

Solubilization of DNAPLs by mixed surfactant: Synergism and solubilization capacity

Baowei Zhao^{a,b,*}, Lizhong Zhu^{b,1}

^a School of Environmental and Municipal Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu Province 730070, China

^b Department of Environmental Science, Xixi Campus, Zhejiang University, Hangzhou 310028, China

Received 7 May 2005; received in revised form 26 August 2005; accepted 27 August 2005

Available online 19 October 2005

Abstract

Efforts to remove the dense nonaqueous phase liquids (DNAPLs) in subsurface by mobilizing them face with risks of driving the contaminants deeper into aquifer zones. In this paper, a synergistical solubilization of DNAPLs by mixed nonionic and anionic surfactant, Triton X-100 (TX100) and sodium dodecylbenzene sulfonate (SDBS) in DNAPL/water systems was presented. Given 1:40 phase ratio of DNAPL:water (v/v), mixed TX100–SDBS exhibited significantly synergistical solubilization for the DNAPLs, trichloroethene (TCE), chlorobenzene (CB) and 1,2-dichlorobenzene (1,2-DCB), respectively, when the total surfactant concentration was up to 1000 mg/L, i.e. the condition when solubilization by the mixture was better than those attainable with individual components by themselves. The synergistical extents depended on the initial ratios of TX100 to SDBS, the initial surfactant concentrations and the properties of DNAPLs. Given the total surfactant concentration, synergistical extents increased with the fraction of SDBS in mixed surfactant. On the other hand, it did with the total surfactant concentration. The solubilization capacity by 3:1, 1:1 and 1:3 of mass ratio of TX100–SDBS were determined and compared with those by single ones. In the view of the mass solubilization ratio (SR), the mixed TX100–SDBS could solubilize more DNAPLs than single SDBS at given surfactant concentration. Reduction in partition of TX100 and synergistic solubilization were responsible for the significant solubilization extent of mixed system. The work presented here demonstrates that mixed nonionic–anionic surfactants would be preferred over the corresponding single surfactants for solubilization remediation of DNAPLs, which could decrease risks of driving the contaminants deeper into aquifers.

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Keywords: DNAPLs; Mixed surfactant; Solubilization; Partitioning; Synergism

1. Introduction

Dense nonaqueous phase liquids (DNAPLs) are widespread environmental contaminants and are more prevalent contaminants found in subsurface. Being denser than the surrounding groundwater, these contaminants are termed dense nonaqueous phase liquids. Specially, DNAPLs may migrate below the water table when they tend to pool on the top of fine-grained strata or become trapped by interfacial force in the form of disconnected ganglia. Further downward migration of the contaminant can occur due to an increase in the hydraulic potential, lateral spreading of a pool to a vertical fracture, or a reduction in inter-

facial tension due to change in subsurface chemistry, which pose the most significant problem due to their location in the aquifer. EPA estimates predict that approximately 60% of the Superfund sites have a medium to high likelihood of containing DNAPLs [1].

Despite the extent of DNAPL contamination problems, consistently successful remediation techniques have not yet been developed. Surfactant injection is a promising new technology for enhancing NAPL remediation, through micelle solubilization and/or mobilization [2–4]. The mobilization mechanism involves the immiscible (two phase) displacement of NAPL as free product. Immiscible displacement is often referred to as mobilization, as discrete NAPL ganglia is envisioned to be mobilized from interstitial pore space as a result of reduction in capillary force. However, the risk of downward migration of DNAPL free product into uncontaminated regions of aquifers has been the primary limitation for the implementation of immiscible displacement technologies for DNAPL remediation. Sol-

* Corresponding author. Tel.: +86 931 4956977; fax: +86 931 4956017.

E-mail addresses: baoweizhao@mail.lzjtu.cn, zhbw2001@sina.com

(B. Zhao), zlz@zju.edu.cn, lzzhu@mail.hz.zj.cn (L. Zhu).

¹ Tel.: +86 571 88273733; fax: +86 571 88273450.

ubilization usually involves the use of micellar surfactant solutions to increase the apparent aqueous solubility of contaminant in a single-phase miscible displacement flood. This approach has been shown to be effective in numerous studies [5–11] and may significantly reduce remediation times compared to pump-and-treat. Solubilization technologies pose less risk of uncontrolled NAPL migration and are less complex to design. Since DNAPLs pose the greatest risk of migration, there is a need for more information on surfactants that are capable of solubilizing DNAPLs and removing them as water continuous, low viscosity, microemulsions without mobilization.

