Solubilization of pyrene by anionic–nonionic mixed surfactants

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Abstract

Surfactant-enhanced remediation (SER) is an effective approach for the removal of sorbed hydrophobic organic compounds from contaminated soils. The solubilization of pyrene by four anionic–nonionic mixed surfactants, sodium dodecyl sulfate (SDS) with Triton X-405 (TX405), Brij35, Brij58, and Triton X-100 (TX100), has been studied from measurements of the molar solubilization ratio (MSR), the micelle–water partition coefficient (K_{mc}), and the critical micelle concentration (CMC). The MSRs of pyrene in mixed surfactants are found to be larger than those predicted according to an ideal mixing rule. The mixing effect of anionic and nonionic surfactants on MSR for pyrene follows the order of SDS–TX405 > SDS–Brij35 > SDS–Brij58 > SDS–TX100 and increases with an increase in the hydrophile–lipophile balance (HLB) value of nonionic surfactant in mixed systems. In addition, the mixture of anionic and nonionic surfactants cause the K_{mc} value for pyrene to be greater than the ideal value in SDS–TX405 mixed system, but to be smaller than the ideal value in SDS–Brij35, SDS–Brij58, and SDS–TX100 mixed systems. Meanwhile, in the four mixed systems, the experimental CMCs are lower than the ideal CMCs at almost all mixed surfactant solution compositions. The mixing effect of anionic and nonionic surfactants on MSR for pyrene can be attributed to the conjunct or the net result of the negative deviation of the CMCs from ideal mixture and the increasing or decreasing K_{mc}.
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1. Introduction

The contamination of soils and water by toxic and/or hazardous organic pollutants is a widespread environmental problem. Various physical, chemical, biological, and their combined technologies have been attempted to remedy organic contaminated soils and groundwater. Hydrophobic organic compounds (HOCs) are of special interest because they are strongly sorbed to soils or sediments. As a consequence, remediation of HOCs in soil–water system is often dependent on the desorption of contaminants from the soil surface [1,2]. It is well known that surfactants can increase the solubility of HOCs by partitioning it into the hydrophobic cores of surfactant micelles. Surfactant-enhanced remediation (SER) has been suggested as a promising technology for the removal of sorbed HOCs. Numerous studies have investigated the enhanced solubility of a contaminant in the presence of surfactants above their critical micelle concentrations (CMC) [3–9]. A few studies have also indicated

the potential for using micellar solubilization to clean up residual and sorbed contaminants from soils [10–14]. Surfactant may also improve microbial remediation of HOCs in soils by affecting the accessibility of the HOCs to microorganisms [15–20].

In the present study, the enhanced solubilization for HOCs has generally been performed in single anionic or nonionic surfactant and the HOCs solubility enhancement properties of surfactants in single surfactant solution are well defined [3–14]. However, recent soil experiments [21–24] have suggested that precipitation for anionic surfactant and the sorption of nonionic surfactant to soil may occur in soil–water systems. Moreover, the sorbed nonionic surfactant has strong retention capability for HOCs. These may result in an increase in remediation times and costs. Meanwhile, the environment factors, temperature, salinity, and pH have obvious effects on the solubilization of single anionic or nonionic surfactant solution for HOCs.

Now, mixed surfactants are of great interest in scientific and industrial application. Surfactants used in practical applications almost always consist of mixtures of surfactant and the solution properties of mixed surfactant systems are often superior in application to that of the individual ones

