmacology surfactants with low CMC values are preferred to transport drugs to reduce the number of free monomers that can precipitate in the blood.[6]

Experimentally, surfactant systems exhibit an exponential decrease in the CMC value with respect to the size of the hydrophobic tail at constant temperature,[7,8] such a behavior has been predicted by theoretical models[9–11] and simulation studies.[12–14] However for very low CMC values a non-exponential decrease of the CMC can be observed starting from a certain length of the hydrophobic component which depends on the surfactant chosen. This phenomenon has been reported in the case of ionic[15–17] and nonionic[18,19] surfactants. This Letter is aimed at understanding and explaining this discrepancy between the experimental CMC observation and expected theoretical behavior.

Theoretical models have been proposed for the formation of micelles in surfactant systems[9–11] in order to calculate the main factors that give rise to micelle shape, phase behavior and the CMC. In particular, a description of cationic dimeric (gemini) surfactants has been realized.[20] These models are based on an arbitrary division of the free energy into several contributions and a direct link to the underlying microscopic system is lost. The CMC is estimated mainly from the free energy contribution related to the transfer of the hydrophobic tail of the surfactant from the bulk to the inner core of an aggregate, together with additional contributions. Since this free energy can be related linearly to the size of the surfactant tail

and the CMC depends on the exponential of the free energy of micelle formation, this results in an exponential decrease of the CMC on increasing the tail length.

Within the computational framework, molecular dynamics (MD) and Monte Carlo (MC) simulations have been widely used to explore micellization,[12,21–25] however problems can be found when trying to determine the CMC. In particular, MC and MD calculations appear to be limited by spatial and temporal factors resulting in: sampling and equilibrium problems, a lack of long time kinetic effects, non-convergence in the aggregate size distribution due to the slow dynamics of the aggregates and in some cases no satisfactory CMC prediction. These effects have been reported in recent MD simulations using graphics processing units for a series of nonionic polyethylene glycol surfactants for hydrophobic tails composed of 6 to 12 carbon atoms.[26]

In a similar fashion, mean field methods have also been used such as the self-consistent field theory in lattice discretized space,[27–29] and in continuous space,[30,31] however the chains representing the surfactants are described by Gaussian distributions which implies the inclusion of overlapping conformations which ignore excluded volume intramolecular interactions terms in the free energy. Another mean field simulation technique that has been successful in predicting the CMC is the so-called single chain mean field (SCMF) theory[32] which has been directly compared with MC[33,34] and MD[35] simulations. Recently, accurate predictions of the CMC for a wide number of polyoxyethylene alkyl ethers surfactants were performed by Gezae Daful et al.[13] where a comparison to experimental values showed an excellent quantitative agreement.

In view of the concerns with standard simulations, which can be expected to be even more important for longer surfactants, the SCMF theory presents itself as an interesting alternative. This method uses the solution of a mean field Hamiltonian and can be applied to relatively long surfactants. The main idea is to use non-overlapping conformations of a single molecule that can be described at any desired coarse-grained level. The interactions with the other molecules and solvent medium are described in terms of mean molecular fields; these fields

take into account the concentrations of the different species of the molecule and an incompressibility condition. The molecular fields are calculated from a self-consistent condition which specifies that the individual molecule conformations depend on the mean molecular fields while these mean fields are calculated from the average values of these individual conformations. The microscopic level is close to the one employed in MC and MD simulations. The main advantage being that the free energy involved in the micellization process can be calculated directly whereas it is difficult to obtain from MC or MD simulations. In this Letter, we employ the SCMF combined with a model for micellization kinetics to calculate the CMC in order to understand the deviations found between experimental data and the expected theoretical exponential decrease. In particular, we have chosen the nonionic gemini surfactant $(H(CH_2)_{n\text{-}2}CHCH_2O(CH_2CH_2O)_mH)_2(CH_2)_6$ synthesized by FitzGerald et al.[19] and denoted as Gem_nEO_m. This system has a strong deviation in the measured CMC with respect to the values predicted by theoretical free energy models as a function of the hydrophobic tail length n.

