Effects of surfactants and salt on Henry's constant of *n*-hexane

Chunping Yang [a,b,*], Fayuan Chen [a,c], Shenglian Luo [a,b], Gengxin Xie [a,c],
Guangming Zeng [a,c], Changzheng Fan [a,c]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
[b] School of Environmental and Chemical Engineering, Nanchang Hangkong University, Nanchang 330063, PR China
[c] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China

ARTICLE INFO

ABSTRACT

n-Hexane biological removal is intrinsically limited by its hydrophobic nature and low bioavailability. The addition of surfactants could enhance the transport of volatile organic compounds (VOCs) and change the gas–liquid equilibrium of VOCs. In this paper, the effects of four surfactants, sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), *tert*-octylphenoxypoly-ethoxyethanol (Triton X-100), polyoxyethylene (20) sorbitan monooleate (Tween 80), and sodium nitrate on apparent Henry's constant of *n*-hexane in surfactant solutions were investigated. The apparent Henry's constants were significantly reduced when surfactants concentrations exceeded their critical micelle concentrations (cmc's). On a cmc basis, the anionic surfactant SDS was found to have the greatest effect on the apparent Henry's constant with CTAB succeeding, then followed by Triton X-100 and Tween 80. However, the apparent Henry's constant of *n*-hexane decreased even more rapidly when Triton X-100, a nonionic surfactant, was added than when the ionic surfactant of SDS or CTAB was applied under identical mass concentration and other conditions. These results suggest that Triton X-100 have the biggest solubilization of *n*-hexane among the four surfactants. Sodium nitrate slightly decreased the apparent Henry's constant of *n*-hexane in surfactant solutions, and could be considered as a cosolvent in the surfactant–(*n*-hexane) solution. In addition, the relationship between apparent Henry's constant and surfactant concentration was further developed.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

n-Hexane, a volatile organic compound (VOC) widely used in many industries, can serve as a solvent in organic synthesis, oil and grease removal, food and chemical industrial processes and other down-stream processes. Like many other VOCs, *n*-hexane is also toxic and can cause odor nuisances, a conclusive reason that precisely indicates the importance of its removal from contaminated streams [1]. The Henry's constant of volatile organic compounds (VOCs) is an important parameter in the determination of the fate and transport of organic contaminants in the environment. Several environmental factors such as temperature, pH, surfactants and dissolved salts can affect the gas–liquid partitioning of a compound [2].

Previous studies reported effects of surfactants and salts on the gas–liquid phase partitioning of other volatile organic compounds (VOCs) such as toluene [3] and chlorinated solvents [4].

Solubilization of benzene by miceller solutions of SDS also was investigated [5]. Unfortunately, the effects of surfactants and salt on the vapor–liquid partitioning of *n*-hexane have not been thoroughly investigated. This brings forward a need for the effects of surfactants on gas–liquid or Henry's constant of *n*-hexane to be evaluated. The effects of surfactants on Henry's constant are important for their ubiquitous status in the environment as a result of their widespread uses in domestic, industrial and environmental fields, including detergency, mineral flotation, oil recovery, and surfactant-enhanced remediation. It is widely known that surfactants can increase the solubility of hydrophobic organic contaminants by partitioning it into the hydrophobic cores of surfactant micelles, they can also affect gas–liquid mass transfer of VOCs.

The poor gas–liquid transfer of hydrophobic VOCs often significantly limits the efficiency of biodegradation. At an organic loading rate of 2.95 g/m³ h and gas empty bed contact time (EBCT) values of 120 s, the average *n*-hexane removal efficiencies reached 50.0% for a hybrid RDB [6] and 57.0% for a multi-layer hybrid rotating drum biofilter (RDB) [7]. The elimination capacity for 18 VOCs with a wide range of Henry's constants evaluated using the 48 h test protocol was influenced greatly by the Henry's constants [8]. Zhu et al. [9] reported that the removal efficiency of the VOCs increased

with decreases in values of Henry's constant and that the influence of organic loadings on biofilter performance varied for different VOCs and seems to be related more particularly to substrate Henry's law constant. Thus, the present study will offer some reference to other researchers interested in the biological removal of *n*-hexane by including surfactant.

