MATERIALS AND INTERFACES

Solubilization of Naphthalene by Pure and Mixed Surfactants

Santanu Paria* and Pak K. Yuet

Department of Chemical Engineering, Dalhousie University, P. O. Box 1000, Halifax, NS, Canada B3J 2X4

Surfactant-enhanced remediation technology has shown promising potential for removing residual organics from contaminated soils and groundwater. Using a homologous series of cationic surfactants, alkylpyridinium bromide, it was found that the molar solubilization ratio (MSR) for naphthalene decreases with decreasing carbon number in the hydrophobic tail. In contrast, with nonylphenyl ethoxylates (nonionic surfactants), the MSR for naphthalene does not show appreciable changes with varying number of ethylene oxide groups in the hydrophilic head. MSR values for naphthalene in the presence of ionic surfactants with similar tail length depend on the charge of the headgroup. In addition, the behavior of naphthalene solubilization using cationic–nonionic and anionic–nonionic surfactant mixtures deviates considerably from that of ideal mixing. More interestingly, however, results from batch and column experiments reveal that the interactions between surfactant molecules and sand surfaces, particularly surfactant adsorption, play a critical role in determining the organics removal efficiency from sand matrixes.

Polycyclic aromatic hydrocarbons (PAHs) such as naphthalene, anthracene, and phenanthrene are hydrophobic pollutants found in contaminated soils and groundwater at many sites, particularly at coal storage, coke oven plants, and areas of coal tar spillage. Because of their low solubility in water, the presence of PAH in the soil matrix constitutes a long-term source of groundwater contamination. Improvement of desorption and removal efficiency of these organics from soil is therefore essential to the remediation of contaminated soils and groundwater.

Surfactant-enhanced remediation (SER) has been proposed as a promising technology for removing residual organics from contaminated aquifers.[1,2] This technology is based primarily on two processes: (i) micellar solubilization and (ii) mobilization of entrapped nonaqueous phase liquid (NAPL) due to reduction of interfacial tension. Below the surfactant's critical micelle concentration (CMC), surfactants exist as monomers and have only minimal effects on the aqueous solubility of organics.[3,4] Micellar solubilization occurs when the surfactant concentration exceeds the CMC, where the aqueous solubility of organics is enhanced by the incorporation of hydrophobic molecules into surfactant micelles.[3–5] The extent of micellar solubilization depends on many factors, including surfactant structure, aggregation number, micelle geometry, ionic strength, temperature, and the size and chemistry of the solubilizate.[6] To quantify the effectiveness of a surfactant in solubilizing a given solubilizate, the molar solubilization ratio, MSR, is defined as the number of moles of organic compound solubilized per mole of surfactant added to the solution.[6] The MSR is calculated as

$$\text{MSR} = (S - S_{\text{CMC}})/(C_{\text{S}} - \text{CMC}) \tag{1}$$

where S is the apparent solubility of organic compound at surfactant concentration C_{S} ($C_{\text{S}} > \text{CMC}$) and S_{CMC} is the apparent solubility of the organic compound at the CMC. Thus,

when solute concentration is plotted against surfactant concentration above the CMC, MSR can be determined from the slope of the linearly fitted line.

The solubilization of PAH by single surfactant systems has been studied extensively.[3,7–15] These studies mainly concentrated on the solubilizing power of different synthetic surfactants and biosurfactants. The study reported by Bernardez and Ghosal[16] shows resonance π-electrons in the PAHs form weak bonds with the nonionic surfactant headgroups and thus solubilized in the shell region of the micelle. Recently, the solubilization of PAH by anionic–nonionic surfactant mixtures has been studied,[17–19] showing positive deviation of the MSR in mixed surfactant systems from the ideal mixture. The theoretical study reported by Ko and Schlautman[20] found that the elution of hydrophobic organic compounds (HOC) from a column partitioned to sorbed surfactants requires a long remediation time due to relatively strong affinity of surfactant sorption to soil minerals as well as slow HOC desorption rates.

In our previous publication[23] we have reported the adsorption of alkylpyridinium bromide surfactants of the sand–water interface, since adsorption is an important parameter in the surfactant-enhanced remediation processes and the mechanism of adsorption can improve the understanding of the process as well. In this paper, we report the solubilization aspect of naphthalene by single- and mixed-surfactant systems. More specifically, we focus on (i) the effects of hydrophobic (tail) and hydrophilic (head) chain length of two homologous series of surfactants on the solubilization of naphthalene, (ii) the difference between cationic and anionic surfactants with the same tail length, and (iii) the effects of tail length of cationic surfactants in the presence of a nonionic surfactant. In addition, we have also attempted to correlate batch solubilization data with naphthalene removal from a sand column, which highlights the importance of surfactant adsorption at sand–water surfaces. The main objectives of this study are (i) to elucidate the relation between surfactant molecular structure and its solubilization capacity of polycyclic aromatic hydrocarbons and (ii) to correlate results from batch solubilization experiments with organics

