



## Emissions of Organic Compounds in Surfactant Solutions under Air Turbulence

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### ABSTRACT

The objective of this study was to investigate the effects of surfactants aggregating the gas-liquid interface on the volatilization rates of the organic compounds. The changes in the overall mass transfer coefficient ( $K_{OL}$ ) and concentration at gas-liquid interface of organic compounds in surfactant (dodecylbenzene sulfonic acid sodium, DBS) solutions under wind speed conditions were used to elucidate the results. The studied compounds consisted of aromatic compounds, benzene, toluene, ethylbenzene, *m*-dichlorobenzene, and propylbenzene with relatively higher Henry's law constants ( $H$ ) and water solubilities ( $S_w$ ), and chlorinated pesticides,  $\alpha$ -endosulfan, heptachlor epoxide, endrin, and dieldrin, with relatively lower  $H$  and  $S_w$ . Various surfactant concentrations, from 0 to 1000 mg/L under various wind speeds from 0 to 6.0 m/s, were used to examine the influence of the surfactant on the volatilization of the test organic compounds. The results indicated that the surfactant in the solution suppressed the volatilization of organic compounds. The degree of volatilization reduction was inversely proportional to the  $S_w$  values of the test organic compounds. The curve profiles for the  $K_{OL}$  values of the organic compounds in the surfactant solutions, relative to the selected wind speed, were divided into the following two stages: the sharp-rise stage and the stable-linearity stage. The critical finding was that the surfactant markedly enhanced the concentrations of the low  $S_w$  compounds at the interface. The wind may cause an unexpected increase in the  $K_{OL}$  value of the low  $S_w$  compound in the solution that contains a high surfactant concentration.

**Keywords:** Volatilization rate; Volatilization reduction; Surfactants; Wind; Interface concentration.

### INTRODUCTION

The emissions of organic compounds from various sources have become a notable problem (Choi and Jo, 2011). The release of these organic compounds into the surrounding environment may cause toxic effects on human health (Dawson and Gokare, 1994; Yeh *et al.*, 2011). Because industrial wastewater contains various organic compounds, the issue regarding emissions of the organic compounds from wastewater treatment plants (WWTPs) has been gradually emphasized (Mayer *et al.*, 1994; Schmid *et al.*, 2001; Lin and Chou, 2006; Oskouie *et al.*, 2008). Over the past decade, numerous researchers developed a series of models to predict the fates of organic compounds in WWTPs (Ince and Inel, 1991; Parker *et al.*, 1993; Hsieh *et al.*, 1994; Melcer, 1994; Bhattacharya *et al.*, 1996). However, these models only provided potential emission amounts of organic compounds under specific environmental conditions. The main disadvantage of these models is the lack of consideration to the interaction among organic compounds and other solutes in the wastewater.

In general, the volatilization of an organic solute from a natural water body is described by the two-film model (Liss and Slater, 1974). In this model, it is assumed that a transition layer exists, through which chemicals pass by molecular diffusion at the interface between the liquid and gas films. The volatilization flux  $Q$  (mass/area-time) can be written as (Mackay and Leinonen, 1975)

$$Q = K_{OL} \left( C_L - \frac{C_G^*}{H} \right) \cong K_{OL} C_L \quad (1)$$

with

$$\frac{1}{K_{OL}} = \frac{1}{k_L} + \frac{1}{Hk_G} \quad (2)$$

where  $H$  represents Henry's law constant (dimensionless);  $K_{OL}$  (length/time) represents the overall mass transfer coefficient;  $k_L$  is the liquid-phase transfer coefficient (length/time);  $k_G$  is the gas-phase transfer coefficient (length/time);  $C_L$  (mass/volume) is the concentration of the bulk liquid; and  $C_G^*$  (mass/volume) is the concentration on the gas side of the interface. The  $(C_G^*/H)$  term in Eq. (1) is usually negligible because of the markedly small  $C_G^*$  in an open surface. The interaction among the organic compounds and other solutes is not considered in the two-film model. Thus, the model is infrequently applied to estimate the

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volatilizations of the organic solutes from wastewater. According to the traditional two-film model, the relationship between  $K_{OL}$  and  $H$  for the high  $H$  solutes is defined difficultly (Chao *et al.*, 2005a). A new model, that is, the surface-depletion rate-limiting (SDRL) model, was developed to describe the effects of  $H$  values on the volatilization rates of organic solutes (Lee *et al.*, 2004a). In traditional two-film model, the decreases in the thickness of gas-film and liquid film were used to interpret the increases in volatilization rates of the organic compounds under the wind and liquid-mixing conditions. For the SDRL model, the ratio of concentration of an organic compound at the interface to that in the bulk phase was incorporated into the model to explain the changes in the  $K_{OL}$  value of an organic solute under various environmental conditions.

