



The effect of agitation on volatilization of naphthalene from solution containing surfactant

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ABSTRACT

The effects of agitation on naphthalene volatilization from solutions with surfactant concentration exceeding critical micelle concentration were studied. Micellar partition coefficient (K_m) and liquid–vapor mass transfer coefficient (K_L) in the presence of three surfactants, i.e., anionic sodium dodecyl sulfate (SDS), cationic cetyltrimethylammonium bromide (CTMAB), and nonionic Tween 20 were determined at different agitation speeds. Both K_m and K_L increased in the agitated solutions, indicating enhanced naphthalene micellization and water–vapor mass transfer due to agitation. The enhancement factor of K_L in surfactant-laden solution was determined to be in the range of 1.3–6.3 (SDS), 0.7–7.9 (CTMAB), and 1.5–7.3 (Tween 20). However, agitation exhibited a greater enhancement on K_L , resulting in a net increased volatilization rate. A conceptual model was developed to describe the dependence of the bulk aqueous phase naphthalene concentration (C_L) on Henry's constant (H), K_L , K_m , and surfactant concentration (S). This study is the first in reporting the combined effects of agitation and surfactant on the volatilization of semi-volatile naphthalene in air–water–micelle system. Results provided insight into the volatile emission as frequently encountered in certain waste streams.

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1. Introduction

Volatilization of volatile and semi-volatile organic compounds (VOCs and SVOCs) from water into atmosphere is an important process in determining the fate and transport of organic contaminants in the environment. In natural waters, volatilization primarily controls the residence time of hydrophobic organic compounds that are resistant to physicochemical and biological degradation [1]. In municipal and industrial wastewater treatment plants, volatilization can lead to the emission of toxic compounds that must be controlled, particularly when regulations on the toxic emission become increasingly stringent in recent years [2–4]. The factors that affect the volatilization are well documented, including organic solute properties, such as diffusion coefficient, aqueous solubility, molecular weight and Henry's law constant [4–8]. Other important factors include wastewater properties such as co-solutes and the operating parameters such as mixing and turbulence across air–water interface caused by agitation and wind currents [9–12]. Unfortunately, both theoretical description

and experimental data have not been substantiated to elucidate how these factors affect the exact rate and extent of volatilization.

From relevant studies reported to date, it is generally believed that volatilization characteristics are highly dependent on compound's Henry's law constant (H). For solutes with very high H such as benzene, toluene, ethylbenzene and xylene, the liquid phase based overall mass transfer coefficient (K_L) approximates the liquid–film mass transfer coefficient (k_L). Since liquid phase resistance dominates, stirring has significant effects on volatilization. For compounds of this category, molecular weight plays a key role in solute volatilization, and the effect of co-solutes was found to be minimal [4]. For solutes with a very low H such as alcoholic or phenolic compounds, gas phase film dominates the mass transfer resistance; hence the overall mass transfer coefficient K_L is approximately equal to the gas–film mass transfer coefficient (k_G). In such a case, volatilization is independent of stirring but significantly impacted by wind velocity [4]. Smith et al. [13] defined the relative volatilities (high vs. low) on the basis of H value and estimated that mass transfer in the liquid phase controls about 95% when a compound has an H value of greater than 4.61 atm L/mol, whereas mass transfer in the gas phase becomes rate-limiting when H is less than 0.013 atm L/mol.

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This present study attempted to investigate how surface-active-agents (i.e., surfactants as co-solutes and micelle) affected the volatilization of naphthalene in an agitated solution. With its intermediate Henry's law constant of 0.483 atmL/mol, naphthalene is a semi-volatile compound and hence significant mass transfer resistance is anticipated in both liquid and gas films. The effects of surfactants on volatilization are of importance because of their ubiquitous nature in the environment as a result of their widespread uses in domestic, industrial and environmental fields such as detergency, mineral flotation, oil recovery, and surfactant-enhanced remediation. It should be noted that surfactants and agitation have opposing effects on air–water mass transfer (volatilization) of VOCs and SVOCs. When present at high concentrations exceeding critical micelle concentrations (CMCs), surfactants are capable of micellizing volatile compounds, rendering organic compounds less volatile. In the meantime, agitation enhances volatilization by increasing mass transfer at the air–water interface.

Several investigators demonstrated the inhibition effect of surfactant solubilization on the volatilization of organic compounds [14–18]. The suppression of volatilization was conducted under equilibrium partitioning in closed systems (EPICs) containing surfactants in an excess of CMCs. Results from these studies showed that surfactants significantly reduced the apparent Henry's law constant (H'), thus decreasing equilibrium vapor phase concentrations. The suppression of volatilization was also demonstrated in a quiescent open container containing mixed surfactants [19]. Mixed anionic–nonionic surfactants were found to synergistically suppress the volatilization of naphthalene.

Moreover, natural waters and wastewaters in an agitated state are of more practical relevance. With surfactant present, the effects of agitation may become complicated because agitation has direct effects on volatilization characteristics of organic compounds as well as indirect effects on volatilization through increased micellar solubilization [20] and reduced apparent Henry's law constant [18]. Until recently, the volatilization characteristics of organic compounds in the presence of surfactant under turbulent mixing condition were only investigated for a few compounds with either a very high H (benzene, toluene, ethylbenzene) or a very low H (hexanol, heptanol, octanol) [4,7,8]. Compounds such as naphthalene with an intermediate H have not been examined with regard to their volatilization characteristics in agitated surfactant solutions.

The objective of this work was to determine the effects of agitation on the micellar solubilization as well as on the volatilization characteristics of semi-volatile compounds in surfactant solutions with various concentrations exceeding CMCs. Three types of surfactants were tested in this study, including an anionic surfactant (sodium dodecyl sulfate, SDS), a cationic surfactant (cetyltrimethylammonium bromide, CTMAB) and a nonionic surfactant (Tween 20). The experimental results and a conceptual model developed in this study are intended to provide some insight into the mechanism and estimation of volatile emission in stirred and surfactant-laden solutions as frequently encountered in certain waste streams as well as natural waters receiving wastewater effluents.

