Henry's Law Constants and Micellar Partitioning of Volatile Organic Compounds in Surfactant Solutions

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Partitioning of volatile organic compounds (VOCs) into surfactant micelles affects the apparent vapor−liquid equilibrium of VOCs in surfactant solutions. This partitioning will complicate removal of VOCs from surfactant solutions by standard separation processes. Headspace experiments were performed to quantify the effect of four anionic surfactants and one nonionic surfactant on the Henry's law constants of 1,1,1-trichloroethane, trichloroethylene, toluene, and tetrachloroethylene at temperatures ranging from 30 to 60 °C. Although the Henry's law constant increased markedly with temperature for all solutions, the amount of VOC in micelles relative to that in the extramicellar region was comparatively insensitive to temperature. The effect of adding sodium chloride and isopropyl alcohol as cosolutes also was evaluated. Significant partitioning of VOCs into micelles was observed, with the micellar partitioning coefficient (tendency to partition from water into micelle) increasing according to the following series: trichloroethane < trichloroethylene < toluene < tetrachloroethylene. The addition of surfactant was capable of reversing the normal sequence observed in Henry's law constants for these four VOCs.

Introduction

Vast quantities of organic solvents have been disposed of in a manner which impacts human health and the environment. One particularly problematic class of solvents consists of chlorinated organic compounds such as trichloroethylene (TCE) and tetrachloroethylene (PCE). These widely used compounds have low water solubilities, low biodegradation potentials, and densities greater than that of water (classified as DNAPLs− dense nonaqueous phase liquids). As a result, spilled DNAPLs settle through the water table until they reach a confining layer where they serve as long term sources of contamination. Significant chronic health effects have been associated with a number of the chlorinated solvents resulting in regulated drinking water concentrations which are orders of magnitude less than the water solubilities of the compounds, generally in the micrograms per liter (ppb) range. Consequently, chlorinated organic solvents receive a significant amount of attention in the environmental arena, from analytical chemistry through biochemistry to remediation engineering.

Many chlorinated solvents are classified as volatile organic compounds (VOCs), exhibiting high vapor pressures as well as a tendency to participate in photochemical reactions. The high vapor pressures, combined with low water solubilities, yield high vapor−liquid partition coefficients as described by the Henry's law constant (H_c) for aqueous samples:

$$H_c = \frac{C_g}{C_l} \qquad (1)$$

where C_g and C_l are the gas- and liquid-phase concentrations, respectively. Environmental scientists and engineers have long taken advantage of the high H_c values for these compounds. In the engineering field, the most common method of dealing with chlorinated solvents dissolved in groundwater is "pump & treat"−withdrawal of groundwater from a contaminated aquifer usually followed by air stripping of the VOCs into the airshed or capture of the VOCs on activated carbon. To design air-stripping processes, H_c for each compound must be known. Fortunately, over the past decade, significant improvements in the accuracy and reproducibility of H_c measurements have been made, enabling improved design of air-stripping systems (*1*−*10*). Unfortunately, while often referred to as a remediation process, pump & treat installations are more accurately viewed as plume containment processes, since many of these installations will require decades of operation and maintenance before the contaminant source is exhausted.

In an effort to directly address the source of the contamination, researchers have been investigating the addition of agents to enhance the solubility of contaminants (*11*−*22*). One such system which recently reached the field demonstration stage is surfactant enhanced aquifer remediation (SEAR). In SEAR processes, surfactants are added at concentrations above that required to create surfactant self-aggregates (micelles). That is, the concentrations are higher than the critical micelle concentration (cmc). These micelles act as high-capacity reservoirs where organic compounds accumulate, thereby creating a high apparent solubility of the organic compounds in the surfactant solution. Using hydraulic gradients, the aqueous surfactant solution is made to flow through the subsurface region containing free phase contaminant to a series of withdrawal wells. The high solubilization capacity of the surfactant solution combined with targeting only the DNAPL source zone yields a dramatically smaller volume of stripping solution as compared to the volume of water generally originating from a pump & treat process. Other

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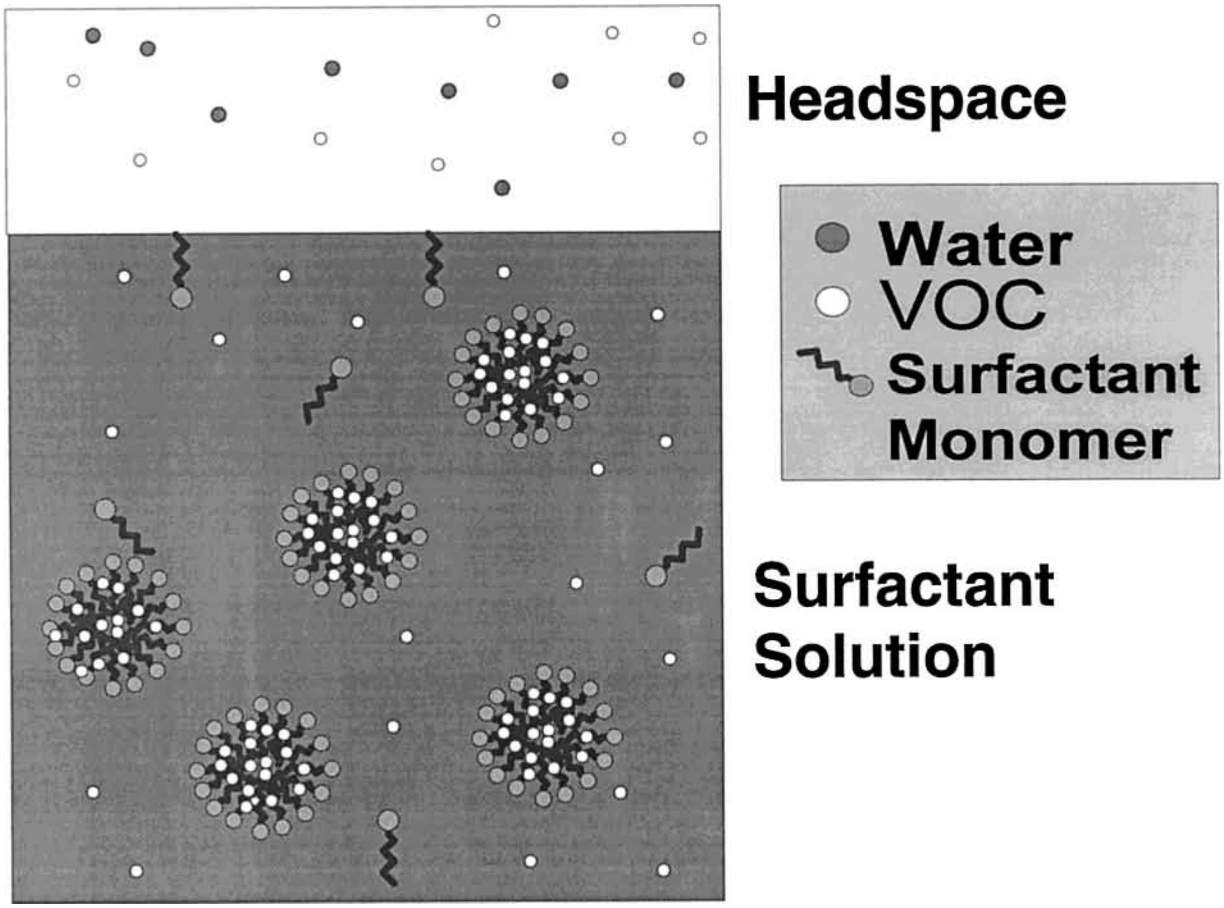


Figure 1. Pictorial representation of micellar, extramicellar, and headspace partitioning of VOCs.

compounds, such as salts or alcohols, may be added to manipulate the properties of the surfactant solution.

