Solubilization of Trichloroethylene by Polyelectrolyte/Surfactant Complexes

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An automated vapor pressure method is used to obtain solubilization isotherms for trichloroethylene (TCE) in polyelectrolyte/surfactant complexes throughout a wide range of solute activities at 20 and 25°C. The polyelectrolyte chosen is sodium poly(styrenesulfonate), PSS, and the surfactant is cetylpyridinium chloride or N-hexadecylpyridinium chloride, CPC. Data are fitted to the quadratic equation $K=K_0(1-\alpha X+\beta X^2)$*, which correlates the solubilization equilibrium constant* (K) *with the mole fraction of TCE* (X) *in the micelles or complexes at each temperature. Activity coefficients are also obtained for TCE in the PSS/CPC complexes as a function of* X*. The general solubilization behavior of TCE in PSS/CPC complexes resembles that of TCE in CPC micelles, as well as that of benzene or toluene in CPC micelles, suggesting that TCE solubilizes in ionic micelles both within the hydrocarbon micellar interior and near the micellar surface. The presence of the polyelectrolyte causes a small decrease in the ability of the cationic surfactant to solubilize TCE, while greatly reducing the concentration of the surfactant present in monomeric form. PSS/CPC complexes may be useful in colloid-enhanced ultrafiltration processes to purify organic-contaminated water.*

Introduction

Colloid-enhanced ultrafiltration (CEUF) methods are novel separation processes for removing organic solutes from aqueous streams (Christian et al., 1990). Micellar enhanced ultrafiltration (MEUF) (Christian and Scamehorn, 1989; Dunn et al., 1985, 1987) is one such technique, in which a micellar solution is added to a contaminated feed stream. The resulting solution is passed through a membrane with pore sizes smaller than the micellar diameter, so that the micelles and solubilized organic solute are removed. Previous MEUF studies indicate that the separations (solute rejections) obtained are usually closely related to equilibrium values inferred from semiequilibrium dialysis (SED) (Christian et al., 1985, 1994; Bhat et al., 1987; Smith et al., 1986; Higazy et al., 1987; Uchiyama et al., 1990, 1994b; Lee et al., 1990, 1991a,b; Kondo et al., 1993; Abe et al., 1993) and vapor pressure experiments (Tucker et al., 1981, 1982; Christian et al., 1982, 1986; Smith et al., 1989).

One important modification of MEUF is the use of polymer/surfactant complexes as the soluble colloid, in place of surfactant micelles alone. Previously, it has been shown that mixtures of a water-soluble anionic polyelectrolyte and a cationic surfactant (with 2:1 or 3:1 excess of anionic charge) retain the ability of the surfactant to solubilize potentially-hazardous organic solutes, while almost entirely preventing loss of the surfactant through the ultrafiltration membrane (Lee et al., 1991b). There have been numerous studies of the formation of complexes in aqueous solution between soluble polyelectrolytes and oppositely charged ionic surfactants (Goddard and Leung, 1992; McQuigg et al., 1992; Carlsson et al., 1989; Brackman et al., 1992; Kido et al., 1991; Gao et al., 1990;

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Tokiwa et al., 1973; Arai and Horin, 1969), and many polymer/surfactant complexes have been shown to have much reduced thermodynamic activities (monomer concentrations) of the surfactants, compared to micellar solutions of these solutes in the absence of added polyelectrolytes.

Except for work from our laboratory (Lee et al., 1991b; Uchiyama et al., 1994b), there have been few studies of the solubilization of organic solutes in polymer/surfactant mixtures throughout wide ranges of relative concentrations of organic solute in the polymer-bound surfactant aggregates. We have shown that a partially-neutralized copolymer of maleic anhydride and vinyl methyl ether (Gantrez S-95) forms complexes with a cationic surfactant, cetylpyridinium chloride (CPC), throughout a wide concentration range. In order to predict the effectiveness of CEUF, utilizing polyelectrolyte/surfactant complexes as the added colloid to bind molecular organic solutes, additional solubilization data are required.

