Water solubility enhancements of PAHs by sodium castor oil sulfonate microemulsions

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Abstract: Water solubility enhancements of naphthalene(Naph), phenantherene(Phen) and pyrene(Py) in sodium castor oil sulfonate(SCOS) microemulsions were evaluated. The apparent solubilities of PAHs are linearly proportional to the concentrations of SCOS microemulsion, and the enhancement extent by SCOS solutions is greater than that by ordinary surfactants on the basis of weight solubilization ratio(WSR). The $\log K_{em}$ values of Naph, Phen, and Py are 3.13, 4.44 and 5.01 respectively, which are about the same as the $\log K_{ow}$ values. At 5000 mg/L of SCOS conccentration, the apparent solubilities are 8.80, 121, and 674 times as the intrinsic solubilities for Naph, Phen, and Py. The effects of inorganic ions and temperature on the solubilization of solutes are also investigated. The solubilization is improved with a moderate addition of Ca^{2+}, Na^+, NH_4^+ and the mixture of Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+. WSR values are enhanced by 22.0% for Naph, 23.4% for Phen, and 24.6% for Py with temperature increasing by 5℃. The results indicated that SCOS microemulsions improve the performance of the surfactant-enhanced remediation(SER) of soil, by increasing solubilities of organic pollutants and reducing the level of surfactant pollution and remediation expenses.

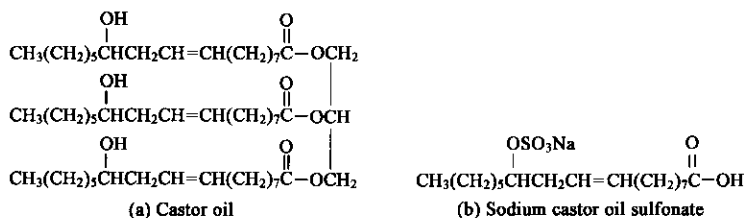**Keywords:** sodium castor oil sulfonate; microemulsion; solubilization; PAHs

Introduction

Contamination of groundwater and soils by organic pollutants has become an issue of increasing worldwide concern, which arouses environmental scientists to explore different approaches for the clean-up of the contaminated soils and groundwater. The chemical, biological, and chemical-biological remediations have received considerable attention due to high efficiency in contrast to pump-and-treat systems and surfactants play key roles in these techniques(Zhu, 1999). Surfactant-enhanced remediation(SER) has been employed to remove nonaqueous phase liquids(NAPLs) from contaminated soils and aquifers(Abdul, 1992; Pinto, 2000; Lagadec, 2000; Taylor, 2001). The key points for SER are (1) to increase the aqueous solubility of NAPLs through the formation of surfactant micelles, and (2) to mobilize the entrapped NAPLs through decrease in NAPL-water interfacial tension. To conform with these requirements, different surface active agents, such as anionic surfactants(Divarakanath, 1999), nonionic surfactants (Dianne, 2000; Cowell, 2000; Zhou, 2000), cyclodextrins(Ko, 2000), humic acids(Van Stempvoort, 2002) and biosurfactants(McCray, 2001), were used to improve the solubilization, mobilization and bioavailability of organic pollutants. However, microemulsion may be a promising approach for the remediation of soils and groundwater, because microemulsion is capable of solubilizing much more oil than that of micellar solution and arising ultralow interfacial tension between the aqueous phase and oil phase (Cui, 1999).

Since J.H.Schulman introduced the term "microemulsion" in 1959, microemulsions have attained increasing significance both in basic research and industry(Schwuger, 1995). Recently, much attention has been paid to its application in SER(Fiorenza, 2000). Richard Martel *et al*.(Martel, 1998a; 1998b) optimized different surfactant-alcohol-solvent (oil-in-water) microemulsions to recover NAPLs from sand columns. Ouyang *et al*.(Ouyang, 1995; 1996) developed a surfactant-enhanced microemulsion(gasoline-in-water) approach for the remediation of NAPLs from contaminated soil columns. Although high recovery was obtained from these studies, the main drawback of this oil removal process was the high concentration

