

# Minimizing losses of nonionic and anionic surfactants to a montmorillonite saturated with calcium using their mixtures

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## Abstract

Losses of surfactants through sorption to soils/sediments, especially to clay minerals, by various chemical interactions such as sorption and precipitation threaten the success of surfactant in enhancing remediation of contaminated soil and groundwater. In this study, the behavior of mixtures of a nonionic surfactant (TX-100) and an anionic surfactant (SDBS) sorbed to a montmorillonite saturated with calcium (Ca-montmorillonite) was investigated, and compared with that of individual surfactants. It is shown that the amounts of both TX-100 and SDBS sorbed to Ca-montmorillonite are significant. However, the amount of either TX-100 or SDBS sorbed can be decreased and minimized when they are mixed with each other. Mixed micelle formation, which causes negative deviation of critical micelle concentrations (CMCs) from the ideal, is responsible for the decrease in sorbed TX-100 and sorbed SDBS in their mixtures. Because of their ability to minimize their amounts sorbed and thus enhance their active concentrations, as observed in mixed TX-100 and SDBS systems, mixed anionic–nonionic surfactants exhibit potential advantages in the area of enhanced soil and groundwater remediation.

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## 1. Introduction

In response to the serious pollution of soil and groundwater by hydrophobic organic contaminants (HOCs), various physical, chemical, biological, and combined technologies have been developed to remediate these contaminated environments [1–3]. Improvement in desorption of HOCs from soils/sediments is a key to remediation technologies. Surfactant, especially through micelle formation, can enhance the mobilization and solubility of HOCs and, thus, improve desorption efficiency [4–7]. Therefore, surfactant-enhanced remediation (SER) has been suggested as a promising technology in the removal of organic contaminants in soil and groundwater for decades [1,8–10].

However, the choice of a successful surfactant to enhance remediation goes beyond selection of a surfactant (or a surfactant system) that efficiently solubilizes or mobilizes HOCs. The surfactant must also be matched to the subsurface conditions so that it remains at an active concentration. Surfactants sorbed to soils/sediments, especially to clay minerals, will, through various chemical interactions such as sorption and precipitation, retard HOCs by enhancing soil/sediment organic carbon content [11–13] and enhance the cost of the operation by reducing the active surfactant concentrations [14–16] and because of surfactant pollution [17]. Clearly, losses of surfactants through sorption to soils/sediments threaten the success of SER technology. Therefore, an attempt should be made minimize losses of surfactant to soils/sediments and thus maintain an active concentration in solution.

Due to the negatively charged surface of most minerals, anionic surfactants and nonionic surfactants can be expected to be sorbed less than cationic surfactants, and have usu-

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ally been chosen in SER technology [18,19]. The amount of a single anionic surfactant or a single nonionic surfactant sorbed to soils/sediments, however, is still significant. For example, sorption of 11.4 mg/g of the anionic surfactant SDBS and 11.9 mg/g of the nonionic surfactant TX-100 to a soil sample (Canadian River Alluvium) has been observed by Rouse and Sabatini [15].

The sorbed losses of nonionic surfactants are attributed primarily to sorption to soils/sediments [14,20]. Sorption of nonionic surfactants to soils/sediments is limited by their critical micelle concentrations (CMCs) and reaches a plateau at their equilibrium concentrations about 1.5 CMCs [20]. The CMC-limited sorption of nonionic surfactants reflects the significant effects in surfactant micelles; in other words, a change in their micelles affects their sorption to soils/sediments. It is also indicated that sorption of nonionic surfactants to soils/sediments depends on both the type and content of soil/sediment clay minerals [20]. The sorbed losses of anionic surfactants, however, are attributed to precipitation between the anionic surfactant ions and the binary cations (e.g.,  $\text{Ca}^{2+}$ ) in soils/sediments [21].

Mixed surfactants are of considerable applied and fundamental interest. Generally, surfactant mixtures exhibit a number of synergistic advantages over the use of a single surfactant type [5,22–25]. In the area of enhanced soil and groundwater remediation, for example, such surfactant systems might show advantageous solubility behavior [22]. Mixed anionic–nonionic surfactants exhibit Cloud points higher than those of the pure nonionic surfactants, along with Krafft points lower than those of the pure anionic surfactants [23,24]. Furthermore, the addition of nonionic surfactants to anionic surfactants in pure solutions can increase the hardness tolerance of anionic surfactants, i.e., decrease precipitation between anionic surfactant ions and multivalent electrolytes such as  $\text{Ca}^{2+}$  [25]. Therefore, mixed anionic–nonionic surfactants could be employed over a wider range of temperature, salinity, and hardness conditions than could individual surfactants in SER technology. However, as single nonionic and anionic surfactants were employed in SER technology in past decades, little information on the application of mixed anionic–nonionic surfactants in SER technology is available. An investigation of the behavior of mixed anionic–nonionic surfactants sorbed to soils/sediments is critical to providing this information.