Literally hundreds of studies have been made of the extent of solubilization of organic compounds by surfactant solutions (Nguyen et al., 1988; Christian and Scamehorn, 1989, 1994). However, relatively few of these provide detailed and accurate solubilization isotherms, that is, measured solubilization results at varying solute activities and mole fractions of the solute in the micelles. In applications of CEUF, it is important to have solubilization results for target solutes throughout a range of activities, as well as derived information about the distribution of organics between the "micellar" and "bulk" pseudophases. In the case of relatively nonvolatile organic solutes, a new SED method has proven to be quite useful in inferring solubilization equilibrium results needed in predicting the effectiveness of CEUF separations (Christian et al., 1985, 1994; Bhat et al., 1987; Smith et al., 1986; Higazy et al., 1987; Uchiyama et al., 1990, 1994a; Lee et al., 1990, 1991a,b; Kondo et al., 1993; Abe et al., 1993).

An automated vapor pressure apparatus developed in our laboratory can be used to obtain highly-accurate solubilization data for volatile organic solutes, such as benzene and the lower molecular weight chlorinated alkanes and alkenes, interacting with surfactants and other nonvolatile solutes (Tucker et al., 1981, 1982; Christian et al., 1982, 1986; Smith et al., 1989). The experimental solute vapor pressure (SVP) results, interpreted with the aid of mass-action and pseudo-phase equilibrium models, lead directly to the determination of equilibrium constants for the self-association of individual solutes and for the formation of specific complexes between the volatile and the nonvolatile solute in aqueous solution. The SVP measurements also provide information about the thermodynamic activity and activity coefficient of a surfactant as a function of intramicellar composition (mole fraction of surfactant and organic solute in the micelle) and temperature.

Chlorinated hydrocarbons such as trichloroethylene (TCE) and tetrachloroethylene (PCE) are widely used as industrial solvents and de-greasers. As a result, groundwater and soil near major industrial sites are frequently polluted with TCE and PCE, posing a threat to local water supplies. In the present work, the SVP method has been used to obtain solubilization data for a chlorinated hydrocarbon, trichloroethylene, solubilized by the complexes of hexadecylpyridinium chloride (CPC) and sodium poly(styrene sulfonate) (PSS). Such results are of direct use in predicting the utility of CEUF as a method for removing TCE and related compounds from contaminated water. In this article, we report solubilization equilibrium constants for TCE in CPC micelles and PSS/CPC complexes, as well as values of the activity coefficient of the solubilized solute, throughout a range of compositions at 20°C and 25°C.

Experimental Procedures

Certified 99+% TCE was obtained from Aldrich Co. High-quality *n*-hexadecylpyridinium chloride monohydrate (cetylpyridinium chloride or CPC) was obtained from Hexcel Co. and used without further purification. The surface tension vs. concentration curve for aqueous CPC solutions showed no minimum and no impurities were observed by HPLC analysis, using UV or conductivity detectors.

An anionic polymer, sodium poly(styrenesulfonate) (PSS), is used as the polyelectrolyte in the present studies. The PSS, from Aldrich Co., has a weight average molecular weight of approximately 70,000 daltons. Preliminary to the vapor pressure experiments, lower molecular weight fractions of PSS are removed with a spiral wound ultrafiltration apparatus described previously (Tucker et al., 1992).

The automated vapor pressure system developed in this laboratory consists of four primary components (Tucker et al., 1981, 1982; Christian et al., 1982, 1986; Smith et al., 1989; Uchiyama et al., 1994b): (1) a high pressure liquid chromatography valve with a 20 μL external sample loop, remote operator, and a thermostatted reservoir (at 50°C) for TCE; (2) a thermostatted bath containing the LC valve and the vapor pressure sample chamber; (3) a high precision pressure transducer (a Paroscientific, Inc. Model 215A was used in the present study); (4) a microcomputer controller reading pressure data via a BCD interface and sending control signals via a parallel output port. The thermostat bath temperature was monitored by a Hewlett-Packard 2804A thermometer through an IEEE-488 interface. Maximum overnight temperature variations of the bath containing the vapor pressure chamber were on the order of 0.003°C.