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* Corresponding author. E-mail: santanuparia@yahoo.com.
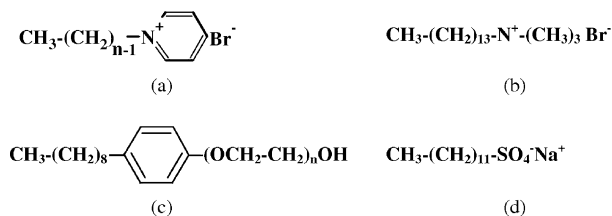
Figure 1. Structures of surfactant molecules used in this study: (a) alkylpyridinium bromide (C_jPB), (b) tetradecyltrimethylammonium bromide (C_{14}TAB), (c) nonylphenyl ethoxylates (NP-n), and (d) sodium dodecyl sulfate (SDS).

removal from a sand-packed column. The findings of this study may be useful in the application of removal of PAHs from the soil matrix using surfactants.

2. Materials and Methods

The cationic surfactants cetylpyridinium bromide (C_{16}PB) and tetradecyltrimethylammonium bromide (C_{14}TAB) were obtained from Aldrich Chemicals and were used as received. Tetradecylpyridinium bromide (C_{14}PB), dodecylpyridinium bromide (C_{12}PB), and decylpyridinium bromide (C_{10}PB) were synthesized in our laboratory and were recrystallized five times from acetone before use. A series of nonionic nonylphenyl ethoxylate (4-$C_9H_{19}C_6H_4(OCH_2CH_2)_nOH$) surfactants, NP-9 (Igepal CO 630, $n = 9$), NP-12 (Igepal CO 720, $n = 12$), and NP-40 (Igepal CO 890, $n = 40$), were obtained from Aldrich, and NP-15 ($n = 15$) was obtained from Nikko Chemicals; all were used as received. The anionic surfactant, ultrapure sodium dodecyl sulfate (SDS) was obtained from J. T. Baker, Japan, and was used as received. The structures of the surfactants used in this study are shown in Figure 1. Naphthalene was obtained from Aldrich. The critical micelle concentration (CMC) of each surfactant was determined by surface-tension measurement. Ultrapure water of 18.2 MΩ resistivity (Barnstead International) was used in all experiments. The sand used for column studies was obtained from Bonar Inc., Canada. The sand density was determined experimentally to be 2.6 g/cm³. The sand surface area is 0.3 m²/g, determined by the methylene blue adsorption method.[21] The pH_{PZC} (point of zero charge) of sand is reported as ~2, and the surface charge becomes more negative up to pH ~11.[22] It is also reported that the surface charge is ~−40 mV at pH 7.

2.1. Sand Sieving and Cleaning. The sand was sieved in a sieve shaker, and the 212−500 μm sized sand was taken for the experiments. The sand was cleaned prior to each experiment according to the procedure given by our previous publication.[23]

2.2. Experimental Measurements. For the batch solubilization experiments, a stock solution of naphthalene (400 mM) was prepared by dissolving naphthalene in pure methanol. Methanol is preferred over higher alcohols because of its negligible effect on solubilization and CMC values.[24] For example, Edwards et al.[3] reported no difference in PAH solubility with or without 1% methanol by volume. For each experiment, 0.185 mL of the stock naphthalene solution was added to 20 mL of surfactant solution in a 25 mL glass vial. The concentration and volume of the stock naphthalene solution used in each experiment was selected to (i) keep the methanol concentration in the test solution to below 1 vol % and (ii) produce an excess of naphthalene in the test solution. The vial was sealed with a screw cap fitted with Teflon-lined septum to prevent loss of naphthalene from water. Kinetics of solubilization show there was no change in the solubility of naphthalene after 24 h, so for this study 24 h equilibrium time was taken.
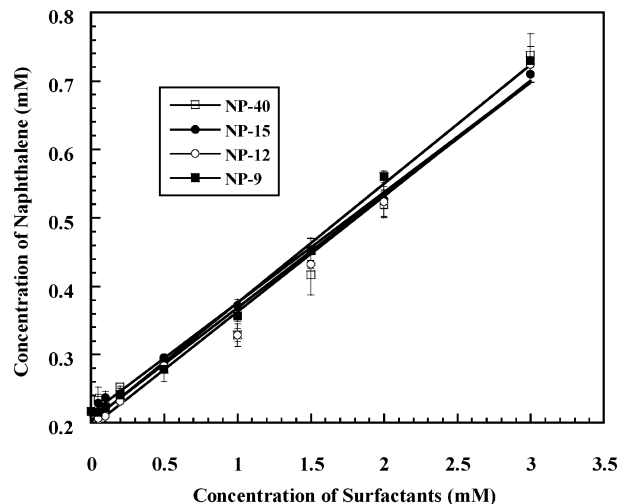
Figure 2. Solubilization of naphthalene in the presence of nonylphenyl ethoxylate surfactants (NP-n). n denotes the number of ethylene oxide groups.

