

Principal Role of the Stepwise Aggregation Mechanism in Ionic Surfactant Solutions Near the Critical Micelle Concentration. Molecular Dynamics Study

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Received: March 20, 2009; Revised Manuscript Received: June 9, 2009

The validity of the assumption on the predominant contribution of the stepwise processes to the ionic micelle formation/destruction in the vicinity of critical micelle concentration was investigated by molecular dynamics simulation. A coarse-grained model was used to describe the surfactant/water mixture. The cluster size distribution was estimated directly from molecular dynamics simulations or obtained from a reduced set of kinetic equations. The good agreement between two approaches shows that the neglect of the terms responsible for cluster fusion/fission is fully justified and that such processes are less important than stepwise aggregation.

1. Introduction

The association of surfactant molecules into aggregates known as micelles is a well-studied phenomenon. Micelles are dynamic objects, and the aggregation number of micelles changes continuously. The kinetics of micellar transformations has been shown to have a significant impact on technological processes involving a rapid increase in interfacial area, such as foaming, wetting, emulsification, solubilization, and detergency.^{1,2} Two main mechanisms of the micelle growth/diminishing can be considered. These mechanisms are the stepwise addition/removal of one surfactant molecule to/from a micelle (the so-called stepwise mechanism) and the merging of two micelles into one or the break-up of a micelle into two aggregates (cluster fusion/fission mechanism).

Aniansson, Wall, and co-workers^{3–5} had developed the theory of the micellar association and dissociation kinetics supposing that these processes proceed by the stepwise mechanism only. To solve the classical kinetic equations, they rewrote them in a form that closely resembles that of the heat conduction between two large metal blocks connected by a thin wire.

The approach of Aniansson and Wall is widely and successfully exploited by various authors up to now (see the paper¹ and the references cited therein). In 1982, Kahlweit⁶ introduced the cluster fusion/fission mechanism into the original formalism, which extended the field of possible applications of the theory to more concentrated solutions and to solutions with a high ionic strength.

In the last several years, a lot of works on computer simulations of surfactants were published; however, almost all of them were devoted to either thermodynamics or structure of micelles,^{7–19} while the kinetic aspects received far less attention.^{20–24} In refs 20 and 21, an autocatalytic replication mechanism of micelle formation was suggested which includes the stepwise growth of micelles followed by their fission. This mechanism was supported by molecular simulations. However, in these works there is no analysis of the dependence of the micelle stability on the simulation cell size which might be crucial according to refs 25–27. In ref 22 the mechanism of micelle destruction into two comparable parts was examined by all-atom computer simulations. The micelle fission progresses

through a dumbbell-like morphology involving the formation of a long and narrow stalk in which the surfactants are highly interdigitated. Such destruction was stimulated by the sharp decrease of the salt concentration in the solution and was found far away from critical micelle concentration (CMC). The authors of ref 23 proposed the theoretical approach on the basis of an effective Fokker–Planck equation with the assumption of only stepwise reactions to describe micelle formation in the lattice model of Larson.²⁸ Multiple relatively short Monte Carlo simulations were used to estimate the components of the Fokker–Planck equation which allows for an adequate reconstruction of the free-energy surface and the statistical characteristics of the thermal noise. A multiscale model of formation and disintegration of spherical nonionic micelles was proposed in ref 24. Different scales of these processes were investigated using a combination of coarse-grained molecular dynamics simulations, the analytical and numerical solution of stochastic differential equations, and the numerical solution of kinetic equations. It was assumed that the dominant mechanism of micelle formation (disintegration) is the stepwise process. The observed discrepancies in the cluster size distribution obtained from a free energy simulation and from the multiscale model were interpreted as an imperfection of the model.

The assumption that the stepwise mechanism plays the principal role has the exceptional merit in the development of various micellization theories. At the moment, however, there is no direct evidence that this assumption is valid. Convenient tools for the examination of the role of stepwise processes are provided by the computer simulation techniques.