The presence of surfactants in the wastewater significantly suppresses the volatilization of organic solutes (Smith *et al.*, 1980; Chao *et al.*, 2000; Lee *et al.*, 2004b). However, few researchers discussed the reason for the reduction in the volatilization of organic compounds in the surfactant solution. In the previous study, the mechanisms for the surfactants that suppressed organic compound volatilizations were elucidated by the solubility enhancement and interface hindrance (Chao *et al.*, 2008). The surfactants in the solution enhance the water solubilities ( $S_w$ ) of the organic compounds with the low  $S_w$  values, which enhances the affinity between the organic solutes and the solution. Especially for the surfactant forming micelles in the solution, the surfactant may highly enhance the apparent solubility of organic compounds with the low  $S_w$  values. Moreover, the surfactants may aggregate at the gas-liquid interface, which hinders the emissions of organic solutes. Because of the characteristics of the surfactants that aggregate at the interface, the surfactant at the interface may attract other organic solutes. The result may lead to the increase in concentration of organic compounds at the gas-liquid interface. A number of previous reports indicated that the wind across the solution surface may blow away the organic solutes at the interface to enhance the volatilization amount (Chao *et al.*, 2005b; Chao, 2009a). If the surfactants attract the aggregation of organic compounds at the interface, the concentrations of the organic compounds at the interface increase. When wind blows across the surfactant solution containing organic compounds, the changes in the  $K_{OL}$  values and concentration at the interface are a noteworthy issue. In this study, the  $K_{OL}$  values of organic compounds with the various  $S_w$  values in the surfactant solution under various wind speeds were measured. The concentrations of the organic compounds at the interface were evaluated by using the SDRL model. The obtained result clarified the effects of the surfactant on the volatilization of the organic solutes.

### SDRL MODEL

The surface-depletion rate-limiting (SDRL) model was used to examine the relationship between the  $K_{OL}$  values of the organic solutes and their physico-chemical properties. This model was originally derived from the modified Knudsen equation and may be written as follows (Chiou *et al.*, 1980) :

$$Q = \alpha\beta\left(\frac{RT}{2\pi M}\right)^{\frac{1}{2}}HC_L \quad (3)$$

where  $M$  is the molecular weight,  $R$  is the gas constant, and  $T$  is the absolute temperature. In this equation  $\alpha = C^*/C$  (dimensionless) represents the concentration ratio at the interface of an organic solute to the bulk phase, and  $\beta$  (dimensionless) is the evaporation coefficient, which is dependent on the atmospheric pressure and air turbulence. The  $\beta$  values of the various organic solutes approach a constant value under a specific environmental condition. If  $\alpha$  is also a constant under a specific environmental condition, Eq. (3) may be deduced as (Lee *et al.*, 2004a)

$$Q = K_{OL}C_L \quad (4)$$

thus,

$$K_{OL} = \alpha\beta H\left(\frac{RT}{2\pi M}\right)^{\frac{1}{2}} \quad (5)$$

In Eq. (5), the parameter  $\beta$  is related to  $k_G$  in the two-film model as

$$k_G = \beta\left(\frac{RT}{2\pi M}\right)^{1/2} \quad (6)$$

The  $\alpha$  factor may in turn be related to the  $k_L$  and  $k_G H$  parameters as

$$\alpha = \frac{k_L}{k_L + k_G H} \quad (7)$$

The  $\alpha$  value for a high  $H$  compound is quite less than 1.0, and the  $\alpha$  value for a low  $H$  compound approaches 1.0. Moreover, the  $\alpha$  value increases with the increasing liquid mixing intensity, and decreases with the increasing wind speed. The more detailed description has been presented in the literature (Lee *et al.*, 2004a).

## METHODS

### Properties of Test Compounds

Laboratory experiments were conducted to investigate the changes in the  $K_{OL}$  values of the selected organic compounds in the surfactant solutions. The test organic compounds consisted of the aromatic compounds with the relatively higher  $S_w$  and  $H$ , and the chlorinated pesticides with the relatively lower  $S_w$  and  $H$ . The aromatic compounds, including benzene, toluene, ethylbenzene, *m*-dichlorobenzene, and propylbenzene were purchased from the Fluka Co. The chlorinated pesticides, including  $\alpha$ -endosulfan, heptachlor epoxide, endrin, and dieldrin were purchased from Chem Service, Inc. The crucial physico-chemical properties of the tested chemicals are listed in Table 1. All of the organic compounds were of analytical grade or higher (with purities > 98 %) and were used as received. The anionic surfactant

**Table 1.** The physico-chemical properties of the test compounds at 298 K.

Compounds	M	Water solubility (mg/L)	<sup>a</sup> H (dimensionless)
Benzene	78	1780	0.225
Toluene	92	515	0.269
Ethylbenzene	106	152	0.321
<i>m</i> -Dichlorobenzene	147	123	0.144
Propylbenzene	120	55	0.281
$\alpha$ -Endosulfan	407	0.51	2.9E-04
Heptachlor epoxide	389	0.275	8.6E-04
Endrin	381	0.25	2.57E-04
Dieldrin	373	0.195	4.37E-05

<sup>a</sup> cited from Mackay and Shiu (1980),  $H = MP^0/RTS_w$ ,  $M$  is molecular weight,  $P^0$  is saturation vapor pressure (Pa),  $S_w$  is the water solubility (mg/L),  $R$  is the gas constant (8.314 Pa·m<sup>3</sup>/mol·K),  $T$  is the absolute temperature (K).

was dodecylbenzene sulfonic acid sodium (DBS), which was supplied by the Riedel de Haën Company. The molecular structure of the surfactant was C<sub>12</sub>H<sub>25</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na. The measured critical micelle concentration (CMC) was 523 mg/L.