After a 24 h equilibration period and subsequent centrifugation at 5000 rpm for 30 min to separate the suspended solids, the concentration of naphthalene was determined by measuring the absorbance at 275 nm wavelength with quartz glass cells of 10 mm path length (Shimadzu spectrophotometer, model UV-1700). An appropriate aliquot of the supernatant was diluted to at least 80% (v/v) methanol prior to analysis.[11] Note that the surfactant concentration was kept the same in both the reference and the measurement cells to minimize the effect of surfactant on UV absorbance for both batch and column experiments. The solubility of naphthalene at each surfactant concentration was calculated as the mean of the triplicate samples. The surface tension was measured by the Wilhelmy plate method using a Kruss K100 tensiometer. The pH values of the experimental solutions were found to be the same as that of pure water (~6.8−7). All experiments were performed at 23 °C.

The column experiments were conducted using a glass column with inner threaded poly(tetrafluoroethylene) (PTFE) caps shielded with O rings at both ends. The column is 30 cm in length and 1.5 cm in diameter. The porosity or void fraction, v_p, of the sand bed was 0.42, calculated according to the following relation,

$$v_p = \frac{V - (m/\rho)}{V} \tag{2}$$

where V is the empty column volume, m is mass of the sand used, and ρ is the sand density. For each set of experiments, 1.5 mL of the 400 mM naphthalene in methanol solution was added to the sand and kept for 30 min at room temperature to evaporate the methanol. The sand was then mixed thoroughly to break the agglomerates and packed into the column. A constant water flow rate of 3.3 mL/min, controlled using a peristaltic pump (Masterflex from Cole Parmer), was used. The effluent from the column was collected in a glass tube at a particular time interval, and only the concentration of naphthalene was analyzed by UV absorbance after centrifugation.

3. Results and Discussion

3.1. Effect of Hydrophilic Chain Length. The solubility of naphthalene in water was measured in this study to be 2.17 × 10^{-4} mol/L, which is comparable to the reported value of 2.44 × 10^{-4} mol/L.[18] Figure 2 depicts the solubility of naphthalene

Table 1. Values of Critical Micelle Concentration (CMC), Molar Solubilization Ratio (MSR), and Partition Coefficient (K_m) for Different Nonionic Surfactants[a]

surfactant	CMC (mM)	MSR	log K_m
NP-9	0.05	0.179 (0.998)	4.582
NP-12	0.07	0.175 (0.995)	4.574
NP-15	0.09	0.164 (0.999)	4.550
NP-40	0.15–0.2	0.173 (0.987)	4.550
C_{14}PB	3.5	0.198 (0.999)	4.614
C_{12}PB	11	0.135 (0.997)	4.315
C_{10}PB	40	0.100 (0.992)	4.226
C_{14}TAB	3	0.202 (0.999)	4.589
SDS	8.5	0.073 (0.999)	4.190

[a] The correlation coefficient of the linear fit for determining the MSR is given in parentheses. The CMC was determined using surface-tension measurements.

in aqueous solutions of NP-9, NP-12, NP-15, and NP-40. Recall that all the NP surfactants have the same hydrophobic tail but different poly(ethylene oxide) (EO) heads (see Figure 1). No appreciable difference in naphthalene solubility can be observed in Figure 2, even though the numbers of EO groups range from 9 to 40. As shown in Table 1, the MSRs for the four NP surfactants are very similar, which indicates that the length of the hydrophilic head of nonylphenyl ethoxylate surfactants is not important in determining the batch solubilization of naphthalene.

In addition to MSR, the effectiveness of solubilization can also be expressed in terms of the partition coefficient, K_m, of the organic compound between micelles and the aqueous phase. The partition coefficient can be written as[3]

$$K_m = X_m/X_a \qquad (3)$$

where X_m and X_a are the mole fractions of solute in micelles and the aqueous phase, respectively. The value of X_m can be calculated as $X_m = MSR/(1+ MSR)$, and X_a can be expressed as $X_a = S_{CMC}V_w$, where $V_w = 0.01805$ L/mol is the molar volume of water. Consequently, eq 3 can be rearranged to yield

$$K_m = \frac{MSR}{S_{CMC}V_w(1 + MSR)} \qquad (4)$$

The K_m values for the four NP surfactants are also listed in Table 1.

3.2. Effect of Hydrophobic Chain Length. Figure 3a depicts the solubilization of naphthalene in solutions of three cationic surfactants (C_jPB; j = 14, 12, 10) of different hydrophobic tail lengths. As shown in the figure, with decreasing tail length, the CMC increases and the abrupt increase in solubilization occurs at a higher concentration. Table 1 lists the CMCs, the MSRs calculated from the slope of the fitted line above the CMC, and K_m for the three C_nPB surfactants. Note that both the MSR and K_m decrease with decreasing hydrophobic chain length. More specifically, as shown in Figure 3b, the MSR increases linearly with the hydrophobic chain length. This increase in solubility is most likely due to the higher affinity of naphthalene toward long-chain hydrocarbon. In addition, long-chain surfactants also have larger micellar aggregation numbers, which provide a larger micellar core region for solubilizing organic molecules.