of ingredients necessary for NAPL dissolution, which made the process expensive. The solvents used(e.g. toluene, xylenes, ethylbenzene, D-limonene, gasoline, etc.) would be potential contaminants to soils and groundwater. A ternary microemulsion of water-rapeseed oil-polyglycoside(APG) significantly extracted pyrene(Py) from a real soil sample and its ingredients(APG and rapeseed oil) are biodegradable (Schwuger, 1995). However, 10% (wt. fraction) of APG would be a great cost for the clean-up of contaminated soils. Thus, these microemulsified systems are not suitable for remediation application. Meanwhile, the information about the effects of the temperature and inorganic salts co-existed with organic pollutants in soils on the performance of microemulsion are not available.

The commercial sodium castor oil sulfonate(SCOS) (Turkey red oil) is the product of natural castor oil sulfonated by concentrated sulfuric acid. SCOS is used as emulsifying and dispersing agents in various applications(Liu, 1995). It is a mixture of castor oil, sodium castor oil sulfonate, sodium castor oil acid, inorganic salts and water and so on. The structures of main ingredients are shown in Scheme 1. SCOS is aptitude for biodegradation due to the unsaturated bonds and hydroxyl groups in the structures of its ingredients. A stable microemulsion(oil-in-water) forms when SCOS is mixed with water. Thus, SCOS microemulsion would solubilize more organic pollutants than the surfactant micelle solutions arise ultralow interfacial tension and expose little contamination risk on the soils and groundwater; meanwhile, abundant resources of castor oil and a simple process for SCOS production would result in a relative low cost if SCOS microemulsion would be used in SER application. Most conventional surfactants are derived from petroleum hydrocarbans(non-reproducible resources). However, SCOS is the product of the reproducible castor oil, which has significance to resources availability.

Scheme 1   Structures of castor oil(a) and sodium castor oil sulfonate(b)

Many microorganisms, including bacteria, algae and fungi, are shown to possess degradative enzymes for the oxidative degradation of PAHs(Cerniglia, 1981). However, the in-situ microbial metabolism of PAHs is limited by low bioavailability and removal of PAHs from contaminated soils and groundwater is governed by the type and concentration of enhancing agents. The objectives of this study are (1) to investigate the solubilization and partition of Naph, Phen and Py in the SCOS microemulsions; (2) to compare the extent of solubilization by SCOS microemulsions with that by the conventional surfactants; (3) to test the effects of inorganic salts and temperature(environmental factors) on solubilization. This study will be a base for the application of SCOS microemulsion in the remediation of contaminated soils and groundwater, and provide a conceptual basis for assessing the potential impact of microemulsions on the behavior of organic contaminants in situations where spilled or waste oils may be emulsified by surfactants.

1   Experimental section

1.1   Materials

The commercial sodium castor oil sulfonate was obtained from Shanghai Chemical Company and used as received. The content of water and inorganic salts were measured as 13.44% and 1.87% respectively, by the weight analysis(Zhong, 1986). A stock solution at concentration of 100.0 g/L was prepared and other solutions for batch equilibrium experiment were prepared by diluting stock solution. At ambient

temperature, the solutions with concentration greater than 1000 mg/L show slight turbidity. Phenanthrene and pyrene with purity of 98% or greater were obtained from Aldrich Chemical Co. and used without further purification. Naphthalene was obtained as analytical grade chemical from Shanghai Yuanhang Chemical Factory. Methanol, used for sample analysis, was obtained as an analytical grade solvent. Deionized water was used throughout the experiments.

