



Monte Carlo simulation of binary surfactant/contaminant/water systems

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ABSTRACT

Surfactant-enhanced remediation (SER) is an effective approach for the removal of absorbed hydrophobic organic compounds (HOCs) from contaminated soils. The solubilization of contaminants by mixed surfactants with attractive and repulsive head–head interactions was studied by measuring the micelle–water partition coefficient (K_C) and molar solubilization ratio (MSR) using the lattice Monte Carlo method. The effect of surfactant mixing on the MSR and K_C of contaminants displayed the following trend: $C_4 > C_3 > C_2$.

Synergistic binary surfactant mixtures showed greater solubilization capacities for contaminants than the corresponding individual surfactants. Mixed micellization parameters, including the interaction parameter β , and activity coefficient f_i , were evaluated with Rubingh's approach.

Synergistic mixed-surfactant systems can improve the performance of surfactant-enhanced remediation of soils and groundwater by decreasing the amount of applied surfactant and the cost of remediation.

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1. Introduction

The contamination of soils and groundwater by hazardous organic pollutants is a widespread environmental problem. The most common chemical pollutants are petroleum hydrocarbons, pesticides, solvents, lead, and other heavy metals.

Natural gas, crude oil, tar, and asphalt are petroleum hydrocarbons composed of various proportions of compounds such as alkanes, aromatics, and polycyclic aromatic hydrocarbons (PAHs). Various physical, chemical, biological, and combined technologies have been developed to remediate organic contaminants in soil–water systems, and these processes are often dependent on the desorption of contaminants from the soil–water surface [1,2].

Surfactant-enhanced remediation (SER) is a promising technology for the removal of organic contaminants such as alkanes. In SER, contaminants from contaminated soil and groundwater are partitioned into the hydrophobic core of surfactant micelles [3].

For several decades, surfactant mixtures have received a considerable amount of attention due to their efficient solubilization, dispersion, suspension, and transportation capabilities [4]. Some surfactant combinations exhibit synergistic properties and provide lower surface tensions and critical micelle concentration (CMC)

values than individual surfactants. The synergistic behavior of surfactant mixtures may allow reduction of the total amount of surfactant used in an application, thereby reducing both the cost and the environmental impact of remediation.

Several experimental studies on the solubilization of organic compounds in mixed surfactants have been conducted [1,3–7]. However, Monte Carlo (MC) simulation studies have been performed only on single-surfactant solutions; to date, no MC simulation studies have been used to investigate mixed surfactant solubilization of organic compounds [8–14].

Talsania et al. [9] used lattice-based MC simulations to investigate the solubilization of solutes in surfactant aggregates; the size and shape of the micelles, CMC, locus of solubilization, and partition coefficients of the solute were determined. In another study, Talsania et al. reported a novel method to study the phase behavior of solutes in the presence and absence of surfactants [10]. In this study, the authors demonstrated that the addition of surfactants to solute–solvent systems initially reduces the solubility of the solutes; however, at higher surfactant concentrations, an increase in the solubility of the solutes was observed.

Kim et al. [15] studied oil chains with various lengths (from T to T₄) in the presence of H₄T₄ surfactants and quantitatively determined the effects of oil on the CMC. Their results showed that the CMC decreased with an increase in the volume fraction of oil in the aqueous phase.

Al-Shannag et al. [16] used the self-consistent mean field (SCMF) theory to describe the properties of a ternary system containing

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oil, water, and surfactant. The authors of this study observed no significant differences between the predicted CMCs and density distributions of SCMF calculations and grand canonical Monte Carlo (GCMC) simulations.

Weers demonstrated experimentally [17] that nonionic–ionic mixtures showed negative deviations from ideal behavior and observed no attractive interactions between surfactant head groups. Systems containing dodecyltrimethylammonium bromide ($C_{12}TAB$)–hexaethyleneglycol mono *n*-dodecyl ether ($C_{12}EO_6$) displayed different solubilization sites for hexanol, which was solubilized in the palisade layer, and decane, which was solubilized in the micellar core. From this evidence, the authors deduced that surfactant–solubilize interactions were as important as surfactant–surfactant interactions.

The experimental studies of Paria et al. [18] on the solubilization of naphthalene by pure and mixed surfactants showed that naphthalene solubilization in ionic–nonionic surfactant mixtures deviated considerably from that of ideal mixing. Although attractive interactions for mixed-micelle formation were detected, naphthalene solubilization was less than predicted by ideal theory.

Zhu et al. measured the maximum additive concentration (MAC), micelle–water partition coefficient (K_C), and CMC of PAHs in sodium dodecylsulfate (SDS)–nonionic mixed surfactants [2,6] and compared the results to the properties predicted by the ideal mixing rule. Interestingly, they found that the MAC and K_C of PAHs in mixed surfactants were greater than those calculated according to the ideal mixing rule.

The solubilization of PAHs in mixed ternary surfactant systems was first studied by Das et al. [4]. Although cationic–cationic–nonionic ternary mixtures showed lower solubilizing efficiencies than their binary cationic–nonionic counterparts, their solubilization efficiency was found to be greater than that of cationic–cationic systems.

The objectives of this study were: (1) to investigate a lattice-based MC model of contaminant solubilization in synergistic and antagonistic binary surfactant micelles with regard to the effect of mixing on the solubilization of contaminants; (2) to determine the micelle–water partition coefficient (K_C) and CMC of mixed surfactants and to use these values to predict the solubilization capacity for contaminants; and (3) to correlate the interaction parameter of mixed-micelle formation to the solubilization interaction parameter (evaluated using regular solution approximation [RSA]) to identify synergism and antagonism in the solubilization capacities of binary surfactant systems.

To date, there are no studies that have used MC simulation methods to study contaminant solubilization in binary surfactant solutions. The present paper is arranged as follows: in Section 2, a detailed account is provided of the coarse-grained lattice model used to study contaminant solubilization in aggregates, and the results are presented and discussed in Section 3. The findings are summarized in Section 4, and concluding remarks are presented.

2. Simulation method

Two main classes of simulation models can be used to study surfactant systems: detailed atomistic models and coarse-grained [19,20] models. In theory, atomistic approaches are more rigorous and accurate. Coarse-grained models, in which several atoms are grouped together, are alternatives to atomistically detailed models and can usually describe micellization; however, coarse-grained models lack the detailed structural information that atomistic models can provide. Coarse-grained models can be classified as continuum or lattice models: continuum models are more realistic, but lattice models are more computationally efficient [21]. Numerous simulation studies using coarse-grained

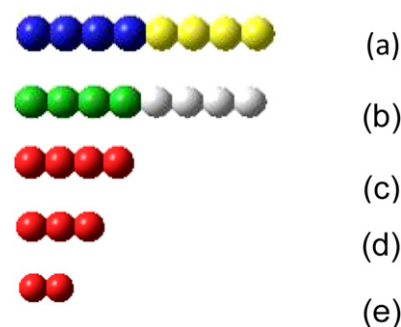


Fig. 1. Schematic diagram of (a) H_4T_4 surfactant, blue balls indicate head groups on the surfactant, and yellow balls indicate tail groups, (b) A_4B_4 surfactant, green balls indicate head groups on the surfactant, and gray balls indicate tail groups, (c–e) C_4 , C_3 , and C_2 contaminants respectively. Red balls represent contaminants. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

continuum [22–28] and lattice [29–36] models have been performed.

