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Investigation of the mixing behavior of surfactants by lattice Monte Carlo simulation

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Abstract We have studied the behavior of binary surfactant mixtures using the Monte Carlo (MC) simulation technique with a three-dimensional lattice model of a binary surfactant mixture, in which the constituent surfactant species are represented by a series of connected grid sites. Head–head interactions, alone and along with tail–tail interactions, among identical surfactant species were varied to imitate non-ideal mixing and to manipulate the net attractions and repulsions between surfactant species. We found that the head–head and tail–tail interactions affect both the mixed critical micelle concentration and distribution of aggregates. The simulation results are analyzed in the light of the phase separation model, which considers micelles as separate bulk pseudo-phase. Our studies reveal that regular solution theories do not present a satisfactory description for such systems. The discrepancies observed between the theoretical and simulation results for the studied systems could be attributed to the nonrandom mixing effect in simulation, which is neglected in regular solution theory.

Keywords Lattice Monte Carlo · Surfactant mixture · Head–head and tail–tail interaction · Regular solution theory

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Introduction

Surfactants (surface active agents) play an important role in many industrial processes and are key ingredients in biological systems and consumer products [1].The amphiphilic character of surfactants leads to the formation of various self-assembled aggregates in water. Surfactant molecules consist of a polar headgroup and one or more hydrocarbon chains. In aqueous solutions, surfactant molecules can arrange themselves into molecular assemblies, known as micelles, if the concentration of the surfactant exceeds a certain critical value. The concentration at which micelles start to form is known as the critical micellar concentration (CMC). However, as has been known for a long time, surfactant mixtures show a very different behavior in comparison with their components [2]. For example, in aqueous solutions of binary surfactant mixtures, synergistic (attractive) interactions between two species produce CMCs lower than solutions with the constituent single surfactants [3]. However, antagonistic interactions in mixtures of hydrocarbon-based and fluorocarbon-based surfactants in aqueous solutions result in CMCs considerably higher than those of the constituent single surfactants [4, 5]. In general, specific interactions (synergistic or antagonistic) between surfactants significantly alter micellar and phase behavior properties [5]. It is therefore necessary to understand the specific interactions of surfactant mixtures in aqueous solution [6].

Clint [7] proposed the phase separation model to describe the mixed micelle formation phenomenon. In this model, surfactant species present in the micellar phase are assumed to mix ideally, allowing calculation of CMC for mixed entities in terms of the overall composition of the

combined components and the CMCs of the individual surfactants [8]. This ideal mixing model has been very successful in describing surfactant mixtures containing very similar surfactant species but fails to adequately describe the majority of mixed surfactant systems, where the surfactant species present in the mixture are quite dissimilar. Rubingh treated non-ideal binary surfactant mixtures using the pseudo-phase separation (PPS) model [9], where non-ideality is included as the activity coefficient of each surfactant in bulk phase. Evaluation of these activity coefficients then becomes the important step. To evaluate these activity coefficients, the excess free energy of mixing, g^E, is expressed as a series expansion. In the PPS model, only the first term is taken, which means that the excess free energy is constrained to be a symmetrical function with respect to micellar composition:

$$g^E = \beta x_1 x_2 \qquad (1)$$

where x_i is the composition of surfactant i in mixed micelles and β is the interaction parameter. This leads to the following expression for the activity coefficients:

$$\ln \gamma_i = \beta (1 - x_i)^2 / kT \qquad (2)$$

Hence, Eq. 2 is for applied calculation of activity coefficients, where γ_i is the activity coefficient of surfactant i, k is the Boltzmann constant, and T is the temperature. The β parameter is the interaction parameter for micellization, which has been interpreted as an enthalpic contribution to non-ideality [9, 10]. The model is also known as regular solution theory, in analogy to assumption of ideal entropy for bulk solutions.

Although the regular solution treatment is simple, it must be noted that the basic assumption in the treatment, i.e., being zero mixing entropy, is not thermodynamically valid for non-ideally mixed micelles. This model should therefore be viewed as a useful empirical model. Furthermore, regular solution treatment is successful mainly with respect to the correlation of mixed critical micelle concentrations with one interaction parameter β [9, 11].

Computer simulation plays a major role in understanding the properties of self-assembling amphiphilic systems. Using characteristic features of a single amphiphile and the interaction parameters of the models, one can effectively obtain a microscopic understanding of thermodynamic properties and a detailed picture of the self-assembled phases through simulation studies. These simulations can be classified into two broad categories: molecular dynamics (MD) simulations and Monte Carlo (MC) simulations.

In MD simulations, Newton's equations of motion are solved for each amphiphile. Some of these MD simulations are very expensive computationally and, therefore some-times require preassembly of structures and a limit on the number of molecules that can be simulated in a reasonable amount of time.

MC simulation studies of surfactant solutions have been used widely in the past 22 years. These methods are generally based on lattice models in which a surfactant molecule is represented as a chain of chemical groups occupying certain grid sites on a two or three-dimensional (3-D) lattice. Extensive work has been done by Larson [12–16], showing that surfactant self-assembly can be achieved by MC simulations without having to resort to any preassembled micellar structure or shape. However, the majority of Larson's work has focused on three-component amphiphile–oil–water systems, and quantitative predictions of phase behavior have been made by using a temperature integration method [17].

