J. Chem. Eng. Data **2003,** *48*, 253−261

Measurement and Estimation of Henry's Law Constants of Chlorinated Ethylenes in Aqueous Surfactant Solutions

Tsutomu Shimotori and William A. Arnold*

Department of Civil Engineering, University of Minnesota, 500 Pillsbury Dr. SE, Minneapolis, Minnesota 55455

Henry's law constants of tetrachloroethylene, trichloroethylene, *cis*-dichloroethylene, and *trans*-dichloroethylene in air−aqueous surfactant systems were experimentally determined by the equilibrium partitioning in closed systems method. Polyoxyethylene (10) octylphenol, sodium dodecyl sulfate, and cetyltrimethylammonium bromide were used as surfactants. The effects of temperature and surfactant concentration were investigated, and the results demonstrated that the Henry's law constants increased as temperature was increased and decreased as surfactant concentration was increased. The decrease in the Henry's law constants became obvious above the critical micelle concentration. The effect of surfactant addition on the Henry's law constant was larger for the more hydrophobic species. The micelle−water partitioning coefficients (K_{mw}) for the chlorinated ethylene-surfactant pairs were estimated from the Henry's law constants. The values of K_{mw} estimated from the Henry's law constants at high surfactant concentrations had a small standard error. On the basis of the experimental data, equations to estimate Henry's law constants in air−aqueous surfactant systems as a function of temperature and surfactant concentration were constructed. All of the equations estimated the experimental data with R^2 values above 0.96.

Introduction

Contamination of groundwater and sediments by chlorinated ethylenes is recognized as a serious environmental problem.[1, 2] Used in dry-cleaning and degreasing operations, these chemicals are commonly found in the environment as a result of spillage or poor disposal practices. These compounds are known to cause health problems such as liver and kidney disorders and are suspected carcinogens.[3] They are listed as priority pollutants, and the Safe Drinking Water Act set maximum contaminant levels of 5 $\mu g \cdot L^{-1}$ for tetrachloroethylene and trichloroethylene.[4] Moreover, once released into the environment, chlorinated ethylenes persist in the subsurface via formation of dense nonaqueous phase liquid pools at the bottom of aquifers because of their low aqueous solubility and high density.[2,5,6] The dense nonaqueous phase liquid pools dissolve slowly and thus continually contaminate passing groundwater.

Pump and treat systems and soil vapor extraction are the most common remediation options to remove the contaminants from saturated and unsaturated zones, respectively. It has been demonstrated that these technologies alone are often impracticable because of the compounds' low aqueous solubility or strong binding to the soil.[2,7,8] To facilitate solubilization and mobilization of dense nonaqueous phase liquid pools, surfactant[2,9−19] or alcohol flushing[2,10,20−23] and heating the subsurface with electrical current[24] or hot fluid[25] have been proposed. Among these, surfactant flushing is currently drawing the attention of many investigators.

The solubility of hydrophobic compounds dramatically increases when the surfactant concentration exceeds the critical micelle concentration.[26−31] Above the critical micelle concentration, surfactants form aggregates of molecules, micelles. In micelles, aggregated surfactant molecules direct their hydrophobic tail inward and hydrophilic head outward.[11,30] Thus, the interior regions of micelles provide a hydrophobic environment into which chlorinated ethylenes preferentially partition, resulting in an increase in the solubility of the chlorinated ethylenes in the solution phase. The partitioning of a solute between the interior and exterior of micelles is governed by the micelle−water partitioning coefficient, K_{mw}.[27, 32] The addition of surfactant also affects gas-solution partitioning, thus changing the Henry's law constant.

These changes in partitioning of contaminants may greatly influence the efficiency of contaminant removal by the subsurface flushing. Knowledge about K_{mw}, therefore, is important in saturated zones, whereas both K_{mw} and Henry's law constants are important in unsaturated zones. After the aqueous surfactant solution is used for flushing, it must be pumped up and treated above ground to remove the contaminants (secondary treatment) so that the water containing the surfactant can be discharged or recycled. The recycle of the used surfactant solutions is important to lower the cost of remediation.[33] The techniques to separate the contaminants from the aqueous surfactant solution include liquid−liquid extraction,[34,35] steam stripping,[33] air stripping,[36] vacuum stripping,[37] and pervaporation.[38,39] The latter four techniques employ principles of gas−solution partitioning, and the Henry's law constant, therefore, is an important design parameter. Increasing the temperature of the solution may enhance the efficiency of subsurface flushing and the secondary treatment. Thus, information regarding K_{mw} and Henry's law constants over a wide range of temperatures is useful.

Although many studies have been performed to determine the Henry's law constants of chlorinated ethylenes, most are limited to the air−water system and narrow temperature ranges.[40−44] Only recently, Vane and Giroux[45]

---

* To whom correspondence should be addressed. E-mail: arnol032@tc.umn.edu. Phone: 1-612-625-8582. Fax: 1-612-626-7750.

10.1021/je025553z CCC: $25.00

extensively studied the effect of surfactants on the Henry's law constants of tetrachloroethylene and trichloroethylene. On the basis of the recognition that additional investigations are needed on this topic, this work provides experimentally determined Henry's law constants of chlorinated ethylenes in air−aqueous surfactant systems and estimated K_{mw} values from the Henry's law constants. This study focused on four chlorinated ethylenes (tetrachloroethylene, trichloroethylene, *cis*-dichloroethylene, *trans*-dichloroethylene), a wider range of temperatures (2 to 70) °C, and a larger range of surfactant concentrations (up to 200 times of the critical micelle concentration) than previously studied. In addition, regression equations for predicting Henry's law constants at a given temperature and surfactant concentration were developed.

Theory

Definition of the Henry's Law Constant and the Micelle−Water Partitioning Coefficient. The conventional Henry's law constant is defined for the air−water system

$$H \equiv \frac{C_{\mathrm{air}}}{C_{\mathrm{water}}} \qquad \left(\frac{\mathrm{mol{\cdot}L^{-1}\ in\ air}}{\mathrm{mol{\cdot}L^{-1}\ in\ water}}\right) \tag{1}$$

where C_{air} and C_{water} are the solute concentration in the air and the water phase, respectively. The Henry's law constant in an air-aqueous surfactant system is defined as follows:

$$H_{\mathrm{app}} \equiv \frac{C_{\mathrm{air}}}{C_{\mathrm{soln}}} = \frac{C_{\mathrm{air}}}{C_{\mathrm{ex}} + C_{\mathrm{mic}}} \qquad \left(\frac{\mathrm{mol{\cdot}L^{-1}\ in\ air}}{\mathrm{mol{\cdot}L^{-1}\ in\ solution}}\right) \tag{2}$$

C_{soln} is the solute concentration in the solution phase. Note that C_{soln} is a sum of the solute's extramicellar phase concentration (C_{ex}) and micellar phase concentration (C_{mic}). These three concentrations refer to the same solution volume. An extramicellar phase is defined as a solution environment outside of the micelles. This definition of Henry's law constant is often regarded as the "apparent" Henry's law constant. For simplicity, both "apparent" Henry's law constants and conventional Henry's law constants are called Henry's law constants in this work unless a special emphasis is needed to distinguish the two definitions. Experimentally determined Henry's law constants in this study are all expressed in the form of eq 2.