The main purpose of our work is to make certain that only the stepwise mechanism is responsible for the micelle growth/diminishing near CMC for the ionic surfactant. We have carried out the molecular dynamics (MD) simulation of ionic surfactant solutions at two concentrations close to CMC and calculated the cluster size distribution by two different ways: directly from the MD trajectories and as the solution of the kinetic equations set assuming the absence of cluster fusion/fission. It will be shown below that the cluster size distribution curves obtained by two different approaches appear to coincide with good accuracy. Since we did not account for processes of cluster fusion/fission while constructing the set of kinetic equations,

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we conclude that such processes do not play an essential role in the micelle growth/diminishing.

2. Model and Simulation Details

The coarse-grained (CG) approach was used for the MD simulations of the surfactant solutions. This approach represents several atoms (e.g., four methylene groups) as one large interaction site (a bead). As a result, the number of pair interactions decreases by an order of magnitude as compared to the united-atom force fields. Moreover, the fast degrees of freedom are eliminated, and a larger time step can be used in the MD algorithm. So the time and the length scale of simulations are increased several times. We use the coarse-grained force field developed by Marrink and co-workers²⁹ to describe a surfactant molecule. It was shown that for various amphiphilic substances this force field provides good agreement with united-atom simulations and experimental results.

Unfortunately, even the CG approach does not allow us to model water solutions of surfactants with long tails in the vicinity of CMC (for example, sodium dodecylsulfate, cetyltrimethylammonium bromide) because the very low CMC of such substances (ca. 10^{-4} mol/L) requires a very large system in computer simulations. It is well-known that the CMC of nonionic surfactants is lower than the CMC of ionic ones and that CMC decreases with increasing length of the hydrophobic part of amphiphilic molecules. For these reasons, we have investigated an ionic surfactant with a short tail. Nevertheless, we believe that the results obtained for the surfactant with a short nonpolar part will also be valid for surfactants with a long tail. At the same time, the choice of a short-tail surfactant as the object of this study allowed us to investigate the effective micellar solution in a relatively small simulation cell.

In our study, all molecules consist of only two types of beads: the hydrophilic bead H and the hydrophobic bead T. Intermolecular interactions are described by Lennard-Jones (LJ) and Coulomb potentials. Both type of beads have the same mass, $m = 72$ amu, and the same geometric parameter of LJ potential, $\sigma = 0.47$ nm. The energetic parameter ε of LJ potential for different pairs takes the following values: $\varepsilon(\text{H-H}) = 5.0$ kJ/mol, $\varepsilon(\text{T-T}) = 3.4$ kJ/mol, $\varepsilon(\text{H-T}) = 1.8$ kJ/mol. Thus, the H-T interaction is less preferable than the H-H or T-T interactions. All LJ interactions are smoothly shifted to zero from 0.9 to 1.2 nm.

The surfactant cation T_2H^+ consists of two T beads (a surfactant tail) and one positively charged H bead (a polar head). All chemical bonds are simulated by the harmonic potential with equilibrium distance $r_{\text{bond}} = \sigma = 0.47$ nm and the force constant $K_{\text{bond}} = 1250$ kJ/mol \cdot nm². The cosine-based angle potential with the equilibrium angle $\theta_0 = 180^\circ$ and force constant $K_{\text{angle}} = 25$ kJ/mol was used for all bond angles. The surfactant anion H^- was modeled as one negatively charged H bead. Four water molecules are represented as one neutral nonpolar H bead. The presence of a polar solvent was taken into account through the relative dielectric permittivity, ε_r . In our calculations, the dielectric permittivity is equal to 40 instead of the original 20; however, at the same time we use the PME long-range electrostatics³⁰ and not the cut-and-shifted Coulomb potential. In ref 31, it was shown that the usage of the long-range electrostatics is very important for the description of general properties of ionic micellar solutions, in particular the cluster size distribution. Since the long-range electrostatic force is stronger than that of the cut-and-shifted potential, we use a greater value of the dielectric permittivity to compensate the increase of the electrostatic contribution to the energy of the system.