In mixed anionic–nonionic surfactant systems, mixed micelles might form, which may differ significantly from the micelles of individual surfactants and exhibit strong deviations from the ideal: the CMCs of mixed surfactants are considerably lower than that of ideal mixing theory would predict [5]. Because the changes in micelles affects the sorption of nonionic surfactants and the addition of nonionic surfactants to anionic surfactants can decrease the precipitation of anionic surfactants, mixed anionic–nonionic surfactants would be expected to sorb less to soils/sediments than individual surfactants.

Montmorillonite, a common soil/sediment clay, more strongly sorbs nonionic surfactants such as TX-100 than other clays and limits the application of nonionic surfactants in SER technology when its content in soils/sediments is high [20,26–30]. For example, Shen [31] compared the sorption of nonionic surfactants to montmorillonite with that of cationic surfactants. According to Jafvert and Heath [21], montmorillonite saturated by  $\text{Ca}^{2+}$  (Ca-montmorillonite) should also exhibit significant precipitation with anionic surfactants. Thus, Ca-montmorillonite would exhibit either significant sorption losses for nonionic surfactants or significant precipitation losses for anionic surfactants. Obviously, minimizing sorption of nonionic surfactants and anionic surfactants to Ca-montmorillonite is key to minimizing losses of surfactants to soils/sediments.

Thus, the behavior of mixtures of a nonionic surfactant (TX-100) and an anionic surfactant (SDBS) sorbed to Ca-montmorillonite were investigated, and the results were compared with those for individual surfactants. The mixed surfactants investigated in this study are also important because it is rare that a single surfactant is present industrial and biological systems. This information may play an important role in the development of commercially viable surfactant systems for enhanced remediation. TX-100 and SDBS were employed in this study because they are widely used in industrial processes and have been suggested for subsurface remediation applications [11,15,32,33].

## 2. Experiments and methods

### 2.1. Sorbent

Ca-montmorillonite was collected from the Inner Mongolia Autonomous Region, China. The specific surface area ( $\text{N}_2$ -BET), organic carbon content ( $f_{oc}$ ) and cation exchange capacity (CEC) are 60.9  $\text{m}^2/\text{g}$ , 0.040%, and 105 mmol/100 g, respectively [34].

### 2.2. Surfactants and analytical methods

The anionic surfactant sodium dodecylbenzene sulfonate (SDBS), with a purity of 95%, was purchased from Tokyo Kasei Kogyo Company. The nonionic surfactant octylphenol polyethoxylate Triton X-100 (TX-100) was purchased from Sigma Chemical Company. They were used without further purification. Formulas, average molecular weights (MWs), and critical micelle concentration (CMCs) are listed in Table 1.

Concentrations of SDBS and TX-100 in the aqueous phase were determined by HPLC with a UV spectrophotometer at a wavelength of 224 nm, flow rate of 1.0 mL/min, and mobile phase of 80% methanol and 20% water. The injection volume was 40  $\mu\text{L}$ . HPLC analysis was performed on a Hitachi instrument (L-7000 series, Japan) with  $\text{C}_{18}$  reverse-phase column (Wakosoil, 250  $\times$   $\varnothing$ 4.6 mm, Japan).

Table 1  
Formula and selected properties of TX-100 and SDBS

Surfactant	Formula	MW (g/mol)	CMC (mg/L)
TX-100	$C_8H_{17}C_6H_4O(CH_2CH_2O)_{9.5}H$	628	167, 130 <sup>a</sup> , 157 <sup>b</sup>
SDBS	$C_{12}H_{25}C_6H_4SO_3^-Na^+$	348.48	963, 732 <sup>b</sup> , 1400 <sup>c</sup>

<sup>a</sup> Ref. [4].

<sup>b</sup> Ref. [23].

<sup>c</sup> Ref. [15].

### 2.3. Measurement of surface tension and critical micelle concentration (CMC)

Surface tensions of TX-100, SDBS, and their mixtures were determined with a Model 20 surface tensiometer, manufactured by Fisher Scientific Company. This instrument operates on the DuNouy principle, in which a platinum–iridium ring is suspended from a torsion balance, and the force (in mN/m) necessary to pull the ring free from the surface film is measured. CMC values of TX-100, SDBS, and their mixtures were estimated from the surface tension of surfactant solutions over a wide concentration range, noting the inflection in the plot of surface tension versus logarithm of surfactant concentrations; the plotted surface tension value was taken when stable readings were obtained for a given surfactant concentration, as indicated by at least three consecutive measurements of nearly the same value.

### 2.4. Batch experiments

A total of 20 mL of surfactant solution was mixed with 0.5 g of Ca-montmorillonite in a 50-mL Erlenmeyer flask with glass cap and shaken on a gyratory shaker at  $(25 \pm 1^\circ C)$  for 12 h. Initial TX-100 and SDBS concentrations

ranged from 0 to 6000 mg/L and from 0 to 5000 mg/L, respectively. Previous experiments showed no significant increase in surfactant sorbed after 12 h. After equilibrium, the solid and aqueous phases were separated by centrifugation (4000 rpm for 30 min). Then, the concentrations of SDBS and TX-100 in the aqueous phase were determined by HPLC. The amounts of SDBS and TX-100 sorbed were calculated by the difference between initial and equilibrium surfactant concentrations.