1.1. Partitioning of ethoxylated nonionic surfactant in DNAPL phase

Ethoxylated nonionic surfactants have received significant attention in surfactant remediation investigations to date due to their relative high solubilization capacity [12,13]. However, one concern with this surfactant remediation that has received attention recently is the partitioning of surfactants between aqueous and organic phase during remediation applications [14–16]. It is found that the partitioning of ethoxylated nonionic surfactant can, especially in the case of polar DNAPLs, such as dichloromethane, chloroform, trichloroethene (TCE), chlorobenzene (CB) and 1,2-dichlorobenzene (1,2-DCB), etc., leads to substantial loss of surfactant, leaving little surfactant remaining in aqueous solution for solubilization [14,16], which would greatly reduce the surfactant flushing efficiency and surfactant recovery in post-groundwater extraction recycling operations. As a result, surfactant partition should be considered while selecting a surfactant for a particular remediation (e.g. the polar DNAPLs) application to minimize surfactant loss.

1.2. Reduction in partitioning losses of nonionic surfactant

In general, anionic surfactant does not partition into the organic phase [17]. However, their solubilization capability for DNAPLs is significantly less than nonionic one's [12,13]. Anionic and nonionic surfactant solutions usually form mixed micelle aggregates that frequently exhibit characteristic properties that are remarkably different from those of individual components [17–19], which would result in the less partitioning of nonionic surfactant and hence more aqueous solubility enhancement of DNAPLs. In our previous research, a novel solubilization of DNAPLs by mixed nonionic and anionic surfactant, Triton X-100 (TX100) and sodium dodecylbenzene sulfonate (SDBS), was studied and compared with those by single ones. Given 1:40 phase ratio of DNAPL:water (v/v) and the total surfactant concentration from 200 to 10,000 mg/L, the mixed TX100–SDBS at the total mass ratios of 3:1, 1:1 and 1:3 exhibited significant solubilization for TCE, CB and 1,2-DCB. The solubilization extent by mixed TX100–SDBS was much larger than by single TX100 and even larger than by single SDBS at the ratios of 1:1 and 1:3, respectively, which was shown in Fig. 1 taking 1,2-DCB as an example. Partition of TX100 into the organic phase greatly affected the solubilization extent. The

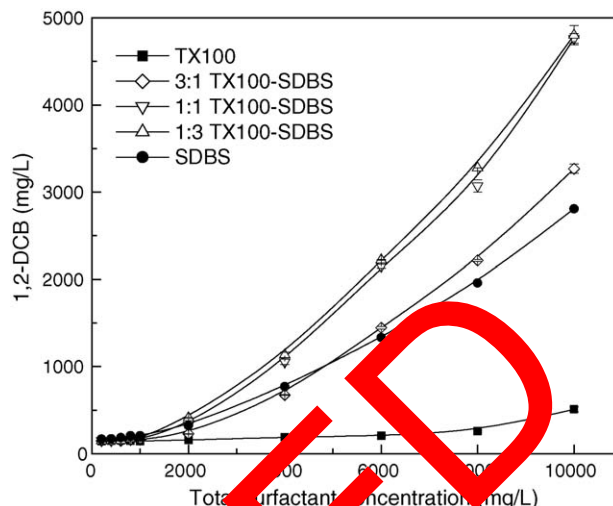


Fig. 1. Aqueous phase solubility of 1,2-DCB vs. total surfactant concentration at 1:40 phase ratio of 1,2-DCB:water (v/v).

TX100 losses into TCE, CB and 1,2-DCB phases were more than 90, 97 and 97%, respectively, when single TX100 was used. No SDBS partitioned into DNAPLs was observed in single or mixed systems. SDBS decreased greatly the partition loss of TX100 into DNAPLs. The extent of TX100 partition decreased with increasing the amount of SDBS, which is shown in Fig. 2 taking 1,2-DCB as an example. The mechanism for reduction of TX100 partition was found. TX100 and SDBS formed mixed micelles in the solution phase. The inability of SDBS to partition into DNAPLs, the mutual affinity of SDBS and TX100 in the mixed micelle controlled the partitioning of TX100 into DNAPL phase.

