

## Volatilization reduction of monoaromatic compounds in nonionic surfactant solutions

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### Abstract

Changes in the overall mass transfer coefficient ( $K_{OL}$ ) of several volatile organic compounds (VOCs) in surfactant (Triton X-100, Triton X-305, and Triton X-405) solutions are investigated. Different surfactant concentrations, from below to above the critical micelle concentration (CMC), are used to examine the possible inhibition effects on the volatilization of VOCs. The volatilization reduction (or the decrease in the  $K_{OL}$  value) of the monoaromatic solutes from the surfactant solutions is considered to be a result of the effects of solubility enhancement and gas–liquid interface hindrance. For the solubility enhancement effect, the extent of volatilization reduction would generally be larger when a surfactant contains less polar ethylene oxide (EO) and when a monoaromatic compound has lower water solubility. On the other hand, gas–liquid interface hindrance may inhibit the volatilization of VOCs due to the aggregation of surfactants at the interface. Both the two-film and surface-depletion rate-limiting (SDRL) models are applied to elucidate the volatilization reduction of VOCs in surfactant solutions.

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**Keywords:** Volatilization rate; Volatilization reduction; Surfactants; Solubility enhancement; Interface hindrance

### 1. Introduction

A significant volume of aqueous effluents containing synthetic VOCs is generated by the large number of wastewater treatment plants (WWTPs). The release of these VOCs from wastewater into the surrounding environment has caused increasing concern about their toxic effects on human health. Over the past decades, numerous researchers have developed a series of models to predict the fate of organic compounds in WWTPs [1–4]. For these proposed models, however, the changes in the volatilization rates of the organic compounds accompanying with the variation in the environmental conditions are poorly clarified. One well-known example is that the effects of surfactants in the wastewater on the volatilization of organic solutes are rarely investigated [5–7]. Since the surfac-

tants are often found in the WWTPs, a comprehensive study for the effects of surfactants on the volatilization of VOCs is necessary to develop a more accurate model to predict the fate of VOCs in the surfactant solutions.

In general, the existence of surfactants in the solution can enhance the apparent solubility of the organic compounds [8,9], which in turn gives a significant inhibition on the volatilization of VOCs. In addition to the solubility enhancement, however, there are other factors that could also reduce the volatilization of the solutes in surfactant solutions. One recognized property of surfactants is that they can aggregate at the gas–liquid interface and may also hinder the volatilization of organic solutes from surfactant solutions [5]. In this study, effects of nonionic surfactants with different EO number on the  $K_{OL}$  values of organic solutes with comparable Henry's law constant ( $H$ , dimensionless) and different water solubility are investigated. The relative suppressing effect of different surfactants on the organic solute volatilization via the solubility enhancement and interface hindrance are discussed. Both the two-film and the

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Table 1  
Water solubility and Henry's law constant for selected VOCs (at 25 °C)

Compounds	Water solubility (mg/l)	Henry's law constant <sup>a</sup> (dimensionless)
Benzene	1780	0.226
Toluene	515	0.270
Bromobenzene	410	0.085
<i>m</i> -Xylene	162	0.282
Ethylbenzene	152	0.322
<i>m</i> -Dichlorobenzene	123	0.145
1,2,4-Trimethylbenzene	57	0.238
Propylbenzene	55	0.282
1,3,5-Trichlorobenzene	25	0.093
1,2,3,4-Tetrachlorobenzene	4.31	0.105
Pentachlorobenzene	0.56	0.395

<sup>a</sup> Values obtained from Mackay and Shiu [10].

surface-depletion rate-limiting (SDRL) model are used to interpret the experimental results.

## 2. Materials and methods

Laboratory experiments were conducted to investigate the changes in the  $K_{OL}$  values of the selected VOCs in different surfactant solutions. The properties of the tested chemicals and experimental approaches were described as follow.