## 3. Results

### 3.1. Effects of SDBS on the sorption of TX-100

Typical isotherms for sorption of TX-100 to Ca-montmorillonite at various initial concentrations of SDBS are shown in Fig. 1. Because of the difficulty in obtaining an accurate fit of TX-100 sorption data to any simple model (i.e., Freundlich or Langmuir), the experimentally determined equilibrium TX-100 concentrations in the aqueous phase and in soil are listed [12,20]. Fig. 2 illustrates the amounts of TX-100 sorbed to Ca-montmorillonite as a function of equilibrium SDBS concentration. In the absence of SDBS, the sorption isotherm of TX-100 is nonlinear, exhibiting a plateau in sorbed TX-100 at its equilibrium concentration, about 1.5 CMCs (see Fig. 1). The plateau amount of TX-100 sorbed is about 140 mg/g, in agreement with the value reported by Lee et al. [13], which means that an additional 3500 mg/L ( $3500 \text{ mg/L} = (140 \text{ mg/g} \times 0.5 \text{ g})/20 \text{ mL}$ ) of TX-100 needed to be added to obtain its aqueous CMC. In the presence of SDBS, when its initial concentrations are lower than 1500 mg/L (corresponding to equilibrium SDBS concentrations below the CMC, shown in Fig. 2), no sig-

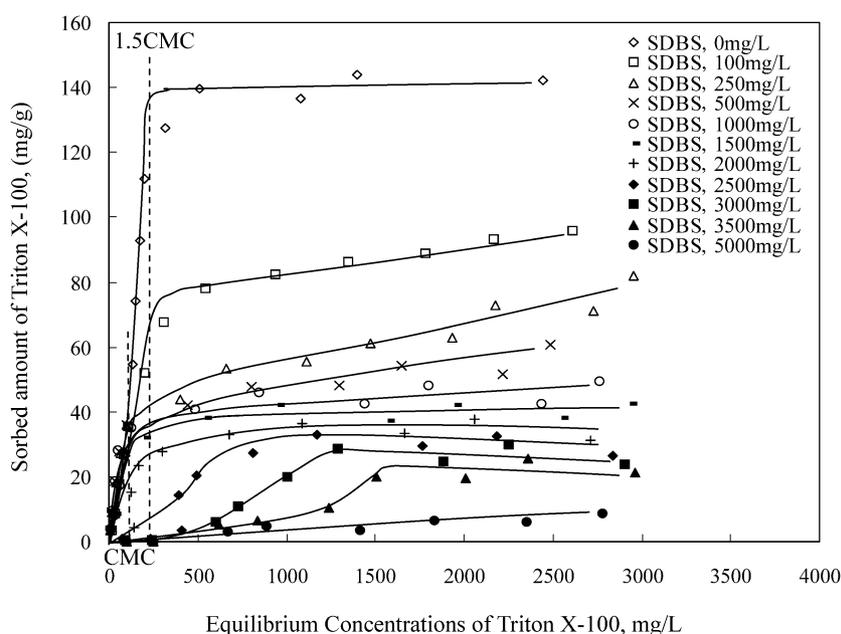


Fig. 1. Typical isotherms for sorption of TX-100 to Ca-montmorillonite at various initial concentrations of SDBS.

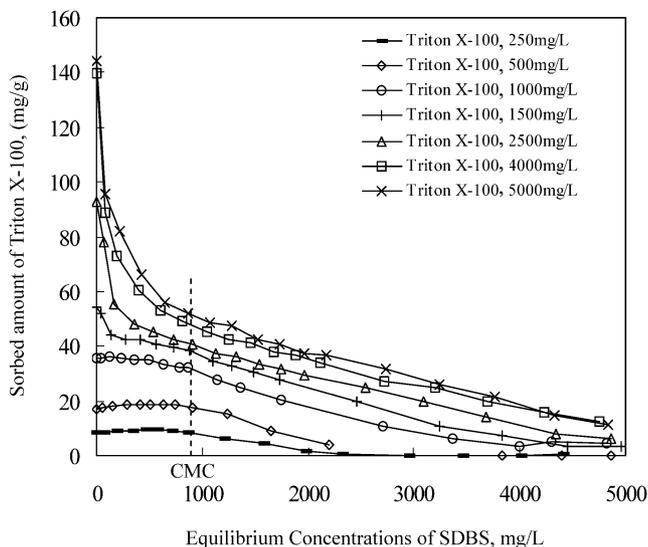


Fig. 2. Amount of TX-100 sorbed to Ca-montmorillonite versus equilibrium concentration of SDBS.

nificant effects of SDBS on sorbed TX-100 are observed at equilibrium TX-100 concentrations below its CMC (corresponding to the initial TX-100 concentrations lower than 1000 mg/L, shown in Fig. 2), but a sharp decrease in sorbed TX-100 by the coexisting SDBS is observed at equilibrium TX-100 concentrations above its CMC. When initial concentrations of coexisting SDBS are higher than 1500 mg/L, a stable decrease in sorbed TX-100 is observed. It is clear that: (1) sorption of TX-100 to Ca-montmorillonite can be reduced by the added SDBS; (2) a high SDBS concentration is needed to reduce the sorption losses of TX-100 at equilibrium TX-100 concentrations below its CMC; and (3) sorption losses of TX-100 can be minimized when the concentration of added SDBS is sufficient.

