



## Reversibly enhanced aqueous solubilization of volatile organic compounds using a redox-reversible surfactant

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### Abstract

Surfactant-enhanced remediation (SER) is an effective method for the removal of volatile organic compounds (VOCs) from contaminated soils and groundwater. To reuse the surfactant the VOCs must be separated from the surfactant solutions. The water solubility of VOCs can be enhanced using reversible surfactants with a redox-active group, (ferrocenylmethyl)dodecyldimethylammonium bromide (Fc12) and (ferrocenylmethyl)tetradecanedimethylammonium bromide (Fc14), above and below their critical micelle concentrations (CMC) under reducing ( $I^+$ ) and oxidative ( $I^{2+}$ ) conditions. The CMC values of Fc12 and Fc14 in  $I^+$  are 0.94 and 0.56 mmol/L and the solubilization of toluene by Fc12 and Fc14 in  $I^+$  for toluene is higher than the solubilization achieved with sodium dodecyl sulfate, cetyltrimethylammonium bromide and Triton X-114. The solubilization capacity of the ferrocenyl surfactants for each tested VOCs ranked as follows: ethylbenzene > toluene > benzene. The solubilities of VOCs by reversible surfactant in  $I^+$  were 30% higher than those in  $I^{2+}$  at comparable surfactant concentrations. The effects of Fc14 concentrations on VOCs removal efficiency were as follows: benzene > toluene > ethylbenzene. However, an improved removal efficiency was achieved at low ferrocenyl surfactant concentrations. Furthermore, the reversible surfactant could be recycled through chemical approaches to remove organic pollutants, which could significantly reduce the operating costs of SER technology.

**Key words:** ferrocenyl surfactant; reversibility; solubility; VOCs

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### Introduction

Contamination of soils and groundwater by organic pollutants is a widespread environmental concern. Volatile organic compounds (VOCs) are one important class of such pollutants (Lee et al., 2004; Soga et al., 2004). The release of VOCs from soils and wastewater into the surrounding environment raises concerns due to their toxic effects on human health. VOCs are known or suspected carcinogens or mutagens, and their ready evaporation into the atmosphere makes them particularly hazardous (Atkinson, 2000; Kim et al., 2001; Nguyen and Dabdub, 2001). Various physical, chemical, biological and their combined technologies have been attempted to remediate organic contaminated soils and groundwater. Improvements in both the desorption efficiency of soils and the mobility and bioavailability of VOCs into water are essential to allow the remediation of organic contaminants from soils and groundwater (Deshpande et al., 1999; Zhao et al., 2005; Zhou and Zhu, 2007). Surfactant-enhanced remediation (SER) is a promising technology for the removal of organic

pollutants, such as VOCs, from contaminated soils and groundwater. Although the surfactant washing of contaminated soils and groundwater with surfactant has been an effective and common approach to date, the surfactant can not be recycled and thus result in high operating costs (Rao et al., 2000; Zhou and Rhue, 2000; Mulligan et al., 2001; Schaerlaekens et al., 2005).

The economics of the SER could be significantly optimized via materials separation and the recycling of surfactants. To reuse the surfactant, the VOCs must be separated from the surfactant solutions. Several methods have been developed for the removal of VOCs from a surfactant solution and the recovery of the surfactant (Quina and Hinze, 1999; Taylor et al., 2001; Cheng and Sabatini, 2007; Kungsanant et al., 2008): (1) air stripping in packed columns, (2) air stripping in hollow fiber membrane columns, (3) vacuum-air stripping in packed columns, and (4) liquid-liquid extraction in hollow fiber columns. However, there are many drawbacks to these four methods. The processes are difficult, costly endeavor and some them are ineffective. Reversible surfactants (ferrocenyl surfactants) have been synthesized and characterized (Saji et al., 1985;

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Aydogan and Abbott, 2001; Bai et al., 2002) to enhance solubility of both organic pollutants and  $I^+$ , which was solubilized to a greater extent than  $I^{2+}$ . Furthermore, the author reported the ease with which the organic pollutants could be separated from the surfactant, making it an attractive system for remediation, as reversibility should allow costs to be reduced.

