



Comparative study on the micelle properties of synthetic and dissolved organic matters

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ABSTRACT

The conductivity of two synthetic surfactants and several natural surfactants, dissolved organic matters (DOMs), as well as their enhancement on phenanthrene solubility were measured in order to compare the formation of micelle by DOMs with synthetic surfactants, and their applicability for promoting hydrophobic organic pollutants' mobility. The DOMs could form micelle structure, similar to the synthetic surfactants. The critical micelle concentration values of the DOMs are lower than those of the synthetic surfactants, and the enhancement of phenanthrene solubility by the DOMs is comparable to or more remarkable than the synthetic surfactants. The partitioning coefficient of phenanthrene to DOM micelles decreased at high DOM concentrations, which is attributed to the structure rearrangement of DOM macromolecules, while no such phenomenon was observed for simple synthetic surfactant micelles. There was an optimum concentration range when applying DOMs to enhance HOCs' solubility and mobility. Synthetic surfactants gave a concentration dependent conductivity plot with two evident regimes, pre-micellar and post-micellar regimes, whereas the DOMs showed a gradual transition between the two regimes. The degree of counterion dissociation (α) of the DOMs was remarkably higher than those of the synthetic ionic surfactants. These results provide insight into DOM micelle structure and micelle forming process with compared to synthetic surfactants, and valuable information on using natural surfactant-enhanced remediation technology.

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1. Introduction

Surfactants are molecules containing simultaneously in their structure a polar headgroup and a nonpolar hydrocarbon tail so that the molecules assume amphiphilic characteristics. At low concentration, surfactants are often present as dispersed molecules (monomers), however, when their concentration is high enough, the surfactant molecules tend to aggregate into micelles with the hydrophobic group located in the center (hydrophobic core) of the cluster and hydrophilic headgroup toward the aqueous phase (hydrophilic shell) [1]. The concentration at which the micelle formation occurs is defined as the critical micelle concentration (CMC). Formation of micelle by surfactant molecules is an important process in the environment, because it can change the solubility and inter-phase transfer of hydrophobic organic compounds (HOCs) in natural or remediation engineering systems. Consequently, the CMC is an important parameter, for a lower CMC value equates to a lower concentration required to initiate the enhanced solubilization and mobility of HOCs. Moreover, the enhancement on HOCs'

mobility varies a lot by different surfactants due to their different micelle properties.

Synthetic surfactants are the common chemicals applied in the remediation of contaminated sites to enhance the mobility of HOCs. However, the use of synthetic surfactants may be limited due to the concern of their environmental persistence and their possible toxicity to ecosystem [1,2]. On the other hand, the surfactant of a natural source allows the development of environmentally friendly surfactant-based remediation technologies. Furthermore, microbial degradation of certain pollutants has been demonstrated to be facilitated by natural surfactants [3].

Dissolved organic matters (DOMs), widespread in water and soil [4,5], are natural amphiphilic molecules with hydrophilic portions composed of both ionic groups ($R-COO^-$) and nonionic groups ($R-OH$), and hydrophobic portions composed of aliphatic chains and aromatic rings [6,7]. DOMs have been found to exhibit surfactant properties, and were used to enhance HOCs' solubility in remediation of contaminated soils [8,9].

However, there are still some disputes in the literatures on whether DOMs can form micelles or not [10]. Early concepts, informed by polymer science, suggested that DOMs comprise randomly coiled macromolecules that have elongated shapes in basic or low-ionic-strength solutions, but become coils in acidic or high-ionic-strength solutions [11]. However, recent information

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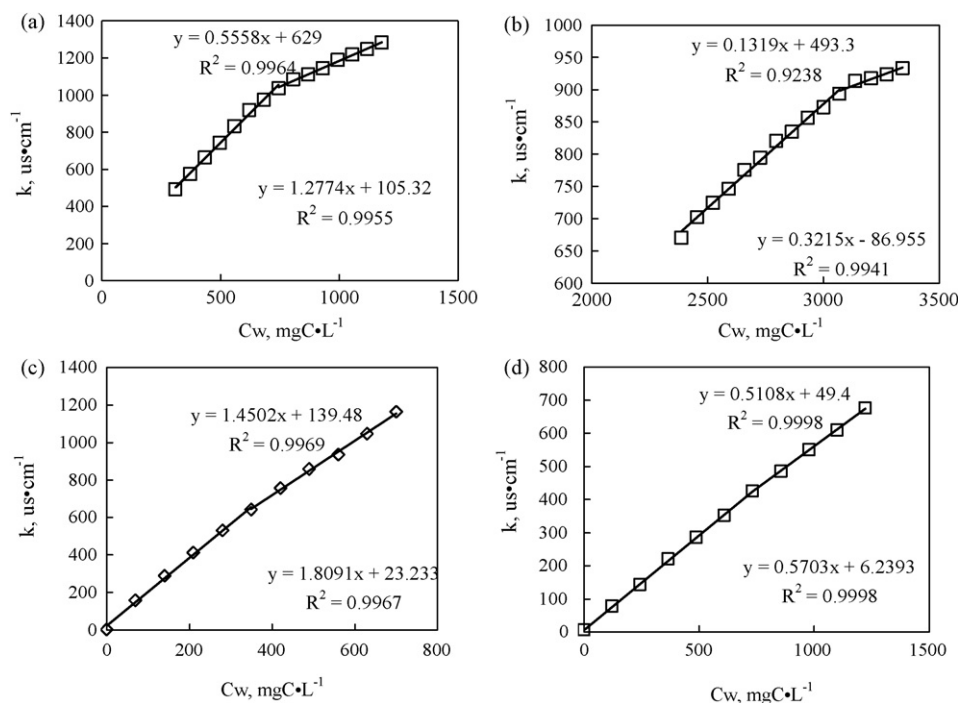