Several MC studies have been performed for the measurement of the micellar properties, such as CMC, micellar shape, micellar size, aggregation number, polydispersity, etc. Care [18] has studied the thermodynamics of cluster formation by calculating the distribution of monomer in clusters. In another work, Panagiotopoulos et al. [19] determined the phase behavior and micellization of several lattice di- and tri-block surfactants in a Larson-type model by histogram-reweighting grand canonical MC simulations on a lattice model.

Several reviews on simulation studies of surfactant solutions have appeared in the literature [20, 21].These reviews contain information about surfactant simulation modeling in general and provide a critical overview of the current state of research in this area. Surprisingly, despite increased interest in mixed surfactant systems, compared with studies of the bulk properties of amphiphiles of a given type using the MC method [12–16, 22, 23], simulation studies are relatively scarce [24, 25]. 3-D lattice-based MC simulations of mixed amphiphile systems have been performed by Zaldivar and Larson [24]. They adjusted the attractions and repulsions between headgroups in order to mimic natural synergistic and antagonistic behaviors. Effect of interactions between the tailgroups in micellization of surfactant mixtures were neglected in their model, and the antagonistic behavior in mixed surfactants is attributed to interspecies head repulsions, while the antagonistic behavior seen in nature in mixed surfactants can be attributed mainly to interspecies tail repulsion. Recently, MC simulations have also been used by Rodriguez et al. [25] to study the behavior of binary surfactant mixtures. In that work, three types of mixed amphiphile systems were investigated. They considered six nonzero interaction energies between two types of amphiphiles and solvents in the solution, and neglected interactions between head-groups or tailgroups of amphiphile molecules.

In previous studies, we described ionic–nonionic surfactant and ionic–ionic surfactant mixtures experimentally by considering two effects not accounted for in regular solution theory, namely nonrandom mixing in the formation of mixed micelles and the effect of head group size [26–28]. In this work, we studied the thermodynamic properties of aqueous solutions of binary surfactant mixtures through lattice MC simulation using the Rodriguez model [29]. By varying the net head–head alone and along with tail–tail interactions between surfactant species, this model captures the non-ideal mixing effects responsible for the synergistic and antagonistic behaviors of surfactant mixtures. Furthermore, relative importance of the interactions between headgroups and tailgroups are evaluated. The simulation results for the mixed surfactant solutions are compared with those obtained from regular solution theory. This is an extension of our earlier work on surfactant mixtures [30].

Model and methods

A 3-D simple cubic lattice with the coordination number of $z=6$ is applied, i.e. only the nearest neighboring interactions are taken into account. In order to minimize any possible size effect, a box with $L=60$ is used for simulation of mixtures. In all the presented results, the excluded volume and periodic boundary conditions are used to mimic the bulk solution. All the lattice sites are occupied either by solvent, surfactant 1 or surfactant 2. Solvent molecules occupy single sites, while surfactant molecules occupy a chain of neighboring sites. Surfactant chains, H_iT_j, have appropriate numbers of H and T beads ($i, j \geq 1$). The second surfactant is also represented by a chain of head beads and tail beads but is denoted by A_iB_j instead. The head and tail beads are typically assumed to be hydrophilic and hydrophobic, respectively. The nature of beads is established through an appropriate assignment of energies of interactions with solvent molecules. All lattice sites not occupied by surfactant molecules are occupied by solvent molecules, denoted here by S. Each lattice site is occupied by only one bead at a time. In this study, only H_4T_4 and A_4B_4 are investigated.

Energy in the system is defined as the sum of all of the nearest-neighbor interactions. Thus, each interaction between pairs of nearest-neighboring sites contributes additively to the total energy. Numerically, each head or tail site interacts with its nearest-neighbors through the specified dimensionless interaction energy, E_{pq}, where p and q represent various types of molecular beads, that is $p, q=$S, H, T, A, B. Therefore, the net energy associated with any configuration is a multiple of ε/kT. This interaction parameter can be related to the Flory–Huggins parameter χ through $\chi = \varepsilon z/kT$. The total internal energy of the system divided by kT is:

$$E_{Total} = \sum_{pq} N_{pq}\varepsilon_{pq} \qquad (3)$$

where N_{pq} is the total number of pq pairs in the system, ε_{pq} is the dimensionless interaction energy, k is the Boltzmann constant and T is temperature. Although this model contains many interaction energies, only some of them are used in practice.

Metropolis algorithm

This study is based on the standard Metropolis algorithm [31]. From all possible configurations for the system, a starting configuration is randomly selected. The total internal energy of this configuration, denoted as E_{old}, is then calculated. Then, another configuration is randomly generated and its energy, E_{new}, is calculated. This trial configuration is accepted based on the following probability:

$$P_{acc.} = Min\left\{1, \exp\left(-\frac{\Delta E}{kT}\right)\right\} \qquad (4)$$

Where ΔE is the difference between the total internal energies of the trial and old configurations, k is the Boltzmann constant and T is temperature. This procedure is continued until equilibrium is attained. The optimum number of MC steps depends on the temperature and concentration of the surfactant molecules. In this work, more than 10^8 moves are performed in order to reach a constant total energy. To avoid pseudo-equilibrium states, some simulations are performed under athermal conditions and the interaction energy is increased at each step, typically in steps of 0.1, until the desired interaction energy is reached. Furthermore, some of the simulations are repeated several times to verify results.