TABLE 1: Composition of the Systems, Simulation Time t , and the Cell Edge Length L

	$N_{\text{surfactant}}$	$N_{\text{water bead}}$	t , ns	L , nm
$c^{(1)}$	512	49152	1600	18.3
$c^{(2)}$	1000	32000	2000	16.3

As a result of the coarseness of the picture (as compared to the all-atom or united-atom approach), the surfactant model used in this work may reproduce several different substances. One of these substances is the octyltrimethylammonium bromide (OTAB): each T bead represents four CH_2/CH_3 groups, the polar head H^+ is a $\text{N}(\text{CH}_3)_3^+$ group, the counterion H^- is Br^- . The CMC of OTAB in water at room temperature is equal to about 0.25 mol/L.^{32,33} Since the structure of the water molecule was lost after coarse-graining, the difference between cations and anions is not reproduced. Therefore, other possible surfactants are sodium octylsulfonate ($\text{C}_8\text{SO}_3\text{Na}$) with CMC equal to 0.11 mol/L³⁴ or sodium octylsulfate ($\text{C}_8\text{SO}_4\text{Na}$) with CMC equal to 0.13 mol/L.³⁵ According to these CMC values of surfactants, we studied the solution of $\text{T}_2\text{H}^+\text{H}^-$ at two different total surfactant concentrations: $c^{(1)} = 0.14$ mol/L and $c^{(2)} = 0.38$ mol/L. Since the concentration $c^{(1)}$ is between CMC for OTAB, $\text{C}_8\text{SO}_4\text{Na}$, and $\text{C}_8\text{SO}_3\text{Na}$, we hoped to obtain the micellar solution as close as possible to its CMC. Concentration $c^{(2)}$ is intentionally taken greater than CMC.

The simulations were performed in the isothermal–isobaric NpT ensemble at temperature $T = 300$ K and pressure $p = 1$ bar. In Table 1, some details of the simulations are given. The time step of the simulations was equal to 0.04 ps. GROMACS 3.2.1 software³⁶ was used for the molecular dynamics simulation.

Surfactant molecules in initial configurations were uniformly distributed in the cubic simulation cell with the edge length L (Table 1). During the several first nanoseconds, fast formation of small clusters occurs, followed by slower relaxation to the equilibrium state. A cluster is defined as a group of surfactant molecules such that at least one tail bead of each surfactant molecule of the group is at the distance no larger than r_{cl} from a tail bead of another amphiphile belonging to the same cluster. We use $r_{\text{cl}} = 0.7$ nm as in work 24. There is some ambiguity in the choice of this value. To estimate the effects of the r_{cl} choice we also performed the analysis of the trajectories with $r_{\text{cl}} = 0.8$ nm, observing no perceptible difference in the cluster size distribution. According to the time evolution of the number of aggregates (Figure 1), the first 500 ns of the simulated

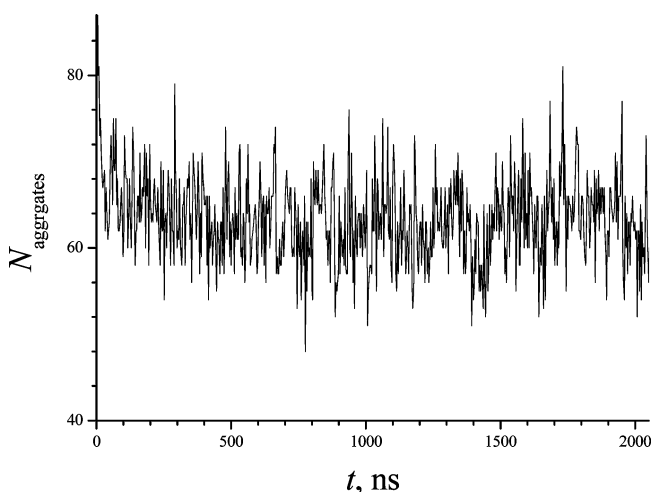
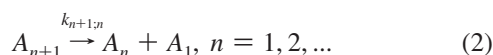
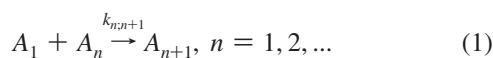


Figure 1. Dependence of the number of aggregates in the simulation cell, $N_{\text{aggregates}}$, on time for $c^{(2)} = 0.38$ mol/L.

trajectory was dismissed as the nonstationary part of the track. After that period, the number of aggregates oscillates near the average value. Significant fluctuations of the number of aggregates during short time periods indicate that micelles have a short lifetime and that intensive exchange by surfactant cations between micelles takes place. Instantaneous configurations were saved each 100 steps (every 4 ps), generating 275 000 and 375 000 equilibrium configurations for the concentrations $c^{(1)}$ and $c^{(2)}$ correspondingly.