### 3.2. Effects of TX-100 on the sorption behavior of SDBS

Typical isotherms for sorption of SDBS to Ca-montmorillonite at various initial concentrations of TX-100 are shown in Fig. 3. At initial concentrations lower than 250 mg/L, TX-100 can significantly reduce the amount of SDBS sorbed at equilibrium SDBS concentrations above its CMC, but exhibits no significant effects on SDBS at equilibrium SDBS concentrations below its CMC. At initial TX-100 concentrations higher than 250 mg/L, the amount of SDBS sorbed to montmorillonite at any equilibrium concentration increases with the coexisting TX-100 at first and then decreases.

It is demonstrated that all isotherms of SDBS exhibit a maximum sorption value at some equilibrium SDBS concentration. For example, the maximum sorption value for SDBS in the absence of TX-100 is about 58 mg/g at equilibrium SDBS concentration, about 1.5 CMCs. Fig. 4 shows the maximum sorption values of SDBS as a function of initial TX-100 concentration. As shown in Fig. 4, the maximum sorption value of SDBS sharply decreases from 58 to 25 mg/g when the initial TX-100 concentration in-

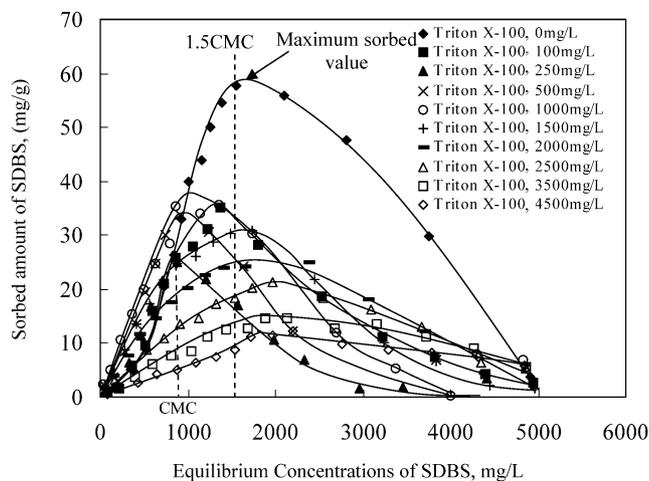


Fig. 3. Typical isotherms for sorption of SDBS to Ca-montmorillonite at various initial concentrations of TX-100.

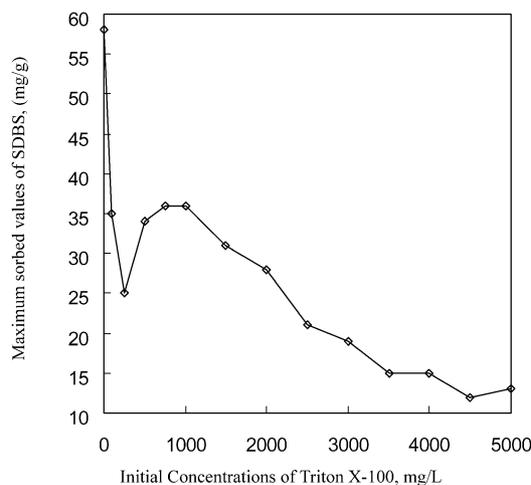


Fig. 4. Maximum amount of SDBS sorbed to Ca-montmorillonite versus initial concentration of TX-100.

creases from 0 to 250 mg/L, and then it increases to 36 mg/g when the initial TX-100 concentration increases to 1000 mg/L; at initial TX-100 concentrations higher than 1000 mg/L, the maximum sorption value of SDBS decreases again.

Fig. 5 shows the amounts of SDBS sorbed at various initial concentrations as a function of equilibrium TX-100 concentration. It is shown that the amount of SDBS sorbed reaches a peak. The peak sorption value increases with an increase in SDBS at first and then decreases. At SDBS concentrations higher than 5000 mg/L, the peak sorption value disappears. Furthermore, the equilibrium concentration of TX-100, at which the peak sorption value of SDBS appeared, increases with an increase in initial SDBS concentrations.