Therefore, the effects of various types of surfactants and salt at different concentrations on the apparent Henry's constant were examined using *n*-hexane as the model hydrophobic VOC in this study. In addition, a simple equation capable of estimating the apparent Henry's constant for a given *n*-hexane–surfactant pair and surfactant concentration is derived. The apparent Henry's constant data we present here should allow other researchers to estimate and extrapolate the influence of surfactant on their own biotreatment facility or subsurface or aquifer conditions. These data are then used to calculate parameters which facilitate modeling of transport, uptake, mobilization, and sorption of organic contaminants such as *n*-hexane.

2. Materials and methods

2.1. Experimental reagents

All chemicals described below were used as received. Analytical grade *n*-hexane (+95%) and methanol (+99.5%) were purchased from Hengxing Chemical Reagent Company (Tianjin, China). The four surfactants studied in this work, anionic surfactant sodium dodecyl sulfate (SDS), nonionic surfactant polyoxyethylene (20) sorbitan monooleate (Tween 80) and cationic surfactant cetyltrimethylammonium bromide (CTAB), were obtained from Sigma–Aldrich (St. Louis, USA). Nonionic surfactant *tert*-octylphenoxypoly-ethoxyethanol (Triton X-100) was purchased from Amresco (Solon, OH, USA). The cmc values of the four surfactants (SDS, CTAB, Triton X-100, Tween 80) are 2.36, 0.335, 0.112, 0.015 g L^{-1}, respectively. Deionized water was used throughout this study.

Surfactants were selected based on their properties, representative types and potential in remediation uses. Among commercial surfactants currently available, nonionic surfactants are considered less toxic and more biodegradable than anionic and cationic ones. The sodium nitrate concentration used in this study is based on the dosage utilized in biofilters [9,10].

2.2. Sample preparation

A concentrated standard solution (stock solution) was prepared as follows: 8 mL of methanol was placed into a 10-mL ground glass volumetric flask equipped with a polyethylene stopper. The flask was then stopped and weighed to the nearest 0.1 mg. In succession, 20 μL *n*-hexane was added just below the methanol level into the flask by appropriate syringes. To obtain a concentration value more precise for *n*-hexane, the mass after it was added was weighed. The resulting solution was carefully diluted to volume with methanol. This concentrated stock solution, made monthly, was stored at 4 °C. Methanol was used as stock solutions for its good partitioning property with the solutes, and was successfully applied for the determination of the Henry's constant of volatile organic compounds such as benzene, toluene [3], chlorinated solvents [4]. The amount of methanol in each bottle was much less than 0.5% (v/v). At such low concentrations, methanol does not affect gas–liquid partitioning [11]. Proper safety procedures and appropriate disposal of solutions should be followed.

2.3. Experimental procedures

The equilibrium partitioning in closed systems (EPICS) procedure, described by [11], was used to determine Henry's constant

values (H). For each aqueous mixture, Henry's constants were measured in six 600 mL serum bottles. Three contained 500 mL of liquid and the other three 50 mL. Bottles were prepared as follows: deionized water or surfactant solutions (50 or 500 mL) was placed into serum bottles sealed with rubber septa. A 100-μL gas-tight syringe with a 5-cm side-port needle was used to deliver approximately 20 μL of the appropriate stock solutions to each serum bottle. The six serum bottles were then incubated (inverted and submerged) for 1 h at a desired temperature (27 °C), in a reciprocating shaker bath (approximately 90 rpm), 1 mL of headspace was withdrawn into a syringe and submitted to GC analysis as described below. Preliminary studies indicated that an incubation period as short as 1 h is sufficient to achieve equilibrium in the serum bottles mentioned.

Data from all possible pairs of serum bottles that were not volume replicates were combined using Gossett's Eq. (6) to generate estimates for H [11]:

$$H = \frac{V_{w2} - rV_{w1}}{rV_{g1} - V_{g2}} \tag{1}$$

where $r = (C_{g1}/M_1)/(C_{g2}/M_2)$ and C_{g1} and C_{g2} are the gas phase concentrations, and M_1 and M_2 are the masses of *n*-hexane in serum bottles one and two, respectively. V_{w1} and V_{w2} are the liquid volumes in serum bottles one and two, respectively, with corresponding headspace volumes V_{g1} and V_{g2}. For linear GC detector response, the ratio of the gas phase concentrations is simply the ratio of the GC peak areas.