However, the superior solubilization extent by mixed surfactant was partially due to the reduction in partitioning of nonionic surfactant. In most cases, when different types of surfactants are purposely mixed, synergism is observed [17–19], i.e. the

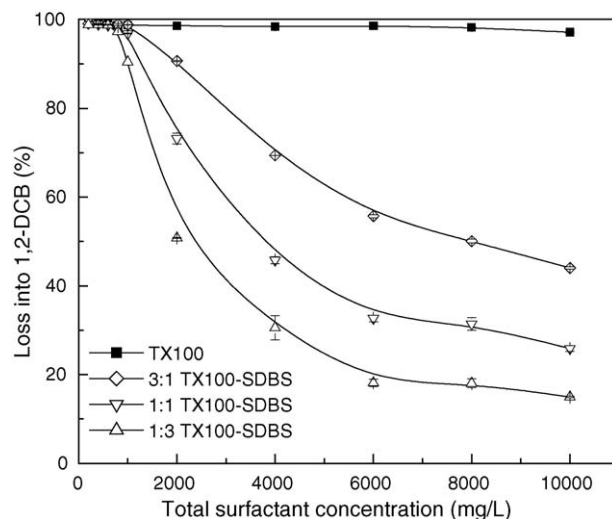


Fig. 2. TX100 losses into 1,2-DCB organic phases vs. total surfactant concentration at 1:40 phase ratio of 1,2-DCB:water (v/v).

condition when properties of the mixture are better than those attainable with individual components by themselves, which could enhance the solubilization capacity of mixed surfactant. To our knowledge, few studies were done to the synergistical solubilization of DNAPLs by mixed anionic–nonionic surfactant. Here, TX100 and SDBS are chosen as the representatives of anionic and nonionic surfactant, and TCE, CB and 1,2-DCB the representatives of polar DNAPLs. The objectives of the present study are (1) to quantify the synergistical extent of DNAPLs solubilization in mixed anionic–nonionic surfactant; (2) to expound the solubilization extents of DNAPLs associated to the mixed micellar phase. The work presented implications for aquifer remediation contaminated by DNAPLs.

2. Experimental

2.1. Chemicals

TX100 was obtained from Sigma Chemical Company and SDBS (purity $\geq 98\%$) was purchased from Tokyo Kasei Kogyo Co., Ltd., respectively, used as received. TCE, CB and 1,2-DCB, with analytical grade, were obtained from Shanghai Chemical Company, China. The characteristics of the selected chemicals are given in Table 1. HPLC-grade methanol was purchased from Shanghai Chemical Institute. Purified water was used for all tests.

2.2. Synergistical solubilization tests

Single TX100, SDBS and mixed TX100–SDBS solution with different total concentration were prepared respectively in flasks. A series of 20 mL of single or mixed surfactant solutions were placed into 25-mL Corex centrifuge tubes with Teflon cap liners. Five hundred microliters of DNAPL was added into each tube. Duplicate samples were prepared for each surfactant concentration solution; these samples were then equilibrated on a reciprocating shaker for 72 h at $25 \pm 1^\circ\text{C}$. (Previous experimental results showed 72 h mixing time to be sufficient for obtaining equilibrium solubilization and partitioning values under mixing conditions.) The samples were subsequently centrifuged on a Model Bio-1000 Primary centrifuger (Hanau, Germany) for 1 h at the speed of 1000 rpm ($290 \times g$) to separate the phases. An appropriate aliquot (2.0, 1.0, 0.5 or 0.2 mL) of the supernatant was then carefully withdrawn with a volumetric pipette

and diluted to 10 mL in flasks with 8.0 mL of methanol, with the rest by water. The diluted samples were analyzed for TX100, SDBS, and DNAPL using Hitachi HPLC (Hitachi, Japan), which was equipped with two pumps, an autosampler, and an ultraviolet spectrophotometer. One hundred microliters of the sample solution was injected into a reverse-phase C18 column (Waters Spherisorb S50DS2, 4.6 mm \times 250 mm). The elution was carried out by pumping methanol and water (80:20, v/v) isocratically at a flow rate of 1.0 mL/min. The temperature of column was kept at 40°C . Standards containing surfactant or DNAPL initially were analyzed as separate standards to determine retention times and to optimize the UV wavelength for detection. The absorbency was measured at a wavelength of 224, 224, 200, 210 and 210 nm for SDBS, TX100, TCE, CB and 1,2-DCB, respectively, and the retention time was 2.72, 11.85, 5.75, 5.89 and 6.82 min, respectively. The quantitation limits of the method, defined as the concentrations that gave a signal-to-noise ratio of 10, were 0, 0.06, 0.015, 0.024 and 0.30 mg/L for SDBS, TX100, TCE, CB and 1,2-DCB, respectively. The calibrations were performed by injecting standard surfactant or DNAPL solution, determining the peak area and plotting the curves of the peak area versus the standard concentration. TX100, SDBS and DNAPL were quantified from the calibration. The amounts of surfactant in DNAPL phase were evaluated by the difference between the initial and equilibrium concentration of surfactant in aqueous phase.