Preliminary to performing SVP measurements on surfactant solutions, we carried out a series of "blank" experiments to obtain the dependence of the partial pressure of TCE on its mole fraction or molarity in aqueous solution. TCE stored in the external reservoir (at 50°C), under its own vapor pressure, was added to the evacuated measuring system containing a weighed amount of pure liquid water (thoroughly degassed prior to addition of the TCE, and stirred throughout the experiment with a magnetic stirrer bar). The inlet valve introduces replicate samples of the volatile liquid of accurately known volume (by flash evaporation), so that the overall composition of the liquid-vapor system as well as the compositions of the individual vapor and liquid phases can be inferred with great precision for each mixture at the measured total pressure. Information about the partial pressure of TCE, which varies nearly linearly with the molar composition of TCE in the very dilute solutions studied, is of course required in interpreting SVP data for TCE in the surfactant solutions.

Analogous SVP experiments were performed, as described above, using in place of pure water, aqueous solutions of the surfactant or the polyelectrolyte/surfactant mixture in the receiving flask. The concentrations of TCE solubilized by the surfactant micelles were inferred by subtracting the concentration of monomeric TCE from the total TCE concentration

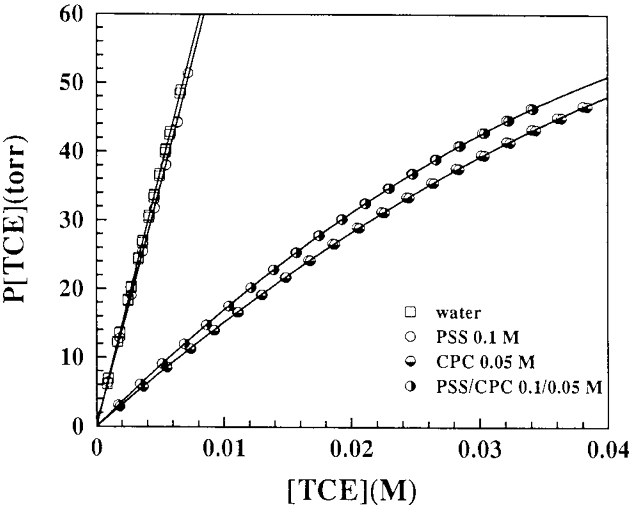

Figure 1. Trichloroethylene fugacity as a function of molarity for solutions in water, 0.1-M PSS, 0.05 M CPC, and 0.1M/0.05-M PSS/CPC at 25°C.

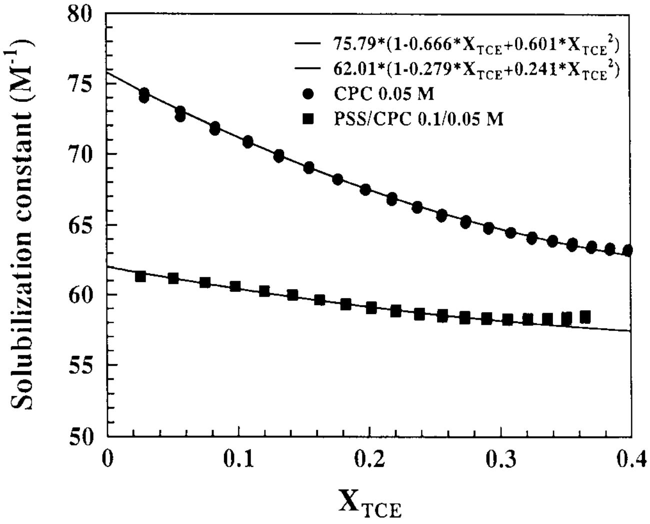

Figure 2. Solubilization constant as a function of mole fraction of TCE in CPC micelles and in the PSS/CPC complex at 25°C.

in the ternary system containing the surfactant *at the same TCE activity*. Slight corrections were made to account for the "salting-out" of TCE by ionic surfactants and for the existence of small concentrations of the surfactant in monomeric (nonmicellar) form (Tucker and Christian, 1982, 1985). The temperature was capable of variation from 15 to 45°C, although the present measurements were performed at 20 and 25°C.