In the present study, the simulation model was employed in a three-dimensional $60 \times 60 \times 60$ cubic lattice with a coordination number of $Z=6$ (i.e., only interactions between neighbors were considered). Standard excluded volumes and periodic boundary conditions were used, and all of the lattice points were assumed to be occupied by a solvent molecule (S), a bead of a contaminant (C) molecule (C_k , $k \geq 1$), or the bead of a surfactant molecule. For convenience, unique nomenclature was employed for each surfactant molecule. The first surfactant was labeled as H_iT_j , with i ($i \geq 1$) head beads and j ($j \geq 1$) tail beads, and the second surfactant was labeled as A_iB_j (Fig. 1). Each bead–bead pair interaction was assigned interaction energy (E_{mn}), where $m, n = S, C, H, T, A, B$.

The total energy of the system divided by $k_B T$ is:

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

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

The only type of move used to modify the configuration was the reptation move. Reptation is an efficient mode of chain rearrangement because each bead on a chain is moved to a new site. Here, one end of the chain was randomly selected to be the lead end for reptation and then one site of the five potentially available nearest neighbors of the lead end was randomly selected (the sixth site was occupied by the bead adjacent to the end and was not considered). If this site was vacant (i.e., occupied by solvent), the lead end was moved to a new site, and all of the other beads on the chain followed the lead end. If the site was not vacant, a move would not occur. In either case, the reptation move was completed, and the new configuration was temporarily recorded as the trial configuration. The probability of acceptance of the move was calculated according to the standard Metropolis algorithm [37]. For any given concentration of contaminant and surfactant, the appropriate number of C_k , H_iT_j , and A_iB_j chains was randomly placed on the lattice sites, and the resulting configuration was considered the initial configuration of the system. The total energy of the initial configuration, E_{old} (normalized by $k_B T$), was calculated. The initial configuration was modified by moving a randomly selected surfactant or contaminant chain, and the new energy, E_{new} , of the trial configuration was then calculated.

Table 1
Interaction energies of the system.

Interaction energies, E_{mn}						
	S	H	T	A	B	C
S	0	0	ε	0	ε	ε
H	0	0	ε	$\pm\varepsilon$	ε	ε
T	ε	ε	0	ε	0	0
A	0	$\pm\varepsilon$	ε	0	ε	ε
B	ε	ε	0	ε	0	0
C	ε	ε	0	ε	0	0

The trial configuration was accepted or rejected according to the following probability:

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

The attempted move (whether successful or unsuccessful) is called an MC step and was repeated until equilibrium was achieved for that particular temperature. More than 10^8 moves were performed to achieve a region of phase space in which the total energy and micelle size growth remained almost constant. These states were selected to be the equilibrium configurations, and the aggregates were characterized under these conditions. Furthermore, some of the simulations were repeated several times to verify the results. To avoid pseudo-equilibrium states, we performed the simulations under athermal conditions. At the highest temperature, $1/\varepsilon$, random initial configuration at given surfactants and contaminant volume fraction was generated. The system was achieved to equilibrium by the sufficient MC step. Then the system was cooled by increasing ε in small increments (0.1), and the resulting configuration was defined as initial configuration for further step. A total 7 step was used, each step being equilibrated for triple the number of MC step as the previous step. The average energy in each temperature was monitored. When the system was cooled to desired interaction energy and averaged energy appears to steady sate (the change in this property became minimized) the system properties snapshots were taken. Interspecies interactions, which consisted of attractive and repulsive forces between the head unit of one surfactant species and the head unit of another species, were used to describe surfactant mixtures. Head–solvent interactions are not necessary for micellization; thus, by setting this interaction energy to zero, hydrophilic interactions between head groups and solvent were created [38].

The interaction energies are shown in Table 1. Except for head–head interactions, all non-zero interaction energies, E_{mn} , presented a constant magnitude of $\varepsilon = 0.7$, as suggested by Rodriguez [39].

The antagonistic behavior of surfactant system observed in nature is often attributed to interspecies tail repulsion. For example, in hydrocarbon–fluorocarbon mixtures, the fluorinated surfactant is oleophobic, which results in repulsion between the tails of the two surfactant species. Although tail–tail interactions (E_{TB}) were not specifically adjusted to mimic such conditions, head–head interactions (E_{HA}) were used to stimulate analogous antagonistic deviations from ideal mixing.

The head–head interaction energy was set to $\varepsilon = 0.7$ and -0.7 . The identical surfactants H_4T_4 and A_4B_4 , which possessed similar structures and displayed similar interactions, were investigated in the present study.

According to snapshots from simulations of the H_4T_4 – A_4B_4 system and contaminants with attractive and repulsive interactions between head groups, the aggregates that formed in the lattice solution consisted of H_4T_4 and A_4B_4 surfactants. Interestingly, aggregates containing only one type of surfactant were not observed (Fig. 2).

Different researchers use various methods for measuring the CMC [33,36,40,41]. We employ the Desplat [36] definition, and the obtained CMC is according to the intercept of a line drawn through high concentration data and the origin of the unit slope.

3. Results and discussion

Critical micelle concentration (CMC) and interactions between surfactants in mixed micelles.

The CMC is a narrow concentration range over which a surfactant solution displays an abrupt change in physicochemical properties.

In an ideal mixed state, the CMC of a mixed surfactant solution, $CMC_{1,2}$, can be calculated using the Clint [42] equation:

$$\frac{1}{CMC_{1,2}} = \frac{X_1}{CMC_1} + \frac{X_2}{CMC_2} \tag{3}$$

where $CMC_{1,2}$, CMC_1 , and CMC_2 are the critical micelle concentrations of mixed surfactant and individual pure components 1 and 2, respectively. X_1 and X_2 are the volume fraction of components 1 and 2 in mixed surfactant solutions, respectively.

Due to interactions between components in mixed micelles, the simulated CMCs of mixed surfactants usually differ from the ideal CMCs. The simulated and ideal CMCs of H_4T_4 – A_4B_4 mixed systems are shown in Fig. 3 as a function of the solution composition. Negative interaction energies between surfactant heads produce negative deviations from ideality (a synergistic system) and decrease the mixed CMC. Alternatively, positive interaction energies between surfactant heads (an antagonistic system) produce positive deviations from ideality and increase the mixed CMC. The CMC values of single and mixed surfactant systems in the aqueous phase and the presence of C_2 , C_3 , and C_4 chains are provided in Table 2.

Synergistic binary mixed surfactant with C_4 contaminant at high MC step did not appear micelle, but rather phase separation occurred.

Rubingh’s regular solution theory model [42,43] can be used to determine negative and positive deviations in the simulated CMC values from the ideal CMCs and the nonideality of mixed binary surfactant systems. According to Rubingh’s theory, deviations in the simulated CMC of mixed surfactant systems from the ideal CMC can be represented by the interaction parameter β , which is expressed as:

$$\beta = \frac{\ln[CMC_{1,2}X_1/CMC_1X_1^M]}{(1 - X_1^M)^2} = \frac{\ln[CMC_{1,2}X_2/CMC_2X_2^M]}{(1 - X_2^M)^2} \tag{4}$$

where X_1^M and X_2^M are the volume fractions of components 1 and 2 in mixed micelles, respectively. A negative value of β indicates that the free energy of micellization is less than that predicted by ideal solution theory, while a positive value of β indicates that the free energy of micellization is greater than the ideal value.