MC moves

Even though the methods used in the literature for chain rearrangement vary from local motions involving only one or two chain segments, such as Verdier–Stockmayer, kink jump moves, to schemes involving the removal and regrowth of chains such as the configuration-bias method, reptation is still efficient under many circumstances. Although the relatively simple algorithm is not a realistic description of the chain motions on a local scale, it leads to a rather quick equilibration of the coil. The main application of this algorithm is for multi-chain systems. The ratio of successful to rejected reptation moves depends on concentration of the amphiphilic molecules. The inefficiency for high amphiphile concentrations is compensated by the

large number of attempted moves. Here, the end of a randomly selected chain is moved to one of the five nearest neighboring sites (the 6th one being occupied by the second bead of the chain). The second bead of the chain is moved to the position previously occupied by the first one, and all the other beads of the chain follow the end site. In this work, reptation moves are used to rearrange the chains on the lattice.

Selection of interaction energies

In our simulations, the surfactant molecules are divided into two parts: a head segment, which interacts favorably with solvent sites, and a tail segment, which interacts repulsively with these sites. Head–solvent interactions are unnecessary for micellization and, thus, an effective surfactant head-solvent hydrophilic interaction may be created by zeroing them.

To describe a surfactant mixture, interspecies interactions are used, consisting of repulsive values between the head (tail) unit of one surfactant species and the tail (head) unit of another one. Simulations are performed using five different sets of parameters. The different interaction energies are shown in Table 1. Since the synergism phenomenon in surfactant mixtures result from the interactions between different head groups, the head–head interaction energies, E_{HA}, are adjusted to control the interactions between surfactant molecules. On the other hand, antagonistic behavior seen in nature is most often attributed to interspecies tail repulsion, one hydrocarbon and the other perfluorinated. In this work, the tail–tail interaction energies, E_{BT}, are also adjusted to control the interactions between surfactant molecules. Except for the head–head and tail–tail interactions, all the non-zero interaction energies, E_{pq}, have constant magnitude of $\varepsilon = 0.7$, as suggested by Rodriguez [29]. The head–head and tail–tail interaction energies are given as multiples of ε.

Identical surfactants H_4T_4 and A_4B_4 with similar structures and interactions are chosen to investigate the net crossing interaction between headgroups and tailgroups. This would allow refinement of the properties defined for surfactant mixture solutions.

Results

Critical micellar concentration

At low surfactant concentrations, individual surfactant molecules are dissolved in solvent, while micelles form at higher concentrations. The threshold concentration, where first micelles appear in the system, is called the CMC point. Unfortunately, CMC is not a well defined point. There are several definitions for the CMC in simulation studies [32, 33]. In this paper, the Israelachvili definition is applied and CMC is assumed to be the concentration at which the number of free surfactants is equal to the number of aggregated surfactants in solution [33]. Thus, for a mixture of surfactants, CMC corresponds to the intersection of a straight line defined by $C^M = C_t/2$, and the curve defined by the simulation data obtained for the total concentration of monomeric surfactants, $C^M = C_1^M + C_2^M$, as in Fig. 1; C_t is the total surfactant concentration and C_i^M is the monomeric concentration of surfactant i. The concentrations are defined as the number of surfactant sites divided by the total number of lattice cells, $60 \times 60 \times 60$ in this work. Figures 1 and 2 show the total monomeric concentration as a function of total concentration of the H_4T_4–A_4B_4 surfactant mixture at a ratio of 50:50, with $E_{HA}=0$ and $E_{HA}=-0.7$. As it can be seen in Fig. 2, at concentrations well above the CMC, a decline in free surfactant concentrations is observed. Experimental evidence also exists for this decrease, which is not predicted by traditional theories for micelle formation [34, 35]. This behavior has been explained by von Gottberg et al. [36] and is due to the nonideality of the micellar solution at high concentrations, where interactions among the aggregates cannot be neglected. Figure 3 shows a snapshot of the simulation box for the H_4T_4–A_4B_4 system with $E_{HA}=-0.7$, indicating the presence of a large number of interacting micelles. From visual inspection of snapshots for all mixed systems studied in this paper, it is observed that the aggregates formed in the lattice solutions consist of both the amphiphiles H_4T_4 and A_4B_4, and not separate aggregates of each amphiphile (Fig. 4).