Three regions can be distinguished in the effects of sorption of TX-100 and SDBS to Ca-montmorillonite: (i) no significant effects at equilibrium SDBS concentrations below its CMC or a sharp decrease in sorbed SDBS at equilibrium SDBS concentrations above its CMC, until the initial

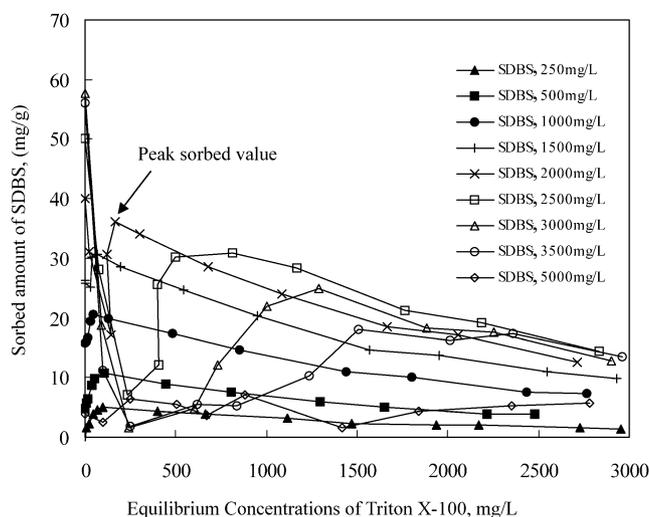


Fig. 5. Amount of SDBS sorbed to Ca-montmorillonite versus equilibrium concentration of TX-100.

TX-100 concentration is about 250 mg/L, followed by (ii) a substantial increase in sorbed SDBS to reach a peak sorbed value with the increase in initial TX-100 concentrations, after which (iii) the amounts of SDBS sorbed decreased again and are minimal when the concentration of added TX-100 dose is sufficient.

### 3.3. Sorption behavior of mixtures of TX-100 and SDBS

Fig. 6 shows the typical curves sorption of mixtures of TX-100 and SDBS to Ca-montmorillonite at various mass ratios of TX-100 to SDBS. It is clear that the amounts of the

mixtures sorbed are lower than those of individual TX-100 at any mass ratios of TX-100 to SDBS and even lower than those of individual SDBS at some concentrations when the mass ratio of TX-100 to SDBS is lower than 3:7. Clearly, the amounts of the mixtures sorbed would be lower than either those of TX-100 or those of SDBS under some conditions (shown in Fig. 6). For example, the amount of mixture sorbed, at a mass ratio of 1:9 and an initial concentration of 3000 mg/L, is about 7 mg/g, which is significantly lower than that of TX-100 (about 115 mg/g) or of SDBS (about 58 mg/g). Furthermore, the amounts of the mixtures sorbed can be minimized when the concentration of both added TX-100 and SDBS are sufficient, as also shown in Figs. 1–5.

### 3.4. Interaction between TX-100 and SDBS in solution

To interpret the sorption behavior of mixtures, it is essential to know the surfactant interaction between TX-100 and SDBS in solution. Mixtures of nonionic and anionic surfactants generally form mixed micelles in solution. Surface tension measurement and nonideal solution theory have been used to investigate the micelle formation of mixed nonionic–anionic surfactants [5,23,35]. Typical surface tension curves of mixed TX-100 and SDBS solutions at various mass ratios of TX-100 to SDBS are shown in Fig. 7. Note the inflection in the plot of surface tension versus logarithm of surfactant concentration, at which the experimental CMCs of surfactants exist.

In an ideal mixed system, the ideal CMC of mixed surfactant solutions at any mole ratio of TX-100 to SDBS can

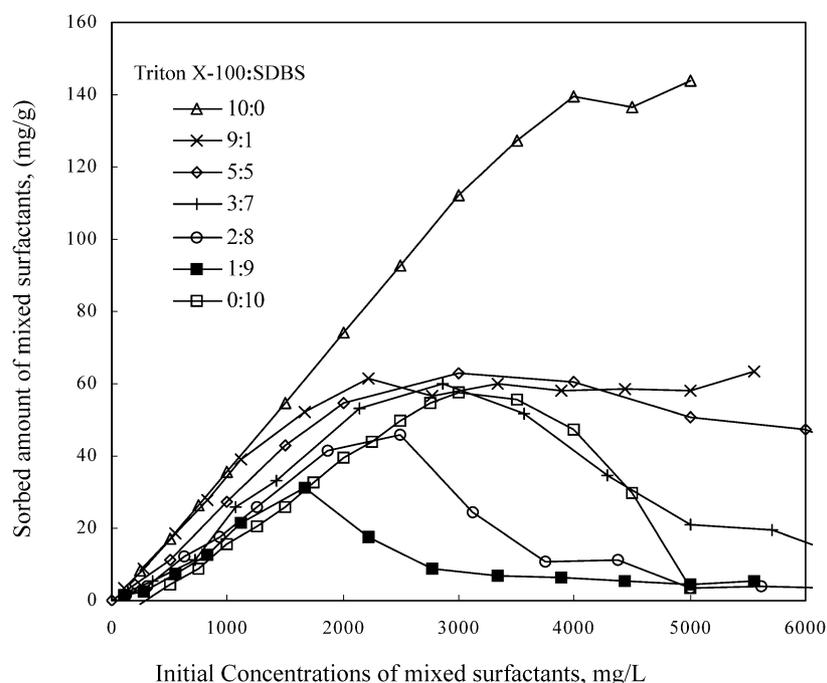


Fig. 6. Typical curves for sorption of mixed surfactants to Ca-montmorillonite at various mass ratios of TX-100 to SDBS.