For ideal mixing, the activity coefficients, f_1 and f_2 , are equal to one by definition. Alternatively, for non-ideal mixing, these parameters deviate from unity. In the regular solution approximation, the excess entropy of mixing is equal to zero, and the activity coefficients can be approximated as:

$$f_1 = \exp \beta(1 - x_1)^2 \tag{5a}$$

$$f_2 = \exp \beta(x_1)^2 \tag{5b}$$

As shown in Table 2, when head–head repulsion occurs, the activity coefficients obtained from simulated data approaches one. In contrast, when head–head attraction occurs, the activity coefficients are significantly less than one [44]. Deviations in the activity coefficients are attributed to repulsion between head groups and the occurrence of degrading interactions between components.

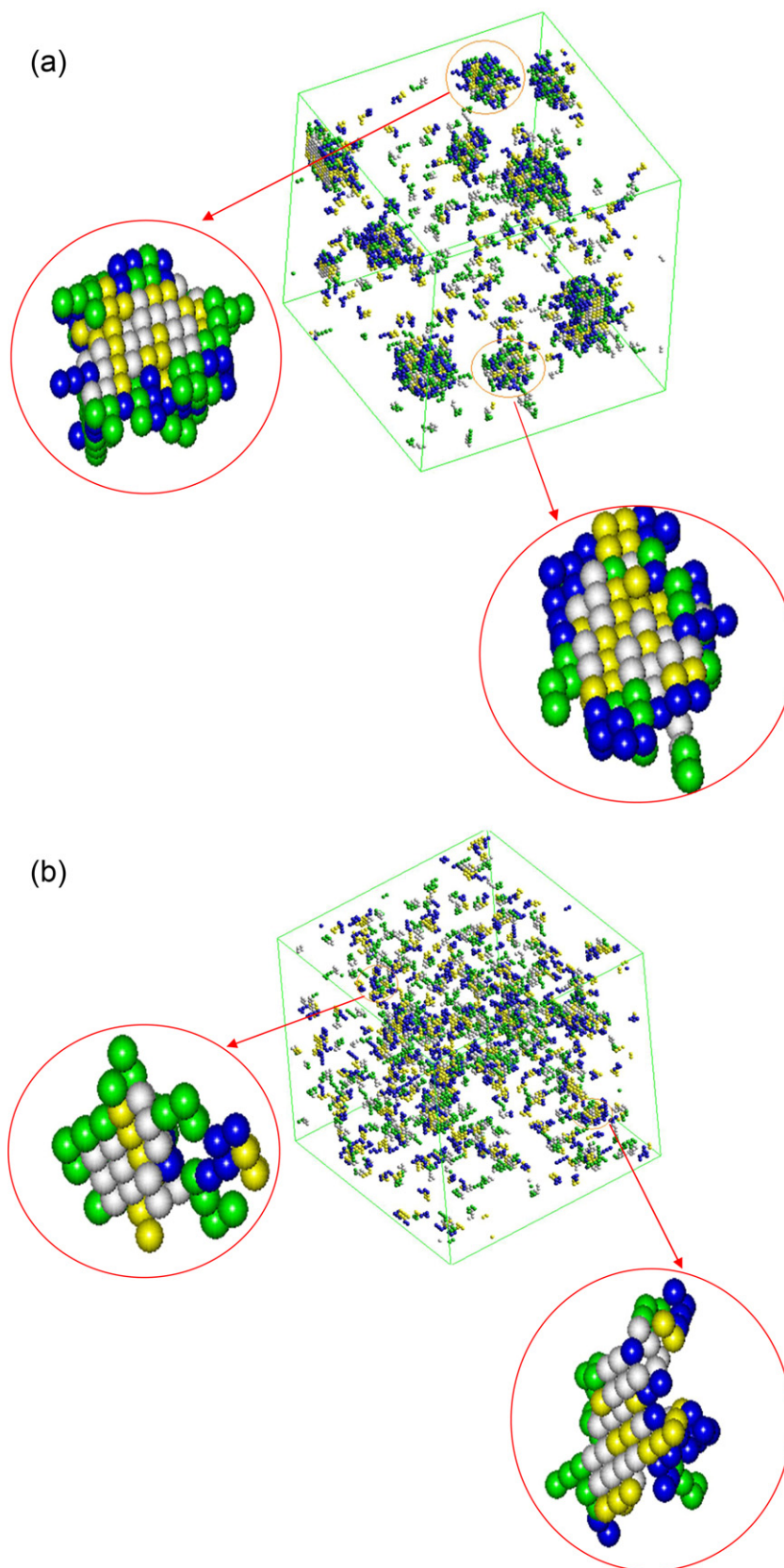


Fig. 2. Typical visualization of a cross-section of a selected micelle with a 50:50 H_4T_4 – A_4B_4 ratio (by volume). When the volume fraction of surfactant was greater than the CMC, (a) $E_{HA} = -0.7$ (b) and $E_{HA} = 0.7$. Blue/green balls represent the heads of surfactants, and yellow/gray balls represent the tails of surfactants.

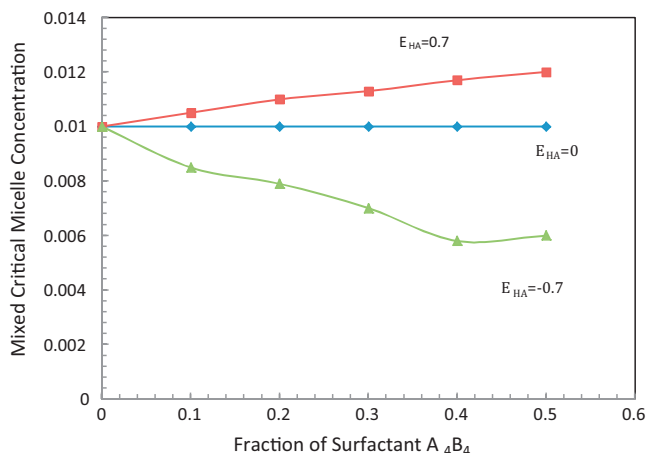


Fig. 3. The mixed-micelle CMC as a function of the concentration of A₄B₄. Each line represents head-head interaction energy. The blue line connecting the diamond symbols represents the ideal mixing of surfactant species.

