



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



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ARTICLE INFO

Article history:

Accepted 28 July 2014

Available online 7 August 2014

Keywords:

Lattice Monte Carlo
Mixed micellization
Gemini surfactant
Conventional surfactant
Synergism

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.

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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 $T_jH_1S_mH_1T_j$. 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 $T_5H_1S_6H_1T_5$ 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 $k_B T$ 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 $T_jH_1S_mH_1T_j$ 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 $k_B T$), 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

contact with another chain element [17]. Lattice size effects are studied by comparing results for different lattice sizes. Some simulations are repeated several times for statistical significance and to confirm the results. To avoid pseudo-equilibrium states, we have performed simulations under athermal conditions. At the highest temperature, $1/\varepsilon$, a random initial configuration at the given surfactant volume fractions is generated. The system is brought to equilibrium by a sufficient number of MC steps. The system is then cooled by increasing ε in small increments, and the resulting configuration is defined as the initial configuration for further steps. A total of 7 steps are used, and each step is equilibrated for triple the number of MC steps used in the previous step. The average energy in each temperature is monitored. When the system is cooled to the desired interaction energy and the average energy appears to have reached a steady state (the change in this property is minimized), snapshots of the system properties are taken.

3. Results and discussion

3.1. Pure gemini surfactant

In an amphiphilic solution, surfactant molecules will form micelles at a definite concentration, referred to as the CMC. Several researchers have used various methods for measuring the CMC based on plots of free monomer concentration against total surfactant concentration (X_t) [28–31]. We have used Desplat's definition of CMC, which describes the CMC as the intercept of a line drawn through high concentration data with a line through the origin of the unit slope [28]. Here, concentrations are defined as volume fractions, which are calculated by dividing the number of surfactant sites by the total number of lattice sites.

$T_jH_1S_6H_1T_j$ gemini surfactants are chosen to analyze the effect of tail length on surfactant solution properties. The CMCs for different gemini surfactant structures are shown in Fig. 2a. In this figure, we plot CMC versus the number of j . Similar to conventional surfactants, increasing the tail segments results in a decrease in CMC. The plot of CMC against j shows a departure from linearity starting at $j=7$. Such behavior is in agreement with several experimental studies [32–38].

Aggregate size distribution is an important property that needs to be determined for a surfactant system. In Fig. 2(b), the aggregate size distribution is plotted for several values of j at a concentration above the CMC (i.e., $X_t=0.07$). It is clear that gemini surfactants with lengthy tails produce larger aggregates, depicted by the value of n at the maximum in n^*X_n , as well as a wider distribution of aggregate sizes, depicted by the width of the peak. All properties were averaged over a number of simulations to avoid errors due to statistical fluctuations.

The typical picture of snapshots for $T_3H_1S_6H_1T_3$ and A_4B_4 surfactant systems is shown in Fig. 3. In comparison to spherical A_4B_4 aggregates, aggregates formed by $T_3H_1S_6H_1T_3$ surfactants in the lattice solution are elongated [17].

3.2. Binary mixture systems

We study mixtures of gemini and conventional surfactants for selected $T_3H_1S_6H_1T_3/A_4B_4$ and $T_{11}H_1S_6H_1T_{11}/A_4B_4$ systems to investigate the composition of the micelles that are produced, aggregation number, and deviation from ideality in the lattice systems.

In the lattice model with two mixed surfactants, it is essential that cross interactions between the different surfactant species are considered. In this study, the following cross interactions were applied for a mixture of gemini and conventional surfactants: T (S) tail beads are repulsed by A head beads, B(S) tail beads are repulsed

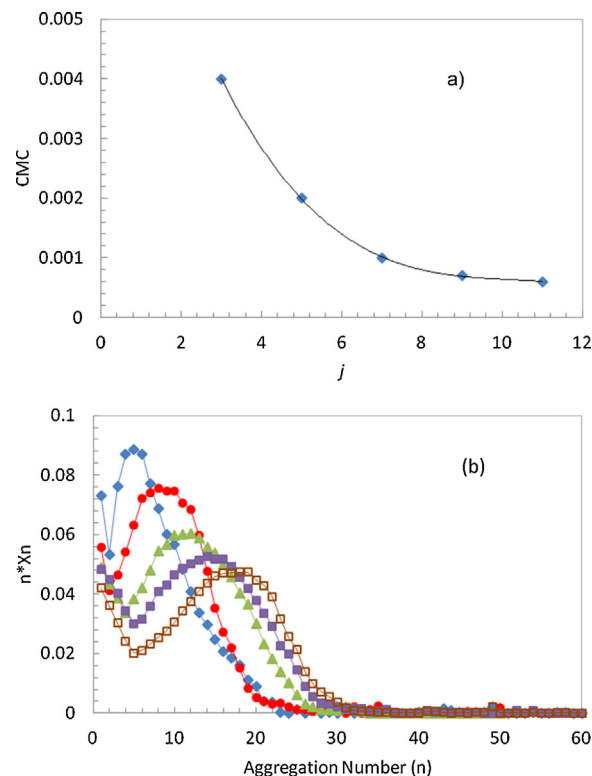


Fig. 2. (a) Variation of CMC for different tail ($T_jH_1S_6H_1T_j$ surfactant system). The solid lines are guides for the eyes. (b) Aggregate size distribution for the $T_3H_1S_6H_1T_3$ (\diamond), $T_5H_1S_6H_1T_5$ (\bullet), $T_7H_1S_6H_1T_7$ (\blacktriangle), $T_9H_1S_6H_1T_9$ (\blacksquare) and $T_{11}H_1S_6H_1T_{11}$ (\square) surfactant systems, where $X_t = 0.07$.

by H head beads, and A head beads are attracted by H head beads. Table 1 outlines these interactions.