To describe nonionic gemini surfactants we used the coarse-grained model developed in a previous work by Gezae Daful et al.[13] for polyethylene oxide alkyl ether surfactants. Two classes of beads with the same diameter are employed, one type representing the group that contains a central carbon atom (C) and the other representing an ethylene oxide unit (EO). All the length units are given in terms of the diameter of the beads: the distance between two consecutive beads is 1.42, and the interactions of a bead with the surrounding fields are given by means of square well potentials with internal and external radii of 1.0 and 1.6 respectively. Finally, the only interactions considered are those between unlike molecular type of the surfactant and the solvent i.e. C-EO, C-Solvent, EO-Solvent with values of 0.34, 3.984 [1] and 0.5 respectively. It should be noted that no additional adjustment of these parameters was made for the gemini surfactants. The chemical formula and a typical configuration of the coarse-grained model adopted in this work is shown in Figure 1 for a $Gem_{12}EO_{10}$ surfactant.

[1]In the original work Ref. 13 a factor of 1.66 was missing and is incorrectly stated, the value should be 3.984 as given in this work in order to reproduce correctly the CMC values.

In the SCMF a set of non-overlapping conformations, $\{\alpha\}$, of the surfactant molecule are

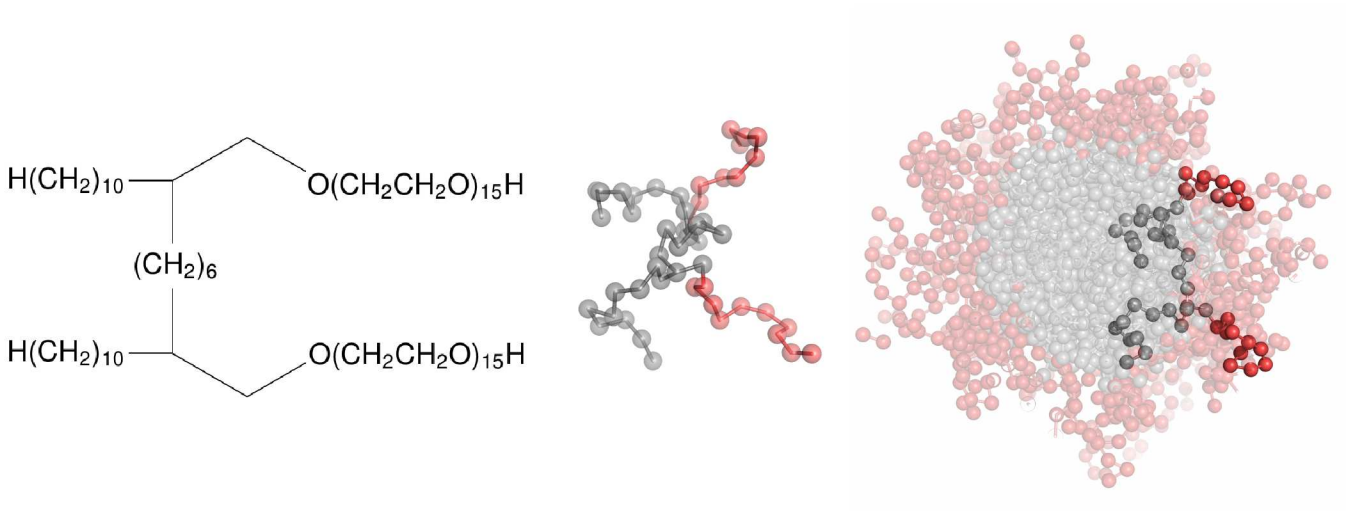


Figure 1: Coarse-grained model for $Gem_{12}EO_{10}$. Left: chemical structure for the selected gemini surfactant. Center: the most probable conformation in the bulk, the groups with a central carbon atom and ethylene oxide unit are represented by grey and red beads respectively. Right: Cross section for an aggregate of 100 gemini surfactants predicted with the SCMF where the most probable configuration is highlighted

generated, each one of these conformations is represented by an associated probability $P[\alpha]$ enabling the calculation of any average property by means of $< A >= \int d\alpha P[\alpha]A[\alpha]$ where $A[\alpha]$ is the quantity measured for each conformation. This probability follows a Boltzmann distribution which means that $P[\alpha] = e^{-H^N_{MF}[\alpha]/kT}/Q$, where $H^N_{MF}[\alpha]$ is the SCMF Hamiltonian for a system containing N surfactants, k is the Boltzmann constant, T the temperature and Q is the partition function which ensures the correct normalization of the probabilities. The mean field Hamiltonian includes: i) the exact internal energy of configuration α, ii) the interaction of the configuration with the surrounding fields of solvent and surfactants molecules calculated in a self-consistent way and iii) a steric repulsion term representing the incompressibility condition of the system. The concentration of aggregates in equilibrium can be extracted from the equality of the chemical potential between aggregated and free surfactants according to the mass action model:[36]