Fig. 1. Conductivity versus surfactant concentration for different surfactants SDBS (a), DDTMA (b), SDOM (c), and PDOM (d). Lines are the best fit of the data using the conventional method (two straight line regression).

obtained using electron spin resonance (ESR) spectroscopic, nuclear magnetic resonance (NMR) spectroscopic, and transmission electron microscopic techniques is not consistent with the “polymer model” [12–14]. A new concept of DOM micellar structure has thus been proposed in which molecules of DOM form micelle-like clusters linked by hydrogen bonds and hydrophobic interactions [15,16]. Consequently, we speculate that if DOM macromolecules can form micelle, the structure and the forming process of the micelle would have some differences from synthetic surfactants, which are important knowledge for applying DOMs as remediation technology. However, until now there was no research focusing on the comparison of micelle forming between natural macromolecular surfactants and synthetic surfactants.

The aim of this work was to examine whether DOMs can form micelle or not, compare the similarity and discrepancy of their micelle forming process with those of the synthetic surfactants, and examine the application feasibility in enhancing HOCs’ mobility by natural surfactants as compared to synthetic surfactants. Hence, the conductivity of several DOMs with natural origin and two synthetic surfactants, an anionic surfactant, sodium dodecylbenzene sulfonate (SDBS) and a cationic surfactant, dodecyltrimethylammonium chloride (DDTMA), and as well as the enhancement of phenanthrene solubility in the presence of these surfactants, were studied.

2. Materials and methods

2.1. Materials

Phenanthrene, sodium dodecylbenzene sulfonate (SDBS), and dodecyltrimethylammonium chloride (DDTMA) were purchased from Acros Corporation (New Jersey, USA), Yingda Chemical Corporation (Tianjin, China), Kemiou Chemical Research Center (Tianjin, China), respectively, and were all of analytical grade.

In this study, three natural DOMs were acquired from natural samples. Sediment sample (Tianjin, China) and pine (*Pinus massoniana* Lamb.) sawdust (<2 mm) were extracted with deionized

water for 24 h using a solid:water ratio of 1:2 for the sediment sample and 1:10 for the pine sawdust at 20 °C. The two extracts are referred to as SDOM and PDOM, respectively. A commercial humic acid (JINKE Chemistry Research Center, China) was extracted for 5 h with deionized water at solid:water ratio of 1:5, and the extracted DOM is referred to as HDOM. All suspensions were centrifuged for 15 min at 5000 rpm and filtered through a 0.45 μm cellulose nitrate filter. The pH of HDOM is around 4, and in this study its pH was adjusted to 8.0 in order to be in consistency with those of SDOM and PDOM. All the DOM solution were analyzed for pH, conductivity, DOC (using a total organic carbon analyzer, TOC-VCPH; Shimadzu, Japan) and absorbance at 254 nm (UV-VIS⁻¹ spectrometer, Shanghai Spectrum Instruments, China). The extracted DOM solution was stored at 4 °C in the dark no longer than 4 d before use. The properties of the three DOMs are summarized in Table S1 (supporting information). The initial solution was diluted by deionized water at different ratios in order to get the designed DOM concentrations.

2.2. Conductivity measurements

Conductivity (κ) measurements were performed using a conductivity meter (Hanna Instruments EC215, Italy), equipped with a conductivity cell having cell constant of 0.943 cm^{-1} . Solutions with a series of surfactant concentrations ranging from below to above the CMC of the surfactant were measured.

2.3. Solubility of phenanthrene in the presence of surfactants

Batch experiments were conducted to determine the extent of solubility enhancement of phenanthrene in the presence of surfactants. Twenty millilitre solutions with a series of surfactant concentrations were placed in 22 mL EPA stander sample vials with Teflon-lined septa and screw caps, and phenanthrene was subsequently added to each vial in the amount slightly more than required to saturate the solution. The initial surfactant concentrations were set at a wide range below and above its CMC in the

solution. The solution also contained 200 mg L⁻¹ NaN₃ as microbial inhibitor. Triplicate samples were prepared for each surfactant concentration; these samples were then equilibrated on a shaker for 48 h at 20 ± 0.5 °C and 150 rpm. The samples were subsequently centrifuged at 4500 × g for 20 min to completely separate the undissolved phenanthrene. Then, about 100 μL of the supernatant was carefully withdrawn with a syringe and analyzed by high performance liquid chromatography (HPLC).