Figure 4a shows the solubilization of naphthalene by two cationic surfactants, C_{14}PB and C_{14}TAB. Although the head-groups of these two surfactants are different (see Figure 1), the areas occupied per molecule are nearly the same (60 Å[2] for C_{14}PB and 61 Å[2] for C_{14}TAB at 30 °C).[25] Consequently, since
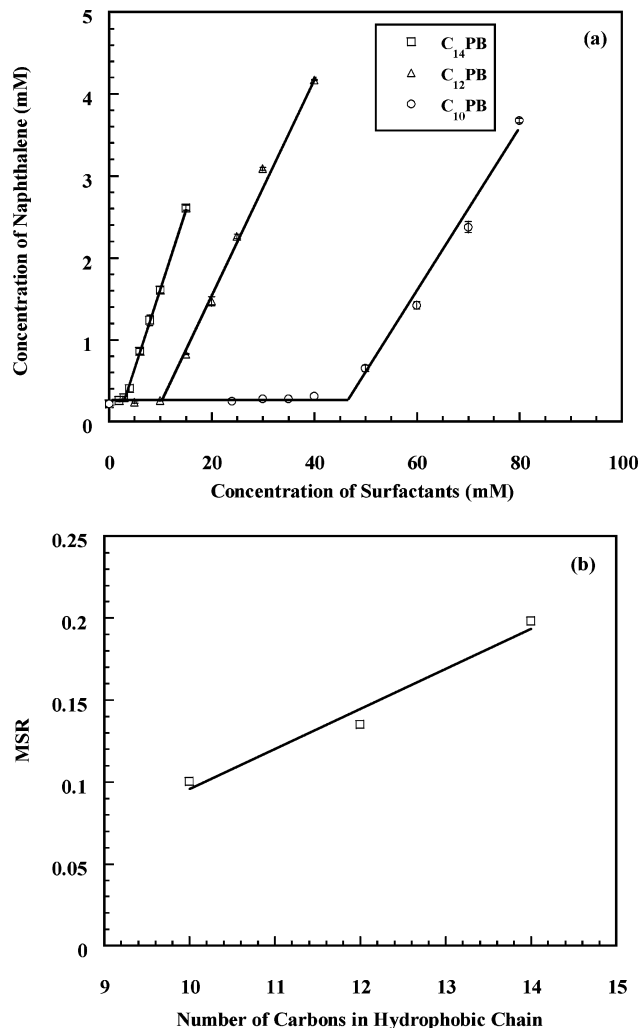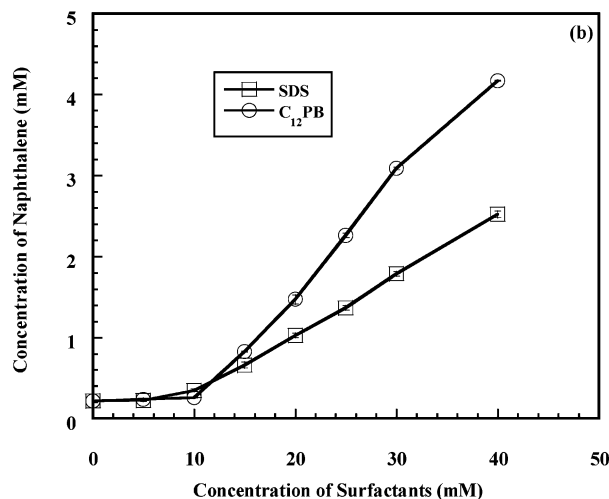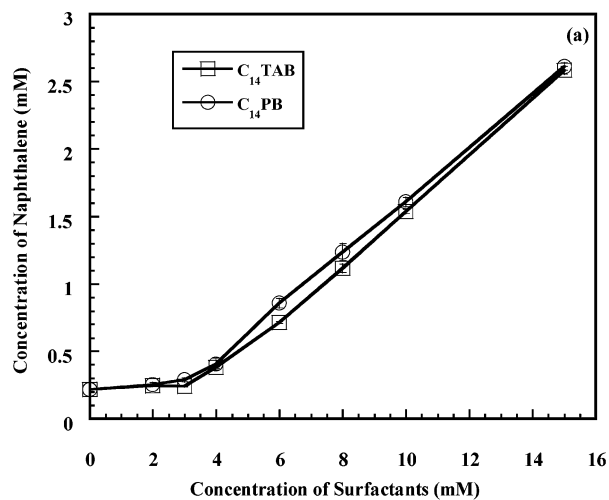

Figure 3. (a) Solubilization of naphthalene in the presence of C_{14}PB, C_{12}PB, and C_{10}PB. (b) Variation of the molar solubilization ratio (MSR) of naphthalene as a function of the hydrophobic chain length of pyridinium bromide surfactants.

they also have identical hydrocarbon tails, their solubilization behavior and MSR values are also very similar (see Table 1).