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[25]. For example, ionic–nonionic mixed surfactants might show advantageous solubilization behavior, exhibiting cloud points higher than those of the single nonionic surfactant, along with Krafft points lower than those of the single anionic surfactant. Mixed surfactants could be employed over a wider range of temperature, salinity, and hardness conditions than the individual surfactant. Thus, in the practical applications, some researchers attempt to use mixed surfactants with an aim to improve the performance of the SER for contaminated soils. However, only a limited number of studies have been reported where the solubilizations of organic compounds in mixed surfactants were examined [26–33]. Then, it is difficult to understand and predict the solubilization behavior of a mixed surfactant system for organic pollutants and the selection of the mixed surfactants for the SER of contaminated soils lacks adequate theoretical basis.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants resulting from the incomplete combustion of fuel and organic matter. The levels of these compounds in the environment are regulated by government agencies because of the genotoxicity of some high molecular weight PAHs. Pyrene is usually considered to be representative of the behavior of many PAHs. PAHs removal from soils and aquifers by natural attenuation mechanisms or traditional remediation efforts such as pump–treat is slow due to the low solubility of these compounds in water. Many microorganisms, including bacteria, algae, and fungi, have been shown to possess degradative enzymes for the oxidative degradation of PAHs [34], however, the in situ microbial degradation of PAHs is limited by their low bioavailability. Various surfactants have been employed with attempts to increase the aqueous-phase concentrations of PAHs, and thus the bioavailability [4,8,17,18]. Removal of PAHs from contaminated soils and groundwater by surfactants is governed mainly by the micelle and/or microemulsion concentrations of surfactants to solubilize or mobilize the pollutants. It has been demonstrated that the solubility of PAH increases linearly with the surfactant concentration above the critical micelle concentration [4] and the addition of surfactant to pure cultures of microorganisms can increase the extent of PAH metabolism [17]. Up till now, few studies have been made with the solubilization of PAHs on mixed surfactants.

The objectives of this study are (1) to investigate the solubilization of pyrene in some anionic–nonionic mixed surfactants and compare with that predicted according to the ideal mixing rule, and (2) to elucidate the cause of mixing effect of anionic and nonionic surfactants on the solubilization for pyrene. The experimental results can be used to understand and predict the solubilization properties of anionic–nonionic mixed surfactant based on that of single surfactant and provide valuable information for the selection of mixed surfactants on the SER of contaminated soils.

2. Materials and methods

2.1. Materials

Pyrene was selected as representative PAHs to model the hydrophobic organic contaminants and obtained from Aldrich Chemical Company, with a purity of 98%. The water solubility of pyrene is 6.04×10^{-7} mol/L at 25 °C [35]. Surfactants were obtained either directly from the manufacturer or through a distributor and were used without further purification. Sodium dodecyl sulfate (SDS) was obtained from Acros Organics, with purity 98%. Triton X-100 (TX100) was obtained from Sigma Chemical Company. Triton X-405 (TX405), Brij35, and Brij58 were purchased from Acros Organics. The structure and properties of surfactants are listed in Table 1. Surfactant solutions were prepared by dissolving the relevant surfactant in deionized water. Pyrene was dissolved in methanol for pyrene stock solutions.

2.2. Experimental procedures

Batch tests for solubilizations of pyrene in mixed surfactant solutions were performed in four different anionic–nonionic mixed surfactants. Each surfactant–pyrene system involved five to seven batch tests with surfactant solutions having a range of concentrations above the CMC. Duplicate tests were performed for each surfactant concentration. The tests were performed in 25 ml Corex centrifuge tubes with Teflon cap liners. Adding 0.5 ml of pyrene stock solution to centrifuge tubes and then allowing the solvent to evaporate to dryness over a period of 12 h. After this evaporation step, 20 ml of mixed surfactant solutions with different concentrations and composition were added to each tube. These samples were then equilibrated on a reciprocating shaker for 24 h at 25 ± 1 °C. The samples were subsequently centrifuged at $6500 \times g$ for 30 min to separate

Table 1
Physicochemical properties of the selected surfactants

Surfactant	Structure	MW	CMC[a] (mmol/L)	HLB[b]
TX100	$C_8H_{17}C_6H_4O(OCH_2CH_2)_{9.5}H$	628	0.21	13.5
Brij58	$C_{16}H_{33}(OCH_2CH_2)_{20}OH$	1123.5	0.0081	15.7
Brij35	$C_{12}H_{25}(OCH_2CH_2)_{23}OH$	1200	0.066	16.9
TX405	$C_8H_{17}C_6H_4O(OCH_2CH_2)_{40}H$	1966	0.904	17.9
SDS	$C_{12}H_{25}SO_4Na$	288	4.84	40.0

[a] Critical micelle concentration.
[b] Hydrophile–lipophile balance, calculated as HLB = % wt. EO/5.

the undissolved solute. An appropriate aliquot of the supernatant was then carefully withdrawn with a volumetric pipette and diluted to 10 ml with 1 ml methanol, with the rest by surfactant–water solution. Pyrene in the solutions was analyzed at 333.6 nm by the Model UV2401PC spectrophotometer. Because the surfactants exhibit broad UV adsorption, the surfactant concentration was kept a constant in both experimental and standard solutions to eliminate the effects of surfactant on determining solubility.