### 2.1. Selected VOCs and surfactants

The selected aromatic VOCs included benzene, toluene, ethylbenzene, *m*-xylene, bromobenzene, propylbenzene, 1,2,4-trimethylbenzene, *m*-dichlorobenzene, 1,3,5-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and pentachlorobenzene. They possessed a comparable  $H$  (from 0.085 to 0.395) but widely different water solubility (from 0.56 to 1780 mg/l), as shown in Table 1. All of the examined VOCs were of analytical grade or better (with purities >98%) and were used as received. The VOCs were purchased from the Fluka Co. with the exception of the three types of chlorinated benzenes, which were purchased from the Sigma Co. The three nonionic surfactants adopted were Triton X-100 (TX-100), Triton X-305 (TX-305), and Triton X-405 (TX-405). The Triton series of surfactants were supplied by the Riedel de Haën Company and were a mixture of different EO number surfactants. The molecular structures, average EO numbers, and CMCs of the surfactants were shown in Table 2.

Table 2  
Molecular weights, CMCs, and molecular formulas of selected commercial surfactants

Surfactant	Molecular weight (g/mol)	CMC (mg/l)	Average molecular formula <sup>a</sup>
TX-100	624	130	C <sub>8</sub> H <sub>17</sub> C <sub>6</sub> H <sub>4</sub> OE <sub>9.5</sub> H
TX-305	1526	1033	C <sub>8</sub> H <sub>17</sub> C <sub>6</sub> H <sub>4</sub> OE <sub>30</sub> H
TX-405	1966	1600	C <sub>8</sub> H <sub>17</sub> C <sub>6</sub> H <sub>4</sub> OE <sub>40</sub> H

<sup>a</sup> E is (CH<sub>2</sub>CH<sub>2</sub>O).

### 2.2. Solubility enhancement of VOCs

Batch experiments were conducted to determine the extent of the solubility enhancement of the VOCs induced by the Triton series of surfactants. Three compounds, bromobenzene, *m*-dichlorobenzene, and propylbenzene, were selected as the target compounds. A series of 25 ml solution with different surfactant concentrations were added to the Corex centrifuge tubes with Teflon-lined screw caps and VOCs with concentrations of 3–5 times their individual water solubility were added to each tube. Duplicate samples of each surfactant concentration were prepared and the average value was recorded. These samples were then equilibrated on a reciprocating shaker at 25 ± 1 °C for 24 h. The solution and insoluble phase were separated by centrifugation at 8000 rpm (7649 × *g*) for 30 min with a Sorvall RC-5C centrifuge. To analyze the VOCs concentrations in the solution, 1-ml aliquots of the solution were taken and extracted with 2 ml of carbon disulfide. The extracted samples were analyzed using a Hewlett-Packard Model 5890A gas chromatograph (GC) equipped with an FID detector.

### 2.3. Volatilization experiments

The initial concentrations of benzene, toluene, bromobenzene, *m*-xylene, ethylbenzene, *m*-dichlorobenzene, 1,2,4-trimethylbenzene, and propylbenzene were set to be 50% their individual water solubility. The above organic solutes were directly added to 100 ml of surfactant solutions with concentrations from 0 to 2500 mg/l. Meanwhile, the stock solutions of 1,3,5-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and pentachlorobenzene in acetone were prepared. The initial concentration of the three chlorinated benzenes in the surfactant solutions was 0.2 mg/l. These solutions were shaken for 24 h to reach a complete mixing state. The solution was then kept stationary until equilibrium was reached. Finally, the solution was poured into a vessel that was placed in a water tank with a controllable temperature. The vessel was a glass dish with 8.0 cm in diameter and with 4.0 cm in height, and the liquid depth was 2.2 cm. The volatilization rates of the VOCs were determined by analyzing the residual concentrations of VOCs in the solution during a given period. For benzene, toluene, bromobenzene, *m*-xylene, ethylbenzene, *m*-dichlorobenzene, 1,2,4-trimethylbenzene, and propylbenzene, 1-ml-solution was sampled at 1-h interval for 6 h. The sampled solutions were extracted with 2 ml carbon disulfide and the extracts were analyzed by a GC using the Hewlett-Packard Model 5890A equipped with an FID detector. The packed column used was 5% sp-1200/1.75% Bentone on 100/120 Supelcopot, 2 m × 1/4 in. For 1,3,5-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and pentachlorobenzene, 1-ml-solution was sampled at 2-h interval for 12 h. The sampled solutions were then extracted with 2 ml *n*-hexane. The determination of these chlorobenzenes was carried out by GC using an ECD (<sup>63</sup>Ni) detector and a glass packed column with 1.5% sp-2250/1.95% sp-2401 liquid phase on a 100-120 Supelcopot.