Determinations of mass solubilization ratio (SR)

A series of 20 mL of single or mixed surfactant solutions at 3:1, 1:1 and 1:3 mass ratio of TX100 to SDBS, ranging from 1000 to 10,000 mg/L, were placed into Corex tubes and 2.0 μL of DNAPL was added into each tube. Duplicate samples were prepared for each surfactant solution; these samples were then equilibrated on a reciprocating shaker and subsequently centrifuged under the condition mentioned above. Phase separation was detected. If there was the residual of DNAPLs (oil droplet), an appropriate aliquot of the supernatant was withdrawn, diluted and analyzed according to the procedure mentioned above; if there was not the residual of DNAPLs, 2.0 μL of DNAPL addition, equilibration and centrifugation were repeated until oil droplet occurred. This procedure neglected the phase ratio, avoided substantial partition of TX100 and ensured the measurement of mass solubilization ratio (SR).

Table 1
Characteristics of the selected chemicals

Chemicals	Molecular formula	Molar weight (g/mol)	IFT ^a (mN/m)	Aqueous solubility (mg/L, 25 °C) ^b	CMC (mg/L) ^c
TCE	C ₂ HCl ₃	131.39	34.5	1100	
CB	C ₆ H ₅ Cl	112.56	37.4	390.7	
1,2-DCB	C ₆ H ₄ Cl ₂	147.00	40.1	92.32	
TX100	C ₈ H ₁₇ C ₆ H ₄ (OCH ₂ CH ₂) _{9,5} OH	625			164.7
SDBS	C ₁₂ H ₂₅ C ₆ H ₄ SO ₃ Na	348.48			963.2

^a Interfacial tension, reported by Zimmerman et al. [14].

^b Aqueous solubility, reported by Yaws [20].

^c The critical micelle concentration, measured in this work.

3. Results and discussion

3.1. Synergistical solubilization

In practical applications, mixtures of surfactants, rather than individual surfactants are often used. In most cases, when different types of surfactants are purposely mixed, synergism is observed, i.e. the condition when properties of the mixture are better than those attainable with individual components by themselves. Synergism has been found in solubilization for hydrophobic organic compounds by anionic–nonionic surfactants [18,19]. To detect synergistical solubilization of mixed surfactant, the solubility enhancement by single surfactant should be firstly viewed.

Data in Fig. 3 show the water solubility enhancements of TCE, CB and 1,2-DCB by single TX100 and SDBS at the concentrations above their CMCs respectively, in which the solubilities increased with increasing surfactant concentrations. From slope of the plot, mass solubilization ratios (SR) were calculated as the number of grams of organic compound solubilized per gram of surfactant added to the solution. In the presence of an excess of hydrophobic organic compound, SR can be obtained as follows:

$$SR = \frac{(S^* - S_{cmc}^*)}{(C_{surf} - CMC)} \quad (1)$$

where S_{cmc}^* (mg/L) is the apparent solubility of a compound at the CMC (mg/L); S^* (mg/L) the total apparent solubility of the compound in micellar solution at a particular surfactant concentration greater than the CMC; and C_{surf} (mg/L) is the surfactant concentration at which S^* is evaluated. Experimental measured values of SR for TX100 and SDBS are listed in Table 2. The solubilization capacity of TX100 for TCE, CB and 1,2-DCB quantified by SR values are 1.47, 1.66 and 1.08 times as those of SDBS, which demonstrates that ethoxylated nonionic surfactants have relative high solubilization capacity.

For binary mixed surfactant systems, S_{mix}^* is defined as the aqueous solubility of solute by mixed surfactants in aqueous phase, and S_{sum}^* , the calculated solubilities of solute in the mixed solutions based on the ideal additivity rule [21–23]. S_{sum}^* was calculated as

$$S_{sum}^* = (S_1^* + S_2^*) - S_w \quad (2)$$

where S_1^* is the apparent solubility of solute in sole nonionic surfactant solution in which nonionic surfactant concentration is equal to that in the binary mixed system; S_2^* is the apparent solubility in sole SDBS solutions in which SDBS concentration