In the aquifer and at extraction wells, the surfactant solution will, at times, contain contaminants at concentrations far exceeding their aqueous solubilities. This extracted surfactant solution must subsequently be disposed of, treated for disposal, or treated for reuse. When no surfactant is present, this system would be equivalent to a standard pump & treat process on a small localized scale and air stripping could be applied as before to remove the VOCs. However, the addition of surfactants may create unmanageable foaming problems for direct vapor−liquid contact technologies such as air stripping, vacuum stripping, or steam stripping. Other separation technologies, such as pervaporation or liquid−liquid extraction, could be applied to avoid foaming.

To predict and assess the performance of processes removing VOCs from surfactant solutions, the partitioning behavior of VOCs between surfactant micelles, the extramicellar aqueous phase, and the headspace must be evaluated. In such systems, the “extramicellar” VOC may be only a small fraction of the total VOC in the system, as shown pictorially in Figure 1. It is this extramicellar VOC which best defines process efficiency, redefining the vapor−liquid equilibrium relationship in air stripper designs. The total amount of VOC accumulated in micelles will also play an important role in process design. While a significant number of literature references are available for ascertaining the H_c of VOCs in water, only limited information is available for the partitioning of VOCs in surfactant solutions (*23*−*28*). Methods for determining this partitioning include vapor pressure and headspace measurements, which are referenced to systems without surfactant. In this paper, the equilibrium partitioning in closed systems (EPICS) headspace method has been used to determine micellar partitioning of VOCs for several VOCs in the presence of surfactants and cosolutes over a range of temperatures.

Experimental Methods

Materials (the mention of trade names or commercial products does not constitute an endorsement or recommendation for use). Solvents, VOCs, and other reagents were purchased from Sigma/Aldrich. The VOCs included toluene (CAS# 108-88-3), TCE (CAS# 79-01-6), PCE (CAS# 127-18-4), and 1,1,1-trichloroethane (TCA, CAS# 71-55-6). As listed in Table 1, five surfactants were studied in this work. Aerosol MA 80-I surfactant (Cytec MA80), sodium dihexyl sulfosuccinate in a mixture of isopropyl alcohol (IPA) and water, was obtained from the manufacturer, Cytec Industries, who indicated that active surfactant constituted 80% by mass of the delivered product. The IPA content, determined by GC analysis, was 5% by mass. DOWFAX 8390 anionic surfactant was obtained from its manufacturer (Dow Chemical). The manufacturer indicated that 35.6% by mass was active surfactant. Sodium dodecyl sulfate (SDS) was purchased from Sigma and was 99+% pure. Triton X-100 (ChemCentral), the only nonionic surfactant included in this study, was also 99+% pure. A fourth anionic surfactant, Isalchem 145 4PO ether sulfate (IC145) (also referred to as Alfoterra 145 by the manufacturer CONDEA Vista) was 34.5 mass % active. Of these, two have been extensively studied in the surfactant literature (Triton X-100 and SDS) and three have been employed in pilot or field demonstrations of SEAR processes (Cytec MA80, DOWFAX 8390, and IC145).

Table 1. Surfactant Properties

surfactant trade name	ionic form	chemical name	cmc (g/L)	MW (g/mol)
Aerosol MA 80-I	anionic	sodium dihexyl sulfosuccinate	7.1[a]	388
DOWFAX 8390	anionic	disodium hexadecyldiphenyloxide disulfonate	0.426[b]	643
Triton X-100	nonionic	t-octylphenoxypolyethoxyethanol	0.112[c]	628
SDS	anionic	sodium dodecyl sulfate	2.36[d]	288
Isalchem 145 4PO ether sulfate	anionic	sodium ($C_{14\ \mathrm{or}\ 15}$ branched alcohol) (propylene oxide)$_4$ ether sulfate	0.0087[e]	553

[a] Calculated from vendor product literature; cmc estimated to drop to 4.2 g/L for a system with 3.0 g/L NaCl and 15.0 g/L IPA. [b] Provided by Dow Chemical. [c] From ref 36. [d] From ref 31 at 25 °C. [e] Provided by CONDEA Vista for surfactant in 0.01 M sodium sulfate.

Headspace Chromatography. Analyses were performed using a Tremetrics 9001 gas chromatograph fitted with a megabore DB624 column. VOCs were eluted using a temperature program of 8 °C per minute from 54 to 126 °C and quantified with a flame ionization detector. After elution of PCE, the latest eluting VOC studied, the oven was heated to 196 °C and then re-equilibrated to the initial temperature. Direct injection of liquid calibration standards verified that detector response was directly proportional to analyte mass over the ranges used in these studies (up to 25 μg for TCA, TCE, and PCE; up to 4 μg for toluene). A headspace autosampler (CombiPAL, LEAP Technologies), equipped with a temperature-stabilized shaking incubator, was used to acquire gas samples via a gastight syringe from sample vials and directly inject these samples into the GC. Vials used with this device had a volume of 21.7 ± 0.1 mL (average measured volume for 10 vials). The headspace above Cytec MA80 solutions had a component that eluted near toluene in the GC chromatogram and interfered with quantification of this VOC. As a result, Henry's law constants were not calculated for toluene in this surfactant. The headspace above Triton X-100 contained a component that eluted near TCE, and constants were also not calculated for this VOC in this surfactant.

EPICS Procedure. The EPICS procedure, described by Gossett (*3*), was used to determine H_c values. An aqueous solution, with or without surfactant, was added to vials in measured volumes. A methanol solution (20−50 μL) of a mixture of TCA, TCE, toluene, and PCE was added to each vial, which was immediately sealed with a crimp cap fitted with a Teflon-surfaced septum. The masses of TCA, TCE, and PCE added were 0.2−0.9 mg, depending on their anticipated volatility in the test mix, with toluene at about 20% that amount. Gossett addressed concerns about the use of mixtures of VOCs in a single trial and about the tolerance for an organic cosolvent such as methanol. The trials reported here stayed within recommended guidelines. Under management by the CombiPAL device, vials were incubated at the equilibration temperature with agitation for 15 min, and then 1 mL of headspace was withdrawn into a heated syringe and submitted to GC analysis. Pilot trials indicated incubation of 12 min or longer was adequate to stabilize headspace VOC concentrations, while incubation for 1 h, especially at higher temperatures, risked greater variability from inadequately sealed vials. Incubator temperatures over the range used in these trials were determined to be within 0.2 °C of the stated value using a calibrated thermistor thermometer.