2. Theoretical considerations

The volatilization of organic solutes from water to air can be described by the classical two-film model. The model assumes that the interface between bulk liquid and air is bounded by a stagnant transition film on each side, across which the solute moves by diffusion [21]. According to the film theory, Fick's second law and

the boundary conditions [22], total naphthalene flux is constant for both the liquid–film and the gas–film. The vapor flux of naphthalene (J) from water to air, on the liquid side, can be expressed as:

$$J \equiv -\frac{V}{A} \frac{dC_L}{dt} = K_L(C_L - C_i) \quad (1)$$

where V is the volume of water, A is the interfacial contact area between air and water, C_L is the solute concentration in the bulk liquid, C_i is the solute concentration on the liquid side of the water–air interface, and K_L is the liquid-based overall mass transfer coefficient [10]. If the solute quickly reaches equilibrium at the water–air interface, then C_i in Eq. (1) can be replaced by C_G^*/H , where C_G^* is the solute concentration on the gas side of the interface. Since C_G^* can be assumed negligible in open container (a condition commonly referred to an infinite dilution or infinite ventilation condition), Eq. (1) becomes:

$$-\frac{V}{A} \frac{dC_L}{dt} = K_L C_L \quad (2)$$

Integrating Eq. (2) and substituting V/A by the depth of the aqueous solution in the open volatilization container (L), one arrives at:

$$C_L = C_0 \exp\left(-\frac{K_L t}{L}\right) \quad (3)$$

where C_0 is initial concentration of the solute. Eq. (3) is commonly written in terms of the first-order volatilization rate constant (k) as follows:

$$C_L = C_0 \exp(-kt) \quad (4)$$

where the volatilization rate constant (k) and the overall mass transfer coefficient (K_L) is related as:

$$k = \frac{K_L}{L} \quad (5)$$

Eqs. (3) and (4) can be used to determine the values of k and K_L directly from experimental data by linear regression. The aforementioned two-film theory, however, does not take into account of the effects of co-solutes such as surfactants. The presence of surfactants changes the partitioning and volatilization characteristics of hydrophobic organic compounds such as naphthalene. Naphthalene is partitioned between micellar phase and the dissolved aqueous phase according to the following mass balance:

$$C_L = C_A + K_m C_A (S - \text{CMC}) \quad (6)$$

Eq. (6) indicates that the apparent solubility (C_L) is the concentration of contaminant dissolved in aqueous phase (C_A) plus the concentration of the micellized contaminant. The latter is linearly proportional to the micellized surfactant concentration ($S - \text{CMC}$), where S is the total surfactant concentration (mg/L) and CMC is the critical micelle concentration (mg/L). The value of the linear proportionality factor, micellar partitioning coefficient K_m (L/mg), has been found to be constant at surfactant concentration above the CMC for a given surfactant–organic system [23].

By dividing both sides of Eq. (6) by C_A and rearrange, one can obtain:

$$\frac{1}{f_{\text{ex}}} = 1 + K_m (S - \text{CMC}) \quad (7)$$

where the extramolecular fraction (f_{ex}) is defined as the ratio of C_A to the total contaminant concentration (i.e., apparent solubility, C_L) in the solution:

$$f_{\text{ex}} \equiv \frac{C_A}{C_L} \quad (8)$$

By plotting $1/f_{\text{ex}}$ vs. $S - \text{CMC}$ on the basis of Eq. (7), one can determine the value of K_m [18].

Besides the effects of micellar partitioning, surfactant also affects the volatilization of solute naphthalene because only the aqueous dissolved form of naphthalene (rather than micellized naphthalene) is participated in liquid–vapor exchange [15,24]. Consequently, C_L in a surfactant-free solution of the classical two-film theory in Eq. (2) should be replaced by C_A or $f_{ex} C_L$ when surfactant micelles are present. Substituting f_{ex} in Eq. (7) into Eq. (2), we can obtain:

$$\frac{dC_L}{dt} = -\frac{K_L C_L}{L[1 + K_m(S - CMC)]} \quad (9)$$

Integration of Eq. (9) results in the first-order kinetics with regard to the decrease in liquid phase naphthalene concentration during the course of volatilization when surfactant micellization is present ($S \geq CMC$):

$$C_L = C_0 \exp\left(-\frac{K_L t}{L[1 + K_m(S - CMC)]}\right) \quad (10)$$

The above equation is analogous to Eq. (4) in describing the volatilization from a surfactant-free solution. This conceptual model clearly indicates that volatilization rate constant due to the presence of surfactant micelles is decreased by a factor of $1/f_{ex}$ or $1 + K_m(S - CMC)$. The model also clearly depicts the opposing effects of K_L and K_m , because they appear in the numerator and denominator of Eq. (10), respectively. Such opposing effects are in agreement with the physical meanings of each parameter. It is evident that volatilization increases with the increasing mass transfer coefficient. In the meantime, micellization reduces dissolved phase solute concentration thereby suppressing volatilization. The utilities and its limitations of Eq. (10) will be further elaborated in subsequent sections of this paper.

3. Experimental

3.1. Chemicals

Naphthalene with a purity of greater than 98% was purchased from Shanghai Yuanhang Reagent Plant, China. An anionic surfactant, sodium dodecyl sulfate (SDS), was purchased from Tokyo Kasei Kogyo Co. Ltd., Japan. A nonionic surfactant, Tween 20 and a cationic surfactant, cetyltrimethylammonium bromide (CTMAB), were purchased from Acros Organics. All of these test surfactants possess a linear aliphatic chain. These surfactants (all analytical reagents except SDS with a chemical purity of 98%) were used as received without further purifications. Surfactant solutions were prepared by dissolving the relevant surfactant in deionized water. The stock solutions of naphthalene were also prepared by dissolving it in deionized water. The physicochemical properties of naphthalene and surfactants used in this study are listed in Table 1 [25].

3.2. Experimental procedures

Experiments were conducted at open surfaces in the laboratory, with the apparatus shown in Fig. 1. The water tank designed

by us was used to control the temperature by water-bath with a heater and a water circulator on the inner wall. The head of a mercury thermometer was dipped below the liquid surface to monitor water temperature. A glass dish of 7.5 cm in diameter and 3.5 cm in height was used to hold the aqueous solution. The solution depth in the dish was maintained at about 2.8 cm, with the volume being approximately 100 mL. During the experiment, the relative humidity of the ambient air ranged from 75% to 85%, and the temperature of air and aqueous solution was kept at 25 ± 1 °C. An air-conditioner ensured stable room temperatures in the laboratory. The naphthalene solutions with or without the presence of surfactant (i.e., SDS, CTMAB, and Tween 20) were maintained at the above-described temperature by keeping the dishes in the water bath. To simulate the needed turbulence level of the aqueous solutions, a Jar Test agitator with adjustable rotational frequency was applied. The stirring blade was 1 cm wide and 6 cm long. The stirring rates adopted were 0, 13, 39, 65, 91 revolutions per minute (rpm), which mimics the turbulent liquid intensity common in most wastewater treatment facilities [4]. The velocity gradients (G) at given rpm values were calculated from liquid volume and blade dimension according to a method described by Lee et al. [12]. The calculated G values corresponding to these stirring rates were 0, 13, 68, 147, 243 s^{-1} , respectively. Before the mixture was agitated, the concentration of naphthalene was tested. The volatilization loss of naphthalene was determined by analyzing the concentration of naphthalene remained in the aqueous solutions. Samples were collected at a 30-min interval for 3 h.