2.4. Analytical methods

Aqueous phenanthrene was quantified by a SCL-10AVP HPLC system (Shimadzu, Japan) equipped with a fluorescence detector and a reverse-phase column (VP-ODS Kromasil C-18, 150 mm × 4.6 mm × 5 μm) [17].

3. Results and discussion

3.1. Conductivity of the surfactants

Fig. 1 shows that the conductivity (κ) of the synthetic surfactants and DOMs increases with their aqueous concentration (C_w) (for ease of comparison, the unit of C_w of both synthetic surfactants and DOMs is shown as mg CL⁻¹). However, the conductivity did not increase at a constant slope within the whole concentration range, and at higher concentrations, a lower slope presents. This is more obvious in the case of the synthetic surfactants. The increase of κ in the premicellar regime (at low C_w) is due to the increase of the concentration of surfactants as monomers. When the surfactant concentration is high enough, micellization occurs. After this point, the slope of the κ - C_w plot decreases for two reasons, i.e., the micelles diffusion, and consequently the charge transport, is slower than those of the monomers [18]; and the ionization degree of the micelles is less than that of monomers [19].

For the DOMs, the changes of the slope are not as sharp as those of SDBS and DDTMA, when their C_w crosses from premicellar regime to postmicellar regime in κ - C_w plot (Fig. 1). DOM molecules are quite large and have polar groups in a random way in their molecular structure, which makes it difficult for DOM molecules to assemble in a regular micelle. This would account for a loose, not compact structure, and a small aggregation number for DOM micelles, as reflected by the much weaker curvature in the κ - C_w plot.

Conventionally, the CMC value is determined by the intersection of the two straight lines in κ - C_w plots above and below the CMC. In addition, the ratio of the slope of the postmicellar region to that of the premicellar region is commonly assumed to be the degree of counter ion dissociation of the micelle (α) [20]. However, it is difficult to analyze a κ - C_w plot with a weak curvature, such as the plots for the DOMs in this study, using this “conventional procedure”. Therefore, another novel method was also adopted to analyze the experimental data in this study, and the expression is described as [21]:

$$\kappa(C_w) = \kappa_0 + A_1 C_w + \Delta C_w (A_2 - A_1) \ln \left(\frac{1 + e^{(C_w - \text{CMC})/\Delta C_w}}{1 + e^{-\text{CMC}/\Delta C_w}} \right) \quad (1)$$

where κ_0 represents the value of κ at $C_w = 0$. The function of $\kappa(C_w)$ could be used to describe κ - C_w plots. It presents two different linear regimes as C_w increases, and a transition point between them. The transition point is the CMC of the surfactant and the transition width is controlled by ΔC_w . Fitting κ - C_w data to Eq. (1), we obtained four parameters: values of CMC, A_1 , A_2 and ΔC_w . In addition, the degree of counterion dissociation (α) can be obtained from the A_2/A_1 ratio. The fitting results are shown in Fig. S1 in Support Information.

Table 1

Critical micelle concentration (CMC) and degree of counterion dissociation (α) for surfactants from conductivity-concentration plots by using two different treatments of the experimental data.

	Conventional				Integration		
	CMC ^a	α^b	$R^2 (<\text{CMC})$	$R^2 (>\text{CMC})$	CMC ^a	α^c	R^2
SDBS	725.7	0.44	0.9955	0.9964	727.0	0.41	0.9992
DDTMA	3060.4	0.41	0.9941	0.9238	3098.2	0.43	0.9970
SDOM	323.9	0.80	0.9967	0.9969	322.1	0.77	0.9993
PDOM	691.6	0.90	0.9998	0.9997	689.2	0.89	0.9999

^a Critical micelle concentration, the unit is mg CL⁻¹.

^b Degree of counterion dissociation of surfactants, obtained by the ratio of the slope of the postmicellar region to that of the premicellar region.

^c Degree of counterion dissociation of surfactants, A_2/A_1 in Eq. (1).

The two methods gave similar results for the CMC and α values (Table 1), although the second method (fitting data to Eq. (1)) is more direct and convenient, especially for DOMs. The average CMC values of the two methods are 323.0, 690.4 mg CL⁻¹ for SDOM and PDOM, respectively, in agreement with previous studies. Terashima et al. [22] reported the CMC of a peat humic acid (HA) of about 1100 mg CL⁻¹, and a compost derived HA with CMC value of 244 mg CL⁻¹ was obtained by Quagliotto et al. [23]. Hayase and Tsubota [24] concluded that the aggregation concentration of natural HAs is related to their origin, molecular weight and structure.