Data from all possible pairs of vials that were not volume replicates were combined using Gossett's eq 6 to generate estimates for H_c (*3*):

$$H_c = \frac{V_{w2} - rV_{w1}}{rV_{g1} - V_{g2}} \tag{2}$$

where $r = (C_{g1}/M_1)/(C_{g2}/M_2)$ and C_{g1} and C_{g2} are the gas-phase concentrations and M_1 and M_2 are the masses of VOC in vials one and two, respectively. V_{w1} and V_{w2} are the liquid volumes in vials one and two, respectively, with corresponding headspace volumes V_{g1} and V_{g2}. For linear GC detector response, the ratio of the gas-phase concentrations is simply the ratio of the GC peak areas. The median of the collection of estimates was taken as the desired Henry's law constant. Estimates of appropriate rank order provided 68% and 95% confidence intervals (*29*, *30*). These confidence intervals were symmetric about the central estimator in terms of rank order but not necessarily symmetric in magnitude. Statistically significant differences between H_c values were assigned using 95% confidence intervals. Error bars shown in figures correspond to the 68% confidence interval (using the larger confidence interval for each point). In many cases, the error bars are smaller than the symbols presented. Typically, 12−18 vials were used to obtain H_c values for a given solvent at a given temperature. Two or three volumes were replicated, for example, fluid volumes of 3, 8, and 16 mL. For several determinations, specific experimental conditions were imposed which simplified the general EPICS equation: two volumes only were compared, and they were constrained so the fluid volume of one equaled the headspace volume of the other (specifically, 5.7 and 16 mL); equal masses of VOCs were added to each vial. The simplified equation for such data is

$$H_c = \frac{v - r}{vr - 1} \tag{3}$$

where v is the ratio of vapor-phase volumes in the two vials and r is the ratio of vapor-phase analyte concentrations. With six replicates at each volume, 36 pairings provided H_c estimates. Those ranked 12th and 25th defined the 68% confidence interval, and those ranked 6th and 31st defined the 95% interval. The simplified calculations were readily carried out in a spreadsheet program, whereas a computer program was written for calculations using data obtained under less constrained experimental conditions.

Six trials were carried out using a procedure described by Robbins et al. (*10*), the results of which were compared to those obtained with Gossett's EPICS procedure. Several different volumes of solvent containing a single concentration of VOCs were placed in headspace vials and worked up by the usual CombiPAL protocol. Two trials were done with Cytec MA80 surfactant and single trials with water and solutions of DOWFAX 8390, SDS, and Triton X-100 surfactants. Data were analyzed by weighted least-squares regression of an equation linearized by reciprocal transformation (*9*). The six trials mimicked ones carried out by the pairwise EPICS technique and generated both large and small Henry's law constants. Linear regressions of transformed GC peak data were weighted for constant errors in the dependent variable and for errors proportional to the magnitude of the dependent variable, since the

Table 2. Henry's Law Constants for TCA, TCE, Toluene, and PCE in No-Surfactant Control Systems[a]

		H_c [(g/L of vapor)/(g/L of liquid)]			
T (°C)	Cosolutes	TCA	TCE	toluene	PCE
30	none	0.750 ± 0.010	0.427 ± 0.007	0.251 ± 0.006	0.800 ± 0.012
40	none	1.147 ± 0.019	0.693 ± 0.009	0.420 ± 0.007	1.303 ± 0.023
40	10 g/L NaCl	1.200 ± 0.040	0.724 ± 0.030	0.447 ± 0.014	1.370 ± 0.075
40	40 g/L IPA	0.984 ± 0.018	0.595 ± 0.012	0.342 ± 0.005	1.061 ± 0.027
40	80 g/L IPA	0.846 ± 0.023	0.508 ± 0.015	0.279 ± 0.009	0.862 ± 0.027
40	3 g/L NaCl and 15 g/L IPA	1.104 ± 0.014	0.664 ± 0.010	0.391 ± 0.003	1.239 ± 0.032
50	none	1.467 ± 0.080	0.922 ± 0.048	0.558 ± 0.034	1.773 ± 0.094
60	none	1.948 ± 0.034	1.273 ± 0.020	0.774 ± 0.012	2.491 ± 0.046

[a] Note: data for systems without cosolutes represent the average of four replicate EPICS experiments. The error noted for these systems represents the standard deviation of the medians for the four experiments. All other errors are the largest of the observed 68% confidence intervals.

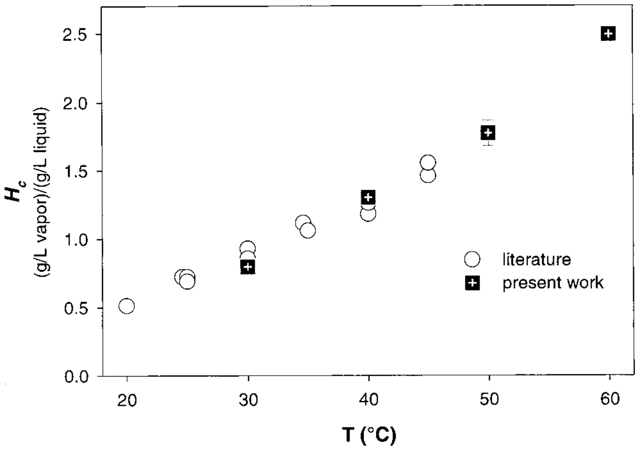


Figure 2. Comparison of Henry's law constants for PCE in water measured in the present study with those in the literature. Vertical error bars indicate 68% confidence intervals. Literature values are from refs 1, 3, 8, and 10.

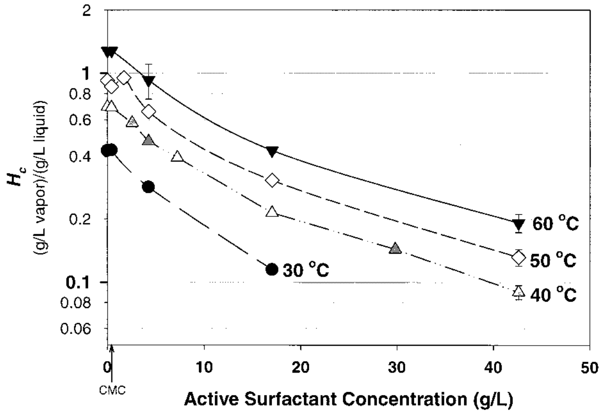


Figure 3. Effect of DOWFAX 8390 surfactant on the H_c values for TCE at 30, 40, 50, and 60 °C. Vertical error bars indicate 68% confidence intervals.

appropriate method of weighting is not known (*9*). For 22 H_c determinations, the values determined via the Robbins technique were within 0.05 H_c units of the values determined using the Gossett method. Neither regression weighting for the Robbins method was clearly superior, and it is reasonable to imagine that a more accurate model would display characteristics of both constant and variable errors. Overall, it was concluded that the Robbins technique generated Henry's law constants comparable to those obtained using the Gossett procedure.