## 2.4. Calculation of $K_{OL}$ values

In general, the volatilization processes of VOCs from water solutions can be viewed as a first order reaction [6,11–13]. The variation of the concentration of the VOCs with time can be expressed as

$$C_L = C_0 \exp(-kt), \quad (1)$$

where  $C_0$  is the initial concentration of the VOCs in the bulk-water phase and  $k$  is the reaction rate constant ( $\text{time}^{-1}$ ). Moreover, the relationship between  $k$  and mass transfer coefficient ( $K_{OL}$ ) can be expressed as

$$k = \frac{K_{OL}}{L}, \quad (2)$$

where  $L$  is the depth of the solution in a container with a uniform cross section. In this study, the  $K_{OL}$  value is estimated from the experimentally determined  $k$  value and the changes in  $K_{OL}$  are used to evaluate the effects of the surfactants on the volatilization of VOCs from surfactant solutions.

## 3. Results and discussion

### 3.1. Effects of surfactants on the $K_{OL}$ values of VOCs

Table 3 lists the  $K_{OL}$  values of VOCs in the surfactant solutions. It is apparent that the  $K_{OL}$  values decrease as

the surfactant concentrations increase. Moreover, the reduction degree of  $K_{OL}$  values observed for a given surfactant is inversely proportional to the water solubility of VOCs, with the increasing order of benzene < toluene < bromobenzene < *m*-xylene < propylbenzene. Another key feature is that the reduction of  $K_{OL}$  values of VOCs in the TX-100 solution is larger than that in the TX-305 or TX-405 solutions. This phenomenon is more noticeable for higher surfactant concentration. Accordingly, it can be experimentally concluded that the effects of surfactants on the VOCs volatilization are closely related to the surfactant concentration, VOCs solubility, and EO number of surfactant.

The effects of surfactant concentration on the volatilization of VOCs are easy to understand. However, a more detailed discussion is needed to understand the relationship between the volatilization reduction and both VOC solubility and surfactant EO number. In general, adding surfactants to a water solution will enhance the apparent solubility of nonionic organic compounds due to the occurrence of a partitioning-like interaction between the surfactants and the nonionic organic compounds [14]. One typical solubility enhancement example is shown in Fig. 1 for 1,3,5-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and pentachlorobenzene in TX-100 solution. Moreover, it is recognized that the partitioning interaction between a surfactant containing a lower amount of polar chains (e.g., TX-100) and a VOC possessing a lower intrinsic solubility (e.g., propylbenzene) would be more effective. A clearer relationship between

Table 3  
 $K_{OL}$  values (cm/min) of selected VOCs as a function of surfactant concentration (mg/l)

Compounds	Surfactant concentration							
	0	250	500	750	1000	1500	2000	2500
<b>TX-100</b>								
Benzene	0.0101	0.0095	0.0092	0.0090	0.0090	0.0088	0.0084	0.0082
Toluene	0.0099	0.0090	0.0088	0.0088	0.0084	0.0080	0.0079	0.0077
Bromobenzene	0.0094	0.0086	0.0084	0.0080	0.0077	0.0075	0.0069	0.0065
<i>m</i> -Xylene	0.0097	0.0086	0.0082	0.0079	0.0075	0.0067	0.0062	0.0056
Ethylbenzene	0.0097	0.0086	0.0082	0.0079	0.0075	0.0069	0.0064	0.0056
<i>m</i> -Dichlorobenzene	0.0095	0.0084	0.0080	0.0075	0.0071	0.0064	0.0058	0.0052
1,2,4-Trimethylbenzene	0.0097	0.0082	0.0073	0.0067	0.0064	0.0056	0.0049	0.0041
Propylbenzene	0.0097	0.0082	0.0075	0.0067	0.0064	0.0056	0.0050	0.0041
<b>TX-305</b>								
Benzene	0.0101	0.0095	0.0094	0.0092	0.0088	0.0088	0.0086	0.0086
Toluene	0.0099	0.0094	0.0092	0.0090	0.0086	0.0082	0.0080	0.0079
Bromobenzene	0.0094	0.0090	0.0088	0.0086	0.0084	0.0080	0.0075	0.0071
<i>m</i> -Xylene	0.0097	0.0090	0.0088	0.0084	0.0080	0.0077	0.0071	0.0067
Ethylbenzene	0.0097	0.0090	0.0088	0.0084	0.0080	0.0077	0.0073	0.0067
<i>m</i> -Dichlorobenzene	0.0095	0.0088	0.0084	0.0082	0.0079	0.0075	0.0071	0.0065
1,2,4-Trimethylbenzene	0.0097	0.0088	0.0084	0.0080	0.0075	0.0071	0.0067	0.0064
Propylbenzene	0.0097	0.0088	0.0084	0.0080	0.0077	0.0071	0.0067	0.0064
<b>TX-405</b>								
Benzene	0.0101	0.0095	0.0094	0.0092	0.0090	0.0088	0.0086	0.0086
Toluene	0.0099	0.0094	0.0092	0.0090	0.0086	0.0084	0.0082	0.0080
Bromobenzene	0.0094	0.0092	0.0092	0.0088	0.0084	0.0082	0.0080	0.0075
<i>m</i> -Xylene	0.0097	0.0092	0.0090	0.0086	0.0082	0.0080	0.0079	0.0073
Ethylbenzene	0.0097	0.0092	0.0090	0.0086	0.0082	0.0080	0.0079	0.0073
<i>m</i> -Dichlorobenzene	0.0095	0.0092	0.0088	0.0086	0.0080	0.0079	0.0075	0.0071
1,2,4-Trimethylbenzene	0.0097	0.0090	0.0086	0.0084	0.0080	0.0077	0.0071	0.0067
Propylbenzene	0.0097	0.0090	0.0086	0.0084	0.0080	0.0077	0.0071	0.0067