$$\frac{X_N}{N} = \left[X_1 e^{-(\mu^0_N - \mu^0_1)/kT}\right]^N, \quad (1)$$

where X_1 and X_N are the concentrations of surfactants in the bulk and those in aggregates of size N, while μ_1^0 and μ_N^0 are the corresponding standard chemical potentials for free chains and surfactants in aggregates of size N respectively. The macroscopic connection with the SCMF is obtained from the relation of eq 1 with the Hamiltonian,[34] which is given as:

$$e^{-(\mu_N^0-\mu_1^0)/kT} \approx \frac{V}{N}\frac{\sum_\alpha e^{-H_{MF}^N[\alpha]/kT}/W(\alpha)}{\sum_\alpha e^{-H_{MF}^1[\alpha]/kT}/W(\alpha)}, \tag{2}$$

where $H_{MF}^1[\alpha]$ refers to the SCMF Hamiltonian for free surfactants in the bulk solution, V and $W(\alpha)$ are the simulation box volume and the statistical weight associated with the Rosenbluth & Rosenbluth method used to generate non-overlapping conformations[37] of the surfactants.

It is possible to establish a direct relationship between the standard chemical potentials and the association/dissociation thermodynamic potential $F(N,\ X_1)$ which gives rise to the energetic barriers[38,39] involved in micelle formation. To do so, we relate the concentration of aggregates given by the mass action model in eq 1 with the dimensionless potential $F(N, X_1)$ by means of

$$\frac{X_N}{N} = X_1 e^{-F(N,\, X_1)}. \tag{3}$$

From the relation between equations 1 and 3 we can state that

$$F(N,\ X_1) = N\frac{(\mu_N^0 - \mu_1^0)}{kT} - (N-1)\log X_1, \tag{4}$$

The first term on the right hand side of eq 4 is related to the interaction between surfactants in aggregates as compared with those in the bulk solution and can be determined by the SCMF method by means of eq 2. The second term is related to the translational entropy of free monomers. From here, the CMC in equilibrium (CMC^{eq}) can be defined as the free surfactant concentration at which $F(M^{agg},\ \mathrm{CMC}^{eq}) = 0$ and $\left.\frac{\partial F(N,\ \mathrm{CMC}^{eq})}{\partial N}\right|_{N=M^{agg}} = 0$ where M^{agg} is the aggregation number in the equilibrium state.

A series of simulations were performed for a set of sixteen gemini surfactants Gem_nEO_m with $n = 6,\ 8,\ 10,\ 12,\ 14,\ 16,\ 18,\ 20$ and $m = 10,\ 15$. Sets of 3 to 8 million conformations were generated to represent the corresponding surfactant configurations. From the solutions of the SCMF equations we can derive all equilibrium properties such as the average volume fractions for aggregates of size N and estimate the standard chemical potentials favoring the micellization process in eq 2, leading to the determination of the association/dissociation potentials from eq 4. In Figure 2 the potential $F(N,\ X_1)$ for three values of the free surfactant