Results and Discussion

H_c values were determined for TCA, TCE, toluene, and PCE in water, in solutions of surfactants, and in aqueous and surfactant systems containing sodium chloride and IPA at concentrations which might be used in surfactant soil remediation processes. Trials were carried out at the temperatures 30, 40, 50, and 60 °C—temperatures which might be utilized in pervaporation separation processes to separate these VOCs from surfactant solutions. A comparison to literature values for an aqueous system (no surfactant) is illustrated in Figure 2 (data from references 1, 3, 8, and 10). Values of H_c for the four VOCs in water determined in the present study were consistent with literature values. H_c values determined in surfactant-free systems are reported in Table 2.

Effect of Surfactant on H_c. The effect of DOWFAX 8390 surfactant on the vapor−liquid partitioning of TCE as a function of surfactant concentration and temperature is illustrated in Figure 3. At all temperatures, H_c decreased as the concentration of surfactant increased. As surfactant is added above the cmc, micelles form, creating hydrophobic zones to which VOCs partition. The more surfactant present, the more hydrophobic regions are available to take up VOC and the less VOC is available to partition into the headspace. Sub-cmc quantities of surfactant should not substantially alter H_c, since no separate hydrophobic zone is available. At the DOWFAX 8390 concentration 1 cmc, there was no significant difference in volatility from that observed for TCE in an entirely aqueous system. The drop in H_c caused by addition of surfactant beyond the cmc was quite dramatic. The H_c value for TCE decreased by a factor of 3 in the presence of 40 cmc DOWFAX 8390 (Figure 3). At a concentration equal to 100 cmc, the headspace partitioning of TCE was quite low at all temperatures, with an H_c of 0.19 even at 60 °C. At this same temperature, $H_c = 1.27$ for TCE in water. Similar trends were observed for the other three VOCs in DOWFAX 8390 and for all VOCs in Triton X-100, Cytec MA80, IC145, and SDS: there were no significant differences in H_c for water with and without 1 cmc surfactant and markedly reduced volatility at higher surfactant concentrations.

While small values of H_c are uncommon for chlorinated VOCs in water, they are clearly achievable for the same VOCs in surfactant solutions. A comparison of 68% confidence intervals as a function of H_c for PCE in all solutions indicated that precision was proportional to the magnitude of H_c. Imprecision was always finite, however, so that the relative imprecision increased without bound as H_c values approached zero. The typical coefficient of variation of 122 trials with PCE, having H_c values ranging from near zero to above 2.5, was 2.2%, expressed as a ratio of $^1/_2$ the 68% confidence interval and the median value that represented H_c. Below $H_c = 0.04$, the regressed coefficient of variation increased beyond 5%. This overview was based solely on

Table 3. Henry's Law Constants for TCA, TCE, Toluene, and PCE in Surfactant Systems[a]

surfactant conc (g/L)	T (°C)	H_c [(g/L of vapor)/(g/L of liquid)]			
		TCA	TCE	toluene	PCE
SDS					
5	30	0.551 ± 0.006	0.305 ± 0.006	0.148 ± 0.007	0.336 ± 0.007
10	30	0.370 ± 0.006	0.199 ± 0.004	0.083 ± 0.002	0.150 ± 0.004
20	30	0.192 ± 0.004	0.091 ± 0.002	<0.04	0.042 ± 0.002
5	40	0.843 ± 0.008	0.497 ± 0.010	0.261 ± 0.006	0.565 ± 0.008
10	40	0.568 ± 0.008	0.324 ± 0.004	0.150 ± 0.003	0.263 ± 0.003
20	40	0.316 ± 0.007	0.171 ± 0.003	0.062 ± 0.004	0.101 ± 0.003
5	50	1.120 ± 0.063	0.695 ± 0.031	0.379 ± 0.008	0.868 ± 0.038
10	50	0.744 ± 0.021	0.445 ± 0.011	0.218 ± 0.006	0.382 ± 0.008
20	50	0.452 ± 0.008	0.262 ± 0.005	0.113 ± 0.004	0.174 ± 0.004
5	60	1.518 ± 0.022	0.977 ± 0.014	0.554 ± 0.010	1.339 ± 0.020
10	60	1.082 ± 0.034	0.674 ± 0.022	0.352 ± 0.011	0.627 ± 0.018
20	60	0.645 ± 0.042	0.391 ± 0.028	0.186 ± 0.019	0.281 ± 0.022
Triton X-100					
0.3	40	1.148 ± 0.010	n/a	0.421 ± 0.006	1.221 ± 0.013
0.6[a]	40	1.086 ± 0.013	n/a	0.390 ± 0.005	1.045 ± 0.024
6[a]	40	0.676 ± 0.011	n/a	0.209 ± 0.004	0.325 ± 0.006
10.5	40	0.551 ± 0.008	n/a	0.160 ± 0.005	0.218 ± 0.008
15[a]	40	0.409 ± 0.008	n/a	0.107 ± 0.005	0.141 ± 0.008
DOWFAX 8390					
0.426	40	1.146 ± 0.022	0.688 ± 0.007	0.410 ± 0.004	1.245 ± 0.033
2.56	40	0.975 ± 0.018	0.580 ± 0.012	0.328 ± 0.009	0.694 ± 0.013
4.26	40	0.814 ± 0.009	0.473 ± 0.004	0.250 ± 0.002	0.469 ± 0.006
7.24	40	0.686 ± 0.011	0.395 ± 0.006	0.205 ± 0.006	0.317 ± 0.006
17.0	40	0.396 ± 0.006	0.214 ± 0.003	0.091 ± 0.003	0.124 ± 0.003
29.8	40	0.268 ± 0.004	0.144 ± 0.004	0.064 ± 0.003	0.075 ± 0.003
42.6[a]	40	0.183 ± 0.007	0.090 ± 0.007	<0.04	<0.04
Cytec MA80 (with 3 g/L NaCl, 15 g/L IPA)					
10	40	1.028 ± 0.021	0.613 ± 0.015	n/a	1.008 ± 0.020
25	40	0.524 ± 0.005	0.302 ± 0.003	n/a	0.255 ± 0.003
40[a]	40	0.297 ± 0.006	0.164 ± 0.004	n/a	0.102 ± 0.004
IC145					
1	40	1.052 ± 0.019	0.628 ± 0.009	0.373 ± 0.009	0.928 ± 0.018
5	40	0.718 ± 0.020	0.403 ± 0.008	0.218 ± 0.009	0.350 ± 0.017
10	40	0.522 ± 0.017	0.283 ± 0.013	0.146 ± 0.007	0.192 ± 0.013
20	40	0.314 ± 0.005	0.164 ± 0.006	0.077 ± 0.006	0.079 ± 0.005

[a] Average of two or more replicated EPICS experiments; largest 68% confidence interval listed.