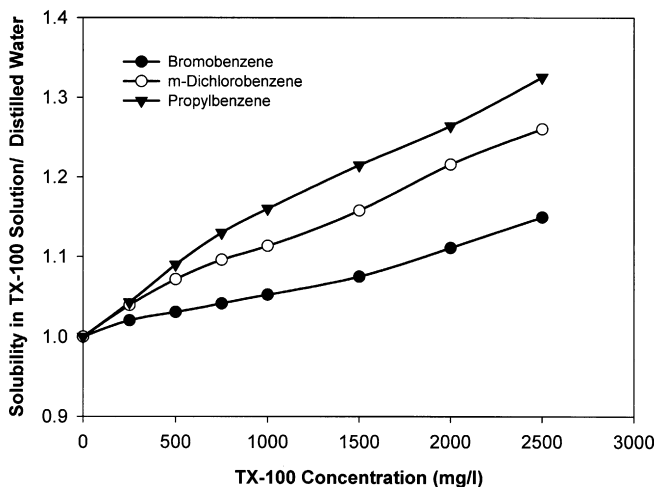


Fig. 1. The dependence of the solubility ratio of bromobenzene, *m*-dichlorobenzene, and propylbenzene in TX-100 solution to in the distilled water on the TX-100 concentrations.

the  $K_{OL}$  values and the water solubility of the examined VOCs is shown in Fig. 2. As demonstrated in Fig. 2, effects of surfactant on the  $K_{OL}$  values are more significant when the VOCs solubility is smaller than 200 mg/l, indicating that less soluble organic compounds possess higher solubility enhancement in a surfactant solution and then, a smaller volatilization rate. On the other hand, the effects of surfactants polarity on the volatilization of VOCs can be seen by the dependence of the ratio of the  $K_{OL}$  value of 1,2,4-trimethylbenzene in surfactant solutions to that of 1,2,4-trimethylbenzene in distilled water on the surfactant concentrations, as shown in Fig. 3. It can be seen that the ratio decreases with the increasing surfactant concentration and the magnitude of the reduction is much greater for the TX-100 solution than for both the TX-305 and TX-405 solutions. Since the examined surfactants are molecularly nonhomogeneous with variable EO numbers and the surfactant with a higher EO number may possess a greater hydrophilic character, the hydrophilicity sequence of the tested surfactants should be with the decrease-