Fig. 4 shows the composition dependence of the mixed CMC for the $T_3H_1S_6H_1T_3/A_4B_4$ and $T_{11}H_1S_6H_1T_{11}/A_4B_4$ mixtures. As shown in Fig. 4, it is obvious that both investigated mixture systems showed synergism, i.e., the CMCs of some mixed systems were lower than the CMCs of the pure surfactants. Synergism in mixed micelle formation has previously been reported by Rosen et al. [3,39] and Zana et al. [13,14] for mixtures of ionic gemini surfactants and various nonionic conventional surfactants.

In an ideal mixed state, the CMC of a mixed surfactant solution, CMC_M , can be calculated using the Clint [40] equation

$$\frac{1}{CMC_M} = \sum_{i=1}^n \frac{X_i}{CMC_i} \quad (3)$$

where CMC_M and CMC_i are critical micelle concentration values of the mixture and component i , respectively; X_i is the mole fraction of respective components in solution.

The ideal CMC_M of the $T_3H_1S_6H_1T_3/A_4B_4$ mixed system is shown in Fig. 4. From this figure, it can be observed that the simulated CMCs of mixed surfactants deviates from the ideal mixed CMC due to interactions between components in mixed micelles [31,41]. Negative interaction energies between head groups of gemini and conventional surfactant produce negative deviations from ideality and decrease the mixed CMC.

Fig. 5(a) shows variation in gemini free monomer concentration, and Fig. 5(b) shows the conventional free monomer concentration as a function of total surfactant concentration at a 50:50 fraction of $T_3H_1S_6H_1T_3/A_4B_4$ mixture. As the total surfactant concentration is increased, the monomer concentration of $T_3H_1S_6H_1T_3$ surfactant remains approximately constant above the CMC_M (Fig. 5(a)) while the individual free monomer concentration of conventional

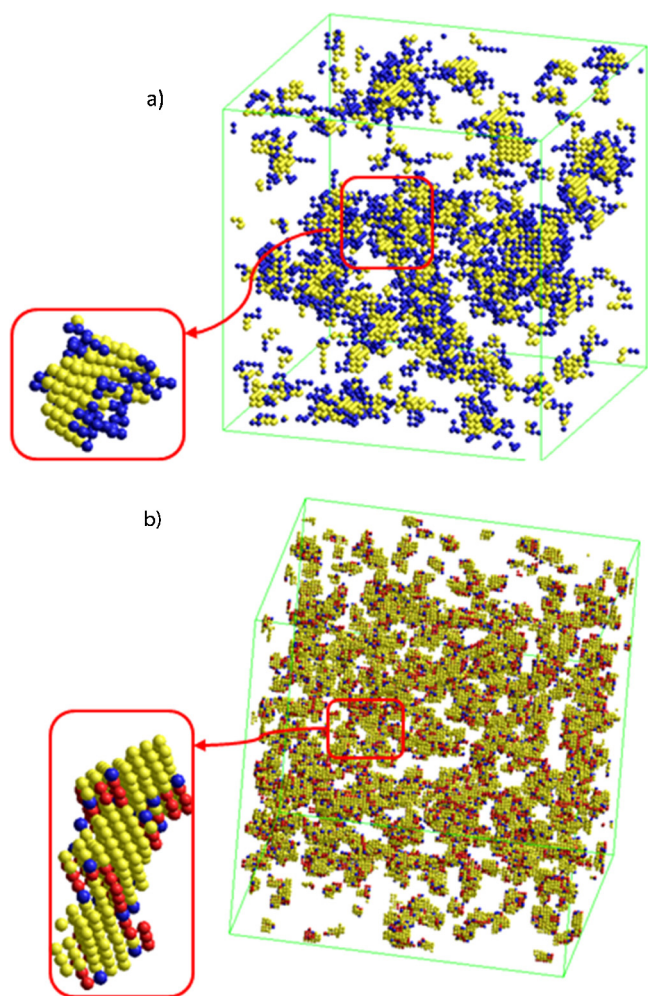


Fig. 3. Snapshot of amphiphilic aggregates for (a) A_4B_4 and (b) $T_{11}H_1S_6H_1T_{11}$ when $X_t = 0.05$. Yellow balls represent the tail of surfactants, blue balls represent the head of surfactants, and red balls represent the spacer.