It is reasonable to assume that the ratio $C_{\mathrm{air}}/C_{\mathrm{ex}}$ is constant and equal to the conventional Henry's law constant regardless of the total surfactant concentration

$$\frac{C_{\mathrm{air}}}{C_{\mathrm{ex}}} \cong H \qquad \left(\frac{\mathrm{mol{\cdot}L^{-1}\ in\ air}}{\mathrm{mol{\cdot}L^{-1}\ in\ solution}}\right) \tag{3}$$

The support for this assumption comes from our finding that surfactant addition below the critical micelle concentration does not affect the Henry's law constant. Note that the surfactant concentration in an extramicellar phase does not exceed the critical micelle concentration at any total surfactant concentration. Surfactant addition beyond the critical micelle concentration increases C_{mic} in eq 2 because the number of micelles increases, whereas the ratio $C_{\mathrm{air}}/C_{\mathrm{ex}}$ remains constant. Thus, the Henry's law constant is expected to decrease with increasing surfactant concentration above the critical micelle concentration.

Table 1. Critical Micelle Concentration Values for the Three Surfactants Used in This Study[a]

	Triton X-100		SDS		CTAB	
t/°C	10^{-3} mol·L^{-1}	g·L^{-1}	10^{-3} mol·L^{-1}	g·L^{-1}	10^{-3} mol·L^{-1}	g·L^{-1}
10			8.67	2.50		
15	0.330	0.0826	8.43	2.43		
20			8.25	2.38		
25	0.323	0.0809	8.16	2.35	0.920	0.335
30			8.23	2.37		
35	0.303	0.0759	8.39	2.42	1.020	0.372
40			8.60	2.48		
45	0.280	0.0701	8.86	2.56	1.155	0.421
50			9.18	2.65		
55	0.290	0.0726	9.61	2.77	1.320	0.481
60			10.16	2.93		
65	0.300	0.0751	10.91	3.15		
75	0.312	0.0781				
85	0.338	0.0846				

[a] Values are from ref 46.

The micelle-water partitioning coefficient, K_{mw}, is often defined as a ratio of a mole fraction of solute in micelles to that in the extramicellar phase[27, 32]

$$K_{\mathrm{mw}} \equiv \frac{\text{mole fraction of solute in micelles}}{\text{mole fraction of solute in extramicelar phase}} = \frac{\dfrac{N^{\mathrm{sol}}_{\mathrm{mic}}}{N^{\mathrm{sf}}_{\mathrm{mic}} + N^{\mathrm{sol}}_{\mathrm{mic}}}}{\dfrac{N^{\mathrm{sol}}_{\mathrm{ex}}}{N^{\mathrm{w}}_{\mathrm{ex}} + N^{\mathrm{sf}}_{\mathrm{ex}} + N^{\mathrm{sol}}_{\mathrm{ex}}}} \cong \frac{\dfrac{N^{\mathrm{sol}}_{\mathrm{mic}}}{N^{\mathrm{sf}}_{\mathrm{mic}}}}{\dfrac{N^{\mathrm{sol}}_{\mathrm{ex}}}{N^{\mathrm{w}}_{\mathrm{ex}}}} \tag{4}$$

where N is the number of moles. The subscripts mic and ex represent the micellar and extramicellar phases, respectively, and the superscripts sol, sf, and w designate the solute, surfactant, and water molecules, respectively. The micelle−water partitioning coefficient is expected to be independent of the surfactant concentration because it is normalized by the number of surfactant molecules.

Estimation of Micelle−Water Partitioning Coefficients. Incorporating eqs 2 and 3 into eq 4 and subsequent mathematical manipulation gives the following relationship between H_{app}, H, and K_{mw} (see the Supporting Information for details):

$$K_{\mathrm{mw}} = \frac{M_{\mathrm{L}}\left(\dfrac{H}{H_{\mathrm{app}}} - 1\right)}{S - S_{\mathrm{CMC}}} \qquad \left(\frac{\text{mole fraction of solute in micelles}}{\text{mole fraction of solute in extramicellar phase}}\right) \tag{5}$$

where M_{L} is the molar concentration of water = 55.5 mol·L^{-1}, S is the total surfactant concentration in mol·L^{-1}, and S_{CMC} is the critical micelle concentration in mol·L^{-1}. The effect of temperature on the volume of water, which is at most 2%, was not considered for M_{L} and S. In this study, K_{mw} values were estimated via eq 5. Experimentally determined Henry's law constants were smoothed via regression using a van't Hoff-type equation before being used in eq 5 in order to remove scatter in the values and allow estimation of K_{mw} over a continuous temperature range (see the Supporting Information for details). Critical micelle concentrations used in this study were obtained from a database[46] and are summarized in Table 1.

Equation to Estimate Henry's Law Constants. It is desirable to have a single equation which estimates the Henry's law constant for a given chlorinated ethylene−

surfactant pair, temperature, and surfactant concentration. A simple transformation of eq 5 results in the following equation:

$$H_{\text{app}} = \frac{H}{\dfrac{K_{\text{mw}}(S - S_{\text{CMC}})}{M_{\text{L}}} + 1}\left(\frac{\text{mol}\cdot\text{L}^{-1}\text{ in air}}{\text{mol}\cdot\text{L}^{-1}\text{ in solution}}\right) \quad (6)$$

In this equation, H, K_{mw}, and S_{CMC} are independent of the surfactant concentration but depend on temperature (T [K]). This implies that H_{app} will be a single function of T and S if the three terms are expressed as a function of T. By assuming a van't Hoff-type behavior for the temperature dependence of H,[47] K_{mw},[45] and S_{CMC},[48] the following equation results:

$$H_{\text{app}} = \frac{e^{A_1+(B_1/T)+C_1\ln T}}{\dfrac{e^{A_2+(B_2/T)+C_2\ln T}(S - e^{A_3+(B_3/T)+C_3\ln T})}{M_{\text{L}}} + 1}\left(\frac{\text{mol}\cdot\text{L}^{-1}\text{ in air}}{\text{mol}\cdot\text{L}^{-1}\text{ in solution}}\right) \quad (7)$$

where A_1, B_1, C_1, A_2, B_2, C_2, A_3, B_3, and C_3 are regression constants. To obtain these constants, H, K_{mw}, and S_{CMC} were regressed independently. Each regression gave three constants, and the obtained constants were incorporated into eq 7 (see the Supporting Information for details). This equation itself, therefore, is not a regression equation.

Experimental Section

Chemicals. All chemicals described below were used as received. Aqueous solutions with different concentrations of polyoxyethylene (10) octylphenol (Triton X-100; 100%, LabChem Inc.), sodium dodecyl sulfate (SDS; 99%, Sigma), and cetyltrimethylammonium bromide (CTAB; 99%, Aldrich) were prepared with Milli-Q (Millipore) water. The surfactant concentrations investigated were (0.13, 0.65, 1.30, 6.50, 13.0, and 26.0) g·L^{-1} for Triton X-100, (2.38, 4.76, 11.9, 23.8, and 47.6) g·L^{-1} for SDS, and (0.36, 0.72, 1.81, 3.61, and 7.22) g·L^{-1} for CTAB. Sahoo et al.[18] injected 0.4 g·L^{-1} of Triton X-100 into groundwater in a surfactant enhanced remediation field experiment and observed concentrations near 0.1 g·L^{-1} from monitoring wells. In this study, a range of concentrations including values both below and above the critical micelle concentration was tested so that the results may help in further developing surfactant based remediation techniques. A methanol (HPLC grade, Pharmco) spiking solution containing tetrachloroethylene (Spectro grade, Kodak), trichloroethylene (A. C. S. grade, Fisher), *cis*-dichloroethylene (97%, Aldrich), and *trans*-dichloroethylene (98%, Aldrich) was prepared. The concentration of each chlorinated ethylene in the spiking solution was 80 mmol·L^{-1}.