The values of the CMC of mixed surfactant solutions at 25 °C were determined as the concentration at sharp breaks in the plots of the surface tension versus the logarithm of surfactant concentration. Surface tensions of mixed surfactant solutions over a wide concentration range were determined with a Model 20 surface tensionmeter, manufactured by Fisher Scientific. Mixed surfactant solutions of varying concentration were made and allowed to equilibrate for approximately 5 h before measurements were made. The plotted surface tension value was taken when stable reading were obtained for a given surfactant concentration, as indicated by at least three consecutive measurements having nearly the same value.

3. Results and discussion

3.1. Mixing effect of anionic and nonionic surfactants on molar solubilization ratio (MSR)

Pyrene solubilization was plotted as a function of mixed surfactant solution concentrations for each data set. As an example, plots of apparent pyrene solubilities versus concentrations of the mixed surfactant solutions, SDS–TX100, SDS–TX405, SDS–Brij58, and SDS–Brij35, in which the mole fraction of nonionic surfactant is 0.5, are shown in Fig. 1. Obviously, the aqueous solubilities of pyrene increased linearly over the range of mixed surfactant concentrations. Similar trends can be observed in all the mixed surfactant solution compositions studied. Similar to single surfactants, anionic–nonionic mixed surfactants also have the potential capacity to enhance the solubilization
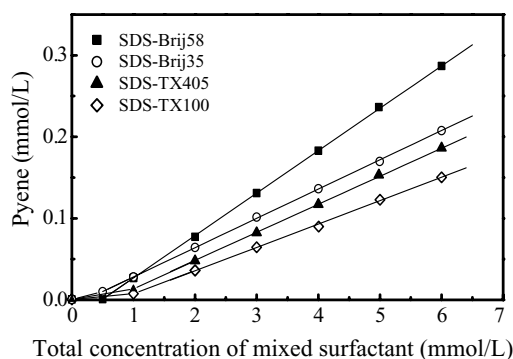
of pyrene in water. The behavior is generally attributed to the incorporation or partitioning of organic solutes within mixed surfactant micelles.

A measure of the solubilization capacity of a surfactant solution for a given solute is known as the molar solubilization ratio (MSR), which is obtained from Edwards et al. [4]. MSR is defined as the number of moles of organic compound solubilized per mole of surfactant added to solution, and can be calculated as follows:

$$\mathrm{MSR} = \frac{S - S_{\mathrm{cmc}}}{C_{\mathrm{s}} - \mathrm{CMC}} \tag{1}$$

where S is the total apparent solubility of the organic compound in surfactant solution at a particular surfactant concentration greater than the CMC, S_{cmc} is the apparent solubility of organic compound at the CMC, and C_{s} is the surfactant concentration at which S is evaluated. All concentrations are expressed in moles per liter. In the presence of excess hydrophobic organic compound, the MSR can be obtained from the slope of the curve in which the solute concentration is plotted against surfactant concentration above the CMC.

To further investigate the role of the solution composition and category of mixed surfactants in the solubilization of pyrene, solubility data were expressed in terms of the MSR. MSRs were obtained from the solubility curves using linear regression procedure. In general, r^2 values of greater than 0.999 were obtained for all pyrene–surfactant systems studied.

Fig. 2 shows the MSRs of pyrene as a function of the mole fraction of nonionic surfactant in different anionic–nonionic mixed surfactants. The MSRs of pyrene increase with an increase in the mole fraction of nonionic surfactant in mixed systems, except for in SDS–TX405 system. In SDS–TX405 system, the MSRs of pyrene have a maximum as the mole fraction of TX405 in mixed system increase.