In the current study, enhancements in the water solubility of VOCs achieved using surfactants have been evaluated. To date, no studies have been conducted on the water solubility of VOCs in reversible surfactant solutions. Two reversible surfactants ((ferrocenylmethyl)dodecyldimethylammonium bromide (Fc12) and (ferrocenylmethyl)tetradecanedimethylammonium bromide (Fc14)) were synthesized, and their capacities to enhance the water solubility of VOCs were evaluated. Results are intended to offer some additional insight into the mechanism of surfactant recycling of surfactant as well as a practical strategy for the pollution control of surfactant-laden aqueous VOCs.

## 1 Materials and methods

Benzene, toluene and ethylbenzene were selected as representative VOCs. All the typical VOCs, dodecyl bromide and tetradecyl bromide were obtained from Sinopharm Chemical Reagent Co. (China) and the purities of VOCs and alkyl bromide were greater than 98%. (Dimethylaminomethyl)ferrocene was purchased from Aldrich Chemical Co. (USA). Ferrocenyl surfactants of (ferrocenylmethyl)dodecyldimethylammonium bromide (Fc12) and (ferrocenylmethyl) tetradecyldimethylammonium bromide (Fc14) were synthesized following procedures in the literature (Saji et al., 1985) and were used without further purification. The purities of Fc12 and Fc14 were determined by  $^1H$  NMR spectroscopy, and they were greater than 96%. Selected physicochemical properties of VOCs and ferrocenyl surfactants are presented in Table 1. The error in measured water solubility of benzene, toluene and ethylbenzene was 7.6%, 6.0% and 5.3%, when compared with literature values (Chao et al., 2008). Doubly distilled water was used in all experiments.

The critical micelle concentrations (CMC) values of ferrocenyl surfactants solutions at 25°C were determined as the concentration at which sharp breaks in the plots of the surface tension versus the surfactant concentration were observed. Surface tensions of surfactant solutions were determined using the method of drop weight at

**Table 1** Selected physicochemical properties of compounds

Compounds	Molecular formula	Molecular weight	Water solubility (mg/L)
Benzene	$C_6H_6$	78	1780 <sup>a</sup> 1915 <sup>b</sup>
Toluene	$C_7H_8$	92	515 <sup>a</sup> 546 <sup>b</sup>
Ethylbenzene	$C_8H_{10}$	106	152 <sup>a</sup> 160 <sup>b</sup>
Fc12	$FcCH_2(CH_3)C_{12}H_{25}$	492	–
Fc14	$FcCH_2(CH_3)C_{14}H_{29}$	520	–

<sup>a</sup> Water solubility of selected VOCs (Chao et al., 2008); <sup>b</sup> observed values reported in the literature (Moroi and Morisue, 1993).

25°C water temperature (Permpasert and Devahastin, 2005). To obtain the precise measurements of surface tension, only values which were reproducible over at least three consecutive measurements were used.

The method for the solubilization of VOCs is described in the literature (Moroi and Morisue, 1993). An excess of chemical was added to a small tube to calculate the changes of mass for selected chemicals. These results indicated that the apparent solubility of VOCs by ferrocenyl surfactants can be described by:

$$M = \frac{M_1 - M_2 - M_3}{V_1} \quad (1)$$

where,  $M$  (mg) is the values of the apparent solubility of VOCs,  $M_1$  (mg) and  $M_2$  (mg) are the total mass of VOCs initially added to the system and measured at the end of the experiment, respectively.  $M_3$  is the mass of VOCs in the gas phase, and  $V_1$  is the liquid volumes.  $M_3$  in the gas phase can be rewritten using Eq. (2) as