Turbidity studies were performed to determine ranges of concentrations of PSS and CPC at which a second phase forms in equilibrium with the homogeneous aqueous solution. At mole ratios of [PSS]:[CPC] greater than or equal to 2:1, the polyelectrolyte/surfactant complex is present in homogeneous aqueous solutions at temperatures throughout the range of measurement. At mole ratios somewhat less than about 2:1, precipitation occurs and redissolution of the precipitate can be slow. The solutions employed in the present experiments were quite clear before, during, and after addition of TCE.

Results

Figure 1 shows plots of the partial pressure of TCE as a function of the concentration of TCE in water, 0.1-M PSS (based on monomer unit concentration), 0.05-M CPC, and 0.1/0.05-M PSS/CPC at 25°C. The partial pressures of TCE increase with increasing concentration of TCE in the solutions. The partial pressure of TCE in a PSS solution at a given total TCE concentration is almost the same as that in water.

At any given partial pressure of TCE (at constant TCE activity), the difference between the concentration of TCE in a surfactant solution (or in polyelectrolyte/surfactant solution) and the concentration of TCE in pure water at the same activity [corrected slightly for a *salting-out effect* (Tucker and Christian, 1985)] corresponds to the concentration of TCE solubilized in the micelle-like complexes. It is, therefore, possible to calculate the solubilization equilibrium constant, which expresses the partitioning of TCE between micelle-like complexes and the bulk phase, almost directly from the SVP data.

We define the solubilization equilibrium constant (K) of TCE in the CPC micelle or PSS/CPC complex by:

$$K = \frac{X_{\mathrm{TCE}}}{C_{\mathrm{TCE}}} \tag{1}$$

where

$$X_{\mathrm{TCE}} = \frac{C_{\mathrm{TCE}}^{\mathrm{agg}}}{C_{\mathrm{TCE}}^{\mathrm{agg}} + C_{\mathrm{CPC}}^{\mathrm{agg}}} \tag{2}$$

is the intramicellar mole fraction of TCE, that is, the ratio of the molar concentration of solubilized TCE, $C_{\mathrm{TCE}}^{\mathrm{agg}}$, to the total molar concentration of the surfactant and organic solute in the complex, $C_{\mathrm{TCE}}^{\mathrm{agg}} + C_{\mathrm{CPC}}^{\mathrm{agg}}$, where C_{TCE} is the molar concentration of unsolubilized or monomeric TCE. The superscript "agg" in Eq. 2 denotes TCE and CPC species present in the surfactant/polyelectrolyte complex. Because preliminary experiments indicated that almost no TCE solubilizes in a PSS solution in the absence of added surfactant, the PSS concentration is not taken into account in deriving values of the mole fraction. An advantage of this definition of K is that it permits comparison with K values for solubilization in micelles in the absence of polyelectrolyte (Lee et al., 1991b). Solubilization results obtained by the SVP method for TCE in CPC solution and mixed solutions of PSS and CPC are shown in Figure 2. Values of the solubilization equilibrium constant for the individual experiments are plotted against the mole fraction of TCE in the CPC micelles or aggregates (attached to PSS) at equilibrium. The solubilization constant in both solutions decreases slightly with increasing mole fraction of TCE in the micelle (or aggregate).

The limiting solubilization constants of TCE in CPC micelles (K_0) have been determined by fitting K vs. X_{TCE} data to a quadratic equation (see Discussion section). K_0 is the value of the solubilization constant in the limit as X_{TCE} approaches zero. As shown in both Figures 2 and 3, the K_0 values in PSS/CPC mixed solutions are smaller by approximately 20% than those in CPC micelles at both temperatures.

The activity coefficient of TCE (γ) is equal to the ratio of the fugacity of the TCE in the micellar or PSS/CPC mixed