In mixed surfactant, the MSR for pyrene can be estimated using the MSR in single surfactant solution based on the ideal mixing rule.

$$\mathrm{MSR}_{\mathrm{ideal}} = \mathrm{MSR}_1 X_1 + \mathrm{MSR}_2 X_2 + \mathrm{MSR}_{\mathrm{water}} \tag{2}$$

Fig. 1. The solubilizations of pyrene in mixed surfactants with 0.5 mol fraction of nonionic surfactant.
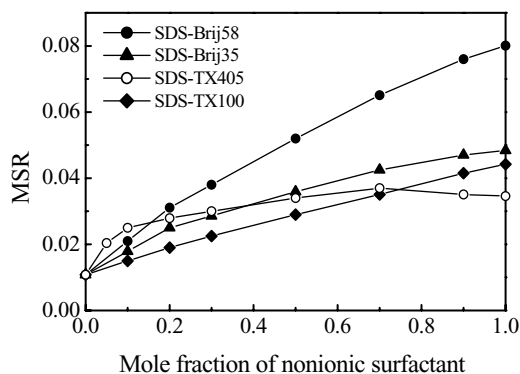

Fig. 2. Molar solubilization ratio (MSR) of pyrene as a function of the solution composition in different mixed surfactants.
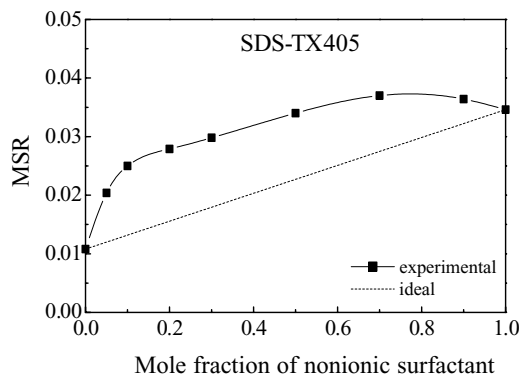
Fig. 3. Comparison of experimental MSR with ideal MSR for pyrene in SDS–TX405 mixed system.

where MSR_{ideal} are the calculated molar solubilization ratio of mixed surfactant for pyrene in the ideal mixed state. MSR_1 and MSR_2 are the molar solubilization ratio for pyrene in single components 1 and 2, respectively. X_1 and X_2 are the mole fraction of components 1 and 2 in mixed surfactant solutions, respectively. MSR_{water} is the molar solubilization ratio of pyrene in pure water (1.09×10^{-8}) and trends to be negligible.

As an example, the comparisons of the MSR_{ideal} of pyrene with the experimental MSR (MSR_{exp}) in SDS–TX405 and SDS–Brij35 mixed systems are shown in Figs. 3 and 4. The results indicate that the MSR_{exp} of pyrene are obviously larger than the MSR_{ideal} at all the mixed surfactant solution composition ranges. Similar tendencies were also observed in SDS–TX100 and SDS–Brij58 mixed systems.

In order to determine fully the mixing effect of the anionic–nonionic surfactant on solubilization for pyrene, the deviation ratio (R) between the MSR_{exp} and the MSR_{ideal} can be evaluated according to the following equation:

$$R = \frac{MSR_{exp}}{MSR_{ideal}} \tag{3}$$

when R is greater than 1, this implies that there is positive mixing effect of anionic and nonionic surfactants on the
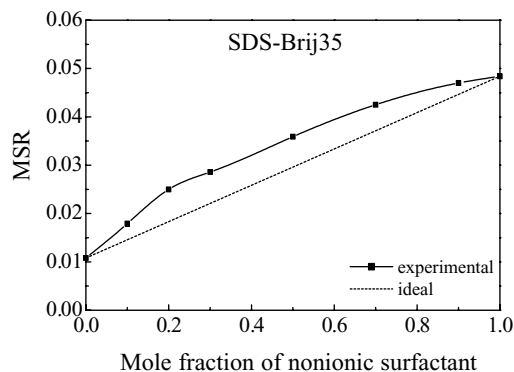