3. Rate Constants in the Quasichemical Approach

As it was said above, we suppose that only stepwise addition/removal of one surfactant cation to/from aggregate gives the main contribution to the micelle formation/desintegration, i.e., the process is described by quasichemical reactions (1, 2)



where A_n is the cluster with the aggregation number n and $k_{n,n+1}$ and $k_{n+1,n}$ are the rate constants of the corresponding reactions. The rate constants are connected with the reaction rates by the following equations

$$v_{n,n+1} = k_{n,n+1} c_1 c_n, \quad n = 1, 2, \dots \quad (3)$$

$$v_{n+1,n} = k_{n+1,n} c_{n+1}, \quad n = 1, 2, \dots \quad (4)$$

where $v_{n,n+1}$ and $v_{n+1,n}$ are the rates of quasichemical reactions 1 and 2 correspondingly and c_n is the concentration of the cluster A_n . The reaction rates are constant at equilibrium so they can be calculated from the MD trajectories by dividing the number of addition/removal acts (1, 2) calculated during the simulation by the time interval. The dependence of concentrations c_n on aggregation number n (i.e., the cluster size distribution) can be obtained directly from the MD simulations. Then the values of the rate constants are easily calculated using eqs 3 and 4. After that, the set of the kinetic eqs 5–7 corresponding to the reactions 1 and 2 should be solved

$$\frac{dc_1}{dt} = \sum_{n=1}^{\infty} (k_{n+1,n} c_{n+1} - k_{n,n+1} c_n c_1) \quad (5)$$

$$\frac{dc_n}{dt} = k_{n-1,n} c_{n-1} c_1 + k_{n+1,n} c_{n+1} - k_{n,n+1} c_n c_1 - k_{n,n-1} c_n, \quad n = 2, 3, \dots \quad (6)$$

$$c^{(j)} = \sum_{n=1}^{\infty} n c_n \quad (7)$$

where $c^{(j)}$ is the total surfactant concentration. These equations do not contain the terms corresponding to cluster fusion/fission processes; i.e., such processes are not accounted for. In equilibrium, all the derivatives dc_n/dt are equal to zero. We truncate the infinite system (eqs 5–7) to M equations supposing $c_n = 0$ when $n > M$. The value of M is naturally equal to the

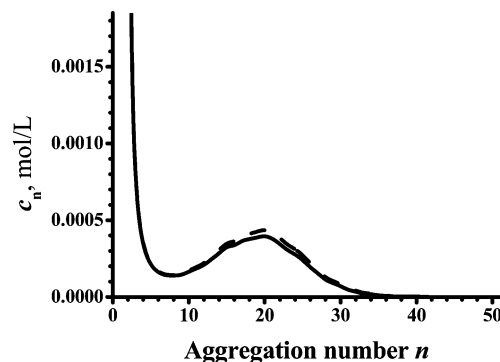


Figure 2. Cluster size distribution for $c^{(1)} = 0.14$ mol/L. Solid line, calculated from the MD trajectories; dashed line, obtained from eqs 8–10.

largest observed aggregation number in the simulation; in our systems, it is equal to 40 and 51 for the concentrations $c^{(1)}$ and $c^{(2)}$ correspondingly. Then we have the set of M linear equations with M variables

$$0 = \sum_{n=1}^{M-1} (k_{n+1,n} c_{n+1} - k_{n,n+1} c_n c_1) \quad (8)$$

$$0 = k_{n-1,n} c_{n-1} c_1 + k_{n+1,n} c_{n+1} - k_{n,n+1} c_n c_1 - k_{n,n-1} c_n, \quad n = 2, 3, \dots, M-1 \quad (9)$$

$$c^{(j)} = \sum_{n=1}^M n c_n \quad (10)$$

We use the simple method to solve the set of the kinetic eqs 8–11, as was described in ref 24. In this method, we need to rewrite eq 9 as follows

$$c_{n+1} = \frac{c_n (k_{n,n-1} + k_{n+1,n} c_1) - k_{n-1,n} c_{n-1} c_1}{k_{n+1,n}}, \quad n = 2, 3, \dots, M-1 \quad (11)$$