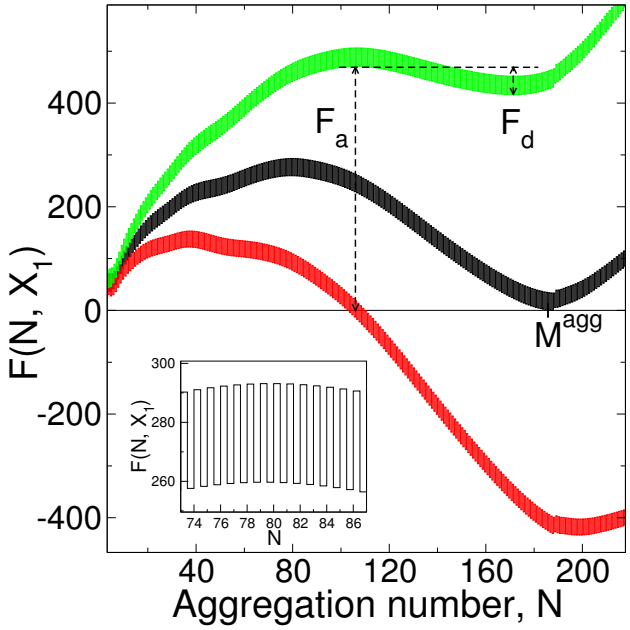


Figure 2: Aggregation potentials $F(N,\ X_1)$ as a function of aggregation number, N, for surfactant $Gem_{16}EO_{10}$ with F_a, F_d and M^{agg} as the association/dissociation barriers and the equilibrium aggregation number respectively. From top to bottom, $X_1 \approx \text{CMC}^{eq}/10$, $X_1 \approx \text{CMC}^{eq}$, $X_1 \approx 10\text{CMC}^{eq}$. The inset shows the maximum for $X_1 \approx \text{CMC}^{eq}$ in the range $N = 73 - 87$

concentration are presented where F_a and F_d, the activation and dissociation energy barriers, are given for the lowest surfactant concentration of $\text{CMC}^{eq}/10$. It should be noted, however, that they are defined for any free surfactant concentration. As can be seen, when $X_1 < \text{CMC}^{eq}$ (green line) the association barrier is higher than the dissociation one meaning that the energetic cost for surfactants to associate into aggregates is higher in comparison to the dissociation, indicating that most surfactants will be in a non-aggregated state. When

$X_1 = \mathrm{CMC}^{eq}$ (black line) the association/dissociation rates are the same indicating that over an interval of time the number of aggregates per unit volume per unit time that associate is the same as the ones that dissociate ($F_a = F_d$). Finally, if $X_1 > \mathrm{CMC}^{eq}$ (red line) the barrier F_a to form aggregates can be more easily overcome, however the dissociation barrier is relatively higher making it more difficult to pass in the opposite direction (i.e. releasing surfactants from the aggregates), leading to the possible formation of aggregates that are not in equilibrium. This last state is of particular importance to understand the experimental results for the gemini surfactants studied in this work.

In order to obtain a reasonable correspondence between the association/dissociation scheme with the step-by-step nature of the micellization process, an entropic contribution related to the probability for surfactants to be in contact with aggregates has to be included in the estimation of the potential $F(N,\ X_1)$ and hence the values of F_a and F_d. This negative contribution is taken to be $-\log \Phi_1$ and modifies the aggregation potential given in eq 4 as follows[38]

$$F\left(N + \frac{1}{2},\ X_1\right) = F(N,\ X_1) - \log \Phi_1, \tag{5}$$

where Φ_1 refers to the free surfactant volume fraction of the system and is taken in this Letter approximately as $X_1 V_{mol}$ with V_{mol} being the single surfactant molecular volume.[8] The effect of such corrections in the association/dissociation potentials can be observed in the inset in Figure 2 which exhibits a step behavior due to the intrinsically discrete mechanism of micelle formation where one chain has to be added at a time. From the information provided by $F(N,\ \mathrm{CMC}^{eq})$ and $F(N + 1/2,\ \mathrm{CMC}^{eq})$ an estimation of the characteristic timescale of micelle formation can be performed by means of $T_a = T_0 e^{F_a}$, where T_0 is the primary association time which is taken to be $T_0 = 6\pi\eta_{sol} R_1^3 / M^{agg} kT$, where η_{sol} is the solvent viscosity and R_1 the surfactant hydrodynamic radius. This time scale is obtained from the relationship of maximum free chain concentration in aggregates with the rate of micelle formation per unit volume and unit time and the dimer lifetime.[38] In our case we have roughly estimated the hydrodynamic radius for each selected surfactant to be in the interval $R_1 \sim 0.42 - 0.56$ nm, in

all cases the aggregation number is around $M^{agg} \sim 54 - 203$, the viscosity of water at 298.15 K is $\eta_{sol} \approx 8.91 \times 10^{-4}$ kg/m.s and $kT \approx 4.11 \times 10^{-3}$ kg.nm^2/s^2. From here we find that T_0 is of the order 10^{-12} s. Given that we are considering micellization as a closed association process carried out by a step-by-step growth, to achieve a complete micellization process at the CMC^{eq} the activation barrier F_a must be overcome. By considering that according to the SCMF results $F_a \sim 35 - 293$, we can infer for $n \geq 12$ (where $F_a > 150$) that the time needed to obtain a complete micelle formation in equilibrium becomes astronomical, $T_a \sim 10^{50} - 10^{100}$ s, leading to the conclusion that it is not feasible to determine experimentally the correct CMC for the longer surfactants in the time scales available in the laboratory.