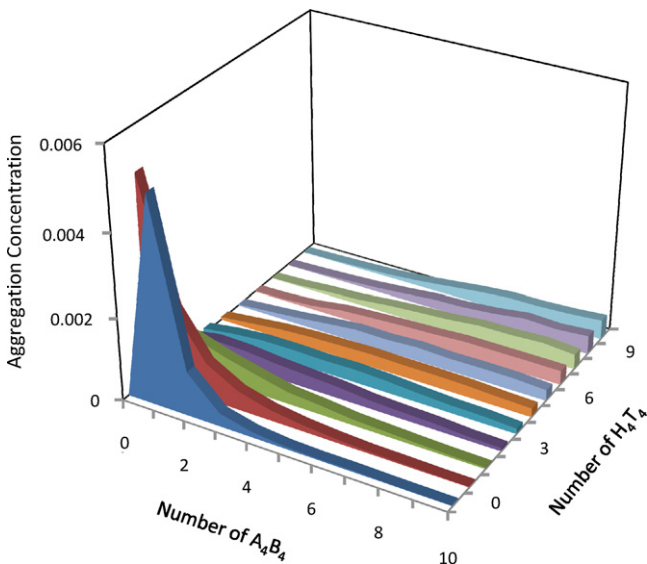


Fig. 4. Volume fraction of a mixed surfactant aggregate as a function of the number of surfactants (H₄T₄ and A₄B₄).

Although some head–head repulsion was observed in the present system, mixed micelles consisted of both surfactants, as shown in Fig. 4. However, the average number of head–head interactions in antagonistic systems was approximately fifteen times lower than that of synergistic systems. Accordingly, in Fig. 2, antagonism was observed in micelles that were rich in A₄B₄ (H₄T₄) and micelles rich in the other surfactant H₄T₄ (A₄B₄). These micelle compositions did not exhibit synergism, which may be due to partial demixing. As shown in Table 2, the CMC decreased with the

addition of a solute, which is in agreement with the simulated results that have been reported in the literature [10,15]. A decrease in the CMC was expected because contaminants stabilize micelles and aid in micellization. When the amount of contaminants was increased, the entropy of the surfactants in the micelle increased; this lowered the CMC and reduced the concentration of free chains. The effect described here has been observed experimentally [9].

3.1. Locus of solubilization

The exact location in the micelle at which solubilization occurred (i.e., the locus of solubilization) was dependent on the nature of the solubilized material. The locus of solubilization is important because it reflects the type of interactions that occur between a surfactant and solubilizate. Solubilization sites have been identified experimentally using X-ray diffraction, ultraviolet spectroscopy, and fluorescence spectroscopy. Based on these studies, solubilization is believed to occur at a number of different sites on a micelle: (1) on the surface of the micelle at the micelle–solvent interface; (2) between hydrophilic head groups; (3) in the palisade layer of the micelle between hydrophilic groups and the first few carbon atoms of hydrophobic groups that comprise the outer core of the micellar interior; (4) deep within the palisade layer; and (5) within the inner core of the micelle. Saturated aliphatic species and other types of nonpolar molecules are solubilized within the core of a micelle, between the ends of hydrophobic groups of surfactant molecules [45]. In addition, the observed density distribution of micellar aggregates and contaminants as a function of the radius of the micelle or the aggregate indicates that the majority of hydrophobic contaminant molecules migrates to the micellar cores [15,16].

The average numbers of solvent–contaminant contacts per solute bead (n_{CS}) and tail–contaminant contacts (n_{CT}) were measured to locate the point of solubilization for binary and single surfactants. A value of n_{CS} near zero indicated that solubilization occurred deep inside the core, whereas larger values indicated that solubilization occurred close to the palisade layer [9]. As shown in Fig. 5, when the volume fraction of surfactant was greater than the CMC of a synergistic system, the n_{CS} of C₃ contaminants in binary surfactant systems was approximately 1.5. As the chain length of the contaminant increased, a reduction in the n_{CS} was detected. The observed changes in the n_{CT} as a function of the volume fraction of surfactant indicate that the average number of contacts between surfactant tails and contaminants increased with an increase in the surfactant concentration and contaminant chain length (Fig. 6). The average number of contaminant–tail contacts for a single contaminant at a constant volume fraction was approximately 1.5. Because contaminants displayed a greater number of tail contacts and fewer solvent contacts, most solubilization occurred near the core of the micelle. The results shown in Figs. 5 and 6 suggest that an increase in the hydrophobicity of the contaminant shifted the locus of solubilization to the core of the micelle. This trend was observed for systems with head–head repulsive interactions. Snapshots from

Table 2
Critical micelle concentration (CMC), interaction parameter (β), and activity coefficients (f_i) of binary surfactant mixtures with a 50:50 H₄T₄–A₄B₄ ratio (by volume). The data were obtained using Rubingh’s method.

System	H ₄ T ₄	H ₄ T ₄ –A ₄ B ₄ ^a			H ₄ T ₄ –A ₄ B ₄ ^b		
	CMC	CMC	β	$f_1 = f_2$	CMC	β	$f_1 = f_2$
–	0.01	0.012	0.7293	1.20	0.006	–2.04	0.60
C ₄	0.009	0.0103	–	–	–	–	–
C ₃	0.0092	0.0108	–	–	0.0053	–	–
C ₂	0.0095	0.011	–	–	0.0055	–	–

^a Repulsive head–head interaction.
^b Attractive head–head interaction.

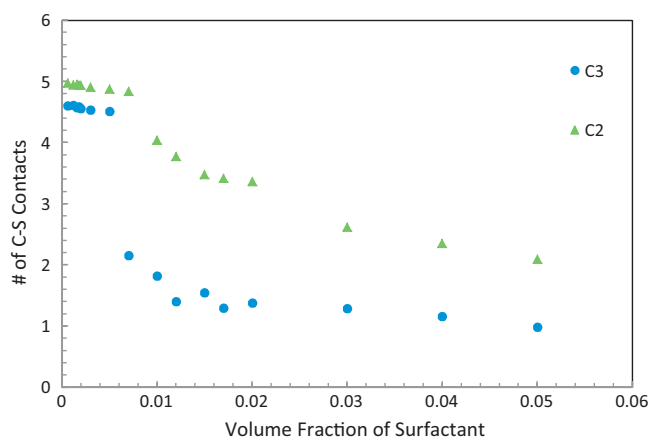


Fig. 5. Simulated number of contaminant–solvent contacts, n_{CS} , as a function of the volume fraction of 50:50 H_4T_4 – A_4B_4 synergistic binary surfactants for a system containing a contaminant volume fraction of 0.001.

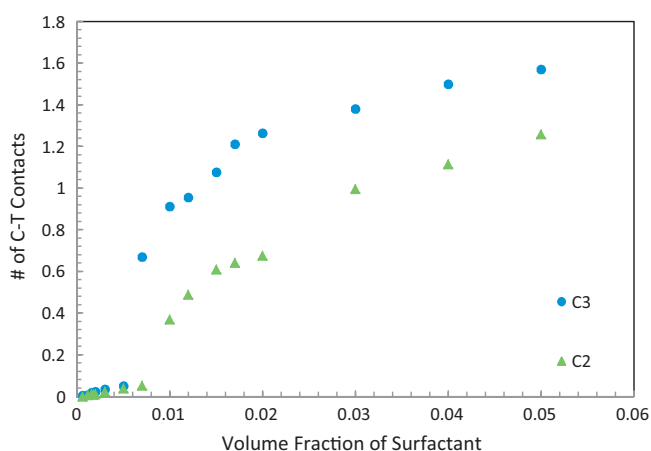


Fig. 6. Simulated number of contaminant–tail contacts, n_{CT} , as a function of the volume fraction of 50:50 H_4T_4 – A_4B_4 synergistic binary surfactants for a system containing a contaminant volume fraction of 0.001.