It is seen from eq 11 that c_3 depends on c_1 and c_2 . In turn, c_4 depends on c_1 , c_2 , and c_3 , and since the latter depends on c_1 and c_2 , then c_4 is the function of c_1 and c_2 only. Applying a similar reasoning for all the c_n ($n > 2$), we obtain that c_n , $n = 3, 4, \dots, M$, depends only on c_1 and c_2 . In other words, eq 11 leads to the inference that the pair of values c_1 and c_2 defines the whole cluster size distribution for the given rate constants $k_{n,n+1}$, $k_{n+1,n}$, $n = 1, 2, \dots, M$. The resulting set of equations is solved as follows. One can choose an arbitrary value of c_1 and find the value of c_2 (i.e., the whole cluster size distribution from eq 11) which satisfies eq 8. After that, the total surfactant concentration is calculated according to eq 10. This procedure is repeated until the equality of the calculated and required total concentration of a surfactant is reached.

4. Results and Discussion

For both concentrations, the simulation time was sufficient to attain smooth cluster size distributions (solid lines in Figures 2 and 3) directly from the time trajectories. In both cases, we see the theoretically predicted shape for micellar solutions³⁷ with the minimum in the region of small clusters (aggregation number from 2 to 12) and the maximum in the region of proper micelles.

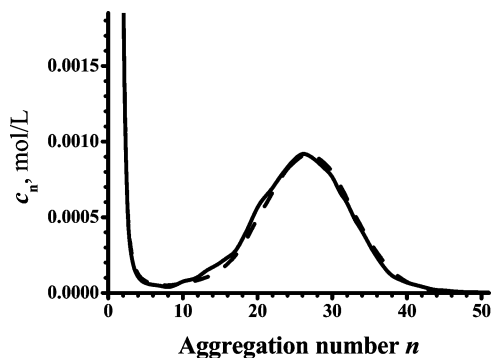


Figure 3. Cluster size distribution for the concentration $c^{(2)} = 0.38$ mol/L. Solid line, calculated from the MD trajectories; dashed line, obtained from eqs 8–10.

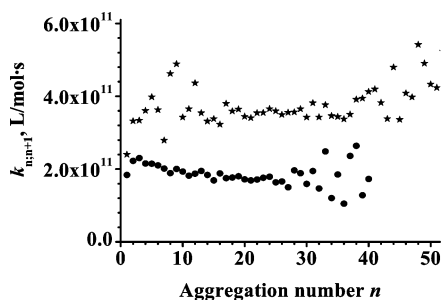


Figure 4. Dependence of the rate constants of reaction 1 on aggregation number. Circles, $c^{(1)} = 0.14$ mol/L; stars, $c^{(2)} = 0.38$ mol/L.

At sufficiently large aggregation number, the micelle concentration falls to zero. Another important feature of the calculated distributions is that the concentration c_1 is significantly larger than other c_n , $n = 2, 3, \dots, \infty$, and therefore it cannot be seen in Figures 2 and 3.

We used the well-known CMC criterion³⁸ according to which CMC is a concentration when the total mass of the nonaggregated surfactant m_{nonaggr} is equal to the total mass of the micelles m_{mic} . In our case, for both concentrations $m_{\text{nonaggr}} < m_{\text{mic}}$, which means that both $c^{(1)}$ and $c^{(2)}$ are greater than CMC. At the same time, m_{nonaggr} and m_{mic} are the values of the same order of magnitude for both concentrations, which indicates that the CMC is not very far.

As described above, the second way to obtain the cluster size distribution is the solution of the set of kinetic equations. First of all, it is necessary to calculate the rates of the quasichemical reactions 1 and 2 which was done by the direct counting of the acts of absorption and emission of surfactant molecules by aggregates. Then the rate constants were obtained using cluster size distribution (solid lines in Figures 2 and 3) and eqs 3 and 4. Figures 4 and 5 show the dependence of $k_{n,n+1}$ and $k_{n+1,n}$ on the aggregation number for both concentrations. A negligible difference can be noticed for the rate constants of surfactant molecule emission (Figure 5), but the difference for rate constants of surfactant molecule absorption in Figure 4 is significant. This surprising fact can be explained by the following reasoning. Let us consider a quasichemical reaction with the equilibrium constant $K_n^{n+1} = c_{n+1}/c_1 \cdot c_n$



According to the micellization theory,^{39,40} we can express c_n as a function of c_1 : $c_n = c_1 \cdot \exp(-W_n/kT)$, where W_n is the work of micelle formation for a micelle with aggregation number n .