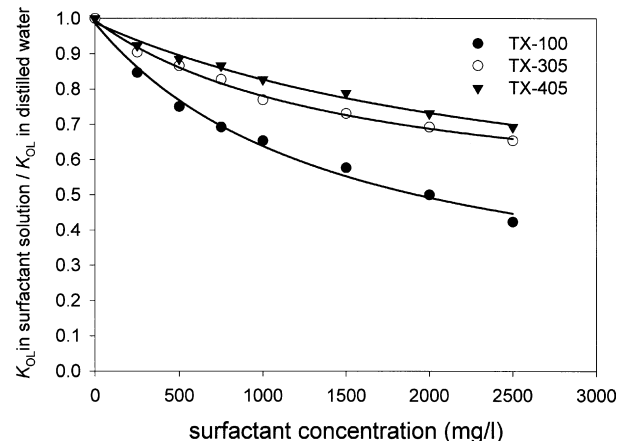


Fig. 3. The dependence of the  $K_{OL}$  ratio of 1,2,4-trimethylbenzene on the surfactant concentrations.

ing order: TX-405 > TX-305 > TX-100. Therefore, the smaller inhibition on the VOCs volatilization with TX-405 and TX-305 may be attributed to the larger hydrophilicity of TX-405 and TX-305, which decreases the partitioning of VOCs to the surfactant phases.

### 3.2. Effects of surfactant micelles on the $K_{OL}$ values of low water solubility compounds

A unique property of the surfactants is the formation of micelles in the solution. When dissolved in water at low concentration, surfactant molecules exist as monomers. The surfactant concentration at which the formation of micelles occurs is called CMC. The presence of surfactants as either monomers or micelles may enhance the apparent solubility of the VOCs. In particular the enhancement may become significant when the surfactant concentration exceeds the CMC. In order to more precisely describe the volatilization reduction of VOCs in surfactant solutions, effects of surfactant concentration on the  $K_{OL}$  values of three chlorinated benzenes with very low water solubility are examined and the results are summarized in Table 4. The three examined monoaromatic compounds are 1,3,5-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and pentachlorobenzene, which have water solubility of ca. 25, 4.31, and 0.56 mg/l, respectively. As expected, the  $K_{OL}$  values are closely related to the water solubility of these organic solutes and the polarity of the selected surfactants. Moreover, the reduction level in the volatilization of the three chlorinated benzenes is higher than that of propylbenzene. As shown in Fig. 4, a distinct and sharp-falling curvature of the  $K_{OL}$  ratio curves is indeed found when the surfactant concentration exceeds the CMC. The resulting higher volatilization reduction may be ascribed to the partitioning of the organic solutes into the micelle phase, which obviously enhances the apparent solubility of the solutes. This indicates that surfactant micelles are far more effective in solubilizing water-insoluble solutes and cause a greater reduction on the volatilization of VOCs.

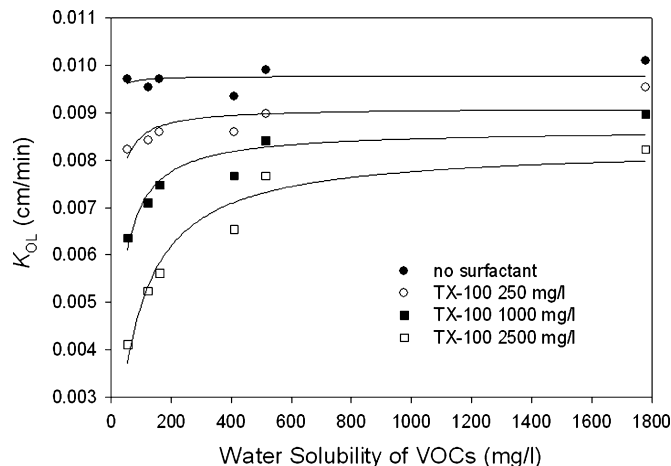


Fig. 2. The dependence of the  $K_{OL}$  values of VOCs in TX-100 solutions on the water solubility of VOCs.