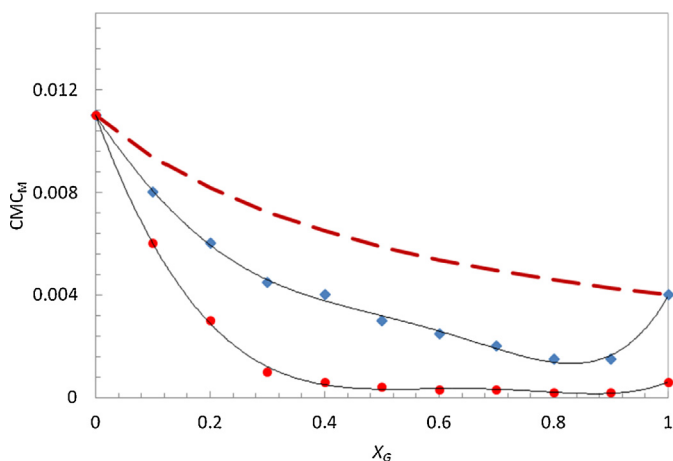


Fig. 4. Variation of the CMC_M with gemini surfactant fraction. $T_3H_1S_6H_1T_3/A_4B_4$ (\blacklozenge), $T_{11}H_1S_6H_1T_{11}/A_4B_4$ (\bullet). The dashed lines are an ideal CMC_M for the $T_3H_1S_6H_1T_3/A_4B_4$ system.

surfactant increases to a maximum and then decreases (Fig. 5(b)). The plot of the A_4B_4 free monomer concentration against the total surfactant concentration for a 50:50 fraction of $T_3H_1S_6H_1T_3/A_4B_4$ mixtures shown in Fig. 5(b) contains two fractures in the curve: (I) the mixed critical micelle concentration (CMC_M), where the

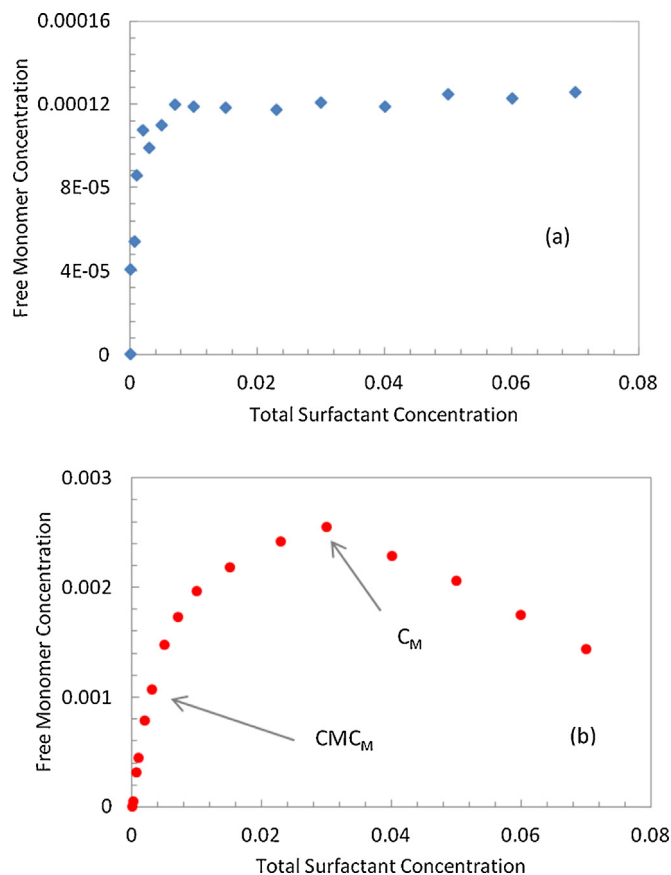


Fig. 5. Free monomer concentration of (a) $T_3H_1S_6H_1T_3$ (\blacklozenge) and (b) A_4B_4 (\bullet) surfactant vs total surfactant concentration for a 50:50 $T_3H_1S_6H_1T_3/A_4B_4$ mixture. C_M : The point where maximum free monomer concentration is achieved.

gemini and conventional surfactants begin to interact and form mixed gemini-rich micelles; and (II) the C_M point, where the free monomer concentration reaches a maximum and then decreases with increasing total surfactant concentration. At the C_M point, the free monomer concentration of A_4B_4 increases gradually as A_4B_4 rich micelles are formed.

When conventional surfactant is incorporated into mixed micelles, an increase in the free monomer concentration with an increasing total concentration is observed. The free monomer concentrations then reach the maximum point (C_M point). From Fig. 5(b), it can be observed that the free monomer concentration will decrease above the maximum point when the total concentration is increased. This behavior normally indicates the appearance of micelles rich in conventional surfactant. Thus, two types of micelles simultaneously exist in the mixed surfactant systems, one rich in gemini surfactant and another rich in conventional surfactant. This behavior is consistent with previous experimental reports regarding single tail surfactants [42,43].

For proof of the above results, we assumed that mixed micelles with 80% of one specific type of surfactant are the rich micelle of that particular surfactant. Fig. 6 shows the concentration of rich micelles for each gemini and conventional surfactant at a 50:50 $T_3H_1S_6H_1T_3/A_4B_4$ surfactant mixture. As shown in Fig. 6(a), conventional-rich micelles have not formed at $X_t = 0.01$ before the C_M point; only gemini-rich micelles have formed. Both types of micelles appear at $X_t = 0.07$ after the C_M point (Fig. 6(b)).