Experimantal Procedures. In this study, the equilibrium partitioning in closed systems method[41,47,49] was used to determine the Henry's law constants. For each experimental condition (i.e., a specific surfactant, surfactant concentration, and temperature combination), five headspace vials (21.6 mL average volume; Chromocol) with different volumes (2, 4, 6, 8, and 10) mL of the surfactant solution were prepared. Each vial was spiked with 5 μL of the spiking solution, and the vial was quickly sealed with a Teflon faced butyl rubber septum and an aluminum crimp cap (Chromtech). The syringe was weighed before and after the injection to determine the mass of the spike solution injected. Concentrations of the chlorinated ethylenes varied from (40 to 200) μmol·L^{-1} each depending on the surfactant solution volume. This concentration range is dilute enough to use eq 2 instead of an activity ratio.[50] The methanol introduced by the spike has been shown to have no effect on the measured Henry's law constant.[41] Although a mixture of the four chlorinated ethylenes was used, experiments using only trichloroethylene confirmed that the measured Henry's law constants of trichloroethylene are the same whether the mixed spike or single component spike was used.

To allow complete equilibration at the desired temperatures, at least 30 min were allowed between the preparation and the sampling of the vials. Vane and Giroux[45] reported that 15 min were sufficient to achieve equilibrium of chlorinated ethylenes in air−aqueous surfactant systems. The vials were left at ambient temperature (~22 °C) for the experiments at room temperatures, and they were cooled in a refrigerator with a water bath for the experiments at refrigerated temperatures (~2 °C). In these experiments, the vials were shaken intermittently by hand. Henry's law constants in SDS and CTAB solutions were not measured at refrigerated temperatures because these surfactants crystallized at temperatures below about 10 °C. For the experiments at (40.0, 50.0, 60.0, and 70.0) °C, the vials were shaken in a constant-temperature incubation chamber by a programmed headspace autosampler (HS2000, ThermoQuest).

After the equilibration at the desired temperature, 200 μL of the headspace gas was withdrawn from the vial with a syringe and analyzed by a gas chromatograph (TraceGC, ThermoQuest) with a GS-GasPro column (J&W Scientific), an FID detector, and a split/splitless injector. For the experiments at (40.0 to 70.0) °C, samples were automatically withdrawn and injected by the autosampler after the incubation period. The autosampler syringe was heated to the incubation temperature. For the experiments at refrigerated and room temperatures, sampling and injection were performed manually.

Results and Discussions

Henry's Law Constants. Table 2 lists the experimentally determined Henry's law constants for tetrachloroethylene, trichloroethylene, *cis*-dichloroethylene, and *trans*-dichloroethylene in Triton X-100, SDS, and CTAB aqueous solutions. A comparison between Henry's law constants determined in this work and those reported by Vane and Giroux[45] (Table 3) shows that these values are similar.

In the error analysis of the Henry's law constants, 95% confidence limits based on replicates were determined by the Student's *t*-method. The relative errors of the Henry's law constants are larger at the refrigerated temperatures and at 70.0 °C. This is true for all of the chlorinated ethylene−surfactant pairs and consistent with the results of other investigators.[41,45,47]

Overall, Henry's law constants increase with increasing temperature and decrease with increasing surfactant concentration. Near or below the critical micelle concentration of each surfactant (0.13 g·L^{-1} for Triton X-100, 2.38 g·L^{-1} for SDS, and 0.36 g·L^{-1} for CTAB), Henry's law constants are not statistically different from those for water. These observations are common to all four chlorinated ethylenes.

Figure 1 shows the ratio of "apparent" Henry's law constants to conventional Henry's law constants in aqueous SDS solutions at 40 °C. It is clear that the more hydrophobic solutes are more susceptible to the surfactant addition. For example, at the highest surfactant concentra-

Table 2. Henry's Law Constants for Chlorinated Ethylenes in Aqueous Surfactant Solutions