Table 4

 $K_{OL}$  values (cm/min) of relatively low solubility VOCs as a function of surfactant concentration (mg/l)

Compounds	Surfactant concentration							
	0	100	250	750	1000	1500	2000	2500
TX-100								
1,3,5-Trichlorobenzene	0.0067	0.0058	0.0047	0.0041	0.0037	0.0028	0.0026	0.0024
1,2,3,4-Tetrachlorobenzene	0.0069	0.0056	0.0045	0.0032	0.0026	0.0021	0.0019	0.0017
Pentachlorobenzene	0.0067	0.0054	0.0036	0.0024	0.0017	0.0015	0.0013	0.0011
TX-305								
1,3,5-Trichlorobenzene	0.0067	0.0064	0.0060	0.0054	0.0052	0.0050	0.0049	0.0045
1,2,3,4-Tetrachlorobenzene	0.0069	0.0064	0.0060	0.0054	0.0050	0.0043	0.0037	0.0034
Pentachlorobenzene	0.0067	0.0058	0.0056	0.0052	0.0047	0.0034	0.0028	0.0022
TX-405								
1,3,5-Trichlorobenzene	0.0067	0.0064	0.0064	0.0062	0.0060	0.0054	0.0049	0.0047
1,2,3,4-Tetrachlorobenzene	0.0069	0.0065	0.0064	0.0060	0.0058	0.0054	0.0047	0.0045
Pentachlorobenzene	0.0067	0.0064	0.0062	0.0058	0.0056	0.0052	0.0043	0.0037

### 3.3. Interface hindrance effect

The above discussion for the effects of surfactants on the volatilization of VOCs is concentrated on the concept of solubility enhancement. However, it should be noted that other factors

may also contribute to the inhibition on the volatilization of VOCs in surfactant solutions. For instance, the surfactants may form a microlayer on the surface of the gas–liquid interface and this aggregate may hinder the escape of VOCs from the liquid–gas interface [5]. This phenomenon may be referred as the interface hindrance effect. The interface hindrance effect can be divided into two parts; the VOCs need to pass through the microlayer formed by the surfactant aggregation on the interface and the surfactant occupies part of the sites at the interface thereby reducing the opportunity of VOCs to contact with the gas phase.

To distinguish the effects of solubility enhancement and interface hindrance on the volatilization reduction, a parameter  $\phi$  is defined. The  $\phi$  value for estimating the relative contribution of the above two factors can be expressed as follows

$$\frac{K_{OL} \text{ in surfactant solution}}{K_{OL} \text{ in distilled water}} = \phi \frac{\text{solubility in distilled water}}{\text{solubility in surfactant solution}} \quad (3)$$

As can be seen in Eq. (3), when the  $\phi$  value is 1, the volatilization reduction will be totally contributed from the changes in the apparent solubility of VOCs. Moreover, a relatively higher  $\phi$  value may correspond to a larger contribution of the solubility enhancement. Fig. 5 shows the dependences of the  $\phi$  values of bromobenzene, dichlorobenzene, and propylbenzene on the surfactant concentrations. It can be seen that all  $\phi$  values are less than 1, indicating the existence of the interface hindrance effect and an effective suppression on the VOC volatilization.

### 3.4. Interpretation with the two-film and SDRL model

The classic theory for describing the volatilization of an organic solute from a dilute solution is the two-film model [15]. For this model, it is assumed that there is a transition layer, through which chemicals pass by molecular diffusion at the interface between the liquid and gas films. The volatilization