3.3. Naphthalene measurement and error analysis

The measurements of naphthalene were detailed in our previous study [19]. Three millilitres of aliquotes for every run were sampled and poured into a 3.5-mL UV cell (1-cm light path) by digital reading pipettes (Acura 821, Socorex, Switzerland). Liquid samples were carefully withdrawn from the test tank for naphthalene measurement using a UV spectrophotometer (UV-2401PC, Shimadzu). It was assumed that the procedure of measuring the naphthalene concentration did not affect the volatilization results because of the short duration of the measuring time (30 s) when compared to the overall experiment (<2%). Naphthalene concentrations were determined at 276 nm with the detection limit of $8 \mu\text{g/L}$. The background UV absorption of each test surfactant was corrected by calibrating with naphthalene-free solutions containing the same surfactant concentration.

A strict regime of quality control and quality assurance was followed at every stage. During experimental processes, deionized water was supplied to the test solution at given time to make up for the water loss due to evaporation. The error introduced by volatilization container due to adsorption was estimated to be less than 0.01%. At each level of turbulence and surfactant concentration, three independent tests were performed. The data presented are the mean values of three measurements with the relative standard deviations of 6.7–10.2%.

Table 1
Selected properties of the test compounds

Compound	Formula	MW (g/mol)	CMC (mg/L)
SDS	$C_{12}H_{25}OSO_3Na$	288	1455
CTMAB	$C_{19}H_{42}BrN$	365	335
Tween 20	$C_{12}H_{23}O_2C_6H_{11}O_4(CH_2CH_2O)_{20}$	1226	60

Compound	Formula	MW (g/mol)	Boiling point (°C)	Vapor pressure (Pa at 25 °C)	Henry's law constant (atm L/mol)	Water solubility (mg/L)	$\log K_{ow}$
Naphthalene	$C_{10}H_8$	128	218	10.4	0.483	32.05	3.36

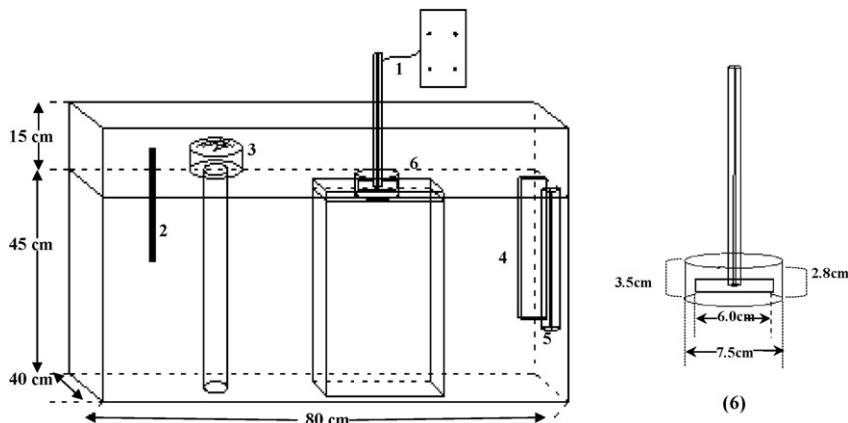


Fig. 1. Experimental apparatus for the study of naphthalene volatilization ((1) Jar Test agitator; (2) mercury thermometer; (3) thermo- and hygrometer; (4) heater; (5) water circulator; (6) glass dish).

4. Results

4.1. Effect of surfactants and agitation on the volatilization rate constant (k)

The effects of three different surfactants (SDS, CTMAB and Tween 20) on the volatilization of naphthalene are compared in the C_L/C_0 vs. volatilization time (t) plot (Fig. 2). Representative data shown in Fig. 2 were obtained under the same surfactant concentration (3000 mg/L) and the same agitation speed (65 rpm or $G = 147 \text{ s}^{-1}$). Due to its moderately high Henry's constant, significant volatilization of naphthalene occurred within 3 h of the experimental duration. When compared with the surfactant-free control, the presence of all three surfactants reduced the rate and extent of naphthalene volatilization. As shown in Fig. 2, the residual naphthalene (C_L/C_0) at the conclusion of the experiment reached 17%, 25% and 45% for Tween 20, SDS and CTMAB, respectively. The volatilization loss ($1 - C_L/C_0$) was the least for cationic CTMAB and the most for nonionic Tween 20. For the effects of three surfactants with the same mass concentration, the decreasing sequence of volatilization rate constant (k) under a given agitation condition is not in agreement with the CMC values (Table 1). This is presumably due

to the fact that k is influenced by other factors as well and is further discussed in subsequent sections.

The inset in Fig. 2 shows the fit of experimental data to the linear regression between $\ln(C_L/C_0)$ and t . Significant linear relationships ($p < 0.05$) for all three surfactants indicate that the first-order kinetic model in Eq. (3), and accordingly Eq. (10) with a lumped rate constant, can be applied to determine the volatilization rate of naphthalene from the surfactant-laden solution. Eq. (3) has been used to describe organic solute volatilization from water under liquid or air turbulent conditions in several studies [4,9,11,26]. Since volatilization rate constant k is related to the overall mass transfer coefficient K_L by Eq. (5), the same linear regression in Fig. 2 can be used to estimate the corresponding K_L value in defining the rate of the overall water–air exchange process.

The values of volatilization rate constant (k) under all test conditions (agitation and surfactant concentrations) of anionic surfactant SDS are depicted in Fig. 3. Similar trends of combined effects of agitation and surfactants were obtained for two other surfactants (data not shown). Experimental data in Fig. 3 indicated that volatilization rate increased with the agitation speed in surfactant-free control as well as five SDS concentrations above CMC. For instance, the k values for the solution containing 3000 mg/L SDS increased from 0.112 h^{-1} in the quiescent condition to 0.629 h^{-1} when the solution was agitated at 91 rpm. It is also noted that the increased volatilization rates due to agitation decreased with the increase in surfactant concentrations, suggesting that the solute's volatilization was impacted more by agitation when surfactant concentrations were lower.

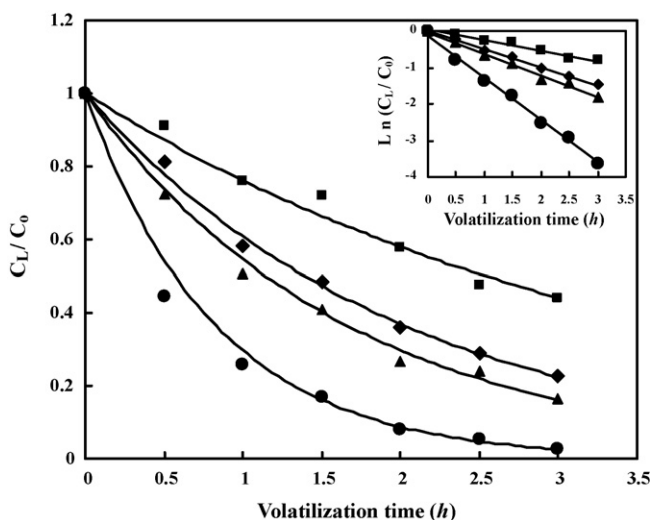


Fig. 2. Kinetics of naphthalene volatilization from a surfactant-free control solution and from solutions containing 3000 mg/L surfactant under 65 rpm agitation speed. Treatments were SDS (◆), CTMAB (■), Tween 20 (▲), and surfactant-free control (●).

