Partitioning effects of nonionic surfactants on the solubilization of single or binary chlorinated solvents: Batch and column experiments

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ABSTRACT

The interaction between surfactants and a dense non-aqueous phase liquid (DNAPL) was investigated. The partitioned amounts of nonionic surfactants to the DNAPL increased with an increase in the surfactant hydrophobicity and a decrease in the interfacial tension. Alcohol enhanced the surfactant loss. With the binary component of the DNAPL, the molar micellar solubilization was not ideal, and the solubilized extent of DNAPL with binary components by the surfactant was larger than with a single component. In surfactant flushing for a DNAPL contaminated sand column, the small amount of partitioned surfactant to the DNAPL facilitated the mobilization of the DNAPL.

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Introduction

Contamination by organic pollutants, such as chlorinated solvents in the subsurface, has been a serious problem [1,2]. They are very toxic to humans and mostly nonbiodegradable. Also, chlorinated solvents form a class of dense non-aqueous phase liquids (DNAPLs), and they make a pool in the bottom of aquifers [3]. Therefore, they are a continuous source of aquifer contamination.

Various technologies, such as thermal treatments, chemical oxidation, soil vapor extraction, bioremediation, the pump and treat method, and surfactant flushing, have been applied to remove chlorinated solvents from the subsurface [2]. The traditional pump and treat method has been proven ineffective because of the low solubility and high density of chlorinated solvents, and a long time is needed for complete removal [4]. Among the various technologies, surfactant flushing, called surfactant enhanced aquifer remediation (SEAR), has been applied as an alternative to the pump and treat method and is the most feasible technology to recover the chlorinated solvents from aquifers [1,4]. This technology enhances DNAPL removal through injection and the subsequent extraction of surfactant solutions.

Surfactant molecules have a hydrophilic head and a hydrophobic tail. At above a certain concentration (critical micellar concentration, CMC), surfactant molecules form micelles that can incorporate the hydrophobic part of the surfactant in their interior and increase the apparent solubility of organic compounds. The process of dissolving organic compounds by incorporation into micelles is termed solubilization. Another characteristic of the surfactant is the concentration of the surfactant molecules in the interface between the DNAPL and water, and it decreases the interfacial tension (IFT). The reduced IFT leads to the mobilization of the DNAPL in the soil pore, and the DNAPL can be removed rapidly. However, the mobilized DNAPL leads to the contamination of the pristine aquifer unless there is a fully impermeable layer below the source zone because the DNAPL is denser than water [2]. The main factor causing solubilization or mobilization is a formulation of surfactant solutions, and surfactant selection is an essential point for proper surfactant formulation. The proper surfactant has been selected by the batch and column test, but the surfactant partitioning was not considered as much. The partitioning of the surfactant to the DNAPL underestimated the solubilization power of the surfactant and the possibility of the occurrence of mobilization. Therefore, experiments of micellar solubilization with surfactant partitioning are needed for the accurate prediction of surfactant flushing.

Several researchers have conducted a partitioning experiment in a water/non-aqueous phase liquid (NAPL) system with batch and column systems. Zimmerman et al. [5] reported that the amount of partitioning of the surfactant to NAPL is significant and that the

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solubilization of NAPL was obtained by considering surfactant partitioning. Cowell et al. [6] reported that the IFT between water and NAPLs and the CMC of the surfactant have some relation to the amount of partitioning of nonionic surfactants. Zhao et al. [7,8] found that, in partitioning in water/chlorinated compounds systems with mixed surfactants, the amount of partitioning of the nonionic surfactant decreased in the presence of anionic surfactants, and the solubilized NAPLs in the micelles increased. In a column test, Bao et al. [9] suggested that the loss of nonionic surfactants to tetrachloroethylene (PCE) led to the delay of PCE solubilization. Park and Bielefeldt [10] found similar results in the solubilization of pentachlorophenol in mineral oil by alkylphenol ethoxylated nonionic surfactants. Sharmin et al. [11] tested the dynamic analysis of the solubilization of PCE with octylphenol ethoxylated nonionic surfactants in a column, and they also found the delay of PCE dissolution.

The partitioning of surfactant to DNAPL affects the mobilization and the solubilization or dissolution. The amount of partitioning of the surfactant on the DNAPLs is large, and it influences the DNAPL removal mechanisms [6]. The amount of surfactant lost to the DNAPL can be orders of magnitude greater than the surfactant lost due to sorption on soils. Additionally, surfactant solutions contain surfactant, co-solvents such as ethanol or butanol, and electrolytes [12]. Most contaminated sites do not contain pure component DNAPL but multi-component DNAPL. Therefore, studying the partitioning of surfactant in a water/DNAPL system in the presence of a co-solvent and multi-component DNAPL is needed for the successful application of surfactant flushing.