For the four surfactants at each concentration evaluated, six possible pairings of two high and low liquid volume serum bottles provided nine possible estimates of Henry's constant in accordance with Eq. (1). The median of the collection of estimates was taken as the desired Henry's constant. Statistically significant differences between H values were assigned using 95% confidence intervals. These confidence intervals were symmetric about the central estimator in terms of rank order but not necessarily symmetric in magnitude. Error bars shown in the figures and Table 1 correspond to the 95% confidence interval.

Table 1
Henry's law constants in deionized water or surfactant solutions in the presence of sodium nitrate.

Surfactant	Surfactant concentration (g/L)	Sodium nitrate concentration (g/L)	H
None	0	0	40.7 ± 2.78
	0	0.5	43.7 ± 4.78
	0	1	44.2 ± 7.07
SDS	2.5	0	19.4 ± 1.22
	2.5	0.5	15.7 ± 1.36
	5	0	7.6 ± 1.67
	5	0.5	6.7 ± 0.68
	5	1	6.4 ± 0.91
CTAB	1	0	28.8 ± 5.66
	1	0.5	15.3 ± 2.04
	2	0	13.6 ± 2.32
	2	0.5	9.7 ± 1.96
	2	1	8.9 ± 2.89
Triton X-100	0.5	0	22.8 ± 5.69
	0.5	0.5	23.0 ± 2.22
	1	0	16.3 ± 1.64
	1	0.5	15.5 ± 0.84
	1	1	16.1 ± 2.34
Tween 80	1.5	0	36.4 ± 7.12
	1.5	0.5	32.5 ± 2.68
	3	0	27.2 ± 3.38
	3	0.5	25.8 ± 5.23
	3	1	23.8 ± 3.34

Note: data for systems represent the average of three replicate EPICS experiments. Errors for Henry's law constants (H) represent 95% confidence limits based on the Student's *t*-method.

2.4. Analytical methods

Headspace concentrations of *n*-hexane in equilibrated serum bottles were measured by gas chromatography (GC) (HP 6890, Series II, Hewlett-Packard, Palo Alto, CA, U.S.A.) equipped with a flame ionization detector (FID) (Hewlett-Packard Co., San Fernando, CA, U.S.A.). The conditions used for the determination of *n*-hexane concentration were as follows: column (Agilent 190915-413) with 30 m × 0.32 mm ID, 0.25 μm film thickness; carrier gas: ultra-pure nitrogen at 27 mL/min; oven temperature: 80 °C isothermal; injector temperature: 120 °C; and detector temperature: 150 °C. The retention time for *n*-hexane under these conditions were 2.5 min.

The sampling procedure was as follows. A serum bottle to be assayed was turned upright from its normal, inverted position in the shaker bath. 1 mL gas-tight syringe was used to obtain a headspace sample.

The combined analytical imprecision associated solely with the processes of headspace sampling and GC injection, and coupled with any imprecision in the GC response while neglected variance associated with initial addition of volatile compounds to bottles and subsequent losses. The analytical imprecision was estimated by replicating headspace analyses in individual bottles. All experiments were done in triplicate.

3. Results and discussion

3.1. Henry's constant of n-hexane in surfactant solutions

The experimentally determined Henry's constant as described in the preceding sections, might best be described in the form of an apparent Henry's constant (H^*) to determine the vapor–liquid partitioning of *n*-hexane in surfactant solutions. Unlike Hc, the apparent Henry's constant (H^*) is a function of surfactant concentration and can be defined as

$$H^* = \frac{C_v}{C_{A,\text{total}}} \tag{2}$$

where $C_{A,\text{total}}$ is the apparent solubility of *n*-hexane, C_v is the vapor-phase concentration of *n*-hexane. H^* values of *n*-hexane determined in surfactants solutions and in surfactants solutions containing sodium nitrate are reported in Fig. 1 and Table 1, respectively.

An accurate and experimentally feasible method for estimate dimensionless H^* is desirable. Although effective methods for VOCs were reported by other researchers [11,12], instruction for VOCs with low water-solubility or high Hc like *n*-hexane have not been presented in reports.

This paper made some modifications on existing experimental procedures from earlier studies [11] to determine the H of *n*-hexane. The Hc of *n*-hexane determined in this study was compared with other reports to testify the accuracy of our experimental procedures applied to lower soluble compounds. Dimensionless Hc was determined to be 40.7 ± 2.78 (Table 1). Other reported values of dimensionless Henry's law constant of hexane were 48.4 at 25 °C [13] and 53 at 25 °C [9], and the hexane partition coefficient (HPC) was 42.4 ± 6.5 at 30 °C [14].