$$M_3 = \frac{PV_g}{1000RT} M_m \quad (2)$$

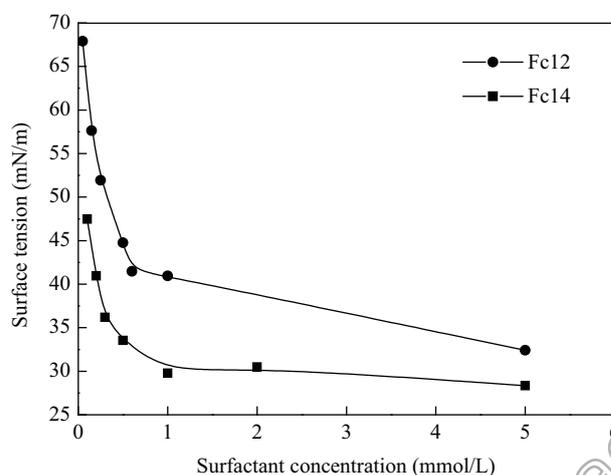
where,  $P$  (Pa) is the saturated vapor pressure of VOCs,  $V_g$  (L) is the gas volume,  $R$  (8.314 J/(mol·K)) is gas constant,  $M_m$  is the molecular weight of the VOCs, and  $T$  is the experimental temperature. Substitution of Eq. (2) into Eq. (1), and rearrangement, yields

$$M = \frac{M_1 - M_2 - \frac{PV_g}{1000RT} M_m}{V_1} \quad (3)$$

## 2 Results and discussion

### 2.1 Surface tension and CMC

The CMC values were obtained through a conventional plot of the surface tension versus the logarithm of the surfactant concentration. Solution surface tensions were significantly reduced with increasing surfactant concentration (Fig. 1). Based upon the surface tension-concentration relationships of Fig. 1, the CMC values of Fc12 and Fc14 were both approximately 0.94 and 0.56 mmol/L, which



**Fig. 1** Plot of surface tension versus Fc12 and Fc14 concentrations in  $I^+$  at 25°C.

**Table 2** Standard free energy of micellisation per mole of micelles

Surfactant	$\Delta G_m^\theta$ (kJ)	CMC <sup>b</sup> (mmol/L)
Sodium dodecyl sulfate (SDS)	-21.6	7.82
Cetyltrimethylammonium bromide (CTMAB)	-29.94	1.12
Triton X-114 (TX114)	-20.45	0.26
Fc12	-31.08	0.94
Fc14	-34.39	0.56

CMC: critical micelle concentration.

are dramatically lower than those of traditional surfactants (SDS (7.82 mmol/L) and CTMAB (1.12 mmol/L)). The standard Gibbs free energy change ( $\Delta G_m^\theta$ ) of micellization per mole of micelles is shown in Table 2. Results from Table 2 indicates that the formation of micelles by ferrocenyl surfactant is effective, as the standard free energy of micellization was significantly lower.

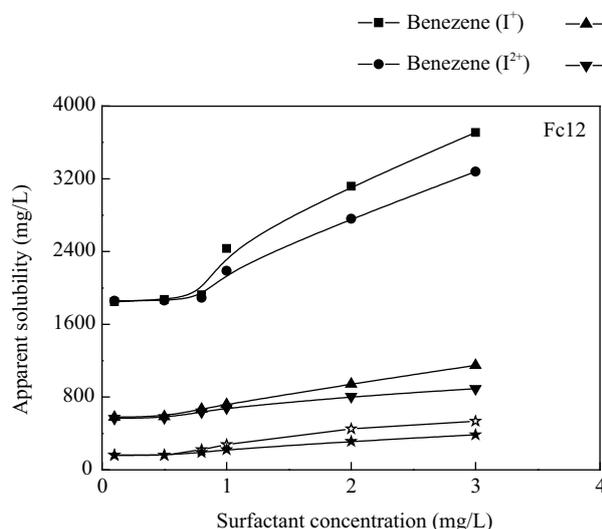
## 2.2 Apparent solubility of ferrocenyl surfactants under reducing ( $I^+$ ) conditions and oxidative ( $I^{2+}$ ) conditions

According to the conventional phase-separation model for surfactants in aqueous solution (Zhu and Chiou, 2001), the solubility enhancement of solute in ferrocenyl surfactants solutions are related to the concentrations of monomer and micelle and the corresponding solute partition coefficients (Yang et al., 2006), in which