	surfactant conc		H_{app}			
t/°C	g·L^{-1}	n[a]	tetrachloroethylene	trichloroethylene	*cis*-dichloroethylene	*trans*-dichloroethylene
			Triton X-100			
2.8	0.13	6	0.27 ± 0.02[b]	0.16 ± 0.00	0.09 ± 0.01	0.17 ± 0.02
24.0		10	0.70 ± 0.03	0.39 ± 0.02	0.16 ± 0.02	0.38 ± 0.02
40.0		10	1.40 ± 0.07	0.76 ± 0.03	0.29 ± 0.01	0.70 ± 0.03
50.0		10	1.93 ± 0.36	1.02 ± 0.13	0.37 ± 0.04	0.91 ± 0.11
60.0		10	2.42 ± 0.50	1.31 ± 0.20	0.48 ± 0.04	1.13 ± 0.15
70.0		20	3.88 ± 0.75	1.85 ± 0.20	0.63 ± 0.04	1.58 ± 0.23
2.3	0.65	16	0.21 ± 0.03	0.14 ± 0.03	0.07 ± 0.02	0.15 ± 0.02
22.8		10	0.58 ± 0.06	0.34 ± 0.04	0.14 ± 0.02	0.34 ± 0.04
40.0		10	1.23 ± 0.12	0.73 ± 0.05	0.28 ± 0.03	0.68 ± 0.03
50.0		6	1.63 ± 0.16	0.98 ± 0.08	0.37 ± 0.00	0.89 ± 0.02
60.0		10	2.01 ± 0.13	1.26 ± 0.10	0.47 ± 0.02	1.11 ± 0.09
70.0		6	2.87 ± 1.17	1.64 ± 0.44	0.59 ± 0.08	1.43 ± 0.33
2.3	1.30	10	0.16 ± 0.01	0.13 ± 0.02	0.07 ± 0.01	0.14 ± 0.01
22.8		10	0.42 ± 0.05	0.31 ± 0.05	0.13 ± 0.02	0.33 ± 0.04
40.0		10	0.89 ± 0.15	0.64 ± 0.09	0.26 ± 0.04	0.64 ± 0.10
50.0		10	1.19 ± 0.12	0.87 ± 0.08	0.35 ± 0.02	0.83 ± 0.07
60.0		16	1.64 ± 0.11	1.15 ± 0.06	0.46 ± 0.02	1.07 ± 0.04
70.0		9	1.89 ± 0.28	1.34 ± 0.18	0.54 ± 0.09	1.27 ± 0.09
2.2	6.50	6	0.08 ± 0.04	0.09 ± 0.04	0.06 ± 0.01	0.13 ± 0.08
23.8		6	0.18 ± 0.06	0.23 ± 0.07	0.12 ± 0.02	0.32 ± 0.06
40.0		10	0.36 ± 0.07	0.43 ± 0.08	0.24 ± 0.06	0.61 ± 0.11
50.0		10	0.47 ± 0.00	0.55 ± 0.00	0.30 ± 0.00	0.74 ± 0.01
60.0		10	0.63 ± 0.02	0.72 ± 0.01	0.39 ± 0.02	0.94 ± 0.02
70.0		6	0.68 ± 0.15	0.85 ± 0.05	0.47 ± 0.03	1.08 ± 0.06
2.3	13.0	9	0.05 ± 0.02	0.07 ± 0.02	0.05 ± 0.02	0.12 ± 0.03
22.7		10	0.10 ± 0.01	0.15 ± 0.01	0.10 ± 0.01	0.27 ± 0.02
40.0		10	0.18 ± 0.02	0.27 ± 0.02	0.18 ± 0.03	0.46 ± 0.05
50.0		10	0.27 ± 0.02	0.37 ± 0.03	0.25 ± 0.02	0.62 ± 0.05
60.0		10	0.36 ± 0.02	0.48 ± 0.01	0.31 ± 0.01	0.77 ± 0.02
70.0		6	0.41 ± 0.06	0.58 ± 0.04	0.39 ± 0.09	0.92 ± 0.09
1.9	26.0	6	0.02 ± 0.01	0.04 ± 0.02	0.03 ± 0.01	0.09 ± 0.04
22.0		6	0.07 ± 0.02	0.10 ± 0.02	0.08 ± 0.02	0.22 ± 0.03
40.0		10	0.11 ± 0.02	0.19 ± 0.04	0.15 ± 0.03	0.38 ± 0.06
50.0		10	0.14 ± 0.02	0.22 ± 0.03	0.18 ± 0.03	0.47 ± 0.06
60.0		10	0.18 ± 0.05	0.30 ± 0.08	0.24 ± 0.15	0.63 ± 0.24
70.0		6	0.21 ± 0.09	0.35 ± 0.07	0.32 ± 0.07	0.70 ± 0.12
			SDS			
22.1	2.38	10	0.55 ± 0.09	0.35 ± 0.06	0.15 ± 0.03	0.37 ± 0.06
40.0		10	1.18 ± 0.13	0.71 ± 0.05	0.28 ± 0.01	0.68 ± 0.04
50.0		10	1.94 ± 0.14	1.08 ± 0.18	0.39 ± 0.07	0.94 ± 0.10
60.0		6	2.43 ± 0.51	1.33 ± 0.17	0.49 ± 0.04	1.16 ± 0.14
70.0		10	3.54 ± 1.08	1.74 ± 0.45	0.59 ± 0.06	1.45 ± 0.28
24.5	4.76	6	0.30 ± 0.03	0.27 ± 0.02	0.13 ± 0.01	0.33 ± 0.03
40.0		10	0.73 ± 0.12	0.61 ± 0.10	0.27 ± 0.04	0.66 ± 0.10
50.0		10	1.14 ± 0.26	0.87 ± 0.16	0.37 ± 0.05	0.89 ± 0.20
60.0		10	1.64 ± 0.17	1.16 ± 0.10	0.47 ± 0.04	1.11 ± 0.08
70.0		10	2.27 ± 0.45	1.50 ± 0.18	0.58 ± 0.03	1.36 ± 0.13
20.2	11.9	10	0.07 ± 0.02	0.12 ± 0.02	0.09 ± 0.02	0.23 ± 0.03
40.0		10	0.27 ± 0.04	0.34 ± 0.06	0.22 ± 0.05	0.51 ± 0.09
50.0		10	0.41 ± 0.08	0.51 ± 0.12	0.30 ± 0.07	0.72 ± 0.12
60.0		10	0.61 ± 0.09	0.71 ± 0.12	0.39 ± 0.07	0.96 ± 0.15
70.0		13	0.84 ± 0.07	0.90 ± 0.09	0.51 ± 0.05	1.04 ± 0.07
21.9	23.8	6	0.05 ± 0.03	0.09 ± 0.03	0.08 ± 0.03	0.21 ± 0.05
40.0		10	0.12 ± 0.03	0.19 ± 0.04	0.16 ± 0.04	0.39 ± 0.06
50.0		10	0.18 ± 0.01	0.27 ± 0.01	0.21 ± 0.01	0.50 ± 0.03
60.0		10	0.26 ± 0.04	0.37 ± 0.05	0.27 ± 0.04	0.64 ± 0.07
70.0		6	0.40 ± 0.22	0.52 ± 0.19	0.35 ± 0.14	0.85 ± 0.13
22.0	47.6	6	0.02 ± 0.01	0.05 ± 0.02	0.06 ± 0.03	0.15 ± 0.03
40.0		10	0.06 ± 0.01	0.11 ± 0.02	0.11 ± 0.01	0.27 ± 0.03
50.0		10	0.09 ± 0.01	0.16 ± 0.01	0.15 ± 0.01	0.36 ± 0.02
60.0		6	0.13 ± 0.02	0.21 ± 0.03	0.18 ± 0.02	0.43 ± 0.12
70.0		6	0.18 ± 0.09	0.30 ± 0.13	0.26 ± 0.11	0.57 ± 0.04
			CTAB			
22.5	0.36	10	0.63 ± 0.06	0.37 ± 0.03	0.15 ± 0.01	0.36 ± 0.03
40.0		10	1.48 ± 0.21	0.79 ± 0.07	0.30 ± 0.02	0.72 ± 0.05
50.0		6	1.73 ± 0.38	0.96 ± 0.07	0.36 ± 0.09	0.88 ± 0.04
60.0		6	2.61 ± 0.26	1.37 ± 0.10	0.51 ± 0.03	1.18 ± 0.11
70.0		6	3.56 ± 1.23	1.76 ± 0.46	0.61 ± 0.11	1.52 ± 0.46

Table 2. (Continued)

	surfactant conc		H_{app}			
t/°C	g·L^{-1}	n^a	tetrachloroethylene	trichloroethylene	*cis*-dichloroethylene	*trans*-dichloroethylene
				CTAB		
20.3	0.72	10	0.49 ± 0.04	0.32 ± 0.02	0.13 ± 0.02	0.34 ± 0.02
40.0		10	1.20 ± 0.12	0.73 ± 0.04	0.27 ± 0.01	0.68 ± 0.03
50.0		10	1.59 ± 0.09	0.94 ± 0.04	0.35 ± 0.02	0.86 ± 0.04
60.0		10	2.19 ± 0.47	1.23 ± 0.18	0.46 ± 0.04	1.09 ± 0.14
70.0		6	3.12 ± 0.75	1.66 ± 0.29	0.59 ± 0.11	1.41 ± 0.20
20.0	1.81	6	0.37 ± 0.16	0.30 ± 0.09	0.13 ± 0.05	0.33 ± 0.09
40.0		10	0.69 ± 0.07	0.56 ± 0.06	0.25 ± 0.03	0.64 ± 0.06
50.0		6	1.15 ± 0.20	0.86 ± 0.15	0.35 ± 0.06	0.84 ± 0.10
60.0		10	1.65 ± 0.21	1.15 ± 0.11	0.46 ± 0.03	1.06 ± 0.11
70.0		6	2.12 ± 0.79	1.40 ± 0.49	0.53 ± 0.23	1.32 ± 0.46
20.5	3.61	6	0.17 ± 0.03	0.20 ± 0.02	0.11 ± 0.01	0.29 ± 0.04
40.0		10	0.44 ± 0.04	0.46 ± 0.04	0.23 ± 0.02	0.59 ± 0.05
50.0		10	0.66 ± 0.06	0.64 ± 0.05	0.31 ± 0.03	0.78 ± 0.06
60.0		10	0.97 ± 0.10	0.88 ± 0.08	0.41 ± 0.03	1.01 ± 0.10
70.0		6	1.34 ± 0.27	1.09 ± 0.29	0.50 ± 0.13	1.18 ± 0.17
21.9	7.22	6	0.12 ± 0.02	0.16 ± 0.03	0.11 ± 0.03	0.29 ± 0.07
40.0		10	0.27 ± 0.02	0.35 ± 0.03	0.21 ± 0.02	0.55 ± 0.04
50.0		6	0.40 ± 0.02	0.49 ± 0.03	0.29 ± 0.02	0.74 ± 0.05
60.0		10	0.59 ± 0.06	0.68 ± 0.07	0.38 ± 0.05	0.94 ± 0.12
70.0		6	0.81 ± 0.07	0.89 ± 0.06	0.46 ± 0.03	1.15 ± 0.05
				water		
1.8	0	10	0.22 ± 0.04	0.14 ± 0.03	0.09 ± 0.03	0.16 ± 0.03
21.6		10	0.64 ± 0.09	0.35 ± 0.05	0.14 ± 0.02	0.34 ± 0.05
40.0		10	1.33 ± 0.13	0.74 ± 0.05	0.29 ± 0.01	0.69 ± 0.05
50.0		10	1.77 ± 0.26	1.00 ± 0.08	0.37 ± 0.02	0.89 ± 0.06
60.0		10	2.52 ± 0.62	1.31 ± 0.24	0.48 ± 0.08(	1.14 ± 0.20
70.0		12	4.16 ± 0.79	2.01 ± 0.34	0.67 ± 0.15	1.67 ± 0.28

[a] Data shown here are average values, and *n* represents the number of Henry's law constant values averaged. [b] Errors for Henry's law constants represent 95% confidence limits based on the Student's *t*-method.