3.2. Effect of surfactant concentration on apparent Henry's constant

The effect of surfactant on H^* of *n*-hexane as a function of surfactant concentration is illustrated in Fig. 1. For comparison purposes, surfactant concentrations are expressed on a mass basis as well as a cmc basis (Fig. 1). H^* values are significantly reduced in the presence of all four surfactants at supra-cmc's (Fig. 1). When surfactant concentration is above the cmc, micelles form, consequently hydrophobic zones are produced into which *n*-hexane partitions. For the four surfactants, H^* decreases as the concentration of surfactant increases. The more surfactant there is, the more hydrophobic zones are available to take up *n*-hexane and the less *n*-hexane is available to partition into the headspace. Sub-cmc quantities of surfactant should not substantially alter H^* since no separate hydrophobic zone is available. This is consistent with other researcher's investigation [4,15].

On the cmc basis, the anionic surfactant SDS showed the greatest effect on H^* value, followed by CTAB, Triton X-100, and Tween 80 (Fig. 1). This order follows the same sequence as the cmc's of the surfactants. At the same cmc level, anionic surfactant SDS had the higher surfactant mass in the solution. At 6.0 cmcs, SDS decreased the value of H^* to 2.4, lower than the value cationic
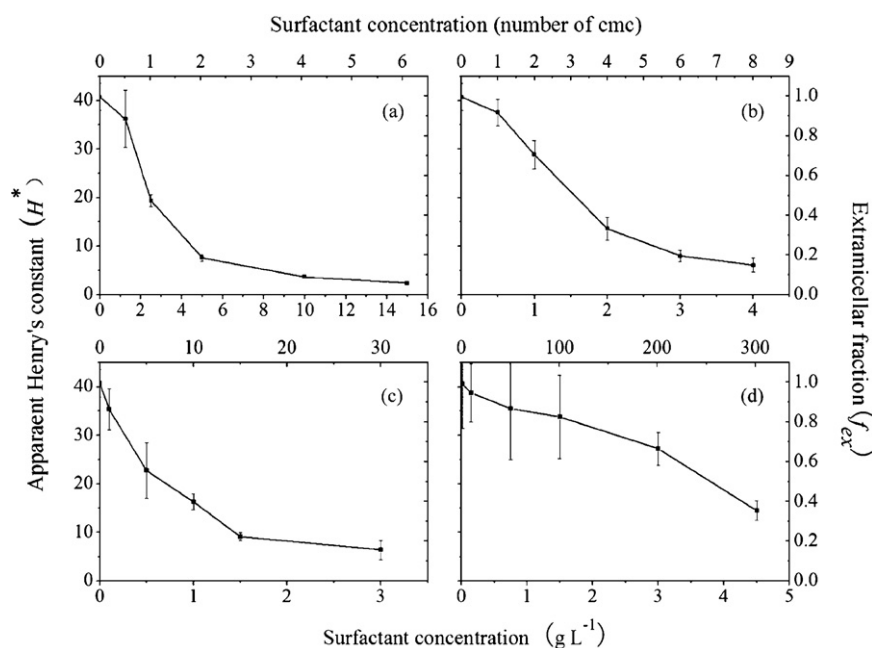

Fig. 1. Effects of surfactant concentration on apparent Henry's constants (H^*) and extramicellar fraction (f_{ex}). (a) SDS, (b) CTAB, (c) Triton X-100, and (d) Tween 80.

surfactant CTAB or nonionic surfactants Triton X-100 and Tween 80 decreased. However, on mass basis, nonionic surfactant Triton X-100 decreased the H^* value more significantly than the ionic surfactant. This is due to the fact that supra-cmc concentrations are achievable using a lower mass of nonionic surfactants. Thus, the H^* determined in Tween 80 solution also should be lower than that in CTAB and SDS solutions. However, the results were contrary to our expectations. On mass basis, Tween 80 had the largest reduction degree of H^* for tetrachloroethylene (PCE), trichloroethylene (TCE), and cis-dichlorethylene (DCE) among the four surfactants SDS, SDBS, Triton X-100 and Tween 80 [15]. This difference may be attributed to the characteristic of micelle created by Tween 80. The micelle core is a non-polar zone with a smaller capacity, and the palisade layer of micelle is polar with a bigger capacity. n-Hexane enters the micelle core predominantly. The solubilization capacity of micelle cores is smaller than that of the palisade layer of micelle where chlorinated solvents (PCE, TCE, DCE) are mainly to be solubilized in.