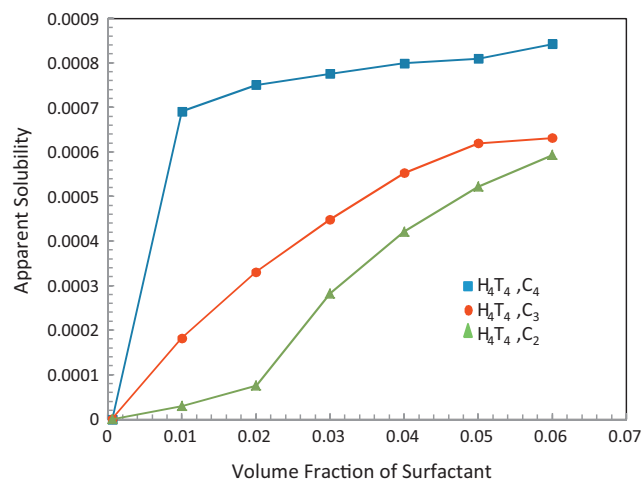


Fig. 8. Enhancement in the water solubility of contaminants by H_4T_4 surfactant solutions.

simulations of synergistic systems shown in Fig. 7 illustrate the loci of contaminant solubilization.

3.2. Enhancement in the water solubility of contaminants by surfactants

The water solubility of contaminants in the presence of H_4T_4 is shown in Fig. 8. The solubility of each contaminant in water was greatly enhanced by the surfactant and increased with an increase in the surfactant concentration due to the solubilization of organic solutes within surfactant micelles. At surfactant concentrations greater than the CMC, the following trend in the water solubility of contaminants was observed: $C_4 > C_3 > C_2$.

The effectiveness of a particular surfactant at solubilizing a given contaminant is known as the molar solubilization ratio (MSR) [46]. The MSR is defined as the number of moles of solubilized compound per number of moles of micellized surfactant and can be calculated by the following equation:

$$MSR = \frac{S - S_{CMC}}{C_S - CMC} \quad (6)$$

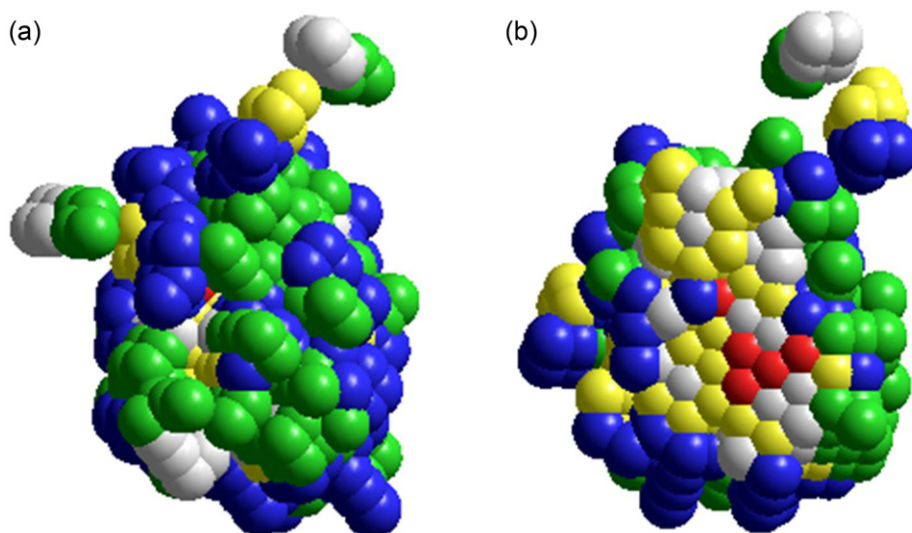


Fig. 7. Snapshots of (a) a micelle, (b) cross-section of micelle with a 50:50 volume fraction of surfactant in a synergistic system. Blue/red balls represent the heads of surfactants, gray/turquoise balls represent the tails of surfactants, and yellow balls represent C_3 contaminants.

where S is the apparent solubility of the contaminant at surfactant volume fractions greater than the CMC, C_S is the surfactant volume fraction at which S is evaluated, and S_{CMC} is the apparent solubility of the contaminant at the CMC.

The effective solubilization can also be expressed in terms of the micelle–water partition coefficient (K_C) of a contaminant between the micelle and the aqueous phase and is defined as [9]:

$$K_C = \frac{C_m}{C_{aq}} \tag{7}$$

where

$$C_m = \frac{\text{Number of Solubilized Contaminants}}{\text{Volume of Aggregates}} \tag{8}$$

and

$$C_m = \frac{\text{Number of Unsolubilized Contaminants}}{\text{Volume of Aqueous Solution}} \tag{9}$$

The $MSRs$ and K_C s of C_4 , C_3 and C_2 contaminants in surfactant solution are shown in Table 3.

Contaminant solubilization caused the micelles to swell, which increased the radius of the micelle and allowed more surfactant chains to aggregate. Thus, larger micelles showed greater solubilization capacities.

3.3. The solubilization of contaminants by mixed-surfactant systems

The ability of synergistic and antagonistic mixed-surfactant systems containing H_4T_4 – A_4B_4 to enhance the water solubility of C_4 , C_3 and C_2 contaminants was investigated, and the results of these simulations were compared to those obtained with single surfactants. The enhancement of the water solubility of contaminants in systems containing H_4T_4 – A_4B_4 / H_4T_4 is shown in Fig. 9. The apparent water solubility of contaminants in synergistic mixed-surfactant solutions was greater than those in single-surfactant solutions at comparable surfactant concentrations. In binary surfactant systems with head–head repulsion interactions, the apparent water solubility of contaminants was nearly equal to that of single surfactants; however, for H_4T_4 , the water solubility of C_2 contaminants was slightly greater.

It was found that for contaminants that were solubilized in the interior of a micelle, the amount of solubilized material increased with an increase in the size of the micelle. It can therefore be postulated that any factor that increases the aggregation number of a micelle will likely increase the solubilization of a contaminant. Mixing surfactants is an efficient method of altering micelle size. For synergistic binary surfactant systems, the aggregation number was greater than that of single-surfactant systems; thus, the solubility of contaminants was higher in synergistic binary surfactant systems. For antagonistic mixed-surfactant systems, head–head repulsion reduced micelle size, and the solubilization of contaminants was relatively low. This result is depicted in Figs. 9 and 10.