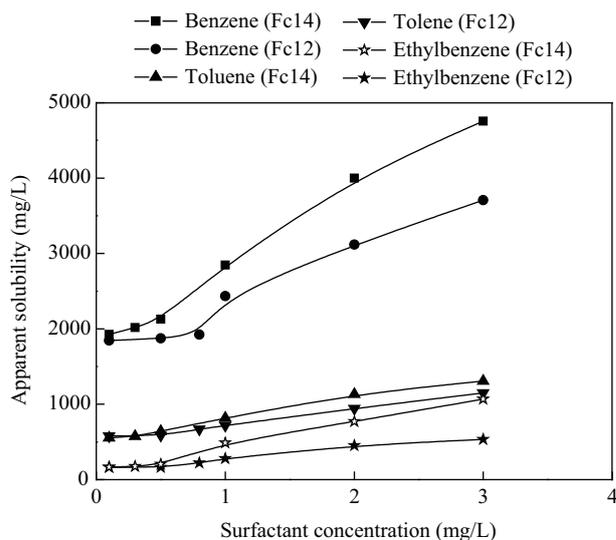
$$f = \frac{S_w^*}{S_w} = 1 + K_{mn}X_{mn} + K_{mc}X_{mc} \quad (4)$$

where,  $S_w^*$  is the apparent solute solubility at the total stoichiometric surfactant concentration of  $X$ ,  $S_w$  is the intrinsic solubility in pure water,  $X_{mn}$  is the concentration of the surfactant as monomers ( $X_{mn} = X$ , if  $X \leq CMC$ ;  $X_{mn} = CMC$ , if  $X \geq CMC$ ), and  $X_{mc}$  is the concentration of the surfactant in micellar form ( $X_{mc} = X - CMC$ ). The  $K_{mn}$  is the partition constant of the solute between monomers and water ( $K = K_{mn}$ , if  $X \leq CMC$ ) and the  $K_{mc}$  is the corresponding partition constant of the solute between micelles and water ( $K = K_{mc}$ , if  $X \geq CMC$ ).

The separation of the concentrations ( $X_{mn}$  and  $X_{mc}$ ) is



**Fig. 2** Effects of ferrocenyl surfactants Fc12 and Fc14 ( $I^+$  and  $I^{2+}$ ) concentration on the apparent solubility of benzene, toluene, and ethylbenzene.



**Fig. 3** Effects of surfactant Fc12 ( $I^+$ ) and Fc14 ( $I^+$ ) concentration on the apparent solubility of benzene, toluene, and ethylbenzene.

carried to accounts for differences in the partition efficiency of the VOCs with monomers and micelles. Using Eq. (4), plots of the apparent solubilities of benzene, toluene and ethylbenzene versus the ferrocenyl surfactants ( $I^+$  and  $I^{2+}$ ) concentration extending from significantly below to significantly above the CMC are shown in Fig. 2. The results indicate that the apparent solubilities of benzene, toluene and ethylbenzene are significantly increased with increasing surfactant concentration. The solubilization of the selected VOCs by Fc12 and Fc14 in  $I^+$  were generally higher than those in  $I^{2+}$  at comparable surfactant concentrations and the solubilities of VOCs in  $I^{2+}$  are reduced by 30%, which demonstrates that the solubilizing power of ferrocenyl surfactants in  $I^+$  is higher than those in  $I^{2+}$ . The solubility enhancements data found for benzene, toluene and ethylbenzene with Fc12 ( $I^+$ ) compared with those found for Fc14 ( $I^+$ ) are illustrated in Fig. 3. The results clearly indicate that the solubilizing capability of Fc14 is higher than that of Fc12.