Similar trend was observed for the solubilization of n-hexane in the solutions of SDS, CTAB, or Triton X-100. The H^* decreased smoothly when the surfactant concentration was beyond the special value (Fig. 1). For instance, the H^* decreased from 3.7 to 2.4 when SDS concentration increased from 10 to 15 g/L, indicating that the dose of surfactant used in solubilization of n-hexane should not be higher than the special value. This trend could be caused by a change in micelle structure as surfactant concentration increases. However, current cmc and micelle structure information are insufficient to characterize this trend properly.

The focus of our work is the effect of surfactants and salt on the Henry's constant of n-hexane. The data determined and solubilization mechanisms discussed analytically are the major contributions of our work. Some basic data about n-hexane solubilization using surfactant was offered. As for the application of surfactant in biofiltration technology for hydrophobic VOCs, in which removal lacks feasibility, more topics should be discussed in future study. It is well known that surfactants may be toxic or inhibitory to microbes, and the effect is a function of surfactant concentrations, surfactant types and microorganism. The optimal dosage of surfactant used in biofilters is yet to be confirmed, due to the insufficiency of information about the effects of surfactants on microorganism activity, and the costs of surfactant are also to be considered.

3.3. Effect of salt on apparent Henry's constant in surfactant solutions

In surfactant-free control trials, the H^* values for n-hexane determined in 0.5 and 1 g/L sodium nitrate solutions are slightly higher than the value measured in deionized water (Table 1). This result shows that H^* is slightly higher in sodium nitrate solution than in deionized water and indicates that n-hexane–sodium nitrate interactions are less favorable than n-hexane–water interactions. It concludes that ion strength could alter gas–liquid phase equilibrium. The experimental results suggest that when the ionic strength reaches values greater than 0.2 M, an increase of at least 10% in Henry's constant can be caused, and this, in turn, favors the partitioning of VOCs into the air phase [16]. Solutes that increase water polarity such as electrolytes, generally resulted in reduced solubility of neutral organic molecules. This effect was associated with a reduction of free water for formation of a cavity in which an organic solute is accommodated [17,18].

However, when compared to the H^* of n-hexane determined in surfactant solutions, the H^* determined after sodium nitrate was added decreased significantly whatever ionic or nonionic surfactants excluding Triton X-100 was added (Table 1). This indicated that sodium nitrate can improve the micelle structure and increase n-hexane solubility. For the ionic and nonionic surfactants, differ-

ent mechanisms existed for the effect of sodium nitrate. For the ionic surfactants, addition of salt reduced the effective charge of the polar groups when surfactant assembles as micelles [19]. Therefore, addition of salt to surfactant solutions enables the micelle to form with smaller numbers at lower surfactant concentration, resulting in a reduction in the cmc. Generally, a log–log relationship exists between the cmc of ionic surfactants and the counter ion concentration [19]. The cmc of SDS decreased when sodium nitrate was added in the SDS solutions, this relationship is as described in [19]:

$$\log[cmc] = -0.55 \log[Na^+] - 3.34 \qquad (3)$$

where the concentrations are in units of moles per liter. According to Eq. (3), the cmc dropped to 1.65 g/L in the presence of 1 g/L sodium nitrate for SDS. Therefore, the relative concentrations of the SDS solution (Table 1) increased from 2 to 3 cmc and the relative actual amount of surfactant as micelle increased from 2.5 to 3.5 g/L when 1 g/L sodium nitrate was added to the SDS solution.

The H^* value in a surfactant concentration in the presence of 0.5 g/L sodium nitrate decreased more dramatically when the surfactant concentration was more close to the cmc and without sodium nitrate (Table 1). While addition of salt is expected to alter the cmc values of almost all anionic surfactants, the net effect on H^* depended on how close the surfactant concentration was to the no-salt cmc [4].