Fig. 4. Comparison of experimental MSR with ideal MSR for pyrene in SDS–Brij35 mixed system.
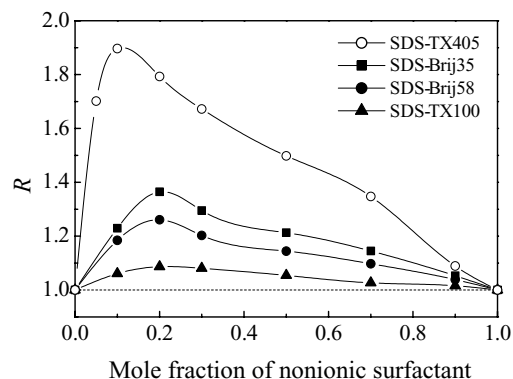

Fig. 5. Deviation ratios (R) as a function of the solution composition in different mixed surfactants.

solubilization and positive deviation of MSRs from ideal mixture.

The deviation ratios (R) as a function of the mole fraction of nonionic surfactant in mixed surfactant solutions are plotted in Fig. 5. The values of R for pyrene are larger than 1 at any solution composition studied, which indicates that these four anionic–nonionic mixed surfactants have positive mixing effect on solubilization for pyrene and MSRs have positive deviation from ideal mixture. The positive deviation of MSRs from ideal mixture follows the order of SDS–TX405 > SDS–Brij35 > SDS–Brij58 > SDS–TX100 and increases with an increase in the hydrophile–lipophile balance (HLB) value of nonionic surfactant in mixed systems. In addition to this, in the four mixed surfactants, the positive deviation of MSRs from ideal mixture has a maximum at the mole fraction of nonionic surfactant between 0.1 and 0.3. Similar results were obtained in the study of Nishikido [26], in which the author investigated the solubilization of yellow OB, a dyestuff, in mixed surfactants of SDS and various dodecyl polyoxyethylene surfactants (POE6, POE29, POE49) and found that the longer the oxyethylene chain length, the larger the dye solubility in the mixed surfactants than for the ideal mixture, and the positive deviation of the dye solubility from the ideal mixture has a maximum with the varying mixed surfactant composition.

3.2. Mixing effect of anionic and nonionic surfactants on micelle–water partition coefficient (K_{mc})

An alternative approach used to quantify the surfactant solubilization is based on the micelle–water partition coefficient (K_{mc}), which represents the distribution of organic compounds between surfactant micelles and the aqueous phase and may be expressed as follows [4]:

$$K_{mc} = \frac{X_m}{X_a} \tag{4}$$

where X_m and X_a are the mole fraction of solute in the micelle and aqueous phase, respectively. The value of X_m

Table 2
Partition coefficients of pyrene in the anionic–nonionic mixed surfactants with solution mole fraction (X_{non}) and micelle mole fraction (X_{non}^m)[a] of nonionic surfactant

		X_{non}						
		0.000	0.100	0.300	0.500	0.700	0.900	1.000
SDS–TX405	X_{non}^m	0.000	0.453	0.574	0.651	0.723	0.829	1.000
	$\ln K_{mc}$	13.74	14.58	14.73	14.88	14.91	14.89	14.88
SDS–Brij35	X_{non}^m	0.000	0.721	0.842	0.901	0.944	0.982	1.000
	$\ln K_{mc}$	13.74	14.24	14.69	14.91	15.11	15.17	15.21
SDS–Brij58	X_{non}^m	0.000	0.919	0.972	0.987	0.994	0.998	1.000
	$\ln K_{mc}$	13.74	14.33	14.97	15.27	15.48	15.61	15.67
SDS–TX100	X_{non}^m	0.000	0.634	0.802	0.881	0.936	0.980	1.000
	$\ln K_{mc}$	13.74	14.06	14.46	14.69	14.89	15.05	15.15

[a] X_{non}^m were calculated by regular solution theory [36,37].

can be calculated from the MSR:

$$X_m = \frac{MSR}{1 + MSR} \tag{5}$$

The mole fraction of organic compound in the aqueous phase (X_a) may be estimated as:

$$X_a = S_{cmc} V_w \tag{6}$$

where S_{cmc} is the apparent solubility of organic compound at the CMC and V_w is the molar volume of water (0.01805 L/mol).