#### Solubility Enhancement of Chlorinated Pesticides

The experiment of solubility enhancement focused on the chlorinated pesticides because the surfactant generates low level solubility enhancement for the aromatic compounds with the higher  $S_w$  values. Batch experiments were conducted to determine the extent of the solubility enhancement of the test chlorinated pesticides when the surfactant concentrations were above and below the CMC. A 25 mL solution with surfactant concentrations from 0 to 1000 mg/L was added to Corex centrifuge tubes with Teflon-lined screw caps, and then chlorinated pesticide concentrations of 3 to 5 times their individual  $S_w$  were added to each tube. These samples were subsequently equilibrated on a reciprocating shaker for 24 h at 25 ± 1°C. 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 solute concentrations in the solution, 1-mL aliquots of the solution were sampled and extracted with 1 mL of *n*-hexane. The extracted samples were analyzed using a Hewlett-Packard Model 6890A gas chromatograph (GC) equipped with an ECD detector. The pesticides were separated on the capillary column (J & W DB-624) with a 30 m × 5.3 mm ID and 3 μm film thickness. The operating temperatures for the injection and the detector were set at 230 and 250°C, respectively. The temperature of the oven was maintained at 220°C. Duplicate samples of each surfactant concentration were prepared, and the average value of solubility enhancement was recorded.

#### Volatilization Experiments

The initial concentrations of the aromatic compounds were set to 50% of their individual  $S_w$ . The initial concentrations for the relatively higher  $S_w$  (> 1000 mg/L) compounds were limited to 500 mg/L. These organic compounds were directly added to 100 mL of surfactant solution, containing surfactant concentrations from 0 to 1000 mg/L. The stock solutions of the chlorinated pesticides in acetone were prepared. Similarly, the initial concentrations of the

chlorinated pesticides in the surfactant solutions were set to 50 % of their individual  $S_w$ . These solutions were shaken for 24 h until completely mixed. The solution was subsequently stationary until equilibrium was reached. The solution was poured into a vessel that was placed in a water tank with a controllable temperature. A blower with a wind speed controller was used to determine the wind speed of interested. The experimental layout has been described elsewhere (Chao, 2009a). The vessel was a glass dish 8.0 cm in diameter and 4.0 cm in height, and the liquid depth was 2.2 cm. The wind speed could be controlled accurately at 0, 0.20, 0.50, 0.80, 1.0, 2.0, 4.0 and 6.0 m/s. The measurement periods varied with the half-lives of the solutes. For the high  $H$  compounds, the experiments were conducted for 1 or 2 hr. For the low  $H$  compounds, the experiments were conducted for 12 to 24 hr. During the experimental period, the solution was maintained at a fixed depth (2.2 cm) via adding the distilled water to the glass dish each hour. The solute concentrations in the water were analyzed by using 1-mL aliquots of the solution for every sampling. After sampling and extraction with 1 mL carbon disulfide for the aromatic compounds or 1 mL of *n*-hexane for the chlorinated pesticides, the extracted samples were analyzed using a Hewlett-Packard Model 6890A gas chromatograph equipped with a FID detector and an ECD detector according to the analysis species. The aromatic compounds were separated on the capillary column (J & W DB-5) with a 30 × 5.3 mm ID and 3 μm film thickness. The operating temperatures for the injection and the detector were set at 200 and 250°C, respectively. The temperature of the oven was maintained at 50°C. The operating conditions for the chlorinated pesticides have been described in the experiment of solubility enhancement.

#### Calculation of $K_{OL}$ Values and $a$ Values

In general, the volatilization processes of organic compounds from water solutions may be regarded as a first order reaction (Peng *et al.*, 1995; Dewulf *et al.*, 1998; Chao *et al.*, 2000; Chao *et al.*, 2005a). The variation of the concentration of the organic compounds with time can be expressed as

$$C_L = C_0 \exp(-kt) \quad (8)$$

where  $C_0$  is the initial concentration in the bulk-water phase and  $k$  is the rate constant (1/time). Moreover, the relationship between  $k$  and  $K_{OL}$  may be expressed as

$$k = \frac{K_{OL}}{L} \quad (9)$$

where  $L$  is the depth of the solution in a container with a uniform cross section. In this study, the  $K_{OL}$  value was estimated from the experimentally determined  $k$  value. The changes in the  $K_{OL}$  values were used to evaluate the effects of the surfactants on the volatilization of the test organic solutes under various wind speeds.

The  $\alpha$  values of the test organic compounds under specific conditions may be estimated based on Eq. (5) after the  $K_{OL}$  values are obtained. The  $\beta$  values for the organic compounds under the specified wind speeds approach a constant. The data is illustrated in Table 2. The experimental process was described in the other report (Lee *et al.*, 2004a; Chao, 2009a). The  $\alpha$  values are obtained when the accurate  $H$  values are determined.