Figure 4b depicts the difference in solubilization between cationic (C_{12}PB) and anionic (SDS) surfactants with identical hydrocarbon chains (C_{12}). Note that the MSR for SDS is only about half of that for C_{12}PB. This considerable difference in solubilization is probably because of the fact that, in addition to residing in the micellar core, naphthalene molecules can also adsorb at the interface of the cationic micelle due to electrostatic interactions between the π-electrons of naphthalene and the positive charges.[26] In contrast, naphthalene molecules would prefer only the interior of the SDS micelle. These results thus suggest that, in the case of ionic surfactants, micellar solubilization of aromatics is affected not only by the hydrophobic chain length but also by the charge of the surfactant.

3.3. Solubilization by Surfactant Mixtures. Parts a and b of Figure 5 show the solubilization of naphthalene by two alkylpyridinium bromide surfactants, C_{14}PB, and C_{12}PB, in the presence of NP-9 at different compositions. As shown in Figure 5a, when the mole fraction of NP-9 (x_{NP-9}) is below 0.5, the solubility of naphthalene in the mixed surfactant system is not significantly different from that in pure C_{14}PB at the same concentration, even though the CMC of the mixture increases from 0.1 mM at x_{NP-9} = 0.5–0.65 mM at x_{NP-9} = 0.05, as shown in Table 2. This behavior is rather different from that of
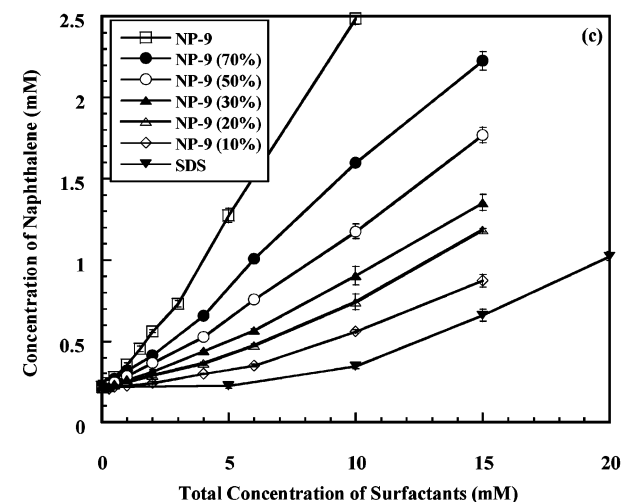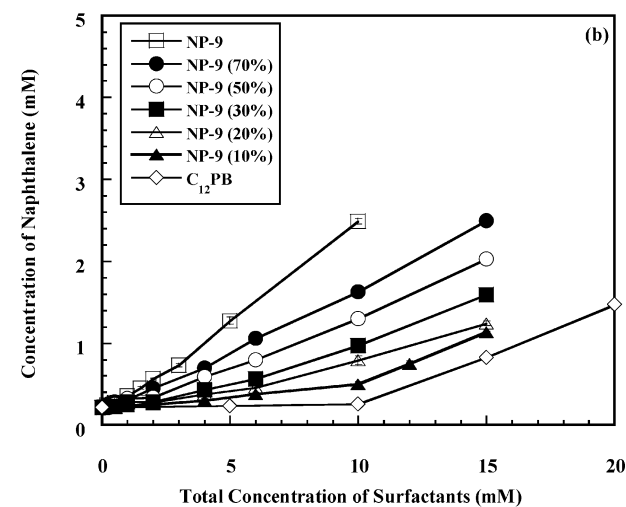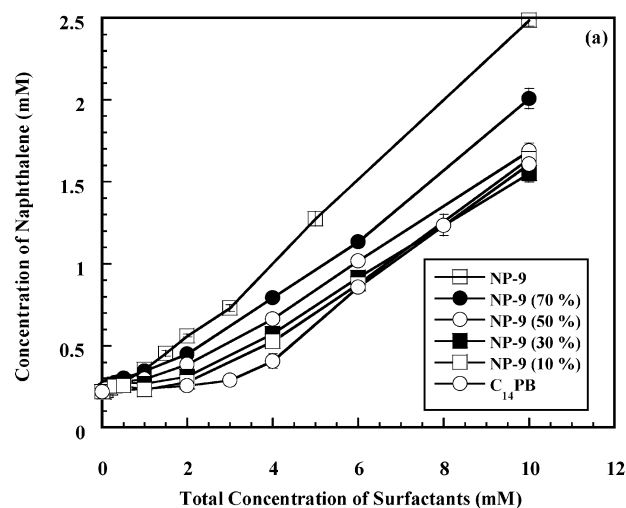
Figure 4. Comparison of solubilization of naphthalene between (a) C_{14}-PB and C_{14}TAB, and (b) C_{12}PB and SDS.

C_{12}PB/NP-9 and C_{10}PB/NP-9 (figure not shown, since similar in nature to that of Figure 5b) mixtures, where gradual variations are observed between the mixed surfactant systems and pure surfactants, as shown in Figure 5b. In addition, with C_{12}PB and C_{10}PB, since the mixture CMC is much lower than that of the pure cationic surfactant, an increase in solubilization in the surfactant mixture occurs at a low total surfactant concentration compared to that of the pure cationic surfactant.