PCE data and was not intended to exactly describe a specific trial with its specific level of experimental variability. Nonetheless, for all the VOCs, we considered that values below $H_c = 0.04$ had inferior precision and should not be reported. Only 6 of 122 H_c values for PCE were below this point. Gossett, too, reported that precision worsens markedly at low H_c and suggested that imprecision in sampling and GC analysis and in dispensing of VOCs is important in the overall precision (*3*).

Effect of Temperature on H_c. Higher temperatures yielded higher values of H_c, although the shapes of the curves in Figure 3 were not affected by temperature. Data for all surfactants are presented in Table 3. Little comparable data exist in the literature for this variety of surfactants, for these types of VOCs, and for this range of temperatures. Anderson reported $H_c = 0.130 \pm 0.009$ for toluene in 0.03 M SDS (8.6 g/L) in the presence of 1.8 g/L NaCl at 23 °C (*23*). Taking into account the differences in SDS concentration, NaCl concentration, and temperature, this is in general agreement with our results for toluene in SDS solutions.

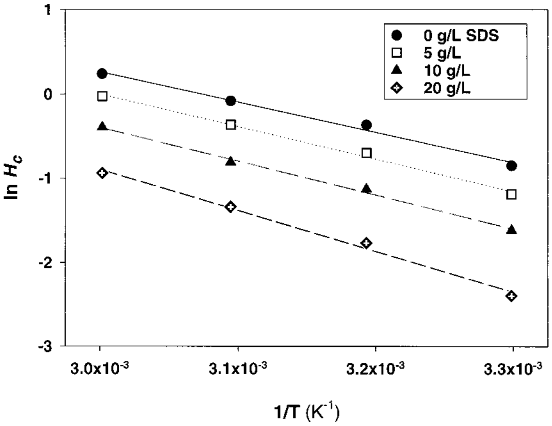


Figure 4. van't Hoff plots of the variation of H_c for TCE with temperature for various SDS concentrations.

The variation of H_c with temperature for VOCs in water is well modeled with the van't Hoff equation (*3*):

$$\ln H_c = A - \frac{B}{T} \tag{4}$$

where A and B are constants for a specific VOC. The temperature variation of H_c for TCE in various SDS solutions is presented as van't Hoff plots in Figure 4. In all cases, the plots were linear with regression r^2 values ranging from 0.990 to 0.996, indicating that, even with surfactant present, the van't Hoff equation fit the data well. The resulting correlation could be used to predict H_c for surfactant solutions at other temperatures. The addition of surfactant resulted in lower intercepts and steeper slopes in such plots. For example, the addition of 20 g/L SDS resulted in a 24% increase in A and a 36% increase in B.

Effect of VOC on H_c Reduction. In principle, the more hydrophobic the VOC, the more readily it will partition into surfactant micelles. This was clearly the case for SDS with TCA, TCE, toluene, and PCE, as displayed in Figure 5 (interpolation lines in the figure were added to assist in observing trends and were not meant to imply that H_c

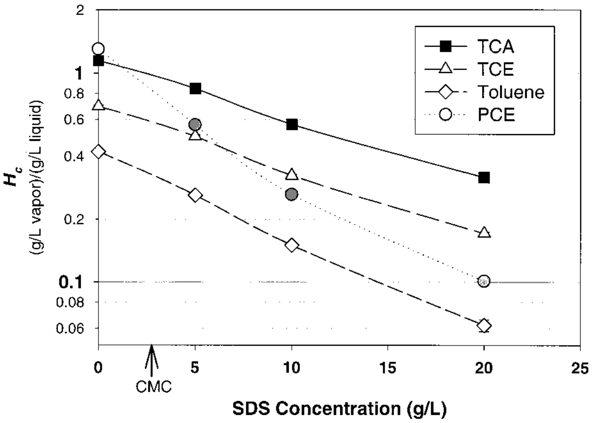


Figure 5. Impact of VOC type on the response of H_c to SDS concentration at 40 °C. Vertical error bars indicate 68% confidence intervals.

below the cmc of SDS is any different from that without SDS). The curves for TCA and TCE exhibit similar shapes while H_c for toluene responds more rapidly to the addition of surfactant. PCE, the most hydrophobic of the four VOCs studied, displays the most dramatic response to increased surfactant levels. In fact, of the four VOCs, PCE is the easiest to remove from water by vapor−liquid stripping but can become the most difficult to remove upon addition of surfactant because of its micellar partitioning. The relatively greater effect of surfactant on PCE than on toluene, TCA, or TCE, seen in Figure 5, was also seen with the other four surfactants: at high surfactant concentrations, the H_c value for PCE was smaller in magnitude than those for TCA and TCE, although it was larger in the absence of surfactant.

Effect of Cosolutes. Alcohols and salts are often added to surfactant-based soil remediation fluids to control the properties of the surfactant and the fluid. Addition of electrolyte to anionic surfactant solutions results in a reduction in the cmc, thereby enabling the formation of micelles at a lower surfactant concentration. For example, addition of sodium ions reduces the effective charge of the polar groups of anionic surfactants, resulting in less repulsion between these groups when surfactant monomers assemble as micelles (*31*). Generally, a log−log relationship exists between the cmc of anionic surfactants and the counterion concentration (*31*). For SDS, this relationship is (from data in ref 31)

$$\log[\mathrm{cmc}] = -0.55 \log [\mathrm{Na}^+] - 3.34 \qquad (5)$$

where concentrations are in units of moles per liter. From vendor literature, the cmc for Cytec MA80 is expected to follow the following relationship:

$$\log[\mathrm{cmc}] = -0.745 \log [\mathrm{Na}^+] - 2.92 \qquad (6)$$

In surfactant remediation processes, alcohols such as IPA may be added to stabilize the solubilization/microemulsion systems and to control the viscosity of the solutions in the subsurface.

To examine the impact of salts and alcohols on H_c, IPA and sodium chloride were used as cosolutes in Cytec MA80 surfactant solutions. Sodium chloride also was studied as a cosolute in the SDS system. A small amount of IPA was already added by the manufacturer of Cytec MA80 to assist in material processing. In surfactant-free control trials, the H_c values determined in 15 g/L IPA and 3 g/L NaCl for TCA, TCE, toluene, and PCE were not significantly different from the values in water at all temperatures studied. Likewise, the values in 10 g/L NaCl were not significantly affected. However, the H_c values determined in 40 g/L IPA were 14−18% below the water H_c values for the four VOCs, whereas those determined in 80 g/L IPA were 26−34% below the water H_c values. The effects of these two concentrations of IPA on H_c were statistically significant at the 5% level.