## RESULTS AND DISCUSSION

### *Effects of Surfactants on Solubility of the Chlorinated Pesticides*

Fig. 1 illustrates the solubility enhancement of various surfactant concentrations on the four pesticides. The  $(S/S_0)$  represents the ratio of solubility for the pesticides in the surfactant solution to those in the distilled water. In general, adding surfactants to the water solution usually enhances the apparent solubility of the organic compounds with the low  $S_w$  values due to the occurrence of a partitioning-like interaction between the surfactants and the organic

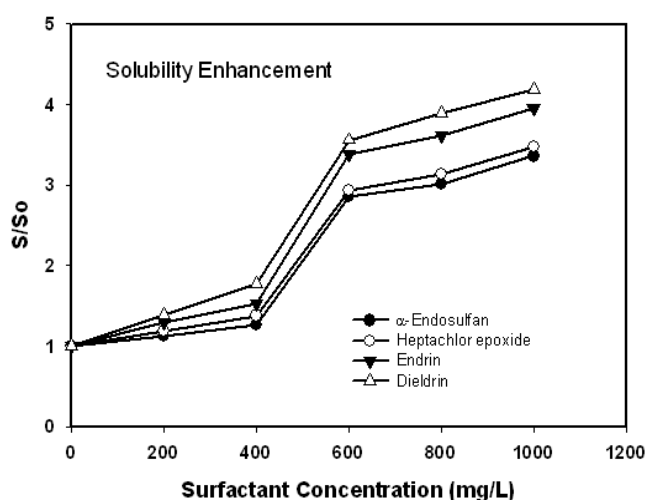
compounds (Kile *et al.*, 1989). The apparent solubilities for the pesticides significantly increase when the expected surfactant concentrations exceed the CMC, which leads to an increase of the  $(S/S_0)$  values of the pesticides by 2.7–4.2 times. According to Eq. (5), the  $K_{OL}$  value of a specified organic compound is proportional to  $\alpha H$ . The  $H$  value of an organic compound is nearly consistent with the ratio of its vapor pressure to the apparent solubility (Mackay and Shiu, 1981; Vane *et al.*, 2000). The surfactant added to the solution cannot significantly reduce the vapor pressure of the pesticide. However, the presence of the surfactant in the solution may reduce the  $H$  value of the organic compound due to a reduction in the solubility. If the  $\alpha$  value is constant, the reduction in the  $K_{OL}$  value is directly proportional to that variety in the  $H$  value. When the surfactant enhances the concentration of organic solutes at the interface, the  $\alpha$  values of the organic compounds vary with the surfactant concentration.

### *Effects of Surfactants on $K_{OL}$ Values of Organic Compounds*

Table 3 lists the  $K_{OL}$  values of the test organic compounds in the surfactant solutions. In general, the  $K_{OL}$  values of high  $H$  organic compounds in the distilled water increase with the decreasing molecular weight, and the  $K_{OL}$  values of low  $H$  organic compounds are proportional to their  $H$  values (Chao, 2009b). In Table 3, the observed  $K_{OL}$  values correspond to the above-mentioned principle. After the surfactant is added to the solution, the  $K_{OL}$  values decrease as the surfactant concentrations increase. Moreover, the degree of reduction of  $K_{OL}$  values for the relatively higher  $S_w$  compounds is markedly lower than those for the relatively lower  $S_w$  compounds. The changes in the  $K_{OL}$  values are dependent of the surfactant concentration and

**Table 2.** The  $\beta$  values ( $\times 10^4$ ) of organic compounds under the given wind speeds (m/s).

Wind speeds	0	0.2	0.5	0.8	1.0	2.0	4.0	6.0
$\beta$ Values	0.196	2.08	2.68	3.51	4.10	5.28	8.41	10.8



**Fig. 1.** The dependence of the solubility enhancement of the chlorinated pesticides on their water solubilities in the DBS surfactant solutions.

**Table 3.**  $K_{OL}$  values (cm/min)  $\times 10^3$  of test organic compounds as a function of surfactant concentration.

Compounds	Surfactant concentrations (mg/L)					
	0	200	400	600	800	1000
Benzene	10.3	10.2	10.1	9.85	9.69	9.59
Toluene	10.1	9.96	9.84	9.57	9.39	9.21
Ethylene	9.62	9.46	9.31	9.07	8.88	8.74
<i>m</i> -Dichlorobenzene	7.38	7.21	7.09	6.81	6.56	6.31
Propylbenzene	8.72	8.53	8.21	7.79	7.42	7.16
$\alpha$ -Endosulfan	1.09	0.97	0.88	0.70	0.57	0.49
Heptachlor epoxide	1.28	1.11	1.01	0.77	0.64	0.54
Endrin	0.93	0.80	0.73	0.54	0.45	0.39
Dieldrin	0.29	0.25	0.22	0.17	0.15	0.13

the  $S_w$  values of the organic compounds. The degree of reduction in the  $K_{OL}$  values for the test compounds indicates the increasing order, as follows: benzene < toluene < ethylbenzene < *m*-dichlorobenzene < propylbenzene <  $\alpha$ -endosulfan < heptachlor epoxide < endrin < dieldrin. On the other hand, the  $K_{OL}$  values of the pesticides reduce significantly when the surfactant concentration exceeds the CMC value (523 mg/L). Regarding the aromatic compounds, the propylbenzene in the solution containing the high surfactant concentration exhibits a notable decrease in the  $K_{OL}$  values. The result corresponds to the fact that the surfactants generate high suppression on the volatilization of the low  $S_w$  organic compounds.