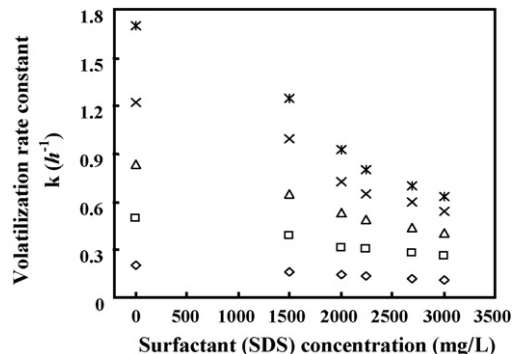


Fig. 3. The volatilization rate constant k (h^{-1}) as a function of surfactant (SDS) concentrations under different agitation speeds. Agitation speeds were 0 rpm (◇), 13 rpm (□), 39 rpm (△), 65 rpm (×), and 91 rpm (*).

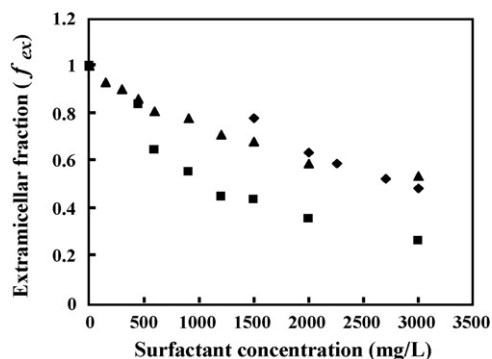


Fig. 4. Dependence of extramicrocellular fraction (f_{ex}) on surfactant concentrations in static and agitated solutions (39 rpm). Surfactants were SDS (◆), CTMAB (■), and Tween 20 (▲).

4.2. Effect of surfactant and agitation on extramicrocellular fraction (f_{ex}) and micellar partition coefficient (K_m)

It is expected that both concentration and type of surfactants affect extramicrocellular fraction (f_{ex}) of naphthalene. A typical plot of such effects is detailed in Fig. 4 for a given agitation speed of 39 rpm ($G = 68 \text{ s}^{-1}$). For all three surfactants, f_{ex} values decreased as surfactant concentration increased. Note that in the surfactant-free control, all naphthalene are present in the form of dissolved phase, hence $f_{ex} = 1$. These surfactant concentration dependant results are expected since more micelles are formed at higher surfactant concentrations relative to its corresponding CMC value. In addition to the effects of surfactant concentrations, the discriminative effects of various surfactants on the f_{ex} can also be observed in this figure. In the range of mass concentration tested, cationic CTMAB had the greatest reduction in f_{ex} of naphthalene. For instance, f_{ex} was 0.633, 0.583, and 0.353 for SDS, Tween 20 and CTMAB solutions, respectively, with surfactant concentration 2000 mg/L and agitation speed 39 rpm ($G = 68 \text{ s}^{-1}$).

Eq. (7) indicates that f_{ex} values depend on both K_m and micellized surfactant concentrations ($S - \text{CMC}$). This equation is used to test if a linear relationship exists between $1/f_{ex}$ and $S - \text{CMC}$ under the experimental conditions. The linear relationships with a slope factor of K_m were demonstrated in a previous study using an equilibrium partitioning in a closed system [18]. Experimental data from this study also demonstrated the positive linear correlation between $1/f_{ex}$ and $S - \text{CMC}$ (Fig. 5). For all three surfactants with five agitation speeds for each surfactant, the resultant R^2 values for all the linear regression lines are greater than 0.96. These results imply that the mass balance of naphthalene between the aqueous and micellized forms in Eq. (6) is satisfied regardless of the nature of the system (i.e., the volatilization loss of naphthalene in an open system).

With the linear relationship between $1/f_{ex}$ and $S - \text{CMC}$, the best estimates of K_m values can be obtained using the least-squares fit through Eq. (7). Table 2 summarizes the K_m values for three surfactants under different agitation speeds. A salient feature of the results shown in Table 2 is the dependence of K_m values on the types of surfactants and the degree of agitation. From Table 2, it is apparent that the K_m values under a given agitation speed were in an increasing order of Tween 20 < SDS < CTMAB. The K_m values (L/g) ranged 0.187–0.401 for Tween 20, 0.354–0.878 for SDS, and 0.523–1.409 for CTMAB under the test conditions. The variations of K_m values among three surfactants cannot be simply interpreted by their test concentrations relative to its corresponding CMC value (Table 1). Rather, it is more likely that micelle structures (shape and size) and the molecular interactions between solute and surfac-