To determine the mixing effect of surfactant systems on the solubilization of contaminants, the deviation ratio (R) between the

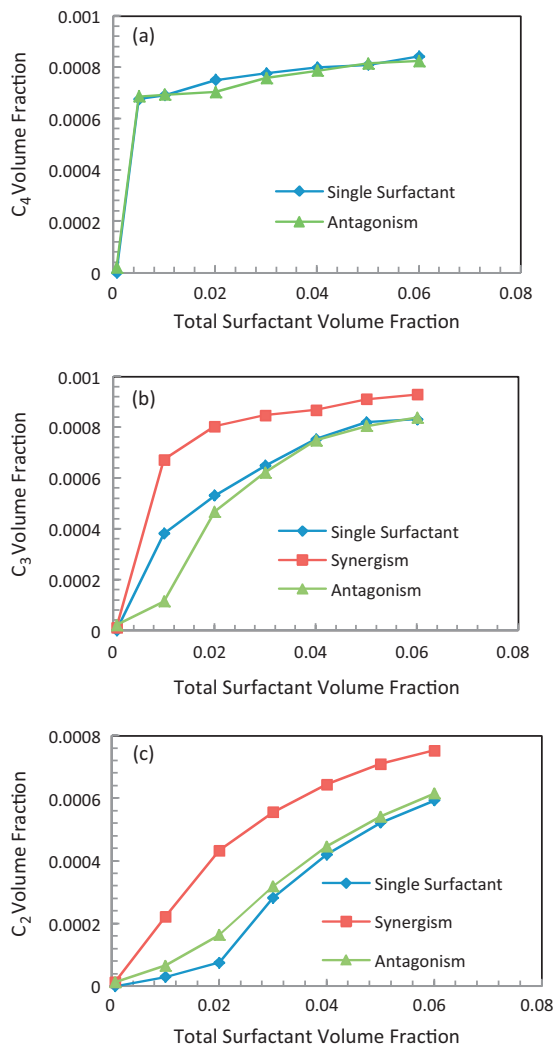


Fig. 9. The solubility of (a) C_4 , (b) C_3 , and (c) C_2 contaminants in single-surfactant and antagonistic and synergistic binary surfactant systems with a surfactant volume fraction of 50:50.

simulated molar solubilization ratio, MSR_{simu} and the ideal value, MSR_{ideal} was calculated by the following equation:

$$R = \frac{MSR_{simu}}{MSR_{ideal}} \tag{10}$$

where $MSR_{ideal} = \sum_i MSR_i \alpha_i$. MSR_i is the simulated MSR of a contaminant in the i th surfactant solution, and α_i is the bulk volume fraction of the contaminant in the mixture. The value of R , which characterizes the nonideality of the mixture with respect to solubilization, is also presented in Table 3.

The surfactants had a positive mixing effect on solubilization when $R > 1$. For both contaminants, the value of R for synergistic H_4T_4 – A_4B_4 surfactant mixtures was greater than 1, indicating that

Table 3
Molar solubilization ratio (MSR), $\ln K_C$ (partition coefficient), deviation ratio (R), and experimental interaction parameter (B) of H_4T_4 and H_4T_4 – A_4B_4 surfactant systems.

System	C_4				C_3				C_2			
	MSR	$\ln K_C$	R	B	MSR	$\ln K_C$	R	B	MSR	$\ln K_C$	R	B
H_4T_4	0.646	5.26	–	–	0.369	2.86	–	–	0.022	0.99	–	–
H_4T_4 – A_4B_4 ^a	0.644	5.17	0.99	3.22	0.171	1.51	0.68	2.83	0.015	0.65	0.46	1.83
H_4T_4 – A_4B_4 ^b	–	–	–	–	0.503	3.69	1.36	5.38	0.078	1.86	3.54	6.76

^a Repulsive head–head interaction.
^b Attractive head–head interaction.

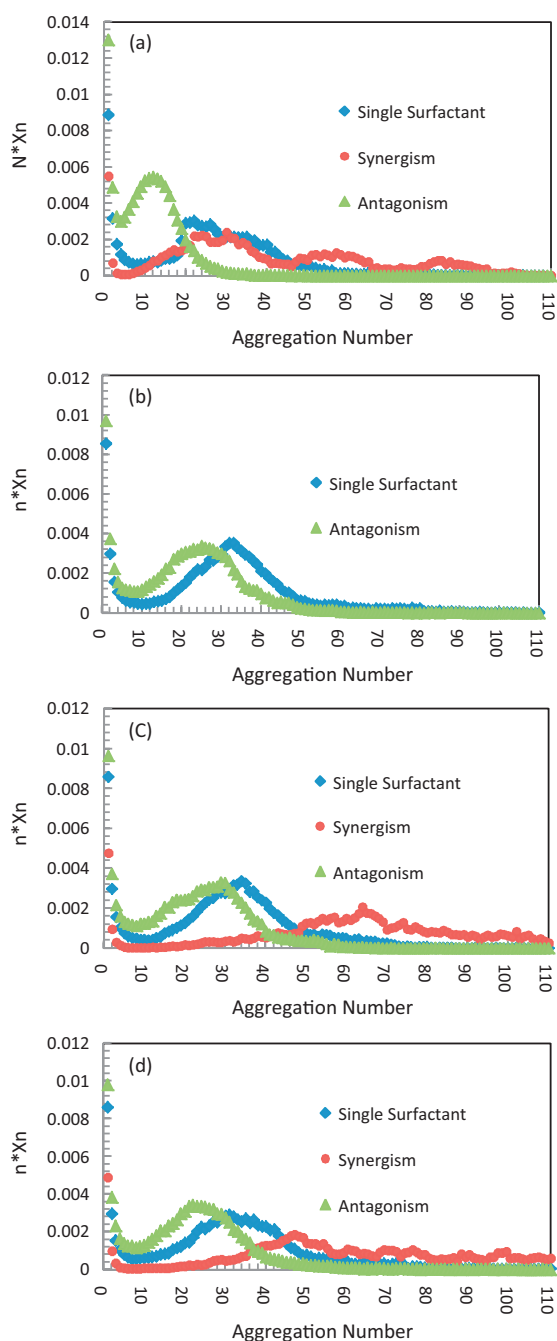


Fig. 10. Aggregate size distribution for (a) C_4 , (b) C_3 , and (c) C_2 contaminants in single and 50:50 antagonistic and synergistic binary surfactant systems at surfactant volume fractions greater than the CMC.

these mixed-surfactant systems had a positive effect on the solubilization of contaminants. The following trend was observed for both the R values of the contaminants and the effect of mixed surfactants on solubilization: $C_2 > C_3$. In the mixed binary H_4T_4 – A_4B_4 system, ideal mixing was similar to that of a single-surfactant system. In single-surfactant systems, C_2 contaminants displayed low solubility. Synergistic surfactant mixing increased solubilization for both contaminants, and the difference in solubilization capacity between mixed binary- and single-surfactant systems was greatest for C_2 contaminants. However, in H_4T_4 – A_4B_4 binary systems with head–head repulsion, the R value for C_4 contaminants was equal to 1, and the effect of mixing was poor. For C_3 and C_2 contaminants in the same binary surfactant systems, the value of R was less than 1.

Treiner et al. [47–50] used regular solution approximation (RSA) to show that the partition coefficient of a neutral organic solute between micellar and aqueous phases in a mixed binary surfactant solution can be represented by the following relationship:

$$\ln K_{C12} = X_1^M \ln K_{C1} + (1 - X_1^M) \ln K_{C2} + BX_1^M(1 - X_1^M) \quad (11)$$

where K_{C12} , K_{C1} , and K_{C2} are the micelle–water partition coefficients of the solute in mixed binary- and single-surfactant systems, respectively, and X_1^M is the volume fraction of surfactant (1) in the micelle. B has the same origin as β in Eq. (4) and does not consider contaminant–contaminant or contaminant–solvent interactions. Thus, if $B = 0$, surfactant mixing is not expected to affect the partitioning of the contaminant. If $B > 0$ ($B < 0$), the value of K_{C12} for a mixed binary surfactant system is larger (smaller) than the predicted value of the ideal mixing rule. According to Zhou et al. [2] B is an empirical parameter that incorporates surfactant–surfactant (in the case of β) and surfactant–contaminant interactions.