Thus, an expression for K_{mc} is

$$K_{mc} = \frac{55.4 \times MSR}{S_{cmc}(1 + MSR)} \tag{7}$$

The K_{mc} of pyrene in the four anionic–nonionic mixed surfactants with different solution composition has been listed in Table 2.

Treiner et al. [28–30] have suggested that the partition coefficient of a neutral organic solute between micelle and aqueous phase in a mixed surfactant may be represented by the relationship

$$\ln K_{mc} = X_1^m \ln K_1 + (1 - X_1^m) \ln K_2 + B X_1^m (1 - X_1^m) \tag{8}$$

where K_1 and K_2 are the micelle–water partition coefficient of a solute for the individual surfactant constituting the mixed micelle, and K_{mc} is the same parameter in the mixed surfactant. X_1^m corresponds to the micelle mole fraction of a surfactant having the value of K_1. B is the experimental

parameter including both the surfactant–surfactant interactions and the surfactant–solute interactions. When there is no mixing effect of surfactant on the partition of the solute, the B coefficient is expected to be zero.

Table 3 listed the analytical functions that represent the experimental data with the average B value at any micelle composition of the anionic–nonionic mixed surfactants. As can be seen from Table 3, the B values for pyrene in SDS–TX405, SDS–Brij35, SDS–Brij58, and SDS–TX100 mixed systems are 1.54, −1.34, −28.3, and −2.81, respectively. Here, there is not distinct relationship between the values of B and the structure of mixed surfactants, because the values of B must depend both on surfactant–surfactant interaction and on surfactant–solute interactions in the mixed micelle. According to the values of B, the mixing effect of anionic and nonionic surfactants on the partition of pyrene is positive in SDS–TX405 mixed system and consistent with the result of positive deviation of MSRs from ideal mixture, which seemingly can be used to interpret the mixing effect of anionic and nonionic surfactants on the solubilization for pyrene. However, the mixing effect of anionic and nonionic surfactants on the partition of pyrene is negative in SDS–Brij35, SDS–Brij58, and SDS–TX100 mixed systems, which are contradictory with the positive deviation of MSRs from ideal mixture. Similar results were also found in the study of Tokuota et al. [32], in which the synergistic solubilization for a hydrophobic synthetic perfume in mixed surfactants of SDS and polyoxyethylene ethers ($C_{16}POE_n$, $n = 20$ and 40) were observed along with the smaller K_{mc} than ideal value. In other studies [22,23], it could also be observed that the mixing effect of

Table 3
Characteristic parameters of the partition equation for pyrene in mixed surfactants

Mixed surfactants	Partition equation[a]
SDS–TX405	$\ln K_{mc} = X_{non}^m 14.88 + (1 - X_{non}^m)13.74 + 1.54 X_{non}^m (1 - X_{non}^m)$
SDS–Brij35	$\ln K_{mc} = X_{non}^m 15.21 + (1 - X_{non}^m)13.74 - 1.34 X_{non}^m (1 - X_{non}^m)$
SDS–Brij58	$\ln K_{mc} = X_{non}^m 15.67 + (1 - X_{non}^m)13.74 - 28.3 X_{non}^m (1 - X_{non}^m)$
SDS–TX100	$\ln K_{mc} = X_{non}^m 15.15 + (1 - X_{non}^m)13.74 - 2.81 X_{non}^m (1 - X_{non}^m)$

[a] Partition equation: $\ln K_{mc} = X_{non}^m \ln K_{non} + (1 - X_{non}^m) \ln K_{SDS} + B X_{non}^m (1 - X_{non}^m)$. X_{non}^m is the mole fraction of nonionic surfactant in mixed micelles. K_{non} and K_{SDS} are the micelle–water partition coefficients of pyrene in nonionic surfactant and SDS, respectively.
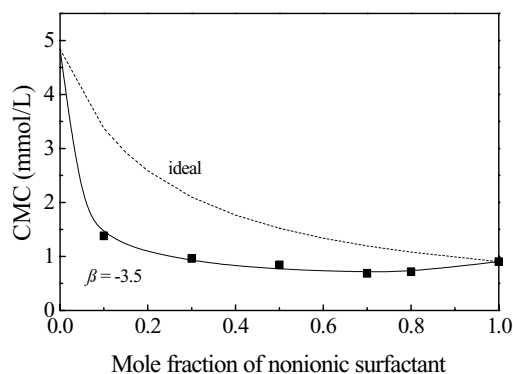
Fig. 6. Comparison of experimental CMCs with ideal CMCs in SDS–TX405 mixed system.