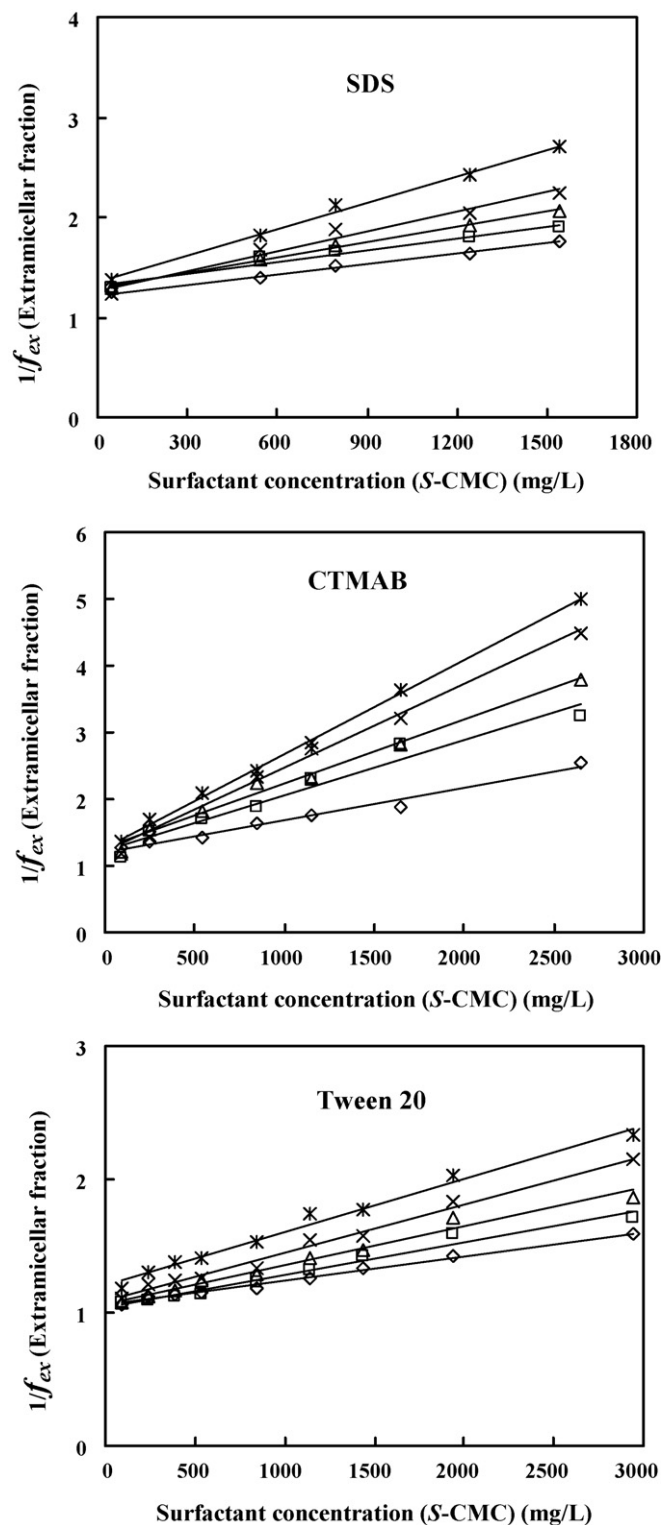


Fig. 5. Linear plots of the inverse extramicrocellular fraction ($1/f_{ex}$) versus the micellized surfactant concentration ($S - \text{CMC}$). Agitation speeds were 0 rpm (◇), 13 rpm (□), 39 rpm (△), 65 rpm (×), and 91 rpm (*).

tant may be responsible for the differences in the micellar partition coefficients. Micelles of cationic CTMAB were reported to undergo a conformational change to swollen micelles that favor the solute solubilization. Specifically, solubilization of aromatic hydrocarbons including naphthalene makes the globular micelles swollen and

Table 2
Micellar partition coefficient (K_m) of naphthalene in surfactant solutions under different agitation speeds

Agitation speed (rpm)	K_m (L/g)		
	SDS	CTMAB	Tween 20
0	0.354	0.523	0.187
13	0.396	0.827	0.247
39	0.512	0.967	0.293
65	0.656	1.257	0.364
91	0.878	1.409	0.401

favors the axial growth of rodlike micelles of CTMAB [27,28]. Fendler and Patterson [29] noted the different solubilization sites of benzene within the micelles of anionic SDS and cationic CTMAB. They observed that solubilized benzene is always located in the interior of hydrophobic core of spherical SDS micelles, whereas for CTMAB micelles, benzene molecules are initially located close to the interface between hydrocarbon and water and then in the micellar interior as more benzene molecules become solubilized.

The dependence of K_m values on agitation is not readily perceived as one compares with other equilibrium-based partitioning coefficients such as K_{ow} and H . Nevertheless, data in Table 2 clearly indicate the increasing K_m values when agitation speed is increased. For example, at the highest agitation speed tested (i.e., 91 rpm), the K_m values increased by 1.1 times for Tween 20, 1.5 times for SDS, and 1.7 times CTMAB. Again, the agitation effects were more pronounced for solutions containing CTMAB, which can be attributed to the same mechanisms as described above. Similar results were reported by Huang and Lee [20], where the effects of agitation on the surfactant solubilization of a solute from air to water were studied. Their results revealed that the solubilization of gaseous naphthalene into agitated surfactant solution is stronger than that obtained from quiescent situation. They indicated that agitation increased the degree of naphthalene entering into micelles.

4.3. Effect on surfactant and agitation on overall mass transfer coefficient (K_L)

The overall mass transfer coefficient (K_L) describing air–water chemical exchange through absorption or volatilization is a complex parameter depending on various physicochemical properties of the solute and hydrodynamic properties of exchanging matrices in agitated vessels. Extensive efforts have been made to develop empirical as well as theoretical models to elucidate K_L in response to various parameters, including a recent study using dimensional analysis to relate K_L to several dimensionless parameters such as Reynolds number, Schmidt number, and Froude number [30]. The attempt of this preliminary study, therefore, was not to develop an explicit model but rather to quantify the effects of two test parameters (surfactant and agitation). Fig. 6 demonstrates the K_L values as a function of agitation speed in surfactant solutions with a typical concentration of 2000 mg/L. The data show that the K_L value increased with increasing agitation speed under the test conditions. For example, K_L in solutions containing 2000 mg/L SDS increased from 1.11×10^{-6} m/s in quiescent condition to 7.23×10^{-6} m/s at 91 rpm ($G = 243 \text{ s}^{-1}$). Fig. 6 also illustrates how K_L values are affected by three different surfactants. The significantly reduced K_L values due to the presence of cationic CTMAB is worth noting. This result is in accord with its favorable micellization by CTMAB micelles as indicated in the preceding section.

The enhanced mass transfer coefficient of naphthalene by agitation can be expressed by an “enhancement factor (EF)”, defined as the ratio of the mass transfer coefficient for agitated surfactant solution to the mass transfer coefficient obtained from quiescent

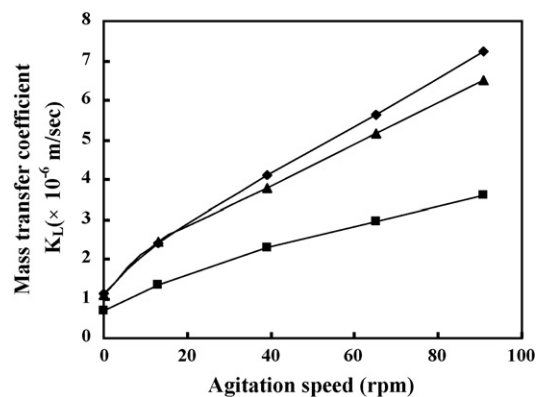


Fig. 6. Effects of agitation speeds on the overall mass transfer coefficient K_L of naphthalene solutions with the same concentration (2000 mg/L) of three surfactants. Surfactants were SDS (◆), CTMAB (■), and Tween 20 (▲).

solution. Owing to the relationship between k and K_L (Eq. (5)), the EF value is also the ratio of the volatilization rate constant for agitated surfactant solution to that of quiescent surfactant-free solution. The EF values in surfactant-laden solutions are summarized in Table 3 with regard to four different agitation speeds. As can be seen from Table 3, the EF values are generally much greater than 1, especially when the agitation speed is at the high end (i.e., 91 rpm). At 91 rpm, the EF values of various surfactant concentrations reached 3.1–6.3, 1.7–7.9, and 3.7–7.3 for SDS, CTMAB, and Tween 20, respectively. If one compares the K_m values (Table 2) vs. K_L values (Table 3), the relative change in the latter are much greater. This implies that although the addition of surfactants suppressed the volatilization due to micellization (increased K_m), the enhanced volatilization as a result of agitation (increased K_L) is greater, resulting in a net volatilization flux from water to air. Under the test conditions (surfactant types and concentrations, agitation speeds), agitation is the dominant factor in controlling the volatilization.