The average CMC values of SDBS and DDTMA are 726.4 and 3079.3 mg CL⁻¹ (Table 1), which are more or less higher than those of DOMs. Quadri et al. [25] found that the CMC values of their surfactant-like humic acids from food and green waste compost were lower than many synthetic ionic surfactants, but they did not give any explanation. Zana et al. [26] reported that when the space chain length of Gemini surfactant (alkanediyl- α,ω -(dimethylalkylammonium bromide)) increased, its CMC decreased. They proposed that when the space chain is long, the degree of conformational freedom is quite high and the headgroups have enough freedom to find a better arrangement, thus favor aggregating. Similarly, we speculate the lower CMC value of the DOMs may be due to their macromolecule characteristics and more complex conformation easier to rearrange. In addition, Zhao and Winnik stated that as macromolecule, the CMC values for block copolymer micelles are normally much lower than those for low molecular weight surfactants [27]. Furthermore, Zhu and Feng [28] reported that mixed anionic-nonionic surfactants could form mixed micelles, and had lower CMC values than single surfactants. Hence, we propose that the lower CMC values of DOMs may also result from the complex structure of DOMs composed of both ionic and nonionic headgroups.

The α values of the DOMs were higher than those of the synthetic surfactants (Table 1), implying that less counter ions balance the coulomb force opposing to the micellization. This can be attributed to an efficient charge shielding by large nonionic headgroups presented in DOMs, especially in PDOM, whose pH (7.1) is lower than that of SDOM (8.0). Torigoe et al. [29] studied the solution properties of poly(amidoamine) dendron surfactants bearing a quaternary ammonium focal group and sugar terminal groups ($C_m\text{qb-GnLac}$, $m = 12, 18, 22$; $n = 0, 1$). They found that the degree of counter ion binding to micelles of $C_m\text{qb-G1Lac}$ was lower than that of $C_m\text{qb-G0Lac}$ surfactants, and attributed it to that the former had more nonionic headgroups relative to the latter [29].

3.2. Solubility enhancement of phenanthrene by surfactants

Fig. 2 shows the solubility enhancement of phenanthrene by the synthetic surfactants (SDBS and DDTMA). There was practically no remarkable enhancement in phenanthrene solubility

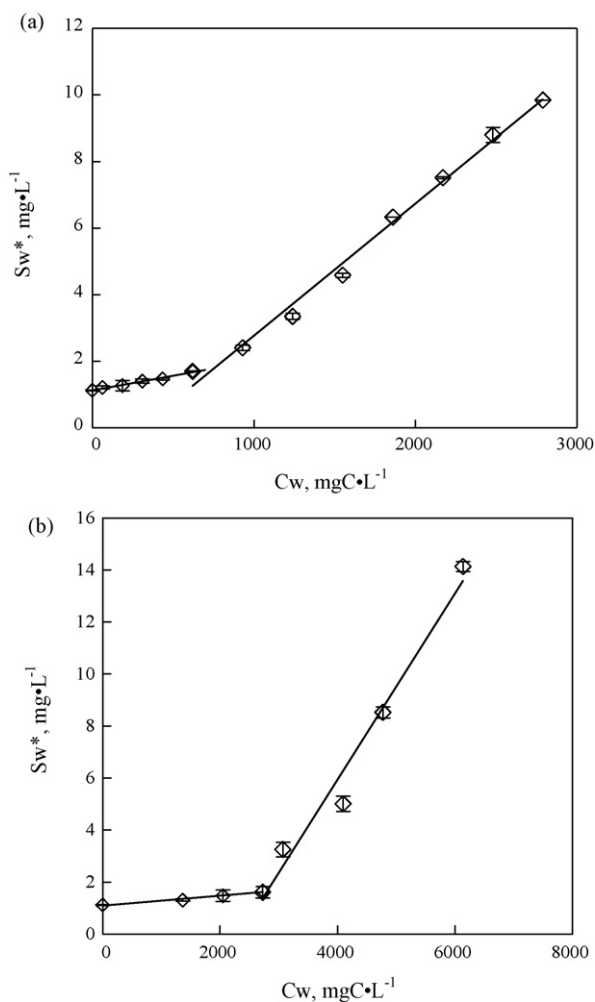


Fig. 2. Water solubility enhancement of phenanthrene as a function of the concentration of synthetic surfactants, SDBS (a) and DDTMA (b) at 20 °C.

below the CMC of the surfactants, while the water solubility of phenanthrene was enhanced greatly by the two surfactants above their CMCs. When the surfactant concentration was 2 times of the corresponding CMC, the apparent solubility of phenanthrene in the presence of SDBS and DDTMA was enhanced to be 4.2 and 9.3 times of its intrinsic solubility in pure water, respectively; whereas at the CMC, the solubility of phenanthrene in surfactant solution increased only by less than 35%. The difference in solubility enhancement by surfactants above and below their CMCs is a result of different ability of micelles and monomers to concentrate phenanthrene through partition interactions. The micelles with hydrophobic cores have markedly greater organic environment compared to the monomers, which favors the partition of HOCs, such as phenanthrene [30].