Mutual interaction of surfactants in mixed micelles, which leads to non-ideality, has been theoretically treated by Rubingh [44,45]

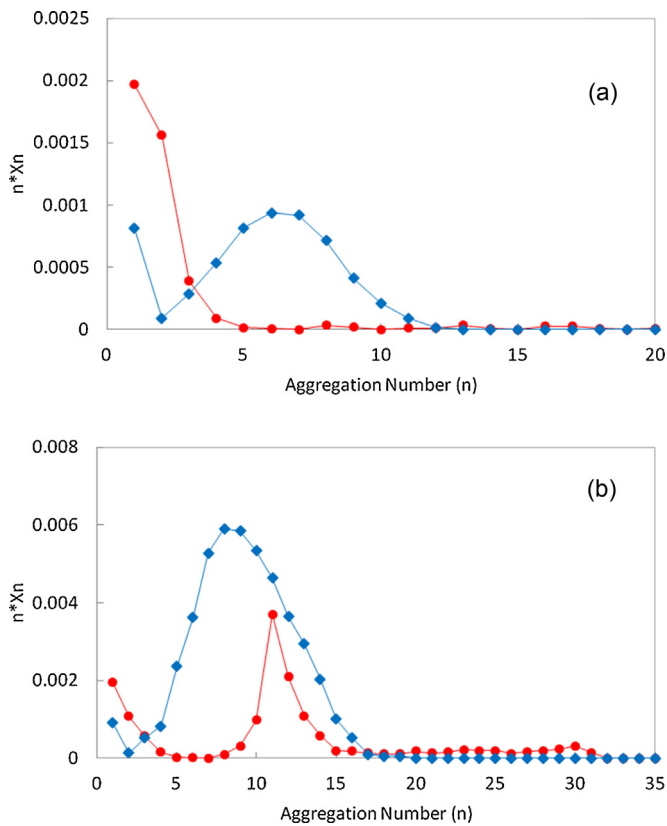


Fig. 6. Aggregate size distribution for 50:50 $T_3H_1S_6H_1T_3/A_4B_4$ surfactant systems: rich micelle of $T_3H_1S_6H_1T_3$ (\blacklozenge) and A_4B_4 (\bullet). (a) Total surfactant concentration is 0.01 (before C_M point). (b) Total surfactant concentration is 0.07 (after C_M point).

in light of regular solution theory. Non-ideality is introduced by including activity coefficients, f_i , in Eq. (3) as follows

$$\frac{1}{CMC_M} = \sum_{i=1}^n \frac{X_i}{f_i CMC_i} \quad (4)$$

for this binary solution,

$$\begin{aligned} f_G &= \exp[\beta(X_G^M)^2] \\ f_C &= \exp[\beta(X_G^M)^2] \end{aligned} \quad (5)$$

where β is an interaction parameter, and f_G , f_C , X_G^M , and X_C^M are the activity coefficients and mole fractions of gemini and conventional surfactant in mixed micelles, respectively. The above expressions are based on regular solution theory, which considers a non-zero enthalpy of mixing and neglects the excess entropy of mixing.

According to Rubingh's theory, deviations of the simulated CMC for mixed surfactant systems from ideal CMC can be represented by the interaction parameter β , which is expressed as

$$\beta = \frac{\ln[CMC_M X_G / CMC_G X_C^M]}{(1 - X_G^M)^2} \quad (6)$$

The deviation of β from zero (and consequently the deviation of f_C and f_G from unity) is generally assumed to result from specific interactions between the surfactant head-groups. Therefore, a negative value of β indicates that the free energy of micellization is less than the value predicted by the ideal solution theory (synergism), and a positive value of β indicates that the free energy of micellization is greater than the ideal value (antagonism). Rubingh's method is applied to evaluate interaction parameter. The β values for the two different systems with attractive interactions between

Table 2

Values of beta obtained from simulation data and regular solution theory.

Mixed surfactant system	Interaction parameter β
$T_3H_1S_6H_1T_3/A_4B_4$	−3.35
$T_{11}H_1S_6H_1T_{11}/A_4B_4$	−6.02

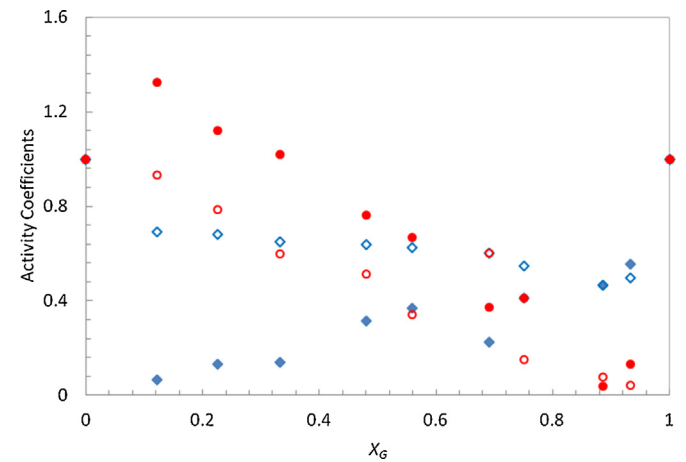


Fig. 7. Activity coefficients (f_i) for the $T_3H_1S_6H_1T_3/A_4B_4$ system: f_1 simulation (\blacklozenge), f_2 simulation (\bullet), f_1 RST (\blacklozenge), and f_2 RST (\bullet).

head groups are listed in Table 2. The magnitude of β is higher for $T_{11}H_1S_6H_1T_{11}/A_4B_4$, and this system deviated significantly from ideality compared to other system.