A close examination of the experimental data was also attempted by plotting K_L vs. velocity gradient (G). The velocity gradient is a measure of stirring power input per unit volume of the liquid. It is non-linearly correlated to the rotational speed, i.e., $G \propto \text{rpm}^{3/2}$, but can be converted from rpm by assumed drag coefficient, solution density, viscosity and blade dimensions [7,10]. A typical plot of K_L vs. G is given in Fig. 7 for CTMAB at 8 surfactant concentrations and 4 agitation intensities for each surfactant concentration. Similar results were also obtained for SDS at 6 different concentrations and Tween 20 at 10 different concentrations (data not shown). Experimental results for all combinations of surfactant concentration–agitation clearly reveal the linear dependence of K_L on G , i.e., K_L linearly increased with increasing G . A more thorough study in the future will warrant the development of a mechanistic model between K_L and G in surfactant-laden solutions as reported by Peng et al. [10].

Table 3
The range of enhancement factors (EFs) in agitated solutions with different agitation speeds

Agitation speed (rpm)	Enhancement factor (EF) ^a		
	SDS	CTMAB	Tween 20
13	1.3–1.9	0.7–2.7	1.5–2.3
39	2.0–3.3	1.1–4.3	2.2–3.9
65	2.7–5.0	1.4–6.8	2.9–5.6
91	3.1–6.3	1.7–7.9	3.7–7.3

^a EF = K_L/K_L' , where K_L = overall mass transfer coefficient in the presence of surfactant, K_L' = overall mass transfer coefficient in surfactant-free solution under quiescent condition.

5. Discussions

Using a semi-volatile and hydrophobic naphthalene as a target compound, this study examined the effects of three different types of surfactants and a range of agitation intensities on micellization and volatilization of naphthalene from air to water matrix. Micellized hydrophobic solutes give rise to a reduced aqueous phase concentration as evidenced by the decreased f_{ex} (Fig. 5), thereby reducing the driving force of air–water mass transfer (Eq. (1)). Although the effects of surfactant monomers are neglected in our experimental analysis, their effects through the formation of a thin film at the air–liquid and liquid–liquid interfaces are well noted and considered to exert additional mass transfer resistance [31,32].

The effects of agitation on naphthalene volatilization in the presence of surfactant have not been explored beyond what is known from the classical two-film theory. Apparently, additional research is warranted on both theoretical and experimental basis. Fig. 8 is to schematically illustrate how agitation affects the dynamics of micellization (hence the solubilization capacity expressed by K_m) and the mass transfer resistance at the air–water interface constituting stagnant liquid and air films. As shown in the diagram, surfactant monomers can aggregate to form close packed resistance barrier layer with hydrophobic tails tending to escape away from the liquid side of the two thin films. The surfactant film thus hinders the chemicals from passing through the liquid [20]. The surfactant molecules adsorbed on surface also retard the surface flow induced by reduced surface tension and increased viscosity [33]. Turbulence in the liquid will shorten the liquid–film distance, thus reducing the diffusion time of the solutes. As a result, the overall mass transfer (volatilization) of naphthalene increases with agitation. In the preceding section, the agitation-induced swelling of micelles was postulated as the surfactant-specific mechanism for enhanced K_m in the case of CTMAB [28,29]. This, however, does not fully explain the enhanced K_m values in agitated solution (Table 2) for two other surfactants. As indicated by Huang and Lee [20], agitation facilitates the hydrophobic solute entering into micelles. This phenomenon can be better interpreted with the surfactant “iceberg structure” depicted in Fig. 8, which was first postulated by Frank and Evan [34]. As can be seen from the figure, water molecules can form a quasi-solid iceberg structure around surfactant molecules or pre-micelles in the system. Because of this structure, it is hard for hydrophobic compounds to penetrate through the iceberg region and be subsequently solubilized by surfactant micelles (Fig. 8a). With proper agitation (Fig. 8b), it is likely that the iceberg structure is broken up or weakened. As a result, it is easier for naphthalene to be trans-

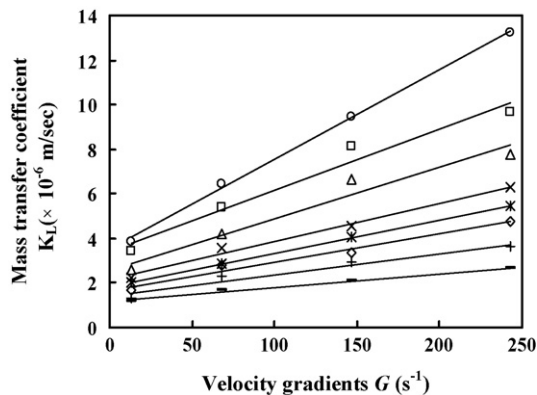


Fig. 7. Relationship between overall mass transfer coefficient K_L and velocity gradient G for solutions with CTMAB concentration of 0 mg/L (○), 450 mg/L (□), 600 mg/L (△), 900 mg/L (×), 1200 mg/L (*), 1500 mg/L (◇), 2000 mg/L (+), and 3000 mg/L (–).

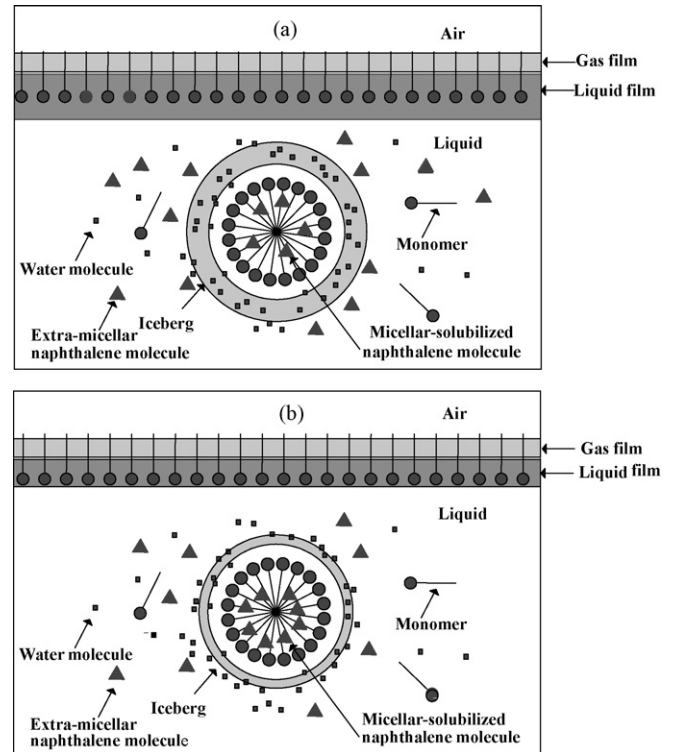


Fig. 8. Schematic of the effects of surfactant monomer barrier layer at the interface and the effects of agitation on liquid-film thickness at air–water interface and “iceberg” thickness of micelles in aqueous solution: (a) before agitation; (b) after agitation.

ported into the hydrophobic cores of the surfactant micelles and the corresponding K_m is increased during the agitation process.