Likewise, for natural surfactants (DOMs), there was also a critical micelle concentration (CMC), below which the apparent aqueous solubility of phenanthrene was not affected significantly, and above which the increase of DOM concentration unambiguously led to an enhancement in the apparent aqueous solubility of phenanthrene (Fig. 3). Previous researches indicated that humic acids (HAs) have an amphiphilic nature because of the presence of both hydrophilic (polar) parts and hydrophobic (nonpolar) parts in their structures [7,11]. Such characters of HAs can lead to form micelle-like aggregates, in which intra- or intermolecular organization produces interior hydrophobic regions separated from aqueous surroundings by exterior hydrophilic layers, and the aggregates can solubilize

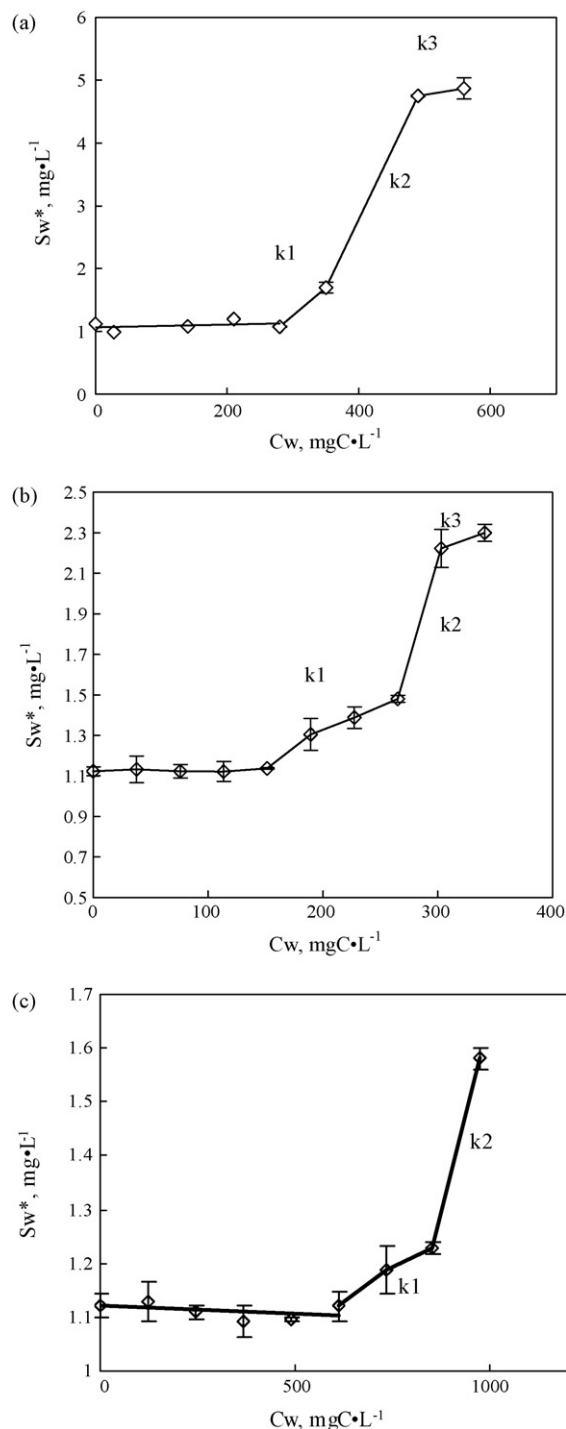


Fig. 3. Water solubility enhancement of phenanthrene as a function of concentration of natural surfactants, SDOM (a), HDOM (b), and PDOM (c) at 20 °C.

HOCs, like the micelles of synthetic surfactants [10,15]. Sutton and Sposito [31] reviewed previous researches of humic substances based on fluorescence quenching, electron spin resonance (ESR) spectroscopy, and nuclear magnetic resonance (NMR) techniques, and concluded that humic substances can form micelles.

Phenanthrene solubility in the presence of the synthetic surfactants (SDBS and DDTMA) above their CMC values could be well described by linear model (Fig. 2). The slope of the lines in Fig. 2 indicates that the apparent solubility of phenanthrene was enhanced by 3.97×10^{-3} and 3.58×10^{-3} mg on the basis of 1 mg C of aqueous SDBS and DDTMA, respectively (Table 2). Unlike the synthetic

Table 2
Solubility enhancement of phenanthrene by natural surfactants (DOMs) and related parameters.

	C (DOM) (mg CL ⁻¹)	Slop (mg mg C ⁻¹)	log K_{mc} (L kg C ⁻¹)	CMC (mg CL ⁻¹)
SDBS	600–2800	3.97×10^{-3}	3.55	748.2
DDTMA	2700–6100	3.58×10^{-3}	3.50	2788.2
SDOM	280–350	8.90×10^{-3} (k_1)	3.90	285.1
	350–490	2.18×10^{-2} (k_2)	4.29	
	490–560	1.70×10^{-3} (k_3)	3.18	
HDOM	150–265	2.93×10^{-3} (k_1)	3.42	139.2
	265–300	1.96×10^{-2} (k_2)	4.24	
	300–340	2.02×10^{-3} (k_3)	3.26	
PDOM	610–855	4.37×10^{-4} (k_1)	2.59	654.8
	855–980	2.89×10^{-3} (k_2)	3.41	

surfactants, phenanthrene solubility in the solution of the natural surfactants (DOMs), increased nonlinearly above their CMCs and fell into several regimes, as evidenced by the significant different slopes (k_1 , k_2 , k_3) (Fig. 3). It can be seen that the slopes of different concentration ranges of the same DOM can have one order of magnitude difference (Table 2).