In Figure 3, the equilibrium CMCs calculated in this work using the SCMF theory for the nonionic gemini surfactants (filled squares) studied in this Letter are shown as well as the available literature experimental values. As can be observed, CMC^{eq} is found to follow

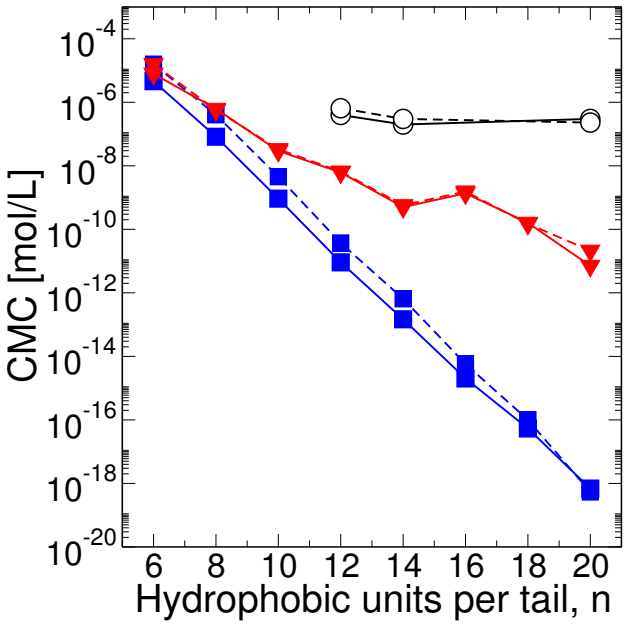


Figure 3: Experimental CMC data (empty circles) as a function of the number of hydrophobic tail units, n, taken from Ref. 19 for nonionic gemini surfactants, predicted equilibrium values from the SCMF (CMC^{eq}, filled squares) and corrected for kinetic factors (CMC^{app}, filled triangles). The lines are just guides for the eye where the dashed line represents Gem$_n$EO$_{15}$ and the solid line Gem$_n$EO$_{10}$

a linear behavior in the logarithmic scale with respect to the number of carbon atoms in the alkyl chain as has already been found in experiments for shorter CxEOy surfactants and has been predicted in theoretical models.[8,13] When the experimental data (empty circles) is compared to the predictions obtained from SCMF for CMC^{eq}, a discrepancy of four orders of magnitude is observed for geminis with the shorter hydrophobic chain ($n = 12$). Such a deviation dramatically increases as the number of methylene CH_2 units rises, reaching a difference of eleven orders of magnitude in the case of $Gem_{20}E_m$. A similar scenario was presented in a previous work[20] for a free energy model for bis(quaternary ammonium bromide) surfactants. The authors justify the difference by suggesting that a recoil or collapse of the free surfactants, an effect not included in the empirical model used, may be responsible for changing the intramolecular interactions and thereby the transfer free energy and result in an increase of the CMC in the experimental systems. However this is not observed in the SCMF calculations performed in this Letter where the free chain conformations are explicitly included in a homogeneous concentration field. Indeed, we have not noted any collapse of the surfactants either in the bulk or in the aggregates as can be observed in Figure 1. Thus we need to look to other possible explanations to understand the discrepancy between experimental and theoretical CMC values and so we turn our attention to the kinetic effects. As already mentioned, from the estimation of the time T_a needed to achieve the micellization process in equilibrium, we can infer that the aggregation process is extremely slow for these systems. However, the formation of aggregates can be modified by means of an arbitrary increase of the free surfactant concentration X_1 above CMC^{eq} following equations 4 and 5, leading to a non-equilibrium formation of micelles in the experimental time scales T^{app} that are typically used. This action of arbitrarily increasing the surfactant concentration above the unattainable CMC^{eq} reduces the activation energy barrier $F_a = \max\{F(N,\ X_1)\}$ until a value F^{app} which can be overcome during the experimental time scale $T^{app} = T_0 e^{F^{app}}$. The observed result will be an equivalent or apparent CMC (referred to here as CMC^{app}) as previously suggested.[38] In this work we arbitrarily consider that the necessary experimen-