Table 3 lists the values of B that were determined by evaluating the least-squares fit of the simulated $\ln K_{C12}$ values (Eq. (11)) of binary surfactant mixtures with attractive and repulsive head–head interactions. For all of the surfactant mixtures, the value of B was positive. In the present study, the values of B and β were not related because B depends on surfactant–surfactant and surfactant–contaminant interactions in mixed micelles.

The B values show that there was a positive mixing effect of A_4B_4 with H_4T_4 in the presence of attractive head–head interactions on the partitioning of C_3 and C_2 contaminants ($B > 1$). These results were consistent with the observed positive deviation in the $MSRs$ from those of an ideal mixture ($R > 1$), which can be used to interpret the mixing effect of A_4B_4 with H_4T_4 on the solubilization of contaminants.

There was a positive mixing effect of A_4B_4 and H_4T_4 in the presence of repulsive head–head interactions on the partitioning of contaminants in H_4T_4 – A_4B_4 mixed systems, as indicated by positive B values. These results conflict with the slight negative deviations in the MSR values from those of an ideal mixture (R was slightly less than 1). Similar contradictory results have also been obtained in studies [3,51,52] on the solubilization of organic compounds in mixed-surfactant systems. A comprehensive analysis of similar mixed-surfactant systems showed that during the micelle formation, contaminant solubilization leads to significant changes in micelle structures like formation of large micelles or partial demixing. Due to the presence of head–head repulsion interactions, large micelles were not formed. Thus, partial demixing occurred in this system, resulting in the observed discrepancy between B and R values.

In systems with attraction between head groups, at a constant concentration of A_4B_4 in water, the CMC of the H_4T_4 surfactant decreased sharply due to the formation of mixed micelles. For example, the CMC decreased from 0.01 to 0.006 in solutions containing a surfactant volume ratio of 50:50. In addition, the K_C (or MSR) values of mixed-surfactant systems may increase. Synergism was attributed to an increase in the MSR or the K_C of the contaminant between the micelle and the aqueous phase and/or a decrease in the CMC of surfactant solutions. For synergistic H_4T_4 – A_4B_4 mixed-surfactant solutions, an increase in $\ln K_{C12}$ was observed as the CMC decreased (Table 3).

In agreement with previous results [44], it was found in this study that head–head interaction energies of equal magnitude but opposite sign do not have the same effects on the mixed-system CMC (Fig. 11). When head–head repulsion occurred, the activity coefficients obtained from simulated data approached one, and β approached zero (Table 2). Hence, this system deviated from ideal behavior, and a slight increase in the CMC was observed. Surprisingly, as shown in Table 3, the value of K_C (MSR) for C_4 , C_3 and

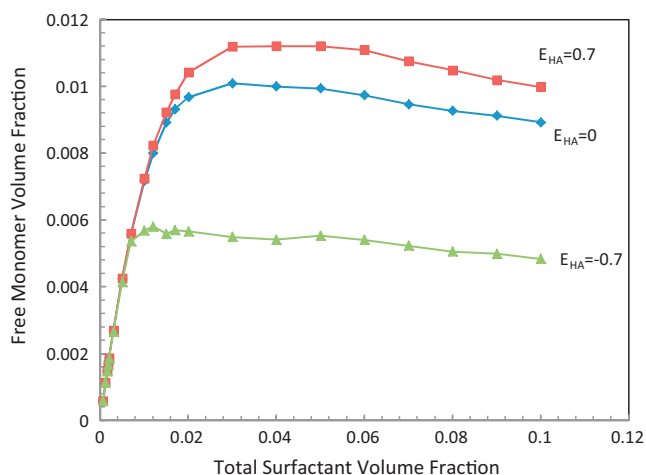


Fig. 11. Concentration of free monomer as a function of the total surfactant concentration for a mixture with a 50:50 volume fraction of H_4T_4 and A_4B_4 and attractive, ideal, and repulsive interactions between head groups.

C_2 contaminants in mixed systems with head–head repulsion was slightly lower than that observed for single H_4T_4 surfactants.

4. Conclusions

In the present study, the solubilization capacities of H_4T_4 and mixed H_4T_4 – A_4B_4 surfactant solutions with repulsive and attractive head–head interactions toward C_4 , C_3 , and C_2 contaminants were determined by conducting MC simulations. The solubilization capacity was quantified in terms of the MSR and $\ln K_C$. In general, the surfactant effect on the solubilization of contaminants displayed the following trend: $C_4 > C_3 > C_2$.

In binary systems containing H_4T_4 – A_4B_4 surfactants with attractive head–head interactions, the solubilization capacity of H_4T_4 was enhanced when A_4B_4 was added. The effect of surfactant mixing was greater on C_2 contaminants than on C_3 contaminants. For systems with repulsive and attractive interactions between head groups, the solubilization capacity increased with an increase in the hydrophobic character of the contaminant.

The results of the present study provide insight on the applicability of Rubingh's regular solution theory (RST) for evaluation of the solubilizing efficiency of binary surfactant systems. With RST, the experimental interaction parameter (B) of binary surfactant systems is predicted using least-squares fitting. The analysis yielded acceptable results, and valuable information was obtained to aid in the selection of appropriate mixed surfactants for the SER of contaminated solutions.

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References

- [1] L. Zhu, S. Feng, Analysis and structure prediction of chlorinated polycyclic aromatic hydrocarbons released from combustion of polyvinylchloride, *Chemosphere* 53 (2003) 459–503.
- [2] W. Zhou, L. Zhu, Solubilization of polycyclic aromatic hydrocarbons by anionic–nonionic mixed surfactant, *Colloids Surf. A: Physicochem. Eng. Aspects* 255 (2005) 145–152.
- [3] Kabir-ud-Dina, M. Shafia, P.A. Bhatb, A.A. Darb, Solubilization capabilities of mixtures of cationic Gemini surfactant with conventional cationic, nonionic