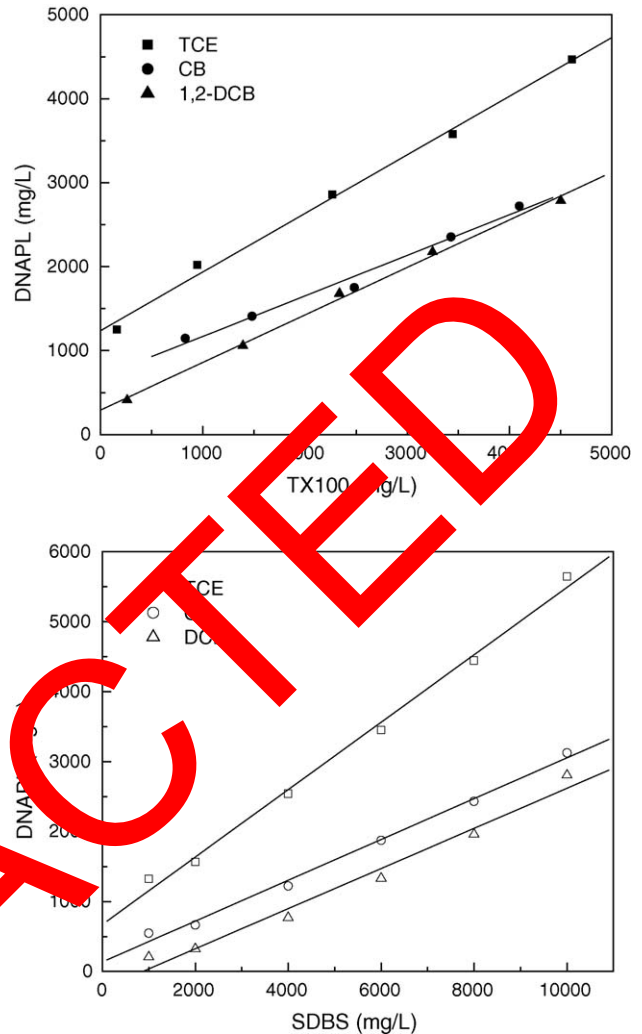


Fig. 3. Solubilization of TCE, CB and 1,2-DCB by TX100 and SDBS micellar solution with phase ratio neglected.

is equal to that in the binary mixed system. Both of them can be obtained from the plots of the apparent solubility of solute versus the concentration of single surfactant (Fig. 3) or calculated from the regression equation (Table 2). S_w is the intrinsic solubility of solute in water. Define the difference ΔS as followed:

$$\Delta S = \frac{(S_{mix}^* - S_{sum}^*)}{S_{sum}^*} \times 100 \quad (3)$$

If the difference ΔS are positively larger than zero, what is the synergistical solubilization is observed. Accordingly the value of ΔS illustrates the extent of synergistic solubilization.

Table 2
Equations of solubilization curves and mass solubilization ratios by TX100 and SDBS with phase ratio neglected

DNAPLs	TX100			SDBS		
	Regression equation	R^2	SR	Regression equation	R^2	SR
TCE	$S_1^* = 0.6976C_1 + 239.6$	0.9952	0.698 ± 0.028	$S_2^* = 0.4818C_2 + 672.74$	0.9944	0.482 ± 0.018
CB	$S_1^* = 0.4844C_1 + 682.01$	0.9900	0.484 ± 0.034	$S_2^* = 0.2916C_2 + 137.6$	0.9942	0.292 ± 0.011
1,2-DCB	$S_1^* = 0.5693C_1 + 282.32$	0.9977	0.569 ± 0.018	$S_2^* = 0.2867C_2 - 248.15$	0.9791	0.287 ± 0.021

Table 3

Comparison of synergistical solubilization extent of TCE, CB and 1,2-DCB by TX100–SDBS at 1:40 phase ratio of DNAPL:water (v/v)

DNAPLs	α_i	$C_{T,i} = 6000 \text{ mg/L}$			$C_{T,i} = 8000 \text{ mg/L}$			$C_{T,i} = 10,000 \text{ mg/L}$		
		ΔS (%)	α_{eq}	$C_{T,\text{eq}}$ (mg/L)	ΔS (%)	α_{eq}	$C_{T,\text{eq}}$ (mg/L)	ΔS (%)	α_{eq}	$C_{T,\text{eq}}$ (mg/L)
TCE	0.75	–	0.50	2809 ± 4.4	–	0.55	3869 ± 9.9	5.5	0.60	5778 ± 49
	0.50	19.8	0.36	4685 ± 39	25.1	0.39	6599 ± 31	45.5	0.41	8425 ± 12
	0.25	36.2	0.21	5717 ± 4.1	44.5	0.22	7696 ± 5.6	57.0	0.22	9587 ± 4.5
CB	0.75	2.4	0.56	3373 ± 120	14.2	0.60	5050 ± 110	27.8	0.64	6894 ± 38
	0.50	8.8	0.40	5011 ± 21	16.9	0.41	6781 ± 13	28.1	0.43	8744 ± 54
	0.25	14.9	0.22	5757 ± 11	17.4	0.22	7669 ± 19	29.8	0.23	9702 ± 5.0
1,2-DCB	0.75	–	0.57	3494 ± 16	–	0.60	4997 ± 20	7.7	0.63	6697 ± 16
	0.50	10.2	0.40	5020 ± 21	15.8	0.41	6744 ± 57	30.1	0.43	8706 ± 32
	0.25	15.1	0.21	5728 ± 13	26.3	0.21	7639 ± 20	45.4	0.22	9626 ± 7.8