The activity coefficients can be calculated from the simulations using

$$f_i = \frac{C_i^f CMC_M}{X_i^M CMC_i} \quad (7)$$

where X_i^M is the micellar composition, and C_i^f is the monomer concentration of component i . The results obtained from simulations and values predicted by the regular solution theory are plotted in Fig. 7. From the figure, it is obvious that there are large discrepancies between the activity coefficient values obtained from the simulation and the predictions from regular solution theory.

The behavior of a binary mixture can be described by introducing the thermodynamic function of mixing. For non-ideal mixtures, excess properties are considered with respect to an ideal solution where the standard state for each component is the pure liquid at the mixture temperature and pressure. At a constant temperature, the excess Gibbs free energy G^E of a mixture depends upon the composition of the mixture. Any expression for the excess Gibbs free energy must obey the following two boundary conditions

$$\text{If } \begin{cases} X_G = 0 & \text{Then } G^E = 0 \\ X_C = 0 & \text{Then } G^E = 0 \end{cases} \quad (8)$$

The excess Gibbs free energy for the non-ideal mixtures is calculated as follows

$$G^E = RT \sum_{i=1}^n X_i^M \ln f_i \quad (9)$$

Fig. 8 shows the values of G^E as a function of micellar composition for the $T_jH_1S_6H_1T_j$ and A_4B_4 mixtures. The activity coefficients are determined by Eq. (7). By increasing the chain length of $T_jH_1S_6H_1T_j$, the preference for gemini surfactant incorporation becomes stronger due to the presence of $T_{11}H_1S_6H_1T_{11}$ in micelles, which results in a more negative excess Gibbs free energy.

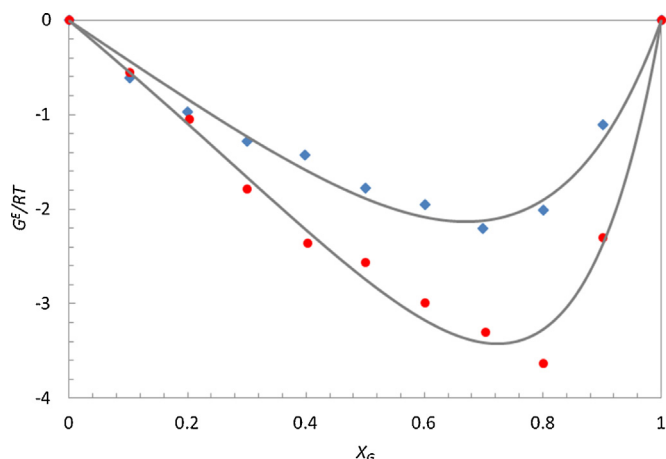


Fig. 8. Excess Gibbs free energy as a function of gemini fraction in mixed micelles for $T_3H_1S_6H_1T_3/A_4B_4$ mixtures: $T_3H_1S_6H_1T_3/A_4B_4$ (♦), $T_{11}H_1S_6H_1T_{11}/A_4B_4$ (●), and (—) curve fit.

Table 3

Results of a least-squares fitting of the three-parameter asymmetric regular solution theory to simulation-derived excess free energy for different tail lengths ($R^2 = 0.9846$).

Mixed surfactant system	P	β^*	P^*
$T_3H_1S_6H_1T_3/A_4B_4$	0.51	−2.14	1.34
$T_{11}H_1S_6H_1T_{11}/A_4B_4$	0.49	−13.09	10.06

In regular solution theory, the excess Gibbs free energy is symmetric and reaches a minimum when the mole fraction of surfactant is 0.5. From Fig. 8, it is obvious that the excess Gibbs free energy is asymmetric with respect to the gemini fraction. As previously mentioned, the trends in the activity coefficients obtained from simulation data were inconsistent with the trend expected from regular solution theory. This conclusion means that the basic assumption of regular solution theory (i.e., mixing entropy is zero) is not thermodynamically valid for describing the non-ideal mixing behavior in such systems. Therefore, we have used a modified version of the Rubingh method to analyze the behavior of this surfactant mixture system. This modified version is based on the following equations for the excess Gibbs energy for mixed micelle formation [46], G^E :

$$\frac{G^E}{RT} = AX_G^M(1 - X_G^M)(BX_G^M - 1) \frac{1}{(1 + CX_G^M)^3} \quad A = \frac{\beta^*}{\rho},$$

$$B = \frac{P^* - \rho P^* - 1}{\rho P^*}, \quad C = \frac{1 - \rho}{\rho} \quad (10)$$

where β^* is the interaction parameter, ρ is the size parameter that reflects differences in the size of the components of the mixture, and P^* is the packing parameter. For gemini and conventional surfactant mixtures, P^* can be employed to represent the constraints on the packing of conventional surfactant in micelles rich in gemini surfactant. The packing constraint is directly related to the non-random mixing in the system.