1.2 Experimental procedures and analytical methods

Procedures for sample equilibration and solubility determination were essentially the same as reported earlier(Zhu, 2001). SCOS solutions were placed in 25 ml Corex centrifuge tubes with Teflon cap liners, and PAHs were added to each tube in an amount slightly more than required to saturate the solution. Duplicate samples were prepared for each concentration of SCOS, these samples were then equilibrated on a Model THZ-C shaker for 24 h at 25 or 20 ± 1 ℃. The samples were subsequently centrifuged at 5000 r/min(2987 g) for 1 h to separate the undissolved solutes. The particles adhering to the glass walls were carefully removed with a cotton swab, and the meniscus was subsequently aspirated to remove any particles suspended on the surface. This centrifugation/cleaning procedure was repeated. An appropriate aliquot of the supernatant was then carefully withdrawn with a pipet and diluted to 25 ml with SCOS-water-methanol solution. Naph, Phen, and Py in solutions were analyzed at 275.8 nm, 250.7 nm, and 334.5 nm on Model UV2401PC spectrophotometer respectively. In order to eliminate the effect of surfactant on analysis, SCOS concentration was kept constant in the standard and experimental solutions; the methanol concentration in the solution was also kept constant at 10%(V/V).

Surface tension was measured by using a Model JZHY-180 tensionmeter on the DuNouy principle.

2 Results and discussion

2.1 Characterization of SCOS microemulsions

Fig. 1 shows a plot of the surface tension as a function of $\log C_{\mathrm{SCOS}}$ at room temperature. No distinct inflection is detected in the plot with concentration extended to 5000 mg/L, which indicates SCOS solutions are different from the micelle solutions. A water-oil-surfactant dispersing system, with transparent or semi-transparent appearance and high mobility, is a microemulsion if no phase separation occurs after it is centrifuged at 100 g of the relative centrifuge force(RCF) for 5 min(Prince, 1977). All SCOS solutions were centrifuged at 2987 g of RCF for 1 h. No phase separation was

Fig.1   Plot of the surface tension versus the log concentration of SCOS solution

observed, which illustrates that SCOS systems are microemulsions formed by castor oil(oil), sodium castor oil sulfonates(surfactant), other surface active ingredients and water.
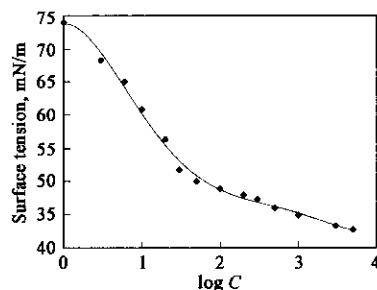
2.2 Solubilization and partition of PAHs in SCOS microemulsions

The relations of the apparent solubilities of Naph, Phen, and Py as a function of SCOS concentrations at 25 ± 1 ℃ are shown in Fig. 2. The expressed SCOS concentrations have not been corrected for the amount of water and inorganic salt in each sample. A linear relation is observed between the apparent solubilities and SCOS concentrations, throughout the range of SCOS concentrations studied. Based on these results, the microemulsified SCOS system is much like a separate bulk phase at all concentrations. This is in contrast to behavior of a conventional surfactant that shows a distinct break in the solubility enhancement (or surface tension) plot in the vicinity of the measured CMC. The linear solubility enhancements of PAHs by SCOS microemulsions can be accounted for by partition equilibrium of solute between the microemulsified phase and the aqueous phase, which can be expressed as(Kile, 1990):

$$S_w^* = S_w(1 + XK_{em}).\qquad(1)$$

Where S_w^* is the apparent solubility in water, S_w is the intrinsic water solubility of the solute, X is the concentration of microemulsion, and K_{em} is the partition coefficient of solute between the microemulsified phase and the aqueous phase. With the quantity of X expressed in g/ml in the solution and solute concentration in both water and microemulsified phase expressed in the same weight-to-weight basis, the resulting K_{em} is a dimensionless quantity. Thus, the K_{em} value can be calculated from the slope and the intercept of the plot.
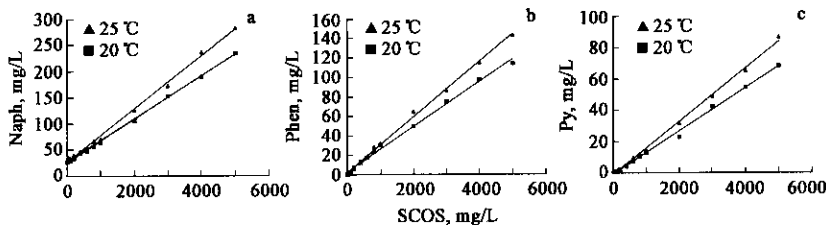