surfactants on the K_{mc} is contrary to that on the solubilization of organic compounds in mixed surfactants. Thus, we suggest that the mixing effect of surfactants on the K_{mc} could not be utilized as the sole factor to account for the mixing effect of surfactants on solubilization for HOCs.

3.3. Mixing effect of anionic and nonionic surfactants on critical micelle concentration

In ideal mixed state, the CMC of mixed surfactant solution can be calculated with ideal solution theory [36].

$$\frac{1}{CMC^{(1+K_g)}} = \frac{X_1}{CMC_1^{(1+K_g)}} + \frac{X_2}{CMC_2^{(1+K_g)}} \quad (9)$$

where X is the mole fraction of components in mixed surfactant solutions. Subscripts 1 and 2 indicate the components 1 and 2, respectively. K_g is the degree of counterion binding to the mixed micelle.

However, due to the interaction between the components of mixed micelle, the experimental CMCs are usually different from the ideal CMCs. In Fig. 6, the CMCs of ideal mixed state in SDS–TX405 mixed system were compared with those of experimental values as a function of the solution composition. It can be found that the experimental CMCs are obviously lower than the ideal CMCs in SDS–TX405 mixed system. Similar results were also obtained for SDS–Brij35, SDS–Brij58, and SDS–TX100 mixed systems.

The regular solution theory has been proven to be remarkably successful in modeling the nonideal behavior of mixed surfactants. According to the regular theory, the deviation of the experimental CMCs from the ideal CMCs in mixed surfactant can be represented with the parameter β, which represents the interaction of components [36,37].

$$\beta = \frac{\ln[X_1 CMC/(X_1^m CMC_1)]}{(1 - X_1)^2} = \frac{\ln[X_2 CMC/(X_2^m CMC_2)]}{(1 - X_2)^2} \quad (10)$$

where X and X^m are the mole fraction of components in the mixed surfactant solutions and the mixed micelles,

respectively, and subscripts 1 and 2 indicate the components 1 and 2, respectively.

The interaction parameter, β, was calculated to be -3.5, -2.6, -2.1, and -1.5 for SDS–TX405, SDS–Brij35, SDS–Brij58, and SDS–TX100 mixed systems from curve fittings, respectively. The larger negative value of β, denotes the great negative deviation of CMCs from ideal mixture. Then, the negative deviation of CMCs from ideal mixture follows the order of SDS–TX405 > SDS–Brij35 > SDS–Brij58 > SDS–TX100, which is same as that of the HLB of nonionic surfactant in mixed systems and that of the mixing effect of surfactants on MSRs for pyrene.

For the anionic–nonionic mixed surfactants there will be significant electrostatic self-repulsion for the anionic and weak steric self-repulsion for the nonionic before mixing. After mixing, the electrostatic self-repulsion of the anionic surfactant will be replaced by ion-dipole attraction interaction between the two different hydrophilic groups of anionic and nonionic surfactant, which result in negative β values and the negative deviation of the CMCs from ideal mixture [38]. When the length of the polyoxyethylene group of the nonionic surfactant becomes larger, then its steric effect becomes larger. There is also the acquisition of a positive charge by the polyoxyethylene group, which should be greater when the length of the polyoxyethylene group is increased. This would cause electrostatic attractive interaction with the anionic surfactant in mixed micelle. Then, with the increase in the length of the polyoxyethylene chain, there is an increased electrostatic attractive interaction between the anionic surfactant and the positively charged polyoxyethylene group of nonionic surfactant, resulting in more negative β values and the deviation of the CMCs from ideal mixture.