Now we consider the capacity of Eq. (10) to describe the behavior of G^E for mixed surfactant systems with gemini surfactants of different tail lengths. The values of β^* , ρ , and P^* are obtained by least-squares fitting to obtain the best possible fit of G^E against the composition of mixed micelles (Fig. 8). As shown in Table 3, increasing the tail length of gemini surfactant results in an increase in the interaction parameter and packing parameter while the size parameters remain constant. This model will successfully predict the behavior of G^E for the gemini and A_4B_4 surfactant mixtures, and this model can be used for different mixed systems

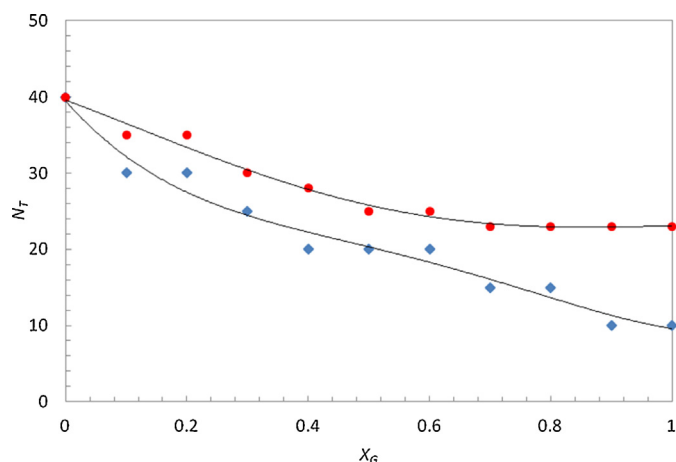


Fig. 9. Variation of the total aggregation number for $T_3H_1S_6H_1T_3/A_4B_4$ mixtures: $T_3H_1S_6H_1T_3/A_4B_4$ (♦), $T_{11}H_1S_6H_1T_{11}/A_4B_4$ (●), and $X_t = 0.07$.

such as conventional–conventional mixtures [46–49] and the gemini–conventional surfactants presented in this work.

Fig. 9 shows the variation of total aggregation number N_T with the mixture composition, X_G , for the studied mixtures. The addition of gemini surfactants to conventional surfactant caused a decrease in the N_T value. The decrease in N_T is obviously associated with the increased average repulsive interaction between surfactant head groups resulting from an increase in X_G .

4. Conclusion

We have presented a Monte Carlo simulation of pure symmetric gemini and binary mixed gemini/conventional surfactant systems on a cubic lattice. The main aim of this work is to predict micellar system properties such as the composition of formed micelles and the size of aggregates for different surfactant systems. The mixture CMC of the gemini/conventional surfactant system exhibited non-ideal behavior and synergism for micelle formation. We have also determined values of the activity coefficient and excess Gibbs free energy using the simulation data and compared the results with regular solution theory for all of the mixed systems studied. The Monte Carlo calculations showed that regular solution theory does not adequately describe the mixed gemini/conventional surfactant system and that the thermodynamic assumptions behind the regular solution theory are incorrect.

References

- [1] Y. Shang, Y. Xu, H. Liu, Y. Hu, The formation and properties of multilamellar vesicles in gemini/SDS/H₂O system, *J. Dispers. Sci. Technol.* 27 (2006) 105–108.
- [2] P.K. Maiti, Y. Lansac, M.A. Glaser, N.A. Clark, Y. Rouault, Self-assembly in surfactant oligomers: a coarse-grained description through molecular dynamics simulations, *Langmuir* 18 (2002) 1908–1918.
- [3] M.J. Rosen, T. Gao, Y. Nakatsuji, A. Masuyama, Synergism in binary mixtures of surfactants 12. Mixtures containing surfactants with two hydrophilic and two or three hydrophobic groups, *Colloids Surf. A: Physicochem. Eng. Asp.* 88 (1994) 1–11.
- [4] R. Zana, Dimeric and oligomeric surfactants. Behavior at interfaces and in aqueous solution: a review, *Adv. Colloid Interface Sci.* 97 (2002) 205–253.
- [5] S. Karaborni, K. Esselink, P.A.J. Hilbers, B. Smit, J. Karthaus, N.M. van Os, R. Zana, Simulating the self-assembly of gemini (dimeric) surfactants, *Science* 266 (1994) 254–256.
- [6] J. Mondal, M. Mahanthappa, A. Yethiraj, Self-assembly of gemini surfactants: a computer simulation study, *J. Phys. Chem. B* 117 (2012) 4254–4262.
- [7] G.P. Sorenson, K.L. Coppage, M.K. Mahanthappa, Unusually stable aqueous lyotropic gyroid phases from gemini dicarboxylate surfactants, *J. Am. Chem. Soc.* 133 (2011) 14928–14931.
- [8] B.A. Pindzola, J. Jin, D.L. Gin, Cross-linked normal hexagonal and bicontinuous cubic assemblies via polymerizable gemini amphiphiles, *J. Am. Chem. Soc.* 125 (2003) 2940–2949.