The objectives of this study were to understand the surfactant partitioning effect between water and DNAPL in batch tests based on the surfactant characteristics. Using a series of nonionic surfactants, the phenomenon of the partitioning of the surfactant in single and binary components DNAPL was observed to elucidate the removal mechanism of chlorinated solvents from porous media using batch and one-dimensional column experiments. The specific objectives are as follows: (1) determine the partitioning behavior of nonionic surfactants into DNAPL, (2) elucidate the solubilization mechanism of chlorinated solvents in micelle by quantifying the molar and volume contributions of chlorinated solvents in surfactant micelle in the solubilization process, (3) determine the alcohol effect on surfactant flushing, and (4) monitor the chlorinated solvents and surfactant concentration in the effluent using a 1-D column.

Materials and methods

Chemicals

Trichloroethylene (TCE), perchloroethylene (PCE), 1-chlorobenzene (MCB), 1,2-dichlorobenzene (DCB), and Triton X (TX) series surfactants were purchased from Sigma-Aldrich Co., Ltd. (St. Louis, MO, USA). TX series are the nonionic surfactant of octhylphenol polyethoxylate with a different number (9.5–30) of ethoxylated chains. The selected properties of the chlorinated solvents and surfactants are summarized in Tables 1 and 2, respectively. Methanol (HPLC grade) was purchased from Merck (Darmstadt, Germany). All other chemicals were purchased from Sigma-Aldrich Chemical and used as received without further purification. Deionized water was prepared by a Millipore water purification system (Branford, MA, USA).

Surfactant partitioning in the batch experiment

Partitioning experiments were conducted by adding 0.5 mL of NAPLs and 10 mL of surfactant solution into a borosilicate glass centrifugal vial with a Teflon lined cap (DAIHAN scientific, Korea).

Table 1
Selected properties of the chlorinated solvents used in this study.

NAPL	MW[a]	Density[b]	Solubility[c]	log K_{ow}[d]	IFT[e]
TCE	131.3	1.464	100	2.42	34.5
PCE	165.8	1.623	9.1	2.88	47.5
MCB	112.6	1.107	43	2.92	39.4
DCB	147.0	1.306	11	3.38	40.1

[a] Molecular weight (g/mol).
[b] Density (g/cm^3).
[c] Aqueous solubility (10^{-4} mol/L).
[d] Octanol/water partitioning coefficient.
[e] Interfacial tension (dynes/cm).

Table 2
Selected properties of the surfactants used in the solubilization and partitioning experiments[a].

Surfactant[b]	Formula[c]	av. MW[d]	HLB[e]	CMC[f]
TX100	$C_8PE_{9.5}$	624.4	13.4	130
TX102	C_8PE_{12}	734.5	14.4	140
TX165	C_8PE_{16}	910.6	15.5	360
TX305	C_8PE_{30}	1526.9	17.3	790

[a] All values were obtained from the product information of Dow Chemical Co.
[b] A series of octhylphenol polyethoxylate.
[c] C: alkyl chain (CH_2), P: phenol group (C_6H_4O), and E: ethoxylated chain (OCH_2CH_2).
[d] Average molecular weight (g/mol).
[e] Hydrophilic-hydrophobic balance.
[f] Critical micellar concentration in distilled water at 25 °C (mg/L).

After shaking in a rolling drum shaker (Vision Scientific, Korea) at 25 °C for 3 days, which was enough time to reach equilibrium, the vial was centrifuged at 5000 rpm for 1 h using a high-speed centrifuge (Hanil Science Inc., Korea) to separate the NAPL from the aqueous phase. The supernatant was transferred and diluted for analysis by high-performance liquid chromatography (HPLC). In some experimental sets, the phases after centrifugation were not separated clearly, and cloudy mesophases formed. Because the mesophases were primarily oil-in-water macroemulsions with surfactant compositions very similar to the bulk NAPL, the oil-in-water emulsion was treated as part of the DNAPL [5]. Each batch experiment was performed in triplicate, and the average values were reported.

Column experiment

A one dimensional flushing experiment was performed in the column (25.4 × 150 mm, Kontes, USA) with Jumunjin filtration sand (Jumumjin Silica Sand Co., Korea), which has the following properties: density, 2.46 g/mL; bulk density, 1.39 g/mL; porosity, 0.42–44; organic contents, 0.41%; and size, 20–30 mesh. The column was filled with 115–120 g sand, and the pore volume (PV) of the sand column was 31.9–33.8 mL. The experimental conditions can be found in Table S1 in the Supporting Information. Initially, deionized water of more than 20 PV flowed at a flow rate of 1 mL/min from the bottom to the top of the column to remove the remaining air. Then, the contamination was carried out by injecting the target pollutants, 1 PV of TCE and/or PCE, with a flow rate of 1 mL/min from the bottom of the column. After the contamination, 10 PV of deionized water was flushed in the reverse direction, from top to bottom, to remove the mobile free pollutants. For surfactant flushing, 40 g/L of the surfactant solutions flowed in the horizontal direction of the column at 1 mL/min.

To observe the possibility of mass transfer limitation, another one-dimensional flushing experiment was performed in a large column (46 mm × 150 mm, Kontes, USA). The column was filled with approximately 400 g of sand, and the PV of the column was