#### **Effects of Wind Speeds on the $K_{OL}$ Values of Organic Compounds in the Surfactant Solution**

In the previous study, an empirical equation was presented to describe the relationship between the  $K_{OL}$  values of the organic compounds in the distilled water and wind speeds. The equation may be written as follows (Chao, 2009a).

$$K_{OL} = K_{OL0} + \frac{au^*}{b + u^*} + cu^* \quad (10)$$

where  $u^*$  is the wind speed (m/s); The parameters  $a$ ,  $b$  and  $c$  represent the characteristic parameters of wind that causes the  $K_{OL}$  value (cm/min) of organic solutes to increase; and  $K_{OL0}$  (cm/min) is the mass transfer coefficient of the organic solute under the still condition. For the high  $H$  compounds, the second term on the right side of Eq. (10) is negligible. The  $K_{OL}$  value of the high  $H$  organic solute almost linearly increases with the increasing wind speeds. For the low  $H$  compounds, the  $K_{OL}$  values that vary with the wind speeds exhibit a two-stage increase. The first stage is a “sharp-rise” stage that is observed at the lower wind speed. The second stage is “stable-linearity” stage that occurs during a continual increase in the wind speed. The characteristics of parameter  $a$ ,  $b$  and  $c$  have been discussed in other report (Chao, 2009a).

Fig. 2 indicates that the  $K_{OL}$  values of the high  $H$  compounds in the surfactant solutions vary with the wind speeds. As expected, the profile of the  $K_{OL}$  value of the organic compound in the surfactant solution is similar to that in distilled water. The  $K_{OL}$  values of the aromatic compounds almost linearly increase with the increasing wind speeds.

Although the surfactant suppresses the emissions of the test organic solutes under the still condition, the five organic compounds in the surfactant solution under the selected wind speeds display similar changes in the  $K_{OL}$  values. This is because the aromatic compounds have the relatively higher  $S_w$  values. The result also implied that, although surfactants in the solution may reduce the  $K_{OL}$  values of the aromatic compounds, the air turbulence may alter the ability of the surfactant to suppress the volatilization of organic solutes. In Fig. 2, when the surfactant concentrations are higher than the CMC, the difference in the  $K_{OL}$  values of the test organic compounds decrease. The result offers a potential phenomenon, that is, the volatilization reduction of the low  $S_w$  organic compound in the surfactant solution under air turbulence may decrease. The result reveals that, in special conditions, the  $K_{OL}$  values of low volatile compounds in the surfactant solution may exceed those of high volatile compounds.

Fig. 3 displays that the  $K_{OL}$  values of the pesticides with the low  $H$  and  $S_w$  values in the surfactant solutions vary with the wind speeds. Because the pesticides have lower  $H$  values, the changes in the  $K_{OL}$  values of the pesticides under the wind speeds are higher than those of the aromatic compounds. Moreover, the change in trend of the  $K_{OL}$  values corresponds to the assumption of the above-mentioned two stages. The four chlorinated pesticides have similar  $S_w$  values. The effects of the solubility enhancement on volatilization of these pesticides are also similar. However, when the surfactant concentration increases, the difference in  $K_{OL}$  values of four pesticides reduce. In particular, the surfactant concentration reaches 1000 mg/L, and the  $K_{OL}$  values of  $\alpha$ -endosulfan are higher than those of heptachlor epoxide under the high wind speeds. The result is not identical with volatilization of the two organic compounds in the distilled water. The unexpected increase is attributed to the change in the concentration of organic solutes at the gas-liquid interface. The wind only affects the volatilization of organic compounds at the gas-liquid interface. The surfactant at the gas-liquid interface can attract the other organic compounds to aggregate at the interface. This result leads to the increase in the concentration of organic solutes at the interface. The organic compounds are blown away from the surface when the wind blows across the surface of the solution. The organic compound with the relatively lower  $S_w$  has a higher concentration at the interface. Consequently, the lower  $S_w$

