

토양/지하수내 난분해성 유기오염물 제거시 계면활성제 흡착 영향 Surfactant Sorption Effects on the Removal of Hydrophobic Organic Compounds (HOCs) from Subsurface

고 석 오

(주)대우 건설기술연구소

요 약 서

본 연구는 오염토양/지하수의 정화를 위하여 사용되는 계면활성제 교정기술의 보다 현실적인 평가를 위하여 토양에 흡착된 계면활성제에 대한 소수성 유기오염물인 Naphthalene과 Phenanthrene의 흡수현상에 대한 연구결과를 나타내었다. 음이온 계면활성제인 Sodium Dodecyl Sulfate (SDS)와 중성 계면활성제인 Tween 80의 흡착곡선은 소수성 꼬리(hydrophobic tails)간의 상호작용에 의하여 S-형 모양을 보이며 이들 흡착된 계면활성제는 Micelle로 존재하는 계면활성제에 비하여 유기오염물에 대한 보다 강한 흡수능력을 나타내었다. 결과에 나타난 흡수능력의 차이는 계면활성제가 흡착되어있거나 Micelle상태로 존재할 경우 다른 구조를 형성하기 때문이라 사료된다. 흡수된 계면활성제와 Micelle의 상호경쟁에 의하여 유기오염물의 부동성(immobility)을 나타내는 분배계수(distribution coefficient)는 계면활성제의 농도에 반비례하였다. 결론적으로 토양/지하수의 오염물 정화를 위하여 계면활성제 교정기술의 적용 시 고정상(solid phase)에 있는 흡착 계면활성제에 의한 유기오염물의 지체현상(retardation)을 고려하여야 한다.

Key Words : Micellar partition coefficient, equilibrium surfactant sorption, HOC partitioning to sorbed surfactant, HOC distribution coefficient

1. INTRODUCTION

The widespread occurrence of hydrophobic organic contaminants (HOCs) in soils and groundwaters has led to intensive studies of the mobility and fate of these compounds in subsurface environments and of their potential remediation. Because of their low solubilities and slow dissolution/desorption rates, HOCs are typically associated with solid surfaces and thus are difficult to remove from subsurface environments with traditional technologies such as groundwater pump-and-treat systems. *In-situ* surfactant-enhanced remediation (SER) utilizing HOC solubility enhancement by surfactant micelles has been suggested as an economically and technically feasible

remediation approach¹⁾⁻⁴⁾. Although surfactants can form a mobile micellar pseudophase and lead to the facilitated transport of solubilized HOCs, they can also be adsorbed by the solid matrix and thereby lead to HOC partitioning to immobile sorbed surfactants and thus, enhanced HOC retardation. Additionally, the sorption of surfactants to subsurface solids leads to an overall higher operating cost because of material losses.

HOC partitioning to micelles and sorbed surfactants may show different characteristics depending on the distribution of surfactant in each phase. Quantitative evaluations of SER processes in terms of costs and efficiency must consider the distribution of surfactant in dissolved and solid (i.e., mobile and immobile, respectively) phases and the subsequent partitioning of HOCs to each phase. Otherwise, the end result may be an over- or under-estimation of SER effectiveness caused by inaccurate predictions of surfactant and HOC transport.

The objectives of this first paper are to (1) study the equilibrium sorption characteristics of an anionic surfactant and nonionic surfactant to a model subsurface soil, (2) examine the partitioning of two HOCs to the adsorbed surfactants within the context of the first objective, and (3) develop overall HOC distribution coefficients that consider sorbed surfactant amounts and the presence of micelles as a function of surfactant dose. Results from this study can then be used to elucidate the role of sorbed surfactants in HOC partitioning and to evaluate HOC removal efficiencies in SER applications.

II. MATERIALS AND METHODS

1. Materials.

The HOCs used in this study were phenanthrene (Aldrich, 99.5+%) and naphthalene (Aldrich, 99+%). An anionic surfactant, sodium dodecyl sulfate (SDS), was obtained from Sigma (99.5+% purity) and used as received. A nonionic surfactant, polyoxyethylene (20) sorbitan monooleate (trade name: Tween 80) was obtained from Aldrich (no purity was reported) and used as received. Kaolinite (Sigma) was used as the model soil without additional treatment.

2. Analytical Methods.

Aqueous phenanthrene and naphthalene concentrations were quantified using a fluorescence spectrophotometer (Photon Technology International). The excitation/emission wavelengths (nm/nm) used were 250/364 and 278/322 for phenanthrene and naphthalene, respectively. The slits were set for bandwidths of 4 nm on the excitation side and 0.5 nm on the emission side. A total organic carbon (TOC) analyzer equipped with an autosampler (low temperature combustion type, Shimadzu Model 5050) was used to determine SDS concentrations in aqueous solutions. Tween 80 concentrations were determined by UV absorbance at the wavelength of 234 nm⁴⁾. Other detailed experimental methods on the HOC micellar solubilization, surfactant sorption and HOC partitioning to sorbed surfactants are described in Ref. 5.