The slope of k_2 is larger than k_1 (Fig. 3), exhibiting that the enhancement in phenanthrene solubility by DOM micelle became stronger. It was reported that oligomeric surfactants, such as the Gemini surfactant are made of molecules in which two or more polar groups are connected by hydrophobic chains of variable length, and they always show gradual transition between pre-micellar and postmicellar regimes [32], correspondingly, their ability for enhancing HOCs' solubility became stronger gradually. Similar phenomenon can be expected for DOMs due to their multi polar macromolecule structure. Different DOM monomers with different headgroups and hydrophobic tails formed micelles at different concentration. Hence, as DOM concentration increased, the DOM micelles formed more completely, and the ability to enhance phenanthrene solubility by DOM micelles became stronger.

The increase in phenanthrene solubility slowed down in the presence of SDOM and HDOM when their concentration were greater than a certain level (Fig. 3a and b), namely the slope k_3 is smaller than k_2 , which suggests a reduction in the partitioning of phenanthrene between DOM and water. The effect of DOM concentration on HOC–DOM interaction has been investigated in several studies, and negative relationships between DOM concentration and binding ability were observed [33–35]. This phenomenon can be attributed to the possible structural changes of DOM micelles when the concentration increases. For synthetic surfactants, increasing surfactant concentration above CMC can only cause the amount and concentration of micelle to increase. On the contrary, DOM macromolecules tend to curl up with continual increasing concentration because of the reduced free space for their movement and decreased intermolecular distance. This rearrangement in macromolecular structure probably hinders the access of phenanthrene to the hydrophobic areas in DOM [36,37]. Hence, an optimum concentration range exists when applying DOMs as a promoter for HOCs' solubility and mobility.

The apparent water solubility of a solute in surfactant solution can be expressed as [38,39]:

$$\frac{S_w^*}{S_w} = 1, \quad X \leq \text{CMC} \quad (2)$$

$$\frac{S_w^*}{S_w} = 1 + K_{mc}(X - \text{CMC}), \quad X \geq \text{CMC} \quad (3)$$

where S_w^* is the apparent solute solubility at a total surfactant concentration of X ; S_w is the intrinsic solute solubility in "pure water"; K_{mc} is the solute partition coefficient between the aqueous micellar phase and water, and the unit is L (kg C)⁻¹. K_{mc} values for the synthetic surfactants were evaluated from the slopes of the linear

lines; whereas K_{mc} values for DOMs were calculated separately for different concentration ranges due to the nonlinearity. The data of K_{mc} , and CMC for each surfactant are presented in Table 2.

CMC values of DOMs based on phenanthrene solubility measurements are in good agreement with the values determined by conductivity measurements, and are lower than the CMC values of the two synthetic surfactants (Table 2), which have been discussed in Section 3.1.

The values of log K_{mc} of the DOMs in this study ranged from 3.18 to 4.29 (Table 2), consistent with several previous studies [34,40]. For examples, Gauthier et al. [40] determined equilibrium constants of PAHs to dissolved humic materials by fluorescence quenching method, and got phenanthrene partition coefficient of 5.0×10^4 mL g⁻¹. Furthermore, Lassen and Carlsen [34] investigated solubility of phenanthrene in humic acids, and reported that the interaction coefficient (K) between phenanthrene and humic acids decreased with increasing humic acid concentration, and K values ranged from 1.1×10^4 to 1.2×10^3 mL g⁻¹ as HA concentration increased from 15 to 181 mg L⁻¹.

The values of log K_{mc} of DOMs are comparable to or higher than those with the synthetic surfactants, suggesting that DOMs are efficient natural surfactants (Table 2). If the unit of K_{mc} (L (kg C)⁻¹) is converted to L mol⁻¹, log K_{mc} value of DOM will be higher than those of synthetic surfactants in a greater extent, since as macromolecular material, DOM generally has more carbon atoms in one mol molecule than synthetic surfactants. Kabir-ud-Din et al. [41] reported that the mixtures of Gemini surfactant with conventional surfactants have higher solubilization capability than respective single ones, and they attributed it to that the mixed micelle with electric dipole has greater radius and larger effective solubilization area. DOM as macromolecular with much polar groups, its micelle must be large and loose, and have larger solubilization area for organic pollutants. Hence, DOM has greater solubilization capability for organic pollutants than conventional synthetic surfactants. Furthermore, considering the environmental friendly characteristics of DOM and its additional capacity to promote microbial activity for further biodegradation of contaminants, DOM presents a promising option for soil washing. To set up an applicable SER technology using DOMs, further research may be needed.