$C_{T,i}$: the initial concentration of TX100–SDBS; $C_{T,\text{eq}}$: the equilibrium concentration of TX100–SDBS in aqueous phase; α_i : the initial mass fraction of TX100 in TX100–SDBS; α_{eq} : the equilibrium mass fraction of TX100 in TX100–SDBS in aqueous phase.

Given 1:40 phase ratio of DNAPL:water (v/v) and the total surfactant concentration from 200 to 10,000 mg/L, the synergistical solubilization by mixed TX100–SDBS at the initial mass ratios of 3:1, 1:1 and 1:3 was detected. The results of synergism for 1,2-DCB by mixed surfactant are shown in Fig. 4. (It should be pointed out that the residual surfactant in aqueous phase was responsible for the synergistic solubilization.) As shown in Fig. 4, significantly synergistic solubilization occurred when the total surfactant concentration went approximately over 6000 mg/L. The situation for TCE and CB were similar to that for 1,2-DCB. The results of synergistic solubilization extents of TCE, CB and 1,2-DCB by TX100–SDBS are listed in Table 3. Given the initial total concentration of TX100–SDBS, ΔS increased with decreasing the mass fraction of TX100 in mixed surfactant; given the initial mass fraction, ΔS increased with increasing the initial total surfactant concentration. The results suggest mixing of anionic with nonionic surfactants could enhance the efficiency of solubilization for DNAPL.

It need be pointed out that the effective concentrations of mixed surfactant in aqueous phase is always less than those of single SDBS when the total concentration were given in DNAPL/water systems, due to the partitioning of TX100 into organic phase. However, the mixed TX100–SDBS exhibited larger solubilization extent than single SDBS did, which predicted the solubilization capacity by mixed TX100–SDBS would be larger than that by single SDBS.

To confirm the results of 1,2-DCB as an example, the solubilization capacity by mixed TX100–SDBS at the mass ratio of 3:1, 1:1 and 1:3 were determined (Note: in SR determination procedure, the substantial partition of TX100 was avoided. The initial ratio of TX100 to SDBS was approximately equal to the ratio in aqueous phase after equilibrium) and compared with

those by single TX100 and SDBS. For mixed TX100–SDBS systems, the mass solubilization ratio, SR_{mix} and SR_{sum} , were obtained from the equations

$$SR_{\text{mix}} = \frac{(S_{\text{mix}}^* - S_{\text{cmc,mix}}^*)}{(C_{\text{surf}} - CMC_{\text{mix}})} \quad (4)$$

$$SR_{\text{sum}} = \frac{(S_{\text{sum}}^* - S_{\text{cmc,sum}}^*)}{(C_{\text{surf}} - CMC_{\text{sum}})} \quad (5)$$

where CMC_{mix} is the critical micelle concentration of mixed TX100–SDBS and CMC_{sum} of mixed TX100–SDBS on the ideal additivity rule at a given ratio (no data shown); S_{cmc}^* (mg/L) the apparent solubility of a compound at CMC_{mix} or CMC_{sum} (mg/L); S^* (mg/L) the total apparent solubility of the compound in mixed micellar solution at a particular surfactant concentration greater than CMC_{mix} or CMC_{sum} ; and C_{surf} (mg/L) is the mixed surfactant concentration at which S^* was evaluated. SR_{mix} and SR_{sum} for 1,2-DCB by mixed TX100–SDBS are listed in Table 4. It is obvious that the mass solubilization ratios by mixed TX100–SDBS in practice, SR_{mix} , are larger than those by single TX100 and SDBS, respectively, while the mass solubilization ratios by mixed surfactant on the ideal additivity rule, SR_{sum} , are larger than that by SDBS but less than that by TX100. In Table 4, ΔSR (%), the extent of solubilization capacity enhancement by mixed TX100–SDBS relative to single ones, is calculated as following:

$$\Delta SR_{\text{mix}} (\%) = \frac{(SR_{\text{mix}} - SR_{\text{single}})}{SR_{\text{single}}} \times 100 \quad (6)$$

$$\Delta SR_{\text{sum}} (\%) = \frac{(SR_{\text{sum}} - SR_{\text{single}})}{SR_{\text{single}}} \times 100 \quad (7)$$

