

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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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 ^a (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

^a 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 ^a
TX-100	624	130	C ₈ H ₁₇ C ₆ H ₄ OE _{9.5} H
TX-305	1526	1033	C ₈ H ₁₇ C ₆ H ₄ OE ₃₀ H
TX-405	1966	1600	C ₈ H ₁₇ C ₆ H ₄ OE ₄₀ H

^a E is (CH₂CH₂O).

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 (⁶³Ni) detector and a glass packed column with 1.5% sp-2250/1.95% sp-2401 liquid phase on a 100-120 Supelcopot.

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