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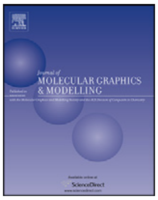

Monte Carlo simulation of binary surfactant/contaminant/water systems

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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.

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 T_4) in the presence of H_4T_4 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–solubilizate 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 continuum [22–28] and lattice [29–36] models have been performed.

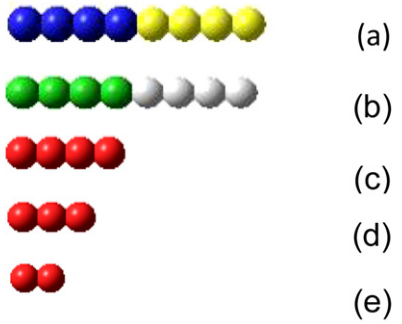

Fig. 1. Schematic diagram of (a) H_4T_4 surfactant, blue balls indicate head groups on the surfactant, and yellow balls indicate tail groups, (b) A_4B_4 surfactant, green balls indicate head groups on the surfactant, and gray balls indicate tail groups, (c–e) C_4, C_3, and C_2 contaminants respectively. 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.)

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, or B.

The total energy of the system divided by k_BT is:

$$E_{Total} = \sum\nolimits_{mn} N_{mn}E_{mn} \tag{1}$$

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_BT), 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.