The solubilization of naphthalene by aqueous mixtures of SDS and NP-9 is depicted in Figure 5c. Note that the nature of the curves is very similar to that for C_jPB/NP-9 surfactant mixtures. Again, enhancement of solubilization over pure SDS starts at a low total surfactant concentration due to the much lower mixture CMC. The results of these studies using cationic−nonionic and anionic−nonionic surfactant mixtures suggest that, at least for NP-9, adding an ionic surfactant would reduce the solubilization capacity for naphthalene. To further characterize these surfactant mixtures with respect to naphthalene solubilization, the MSR for the mixed surfactant systems was determined as a function of the mole fraction of NP-9 and shown in Figure 6a. In general, the MSRs in mixed surfactant systems are lower than that in pure NP-9 (MSR = 0.18). A deviation ratio, R, can also be calculated as

$$R = MSR_{exp}/MSR_{ideal} \qquad (5)$$

where MSR_{exp} is the experimentally determined MSR (see Figure 7a) and MSR_{ideal} is the MSR of naphthalene in a binary

Figure 5. Solubilization of naphthalene in aqueous mixtures of (a) C_{14}PB and NP-9, (b) C_{12}PB and NP-9, and (c) SDS and NP-9. The composition is given in parentheses as the mole percent of NP-9.

surfactant mixture based on ideal mixing, i.e.,

$$MSR_{ideal} = MSR_A X_A + MSR_B X_B \qquad (6)$$

where MSR_A (MSR_B) is the MSR in solution of pure surfactant A (B) and X_A (X_B) is the mole fraction of surfactant A (B) in the mixture of surfactants. This deviation ratio, which characterizes the mixture nonideality with respect to solubilization, is

Table 2. Critical Micelle Concentrations of Mixtures of Alkylpyridinium Bromide (C_nPB) and the Nonionic Surfactant NP-9

|	CMC (mM)		
$x_{NP-9}{}^a$	$C_{14}PB$/NP-9	$C_{12}PB$/NP-9	$C_{10}PB$/NP-9
0.05	0.65	1	1.1
0.1	0.4	0.5	1
0.2	0.3	0.3	0.5
0.3	0.2	0.25	0.3
0.5	0.1	0.15	0.25
0.7	0.08	0.1	0.2

^{a} x_{NP-9} = mole fraction of NP-9.
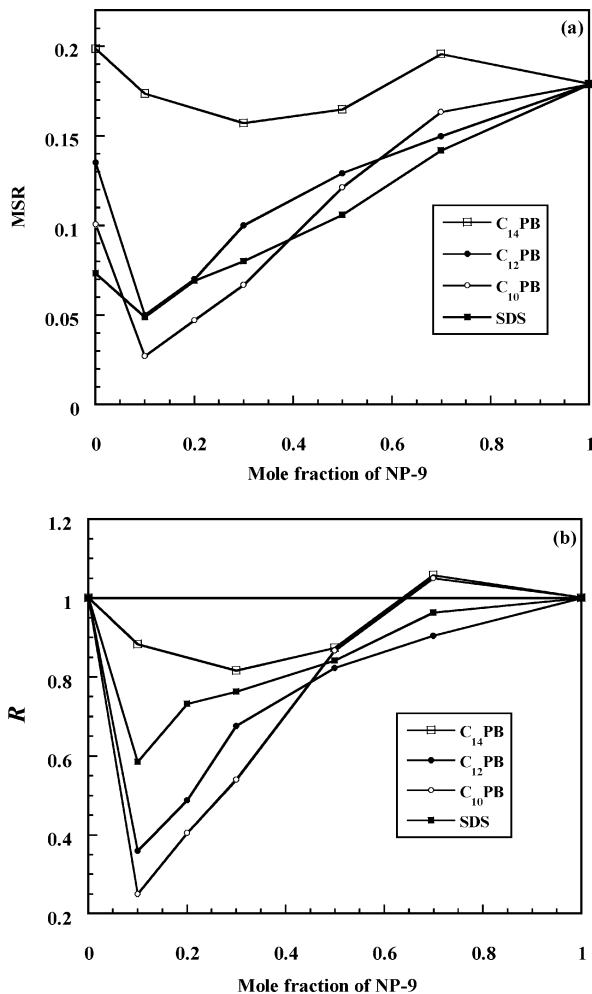
Figure 6. (a) Comparison of the molar solubilization ratio (MSR) of naphthalene in different mixed surfactant systems. (b) Deviation ratio, R, as a function of mole fraction of NP-9 in different mixed surfactant systems.

shown in Figure 6b as a function of the NP-9 mole fraction. Note that MSR_{exp} is generally lower than MSR_{ideal} ($R < 1$), and the deviations are more pronounced at low mole fractions of NP-9, with the extent of deviation in the cationic surfactant series increasing as $C_{14}PB < C_{12}PB < C_{10}PB$. In addition, a comparison between $C_{12}PB$ and SDS also shows that, with the same hydrocarbon chain length, the deviation is more pronounced with cationic surfactant.