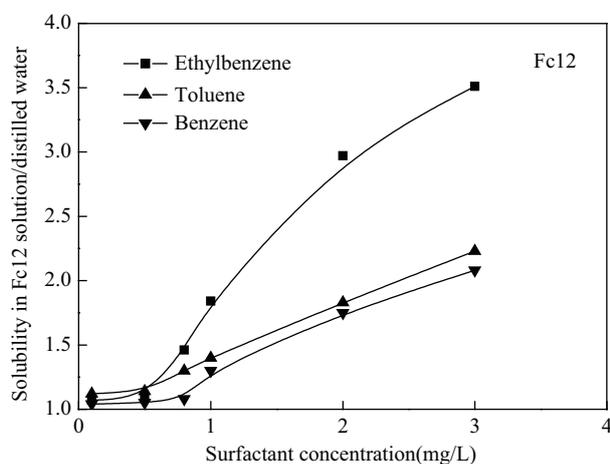
In general, adding surfactant to a water solution will enhance the apparent solubility of organic pollutants due

to the formation of micelles and the occurrence of a partitioning-like interaction between the surfactants and organic pollutants (Zhou and Zhu, 2007). The effects of ferrocenyl surfactants on apparent water solubility of VOCs can be seen by the dependence of the  $f$  values of benzene, toluene and ethylbenzene in Fc12 and Fc14 solutions to that of selected VOCs in distilled water on the surfactant concentrations, as shown in Fig. 4. It can be seen that the ratio increases with the increasing surfactant concentrations and the magnitude of the  $K_{mc}$  is much greater for ethylbenzene than for either benzene or toluene in ferrocenyl surfactants. The partitioning interaction between ferrocenyl surfactants containing less polar chains and VOCs possessing a lower intrinsic solubility would be more effective. Thus, in terms of solubilization capability by ferrocenyl surfactants, the solubilities of benzene, toluene and ethylbenzene can be ranked as follows: ethylbenzene > toluene > benzene.

Equation (4) can be used to determine  $K_{mc}$  by the least-squares fit of the linear plot between  $f$  and surfactant concentration ( $X$ ). The  $K_{mc}$  values of benzene, toluene and ethylbenzene are summarized in Table 3. The  $K_{mc}$  values of benzene, toluene and ethylbenzene in Fc14 solution are higher than that in Fc12 solution. This phenomenon became more obvious at higher surfactant concentrations. Accordingly, it can be experimentally concluded that the effects of ferrocenyl surfactants on the selected VOCs are closely related to the micellar partitioning. The resulting higher solubility power may be ascribed to more ready formation of micelles and partitioning of organic solutes into the micelle phase, which clearly enhances the apparent solubility of the solutes. This indicates that surfactant micelles are very effective in solubilizing water-insoluble solutes.

**Table 3**  $K_{mc}$  values of benzene, toluene and ethylbenzene in Fc14 and Fc12 solutions

Ferrocenyl Surfactants	$K_{mc}$		
	Benzene	Toluene	Ethylbenzene
Fc12	729	898	1875
Fc14	1140	1628	3374



### 2.3 Effect of ferrocenyl surfactants on removal efficiency.

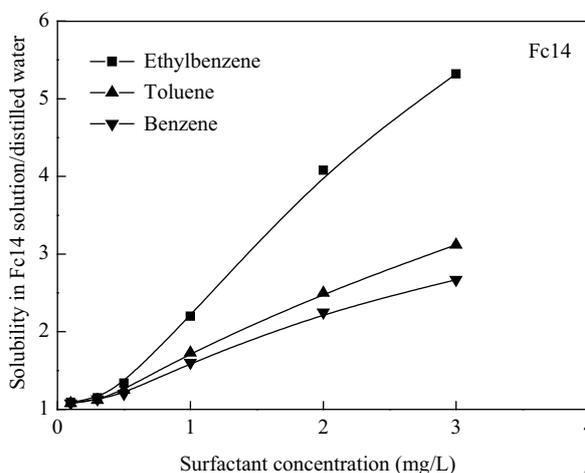
The removal efficiency ( $R$ ) for VOCs can be evaluated according to the following Eq. (5):