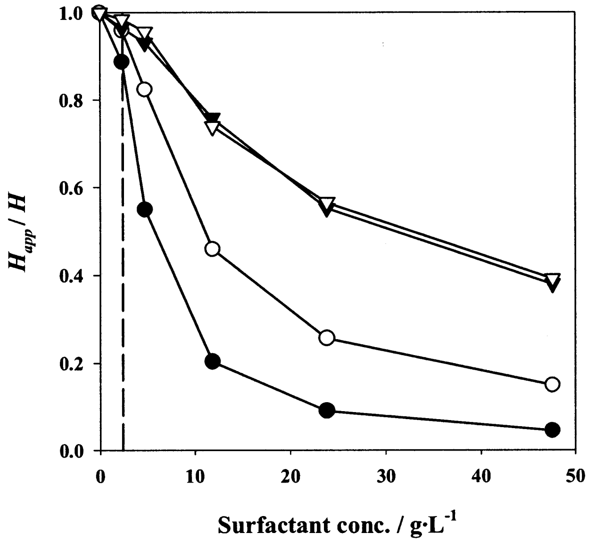

Figure 1. Decrease of Henry's law constants by surfactant addition for the four chlorinated ethylenes studied. The experimental temperature is 40 °C, and SDS is used as the surfactant. The symbols represent: tetrachloroethylene, ●; trichloroethylene, ○; *cis*-dichloroethylene, ▼; and *trans*-dichloroethylene, ▽. Data points for each compound are connected by solid lines. The vertical dashed line shows the critical micelle concentration of SDS at 40 °C.

tion (47.6 g·L^{-1}), the ratio is 0.05, 0.16, and 0.40 for tetrachloroethylene, trichloroethylene, and the dichloroethylenes, respectively.

Estimated Micelle−Water Partitioning Coefficients. Figure 2 displays estimated (via eq 5) values of K_{mw} for trichloroethylene in (a) Triton X-100, (b) SDS, and (c) CTAB aqueous solutions as a function of surfactant concentration. Theoretically, K_{mw} should be independent of the surfactant concentration, but the estimated values at low surfactant concentrations are scattered. This is due to error that results from applying eq 5 when S is close to the critical micelle concentration. The values of K_{mw} are stable at higher surfactant concentrations. It is reasonable, therefore, to exclusively use Henry's law constants at surfactant concentrations significantly larger than critical micelle concentration for the estimation of K_{mw}.

Table 4 summarizes estimated values of K_{mw} for all chlorinated ethylene−surfactant pairs as a function of temperature. For the reason mentioned above, the values of K_{mw} in the table are based on averages over (6.50 to 26.0) g·L^{-1} for Triton X-100, (11.9 to 47.6) g·L^{-1} for SDS, and (1.81 to 7.22) g·L^{-1} for CTAB. The temperature effect varies for each solute−surfactant pair. The decreasing trend for tetrachloroethylene/SDS and trichloroethylene/SDS systems with increasing temperature is consistent with the observations of Vane and Giroux.[45] Comparing the four chlorinated ethylenes, K_{mw} follows the order tetrachloroethylene > trichloroethylene > *cis*-dichloroethylene ~ *trans*-dichloroethylene for all surfactants. This trend is consistent with the order of hydrophobicity of these compounds, and thus, surfactants have larger solubilization effects on the more hydrophobic compounds.

To assess the errors associated with K_{mw}, the standard errors of H and H_{app} were initially calculated based on the van't Hoff-type equation,[51] and error propagation was applied to eq 5 to estimate the standard error associated with K_{mw}. Reflecting the error of the Henry's law constants, the relative error of K_{mw} is also large at refrigerated temperatures and 70 °C. Errors are within ±10% of the K_{mw} values in 76% of the cases.

A comparison between values of K_{mw} in this work and those reported by other investigators is shown in Table 5.

Table 3. Comparison of Henry's Law Constants

	surfactant conc	H_{app}	
t/°C	g·L^{-1}	this work	Vane and Giroux[45]
	Triton X-100/Tetrachloroethylene		
21.6	0	0.64 ± 0.09	
24.0	0.13	0.70 ± 0.03	
40.0	0.13	1.40 ± 0.07	
	0.3		1.221 ± 0.013[a]
	0.6		1.045 ± 0.024
	0.65	1.23 ± 0.12	
	1.30	0.89 ± 0.15	
	6.0		0.325 ± 0.006
	6.50	0.36 ± 0.07	
	10.5		0.218 ± 0.008
	13.0	0.18 ± 0.02	
	15.0		0.141 ± 0.008
	26.0	0.11 ± 0.02	
	SDS/Tetrachloroethylene		
40.0	4.76	0.73 ± 0.12	
	5.0		0.565 ± 0.008
	10.0		0.263 ± 0.003
	11.9	0.27 ± 0.04	
	20.0		0.101 ± 0.003
	23.8	0.12 ± 0.03	
50.0	4.76	1.14 ± 0.26	
	5.0		0.868 ± 0.038
	10.0		0.382 ± 0.008
	11.9	0.41 ± 0.08	
	20.0		0.174 ± 0.004
	23.8	0.18 ± 0.01	
60.0	4.76	1.64 ± 0.17	
	5.0		1.339 ± 0.020
	10.0		0.627 ± 0.018
	11.9	0.61 ± 0.09	
	20.0		0.281 ± 0.022
	23.8	0.26 ± 0.04	
	SDS/Trichloroethylene		
40.0	4.76	0.61 ± 0.10	
	5.0		0.497 ± 0.010
	10.0		0.324 ± 0.004
	11.9	0.34 ± 0.06	
	20.0		0.171 ± 0.003
	23.8	0.19 ± 0.04	
50.0	4.76	0.87 ± 0.16	
	5.0		0.695 ± 0.031
	10.0		0.445 ± 0.011
	11.9	0.51 ± 0.12	
	20.0		0.262 ± 0.005
	23.8	0.27 ± 0.01	
60.0	4.76	1.16 ± 0.10	
	5.0		0.977 ± 0.014
	10.0		0.674 ± 0.022
	11.9	0.71 ± 0.12	
	20.0		0.391 ± 0.028
	23.8	0.37 ± 0.05	

[a] Uncertainties for Henry's law constants from Vane and Giroux were reported as 68% confidence limits.

Overall, values of K_{mw} are comparable, except for Triton X-100/tetrachloroethylene at 17.0 °C compared with West.[31] Considering that K_{mw} for Triton X-100/tetrachloroethylene at 40.0 °C determined in this work is comparable to the value of Vane and Giroux,[45] and the error associated with K_{mw} at 17.0 °C in this work is less than ±5%, it is likely that our value is accurate.