Table 4

SR for 1,2-DCB by single TX100, SDBS and mixed TX100–SDBS with phase ratio neglected

TX100–SDBS	SR_{sum}	SR_{mix}	ΔSR_{sum} , % relative to SDBS	ΔSR_{mix} , % relative to SDBS
3:1	0.478 ± 0.019	0.742 ± 0.034	66.4	159
1:1	0.451 ± 0.022	0.821 ± 0.028	57.1	186
1:3	0.343 ± 0.020	0.753 ± 0.023	19.7	162

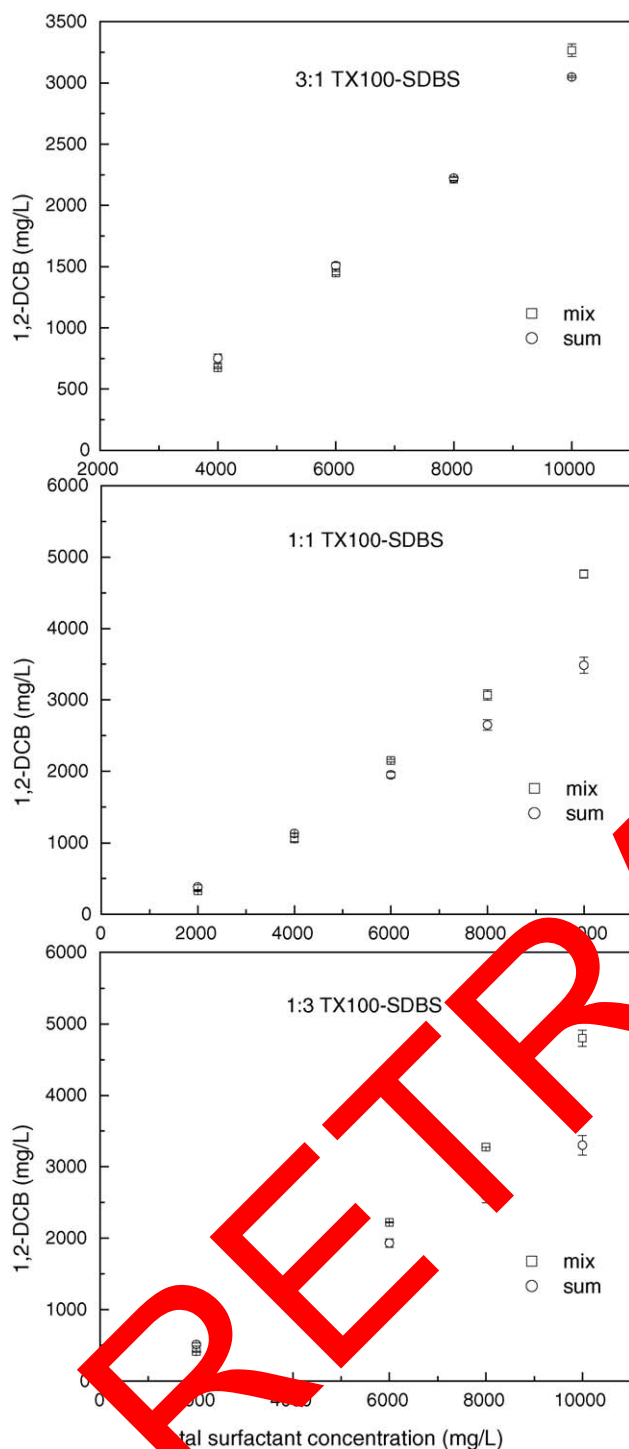


Fig. 4. Synergistic solubilization of 1,2-DCB by TX100-SDBS at 1:40 phase ratio of 1,2-DCB:water (v/v).

where the SR_{single} stands for the mass solubilization ratio by single surfactant. The results of SR shows that the solubilization capacity of mixed surfactant in practice is superior to single TX100 and single SDBS while the solubilization capacity of mixed surfactant on the ideal additivity rule is only superior to single SDBS.