Electrolytes have salting-out or salting-in effects on nonionic surfactants. Salting-in effect is the increase of solubility of solute in water when salt is added to the solution, while salting-out effect is the decrease of solubility of solute in water when salt is added. When salting-out effect occurs, the value of cmc decreases and it is vice versa with salting-in. Moreover, the addition of electrolytes could decrease the cloud point of nonionic surfactants by the salting-out effect. Decreases in cmc and increases in micellar aggregation numbers lead to larger micelles. Sodium chloride decreases the cloud point of the surfactant and increases the dehydration of ethoxy groups on the outer surface of the micelles due to the salting-out effect [20]. When sodium nitrate was added to Tween 80 solutions, the salting-out effect occurred between micelle and the salt, which enlarges the volume of micelles. Consequently, more n-hexane entered the core of the micelle, and the partitioning between the gas phase and the liquid phase (H^*) decreased. When sodium nitrate was added in Triton X-100 solutions, similar response to salt was expected. However, the H^* did not undergo any observable change in the presence of sodium nitrate. This was possibly because the concentration of sodium nitrate was not high enough to cause the salting-out effect on micelles. The difference in structure between Triton X-100 and Tween 80 could help explain these phenomena.

In the surfactant–salt–(n-hexane) system, the H^* decreased more significantly with an increase of surfactant concentration in the presence of 0.5 g/L sodium nitrate. This indicated that surfactant played a predominate role in the decrease of the H^* of n-hexane in this system. In the surfactant solution, sodium nitrate could be considered as a cosolvent.

3.4. Effect of surfactant concentration on extramicellar fraction

The EPICS method considers the liquid concentration in the denominator of the Henry's constant expression (Eq. (2)) as the total concentration of n-hexane solubilized in the surfactant solution, both in micelles and in the extramicellar water region. Unless significant amounts of non-surfactant modifiers, such as salts, have been added to the solution, the Hc of n-hexane in the extramicellar water will not be affected by the surfactant. Thus, the extramicellar concentration of n-hexane can be calculated from the headspace concentration above a given surfactant solution and the Hc for

A=0.0034 B=0.027 R²=0.99 A=0.001 B=0.037 R²=0.98

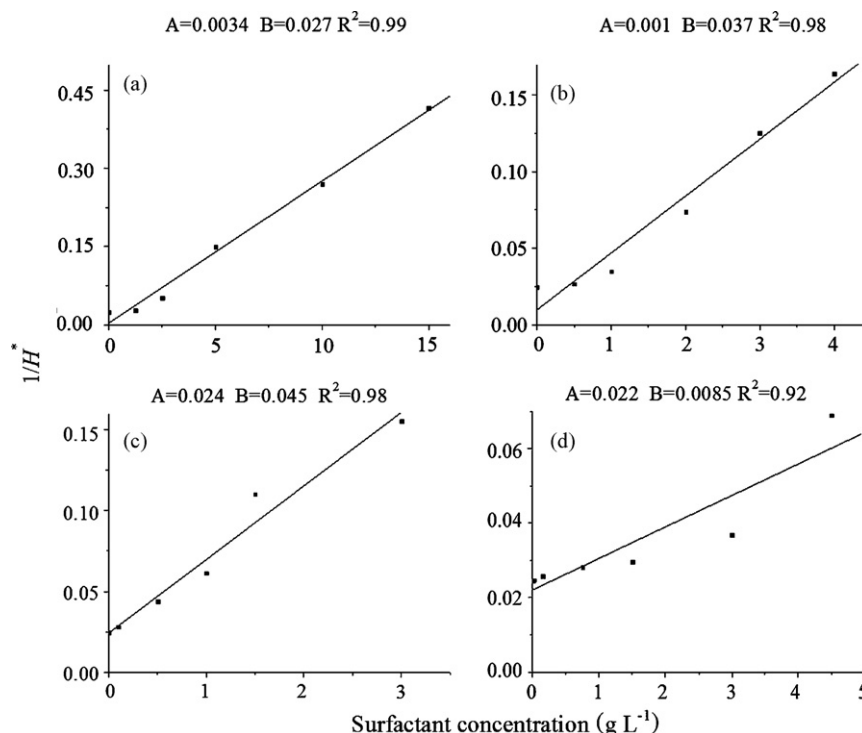A=0.024 B=0.045 R²=0.98 A=0.022 B=0.0085 R²=0.92

Fig. 2. $1/H^*$ as a function of surfactant concentration for (a) SDS, (b) CTAB, (c) Triton X-100, and (d) Tween 80.

the n-hexane in water void of surfactant. Likewise, the extramicellar fraction of n-hexane in the solution can be calculated from the Henry's constant (H) measured with surfactant (H^*) and that measured without (Hc):

$$f_{ex} = \frac{H*}{Hc} \tag{4}$$

where f_{ex} is the extramicellar fraction of n-hexane in the solution.