Table 1 Interaction energies for all the systems studied

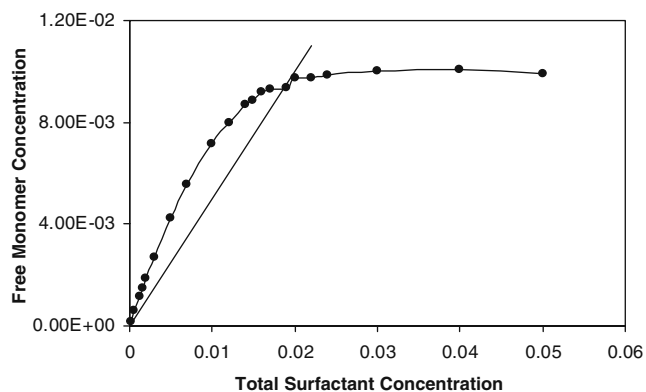|	Interaction energies, $E_{\alpha\beta}$									
System	Surfactant H_4T_4			Surfactant A_4B_4				Cross Interactions		
	E_{HS}	E_{TS}	E_{HT}	E_{AS}	E_{BS}	E_{AB}	E_{BT}	E_{HA}	E_{AT}	E_{HB}
1	0	ε	ε	0	ε	ε	0	$-\varepsilon$	ε	ε
2	0	ε	ε	0	ε	ε	0	$-\varepsilon_{/2}$	ε	ε
3	0	ε	ε	0	ε	ε	0	0	ε	ε
4	0	ε	ε	0	ε	ε	$\varepsilon_{/2}$	$-\varepsilon$	ε	ε
5	0	ε	ε	0	ε	ε	ε	$-\varepsilon$	ε	ε

Fig. 1 Free monomer concentration vs total surfactant concentration for a 50:50 mixture of H_4T_4–A_4B_4 on a box of size $60 \times 60 \times 60$. The interaction energies for this system are given in Table 1 as system 3

The head–head and tail–tail interaction energies affect the average free monomer concentration. Figure 5 indicates the impact of head–head and tail–tail interaction energies (E_{HA}, E_{BT}) on the CMC. The net attraction between headgroups causes a negative deviation from Rault's law and reduces the mixed CMC, while when the attraction is accompanied by repulsion between tailgroups, a positive deviation from Rault's law and a higher mixed CMC is observed. In Fig. 6, CMC is plotted versus relative composition of the surfactant mixture, while interactions between surfactant species are assumed to be constant. Each curve corresponds to a system with different interactions between headgroups alone and along with tailgroups of the surfactants present in solution. As expected, considering the similarity in surfactant structures and interactions, the mixed CMC curve is symmetrical with composition. Comparisons between system 1 with 4 and 5 reveal that interactions between headgroups and tailgroups do not produce same effect on the mixed CMC. Unlike the experimental data reported by Hoffmann and Pössnecker [2], the effect of interactions between tailgroups is more significant (Figs. 5, 6). In this work, only short range
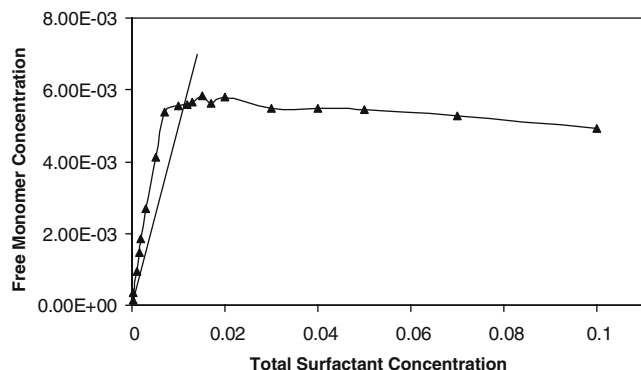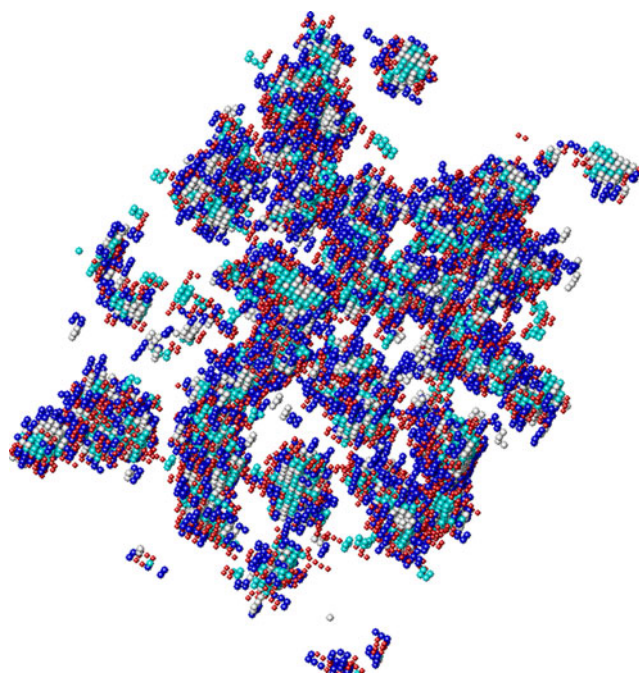