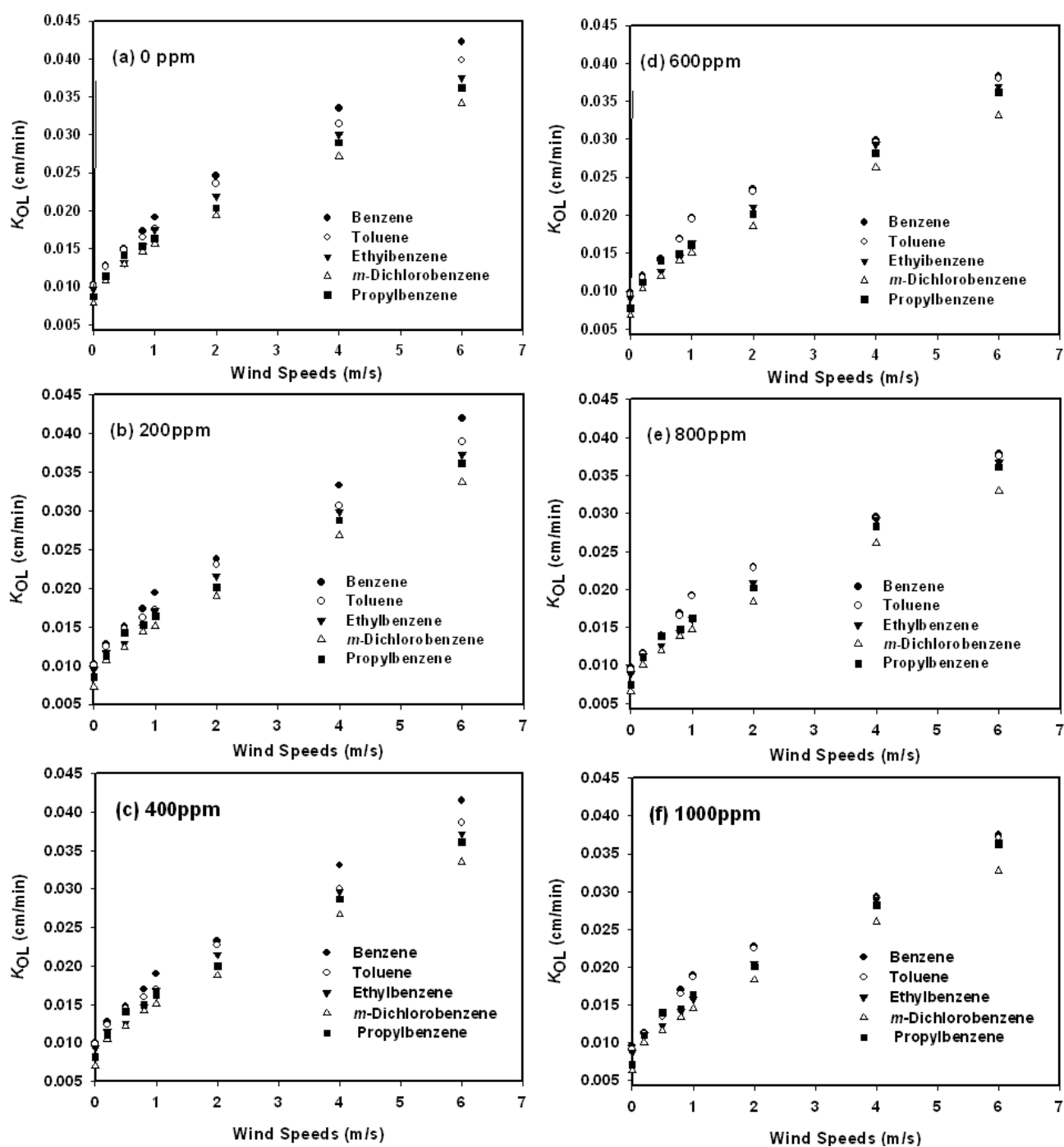


Fig. 2. Changes in  $K_{OL}$  values of aromatic compounds in the surfactant solutions under various wind speeds.

organic compounds generate the higher increase in the  $K_{OL}$  values. In the past study, the  $K_{OL}$  values of organic compounds with low  $H$  ( $H < 0.001$  dimensionless) were proportional to their  $H$  values (Chao, 2009b). In addition, the organic compounds with the similar physico-chemical properties underwent identical changes in their  $K_{OL}$  values under various wind speeds (Chao *et al.*, 2005b). The finding indicated that the surfactants may alter the principle.

#### Changes in $\alpha_s$ Values of Organic Compounds in the Surfactant Solution

According to the SDRL model, the volatilization reduction may be explained by the decrease in the  $H$  value and the changes in the  $\alpha$  value. The presence of surfactant in the solution may alter the  $H$  values. Eq. (5) must be modified as

$$K_{OL} = \alpha_s \beta \left( \frac{RT}{2\pi M} \right)^{1/2} H^* \quad (11)$$

where  $\alpha_s$  is regarded as the concentration ratio between the interface and bulk phase of an organic solute in a surfactant solution; and  $H^*$  is Henry's law constant of an organic