- and anionic surfactants towards polycyclic aromatic hydrocarbons, *J. Hazard. Mater.* 167 (2009) 575–581.
- [4] A.A. Dar, G.M. Rather, A.R. Das, Mixed micelle formation and solubilization behavior toward polycyclic aromatic hydrocarbons of binary and ternary cationic–nonionic surfactant mixtures, *J. Phys. Chem. B* 111 (2007) 3122–3132.
- [5] L.Z. Zhu, C.T. Chiou, Water solubility enhancements of pyrene by single and mixed surfactant solutions, *J. Environ. Sci. (China)* 13 (2001) 491–496.
- [6] W. Zhou, L. Zhu, Solubilization of pyrene by anionic–nonionic mixed surfactants, *J. Hazard. Mater.* 109 (2004) 213–220.
- [7] S. Paria, P.K. Yuet, Solubilization of naphthalene by pure and mixed surfactants, *Ind Eng Chem Res* 45 (2006) 3552–3558.
- [8] R.G. Larson, Monte Carlo lattice simulation of amphiphilic systems in two and three dimensions, *J. Chem. Phys.* 89 (1988) 1642–1651.
- [9] S.K. Talsania, Y. Wang, R. Rajagopalan, K.K. Mohanty, Monte Carlo simulations for micellar encapsulation, *J. Colloid Interface Sci.* 190 (1997) 92–103.
- [10] S.K. Talsania, L.A. Rodríguez-Guadarrama, K.K. Mohanty, Phase Behavior, Solubilization in surfactant–solvent systems by Monte Carlo simulations, *Langmuir* 14 (1998) 2684–2692.
- [11] R.G. Larson, Monte Carlo simulation of model amphiphile–oil–water systems, *J. Chem. Phys.* 83 (1985) 2411–2421.
- [12] R.G. Larson, Self assembly of surfactant liquid crystalline phases by Monte Carlo simulation, *J. Chem. Phys.* 91 (1989) 2479–2489.
- [13] R.G. Larson, Monte Carlo simulation of microstructural transitions in surfactant systems, *J. Chem. Phys.* 96 (1992) 7904–7919.
- [14] R.G. Larson, Simulation of lamellar phase transitions in block copolymers, *Macromolecules* 27 (1994) 4198–4203.
- [15] S.Y. Kim, A.Z. Panagiotopoulos, Ternary oil–water–amphiphile systems: self-assembly and phase equilibria, *Mol. Phys.* 100 (2002) 2213–2220.
- [16] M. Al-Shannag, M. Matouq, Z. Al-Anber, Simulation of surfactant–oil–solvent ternary system: mean field theory, *Asia J. Chem.* 20 (2008) 4021–4030.
- [17] J.G. Weers, Solubilization in mixed micelles, *JAOCs* 67 (1990) 340–345.
- [18] S. Paria, P.K. Yuet, Solubilization of naphthalene by pure and mixed surfactants, *Ind. Eng. Chem. Res.* 45 (2006) 3552–3558.
- [19] W.M. Gelbart, A. BenShaul, The new science of complex fluids, *J. Phys. Chem.* 100 (1996) 13169–13189.
- [20] J.C. Shelley, M.Y. Shelley, Computer simulation of surfactant solutions, *Curr. Opin. Colloid Interface Sci.* 5 (2000) 101–110.
- [21] D.W. Cheong, A.Z. Panagiotopoulos, Monte Carlo simulations of micellization in model ionic surfactants: application to sodium dodecyl sulfate, *Langmuir* 22 (2006) 4076–4083.
- [22] D. Viduna, A. Milchev, K. Binder, Monte Carlo simulation of micelle formation in block copolymer solutions, *Macromol. Theory Simul.* 7 (1998) 649–658.
- [23] A. Milchev, A. Bhattacharya, K. Binder, Formation of block copolymer micelles in solution: a Monte Carlo study of chain length dependence, *Macromolecules* 34 (2001) 1881–1893.
- [24] B. Smit, K. Esselink, P. Hilbers, N.v. Os, Computer simulations of surfactant self-assembly, *Langmuir* 9 (1993) 9–11.
- [25] F.v. Gottberg, K. Smith, T. Hatton, Stochastic dynamics simulation of surfactant self-assembly, *J. Chem. Phys.* 106 (1997) 9850–9858.
- [26] C.M. Wijmans, P. Linse, Modeling of nonionic micelles, *Langmuir* 11 (1995) 3748–3756.
- [27] S. Karaborni, N.v. Os, K. Esselink, P. Hilbers, Molecular dynamics simulations of oil solubilization in surfactant solutions, *Langmuir* 9 (1993) 1175–1178.
- [28] B.J. Palmer, J. Liu, Effects of solute–surfactant interactions on micelle formation in surfactant solutions, *Langmuir* 12 (1996) 6015–6021.
- [29] P.H. Nelson, G.C. Rutledge, T.A. Hatton, On the size and shape of self-assembled micelles, *J. Chem. Phys.* 107 (1997) 10777–10782.
- [30] A.Z. Panagiotopoulos, M.A. Floriano, S.K. Kumar, Micellization, Phase separation of diblock and triblock model surfactants, *Langmuir* 18 (2002) 2940–2948.
- [31] A. Bernardes, V. Henriques, P. Bisch, Monte Carlo simulation of a lattice model for micelle formation, *J. Chem. Phys.* 101 (1994) 645–651.
- [32] A.D. Mackie, A.Z. Panagiotopoulos, I. Szleifer, Aggregation behavior of a lattice model for amphiphiles, *Langmuir* 13 (1997) 5022–5031.
- [33] 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.
- [34] M.A. Floriano, E. Caponetti, A.Z. Panagiotopoulos, Micellization in model surfactant systems, *Langmuir* 15 (1999) 3143–3151.
- [35] C.M. Care, Cluster size distribution in a Monte Carlo simulation of the micellar phase of an amphiphile and solvent mixture, *J. Chem. Soc., Faraday Trans.* 83 (1987) 2905–2912.
- [36] 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.
- [37] 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.
- [38] R.G. Larson, M. Zaldivar, Lattice Monte Carlo simulations of dilute mixed micelles, *Langmuir* 19 (2003) 10434–10442.
- [39] 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.
- [40] M. Zaldivar, R.G. Larson, Lattice Monte Carlo simulations of dilute mixed micelles, *Langmuir* 19 (2003) 10434–10442.
- [41] 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.

- [42] J.H. Clint, Micellization of mixed nonionic surface active agents, *J. Chem. Soc., Faraday Trans.* 171 (1975) 1327–1334.
- [43] P.M. Holland, D.N. Rubingh, Nonideal multicomponent mixed micelle model, *J. Phys. Chem.* 87 (1983) 1984–1990.
- [44] 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.
- [45] M.J. Rosen, *Surfactant and Interfacial Phenomena*, John Wiley & Sons, New York, 1989.
- [46] D.A. Edwards, R.G. Luthy, Z. Liu, Solubilization of polycyclic aromatic hydrocarbons in micellar nonionic surfactant solutions, *Environ. Sci. Technol.* 25 (1991) 127–133.
- [47] C. Treiner, M. Nortz, C. Vaution, F. Puisieux, Micellar solubilization in aqueous binary surfactant systems: Barbituric acids in mixed anionic + nonionic or cationic + nonionic mixtures, *J. Colloid Interface Sci.* 125 (1988) 261–270.
- [48] C. Treiner, M. Nortz, C. Vaution, Micellar solubilization in strongly interacting binary surfactant systems, *Langmuir* 6 (1990) 1211–1216.
- [49] C. Treiner, A.A. Khodja, M. Fromon, Micellar solubilization of 1-pentanol in binary surfactant solutions: a regular solution approach, *Langmuir* 3 (1987) 729–735.
- [50] C. Treiner, The thermodynamics of micellar solubilization of neutral solutes in aqueous binary surfactant systems, *Chem. Soc. Rev.* 23 (1994) 349–356.
- [51] S. Sun, W.P. Inskeep, S.A. Boyd, Sorption of nonionic organic compounds in soil–water systems containing a micelle-forming surfactant, *Environ. Sci. Technol.* 29 (1995) 903–913.
- [52] Y. Tokuota, H. Uchiyama, M. Abe, S.D. Christian, Solubilization of some synthetic perfumes by anionic–nonionic mixed surfactant systems, *J. Phys. Chem.* 98 (1994) 6167–6171.