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Mixed micellization of gemini and conventional surfactant in aqueous solution: A lattice Monte Carlo simulation

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ABSTRACT

In the current study, we have investigated the micellization of pure gemini surfactants and a mixture of gemini and conventional surfactants using a 3D lattice Monte Carlo simulation method. For the pure gemini surfactant system, the effects of tail length on CMC and aggregation number were studied, and the simulation results were found to be in excellent agreement with the experimental results. For a mixture of gemini and conventional surfactants, variations in the mixed CMC, interaction parameter β, and excess Gibbs free energy G^E with composition revealed synergism in micelle formation. Simulation results were compared to estimations made using regular solution theory to determine the applicability of this theory for non-ideal mixed surfactant systems. A large discrepancy was observed between the behavior of parameters such as the activity coefficients f_i and the excess Gibbs free energy G^E and the expected behavior of these parameters as predicted by regular solution theory. Therefore, we have used the modified version of regular solution theory. This three parameter model contains two parameters in addition to the interaction parameters: the size parameter, ρ, which reflects differences in the size of components, and the packing parameter, P^*, which reflects nonrandom mixing in mixed micelles. The proposed model provides a good description of the behavior of gemini and conventional surfactant mixtures. The results indicated that as the chain length of gemini surfactants in mixture is increased, the size parameter remains constant while the interaction and packing parameters increase.

1. Introduction

In recent years, novel surfactants such as gemini surfactants have attracted much attention for a wide variety of applications, including the separation of biomaterials, drug delivery, soil remediation, enhanced oil recovery, and nanotechnology. This widespread interest is due to the surfactants' unique properties, which include lower CMC values and higher efficacy in decreasing the surface tension of water compared to the surfactants' corresponding monomers. Gemini surfactants are a special type of surfactant that contain two identical amphiphilic moieties connected by a spacer [1,2]. Although the spacer in gemini surfactants is usually hydrophobic, gemini surfactants with hydrophilic spacers have also been synthesized [3]. The behavior of gemini surfactants at interfaces as well as in aqueous solutions has been reviewed by Zana [4]. The lyotropic liquid crystal phase behavior of aggregates formed by gemini surfactant molecules has garnered interest because of the unusually large range of concentrations for which the aggregates exhibit different morphologies [5–9].

Because of their high price, using gemini surfactants in combination with conventional surfactants is desirable. Generally, mixed micelle solutions that contain surfactants with similar structures show ideal mixing behavior. On the other hand, mixed surfactant systems that consist of gemini and single chain surfactants (in which the single chain surfactant is the monomeric block of the gemini surfactant) have exhibited non-ideal synergistic behaviors due to predominantly hydrophobic interactions. This behavior occurs when double tails of gemini surfactants are packed together with single tails of conventional surfactants in mixed systems [10–13].

An experimental study by Rosen et al. demonstrated that synergism in mixed systems containing cationic gemini surfactants and conventional anionic surfactants is significant [10]. Zana et al.

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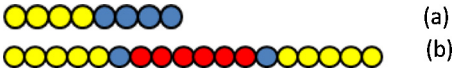

Fig. 1. Schematic diagram of (a) A_4B_4 surfactant, (b) $T_5H_1S_6H_1T_5$ surfactant. Blue balls indicate head groups on the surfactant, yellow balls indicate tail groups, and red balls indicate spacer groups on the surfactant. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

[13,14] have also investigated synergistic behaviors for micelle formation in mixed systems of non-ionic conventional surfactants and ionic gemini surfactants.

Because of the importance of this type of system, a computer simulation of gemini surfactants would be very helpful. Nevertheless, very few Monte Carlo simulation studies of gemini surfactants have been performed. These studies have focused on the impact of parameters such as tail length, head spacing, and asymmetric structure on the properties of micellization in aqueous solutions [15–17]. In micellar aggregates formed by single tail surfactants, cross-linking phenomena have been investigated by adding a few moles of gemini surfactants [18]. Behjatmanesh et al. [19] have investigated the self-assembly of dimeric chains surfactants without spacers using lattice Monte Carlo simulations. It has been found that if the spacer group is absent, the CMC of the dimeric surfactant is much lower than the CMC of its similar single chain.

We have undertaken a systematic study of spontaneous micellization of pure gemini surfactants and a mixture of gemini and conventional surfactants in aqueous solutions using a lattice Monte Carlo simulation. An enormous number of Monte Carlo simulations studying the self-assembly of surfactants have been carried out for lattice models. Such models already cover the fundamental features of aggregate formation including the thermodynamic properties and cluster size distributions [20–25]. Our results will certainly be qualitative in nature as the simple lattice model is able to predict the properties of mixing behavior of binary mixed surfactant systems.