- [9] W. Shinoda, R. DeVane, M.L. Klein, Coarse-grained molecular modeling of non-ionic surfactant self-assembly, *Soft Matter* 4 (2008) 2454–2462.
- [10] L. Liu, M.J. Rosen, The interaction of some novel diquatary gemini surfactants with anionic surfactants, *J. Colloid Interface Sci.* 179 (1996) 454–459.
- [11] M.S. Bakshi, J. Singh, K. Singh, G. Kaur, Mixed micelles of cationic gemini with tetraalkyl ammonium and phosphonium surfactants: the head group and hydrophobic tail contributions, *Colloids Surf. A: Physicochem. Eng. Asp.* 234 (2004) 77–84.
- [12] M.S. Bakshi, K. Singh, Synergistic interactions in the mixed micelles of cationic gemini with zwitterionic surfactants: fluorescence and Krafft temperature studies, *J. Colloid Interface Sci.* 287 (2005) 288–297.
- [13] R. Zana, H. Lévy, K. Kwetkat, Mixed micellization of dimeric (gemini) surfactants and conventional surfactants. I. Mixtures of an anionic dimeric surfactant and of the nonionic surfactants C₁₂E₅ and C₁₂E₈, *J. Colloid Interface Sci.* 197 (1998) 370–376.
- [14] R.G. Alargova, I.I. Kochijashky, M.L. Sierra, K. Kwetkat, R. Zana, Mixed micellization of dimeric (gemini) surfactants and conventional surfactants: II. CMC and micelle aggregation numbers for various mixtures, *J. Colloid Interface Sci.* 235 (2001) 119–129.
- [15] P.K. Maiti, D. Chowdhury, A microscopic model of gemini surfactants: self-assemblies in water and at air–water interface, *J. Chem. Phys.* 109 (1998) 5126–5133.
- [16] P.K. Maiti, D. Chowdhury, Micellar aggregates of gemini surfactants: Monte Carlo simulation of a microscopic model, *Europhys. Lett.* 41 (1998) 183–188.
- [17] D.R. Jackson, A. Mohareb, J. MacNeil, M.S.G. Razul, D.G. Marangoni, P.H. Poole, Simulations of a lattice model of two-headed linear amphiphiles: influence of amphiphile asymmetry, *J. Chem. Phys.* 134 (2011) 204503–204507.
- [18] P.K. Maiti, K. Kremer, O. Flimm, D. Chowdhury, D. Stauffer, Cross-linking of micelles by gemini surfactants, *Langmuir* 16 (2000) 3784–3790.
- [19] R. Behjatmanesh-Ardakani, M. Farsad, On the difference between self-assembling process of monomeric and dimeric surfactants with the same head to tail ratio: a lattice Monte Carlo simulation, *J. Chem.* 2013 (2013) 525948–525954.
- [20] D. Brindle, C. Care, Phase diagram for the lattice model of amphiphile and solvent mixtures by Monte Carlo simulation, *J. Chem. Soc., Faraday Trans.* 88 (1992) 2163–2166.
- [21] R.G. Larson, Monte Carlo simulation of microstructural transitions in surfactant systems, *J. Chem. Phys.* 96 (1992) 7904–7919.
- [22] L.A. Rodríguez-Guadarrama, S.K. Talsania, K.K. Mohanty, R. Rajagopalan, Thermodynamics of aggregation of amphiphiles in solution from lattice Monte Carlo simulations, *Langmuir* 15 (1999) 437–446.
- [23] L.A. Rodríguez-Guadarrama, S. Ramanathana, K.K. Mohantya, V. Vasquez, Molecular modeling of binary mixtures of amphiphiles in a lattice solution, *Fluid Phase Equilib.* 226 (2004) 27–36.
- [24] R. Davis, A.Z. Panagiotopoulos, Micellization and phase separation in binary amphiphile mixtures, *Mol. Phys.* 190 (2009) 2359–2366.
- [25] U. Reimer, M. Wahab, P. Schiller, Monte Carlo simulation of the adsorption equilibrium of a model surfactant solution on hydrophilic solid surfaces, *Langmuir* 17 (2001) 8444–8450.
- [26] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller, E. Teller, Equation of state calculations by fast computing machines, *J. Chem. Phys.* 21 (1953) 1087–1093.
- [27] A.T. Bernardes, V.B. Henriques, P.M. Bisch, Monte Carlo simulation of a lattice model for micelle formation, *J. Chem. Phys.* 101 (1994) 645–650.
- [28] J.C. Desplat, C.M. Care, A Monte Carlo simulation of the micellar phase of an amphiphile and solvent mixture, *Mol. Phys.* 87 (1996) 441–445.
- [29] J.N. Israelachvili, D.J. Mitchell, B.W. Ninham, Theory of self-assembly of hydrocarbon amphiphiles into micelles and bilayers, *J. Chem. Soc., Faraday Trans.* 22 (1976) 1525–1568.