3.4. The mechanism for mixing effect of anionic and nonionic surfactants on solubilization for pyrene

There are various mechanisms by researchers to interpret the mixing effect of surfactants on solubilization for organic compounds. For example, Nishikido [26] considered that the positive deviation from ideal mixture could be attributed to an increase in the compactness of polyoxyethylene chains compared with that in single micelles, and the extent of the increase in compactness is greater for the longer polyoxyethylene chain. A different interpretation suggested by Tokuota et al. [32] was that for hydrophobic organic compounds, the effective solubilization area in the mixed micelles becomes larger than that of the single surfactant micelles as a result of an increase in the radius of the mixed micelle including the electric double. Actually, these interpretations ascribed the mixing effect to the changes of structure and properties of mixed micelles, which are the results of the interaction between the components of mixed surfactant, attractive or repulsive. Among these changes, the micelle–water partition coefficient and the CMC are the two important factors usually discussed influencing the solubilization of mixed surfactant for organic compounds.

The solubility of pyrene increased linearly over the range of mixed surfactant concentrations above the CMC. The behavior is generally attributed to the incorporation or partitioning of organic solutes within mixed micelles. The solubilization of pyrene in mixed micelle has a crucial role for that of pyrene in mixed surfactant solutions with concentrations above the CMC, and can be expressed as follows.

$$S_{mic} = C_{mc} K_{mc} S_w \qquad (11)$$

where

$$C_{mc} = C - CMC \qquad (12)$$

and S_{mic} is the concentration of pyrene partitioned into mixed micelles, C_{mc} is the concentration of mixed surfactant in micellar form, K_{mc} is the micelle–water partition coefficient, S_w is the concentration of pyrene dissolved in water, and C is the total mixed surfactant concentration.

From Eq. (11), we can see that C_{mc} and K_{mc} are two important factors influencing the solubilization of pyrene in mixed surfactant. In discussing the mixing effect of surfactants on solubilization for pyrene, the mixing effect on the C_{mc} and K_{mc} must be considered simultaneously. The positive mixing effect on the C_{mc} is the embodiment of the negative deviation of the CMCs from ideal mixture and increases as that becomes greater.

For the solubilization of pyrene in SDS–TX405 mixed system, both the mixing effect on the C_{mc} and K_{mc} are positive, the conjunct effect of which results in the greater positive deviation of MSRs from ideal mixture. However, for the solubilization of pyrene in SDS–Brij35, SDS–Brij58 or SDS–TX100 mixed systems, the mixing effect on the C_{mc} is positive along with the negative mixing effect on the K_{mc}, thus the positive deviation of MSRs from ideal mixture is the net result of the two opposing effects. Meanwhile, the positive deviation of MSRs for pyrene from ideal mixture increases as the negative deviation of experimental CMCs from ideal mixture becomes greater, but which has not definite relation with the mixing effect on the K_{mc}. These results demonstrate that the negative deviation of the CMCs from ideal mixture plays a crucial role for the mixing effect of anionic and nonionic surfactants on solubilization for pyrene.

4. Conclusions

The solubilities of pyrene increased linearly over the range of mixed surfactant concentrations above the CMC, which illustrates the potential capacity of anionic–nonionic mixed surfactants to enhance the solubilization of pyrene in water. Anionic–nonionic mixed surfactants have mixing effect on solubilization for pyrene. The mixing effect is closely related to HLB of the nonionic surfactant in mixed surfactant systems. The attractive interaction between the components of mixed surfactant results in the changes of structure and properties of mixed micelle, of which the negative deviation of

the CMC from ideal mixture and the increasing or decreasing K_{mc} are two important factors influencing the solubilization of mixed surfactant for pyrene. The positive deviation of MSRs for pyrene from ideal mixture is the conjunct or the net result of the two factors, but the negative deviation of the CMC from ideal mixture plays a crucial role. We can draw a conclusion that the larger the HLB of nonionic surfactant in mixed systems, the greater the attractive interaction between the components of mixed surfactants, which results in the greater negative deviation of the CMC from ideal mixture, and then the mixing effect of anionic and nonionic surfactants on solubilization for pyrene becomes greater. The results can provide valuable information for the selection of mixed surfactant for the SER of contaminated soils.

Acknowledgements

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