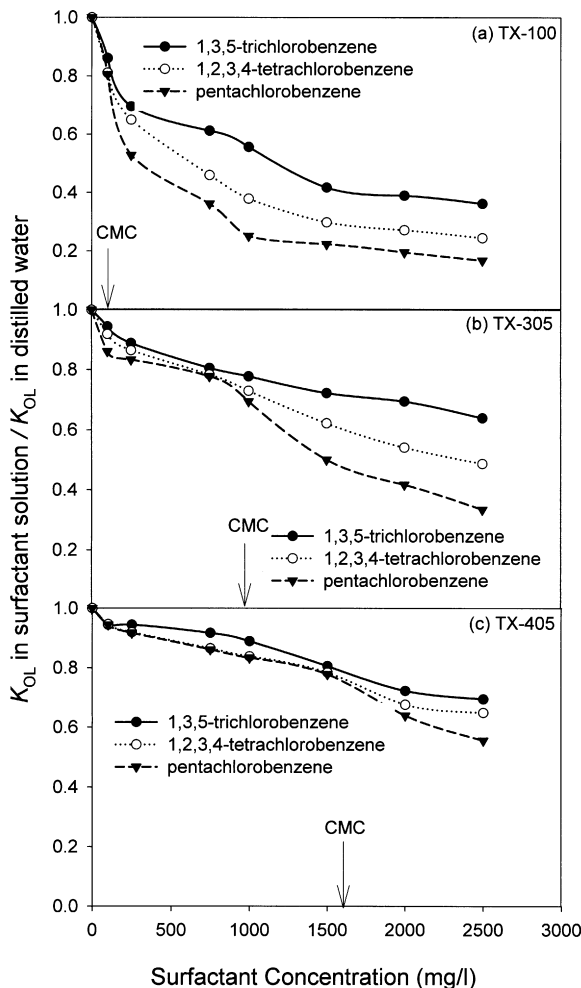


Fig. 4. The dependence of the  $K_{OL}$  ratio of 1,3,5-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and pentachlorobenzene on the surfactant concentrations.

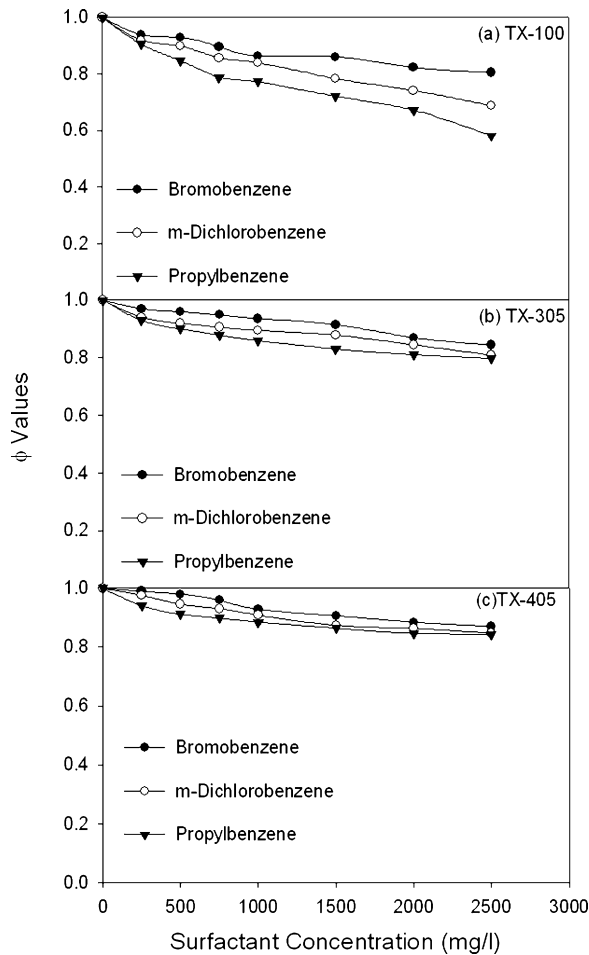


Fig. 5. The variation of  $\phi$  values with the surfactant concentrations.

flux  $Q$  (mass area time<sup>-1</sup>) can be written as [16]

$$Q = K_{OL} \left( C_L - \frac{C_G^*}{H} \right) \cong K_{OL} C_L \quad (4)$$

with

$$\frac{1}{K_{OL}} = \frac{1}{k_L} + \frac{1}{Hk_G} \quad (5)$$

where  $H$  is Henry's law constant (dimensionless),  $K_{OL}$  (length time<sup>-1</sup>) is the overall mass transfer coefficient,  $k_L$  is the liquid-phase transfer coefficient (length time<sup>-1</sup>),  $k_G$  is the gas-phase transfer coefficient (length time<sup>-1</sup>),  $C_L$  (mass volume<sup>-1</sup>) is the concentration of the bulk-liquid phase, and  $C_G^*$  (mass volume<sup>-1</sup>) is the concentration on the gas side of the interface. The  $(C_G^*/H)$  term in Eq. (4) is usually negligible due to the  $C_G^*$  in an open surface being very small. On the other hand, our previous investigation [17] presents an alternative approach to describe the volatilization of an organic solute from the solutions, which is called surface-depletion rate-limiting model. This model was originally derived from the modified Knudsen equation and could be written as follow [18]

$$Q = \alpha\beta \left( \frac{RT}{2\pi M} \right)^{1/2} H C_L, \quad (6)$$

where  $M$  is the molecular weight,  $R$  is the gas constant, and  $T$  is the absolute temperature. In Eq. (6),  $\alpha$  (dimensionless) represents the ratio of concentration of an organic solute at interface to that in the bulk phase and  $\beta$  (dimensionless) is the evaporation coefficient, which is dependent on the atmospheric pressure and air turbulence. It has been experimentally concluded that the  $\beta$  values of different organic solutes approach a constant value under a given environmental condition [17]. If  $\alpha$  is also a constant under a given environmental condition, Eq. (6) can be written as