tal time to observe a complete micellization for the geminis in the laboratory is $T^{app} = 1$ m, this is equivalent to a reduction of F_a until $F^{app} \approx 30$ resulting in a correction in the CMC predicted values seen in Figure 3 (filled triangles). The CMC^{app} and CMC^{eq} from the SCMF scheme show a relative difference that increases progressively to 10^7 with respect to the number of hydrophobic units in the gemini surfactants. Comparing the CMC^{app} with the experimental values we observe an improved agreement, where the predicted values are now within a factor of 10^2 of the experimental values when $n = 12$ or $n = 14$. However the difference between these values increases for $n = 20$ to a relative difference of about 10^4. Although no experimental CMC values are available in the case of $n = 16,\ 18$ we can expect an intermediate difference between these two values when comparing with the predicted CMC^{app}, in contrast to $n = 6,\ 8,\ 10$ where minor discrepancies can be expected. Experimental data is unfortunately also unavailable for these shorter surfactants. The cause of the deviation between CMC^{app} and the experimental CMC is still unclear, however we have not considered the possible effects of the loss of surfactants due to adsorption and how this might affect the equilibrium CMC and equivalent CMC^{app} predicted values. In this respect FitzGerald et al.[19] suggested that for measured CMCs close to $10^{-7} - 10^{-6}$ mol/L it is plausible to estimate that the concentration of free surfactants in the bulk should be around $10^{-10} - 10^{-8}$ mol/L. Such an assertion is based on the assumption that an important amount of surfactant can be adsorbed onto the walls of the recipient that contains the solution leading to an increase in the measured experimental CMC. This means that an experimental CMC of around 10^{-7} mol/L would possibly correspond to 10^{-10} mol/L in the bulk, which is of the same order of magnitude with the predicted CMC^{app} in this Letter for $n = 12,\ 14$ and relatively close in the case of $n = 20$.

According to our calculations for geminis with $n = 6,\ 8,\ 10$ we have observed that the aggregation numbers N corresponding to the association barriers $F^{app} = \max\{F(N,\ \text{CMC}^{app})\}$ lie in the range $10 \leq N \leq 20$. In every case this barrier is easily overcome producing a small relative difference between the apparent and equilibrium CMC as can be observed in

Figure 3. This is contrary to the case when geminis with $n \geq 12$ are considered where the barriers F^{app} are usually found in the range $N \leq 10$. At these very low aggregate numbers the limit of validity of our spherical mean-field approximation can be reached and it would be interesting to check these calculations with other techniques. However, precisely in the case of these longer gemini such as $Gem_{20}EO_{15}$ there are seventy six beads representing each surfactant and we expect that the mean-field approximation may be reasonable even at very low aggregation numbers. Furthermore, the inclusion of the standard chemical potential difference $(\mu_N^0 - \mu_1^0)/kT$ in the corresponding association/dissociation potentials $F(N,\ X_1)$ for very small aggregation numbers, such as dimers and trimers which are currently missing from our mean field approach and kinetic calculations are expected to lead to an increase of CMC^{app}. This change is not expected to be large and would give rise to an improved agreement with experimental data. We thus believe that despite these limitations to our calculations, our overall conclusions will not be significantly affected, namely that the difference between the simulation SCMF value and the experimental one can be attributed to both to kinetic and adsorption effects in the experimental measurements.

In order to identify the effect on CMC^{app} determined with SCMF and kinetic theory with respect to the timescale used to study micellization in the laboratory, T^{app}, a series of calculations with T^{app} = 1 s, 1 h and 6 h were performed. The CMC^{app} obtained in every case show a tendency to decrease with respect to increasing T^{app} as expected. In the extreme cases a decrease of two orders of magnitude and an increase of one order of magnitude was obtained for T^{app}=6 h and T^{app}=1 s respectively with respect to our reference time of 1 m. These results reveal that, although the kinetic effects are susceptible to changes in the laboratory time scales, the changes are not so large as to affect our overall conclusions. To finish, we propose that the experimental values disagree with the theoretical predictions for the gemini surfactants studied in this work because they are not true equilibrium values. This is a consequence of the extremely large time scales found for the equilibration of micelles for these low concentrations values leading to apparent CMCs that are orders of magnitude

above the equilibrium values. When these kinetic factors are used to estimate an apparent CMC, and are combined with the possible adsorption effects on the experimental equipment as reported in the literature, we are able to find the same order of magnitude between the experimental CMCs and our predicted values. We also observe a change in the exponential decrease of the CMC with tail length where the CMC decreases less rapidly in our calculations. Although we have only calculated the case for nonionic gemini surfactants we expect the same conclusions to be valid for all surfactants with sufficiently low CMCs.

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