Experimental data showing the inverse relationship between f_{ex} and surfactant concentration are presented in Fig. 1, where both mass and cmc based surfactant concentrations are plotted for a comparison. All three types of surfactants were capable of significantly reducing f_{ex} for the n-hexane tested. However, the response of f_{ex} to changes in surfactant concentration was not necessarily the same. At the surfactant concentrations tested, on a number of cmc basis, SDS and CTAB were most efficient at reducing f_{ex}, primarily due to the relatively high cmc of these surfactants. For Tween 80, little effect on f_{ex} was noted when the concentrations of Tween 80 were less than 100 cmc. These results corresponded to a lower mass concentration compared to other surfactants tested.

The f_{ex} is a function of H^*, and the f_{ex} and H^* changed in a similar trend in the presence of a surfactant. However, the f_{ex} represented the extramicellar fraction of n-hexane dissolved in liquid phase, while the H^* represented the partitioning between gas phase and liquid phase. The knowledge of f_{ex} in a surfactant solution could be helpful for better understanding of the transport of n-hexane in the solution system.

3.5. Equation for estimation of Henry's constants

A simple equation which can estimate the apparent Henry's constant for a given n-hexane–surfactant pair, temperature, and surfactant concentration is desirable and beneficial to reasonable surfactant application in bioremediation. Zhang et al. [15] presented an equation for the estimation of the f_{ex} value found to be a

function of K_m and micellized surfactant concentration (S-cmc).

$$\frac{1}{f_{ex}} = 1 + K_m(S\text{-cmc}) \tag{5}$$

In combining Eqs. (4) and (5) the following equation emerged:

$$\frac{1}{H*} = \frac{1}{Hc} + \frac{1}{Hc}K_m(S\text{-cmc}) \tag{6}$$

The proportionality constant, K_m (L/mg), is the micellar partition coefficient. Eq. (6) is valid by assuming a constant cmc, with no changes in micelle shape and size during solubilization, and a constant K_m value independent of S. This implies that H^* is a function of S at a given temperature. In this case, the relationship between $1/H^*$ and S can be simply expressed as such form $Y = A + B\,S$ on the basis of the assumptions above.

For SDS, CTAB, Triton X-100, and Tween 80, the model (Eq. (6)) was used to correlate decreases in H^* of n-hexane to the corresponding surfactant concentrations. Parameters A and B were determined directly using Oringin software (Version 8.0, OriginLab Corporation, USA), and the parameter values for different surfactants are listed in Fig. 2. According to Eq. (6), parameter A is a function of Hc, K_m, and cmc; parameter B is a function of Hc and K_m. The linear correlation coefficients obtained from the plots of $1/H^*$ vs S for the four surfactants ranged from 0.92 to 0.99, on an average of 0.97. This shows that the experimental data correlated with this equation for the estimation of Henry's constant pretty well. The data for SDS had the best correlation with the equation among the four surfactants. The linear correlation coefficients reduced along with the decrease of cmc of surfactants, and seemed to be a function of the value of cmc.

4. Conclusions

The apparent Henry's constant of n-hexane decreased significantly when the concentration of surfactants SDS, CTAB, Triton X-100, or Tween 80 exceeded the cmc. All the four surfactants tested had high solubilization capacity for n-hexane. Triton X-100

had the best performance when decrease of the apparent H^* of n-hexane was conducted at lower dosages.

Sodium nitrate decreased the solubility of n-hexane in surfactant-free solutions and increased in surfactant solutions. Salt could be considered as a cosolvent for n-hexane in the surfactant–salt–(n-hexane) system.

The extramicellar fraction of n-hexane which could help in the understanding of the reason for the significant decrease of transfer of n-hexane in micellar phase in the presence of surfactants. More n-hexane was solubilized in micelle core, which enhanced the transport of n-hexane.