$$Q = K_{OL} C_L \quad (7)$$

with

$$K_{OL} = \alpha\beta H \left( \frac{RT}{2\pi M} \right)^{1/2}. \quad (8)$$

It should be noted that the validity of SDRL model for the description of the experimental data is verified with the well fitting results between the experimental data and the first order reaction (see Eqs. (1), (7) and (8)).

For the effects of solubility enhancement on the volatilization of VOCs, we can take the discussion focusing on the variation of  $H$  value because of the  $H$  value of an organic compound is defined as the ratio of the partial pressure to the water solubility in equilibrium [10]. According to the definition of  $H$ , solubility enhancement induced by the surfactants will introduce a decrease in the  $H$  value of an organic solute. Since SDRL model indicate that the  $K_{OL}$  value is proportional to the  $H$  value, they can be used to explain properly the effects of solubility enhancement on the volatilization of VOCs. However, the volatilization reduction of VOCs induced by the solubility enhancement was difficultly interpreted by the two-film. The reason has been presented in previous investigation [19,20].

The two-film model indicates that diffusion is the primary mechanism by which compounds pass through the films. This means that the volatilization rates of the organic solutes are mainly related to the solute's molecular weight or diffusion coefficient. Since the aggregation of surfactants at the interface will change the properties of the liquid film, the surfactant at the interface should be regarded as another phase if the interface hindrance effect is taken into account. The relationship between the  $K_{OL}$  value and the transfer coefficients in respective phases in Eq. (5) can be modified as

$$\frac{1}{K_{OL}} = \frac{1}{k_L} + \frac{1}{Hk_G} + \frac{1}{k_S}, \quad (9)$$

where  $k_S$  (length time<sup>-1</sup>) is the surfactant-phase transfer coefficient of an organic compound at the interface. Since the affinity of organic solutes with respect to the surfactants is regarded as a key point to determine the  $k_S$ , the  $k_S$  value is a function of the water solubility of the solutes and the polarity of the surfactants. This hypothesis is supported by the result that less-soluble compounds (e.g., propylbenzene) and low polarity surfactants (e.g., TX-100) have the relatively lower  $\phi$  values (see Fig. 5). For SDRL model, the volatilization reduction of VOCs induced by the interface hindrance effect may be properly interpreted by the decrease in the  $\alpha$  value. Since the  $\alpha$  value is thought of as the

concentration ratio between the interface and bulk phase of an organic solute in a surfactant solution, the concentration reduction of VOCs at the liquid–gas interface induced by the interface hindrance effect may introduce a decrease in the  $\alpha$  value, which in turn decreases the  $K_{OL}$  value (see Eq. (8)).

#### 4. Conclusions

The results reported show very striking differences in the volatilization rates of the monoaromatic compounds in the selected surfactant solutions. It is found that the presence of surfactants will suppress the volatilization rates of the VOCs due to the solubility enhancement and the interface hindrance. For the solubility enhancement effect, the  $K_{OL}$  value is a function of the concentration of the surfactant, the water solubility of organic solutes, and the surfactant polarity. The extent of the reduction is larger for a water solution containing a surfactant that possesses a lower amount of polar EO number and a monoaromatic compound that has lower water solubility. Moreover, when the surfactant concentration is above the CMC, the less-soluble VOCs are partitioned into the micelles, causing greater impact on the volatilization reduction. The interface hindrance effect means that the surfactants may occupy sites in the interface, also causing obvious volatilization reduction. It can be concluded that at low surfactant concentrations, as generally found in the natural waters, the effects of the surfactants on the volatilization of relatively water-soluble solutes is insignificant but may become important for extremely insoluble solutes (for instance, pentachlorobenzene). When the surfactant concentration is far above the CMC, however, surfactants would have significant impacts on the volatilization of a wide range of organic pollutants. The suppression mechanisms for the volatilization of VOCs from surfactant solutions can be properly interpreted by the SDRL model and a slightly modified two-film model.

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