Fig. 3 Typical visualization of a simulation box with $E_{HA}=-0.7$ at a ratio of 50:50. *Blue/red points* Tails of two surfactants, *gray/turquoise points* heads of two surfactants
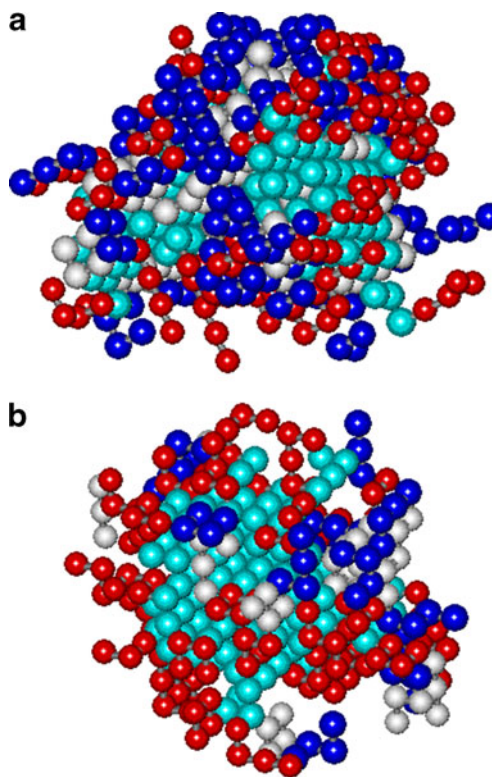

Fig. 4 Typical visualization of a micelle with **a** $E_{HA}=-0.7$ at a ratio of 50:50, and **b** $E_{HA}=-0.7$ along with $E_{BT}=0.7$ at a ratio of 50:50. *Blue/red points* Tails of two surfactants, *gray/turquoise points* heads of two surfactants
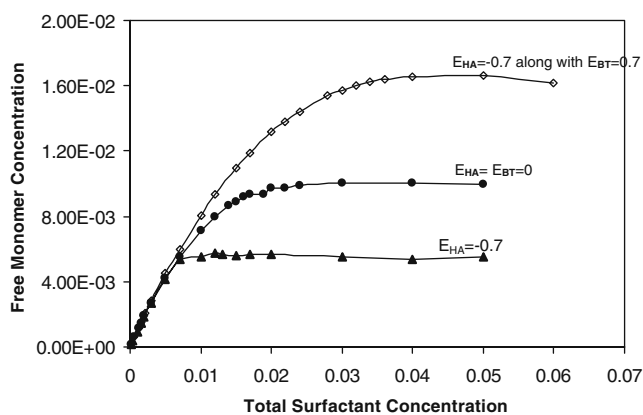

Fig. 2 Free monomer concentration vs total surfactant concentration for a 50:50 mixture of H_4T_4–A_4B_4 on a box of size $60 \times 60 \times 60$. The interaction energies for this system are given in Table 1 as system 1

Fig. 5 Free monomer concentration vs total surfactant concentration for a 50:50 mixture of H_4T_4–A_4B_4

interactions between headgroups and tailgroups are considered, and since the tailgroups are more confined to the micellar core, in contrast to the headgroups, it is more difficult to separate phases from each other. However, for systems with long-range attractions between headgroups and short-range repulsions between tailgroups, the effects of attraction on the mixed CMC are expected to be greater. This possibility should be examined in future research.

Cluster distribution

Aggregate size distribution is one of the most important factors in self-assembled systems. Two maxima are detected when the proportion of the monomers present in n (nxn) clusters is plotted versus n—one for the monomer and the other for the micelle [37]. Wider distribution indicates higher polydispersity. As can be seen in Figs. 7
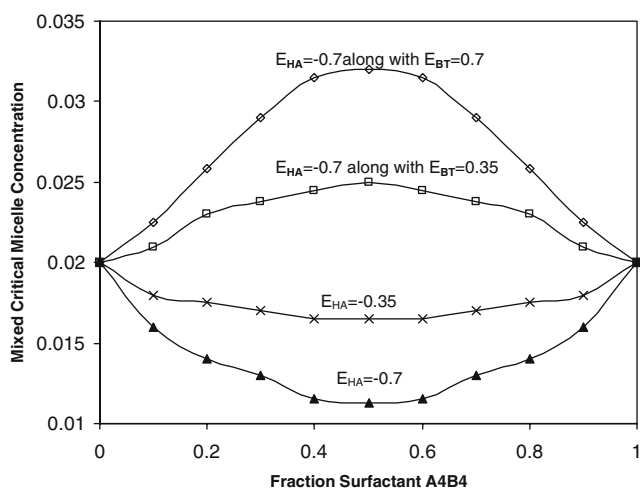

Fig. 6 Mixed micelle critical micellar concentration (CMC) as a function of the concentration of A_4B_4. Each line represents a different value for the head–head interaction energies and the head–head along with tail–tail interaction energies
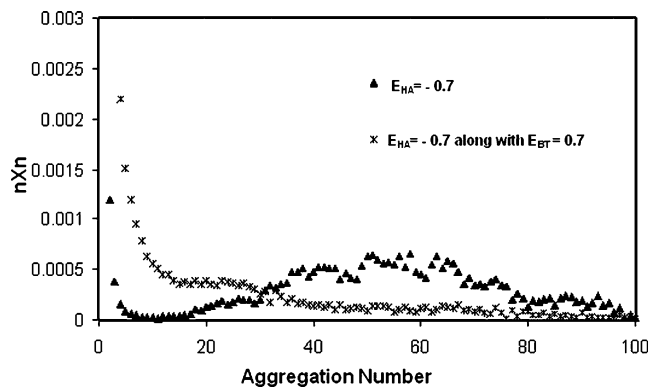