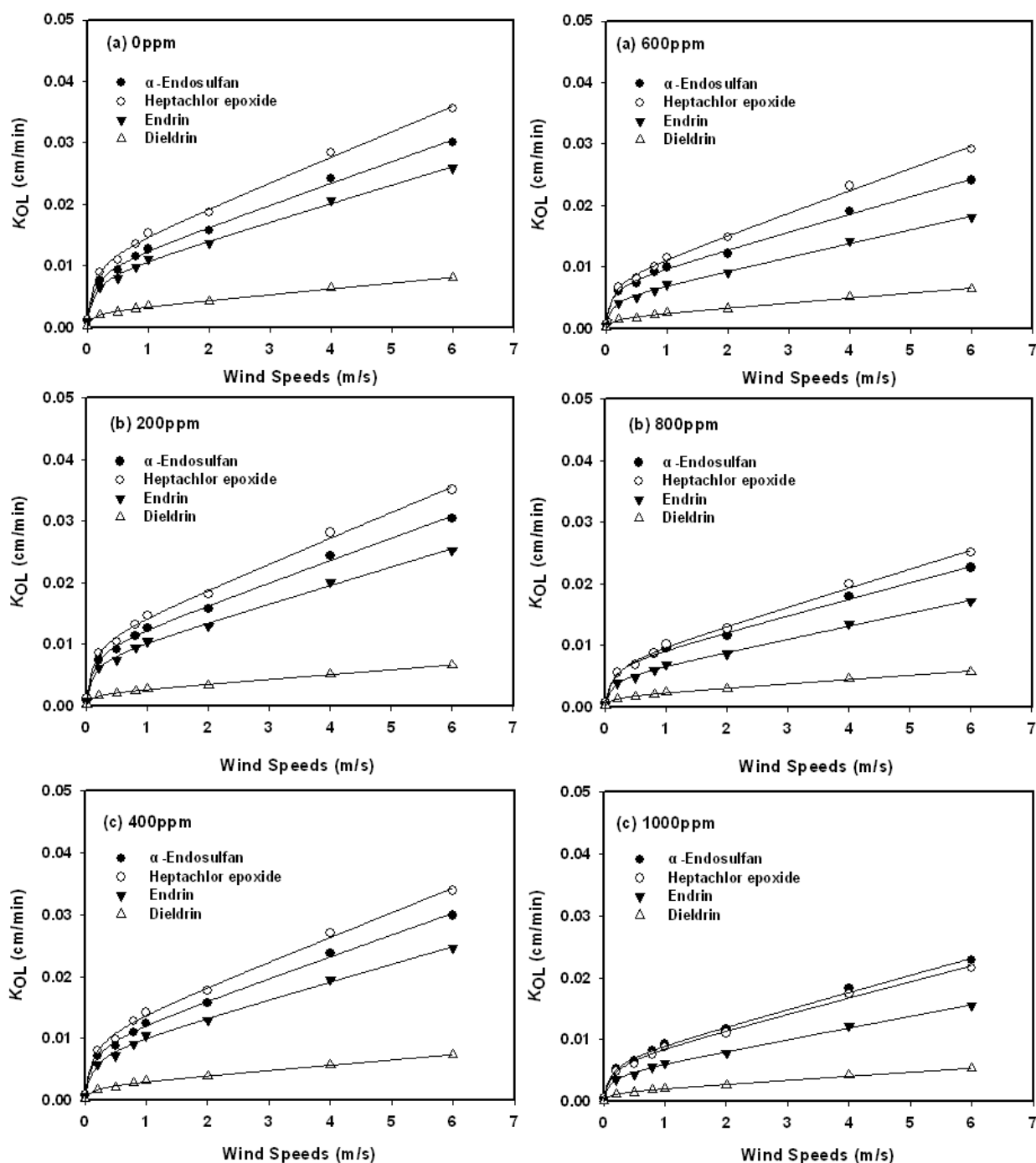


Fig. 3. Changes in the  $K_{OL}$  values of chlorinated pesticides in the surfactant solutions under various wind speeds.

compound in the surfactant solution. The  $H^*$  values in Eq. (11) are assumed to be equal to the  $H$  values because the effects of the solubility enhancement on the aromatic compounds with the high  $S_w$  are less-obvious. Regarding the chlorinated pesticides, the  $H^*$  values are estimates through the  $H$  values obtained from literature divided by  $(S/S_o)$ .

The  $\alpha_S$  values of the test organic compounds under the still condition are presented in Table 4. The  $\alpha$  values of the organic compounds in the distilled water were defined in the previous study. The  $\alpha$  value is equal to or less than 1.0 and the  $\alpha$  value is inversely proportional to the  $H$  value of

the organic compound. When the  $H$  values (dimensionless) of the organic compounds are less than 0.001, their  $\alpha$  values approach 1.0. In Table 4, the  $\alpha_S$  values of the aromatic compounds with the high  $H$  are markedly lower than 1.0. The result is consistent with the prior description. The  $\alpha_S$  values of the chlorinated pesticides in the distilled water ranged from 0.40 to 1.73. The potential bias result from  $H$  values was obtained from the relevant literature. The chlorinated pesticides exhibit the characteristics of the low  $S_w$  and vapor pressure. The estimated  $H$  values generated the relatively higher inaccuracy. When the surfactant was

**Table 4.**  $\alpha$  values of test organic compounds as a function of surfactant concentration.

Compounds	Surfactant concentrations (mg/L)					
	0	200	400	600	800	1000
Benzene	0.0055	0.0054	0.0054	0.0052	0.0051	0.0051
Toluene	0.0049	0.0048	0.0047	0.0046	0.0045	0.0044
Ethylene	0.0042	0.0041	0.0040	0.0039	0.0039	0.0038
<i>m</i> -Dichlorobenzene	0.0089	0.0082	0.0081	0.0078	0.0075	0.0072
Propylbenzene	0.0046	0.0045	0.0043	0.0041	0.0039	0.0038
$\alpha$ -Endosulfan	1.02	1.03	1.05	1.62	1.77	1.82
Heptachlor epoxide	0.40	0.41	0.43	0.68	0.72	0.73
Endrin	0.96	1.05	1.15	1.67	1.77	1.82
Dieldrin	1.73	1.83	2.17	3.30	3.60	3.75