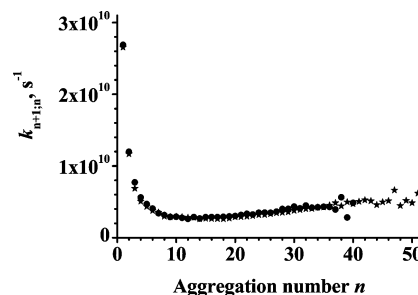


Figure 5. Dependence of the rate constants of reaction 2 on aggregation number. Circles, $c^{(1)} = 0.14$ mol/L; stars, $c^{(2)} = 0.38$ mol/L.

So, $K_n^{n+1} = (1/c_1) \exp(-(W_{n+1} - W_n)/kT)$. The difference $W_{n+1} - W_n$ can be positive or negative and has a weak dependence on the total surfactant concentration. At the same time, c_1 for ionic surfactants decreases with the increase of the total surfactant concentration,^{41–44} and its dependence on surfactant concentration is stronger than that for $\exp(-(W_{n+1} - W_n)/kT)$. That is why the equilibrium constant K_n^{n+1} depends on the total surfactant concentration. On the other hand, $K_n^{n+1} = (k_{n,n+1}/k_{n+1,n})$. Therefore, the ratio of the removal and addition rate constants increases with the increase of the total surfactant concentration. Our calculations are in agreement with this reasoning and experimental observations: the values of c_1 are 0.017 mol/L and 0.009 mol/L for $c^{(1)}$ and $c^{(2)}$ correspondingly; the ratio $k_{n,n+1}/k_{n+1,n}$ increases with the total concentration. It is worth mentioning that in the literature the assumption of independence of rate constants for reactions 1 and 2 on concentration is often used. Our study shows that this approximation is not quite correct for ionic surfactants.

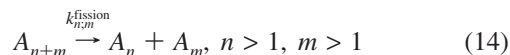
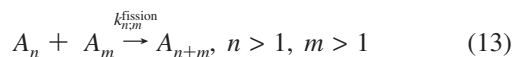
One can notice that the dependence of the additional rates on the micellar aggregation number (Figure 4) is very noisy. However, a careful examination shows that the large scattering occurs only in the regions where the concentration of micelles is quite small (Figures 2 and 3) and is therefore caused by insufficient statistics. In the regions of monomers and proper micelles, the dependence behaves quite well. Thus, it is unlikely that the “noisy” regions may have a significant impact on the results obtained from the rate constants.

In ref 3, the data for the stepwise rate constants of sodium alkylsulfates at 298 K were given. Our model of the surfactant is close to sodium octylsulfate for which the rate constant of stepwise removal is equal to 10^8 s^{-1} . The average value of the removal rate constant in our calculations is equal to $3 \cdot 10^9 \text{ s}^{-1}$. It should be noted that the time in the CG model²⁹ does not correspond to the real time (that was mentioned by the authors of the original force field). CG time is approximately four (or more) times “faster” than real time. Taking the time scale into account, the difference between the rate constant values is less than 1 order of magnitude. As the CG model is semiquantitative, such an agreement with the experimental data can be considered as satisfactory.

The obtained values of the rate constants allow one to solve the set of kinetic equations (eqs 8–10) and thus to obtain the cluster size distribution (dashed lines in Figures 2 and 3). These curves almost coincide with the curves obtained directly from the MD trajectories. Since we did not account for cluster fission and fusion processes in the set of kinetic equations, the results draw the conclusion that in an equilibrium mixture of ionic surfactants near the CMC the processes of stepwise change of aggregation number play the most significant role.