Fig. 2   Water solubility enhancements of Naph(a), Phen(b) and Py(c) by SCOS microemulsions

The calculated K_{em} values (on the water and inorganic salts free basis) and comparison of solubilization extent for Naph, Phen, and Py are shown in Table 1. The $\log K_{em}$ values for Naph, Phen, and Py are 3.13, 4.44, and 5.01 respectively. This difference is characteristic of equilibrium partitioning of solutes between organic phase and water, in which the equilibrium partition constant is inversely related to the solute solubility in water(S_w). So the solubilization extent for Naph, Phen, and Py by SCOS microemulsions is in the order Py > Phen > Naph, which is also obtained from the ratios of solute solubility at 5000 mg/L of SCOS concentration($S_{w,5000}$) to the intrinsic water solubility(S_w). Compared with octanol-water partition coefficient, $\log K_{em}$ for Naph is slightly lower than $\log K_{ow}$, while for Phen equivalent to and for Py greater than the corresponding $\log K_{ow}$, which shows that SCOS microemulsions possess the ability to solubilize nonpolar organic compound to a relative large degree. A linear relation is obtained between $\log K_{em}$ values and $\log K_{ow}$ values, with a regression coefficient square equal to 0.9983, as shown in Fig. 3.

Table 1   Comparison of water solubility enhancements of Naph, Phen and Py at $25 \pm 1^{\circ}\text{C}$

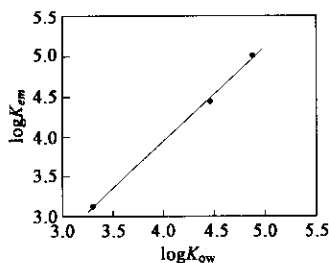| PAHs	S_w, mg/L	$S_{w,5000}^*$, mg/L	Ratio, $S_{w,5000}^* / S_w$	$\log K_{ow}$	$\log K_{em}$
Naph	32.05	283	8.80	3.30	3.13
Phen	1.182	143	121	4.46	4.44
Py	0.1294	87.2	674	4.88	5.01

Fig. 3   Plot of $\log K_{em}$ versus $\log K_{ow}$

2.3   Comparison of solubilization by SCOS microemulsions with surfactant micellar solutions

In view of the unique composition of SCOS microemulsions, it is of interest to compare the solubilization extent of PAHs by SCOS microemulsions from this study with that by the conventional surfactant solutions from the earlier work. Weight solubilization ratio (WSR) is a common parameter, which quantitatively expresses the solubilizing capacity of a solute by unit weight of surface-active agent. For solubilization by microemulsions, it is defined as

$$WSR = (S_w^* - S_w)/X. \qquad (2)$$

Where S_w^* (mg/L) is the apparent solubility of solute at X (mg/L) of microemulsion concentration. S_w (mg/L) is the intrinsic solubility of solute. For solubilization by micellar solution,