Fig. 7 Aggregate size distribution for H_4T_4–A_4B_4 at a ratio of 50:50 at C_t greater than CMC

and 8, high concentrations of clusters with small aggregation numbers serve as a sign of premicellar phenomena. Some authors have argued that a reduction in monomer concentration is insufficient as a signature of micellar organization, and that, to unambiguously identify the onset of micellization, there should not only be a drop in monomer concentration, but the plot of the proportion of monomers in clusters of size n as a function of aggregation number must also show a local minimum and maximum [18, 38]. Therefore, both the monomer volume fraction and the distribution of monomer amount, as a function of aggregation number, were determined for all the systems studied. Figures 7, 8 and 9 show the plots of aggregate size distribution for a 50:50 H_4T_4–A_4B_4 mixture having different interactions between headgroups and tailgroups. It is noteworthy that the difference in cluster distribution arises solely from the interactions among headgroups or tailgroups. A comparison between systems 1 and 5 reveals that tail–tail repulsions deter micellization by increasing the CMC (Fig. 5), and by decreasing (Fig. 7) distribution of larger micelles. Since the tailgroups are more confined in
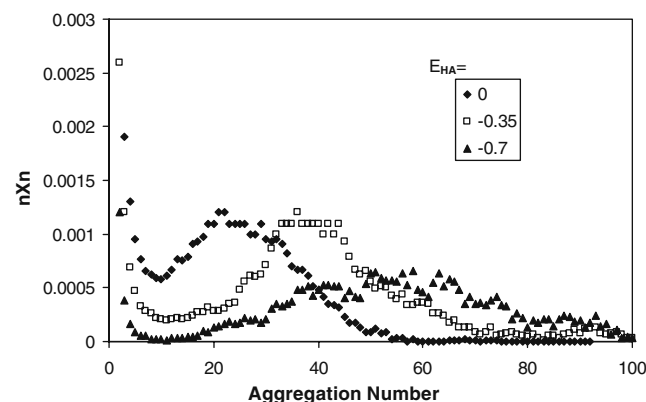

Fig. 8 Aggregate size distribution for the H_4T_4–A_4B_4 mixture at a ratio of 50:50 and with different interactions between the head groups; C_t greater than CMC
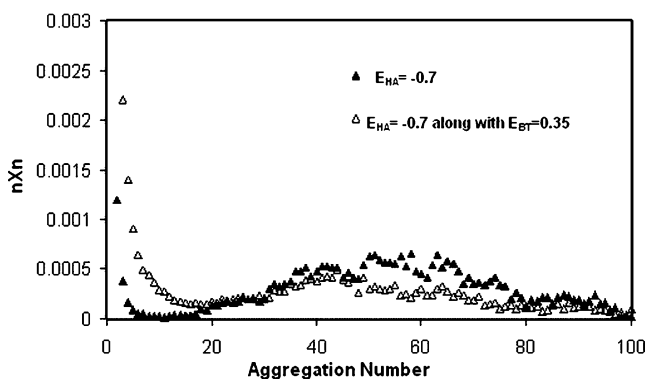
Fig. 9 Aggregate size distribution for the H_4T_4–A_4B_4 surfactant mixture at a ratio of 50:50 at C_t greater than CMC

the micellar core compared to the headgroups, surfactant molecules prefer to reduce the contacts between them. Therefore, the tail–tail repulsions lead to a decrease in the distribution of larger micelles. As this repulsion is decreased, micelles with larger size are observed (Fig. 8).

By comparing systems 1 and 3, it can be concluded that, like the tail–tail repulsions, head–head attractions produce dissimilar effects. Head–head attractions may decrease the CMC (Fig. 5) and distribution of micelles with smaller size. In fact, in the absence of head–head attractions, free monomers would have sufficient time to form small aggregates in solution (Fig. 8). Hence, the premicellar concentration of free amphiphiles is increased.

Determination of interaction parameters

Theory

Binary surfactant mixtures have traditionally been investigated using the PPS approach, in which the micelles are treated as a separate and infinite phase in equilibrium with the monomer phase [7, 9, 39–41]. Although surfactant aggregates do not form a true thermodynamic phase due to their large size, many of their thermodynamic properties approximate those of a true separate phase. Fundamentally, the PPS model represents a limiting case in which micellar aggregates approach infinite size. In fact, calculation using a mono disperse mass action model suggests that the phase separation model provides a good approximation for aggregates of 50 surfactant molecules or more [42]. By treating surfactant aggregates as a separate phase, the chemical potential of surfactant species in each phase may be assumed to be equal while the system is at equilibrium.

In this approach,

$$\mu_i = \mu_i^M \tag{5}$$

where μ_i and μ_i^M are the chemical potential of i species in solution and mixed micelle, respectively. Mixing behavior

of surfactants in the micelle could also be described according to this equation. For mixed surfactant component i in solution:

$$\mu_i = \mu_i^\circ + RT \ln C_i^f \tag{6}$$

where μ_i° is standard chemical potential and C_i^f is monomer concentration of component i.