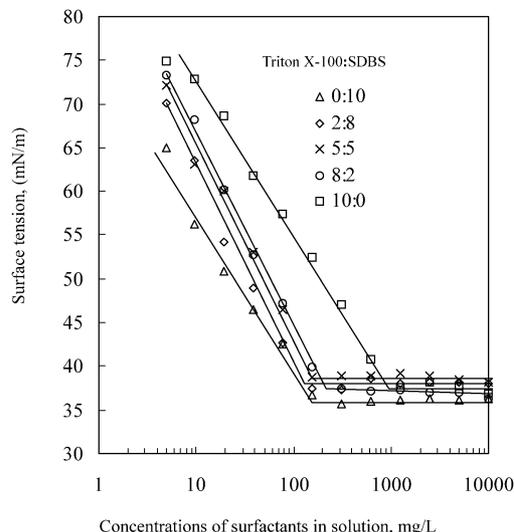


Fig. 7. Typical surface tension curves of surfactants at various mass ratios of TX-100 to SDBS.

be predicted with ideal solution theory [5],

$$\frac{1}{\text{CMC}_{\text{ideal}}} = \frac{\alpha}{\text{CMC}_{\text{TX-100}}} + \frac{1-\alpha}{\text{CMC}_{\text{SDBS}}}, \quad (1)$$

where  $\alpha$  is the mole ratio of TX-100 in the mixed solutions and thus  $1-\alpha$  is the mole ratio of SDBS in the mixed solutions.  $\text{CMC}_{\text{TX-100}}$  and  $\text{CMC}_{\text{SDBS}}$  are the CMCs of TX-100 and SDBS, respectively.  $\text{CMC}_{\text{ideal}}$  is the predicted CMC of mixed surfactant solutions at any mole ratio of TX-100 to SDBS in ideal systems.

Due to the interaction between TX-100 and SDBS in mixed solutions, the experimental CMC of a mixed surfactant solution ( $\text{CMC}_{\text{exp}}$ ) is always different from  $\text{CMC}_{\text{ideal}}$ . As listed in Table 2,  $\text{CMC}_{\text{exp}}$  is obviously less than  $\text{CMC}_{\text{ideal}}$  at any mass ratio of TX-100 to SDBS. According to non-ideal solution theory [5,35], the deviation of  $\text{CMC}_{\text{exp}}$  from  $\text{CMC}_{\text{ideal}}$  can be represented by the parameter  $\beta$ , which also represents the interaction between TX-100 and SDBS in mixed solutions,

$$\begin{aligned} \beta &= \frac{\ln(\alpha \text{CMC}_{\text{exp}} / X_{\text{SDBS}}^{\text{M}} \text{CMC}_{\text{SDBS}})}{(1 - X_{\text{SDBS}}^{\text{M}})^2} \\ &= \frac{\ln(\alpha \text{CMC}_{\text{exp}} / X_{\text{TX-100}}^{\text{M}} \text{CMC}_{\text{TX-100}})}{(1 - X_{\text{TX-100}}^{\text{M}})^2}, \end{aligned} \quad (2)$$

where  $X_{\text{TX-100}}^{\text{M}}$  and  $X_{\text{SDBS}}^{\text{M}}$  are the mole ratios of TX-100 and SDBS in the total surfactant in the mixed micelles, respectively.  $X_{\text{TX-100}}^{\text{M}}$  and  $X_{\text{SDBS}}^{\text{M}}$  can be calculated with, respectively,

$$\begin{aligned} &(X_{\text{SDBS}}^{\text{M}})^2 \ln(\alpha \text{CMC}_{\text{exp}} / X_{\text{SDBS}}^{\text{M}} \text{CMC}_{\text{SDBS}}) \\ &/ ((1 - X_{\text{SDBS}}^{\text{M}})^2 \ln[(1 - \alpha) \text{CMC}_{\text{exp}} \\ &/ (1 - X_{\text{SDBS}}^{\text{M}}) \text{CMC}_{\text{TX-100}}]) = 1 \end{aligned} \quad (3)$$

Table 2

Interaction parameters ( $\beta$ ) and CMCs of TX-100 and SDBS at various mass ratios of TX-100 to SDBS

TX-100: SDBS mass ratios	$\alpha$	$\text{CMC}_{\text{ideal}}$ (mmol/L)	$\text{CMC}_{\text{exp}}$ (mmol/L)	$X_{\text{SDBS}}^{\text{M}}$	$X_{\text{TX-100}}^{\text{M}}$	$\beta$
0:10			2.764			
1:9	0.3096	1.791	0.6177	0.7752	0.2248	-3.45
2:8	0.4346	1.292	0.5223	0.7353	0.2647	-3.35
3:7	0.5446	0.9882	0.5243	0.7125	0.2875	-2.93
4:6	0.6420	0.7842	0.4043	0.6754	0.3246	-2.89
5:5	0.7290	0.6376	0.3725	0.6295	0.3705	-3.14
6:4	0.8071	0.5271	0.3289	0.5943	0.4057	-2.76
7:3	0.8777	0.4410	0.2756	0.5320	0.4680	-3.67
8:2	0.9417	0.3719	0.2527	0.4646	0.5354	-4.33
10:0			0.2679			

and

$$\begin{aligned} &(X_{\text{TX-100}}^{\text{M}})^2 \ln(\alpha \text{CMC}_{\text{exp}} / X_{\text{TX-100}}^{\text{M}} \text{CMC}_{\text{TX-100}}) \\ &/ ((1 - X_{\text{TX-100}}^{\text{M}})^2 \ln[(1 - \alpha) \text{CMC}_{\text{exp}} \\ &/ (1 - X_{\text{TX-100}}^{\text{M}}) \text{CMC}_{\text{SDBS}}]) = 1. \end{aligned} \quad (4)$$