Table 4. Henry's Law Constants for TCA, TCE, Toluene, and PCE in Solutions of Cytec MA80 Surfactant with Cosolutes NaCl and IPA and SDS with NaCl. Equilibration Temperature of 40 °C

	H_c [(g/L of vapor)/(g/L of liquid)]			
surfactant solution	TCA	TCE	toluene	PCE
25 g/L Cytec MA80 with				
0 g/L NaCl,[a] 15 g/L IPA	0.604	0.352	n/a	0.341
3 g/L NaCl,[a] 15 g/L IPA	0.524[b]	0.302[b]	n/a	0.255[b]
10 g/L NaCl,[a] 15 g/L IPA	0.438[b]	0.253[b]	n/a	0.177[b]
40 g/L Cytec MA80 with				
3 g/L NaCl, 15 g/L IPA	0.297	0.164	n/a	0.102
3 g/L NaCl, 40 g/L IPA	0.271[b]	0.154	n/a	0.102
3 g/L NaCl, 80 g/L IPA	0.221[b]	0.120[b]	n/a	0.078[b]
10 g/L SDS with				
0 g/L NaCl[c]	0.568	0.324	0.150	0.263
3.8 g/L NaCl[c]	0.509[b]	0.295[b]	0.135[b]	0.202[b]
20 g/L SDS with				
0 g/L NaCl	0.316	0.171	0.062	0.101
3.8 g/L NaCl	0.323	0.182	0.074	0.099

[a] cmc of Cytec MA80 is 7.1, 4.2, and 1.7 g/L at 0, 3, and 10 g/L NaCl, respectively, as per eq 6. [b] Statistical significance at the 5% level for the effect of NaCl or IPA. [c] cmc of SDS is 2.36 g/L at 0 g/L NaCl and 0.59 g/L at 3.8 g/L NaCl at 25 °C, as per eq 5.

The consequences of altering the cmc of Cytec MA80 and SDS surfactant by the addition of salt and the effects of IPA addition on the H_c values for TCA, TCE, and PCE in Cytec MA80 are itemized in Table 4. At 25 g/L (active) Cytec MA80, distribution coefficients were significantly lower at both 3 g/L and 10 g/L NaCl. For the 40 g/L Cytec MA80 system, the addition of 40 g/L IPA decreased H_c by a few percent and 80 g/L IPA decreased H_c by 25%, so the relative effect approximated that seen in the surfactant-free control trials. However, the magnitude of the decreases was small and the differences were not statistically significant except in one instance. While addition of salt is expected to alter the cmc values of almost all anionic surfactants, the net effect on H_c will depend on how close the surfactant concentration is to the no-salt cmc. For example, Cytec MA80 has a cmc of 7.1 g/L with no salt (vendor data). According to eq 6, the cmc drops to 4.2 g/L in the presence of only 3 g/L NaCl. As a result, the 25 g/L Cytec MA80 system shown in Table 4 would have a relative cmc concentration of 3.5 cmc with no salt but 6.0 cmc with 3 g/L NaCl, resulting in the actual amount of surfactant present as micelles rising from 17.9 to 20.8 g/L. For SDS at 10 g/L, the amount of surfactant present as micelles increases 24% from 7.6 g/L at 0 g/L NaCl to 9.4 g/L at 3.8 g/L NaCl. This change in cmc results in a 10−23% reduction in H_c, as shown in Table 4. However, for SDS at 20 g/L, the same change in salt concentration only changes the amount of surfactant present as micelles by 10%, from 17.6 g/L to 19.4 g/L, with no discernible impact on H_c. For anionic surfactants with even lower cmc's, such as DOWFAX 8390, the impact of salt addition on H_c should be nearly undetectable at typical surfactant mass concentrations used for soil remediation.

Temperature, too, affects the cmc of surfactants, less so in anionics than in nonionics. For example, the cmc of SDS

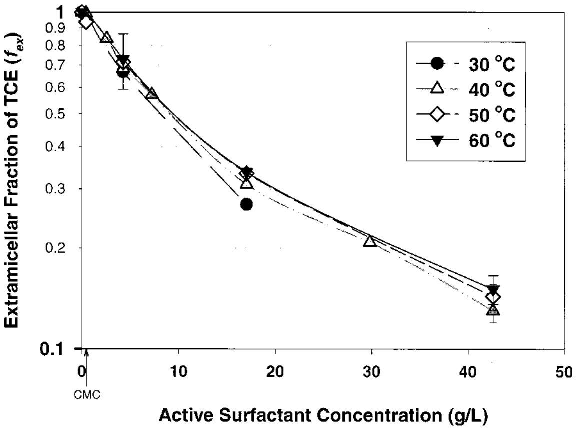


Figure 6. Variation of the fraction of TCE which is extramicellar (f_{ex}) with DOWFAX 8390 concentration at 30, 40, 50, and 60 °C. Vertical error bars indicate 68% confidence intervals.

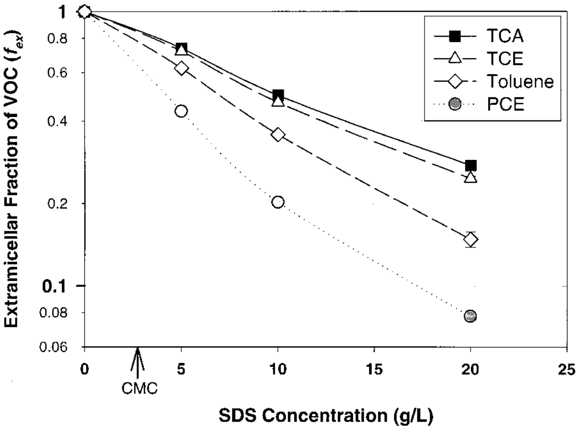


Figure 7. Effect of SDS concentration on the fraction of VOC which is extramicellar (f_{ex}) for TCA, TCE, toluene, and PCE at 40 °C. Vertical error bars indicate 68% confidence intervals.

increases from 2.36 g/L at 25 °C to 2.48 g/L at 40 °C (*31*). The cmc of nonionic surfactants generally decreases with increasing temperature. For anionics, the effect of temperature on the cmc is not nearly as pronounced as the effect of salt concentration.