The negative deviation of R ($R < 1$) in the cationic−nonionic surfactant mixtures may be partly explained by (i) a reduction in surface adsorption of the naphthalene molecules and (ii) the close packing of molecules in the mixed micelles. As stated earlier, in the case of cationic micelles, naphthalene molecules can reside in the micellar core as well as adsorb at the micelle interface due to the attraction between the π-electrons and the positively charged micelle. In a mixture of cationic and nonionic
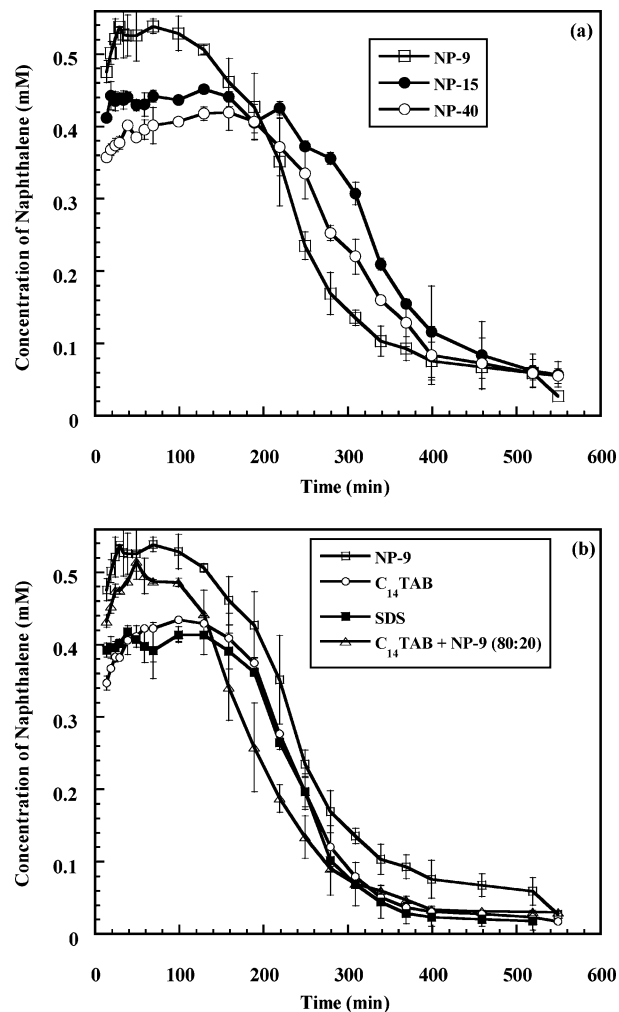
Figure 7. Outlet concentration of naphthalene from the sand column as a function of time in the presence of (a) NP-9, NP-15, and NP-40 at 2 mM concentration. (b) NP-9 (2 mM), $C_{14}TAB$ (5 mM), SDS (13.5 mM), and mixture of 80 mol % $C_{14}TAB$ and 20 mol % NP-9 (5 mM).

surfactants, the nonionic surfactants in the mixed micelle may partially shield the charges of the micelle, hence reducing the adsorption. In addition, the surfactant molecules may be more closely packed in a mixed cationic−nonionic micelle due to a reduction in electrostatic repulsion among the surfactant heads, which may also help to reduce micellar solubilization.[27] The close packing of surfactant molecules also occurs when the hydrophobic chain lengths are very similar, which may contribute to the increase in deviation from $C_{10}PB$ to $C_{14}PB$. The difference in deviation between SDS and $C_{12}PB$ may also be explained in terms of adsorption of naphthalene molecules at the micellar surface as noted above.

3.4. Solubilization Studies Using Sand Column. As noted earlier, one of the primary objectives of this study is to facilitate the design of surfactant-enhanced remediation of contaminated soils by elucidating the relations between the molecular structure of surfactants and the solubilization of PAH. A sand column was therefore used to study the removal of naphthalene using surfactant solutions. Naphthalene removal efficiency of surfactants from a sand column we consider in terms of maximum concentration of naphthalene shows in the outlet aqueous phase when the surfactant is passed through the column. For this, we chose different concentrations for different surfactants, where the surfactants will show similar solubilization capacities in the batch. Figure 7a shows the outlet naphthalene concentration as a function of time from a sand column in the presence of