Calculated interaction parameters,  $\beta$ , at various mass ratios of TX-100 to SDBS are also listed in Table 2 and change with the mass ratio.  $\beta$  values from -2.76 to -4.33 are negative at any mass ratio of TX-100 to SDBS. The more negative  $\beta$  value of the mixed systems indicates the stronger attraction between TX-100 and SDBS in solution. The deviation of  $\text{CMC}_{\text{exp}}$  from  $\text{CMC}_{\text{ideal}}$  and the negative values of  $\beta$  indicate the formation of mixed micelles in TX-100 and SDBS solutions [5,35].

#### 4. Discussion

To interpret the behavior of mixtures of TX-100 and SDBS sorbed to Ca-montmorillonite, it is essential to have knowledge of the interactions between TX-100 and SDBS in solution and on a solid surface, the interactions between individual surfactants and a solid surface, the interactions between their mixtures and a solid surface, and the effects of surface-accumulated surfactants on the properties of a solid surface. A phenomenon unique to surfactants in solution is aggregation, i.e., the self-assembly of molecules into dynamic clusters called micelles when concentrations of surfactants are higher than their CMCs. Surfactant aggregation may also occur at solid-water interfaces. With an increase in surfactant concentrations, surfactant monomers sorbed to a solid surface begin to aggregate and form micelle-like structures called admicelles or hemimicelles, depending on whether the aggregates have one or two surfactant layers. Once these structures form on a solid surface, sorption of additional surfactant may rapidly increase until a complete bilayer of surfactant covers the solid surface. For individual surfactants, both monomers and micelles/admicelles exist in

surfactant solution or on a solid surface. Similarly, mixed micelles in solution, which are identified by the deviation of  $CMC_{exp}$  from  $CMC_{ideal}$  (Table 2), and mixed admicelles on a solid surface are also expected to form in mixed surfactant systems. Therefore, SDBS monomers, SDBS micelles, TX-100 monomers, TX-100 micelles, and mixed micelles are present in mixed SDBS and TX-100 solutions. Also, SDBS monomers, SDBS admicelles, TX-100 monomers, TX-100 admicelles, and mixed admicelles exist on a solid surface in the mixed surfactant systems.

As shown in Figs. 1–6, the sorption of TX-100 alone or SDBS alone to Ca-montmorillonite is significant. Therefore, even when large concentrations are added, TX-100 and SDBS do not remain active when they are individually used to remediate contaminated soils with a high content of Ca-montmorillonite. In the absence of SDBS, sorption by hydrogen bonding on the surface of Ca-montmorillonite is considered to be the most important mechanism in TX-100 losses [31]. As identified by Jafvert and Heath [21], precipitation between SDBS ionic and  $Ca^{2+}$  on the surface of Ca-montmorillonite is considered to be the most probable cause of the observed losses of SDBS in the absence of TX-100. Because of counterion binding of  $Ca^{2+}$  into any micelles that form [25], the precipitates redissolve when the equilibrium SDBS concentrations are above 1.5 CMCs. However, the different effects of TX-100 on the behavior of SDBS sorbed to Ca-montmorillonite in region i indicate that the mechanism for sorption of SDBS alone to the surface of Ca-montmorillonite at equilibrium SDBS concentrations below its CMC is different from that at equilibrium SDBS concentrations above its CMC. Admicelle formation on the solid surface should be considered to be an additional loss of individually used SDBS at equilibrium concentrations above its CMC [8], in addition to the precipitation of SDBS monomer at equilibrium concentrations below its CMC. The different sorption behavior of TX-100 at equilibrium concentrations below its CMC and above its CMC in the presence of SDBS at equilibrium concentrations below its CMC (Figs. 1 and 2) indicates the different mechanisms for sorption of individually used TX-100 to the surface of Ca-montmorillonite, too. The monomer sorption of TX-100 by hydrogen bonding [14,31] and additional admicelle formation on the solid surface can also be employed to explain these differences [8].