III. RESULTS AND DISCUSSION

1. Micellar Solubilization of HOCs.

The general results show that the more hydrophobic compound, phenanthrene, has a larger partition coefficient than naphthalene and that the nonionic surfactant (Tween 80) has larger K_{mic} values than does the anionic surfactant (SDS), agreeing with observations in previous studies^{1), 6), 7)}.

2. Surfactant Sorption on Kaolinite.

SDS sorption isotherms exhibited the characteristic S-shaped curves as shown in Fig. 1. In region II, the sharp rise in the isotherm indicates the association between SDS molecules at the surface, presumably through lateral interactions of their hydrophobic tails, and the formation of hemimicelles and/or admicelles. The leveling-off of sorption that occurs in region III corresponds to either an increase in electrostatic repulsion between the anionic head groups, complete surface coverage, and/or the attainment of a constant surfactant monomer concentration in the aqueous phase. It is noteworthy that the sorption of SDS begins to level out near its critical micelle concentration (CMC), but that the isotherm becomes flat only above the CMC.

Tween 80 sorption to kaolinite also shows a high degree of nonlinearity and an S-shaped curve; however, most of the sorption occurs above the CMC (Figure 1). Tween 80 results also show a continuation of sorption well beyond the CMC; in fact, only one data point fell below the CMC (Figure 1). Similarly to SDS sorption, the Tween 80 isotherm region exhibiting very low sorption amounts most likely has only moderately favorable conditions for sorbate-sorbent interactions and the steeper isotherm region results from interactions between adsorbed surfactant molecules that form hemimicelles and/or admicelles.

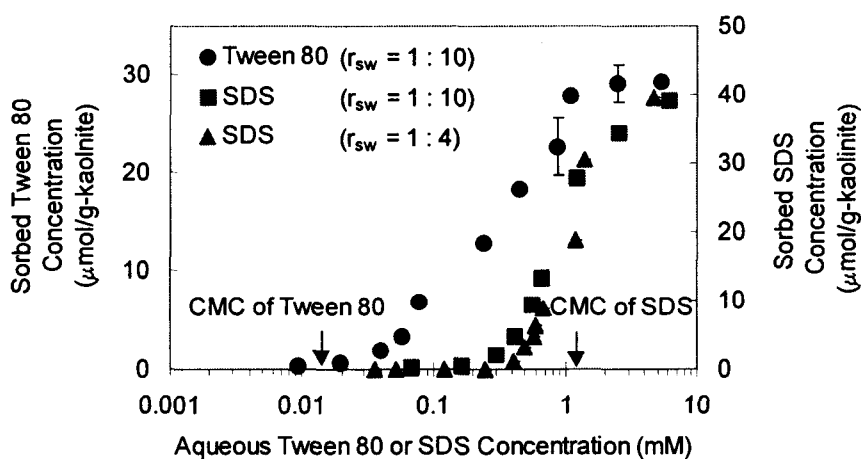


Figure 1. Surfactant sorption isotherm on kaolinite (pH 4.6, I.S. = 0.1M)

3. HOC Partitioning to Sorbed Surfactants.

HOC partitioning between immobile and mobile phases as a function of aqueous surfactant concentration is shown in Fig. 2. At low surfactant concentrations, K_D values increased with increasing sorbed surfactant concentration. As the aqueous phase concentration increases and thus competes with sorbed surfactant, the K_D values are decreasing. Results for HOC partitioning in the presence of sorbed surfactant and micelles demonstrate that large differences can exist in the HOC sorption capacity of surfactant aggregates in micellar versus sorbed forms. This can be seen quite readily by calculating sorbed surfactant partition constants as a function of surfactant dose from the experimental HOC distribution coefficients. The distribution coefficient defines the HOC mass balance and can be expressed as:

$$K_D = \frac{C_{immob}}{C_{mob}} = \frac{S_{sorb} K_{ss} + K_{min}}{1 + S_{mic} K_{mic}}$$

where C_{immob} (mol/g-kaolinite) and C_{mob} (mol/L) are the immobile and mobile HOC concentrations, respectively, S_{sorb} is the sorbed surfactant concentration (mole/g-kaolinite), and K_{min} (L/g-kaolinite) is the HOC sorption constant to the bare kaolinite surface. From our previously-determined values for micellar solubilization (K_{mic}), surfactant distribution (S_{sorb} and S_{mic}) and HOC sorption to kaolinite (K_{min}), HOC partition coefficient to sorbed surfactant, K_{ss} , can be calculated for each distribution data point.