different NP surfactants (NP-9, NP-15, and NP-40) at 2 mM concentration. As discussed earlier, the solubility of naphthalene in these surfactant solutions are very similar as measured in batch experiments (see Figure 2 and Table 1). However, Figure 7a seems to indicate that the removal efficiency of naphthalene from a sand column decreases with an increasing number of EO groups in the hydrophilic chain of the NP surfactant. Note that the maximum solubilization for NP-9 is very similar to that determined in the batch experiments, which is indicated by the upper bound of the *y*-axis in Figure 7a. In contrast, the maximum values for NP-15 and NP-40 are lower than that of NP-9. This discrepancy between the results from batch and column experiments may be due to the difference in adsorption density of NP surfactants on the solid surfaces. Indeed, the order of removal efficiency in the sand column (NP-9 > NP-15 > NP-40) follows the same trend as that of the molecular adsorption density of NP surfactants on sand surfaces. Measurements from a separate batch adsorption study show that the area occupied per surfactant molecule is 213.9 $Å^2$ for NP-9, 384.6 $Å^2$ for NP-15, and 1257.2 $Å^2$ for NP-40. The area occupied per molecule is calculated as

$$A_m = \frac{S \times 10^{26}}{\Gamma N_A} \tag{7}$$

where A_m is area occupied per surfactant molecule in $Å^2$, S is the specific surface area of sand in m^2/g, and Γ is the amount of surfactant adsorbed at saturation in mol/g. This difference in adsorption density suggests that when more surfactant molecules are adsorbed on the sand surface, more naphthalene molecules can be removed from a sand pack column due to detergency action.

Figure 7b shows a comparison of solubilization efficiency among $C_{14}TAB$, SDS, NP-9, and a mixture of 80 mol % C_{14}-TAB and 20 mol % NP-9. The concentration of each surfactant was selected so that the solubilization capacities are the same on the basis of the batch experiments. Note that the curves for $C_{14}TAB$ and SDS are very similar, but they are different from those for NP-9 and the $C_{14}TAB$/NP-9 mixture. The areas occupied per $C_{14}TAB$ and SDS molecules on sand surfaces were determined in a separate batch adsorption study to be 66.4 and 199 $Å^2$, respectively. However, in analyzing these results, it is important to keep in mind that adsorption of cationic surfactants on negatively charged surfaces (fresh sands not coated with naphthalene) would effectively hydrophobize the surfaces.[28] Consequently, as the naphthalene molecules are removed from the sand surface due to detergency action and subsequently solubilized in micelles, it is possible that some naphthalene molecules may reattach on the hydrophobized sand surface. Thus, even though the adsorption density of $C_{14}TAB$ is higher than that of SDS, $C_{14}TAB$ does not show a significantly better removal efficiency of naphthalene than SDS.

Comparing the curves for pure $C_{14}TAB$ and the $C_{14}TAB$/NP-9 mixture in Figure 7b, we also see that naphthalene removal from the sand column is enhanced by the addition of 20 mol % NP-9. As in the case of pure NP surfactants shown in Figure 7) (see discussion above), this behavior is apparently different from the observations made in the batch experiments for the $C_{14}PB$/NP-9 mixtures (see Figures 5a and 6). Several factors may have contributed to this difference:

(1) Experimental evidence (data not shown) has indicated that the adsorption of NP surfactants is mainly through the interactions between the hydrophobic tail and the sand surface. This implies that the formation of a mixed surfactant layer on the sand surface because of the adsorption of both NP-9 and C_{14}-TAB may effectively reduce the reattachment of naphthalene.

(2) The surfactant mixture composition within the void volume of the sand column may be different from that in the inlet solution. More specifically, enrichment of NP-9 may occur within the void volume due to the preferential adsorption of $C_{14}TAB$, thus enhancing the solubilization capacity of naphthalene.

4. Conclusion

The present study represents a systematic investigation on the effects of surfactant molecular structure on the solubilization of naphthalene. Among other results, it was found, using batch solubilization experiments, that (i) the solubilization capacity of naphthalene by the cationic alkylpyridinium bromide surfactant increases with increasing hydrophobic chain length and (ii) the MSR of naphthalene by anionic−nonionic and cationic−nonionic mixed surfactant systems deviates negatively ($R < 1$) from ideal solubilization. Comparison between cationic and anionic surfactants shows cationic surfactants have higher solubilization capacity than that of cationic surfactants. In addition, a series of column studies have indicated that the nonionic NP surfactants are more efficient in removing naphthalene from a sand column than cationic or anionic surfactants.

A key aspect in using surfactants for in situ soil remediation is the effect of soil matrix on the behavior of the surfactant solution. As revealed in this study, the interactions between surfactants and sand surfaces can play a major role in determining the solubilization capacity, and therefore the removal efficiency, of organics in sand matrixes. More specifically, results of the batch experiments have shown that solubilization of naphthalene by the nonionic NP surfactants does not vary significantly with the number of EO groups, but the efficiency of naphthalene removal from a sand column was found to increase with decreasing number of EO groups. These observations point to the importance of surfactant molecular structure (e.g., hydrophobic tail length and cationic vs nonionic surfactants, etc.) and its relation to the sand surface. Indeed, the situation with soil is even more complex because of the presence of other components such as clay. Nevertheless, the results presented here should contribute to our understanding of naphthalene solubilization by solutions of single surfactant and surfactant mixtures, which would lead to a better design of SER process, particularly with respect to the selection of the surfactant systems.

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