The effect of tail length on the composition of the formed micelles, the aggregation number, and deviation from the ideal behavior of mixed surfactant systems are investigated in this study. In addition, the simulation results are compared to the estimations based on regular solution theory. To our knowledge, the investigation of the mixed systems containing gemini and conventional surfactants via Monte Carlo simulation has not been carried out to date.

2. Simulation method

A system of various surfactants on a three-dimensional cubic lattice with a coordination number of $Z = 6$ (i.e., only interactions between nearest neighbors are considered) is modeled. To minimize any possible size effects, a box of size $L = 100$ is chosen. Standard excluded volume and periodic boundary conditions are used in all three dimensions. Each water molecule occupies a single lattice site (W), and surfactant molecules occupy chains of neighboring sites. The conventional surfactant chains are labeled as A_iB_j, with i ($i \geq 1$) head beads and j ($j \geq 1$) tail beads. The gemini surfactant chains are labeled as $T_jH_iS_mH_iT_j$. S ($m \geq 1$) is used to specify spacer beads positioned between the head groups. Head units are assumed to be hydrophilic, but the tail and spacer are hydrophobic. Each site not occupied by conventional or gemini surfactant is occupied by a solvent molecule. Here, A_4B_4 conventional surfactant and $T_jH_1S_6H_1T_j$ symmetric gemini surfactant are studied. A typical representation of gemini and conventional surfactants is shown in Fig. 1.

Energy in the system is calculated as the sum of all the nearest neighbor interactions. Thus, interactions between each pair of nearest neighbor beads contribute additively to the total energy.

Table 1
Interaction energies for gemini and conventional surfactants.

Interaction energies, ε_{pq}						
	W	H	T	S	A	B
W	0	0	0.7	0.7	0	0.7
H	0	1.5	0.7	0.7	-0.7	0.7
T	0.7	0.7	0	0	0.7	0
S	0.7	0.7	0	0	0.7	0
A	0	−0.7	0.7	0.7	0	0.7
B	0.7	0.7	0	0	0.7	0

A dimensionless interaction energy (ε_{pq}) is assigned for each bead–bead pair interaction, where p, q = W, T, H, S, A, or B. The total energy of the system divided by k_BT is

$$E_{Total} = \sum_{pq} N_{pq}\varepsilon_{pq} \quad (1)$$

where N_{pq} is the total number of pq pairs in the system, k_B is the Boltzmann constant, and T is the temperature. In Eq. (1), interactions between adjacent beads of different chains are considered. The dimensionless interaction energies (ε_{pq}) can be set independently of each other; however, ε_{pq} and ε_{qp} are not considered to be distinct.

Table 1 summarizes the interaction energies chosen for this work. The repulsive values are allocated to the head–tail (spacer) and tail (spacer)–solvent units of the surfactant molecules. It should be mentioned that the interaction parameters that we used are close to Rodriguez's parameters [22]. Furthermore, the electrostatic repulsion effects of heads in gemini surfactants are incorporated by assigning $\varepsilon_{HH} = +1.5$. To describe a surfactant mixture, interspecies interactions are accounted for the governed interaction energies.

Reptation is the only move used to rearrange configurations. Reptation is an efficient mode of chain rearrangement because each bead on a chain moves to a new site. The probability of accepting the move is calculated according to the standard Metropolis algorithm [26]. For any given concentration of surfactants, the appropriate values of A_iB_j, and $T_jH_iS_mH_iT_j$ chains are randomly set on the lattice sites, and the resulting configuration is considered the initial configuration of the system. The total energy of the initial configuration, E_{old} (normalized by k_BT), is calculated. The initial configuration is rearranged by moving a randomly selected surfactant chain, and the new energy, E_{New}, of the trial configuration is then calculated. The trial configuration is accepted or rejected according to the following probability

$$P = \min\{1, \exp[-(E_{New} - E_{old})]\} \quad (2)$$

This attempted move (whether successful or unsuccessful) is called a MC step and is repeated until equilibrium is achieved for that particular temperature. The optimal number of MC steps depends on the temperature and concentration of the surfactant molecules. A large set of equilibrium configurations may be generated, and the average properties calculated from this set of configurations. However, such data are reliable only after a few tests [27]: (i) against the possibility of metastability; (ii) control of relaxation times (in the MC step units); and (iii) lattice size effects. To test effects (i) and (ii), the results obtained for the total energy of the system for two opposite initial configurations (one completely random (sample of high temperatures) and a second completely ordered configuration (sample of low temperatures)) are compared. More than 10^8 moves are performed to achieve a region of phase space in which the total energy and micelle size growth remained almost constant. These states are selected to be the equilibrium configurations, and the aggregates are characterized under these conditions. Aggregates are defined as clusters in which every tail, head, and spacer have at least one neighbor