$$WSR = (S_w^* - S_{w,cmc}^*)/(X - X_{cmc}). \qquad (3)$$

Where S_w^* (mg/L) is the apparent solubility of solute at X(mg/L) of surfactant concentration, while $S_{w,cmc}^*$ (mg/L) is the apparent solubility at X_{cmc}(mg/L) (CMC) of surfactant concentration. The value of WSR can be calculated from the slope of solubility curves. Table 2 shows WSR values(on water and inorganic salts free basis) for Naph, Phen, and Py from this study and the earlier work. WRS values for Naph, Phen, and Py by SCOS are greater than that for corresponding solutes by nonionic and anionic surfactants, except that WSR values for Naph, Phen and Py by Brij 30, for Naph and Phen by Tergitol NP-10, and for Naph by Triton X-100 are greater than that for corresponding solutes by SCOS. However, Brij 30, with 4 of polyoxyethlene number, is not suitable for remediation application due to its low solubility in water. Naph is volatile compound and its accumulation in soils is not a concern. From these points of view, SCOS mocroemulsions possess a high ability to enhance water solubility of PAHs. Because WSR by surfactant below CMC is largely smaller than that above CMC, correspondingly, WSR by SCOS microemulsion at low concentrations is much greater than that by surfactant below CMC. As mentioned above, SCOS forms stable emulsion in water and thus behave much like a bulk organic phase in concentrating organic solutes. In addition, a microemulsified droplet can be considered as a micelle in which some oil(e. g castor oil) is solubilized, so the former holds larger volume than the latter to contain organic solutes. Anyhow, microemulsified droplets exist even though the microemulsion concentrations go much down, but surfactants exist as monomers in aqueous solution below CMC, which have no significant effects on water solubility enhacements of organic solutes. Consequently, SCOS microemulsions are superior to the conventional surfactant micelle solutions for the solubilization of organic pollutants.

2.4 Influence of temperature on solubilization

An increase in temperature from 20 to 25 ℃ results in WSR values increasing by 22.0% , 23.4% , and 24.6% for Naph, Phen, and Py, respectively, as shown in Fig.2. The temperature effect can be attributed to (1) changes in the aqueous solubility of PAHs and (2) changes in the properties of microemulsified phase. Temperature increase enlarges the volume of microe-mulsified phase, thus can include more solute molecules.

2.5 Effects of inorganic cations on solubilizations

The performance of microemulsion formed by anionic surfactant is strongly affected by the presence of electrolytes in the solution (Cui, 1999). This is particularly important in field application, since in such situation, subsurface matrix solutions contain electrolytes such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and NH_4^+ . The influence of common inorganic cations in soils on the solubilization of PAHs at 25 ± 1 ℃ was investigated.

Table 2 Comparison of WSR values of Naph, Phen and Py by SCOS with that by surfactants at 25 ± 1℃

Surfactant	Chemical name	PAHs	WSR
Brij 30[a]	Lauryl polyoxyethene(4) ether	Naph	1.12×10^{-1}
		Phen	7.45×10^{-2}
		Py	3.98×10^{-2}
Igepal CA-720[a]	Octylphenyl polyoxyethylene(12) ether	Naph	5.63×10^{-2}
		Phen	2.51×10^{-2}
		Py	1.17×10^{-2}
Tegitol NP-10[a]	Nonylphenyl polyoxyethylene(10.5) ether	Naph	6.70×10^{-2}
		Phen	4.17×10^{-2}
		Py	1.70×10^{-2}
Triton X-100[a]	Octylphenyl polyoxyethylene(9.5) ether	Naph	6.92×10^{-2}
		Phen	3.16×10^{-2}
		Py	1.14×10^{-2}
APFO[b]	Ammonium perfluorooctanoate	Naph	1.24×10^{-3}
		Phen	9.54×10^{-5}
		Py	1.92×10^{-5}
SDBS[c]	Sodium dodecyl phenyl sulfate	Naph	1.43×10^{-2}
		Phen	3.32×10^{-3}
		Py	–
SCOS	Sodium castor oil sulfonate	Naph	6.06×10^{-2}
		Phen	3.77×10^{-2}
		Py	2.03×10^{-2}