The preceding discussions reinforce our experimental results that both K_L and K_m are agitation-dependent. In deriving Eq. (10), we also assumed solute concentration on the gas side of the interface (C_G^*) to be negligible, and therefore the second term of Eq. (1) containing Henry's law constant ($C_i = C_G^*/H$) was dropped. While this assumption holds true for compounds with moderate to high volatility in open container systems with infinite dilution (ventilation), we can develop a more general conceptual model by assuming a small but constant concentration on the gas side of the interface (C_G^0). If air above the liquid is stagnant or where a background concentration exists, C_G^0 in place of C_G^* is more appropriate. By substituting C_i with C_G^0/H^* and C_L with $C_L f_{ex}$ and rearrange the equation, we have:

$$\frac{dC_L}{dt} = -\frac{K_L}{L} \left(C_L f_{ex} - \frac{C_G^0}{H^*} \right) \quad (11)$$

In Eq. (11), the apparent Henry's law constant (H^*) is used since solute's volatility is reduced in the presence of surfactants [15–18]. Integration of the above equation and substitution with Eq. (7) for f_{ex} , the following model can be derived to better illustrate how volatilization is affected by several parameters described in this paper:

$$C_L = \left\{ C_0 - \frac{C_G^0 [1 + K_m(S - CMC)]}{H^*} \right\} \exp \left\{ -\frac{K_L}{L} \frac{t}{(1 + K_m(S - CMC))} \right\} + \frac{C_G^0 [1 + K_m(S - CMC)]}{H^*} \quad (12)$$

As demonstrated in this work, agitation has an effect on K_L , K_m , and H^* . However, it is not directly apparent that why agitation as a main variable is not included in the model (Eq. (12)). The agitation-dependent experimental values of K_L , K_m , and H^* should be determined under the specific test condition. Caution should be exercised when experimental conditions varied and extrapolation from lab to real world system should be cautious because agitation (or mixing in general) between these two settings can be very different in terms of both the quality and quantity of mixing. Additional work is needed to establish explicit correlations between agitation and these model parameters in a pilot setting. Nevertheless, Eq. (12) should be applicable to broader conditions than the one considered in this study, such as conditions with agitated liquid and/or turbulent air-flow. In such a case, model parameters such as K_L , K_m and H^* are considered as lump sum parameters that should be determined under a specific set of conditions. In Eq. (12), initial concentration of the solute (C_0) and total surfactant concentration (S) can be measured directly while solute concentration on the gas side of the interface (C_G^0) should be determined indirectly from experimental data.

Note that Eq. (12) becomes Eq. (10) when the compound has very large H^* or when its vapor phase concentration can be assumed to be zero. A special case is when surfactant concentration is small ($S \leq \text{CMC}$), and the change in Henry's constant is insignificant ($H^* \approx H$), then Eq. (12) becomes:

$$C_L = \left(C_0 - \frac{C_G^0}{H} \right) \exp \left(-\frac{K_L t}{H} \right) + \frac{C_G^0}{H} \quad (13)$$

Although the derivations of Eqs. (10) and (12) were intended to describe volatilization (water-to-air) process, a slight modification can be made such that the models can be applied to absorption (air-to-water) process when solute micellization by surfactant is present. In volatilization, the two controlling factors (K_L and K_m) have competing effects on the rate of volatilization. In the case of naphthalene, K_L dominates the effects under the experimental conditions, resulting in a net volatilization flux. Conversely in absorption process, both factors facilitate volatile solutes to be absorbed from air into the solution. Agitation will always enhance the rate and extent of absorption in the surfactant-laden solutions [20]. As such, the effects of agitation on the liquid-vapor exchange of organic compounds in the presence of surfactants depend on the initial bulk phase concentrations of organic compounds.

Since surfactants are commonly employed in domestic, industrial, and environmental applications, their effects on interfacial mass transfer of environmental contaminants are important. Toxic volatile emissions should be kept at minimal because of their potential fire hazard, and threat to workplace health and safety. With this regard, surfactants or foams have been used to suppress volatile emissions [35,36]. In other cases such as air stripping processes for the treatment of surfactant-laden soil washing/flushing waste streams, the presence of surfactants is troublesome in an effort to maximize the VOCs removal [24,33,37]. The experimental data as well as the model developed in this study provided insight to volatile emission in surfactant-laden solutions as frequently encountered in these waste streams as well as natural waters receiving wastewater effluents.

6. Conclusions

A simplified conceptual model is developed to describe the volatilization as a function of air-water overall mass transfer coefficient (K_L), micellar partition coefficient (K_m), Henry's law constant (H), and micellized surfactant concentration ($S - \text{CMC}$).

The model and experimental results reveal that K_L and K_m have opposing effects on volatilization and both are agitation-dependant under the experimental conditions. While K_L is linearly increased with increasing velocity gradient (G), K_m is increased as agitation speed is increased and the increased K_m due to agitation is likely dependent on the nature of surfactant and its interaction with solubilisate. Since K_L dominates the effects of agitation, a net volatilization was obtained for naphthalene regardless of the reduced volatility (H) and extramolecular fraction of naphthalene (f_{ex}) as a result of surfactant micellization. The volatilization rate constant (k) of naphthalene is increased with increasing agitation speeds and decreasing surfactant concentrations. For the effects of three surfactants with the same mass concentration, the decreasing sequence of volatilization rate constant (k) under a given agitation condition is not in agreement with the increasing order of K_m . This is presumably due to the fact that k is influenced by all concerned factors including K_L , K_m , S and CMC value, as can be seen from the model. Results also indicated that volatilization can be described by a pseudo first-order kinetics with respect to the bulk liquid phase concentration of naphthalene. It can also be generally concluded that the effects of agitation on the liquid-to-vapor (volatilization) or vapor-to-liquid (absorption) exchange of organic compounds depend on the initial bulk phase concentration of organic compounds.