For a micelle of pure ith component:

$$\mu_i^{\circ M} = \mu_i^\circ + RT \ln C_i^M \tag{7}$$

Where C_i^M is the CMC for the pure component i. For a mixed micelle:

$$\mu_i^M = \mu_i^{\circ M} + RT \ln \gamma_i x_i \tag{8}$$

where χ_i and γ_i are the mole fraction and activity coefficient of surfactant i in the mixed micelles, respectively. Equations 6–8 may be rewritten as a general Eq. 9:

$$C_i^f = \gamma_i x_i C_i^M \tag{9}$$

By simply rearranging this basic equation and mass balance, monomer concentrations and mixed micellar composition in binary surfactant systems could easily be calculated according to the following equations:

$$\frac{1}{C^M} = \sum_{i=1}^{n} \frac{\alpha_i}{\gamma_i C_i^M} \tag{10}$$

$$x_1 = \frac{-(C - \Delta) + \left[(C - \Delta)^2 + 4\alpha C\Delta \right]^{1/2}}{2\Delta} \tag{11}$$

$$C_1^f = \frac{-(C - \Delta) + \left[(C - \Delta)^2 + 4\alpha C\Delta \right]^{1/2}}{2 \cdot \left(\gamma_2 C_2^M / \gamma_1 C_1^M - 1 \right)} \tag{12}$$

$$C_2^f = \left(1 - \frac{C_1^f}{\gamma_1 C_1^M} \right) \gamma_2 C_2^M \tag{13}$$

$$\Delta = \gamma_2 C_2^M - \gamma_1 C_1^M \tag{14}$$

where x_1 is the mole fraction of surfactant 1 in the mixed micelles, γ_i ($i=1, 2$) is the activity coefficient of component i in mixed micelles, C^M is the CMC for the mixed surfactant system, C is the total concentration of surfactant in the mixture, and α is the overall mixing ratio of surfactant 1 in the binary mixture. For ideal mixing, the activity coefficients γ_1 and γ_2 are defined unity. In regular

Table 2 β values obtained from the simulation data and the regular solution theory

System	Interaction parameter (β)
$E_{HA}=-0.7$	-1.96
$E_{HA}=-0.35$	-0.78
$E_{HA}=-0.7$, $E_{BT}=0.35$	0.91

solution approximation, where excess entropy of mixing is zero, the activity coefficients could be approximated as:

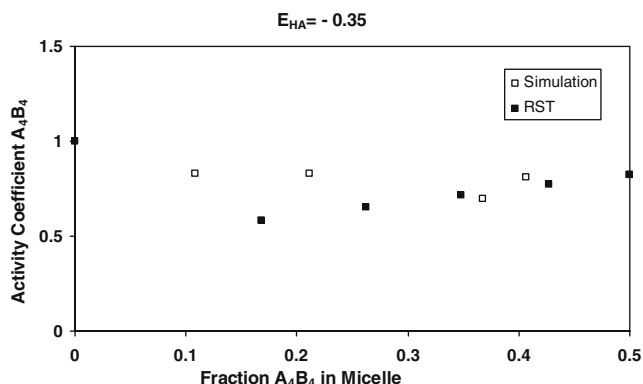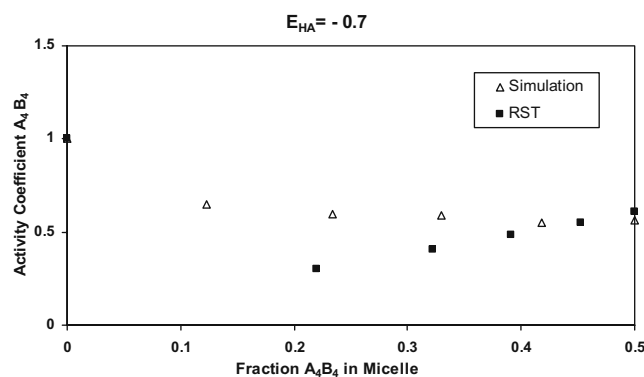$$\gamma_1 = \exp \beta (1 - x_1)^2 \quad (15)$$

$$\gamma_2 = \exp \beta x_1^2 \quad (16)$$

where β is an interaction parameter that could be interpreted as representing the excess heat of mixing divided by the thermal energy. From lattice theory, β can be expressed in terms of molecular level interactions as:

$$\beta = \frac{E_{11} + E_{22} - 2E_{12}}{kT} \quad (17)$$

where E_{11} and E_{22} are interaction energies between the surfactant species in pure micelles, and E_{12} is the interaction energy between the surfactant species in mixed micelles. Therefore, the value of β would give an idea of the degree of interaction between monomers in the micelle. A negative value for β indicates a net attraction between the monomers in mixed micelles and a positive value reveals a net repulsion, as for some hydrocarbon and fluorocarbon mixtures. According to Rubingh's treatment, the interaction parameter β for mixed micelle formation in an aqueous medium can be calculated with the following equation:
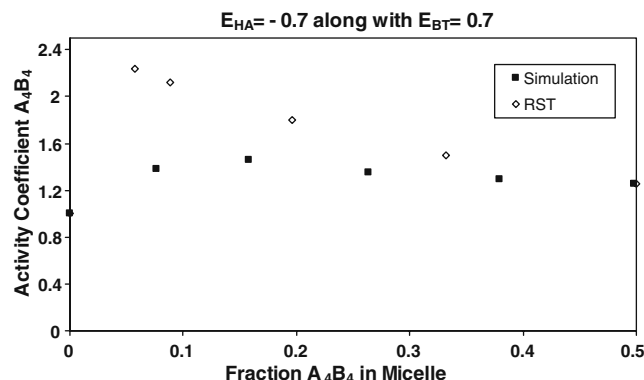
$$\beta = \frac{\ln \left[\alpha_1 C^M / \chi_1 C_1^M \right]}{(1 - x_1)^2} \quad (18)$$

Fig. 11 Activity coefficients for the H_4T_4–A_4B_4 mixture and with $E_{HA}=-0.7$

where χ_1 is the mole fraction of surfactant 1 with respect to the total surfactant in the mixed aggregate, and C_1^M and C^M are the CMCs for surfactant 1 and mixture, respectively, at the mole fraction, α_1.