Equations for the Estimation of Henry's Law Constants. The nine parameters for eq 7 determined by the regression of H, K_{mw}, and S_{CMC} are provided in Table 6. The R^2 values are at least 0.96, and the estimated values are within ±10% of the experimental values in 83% of the cases. An illustrated comparison between the estimated (via eq 7) values and the corresponding experimental values of Henry's law constants for the four chlorinated

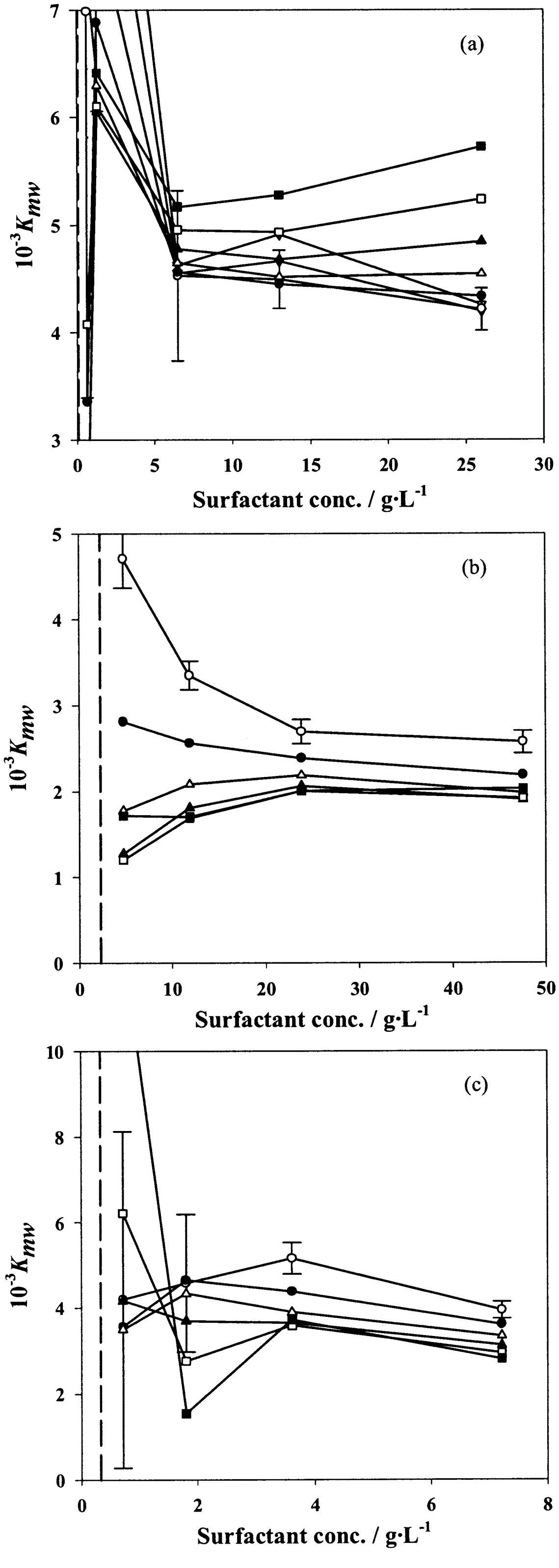

Figure 2. Micelle−water partitioning coefficients (K_{mw}) of trichloroethylene in (a) Triton X-100, (b) SDS, and (c) CTAB aqueous solutions estimated (via eq 5) at different surfactant concentrations. Different symbols represent different temperatures: 2.0 °C, ▽; 10.0 °C, ▼; 20.0 °C, ○; 30.0 °C, ●; 40.0 °C, △; 50.0 °C, ▲; 60.0 °C, □; and 70.0 °C, ■. Data points for each temperature are connected by solid lines. Error bars for 20.0 °C data are shown. The vertical dashed line represents the critical micelle concentration of each surfactant at 25 °C.

Table 4. Micelle−Water Partitioning Coefficients

t/°C	$10^{-3}K_{mw}$			
	tetrachloroethylene	trichloroethylene	*cis*-dichloroethylene	*trans*-dichloroethylene
	Triton X-100			
2.0[a]	14.80 ± 0.90[b]	4.60 ± 0.36	3.73 ± 0.59	1.64 ± 0.23
10.0	14.52 ± 0.64	4.47 ± 0.31	2.86 ± 0.26	1.44 ± 0.18
20.0	14.57 ± 0.50	4.41 ± 0.29	2.13 ± 0.09	1.29 ± 0.16
30.0	15.02 ± 0.45	4.45 ± 0.28	1.68 ± 0.11	1.21 ± 0.15
40.0	15.88 ± 0.39	4.57 ± 0.27	1.42 ± 0.13	1.21 ± 0.14
50.0	17.18 ± 0.36	4.77 ± 0.27	1.30 ± 0.12	1.27 ± 0.14
60.0	18.99 ± 0.53	5.04 ± 0.29	1.30 ± 0.09	1.39 ± 0.15
70.0	21.46 ± 1.00	5.39 ± 0.36	1.41 ± 0.10	1.56 ± 0.19
	SDS			
20.0	12.49 ± 0.55	2.87 ± 0.08	1.11 ± 0.06	0.78 ± 0.05
30.0	9.25 ± 0.25	2.38 ± 0.05	0.78 ± 0.03	0.65 ± 0.03
40.0	7.55 ± 0.16	2.08 ± 0.03	0.60 ± 0.02	0.57 ± 0.02
50.0	6.75 ± 0.14	1.92 ± 0.03	0.52 ± 0.02	0.54 ± 0.02
60.0	6.56 ± 0.18	1.87 ± 0.05	0.52 ± 0.02	0.54 ± 0.03
70.0	6.89 ± 0.31	1.91 ± 0.08	0.59 ± 0.04	0.59 ± 0.05
	CTAB			
20.0	13.58 ± 1.32	4.56 ± 0.55	3.92 ± 0.24	1.43 ± 0.18
30.0	12.99 ± 0.75	4.21 ± 0.34	2.53 ± 0.16	1.13 ± 0.14
40.0	12.18 ± 0.48	3.86 ± 0.28	1.64 ± 0.14	0.98 ± 0.10
50.0	11.20 ± 0.45	3.49 ± 0.24	1.12 ± 0.12	0.96 ± 0.08
60.0	10.10 ± 0.59	3.10 ± 0.28	0.87 ± 0.13	1.05 ± 0.15
70.0	8.92 ± 0.89	2.69 ± 0.51	0.87 ± 0.25	1.27 ± 0.30

[a] K_{mw} can be estimated using eq 5 at temperatures where Henry's law constants have not been measured experimentally. [b] Uncertainties for K_{mw} are standard errors based on the linear regression and an error propagation method.[51]

Table 5. Comparison of Micelle−Water Partitioning Coefficients

surfactant/chlorinated ethylene	t/°C	$10^{-3}K_{mw}$		
		this work	Vane and Giroux[45] (adjusted)	West[31]
Triton X-100/tetrachloroethylene	17.0	14.51 ± 0.69		29.51
	40.0	15.88 ± 0.39	17.93 ± 1.44[a,b]	
Triton X-100/trichloroethylene	17.0	4.07 ± 0.30		3.09
Triton X-100/*cis*-dichloroethylene	17.0	2.14 ± 0.32		0.96[c]
Triton X-100/*trans*-dichloroethylene	17.0	1.15 ± 0.18		
SDS/tetrachloroethylene	30.0	9.25 ± 0.25	11.43 ± 4.89	
	40.0	7.55 ± 0.16	9.16 ± 1.67	
	50.0	6.75 ± 0.14	7.55 ± 1.05	
	60.0	6.56 ± 0.18	6.27 ± 1.00	
SDS/trichloroethylene	30.0	2.38 ± 0.05	2.78 ± 0.56	
	40.0	2.08 ± 0.03	2.55 ± 0.22	
	50.0	1.92 ± 0.03	2.22 ± 0.17	
	60.0	1.87 ± 0.05	1.94 ± 0.11	

[a] The definition of K_{mw} used in ref 45 is different from eq 4. Adjustment was necessary for the comparison: K_{mw} (definition in this work) = $M_L K_{mw}$ (definition by Vane and Giroux) [b] The errors represent 95% confidence limits. [c] No distinction of the isomers mentioned.