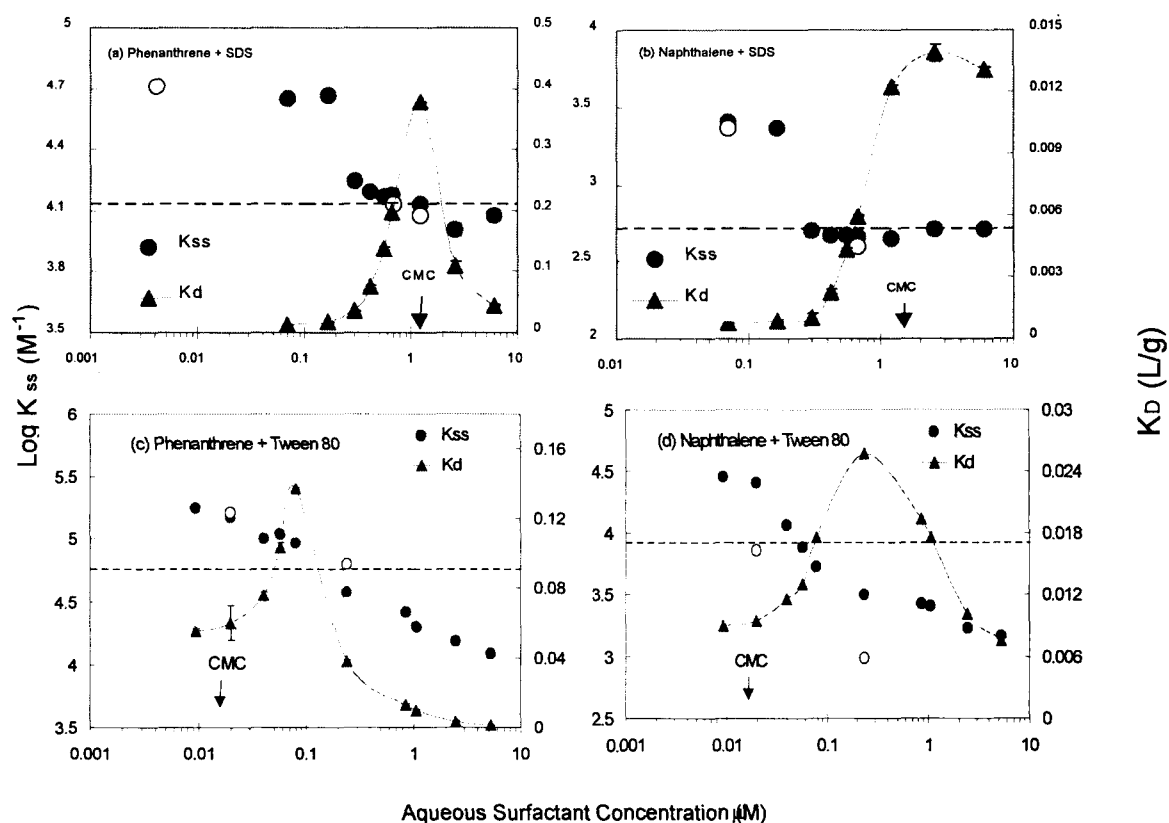


Figure 2. HOC distribution and sorbed surfactant partition coefficients

In all cases, K_{ss} values were larger for the more hydrophobic HOC (phenanthrene) and for the nonionic surfactant (Tween 80). For both SDS and Tween 80, the average K_{ss} values calculated for phenanthrene and naphthalene were always larger than the K_{mic} values at equivalent HOC concentrations. Presumably it results from geometric differences between sorbed and dissolved surfactant aggregate structures. From a practical standpoint, the higher affinity for HOCs exerted by the sorbed surfactants will adversely affect SER applications and will require higher surfactant doses to achieve the target removal efficiency.

IV. CONCLUSION

In any evaluation of SER applications, surfactant doses that decrease the distribution coefficient below that without surfactant addition must be quantified. Very often, only one partition coefficient value for HOC partitioning to sorbed surfactants has been reported in the literature, presumably because that experimental sorption data mainly covers the sorption regions where the surfactant molecule interactions dominate at the surface. However, all of the characteristic sorption regions will develop during an *in-situ* SER application as the surfactant front (i.e., mass transfer zone) advances through the porous medium. Therefore, in addition to the adverse effect of sorbed surfactant on the retardation of HOC transport, the relative role of regional HOC partition coefficients to sorbed surfactant should also be considered in SER processes. Also, the solid-to water ratio (or porosity) for the particular subsurface system must be taken into account when the surfactant sorption is quantified.

REFERENCES

- 1) Kile, D.E. and Chiou, C.T., Water solubility enhancement of DDT and trichlorobenzene by some surfactant below and above the critical micelle concentration. *Environ. Sci. Technol.* 23, pp832-838 (1989).
- 2) Abdul, A.S., Gibson, T.L. and Rai, D.N. Selection of surfactant for the removal of petroleum products from shallow sandy aquifers. *Ground Water*, 28, pp920-926 (1990).
- 3) Diallo M.S., Abriola, L.M. and Weber W.J. Solubilization of nonaqueous phase liquid hydrocarbons in micellar solutions of dodecyl alcohol ethoxylates. *Environ. Sci. Technol.* 28, pp 1829-1837 (1996)
- 4) Pennell, K.D., Abriola, L.M. and Weber, W.J. Surfactant-enhanced solubilization of residual dodecane in soil columns: 1. experimental investigation. *Environ. Sci. Technol.* 27, pp2332-2340 (1993).
- 5) Ko, S.-O. Electrokinetic/Surfactant-Enhanced Remediation of Hydrophobic Organic Contaminants in Low Permeability Subsurface Environment, Ph.D. Dissertation, Texas A&M University, College Station, Texas (1998).