- [30] V. Kapila, J.M. Harris, P.A. Deymier, S. Raghavan, Effect of long-range and steric hydrophilic interactions on micellization of surfactant solutions: a Monte Carlo study in 2-D, *Langmuir* 18 (2002) 3728–3736.
- [31] M. Zaldivar, R.G. Larson, Lattice Monte Carlo simulations of dilute mixed micelles, *Langmuir* 19 (2003) 10434–10442.
- [32] R. Zana, J. Xia, Gemini Surfactants: Synthesis, Interfacial and Solution-Phase Behavior, and Applications, Marcel Dekker Inc, New York, 2004.
- [33] R. Zana, H. Lévy, Alkanediyl- α,ω -bis(dimethylalkylammonium bromide) surfactants (dimeric surfactants). Part 6. CMC of the ethanediyl-1,2-bis(dimethylalkylammonium bromide) series, *Colloids Surf. A: Physicochem. Eng. Asp.* 127 (1997) 229–232.
- [34] F. Devínský, I. Lacko, F. Bittererová, L. Tomečková, Relationship between structure, surface activity, and micelle formation of some new bisquaternary isosteres of 1,5-pentanediammonium dibromides, *J. Colloid Interface Sci.* 114 (1986) 314–322.
- [35] M. Frindi, B. Michels, H. Levy, R. Zana, Alkanediyl- α,ω -bis(dimethylalkylammonium bromide) surfactants. 4. Ultrasonic absorption studies of amphiphile exchange between micelles and bulk phase in aqueous micellar solution, *Langmuir* 10 (1994) 1140–1145.
- [36] L.D. Song, M.J. Rosen, Surface properties, micellization, and premicellar aggregation of gemini surfactants with rigid and flexible spacers, *Langmuir* 12 (1996) 1149–1153.
- [37] R. Zana, M. Benrraou, R. Rueff, Alkanediyl- α,ω -bis(dimethylalkylammonium bromide) surfactants. 1. Effect of the spacer chain length on the critical micelle concentration and micelle ionization degree, *Langmuir* 7 (1991) 1072–1075.
- [38] R. Zana, Critical micellization concentration of surfactants in aqueous solution and free energy of micellization, *Langmuir* 12 (1996) 1208–1211.
- [39] M.J. Rosen, H. Zhu, T. Gao, Synergism in binary mixture of surfactants: 11. Mixtures containing mono- and disulfonated alkyl- and dialkylidiphenylethers, *J. Colloid Interface Sci.* 157 (1993) 254–259.
- [40] J.H. Clint, Micellization of mixed nonionic surface active agents, *J. Chem. Soc., Faraday Trans.* 1 (71) (1975) 1327–1334.
- [41] N. Poorgholami-Bejarpasi, S.M. Hashemianzadeh, S.M. Mousavi-khoshdel, B. Sohrabi, Role of interaction energies in the behavior of mixed surfactant systems: a lattice Monte Carlo simulation, *Langmuir* 26 (2010) 13786–13796.
- [42] C.C. Ruiz, J. Aguiar, Interaction, stability, and microenvironmental properties of mixed micelles of Triton X100 and n-alkyltrimethylammonium bromides: influence of alkyl chain length, *Langmuir* 16 (2000) 7946–7953.
- [43] B.M. Razavizadeh, M. Mousavi-Khoshdel, H. Gharibi, R. Behjatmanesh-Ardakani, S. Javadian, B. Sohrabi, Thermodynamic studies of mixed ionic/nonionic surfactant systems, *J. Colloid Interface Sci.* 276 (2004) 197–207.
- [44] P.M. Holland, D.N. Rubingh, Nonideal multicomponent mixed micelle model, *J. Phys. Chem.* 87 (1983) 1984–1990.
- [45] P.M. Holland, D.N. Rubingh, *Mixed Surfactant Systems*, American Chemical Society, Washington, DC, 1992, pp. 40.
- [46] H. Gharibi, S. Javadian, B. Sohrabi, R. Behjatmanesh, Investigation of interaction parameters in mixed micelle using pulsed field gradient NMR spectroscopy, *J. Colloid Interface Sci.* 285 (2005) 351–359.
- [47] S. Javadian, H. Gharibi, Z. Bromand, B. Sohrabi, Electrolyte effect on mixed micelle and interfacial properties of binary mixtures of cationic and nonionic surfactants, *J. Colloid Interface Sci.* 318 (2008) 449–456.
- [48] B. Sohrabi, H. Gharibi, B. Tajik, S. Javadian, M. Hashemianzadeh, Molecular interactions of cationic and anionic surfactants in mixed monolayers and aggregates, *J. Phys. Chem. B* 112 (2008) 14869–14876.
- [49] S. Javadian, H. Gharibi, H.T. Fallah, Adsorption and micellar properties of binary ionic/nonionic surfactant mixtures in ethylene glycol + water, *J. Chem. Eng. Data* 55 (2010) 1122–1130.