This paper has proven that these four surfactants can improve the solubility and partition of hydrophobic VOC, n-hexane, in water, and showed the potential to improve mass transfer of n-hexane in biofilter systems. However, the optimal dosage of surfactant used in biofilters is yet to be confirmed, due to the insufficiency of information about the effects of surfactants on microorganism activity, and the costs of surfactant are also to be considered. Further investigations on these topics are needed.

Acknowledgements

References

[1] T.R. Card, Fundamentals: Chemistry and Characteristics of Odors and VOCs, McGraw-Hill, New York, 1998.

[2] J. Staudinger, P.V. Roberts, A critical compilation of Henry's law constant temperature dependence relations for organic compounds in dilute aqueous solutions, Chemosphere 44 (2001) 561–576.

[3] M.A. Anderson, Influence of surfactants on vapor–liquid partitioning, Environ. Sci. Technol. 26 (1992) 2186–2191.

[4] 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.

[5] P.D. Todorov, P.A. Kralchevsky, N.D. Denkov, G. Broze, A. Mehreteab, Kinetics of solubilization of n-decane and benzene by micellar solutions of sodium dodecyl sulfate, J. Colloid Interface Sci. 245 (2002) 371–382.

[6] C.P. Yang, M.T. Suidan, X.Q. Zhu, B.J. Kim, G.M. Zeng, Effect of gas empty bed contact time on performances of various types of rotating drum biofilters for removal of VOCs, Water Res. 42 (2008) 3641–3650.

[7] C.P. Yang, H. Chen, G.M. Zeng, X.Q. Zhu, M.T. Suidan, Performance of rotating drum biofilter for volatile organic compound removal at high organic loading rates, J. Environ. Sci. 20 (2008) 285–290.

[8] M.A. Deshusses, C.T. Johnson, Development and validation of a simple protocol to rapidly determine the performance of biofilters for VOC treatment, Environ. Sci. Technol. 34 (2000) 461–467.

[9] X.Q. Zhu, M.T. Suidan, A. Pruden, C.P. Yang, C. Alonso, B.J. Kim, R.J. Kim, Effect of substrate Henry's constant on biofilter performance, J. Air Waste Manage. Assoc. 54 (2004) 409–418.

[10] C.P. Yang, M.T. Suidan, X.Q. Zhu, B.J. Kim, Comparison of single-layer and multi-layer rotating drum biofilters for VOC removal, Environ. Prog. 22 (2003) 87–94.

[11] J.M. Gossett, Measurement of Henry's law constants for C_1 and C_2 chlorinated hydrocarbons, Environ. Sci. Technol. 21 (1987) 202–208.

[12] G.A. Robbins, S.Y. Wang, J.D. Stuart, Using the static headspace method to determine Henry's law constants, Anal. Chem. 65 (1993) 3113–3118.

[13] C.P. Yang, Rotating drum biofiltration, PhD dissertation, Department of Civil and Environmental Engineering, University of Cincinnati, Cincinnati, OH, USA, 2004.

[14] A. Vergara-Fernández, B. Van, S. Haaren, Revah, Phase partition of gaseous hexane and surface hydrophobicity of *Fusarium solani* when grown in liquid and solid media with hexanol and hexane, Biotechnol. Lett. 28 (2006) 2011–2017.

[15] C.L. Zhang, G. Zheng, C.M. Nichlos, 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.

[16] J. Peng, A. Wan, Effect of ionic strength on Henry's constants of volatile organic compounds, Chemosphere 36 (1998) 2731–2740.

[17] N. Ni, M.M. El-Sayed, T. Sanghvi, S.H. Yalkowsky, Estimation of the effect of NaCl on the solubility of organic compounds in aqueous solutions, J. Pharm. Sci. 89 (2000) 1620–1625.

[18] E.K. Kim, D.H. Lee, B.W. Yum, H.W. Chang, The effect of ionic strength and hardness of water on the non-ionic surfactant-enhanced remediation of perchloroethylene contamination, J. Hazard. Mater. 110 (2004) 85–92.

[19] M.J. Rosen, Surfactants and Interfacial Phenomena, third ed., Wiley-Interscience, New York, 2004.

[20] R. Carabias-Martínez, E. Rodríguez-Gonzalo, B. Moreno-Cordero, J.L. Pérez-Pavón, C. García-Pinto, E.F. Fernández Laespada, Surfactant cloud point extraction and pre-concentration of organic compounds prior to chromatography and capillary electrophoresis, J. Chromatogr. A 902 (2000) 251–265.