Calculation of Extramicellar Fraction of VOC. H_c for surfactant solutions might best be described as an "apparent H_c", designated as H_c*, since the EPICS method considers the liquid concentration in the denominator of the Henry's law expression (eq 1) as the total concentration of VOC solubilized in the surfactant solution, both in micelles and in the extramicellar water region. Unless significant amounts of nonsurfactant modifiers, such as alcohols or salts, have been added to the solution, the H_c of a VOC in the extramicellar water is not affected by the surfactant. Thus, the extramicellar concentration of VOC can be calculated from the headspace concentration above a given surfactant solution and the H_c for the VOC in water void of surfactant ($H_c°$). Likewise, the fraction of VOC in the solution which is extramicellar can be calculated from the H_c measured with surfactant and that measured without:

$$f_{ex} = \frac{H_c[\text{with surfactant}]}{H_c[\text{no surfactant}]} = \frac{H_c^*}{H_c^\circ} \tag{7}$$

where f_{ex} is the extramicellar fraction of VOC in the system. Equation 7 can also be used for surfactant systems containing alcohols and salts as long as the H_c used in the denominator is determined in the same solution matrix as was used for the surfactant tests. The calculated values of f_{ex} for the H_c data in Figures 3 and 5 are shown in Figures 6 and 7, respectively. The f_{ex} data in Figure 7 show the impact of VOC hydrophobicity on micellar partitioning. In the presence of 10 g/L SDS, slightly more than 20% of the PCE is extramicellar while almost 50% of the TCA is outside the micelles. In addition, while temperature has a marked impact on the magnitude of H_c (as seen in Figure 3), it does not dramatically impact f_{ex}, as evidenced by the overlapping curves in Figure 6. As a result, a surfactant solution at 30 °C will have approximately the same fraction of VOC in micellar form as one at 60 °C. The general trend is that f_{ex} increases slightly with increasing temperature. Valsaraj et al. calculated a very slight decrease in micellar partitioning for increasing temperature (25 to 33 °C) for chloroform and carbon tetrachloride in sodium dodecyl benzenesulfonate, although the difference was within the stated error tolerance (*28*).

Surfactant Effects on Micellar Partitioning. f_{ex} data for VOCs in solutions of IC145, DOWFAX 8390, Cytec MA80, and Triton X-100 are shown in Figure 8, presented in the same manner as the SDS data was in Figure 7. All surfactants were capable of significantly reducing f_{ex} for the VOCs tested. However, the response of f_{ex} to changes in surfactant concentration was not necessarily the same. Analysis of this point is complicated by the various ways in which surfactant concentration can be characterized, such as in units of surfactant mass per volume, number of cmc, and surfactant molarity. Regardless of the units selected, the surfactant molecules actually affecting f_{ex} are only those molecules in micellar form; thus, f_{ex} for the different surfactants should be compared to the micellar surfactant concentration. The concentration of surfactant in micellar form (referenced to the total solution volume) S_m is equal to the total surfactant concentration S minus the cmc of that surfactant:

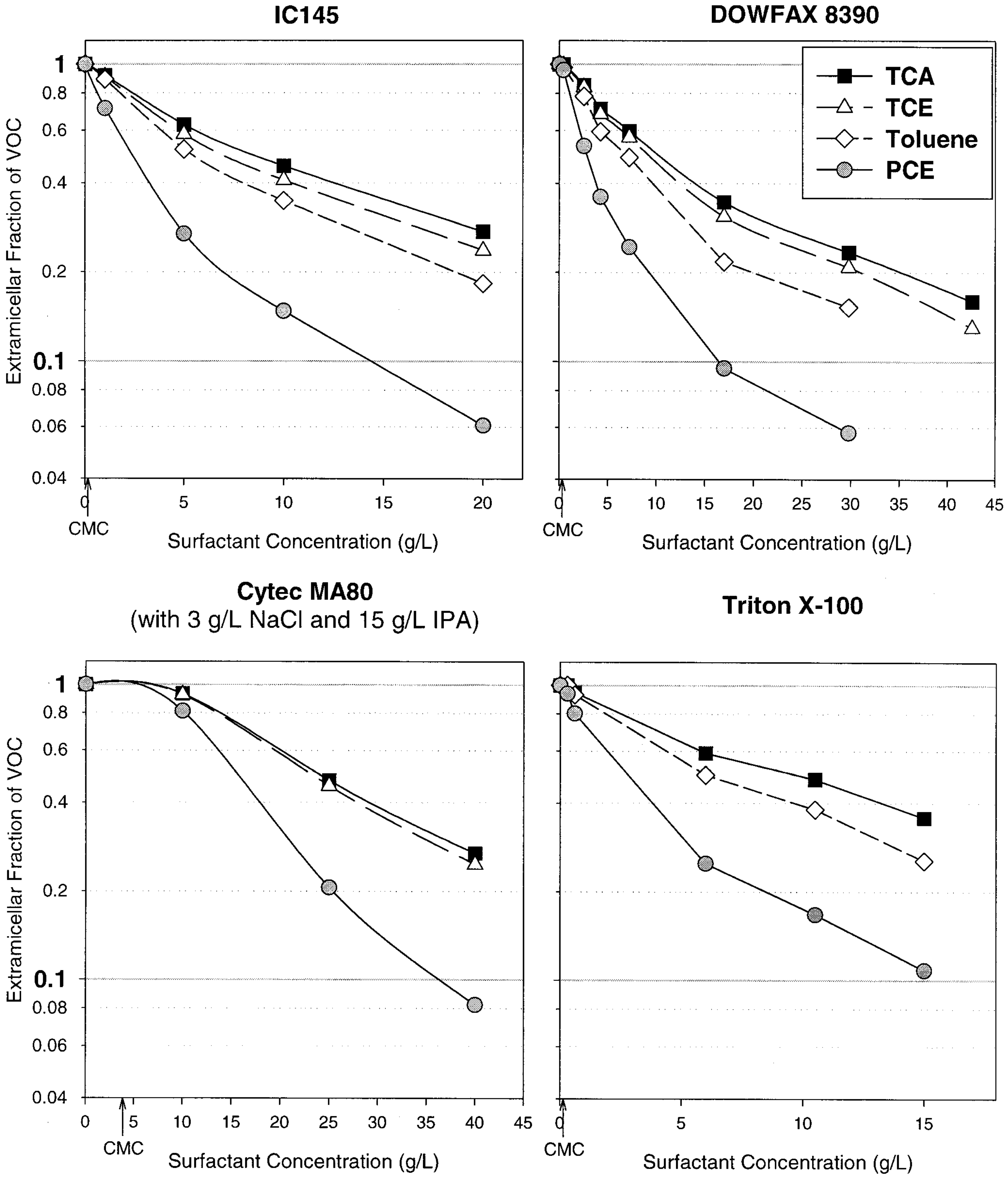
$$S_m = S - \text{cmc} \tag{8}$$

A comparison of the variation of f_{ex} for PCE with S_m for the three sets of concentration units is presented in Figure 9. As seen in the figure, each gram per liter of SDS, DOWFAX 8390, IC145, and Triton X-100 above the respective cmcs reduces the f_{ex} for PCE to approximately the same extent. Cytec MA80 requires about twice the mass concentration of the other three to achieve the same reduction in f_{ex}. On a number of cmc basis, Cytec MA80 and SDS are most efficient at reducing f_{ex}, primarily due to the relatively high cmc of these surfactants. On a molarity basis, DOWFAX 8390, IC145, and Triton X-100 are the most effective at reducing f_{ex}, with Cytec MA80 the least effective.