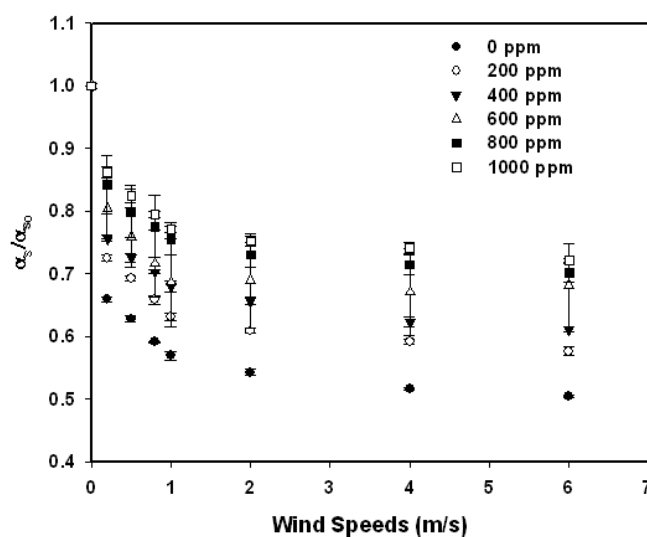
added to the solution, the  $\alpha$ s values of pesticides increased with the increasing surfactant concentrations. As previously described, the surfactant may attract the low  $S_w$  organic compounds to aggregate at the interface. The observed  $\alpha$ s values can correspond to the earlier hypothesis that may be higher than  $\alpha$  values.

#### Effects of Wind on the Concentration of Chlorinated Pesticides at the Interface

This study focused on the changes in the  $\alpha$ s values of pesticides because the effects of the surfactant and wind on the  $\alpha$ s values of the test aromatic compounds were less-obvious. Due to inconsistent  $\alpha$ s values, the estimated  $\alpha$ s values of the pesticides varied in the distilled water under a still condition, which caused difficulty in obtaining a comparable result. The  $\alpha$ s ratio ( $\alpha_s/\alpha_{s_0}$ ) of wind speed under a still condition is an excellent parameter to elucidate the characteristics of the  $\alpha$ s values for the low  $S_w$  organic compounds in the surfactant solutions. The expected differences in the  $\alpha$ s ratios were small because the selected pesticides exhibit similar  $S_w$  and low  $H$  values. Fig. 4 illustrates the relationship of the average  $\alpha$ s ratio for all of the test chlorinated pesticides and standard deviation in comparison to the various surfactant concentrations under the various wind speeds. The average  $\alpha$ s ratio indicates a

small standard deviation. The result demonstrated that the average  $\alpha$ s ratio may represent the characteristics of the individual  $\alpha$ s for the four chlorinated pesticides.

In Fig. 4, the characteristics of the average  $\alpha$ s ratios are a sharp-falling curvature when the wind blows across the solution face. The wind may reduce the concentration of the organic compounds at the interface, which was explained in other report (Chao *et al.*, 2005b). The drop in the curvatures of the average  $\alpha$ s ratios is smooth if the wind speeds increase continuously. The  $\alpha$ s ratios increase when the surfactant concentration increases under the same air turbulence condition. The higher surfactant concentration in the solution causes the higher apparent  $S_w$  values of the organic compounds. Similarly, the higher surfactant concentration in the interface also causes the higher organic compounds at the interface. Although air turbulence leads to the organic compounds escape from the interface, the higher surfactant concentration can hold the higher concentration of the organic compounds at the interface. The results in this study demonstrated that the surfactants in the solution attract the low  $S_w$  organic compounds to aggregate at the gas-liquid interface. However, the surfactants increase the hindrance at the interface, leading to the volatilization reduction. The aggregated concentrations of the organic compounds at the interface are proportional to the surfactant concentration

**Fig. 4.** The average  $\alpha_s/\alpha_{s_0}$  ratios of chlorinated pesticides in the surfactant solutions under various wind speeds.



and inversely proportional to the  $S_w$  values. The organic compounds with the higher concentration at the interface generate the higher  $K_{OL}$  values under air turbulence because the wind blows the organic compounds at the interface away from the solution surface. This is the reason that the  $K_{OL}$  value of  $\alpha$ -endosulfan is higher than that of heptachlor epoxide in the solution containing the high surfactant concentration under the high wind speeds.

## CONCLUSIONS

This study applied the changes in the  $K_{OL}$  values and concentrations at the gas-liquid interface of the test organic compounds to examine the effects of the surfactants and wind speeds on the volatilization of organic compounds with various  $S_w$  values. According to the SDRL model, it is possible to estimate the concentration of organic compounds at the interface. The results demonstrated that the surfactants effectively reduced the  $K_{OL}$  values of the low  $S_w$  organic compounds and enhanced the concentration of the low  $S_w$  organic compounds at the interface. The effects of the surfactant on the high  $S_w$  organic compounds were less notable. Moreover, when wind blows the surfactant solution surface, the  $K_{OL}$  values of low  $S_w$  organic compounds may generate the higher increase rate. This reason is attributed to the surfactants attract the organic compounds with the low  $S_w$  to aggregate at the gas-liquid interface. The wind blows across the solution surface to blow the organic compounds at the interface away from the solution. The result reveals the concentration of organic compounds at the gas-liquid interface is the critical factor to determine the volatilization of the organic compound.

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