4. Conclusions

DOMs can form micelle structure like synthetic surfactants. However, there are also some differences in micelle formation process between natural (DOM) and synthetic surfactants due to the multi polar macromolecular structure and nonionic and ionic headgroups mixture properties of DOMs. DOMs showed a gradual transition from below to above CMC, whereas the transition of synthetic surfactants was sharp. Phenanthrene solubility increased with the concentration of both DOMs and synthetic surfactants above their CMC. However, partitioning coefficients of phenan-

threne to DOM micelles changed with DOM concentrations, and partition did not increase obviously when DOM concentration was greater than a certain level in some cases, while this phenomenon did not occur for the synthetic surfactants. Furthermore, the degree of micellar ionization of DOM was higher than that of synthetic surfactants. All these results give deep insight into the formation of micelle structure of DOMs, and provide valuable information on using DOMs as a natural surfactant in remediation of contaminated sites.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.09.098.

References

- [1] G.G. Ying, Fate, behaviour and effect of surfactants and their degradation products in the environment, *Environ. Int.* 32 (2006) 417–431.
- [2] J.C. Mata-Sandoval, J. Karns, A. Torrents, Influence of rhamnolipids and Triton X-100 on the biodegradation of three pesticides in aqueous phase and soil slurries, *J. Agric. Food Chem.* 49 (2001) 3296–3303.
- [3] E. Kaczorek, L. Chrzanowski, A. Pijanowska, A. Olszanowski, Yeast and bacteria cell hydrophobicity and hydrocarbon biodegradation in the presence of natural surfactants: phamnlipids and saponins, *Bioresour. Technol.* 99 (2008) 4285–4291.
- [4] M. Corvasce, A. Zsolnay, V. D'Orazio, R. Lopez, T.M. Miano, Characterization of water extractable organic matter in a deep soil profile, *Chemosphere* 62 (2006) 1583–1590.
- [5] B. Lam, A. Baer, M. Alae, B. Lefebvre, A. Moser, A. Williams, A.J. Simpson, Major structural components in freshwater dissolved organic matter, *Environ. Sci. Technol.* 41 (2007) 8240–8247.
- [6] O.C. Zafriou, J. Jousset-Dubien, R.G. Zepp, R.G. Zika, Photochemistry of natural waters, *Environ. Sci. Technol.* 18 (1984) 358A–371A.
- [7] H.R. Schulten, M. Schnitzer, Chemical model structures for soil organic matter and soils, *Soil Sci.* 162 (1997) 115–130.
- [8] W.P. Johnson, G.L. Amy, Facilitated transport and enhanced desorption of polycyclic aromatic hydrocarbons by natural organic matter in aquifer sediments, *Environ. Sci. Technol.* 29 (1995) 807–817.
- [9] P. Conte, A. Agretto, R. Spaccini, A. Piccolo, Soil remediation: humic acids as natural surfactants in the washing of highly contaminated soils, *Environ. Pollut.* 135 (2005) 515–522.
- [10] T.F. Guetzlhoff, J.A. Rice, Does humic acid form a micelle? *Sci. Total Environ.* 152 (1994) 31–35.
- [11] R.P. Schwarzenbach, P.M. Gschwend, D.M. Imboden, *Environmental Organic Chemistry*, second ed., John Wiley & Sons, 2004.
- [12] J.A. Ferreira, O.R. Nascimento, L. Martin-Neto, Hydrophobic interactions between spin-label 5-SASL and humic acid as revealed by ESR spectroscopy, *Environ. Sci. Technol.* 35 (2001) 761–765.
- [13] A.J. Simpson, W.L. Kingery, D.R. Shaw, M. Spraul, E. Humpfer, P. Dvortsak, The application of ¹H HR-MAS NMR spectroscopy for the study of structures and associations of organic components at the solid-aqueous interface of a whole soil, *Environ. Sci. Technol.* 35 (2001) 3321–3325.
- [14] M. Kerner, H. Hohenberg, S. Ertl, M. Reckermann, A. Spitz, Self-organization of dissolved organic matter to micelle-like microparticles in river water, *Nature* 422 (2003) 150–154.
- [15] R. von Wandruszka, The micellar model of humic acid: evidence from pyrene fluorescence measurements, *Soil Sci.* 163 (1998) 921–930.
- [16] A.J. Simpson, W.L. Kingery, M.H.B. Hayes, M. Spraul, E. Humpfer, P. Dvortsak, R. Kersebaum, M. Godejohann, M. Hofmann, Molecular structures and associations of humic substances in the terrestrial environment, *Naturwissenschaften* 89 (2002) 84–88.
- [17] H.W. Sun, Z.L. Zhou, Impacts of charcoal characteristics on sorption of polycyclic aromatic hydrocarbons, *Chemosphere* 71 (2008) 2113–2120.
- [18] M.J. Avena, K.J. Wilkinson, Disaggregation kinetics of a peat humic acid: mechanism and pH effects, *Environ. Sci. Technol.* 36 (2002) 5100–5105.
- [19] A. Dominguez, A. Fernandez, N. Gonzalez, E. Iglesias, L. Montenegro, Determination of critical concentration of some surfactants by three techniques, *J. Chem. Educ.* 74 (1997) 1227–1231.