Table 6. Parameters for Estimation of Henry's Law Constants via eq 7[a]

surfactant/chlorinated ethylene	A_1	B_1	C_1	A_2	B_2	C_2	A_3	B_3	C_3	R^2
Triton X-100/tetrachloroethylene	128.23	−9086	−17.22	−166.48	7606	26.43	−180.92	8196	25.51	0.992
Triton X-100/trichloroethylene	123.56	−8615	−16.77	−110.54	5232	17.8	−180.92	8196	25.51	0.995
Triton X-100/*cis*-dichloroethylene	105.99	−7298	−14.61	−358.88	18016	53.71	−180.92	8196	25.51	0.991
Triton X-100/*trans*-dichloroethylene	122.31	−8235	−16.78	−304.74	14277	46.33	−180.92	8196	25.51	0.993
SDS/tetrachloroethylene	128.23	−9086	−17.22	−537.88	26677	80.33	−258.25	11299	37.83	0.978
SDS/trichloroethylene	123.56	−8615	−16.77	−316.76	15927	47.6	−258.25	11299	37.83	0.993
SDS/*cis*-dichloroethylene	105.99	−7298	−14.61	−745.76	36485	110.61	−258.25	11299	37.83	0.966
SDS/*trans*-dichloroethylene	122.31	−8235	−16.78	−417	20381	62.34	−258.25	11299	37.83	0.987
CTAB/tetrachloroethylene	128.23	−9086	−17.22	175.98	−7108	−25.04	−154.7	5849	22.48	0.992
CTAB/trichloroethylene	123.56	−8615	−16.77	150.57	−5803	−21.54	−154.7	5849	22.48	0.985
CTAB/*cis*-dichloroethylene	105.99	−7298	−14.61	−274.38	16073	40.11	−154.7	5849	22.48	0.983
CTAB/*trans*-dichloroethylene	122.31	−8235	−16.78	−727.31	34668	108.5	−154.7	5849	22.48	0.976

[a] Valid temperature ranges: (2 to70) °C for Triton X-100, (18 to70) °C for SDS and CTAB. Valid surfactant concentration ranges: (0.13 to 26.0) g·L^{-1}for Triton X-100, (2.38 to 47.6) g·L^{-1} for SDS, (0.36 to 7.22) g·L^{-1} for CTAB.

ethylenes is included in the Supporting Information (Figure S-1). One minor problem is that 80% of the computed values for SDS are lower than the experimental values. This systematic underestimation may be due to the slight (but not statistically significant) increase in K_{mw} values between 60 and 70 °C (Table 4). The apparent increase of K_{mw} is exaggerated in the regression treatment, and as a result, Henry's law constants are underestimated.

To reduce the number of parameters, the critical micelle concentration could be assumed to be independent of temperature. In that case, the accuracy of the estimated values decreases at low surfactant concentrations near the critical micelle concentration compared with the nine-parameter equation. As a result, the R^2 value can be as low as 0.93. The reduced estimation equation, although not shown here, is a good approximation at high surfactant concentrations, whereas the temperature dependence of the critical micelle concentration should be taken into account if a lower concentration range is covered.

Supporting Information Available:

Derivations and explanations leading to eqs 5 and 7 and plots of estimated versus experimental values of Henry's law constants for the four chlorinated ethylenes. This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgment

We thank professors Paul Capel and Matt Simcik at the University of Minnesota for reviewing the draft of this article and giving beneficial comments.

Literature Cited

(1) Westrick, J. J.; Mello, J. W.; Thomas, R. F. The Groundwater Survey. *J. Am. Water Works Assoc.* **1984**, *76*(5), 52−59.

(2) National Research Council *Alternatives for Groundwater Cleanup*; National Academy Press: Washington, DC, 1994.

(3) Gist, G. L.; Burg, J. A. R. Trichloroethylene−A Review of the Literature from a Health Effects Perspective. *Toxicol. Ind. Health* **1995**, *11*(3), 253−307.

(4) National Archives and Records Administration *40CFR141.61 Maximum Contaminant Levels for Organic Contaminants*, (revised July 1, 2000) [Online] Available: http://www.access.gpo.gov/nara/cfr/waisidx_99/40cfr141_99.html [November, 2002].

(5) Knox, R. C.; Sabatini, D. A. Transport and Remediation of Subsurface Contaminants. *Transport and Remediation of Subsurface Contaminants*; American Chemical Society: Washington, DC, 1992.

(6) Mackay, D. M.; Cherry, J. A. Groundwater Contamination: Pump-and-treat Remediation. *Environ. Sci. Technol.* **1989**, *23*, 3(6), 630−636.

(7) Horvath, A. L. *Halogenated Hydrocarbons*; M. Dekker: New York, 1982.

(8) Mackay, D.; Shiu, W. Y.; Ma, K. C. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Vol III, Volatile Organic Chemicals*; Lewis Publishers: Chelsea, MI, 1992.

(9) Lee, M. The Remediation of Tetrachloroethylene by Surfactant Flushing in Both the Saturated and the Unsaturated Zone. *Environ. Technol.* **1998**, *19*, 1073−1083.

(10) Boving, T. B.; Brusseau, M. L. Solubilization and Removal of Residual Trichloroethene from Porous Media: Comparison of Several Solubilization Agents. *J. Contam. Hydrol.* **2000**, *42*, 51−67.

(11) Sabatini, D. A.; Knox, R. C.; Harwell, J. H. *Emerging Technologies in Surfactant-Enhanced Subsurface Remediation*. In *Surfactant Enhanced Subsurface Remediation*; American Chemical Society: Washington, DC, 1995.

(12) Pennel, K. D.; Abriola, L. M.; Weber, W. J. Surfactant-Enhanced Solubilization of Residual Dodecane in Soil Columns. 1. Experimental Investigation. *Environ. Sci. Technol.* **1993**, *27*, 2332−2340.

(13) Clarke, A. N.; Mutch, R. D.; Wilson, D. J. Design and Implementation of Pilot Scale Surfactant Washing/Flushing Technologies Including Surfactant Reuse. *Water Sci. Technol.* **1992**, *26*(1−2), 127−135.

(14) Sahoo, D.; Smith, J. A. Enhanced Trichloroethylene Desorption from Long-Term Contaminated Soil Using Triton X-100 and pH Increases. *Environ. Sci. Technol.* **1997**, *31*, 1910−1915.

(15) Lee, M.; Fountain, J. C. The Effectiveness of Surfactants for Remediation of Organic Pollutants in the Unsaturated Zone. *J. Soil Contam.* **1999**, *8*(1), 39−62.

(16) Walker, R. C.; Hofstee, C.; Dane, J. H.; Hill, W. E. Surfactant Enhanced Removal of PCE in a Partially Saturated, Stratified Porous Medium. *J. Contam. Hydrol.* **1998**, *34*, 31−46.

(17) Abdul, A. S.; Gibson, T. L. Laboratory Studies of Surfactant-Enhanced Washing of Polychlorinated Biphenyl from Sandy Material. *Environ. Sci. Technol.* **1991**, *25*, 665−671.

(18) Sahoo, D.; Smith, J. A.; Imbrigiotta, T. E.; McLellan, H. M. Surfactant-Enhanced Remediation of a Trichloroethylene-Contaminated Aquifer. 2. Transport of TCE. *Environ. Sci. Technol.* **1998**, *32*, 1686−1693.

(19) Fountain, J. C. Field Tests for Surfactant Flooding. *Transport and Remediation of Subsurface Contaminants*; American Chemical Society: Washington, DC, 1992.

(20) Falta, R. W. Using Phase Diagrams to Predict the Performance of Cosolvent Floods for NAPL Remediation. *Groundwater Monit. Rem.* **1998**, *Summer*, 94−102.