Beta calculations

According to this model, the two surfactants form an ideal mixture when $\beta=0$. A negative value for β indicates deviation from the ideal behavior; the more negative the value of β, the stronger the attractive interaction between surfactant molecules. Negative β values have commonly been ascribed to the interactions between headgroups, while positive β values would indicate the incompatibility of the surfactant species and thus represent a measure of the antagonistic behavior of the surfactants. Rubingh's method is applied to calculate χ_i as a monomer concentration in mixed micelles, and evaluate β. The β values for the three different systems are listed in Table 2. For the H_4T_4–A_4B_4 system, $E_{HA}=-0.7$ along with $E_{BT}=0.7$, application of regular solution theory would give different values between 1.88 and 8.38 for β. So, it is almost impossible to

Fig. 10 Activity coefficients for the H_4T_4–A_4B_4 mixture and with $E_{HA}=-0.35$

Fig. 12 Activity coefficients for the H_4T_4–A_4B_4 mixture and with $E_{HA}=-0.7$ and $E_{BT}=0.7$

decide whether the interaction parameter obtained from the simulation data and regular solution theory is smaller or higher than +2, meaning mixing or demixing. This could be due to the error of interaction parameter in the regular solution theory. As pointed out earlier by Hoffmann and Pössnecker [2], the error of β increases strongly when one component dominates the micelle. It has a minimum value at $x = 0.5$ and increases with deviation from the point of equimolar micellar composition. Thus, 1.88 is a more acceptable value for β, which is calculated for a mixture of two surfactants with a ratio of 50:50. In addition, this conclusion is in reasonable agreement with the visual inspections of configurations during the simulations. Our simulation shows that the aggregates formed in this system consist of both H_4T_4 and A_4B_4 surfactants (Fig. 4).

When both surfactants are mixed ideally, activity coefficients are equal to unity. This is normally the case when there is no interaction between the surfactants. As deviation from the ideal mixing is investigated by varying head–head and tail–tail interactions between the two surfactants, determination of the activities is critical for accurate representation of non-ideality of the micellar phase. The activity coefficients can be calculated from the simulations using:

$$\gamma_1 = \frac{\alpha_1 C^M}{x_1 C_1^M} \quad \text{and} \quad \gamma_2 = \frac{\alpha_2 C^M}{x_2 C_2^M} \tag{19}$$

Simulation results are shown in Figs. 10, 11, and 12. In addition, predictions of activity coefficients based on regular solution theory are shown in these figures. The value of β used in calculating the activity coefficients is taken from Table 2. As can be seen in Figs. 10, 11, and 12, there are large discrepancies between the activity coefficient values obtained from simulation and predictions from regular solution theory. These figures indicate that discrepancy between simulation and theory increases with the increasing interactions. In other words, when there is head–head interaction along with tail–tail repulsion (Fig. 12), we observe the largest discrepancy between theory and simulation. On the other hand, the least discrepancy between theory and simulation is observed for the system $E_{HA} = -0.35$. In fact, due to these specific interactions (repulsion or attraction), the mixing process is not completely random in these systems, whereas regular solution theory treats the mixed systems as ideally mixed from the viewpoint of randomness in mixing. Thus, it is reasonable to conclude that the observed discrepancy between simulation and theory is due to the nonrandom mixing effect that is neglected in theory. On the other hand, surfactant aggregates are not a true thermodynamic phase. In fact, results from the mass action model show this approxima-

tion to hold for aggregates with 50 or more monomers [42]. By looking at Figs. 7 and 8, it is obvious that the aggregates formed in mixed systems, which there are head–head interactions along with repulsions between tailgroups ($E_{HA} = -0.7$ along with $E_{BT} = 0.7$), are too small to be considered as pseudo-phase. This fact also makes totally random mixing invalid for these systems. These results are in good agreement with experimental results [2, 43].

Summary and conclusions

A simple cubic lattice model is presented for binary mixed surfactants in order to investigate the non-ideal mixing behavior of surfactant systems. The model illustrates the synergistic and antagonistic behaviors characteristic of surfactant mixtures by varying the net cross interactions between headgroups and tailgroups of the surfactants species. Simulation results indicate that the head–head and tail–tail interactions affect the mixed CMC and aggregation size distribution. Furthermore, short-range interactions among tailgroups have greater effects on the properties of such systems compared to short-range attractions among headgroups. Our studies on mixed surfactant systems have revealed that large discrepancies exist between results obtained from simulation and predictions based on regular solution theory. This may result from the fact that regular solution theory does not account for the nonrandom mixing observed in simulations.

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