- [20] M. Perez-Rodriguez, G. Perieto, C. Rega, L.M. Varela, F. Sarmiento, V.A. Mosquera, Comparative study of the determination of the critical micelle concentration by conductivity and dielectric constant measurements, *Langmuir* 14 (1998) 4422–4426.
- [21] P. Carpena, J. Aguiar, P. Bernaola-Galvan, C.C. Ruiz, Problems associated with the treatment of conductivity–concentration data in surfactant solutions, *Langmuir* 18 (2002) 6054–6058.
- [22] M. Terashima, M. Fukushima, S. Tanaka, Influence of pH on the surface activity of humic acid: micelle-like aggregate formation and interfacial adsorption, *Colloids Surf. A* 247 (2004) 77–83.
- [23] P. Quagliotto, E. Montoneri, F. Tambone, F. Adani, R. Gobetto, G. Viscardi, Chemicals from wastes: compost-derived humic acid-like matter as surfactant, *Environ. Sci. Technol.* 40 (2006) 1686–1692.
- [24] K. Hayase, H. Tsubota, Sedimentary humic acid and fulvic acid as surface active substances, *Geochim. Cosmochim. Acta* 47 (1983) 947–952.
- [25] G. Quadri, X. Chen, J.W. Jawitz, F. Tambone, P. Genevini, F. Faoro, F. Adani, Biobased surfactant-like molecules from organic wastes: the effect of waste composition and composting process on surfactant properties and on the ability to solubilize tetrachloroethene (PCE), *Environ. Sci. Technol.* 42 (2008), pp. 2618–2623.
- [26] R. Zana, M. Benraou, R. Rueff, Alkanediyl- α,ω -(dimethylalkylammonium bromide) surfactants. 1. Effect of the spacer length on the critical micelle concentration and micelle ionization degree, *Langmuir* 7 (1991) 1072–1075.
- [27] C. Zhao, M.A. Winnik, Fluorescence probe techniques used to study micelle formation in water-soluble block copolymers, *Langmuir* 6 (1990) 514–516.
- [28] L. Zhu, S. Feng, Synergistic solubilization of polycyclic aromatic hydrocarbons by mixed anionic–nonionic surfactants, *Chemosphere* 53 (2003) 459–467.
- [29] K. Torigoe, A. Tasaki, T. Yoshimura, K. Sakai, K. Esumi, Y. Takamatsu, S.C. Sharma, H. Sakai, M. Abe, Synthesis and aqueous solution properties of PAMAM dendron surfactants bearing a quaternary ammonium focal group and sugar terminal groups, *Colloids Surf. A* 326 (2008) 184–190.
- [30] D.K. Kile, C.T. Chiou, Water solubility enhancements of DDT and trichlorobenzene by some surfactants below and above the critical micelle concentration, *Environ. Sci. Technol.* 23 (1989) 832–838.
- [31] R. Sutton, G. Sposito, Molecular structure in soil humic substances: the new view, *Environ. Sci. Technol.* 39 (2005) 9009–9015.
- [32] F.M. Menger, C.A. Littau, Gemini surfactants: synthesis and properties, *J. Am. Chem. Soc.* 113 (1991) 1451–1452.
- [33] P.F. Landrum, S.R. Nihart, B.J. Eadie, W.S. Gardner, Reverse-phase separation method for determining pollutant binding to Aldrich humic acid and dissolved organic carbon of natural waters, *Environ. Sci. Technol.* 18 (1984) 187–192.
- [34] P. Lassen, L. Carlsen, The effect of humic acids on the water solubility and water–organic carbon partitioning of fluorine and its nso-heteroanalogues: carbazole, dibenzofuran, and dibenzothiophene, *Chemosphere* 38 (1999) 2959–2968.
- [35] B. Pan, S. Ghosh, B. Xing, Dissolved organic matter conformation and its interaction with pyrene as affected by water chemistry and concentration, *Environ. Sci. Technol.* 42 (2008) 1594–1599.
- [36] P. Lassen, L. Carlsen, Solubilization of phenanthrene by humic acids, *Chemosphere* 34 (1997) 817–825.
- [37] J. Akkanen, J.V.K. Kukkonen, Measuring the bioavailability of two hydrophobic organic compounds in the presence of dissolved organic matter, *Environ. Toxicol. Chem.* 22 (2003) 518–524.
- [38] M. Terashima, M. Fukushima, S. Tanaka, Evaluation of solubilizing of humic aggregate basing on the phase-separation model, *Chemosphere* 57 (2004) 439–445.
- [39] P. Wang, A.A. Keller, Partitioning of hydrophobic organic compounds within soil–water–surfactant systems, *Water Res.* 42 (2008) 2093–2101.
- [40] T.D. Gauthier, E.C. Shane, W.F. Guerin, W.R. Seitz, C.L. Grant, Fluorescence quenching method for determining equilibrium constants for polycyclic aromatic hydrocarbons binding to dissolved humic materials, *Environ. Sci. Technol.* 20 (1986) 1162–1166.
- [41] M.S. Kabir-ud-Din, P.A. Bhat, A.A. Dar, Solubilization capabilities of mixtures of cationic Gemini surfactant with conventional cationic, nonionic and anionic surfactants towards polycyclic aromatic hydrocarbons, *J. Hazard. Mater.* (2009), doi:10.1016/j.jhazmat.2009.01.022.