(21) Lunn, S. R. D.; Kueper, B. H. Removal of Pooled Dense, Nonaqueous Phase Liquid from Saturated Porous Media Using Upward Gradient Alcohol Floods. *Water Resour. Res.* **1997**, *33*, 2207−2219.

(22) Imhoff, P. T.; Gleyzer, S. N.; McBride, J. F.; Vancho, L. A.; Okuda, I.; Miller, C. T. Cosolvent-Enhanced Remediation of Residual Dense Nonaqueous Phase Liquids: Experimental Investigation. *Environ. Sci. Technol.* **1995**, *29*, 1966−1976.

(23) Brands, D.; Farley, K. Importance of Phase Behavior on the Removal of Residual DNAPLs from Porous Media by Alcohol Flooding. *Water Environ. Res.* **1993**, *65*, 869−878.

(24) Heron, G.; van Zutphen, M.; Christensen, T. H.; Enfield, C. G. Soil Heating for Enhanced Remediation of Chlorinated Solvents: A Laboratory Study on Resistive Heating and Vapor Extraction in a Silty, Low-Permeable Soil Contaminated with Trichloroethylene. *Environ. Sci. Technol.* **1998**, *32*, 1474−1481.

(25) Imhoff, P. T.; Frizzell, A.; Miller, C. T. Evaluation of Thermal Effects on the Dissolution of a Nonaqueous Phase Liquid in Porous Media. *Environ. Sci. Technol.* **1997**, *31*, 1615−1622.

(26) Edwards, D. A.; Luthy, R. G.; Liu, Z. Solubilization of Polycyclic Aromatic Hydrocarbon in Micellar Nonionic Surfactant Solutions. *Environ. Sci. Technol.* **1991**, *25*, 127−133.

(27) Valsaraj, K. T.; Gupta, A.; Thibodeaux, L. J.; Harrison, D. P. Partitioning of Chloromethanes between Aqueous and Surfactant Miceller Phases. *Water Res.* **1988**, *22*(9), 1173−1183.

(28) Kile, D. E.; Chiou, C. T. Water Solubility Enhancements of DDT and Trichlorobenzene by Some Surfactants below and above the Critical Micelle Concentration. *Environ. Sci. Technol.* **1989**, *23*, 832−838.

(29) Jafvert, C. T.; Van Hoof, P. L.; Heath, J. K. Solubilization of Non-Polar Compounds by Non-Ionic Surfactant Micelles. *Water Res.* **1993**, *28*(5), 1009−1017.

(30) Ottewill, R. H. Introduction. *Surfactants*; Academic Press: London, 1984.

(31) West, C. C. Surfactant-Enhanced Solubilization of Tetrachloroethylene and Degradation Products in Pump and Treat Remediation. *Transport and Remediation of Subsurface Contaminants*; American Chemical Society: Washington, DC, 1992.

(32) Pennel, K. D.; Adinolfi, A. M.; Abriola, L. M.; Diallo, M. S. Solubilization of Dodecane, Tetrachloroethylene, and 1, 2-Dichlorobenzene in Micellar Solutions of Ethoxylated Nonionic Surfactants. *Environ. Sci. Technol.* **1997**, *31*, 1382−1389.

(33) Krebs-Yuill, B.; Harwell, J. H.; Sabatini, D. A.; Knox, R. C. Economic Considerations in Surfactant-Enhanced Pump-and-Treat Remediation. *Surfactant Enhanced Subsurface Remediation*; American Chemical Society: Washington, DC, 1995.

(34) Hasegawa, M. A.; Sabatini, D. A.; Harwell, J. H. Liquid−Liquid Extraction for Surfactant-Contaminant Separation and Surfactant Reuse. *J. Environ. Eng. (N.Y.)* **1997**, *123*(7), 691−697.

(35) Cheng, H.; Sabatini, D. A.; Kibbey, T. C. G. Solvent Extraction for Separating Micellar-Solubilized Contaminants and Anionic Surfactants. *Environ. Sci. Technol.* **2001**, *35*(14), 2995−3001.

(36) Lamarche, P.; Droste, R. L. Air-Stripping Mass Transfer Correlations for Volatile Organics. *J. Am. Water Works Assoc.* **1989**, *January*, 78−89.

(37) Choori, U. N.; Scamehorn, J. F.; O'Haver, J. H.; Harwell, J. H. Removal of Volatile Organic Compounds from Surfactant Solutions by Flash Vacuum Stripping in a Packed Column. *Groundwater Monit. Rem.* **1998**, *Fall*, 157−165.

(38) Jiang, J.; Vane, L. M.; Sikdar, S. K. Recovery of VOCs from Surfactant Solutions by Pervaporation. *J. Membr. Sci.* **1997**, *136*, 233−247.

(39) Fujii, Y. (NOK corp.) *Method for Separating Organic Chlorine Compound from Aqueous Solution Containing the Same*, Japan Patent No. 09-103654, April 22, 1997.

(40) Leighton, D. T.; Calo, J. M. Distribution Coefficients of Chlorinated Hydrocarbons in Dilute Air−Water Systems for Groundwater Contamination Applications. *J. Chem. Eng. Data* **1981**, *26*, 382−385.

(41) Gossett, J. M. Measurement of Henry's Law Constants for C_1 and C_2 Chlorinated Hydrocarbons. *Environ. Sci. Technol.* **1987**, *21*, 202−208.

(42) Munz, C.; Roberts, P. V. Air−Water Phase Equilibria of Volatile Organic Solutes. *J. Am. Water Works Assoc.* **1987**, *May*, 62−69.

(43) Mackay, D.; Shiu, W. Y. A Critical Review of Henry's Law Constants for Chemicals of Environmental Interest. *J. Phys. Chem. Ref. Data* **1981**, *10*(4), 1175−1199.

(44) Hansen, K. C.; Zhou, Z.; Yaws, C. L.; Aminabhavi, T. M. Determination of Henry's Law Constants of Organics in Dilute Aqueous Solutions. *J. Chem. Eng. Data* **1993**, *38*, 546−550.

(45) Vane, L. M.; Giroux, E. L. Henry's Law Constants and Miceller Partitioning of Volatile Organic Compounds in Surfactant Solutions. *J. Chem. Eng. Data* **2000**, *45*(1), 38−47.

(46) Mukerjee, P.; Mysels, K. J. *Critical Micelle Concentrations of Aqueous Surfactant Systems*; National Bureau of Standards: Washington, DC, 1971.

(47) Heron, G.; Christensen, T. H.; Enfield, C. G. Henry's Law Constant for Trichloroethylene between 10 and 95 °C. *Environ. Sci. Technol.* **1998**, *32*, 1433−1437.

(48) Chen, L.; Lin, S.; Huang, C.; Chen, E. Temperature dependence of critical micelle concentration of polyoxyethylenated nonionic surfactants. *Colloids Surf. A* **1998**, *135*, 175−181.

(49) Lincoff, A.; Gossett, J. *The Determination of Henry's Law Constant for Volatile Organic by Equilibrium Partitioning in Closed Systems*. In *Gas Transfer at Water Surfaces*; D. Reidel Publishing Company: Boston, MA, 1984.

(50) Munz, C.; Roberts, P. V. Effects of Solute Concentration and Cosolvents on the Aqueous Activity Coefficient of Halogenated Hydrocarbons. *Environ. Sci. Technol.* **1986**, *20*, 830−836.

(51) Bennett, C. A.; Franklin, N. L. *Statistical Analysis in Chemistry and the Chemical Industry*; John Wiley & Sons: New York, 1954.

Received for review May 21, 2002. Accepted November 27, 2002. We are grateful to the Department of Civil Engineering for their endowment of the Rose and Joseph Ling Environmental Engineering Fellowship to T.S., which enabled this research.

JE025553Z