All existing aggregation mechanisms contribute to the cluster size distribution obtained from MD calculations. It is obvious

that the solution of the complete set of kinetic equations which includes fusion/fission processes will also give the same cluster size distribution. Neglecting fusion/fission processes, we construct the reduced set of kinetic equations, which differs from the complete set by the absence of $k_{n,m}^{\text{fusion}} \cdot c_n \cdot c_m$ and $k_{n,m}^{\text{fission}} \cdot c_{n+m}$ terms. These terms account for the contributions from the following processes



As the rate constants of stepwise processes (eqs 1 and 2) were obtained from MD calculations without any presuppositions, they should have the same values in the complete and reduced kinetic sets. That is why the coincidence of solutions of the complete and reduced sets means that the extra terms in the complete set have negligible values and therefore the fusion/fission processes have a very small contribution to the dynamic equilibrium.

However, a question still arises: are there any possibilities that the solution of the reduced set coincides with the distribution from MD simulations while fusion/fission processes are significant? To clarify this question, we suggest the following thought experiment. Let us imagine that in equilibrium micellar solution, the processes 13 and 14) do not occur at all. This means that the rates of reactions 13 and 14 are equal to zero, and consequently the rate constants $k_{n,m}^{\text{fission}}$ and $k_{n,m}^{\text{fusion}}$ are equal to zero as well, while the rate constants $k_{n,n+1}$ and $k_{n+1,n}$ of reactions 1 and 2 are not. In such a case, it is obvious that the complete and reduced sets are identical, and the solution of these sets will give the cluster size distribution. Let us now assume that the rate constants $k_{n,m}^{\text{fission}}$ and $k_{n,m}^{\text{fusion}}$ change their values and become nonzero, while the values of the stepwise rate constants remain unchanged. Then the micellar equilibrium will be broken, and after establishing a new equilibrium, the new distribution will appear. Since the stepwise rate constants do not change, the solution of the reduced set also will be unchanged and will not coincide with new cluster size distribution. Is it possible that after the change of rate constants the equilibrium will not be disturbed? It is, but only if for all of the numerous reactions (13, 14) the equilibrium will remain undisturbed. It looks extremely unlikely that such an event can occur for two different concentrations of the surfactant.

It was also found from the MD trajectories that more than 97% of acts of aggregation number change are realized by the stepwise mechanism, which is another reason in favor of the exclusive role of this mechanism. The cluster fusion/fission events were so rare that it was impossible to calculate the corresponding rate constants. Actually the remaining 3% of events were the acts involving dimers, trimers, and other small clusters. No acts involving only proper micelles (with the aggregation number more than 10) were observed, but we can obtain an upper estimate of the fusion/fission rate constants. Let us assume that each fusion and fission process occurs only once during the simulation time and then calculate the rate constants from equations similar to eqs 3 and 4. The largest values thus obtained are listed in Table 2. We can see that compared to the stepwise rate constants the upper estimates of the rate constants for the micelle fission/fusion are less by 5 and 4 orders of magnitude correspondingly.

TABLE 2: Upper Estimates of the Rate Constants for Fusion/Fission Processes

	$k_{\text{fission}}^{\text{max}}, \text{ s}^{-1}$	$k_{\text{fusion}}^{\text{max}}, \text{ L/mol} \cdot \text{s}$
$c^{(1)}$	1500	8.6×10^6
$c^{(2)}$	4000	7.7×10^7

5. Conclusions

The MD simulations of the ionic surfactant were carried out in the frame of the coarse-grained approach. On the basis of the molecular trajectories, the rate constants were calculated together with the aggregate size distribution. The latter was also estimated by the solution of the set of the kinetic equations using the rate constants obtained from the MD calculations.

The conclusion on the predominant role of stepwise aggregation mechanism was made according to the coincidence of the cluster size distributions obtained by MD calculations and by solution of the reduced set of the kinetic equations. This qualitative result is valid for the micellar solutions of ionic surfactants in the concentration range close to CMC when the average shape of micelles is spherical. As the concentration increases, the growth of micelles and the change of their shape take place, which can result in the increase of the contribution of the cluster fusion/fission mechanism.

The influence of the total ionic surfactant concentration on the rate constants of stepwise addition was revealed. The increase of the rate constants along with the total concentration can be explained by the dependence of the pre-exponential factor of the equilibrium constant on the total concentration, which was confirmed by the experimental and theoretical investigations.

Acknowledgment. This work was partly supported by Russian Foundation for Basic Research (grant 07-03-00367-a) and the Grant of the President of the Russian Federation for State Support of the Leading Scientific Schools (no. NSH-3020.2008.3).

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JP9025305