3.2. Explanation of the solubilization extents

As shown in Fig. 1, at low total surfactant concentrations (≤ 1000 mg/L), no significant solubility enhancements for DNAPLs by both single and mixed surfactants were observed. Although TX100 possesses a low CMC (Table 1), the great partitioning loss led to little amount of TX100 molecules in water phase to form micelle and to solubilize DNAPLs. As for SDBS, no partitioning loss occurred in DNAPL/water systems. However, the CMC of SDBS is 963 mg/L. Thus most of SDBS stayed in water phase as monomers. Surfactant monomers exhibit no significant solubilization for hydrophobic organic compounds [13]. In the mixed surfactant systems, the loss extent of TX100 was also substantial (Fig. 2). Therefore, no obvious solubilization distinction among single and mixed surfactant systems was found.

In DNAPL/water systems, when the total surfactant concentration increased from 1000 to 6000 mg/L, large solubility distinction occurred (Fig. 1). Single TX100 showed no significant solubilization due to its great partitioning, while single SDBS enhanced the solubility linearly with the SDBS concentration above 1000 mg/L. For mixed TX100-SDBS, the partitioning loss of TX100 sharply decreased due to the increasing amount of SDBS (Fig. 2) and the CMC_{mix} was reached at about 1000 mg/L of the total surfactant concentration. No distinctive synergistic solubilization was found in this range of surfactant dosage so the solubilization by the mixed TX100-SDBS could be considered as that by mixed ones on the ideal additivity rule, whose solubilization capacity (SR_{sum}) was larger than that of single SDBS. However, partition of TX100 in 3:1 TX100-SDBS system was relatively great. Thus, the aqueous solubilities of DNAPLs with 3:1 TX100-SDBS were intermediate between those with single TX100 and SDBS. 1:1 and 1:3 TX100-SDBS significantly enhanced DNAPL solubility and the solubilization extents were greater than that by single SDBS due to a large decrease in partition of TX100 and the high solubilization capacity (SR_{sum}) relative to SDBS.

When the total surfactant concentration increased above 6000 mg/L, the distinction among solubility enhancements was obvious, as clearly indicating by the slopes of solubilization curve above 6000 mg/L (Fig. 1). Great losses of single TX100 were found in DNAPL/water systems, rendering TX100 less efficient for solubilization. In contrast, single SDBS enhanced the solubility linearly with the SDBS concentration increasing. For the mixed surfactant systems, on the one hand, the partitioning loss was greatly decreased; on the other hand, a significant synergistic solubilization occurred and the SR_{mix} were much larger than SR by single SDBS. Thus, the mixed TX100-SDBS with the ratios tested enhanced much more significantly the aqueous phase solubility of DNAPLs than single SDBS did.

Typical values of IFT for NAPLs and water are 30–50 dyn/cm. Earlier results indicate that for displacement of the oil in the pores and capillaries in subsurface media, an aqueous solution-oil interfacial tension (IFT) $< 10^{-3}$ dyn/cm is generally required [3,17], which is defined as ultralow IFT. In addition, The amount of oil that a surfactant can solubilize is related to the reduction of the IFT, given by the equation $IFT = C/S$, where

IFT is in dyn/cm, S is the solubilization ratio (the volume of organic liquid solubilized in the microemulsion divided by the volume of surfactant) (mL/mL), and C is a constant equal to 0.3 for hydrocarbons and chlorocarbons [12]. Based on calculations by Pope and Wade [24], IFTs on the order of 1 dyn/cm result in solubilization ratios on the order of 0.6, which correspond to DNAPL concentrations in the microemulsion on the order of 30,000 mg/L when surfactant concentration is about 3 wt.%. From discussion above, the surfactant systems studied here would not lead to ultralow IFT.

4. Conclusions

In DNAPL/water system, the solubilization extent of DNAPL in the aqueous phase depends on the effective concentration of surfactants, the critical micelle concentration and the solubilization capacity in the aqueous phase. The mixed TX100–SDBS is superior to the relevant single ones mainly due to the reduction in nonionic surfactant partition and the high solubilization capacity. The greater the apparent solubilization for a given systems, the fewer pore volumes of surfactant solution are needed, which reduces capital expenditure and the operation cost (equipment and manpower). Remediation of DNAPLs with surfactants via enhancing solubilization is considered to be more favorable over that by mobilization because of the risks on spreading the contamination using the latter approach. The results demonstrate that mixed nonionic–anionic surfactants may be a preferred substitution for single surfactants.

Acknowledgements

This study was financially supported by the National Natural Science Foundation of China (No. 20077010), the Qinlan Talent Project of Lanzhou Jiaotong University, the Young Scientist Fund of Gansu Province (3ZS02-1-05-023), and the National Excellent Young Scientist Fund of China (No. 20125719).

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