The sharp decrease in sorbed SDBS at equilibrium SDBS concentrations above its CMC and at initial TX-100 concentrations below 250 mg/L (Figs. 3–5) may be due to the mixed micelles formed in solutions. Once mixed micelles are present in solutions, they prevent SDBS monomers from forming admicelles on the solid surface and redissolve the precipitates of SDBS due to counterion binding of  $Ca^{2+}$  to any mixed micelles that form [25]. Stellner and Scamehorn determined that mixed micelle formation is the mechanism by which precipitation of anionic surfactant in solution decreases when nonionic surfactant is added [25]. Also, the sharp decrease in sorbed TX-100 at equilibrium TX-100 concentrations above its CMC and at equilibrium SDBS con-

centrations below its CMC (Figs. 1 and 2) can be explained by mixed micelle formation in solution. In other words, mixed micelles in solutions prevent TX-100 monomers from forming admicelles on the solid surface.

The amount of sorbed SDBS remained relatively constant at equilibrium SDBS concentrations below its CMC and at initial TX-100 concentrations below 250 mg/L, as illustrated in Fig. 3. Though mixed micelles may form under these conditions (see Table 2), the amount of mixed micelles in solution is small at such low concentrations. The relatively constant amount of sorbed SDBS indicates that more mixed micelles are needed to decrease the precipitation of anionic surfactant. Similarly, the relatively constant amount of TX-100 sorbed at both equilibrium SDBS concentrations and equilibrium TX-100 concentrations below their respective CMCs (see Figs. 1 and 2) indicates that more mixed micelles are needed to inhibit the hydrogen bonding between TX-100 monomers and the active sites on surface of montmorillonite.

In region ii of the effects of TX-100 on the behavior of SDBS, the amount of SDBS sorbed to montmorillonite increases with an increase in sorbed TX-100, and the equilibrium concentration of TX-100 at which sorption of SDBS peaks is where sorption of TX-100 plateaus (shown in Figs. 1 and 5), which suggests that sorbed TX-100 has significant effects on the behavior of SDBS sorbed to montmorillonite. The losses of SDBS in the absence of TX-100 are due primarily to precipitation rather than sorption because of the strong electrostatic repulsion between the negative charges of SDBS and the Ca-montmorillonite surface. When the Ca-montmorillonite surface is coated by TX-100, however, which has a slight positive charge, the negative charge on the surface decreases, i.e., the positive charge on the surface is enhanced, and therefore, sorption of SDBS by electrostatic attraction is significant [36]. Also, TX-100 is sorbed to and mixed admicelles form on the surface of Ca-montmorillonite, which may strongly attract SDBS. Therefore, three possible mechanisms can be employed to explain the enhanced sorption of SDBS by sorbed TX-100: (1) the direct attraction by sorbed TX-100, (2) the attraction by mixed admicelles formed on the solid surface, and (3) reduction of the negative charge and then enhancement of electrostatic attraction on the Ca-montmorillonite surface by sorbed TX-100. However, sorption of TX-100 considerably decreases while sorption of SDBS increases rapidly to reach the maximum sorption value (shown in Figs. 2 and 5), which indicates that the attraction of TX-100 by the surface-accumulated SDBS or mixed admicelles is insignificant. If the enhanced sorption of SDBS by sorbed TX-100 is due to mechanism (1) or mechanism (2), sorption of TX-100 should also be increased significantly with the rapid accumulation of SDBS on the Ca-montmorillonite surface. In other words, the direct attraction of SDBS by both sorbed TX-100 and mixed admicelles on the solid surface is insignificant; i.e., the most probable mechanism for the enhanced sorption of SDBS by TX-100 is the electrostatic attraction between

SDBS and the positive charge on the Ca-montmorillonite surface enhanced by sorbed TX-100. However, the electrostatic attraction for TX-100 is insignificant. The stable decrease in sorbed TX-100 is due primarily to the abundant mixed micelle formation in solution, which inhibits the hydrogen bonding between TX-100 monomers and surface active sites.

In region iii of the effects of TX-100 on the behavior of SDBS, where abundant mixed micelles are present, sorbed SDBS decreases again with an increase in equilibrium TX-100 concentrations (shown in Fig. 5). This decrease can be explained by the cooperative interactions of mixed micelles that inhibit electrostatic attraction between SDBS and the montmorillonite surface and redissolve the precipitates by counterion binding of  $\text{Ca}^{2+}$  into them.

Clearly, the losses of TX-100 used alone to Ca-montmorillonite are determined by the sorption due to hydrogen bonding and admicelle formation on the Ca-montmorillonite surface. The losses of SDBS used alone to Ca-montmorillonite are determined by precipitation with surface  $\text{Ca}^{2+}$  and admicelle formation on solid surface. The loss of mixed TX-100 and SDBS to Ca-montmorillonite is a very complex process, governed by various interactions between surfactant monomers, micelles, mixed micelles, and the clay, and further complicated by the surface charge changes of the clay when surfactants accumulate on the surface. The overall losses of surfactants are highly sensitive to their concentrations and their specific properties, especially the surface-sorbed TX-100 and the amount of mixed micelles in solution. However, the loss of either TX-100 or SDBS to Ca-montmorillonite can be decreased and minimized by mixing them because of the formation of a strong stable phase, i.e., mixed micelles in solution. The decrease in loss of TX-100 is more important because TX-100 exhibits stronger solubility for HOCs than SDBS [4,15]. This information is very valuable in the development of commercially viable surfactant systems for enhanced remediation.

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