A more theoretical method of gauging surfactant effectiveness is to define a partition coefficient K for partitioning of VOC between the micellar pseudophase and the aqueous extramicellar region (*26, 28, 32, 33*):

$$K\ (\text{L/mol}) = \frac{x_m}{C_{ex}} \tag{9}$$

where C_{ex} is the extramicellar concentration of VOC (in units of mol/L) and x_m is the mole fraction of VOC in the micellar region. K should be independent of surfactant concentration unless the micellar structure changes with concentration (*32*). The mole fraction of VOC in the micellar


IC145

DOWFAX 8390

Cytec MA80
(with 3 g/L NaCl and 15 g/L IPA)

Triton X-100

Figure 8. Effect of surfactant concentration on the fraction of VOC which is extramicellar (f_{ex}) for IC145, DOWFAX 8390, Cytec MA80, and Triton X-100 at 40 °C. Note: error bars excluded for clarity.

region is defined as:

$$x_m = \frac{C_m}{C_m + S_m} \tag{10}$$

where C_m is the molar concentration of VOC in micelles (referenced to the total solution volume). The total VOC concentration in the surfactant solution is the sum of C_m and C_{ex}. For solutions dilute in VOC (as was the case in this study), $C_m \ll S_m$, and Eq 9 becomes

$$K \approx \frac{C_m}{C_{ex} S_m} \tag{11}$$

Substituting f_{ex} for C_m and C_{ex} in eq 11 yields

$$K \approx \frac{1 - f_{ex}}{f_{ex}} \frac{1}{S_m} \tag{12}$$

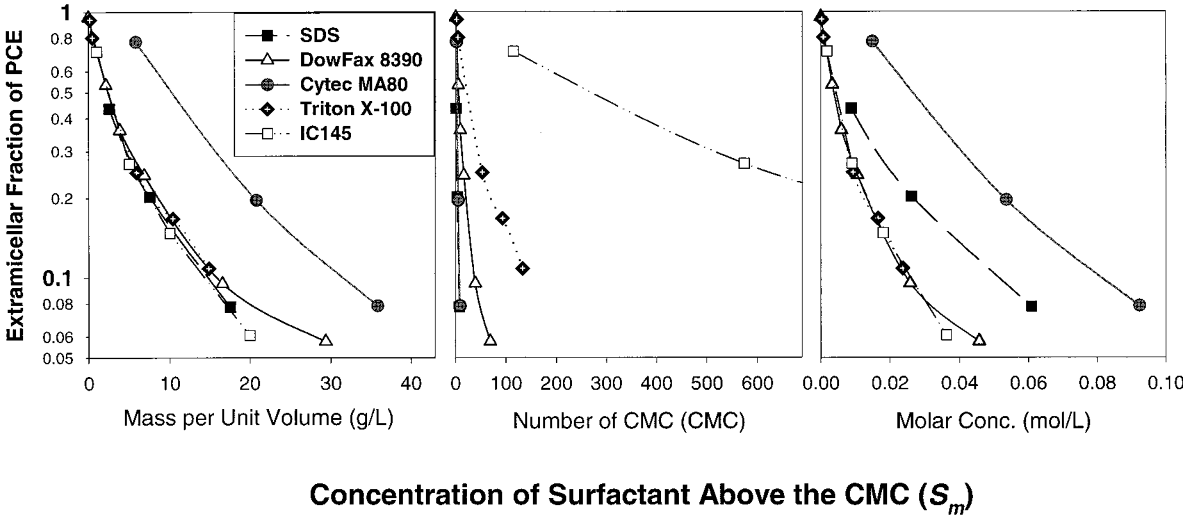


Figure 9. Effect of surfactant concentration on the extramicellar fraction (f_{ex}) of PCE for all surfactants evaluated as a function of the concentration units selected. Note: error bars excluded for clarity.

Table 5. Calculated Values of the Micellar Partitioning Coefficient *K* for the VOCs and Conditions in Table 3 with 95% Confidence Limits Provided

		K (L/mol)			
surfactant	*T* (°C)	TCA	TCE	toluene	PCE
SDS	30	43 ± 5	50 ± 10	78 ± 2	206 ± 88
	40	41 ± 2	46 ± 4	78 ± 17	165 ± 30
	50	36 ± 1	40 ± 3	59 ± 6	136 ± 19
	60	32 ± 1	35 ± 2	48 ± 4	113 ± 18
Triton X-100	40	72 ± 6	n/a	110 ± 14	323 ± 26
DOWFAX 8390	40	71 ± 5	84 ± 10	119 ± 17	329 ± 38
Cytec MA80 (with 3 g/L NaCl, 15 g/L IPA)					
	40	18 ± 14	20 ± 16	n/a	69 ± 60
IC145	40	69 ± 5	83 ± 6	110 ± 13	350 ± 77

Thus, Henry's law constant data can be used to calculate a micellar partitioning coefficient. In this manner, *K* was calculated from the H_c data in Tables 2 and 3 and the surfactant properties in Table 1. Results are shown in Table 5. A value of *K* was calculated for each surfactant concentration, and then values for all concentrations of the same surfactant at the same temperature were averaged. The averages and 95% confidence intervals are presented in the table. The *K* values for SDS, IC145, DOWFAX8390, and Triton X-100 did not exhibit any distinct concentration trends. However, *K* for Cytec MA80 increased markedly with concentration over the three surfactant concentrations studied for all VOCs, independent of temperature. For example, *K* for TCA in Cytec MA80 increased from 5 to 29 L/mol as total surfactant concentration increased from 1 to 4 g/L. This trend could be caused by a change in micelle structure as surfactant concentration increases. However, current cmc and micelle structure information for Cytec MA80 is insufficient to properly characterize this trend.

The partitioning coefficients in Table 5 indicate that DOWFAX 8390, IC145, and Triton X-100 have the highest partitioning coefficients of the five surfactants for all VOCs studied, while Cytec MA80 has the lowest. The partitioning coefficient increased according to the following series of VOCs: TCA < TCE < toluene < PCE. Further, the SDS data show that *K* decreases with increasing temperature. This trend in *K* is consistent with observations from Figure 6 that less VOC partitions to micelles as temperature increases. The data for TCA in Triton X-100 presented in Table 5 are consistent with previous results from our group. In that work, a value of $K = 74$ L/mol (reported in unitless form as $K = 4130$) was determined for TCA in Triton X-100 at 30 °C on the basis of experiments using the EPICS procedure, but with manual sample acquisition and injection (*34*). In addition, researchers at the University of Oklahoma have reported *K* values of 105 L/mol for TCE in DOWFAX 8390, which is reasonably consistent with that presented in Table 5 (*35*). Finally, the trend of lower *K* with increasing temperature is consistent with previously reported data for TCE in *N*-hexadecylpyridinium chloride (*26*).

In general, the results indicate that PCE may be the hardest of the four VOCs to remove from typical SEAR solutions and that significant amounts of VOC could be present in the micellar region. Designers of separation processes will need to account for both reduced vapor−liquid equilibrium as well as the amount of NAPLs held in the micellar "reservoirs". The EPICS headspace procedure provides a relatively convenient method for obtaining this information.

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