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References

- [1] J.E. Baker, S.J. Eisenreich, Concentrations and fluxes of polycyclic aromatic hydrocarbons and polychlorinated biphenyls across the air-water interface of Lake Superior, *Environ. Sci. Technol.* 24 (1990) 342–352.
- [2] L.C. Liao, D.J. Lee, Estimation of VOCs and semivolatiles emission rate from an intermittently aerated bioreactor, *Ind. Eng. Chem. Res.* 36 (1997) 881–887.
- [3] J.-M. Chern, S.-R. Chou, Volatile organic compound emission rates from mechanical surface aerators: mass transfer modeling, *Ind. Eng. Chem. Res.* 38 (1999) 3176–3185.
- [4] H.-P. Chao, J.-F. Lee, C.-K. Lee, H.-C. Huang, Volatilization characteristics of organic compounds in the coagulation process, *J. Environ. Eng. ASCE* 131 (2005) 1253–1259.
- [5] E. Atlas, R. Foster, C.S. Giam, Air-sea exchange of high molecular weight organic pollutants: laboratory studies, *Environ. Sci. Technol.* 16 (1982) 283–286.
- [6] J.E. Woodrow, J.N. Seiber, Correlation techniques for estimating pesticide volatilization flux and downwind concentrations, *Environ. Sci. Technol.* 31 (1997) 523–529.
- [7] C.-K. Lee, H.-P. Chao, J.-F. Lee, Effects of organic solutes properties on the volatilization processes from water solutions, *Water Res.* 38 (2004) 365–374.
- [8] H.-P. Chao, J.-F. Lee, C.-K. Lee, H.-C. Huang, An alternative method for predicting organic solute volatilization rates under gas and liquid turbulence, *Chemosphere* 59 (2005) 711–720.
- [9] Y. Cohen, W. Cocchio, D. Mackay, Laboratory study of liquid-phase controlled volatilization rates in the presence of wind waves, *Environ. Sci. Technol.* 12 (1978) 553–558.
- [10] J. Peng, J.K. Bewtra, N. Biswas, Effect of turbulence on volatilization of selected organic compounds from water, *Water Environ. Res.* 167 (1995) 101–107.
- [11] J. Dewulf, H.V. Langenhove, B. Heireman, The air/water exchange of volatile organic compounds from waters in the transient and turbulent regime, *Water Res.* 32 (1998) 2106–2112.
- [12] J.-F. Lee, H.-P. Chao, C.T. Chiou, M. Manes, Turbulence effects on volatilization rates of liquids and solutes, *Environ. Sci. Technol.* 38 (2004) 4327–4333.
- [13] J.H. Smith, D.C. Bomberger, D.L. Haynes, Prediction of the volatilization rates of high-volatility chemicals from natural water bodies, *Environ. Sci. Technol.* 14 (1980) 1332–1337.
- [14] K.T. Valsaraj, A. Gupta, L.J. Thibodeaux, D.P. Harrison, Partitioning of chloromethanes between aqueous and surfactant micellar phases, *Water Res.* 22 (1988) 1173–1183.

- [15] M.A. Anderson, Influence of surfactants on vapor–liquid partitioning, *Environ. Sci. Technol.* 26 (1992) 2186–2191.
- [16] L.M. Vane, E.L. Giroux, Henry's law constants and micellar partitioning of volatile organic compounds in surfactant solutions, *J. Chem. Eng. Data* 45 (2000) 38–47.
- [17] T. Shimotori, W.A. Arnold, Measurement and estimation of Henry's law constants of chlorinated ethylenes in aqueous surfactant solutions, *J. Chem. Eng. Data* 48 (2003) 253–261.
- [18] C. Zhang, G. Zheng, C.M. Nichols, Micellar partitioning and its effects on Henry's law constants of chlorinated solvents in anionic and nonionic surfactant solutions, *Environ. Sci. Technol.* 40 (2006) 208–214.
- [19] X. Shen, Y. Sun, Z. Ma, P. Zhang, C. Zhang, L. Zhu, Effects of mixed surfactants on the volatilization of naphthalene from aqueous solutions, *J. Hazard. Mater.* 140 (2007) 187–193.
- [20] H.L. Huang, W.-M.G. Lee, Enhanced naphthalene solubility in the presence of sodium dodecyl sulfate: effect of critical micelle concentration, *Chemosphere* 44 (2001) 963–972.
- [21] P.S. Liss, P.O. Slater, Flux of gases across the air–sea interface, *Nature* 247 (1974) 181–184.
- [22] R.B. Bird, W.E. Stewart, E.N. Lightfoot, *Transport Phenomena*, Second ed., John Wiley, New York, 2002.
- [23] M.J. Rosen, *Surfactants and Interfacial Phenomena*, John Wiley, New York, 1989.
- [24] H.-P. Chao, J.-F. Lee, L.-C. Juang, C.-H. Kuo, G. Annadurai, Volatile organic compounds emission from contaminated soil during surfactant washing, *Environ. Eng. Sci.* 23 (2006) 923–932.
- [25] C.L. Yaws (Ed.), *Chemical Properties Handbook*, McGraw-Hill, Beijing, 1999, p. 383.
- [26] D. Mackay, A.T.K. Yeun, Mass transfer coefficients correlations for volatilization of organic solutes from water, *Environ. Sci. Technol.* 17 (1983) 211–223.
- [27] P.K. Vinson, J.R. Bellare, H.T. Davis, W.G. Miller, L.E. Scriven, Direct imaging of surfactant micelles, vesicles, discs, and ripple phase structures by cryo-transmission electron microscopy, *J. Colloid. Interface Sci.* 142 (1991) 74–91.
- [28] A. Heindl, J. Strnad, H.-H. Kohler, Effects of aromatic solubilisates on the shapes of CTABr micelles, *J. Phys. Chem.* 97 (1993) 742–746.
- [29] J.H. Fendler, L.K. Patterson, Solubilization of benzene in aqueous cetyltrimethylammonium bromide measured by differential spectroscopy (Comment), *J. Phys. Chem.* 75 (1971) 3907.
- [30] M.M.P. Zieverink, M.T. Kreutzer, F. Kapteijn, J.A. Moulijn, Gas–liquid mass transfer in benchscale stirred tanks—fluid properties and critical impeller speed for gas induction, *Ind. Eng. Chem. Res.* 45 (2006) 4574–4581.
- [31] I. White, Effect of surfactants on the evaporation of water close to 100 °C, *Ind. Eng. Chem. Fundam.* 15 (1976) 53–59.
- [32] A.M. Dehkordi, S. Ghasemian, D. Bastani, N. Ahmadpour, Model for excess mass-transfer resistance of contaminated liquid–liquid systems, *Ind. Eng. Chem. Res.* 46 (2007) 1563–1571.
- [33] U.N. Choori, J.F. Scamehorn, J.H. O'Haver, J.H. Harwell, Removal of volatile organic compounds from surfactant solutions by flash vacuum stripping in a packed column, *Ground Water Monit. Rem.* 12 (1998) 157–165.
- [34] H.S. Frank, M.W. Evans, Free volume and entropy in condensed systems. III. Entropy in binary liquid mixtures; partial molal entropy in dilute solutions; structure and thermodynamics in aqueous electrolytes, *J. Chem. Phys.* 13 (1945) 507–532.
- [35] P.S. Gautam, K.K. Mohanty, Novel aqueous foams for suppressing VOC emission, *Environ. Sci. Technol.* 38 (2004) 2721–2728.
- [36] C.-C. Wu, W.-M.G. Lee, Control of vaporous naphthalene by scrubbing with surfactants, *J. Environ. Eng. ASCE* 130 (2004) 276–281.
- [37] T.C.G. Kibbey, K.D. Pennell, K.F. Hayes, Application of sieve-tray air strippers to the treatment of surfactant-containing wastewaters, *AIChE J.* 47 (2001) 1461–1470.