$$R = \frac{S_{w1}^* - S_{w2}^*}{S_{w1}^* - S_w} \quad (5)$$

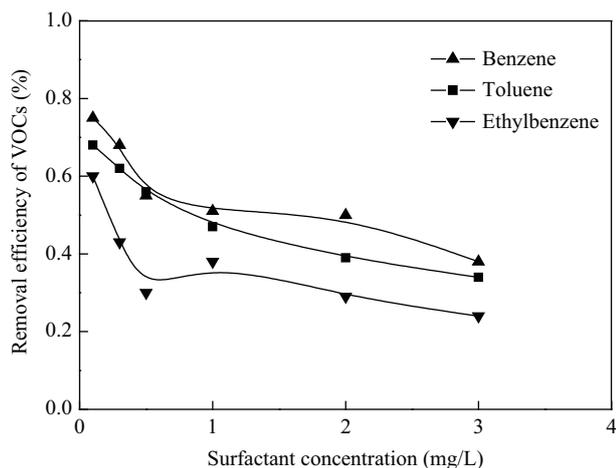
where,  $S_{w1}^*$  (mg/L) and  $S_{w2}^*$  (mg/L) are the apparent water solubilities of VOCs in ferrocenyl surfactants ( $I^+$  and  $I^{2+}$ ) solution, respectively. Figure 5 depicts the removal efficiency of benzene, toluene and ethylbenzene by the Fc14 ( $I^+ \rightarrow I^{2+}$ ) solution. Results from Fig. 5 show that a distinct and rapid decrease in the  $R$  ratio is found when the surfactant concentration exceeds the CMC. The slopes in Fig. 5 further show that the  $R$  values are higher at low surfactant concentrations. As can be seen, the values of  $R$  decrease with increasing surfactant concentration and the magnitude of  $R$  is much greater for benzene than for either ethylbenzene or toluene in ferrocenyl surfactant solutions. This is due to the higher intrinsic solubility of benzene and its weaker partitioning interaction than that of toluene or ethylbenzene. The effect of surfactant concentrations on removal efficiency of selected VOCs was therefore as follows: benzene > toluene > ethylbenzene.

### 2.4 Comparison of solubility capacity between ferrocenyl surfactants and traditional surfactants

The solubilization potential of toluene in typical surfactant solutions can be further evaluated from the micellar partitioning coefficients summarized in Table 4. As can be seen, nonionic surfactants present improved micellar solubilization of toluene than cationic and anionic surfactants. The  $K_{mc}$  value of Fc14 is the highest obtained for toluene of the five surfactants tested, excluding TX114. The solubilization enhancement observed for toluene by ferrocenyl surfactants, as judged by the  $K_{mc}$  values, were approximately 2.5 and 25 times higher than CTMAB and SDS, respectively. As a result, the solubilizing capacity of ferrocenyl surfactants is higher than those of traditional surfactants. This discrepancy cannot be explained simply by their difference in aggregation number and the molar



**Fig. 4** Dependence of the solubility ratio of benzene, toluene, and ethylbenzene in Fc12 and Fc14 solutions to in the distilled water on the Fc14 concentrations.



**Fig. 5** Effects of Fc14 ( $I^+$ ) concentration on removal efficiencies of benzene, toluene, and ethylbenzene.

**Table 4** Micellar partitioning coefficients ( $K_{mc}$ ) of toluene in the presence of surfactants

Surfactant	$K_{mc}$	Alkyl chain length
SDS	130 <sup>a</sup>	12
CTMAB	1378 <sup>b</sup>	16
TX114	4943 <sup>b</sup>	15
Fc12	1875 <sup>b</sup>	12
Fc14	3374 <sup>b</sup>	14

<sup>a</sup> Micellar partitioning coefficients (Anderson 1992); <sup>b</sup> observed values at 25°C.

volume of the surfactant molecule (Hill and Ghoshal, 2001). It appears that the surfactant's structure is also important to its solubilization capacity.

### 3 Conclusions

In this study, a simple apparatus was used to determine the solubilization of benzene, toluene and ethylbenzene with ferrocenyl surfactants. The CMC values of Fc12 and Fc14 ( $I^+$ ) are 0.94 and 0.56 mmol/L and the solubilizing capacity of Fc12 and Fc14 in  $I^+$  for selected VOCs was higher than those in  $I^{2+}$ . The solubility of the VOCs can be ranked as follows: ethylbenzene > toluene > benzene. The impact of the concentration of ferrocenyl surfactants on VOCs removal efficiency was evident with removal efficiency following the series: benzene > toluene > ethylbenzene. The removal efficiency was higher at low ferrocenyl surfactants concentrations.

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