Notes: a. Edwards, 1991; b. Chun, 2002; c. An, 2002

The solubilizations of Py by SCOS microemulsions in the presence of 1.0, 5.0, 10, 20, 50, 70, and 100 mmol/L of NaCl were tested. The quantity of inorganic salts in SCOS reagent was not included. 1.0 mmol/L of NaCl has no distinct effect on the solubilization in contrast to the control solution (no NaCl addition). 5.0, 10, 20, and 50 mmol/L of NaCl increase WSR values by 2.0%, 4.9%, 13.3% and 9.4% respectively. However, 70 mmol/L of NaCl results in the precipitation of SCOS and decrease in solubility of Py, while 100 mmol/L of NaCl does more distinctly. The influence of NH_4Cl is somewhat the same as that of NaCl. No change in WSR values occurs in the presence 1.0 or 5.0 mmol/L of NH_4Cl. WSR values increase by 5.9%, 14.8%, and 13.8% in the presence of 10, 20, and 50 mmol/L of NH_4Cl. Precipitation of SCOS also occurs in the presence of 70 and 100 mmol/L of NH_4Cl. The effects of Ca^{2+} were tested at 0.1, 0.2, 0.5, 0.8, 1.0, 2.0, and 4.0 mmol/L of $CaCl_2$. For $CaCl_2$ concentrations at 0.5, 0.8, 1.0, and 2.0 mmol/L, water solubility of Py increase as a function of SCOS concentration and WSR values increase by 2.5%, 7.4%, 13.3%, and 31.5%, while 0.1 or 0.2 mmol/L of $CaCl_2$ has no effect on solubilization of SCOS. Precipitation occurs in the presence of 4.0 mmol/L $CaCl_2$. The influences of NaCl, NH_4Cl and $CaCl_2$ on WSR values of Py are shown in Table 3. From the results above, it is shown that cation ion has both positive and negative effect on the solubilization of Py. A moderate addition of inorganic salts enhances solubilization. This could be attributed to the static electric screen of "anionic heads" of surfactants by cation ions, which decrease the repulsion among "anionic heads" and increase the number of surfactants in the microemulsified phase, and then enlarge the volume of microemulsified droplets. However, a large amount of salts result in precipitation of anionic surfactant and destroy the structure of microemulsion.

Table 3　Influences of NaCl, NH_4Cl and $CaCl_2$ on WSR values of Py

	NaCl, mmol/L				NH_4Cl, mmol/L				$CaCl_2$, mmol/L			
	5.0	10	20	50	5.0	10	20	50	0.5	0.8	1.0	2.0
WSR	0.0207	0.0213	0.0230	0.0222	0.0203	0.0215	0.0233	0.0231	0.0208	0.0218	0.0230	0.0267
R^2	0.9970	0.9986	0.9995	0.9923	0.9980	0.9984	0.9992	0.9898	0.9966	0.9952	0.9990	0.9920
△WSR, %	2.0	4.9	13.3	9.4	0.0	5.9	14.8	13.8	2.5	7.4	13.3	31.5

Table 4　Influence of the mixed salts(5.0 mmol/L of cation) on WSR values of PAHs

PAHs	No inorganic salt		Mixed inorganic salts		
	WSR	R^2	WSR	R^2	△WSR, %
Naph	0.0602	0.9969	0.0700	0.9874	16.3
Phen	0.0377	0.9978	0.0534	0.9985	41.6
Py	0.0203	0.9972	0.0233	0.9964	14.8

The influence of mixed cations on solubilization is also investigated, as shown in Table 4. $CaCl_2$, NH_4Cl, $MgCl_2$, NaCl, and KCl were mixed together, with each cation ion concentration equal to 1.0 mmol/L. 5.0 mmol/L of mixed cation concentration is at levels representative of soil solution concentration. The solubilities of Naph, Phen and Py are linearly proportional to the concentration of SCOS in the presence of the mixed inorganic salts and WSR values increase by 16.3%, 41.6% and 14.8% for Naph, Phen and Py, respectively, which illustrates the solublization extent by SCOS would be enhanced by electrolytes in subsurface water in field application.

3　Conclusions

SCOS microemulsion significantly enhances the solubilities of Naph, Phen and Py due to its unique properties. The capacity of solubility enhancement by SCOS microemulsions is greater than that by the conventional nonionic and anionic surfactants on the basis of WSR. Temperature increase and suitable quantity of inorganic cations can enhance the solubilization capacities of SCOS microemulsions on PAHs. The results suggested that SCOS would improve the performance of the surfactant-enhanced remediation

(SER) of soils by increasing the bioavailability and biodegradation of non-aqueous-phase organic pollutants and reducing the level of surfactant pollution and remediation expenses. The data also indicated the potential impact of microemulsion on the transport and fate of organic contaminants in environment.

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