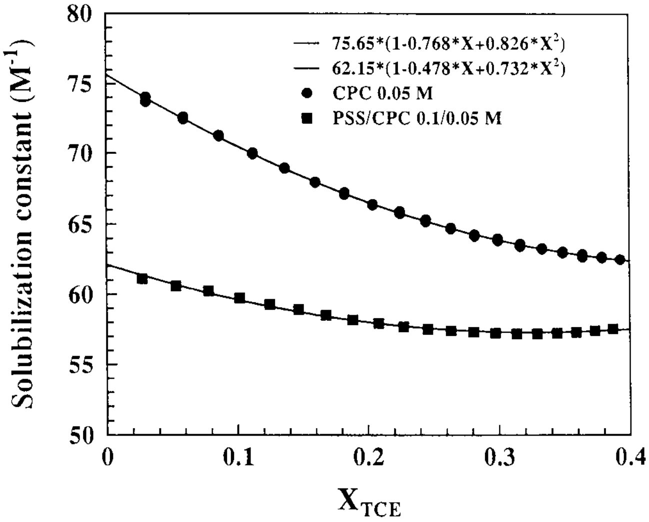

Figure 3. Solubilization constant as a function of mole fraction of TCE in CPC micelles and in the PSS/CPC complex at 20°C.

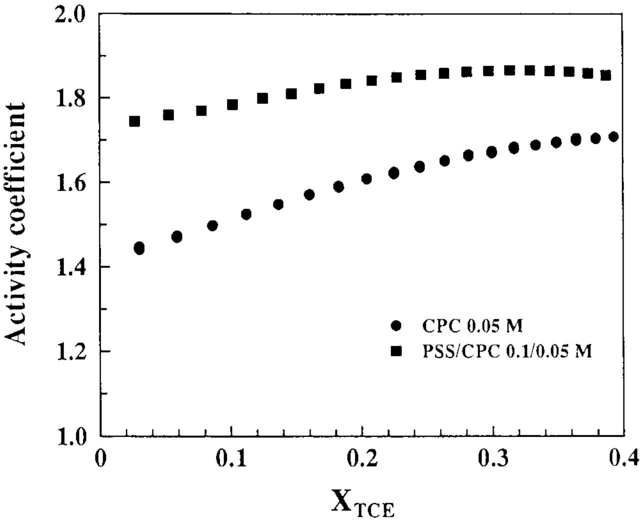

Figure 5. Activity coefficient of TCE in micelle and in the PSS/CPC complex at 20°C.

solution (P) to the fugacity of pure TCE (P^0) at the given temperature, divided by X_{TCE}. The fugacity and partial pressure of TCE are assumed to be equal since the vapor pressure of TCE is only 73.31 torr at 25°C. The solubilization equilibrium constant and the activity coefficient of TCE are inversely related at any given temperature; the limiting value of the Henry's law constant for the TCE in water is required in converting between K and γ (Lee et al., 1990; Christian and Scamehorn, 1989). Figures 4 and 5 show the relationship between the activity coefficient of TCE and the mole fraction of TCE in CPC micelles and in the PSS/CPC complex at 25 and 20°C, respectively. The activity coefficient increases from a value of about 1.4 at infinite dilution to a maximum of approximately 1.6 as the mole fraction of TCE in the micelle approaches ~0.4. On the other hand, the activity coefficient of TCE in the PSS/CPC complex increases slightly from a value of approximately 1.7 at infinite dilution. The activity coefficients of TCE at 25°C are slightly larger than those at 20°C.

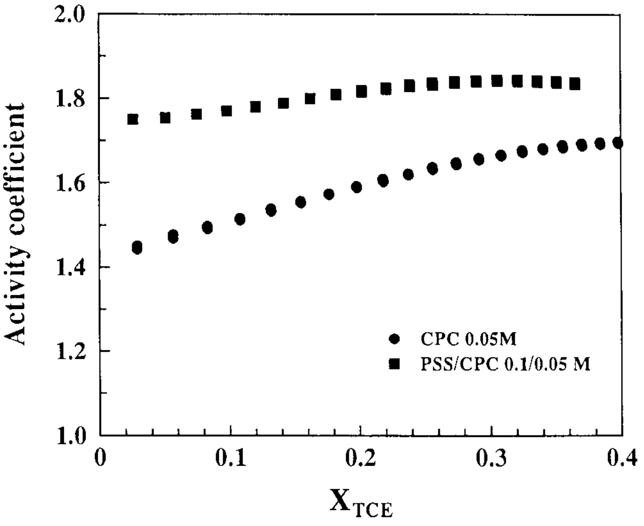

Figure 4. Activity coefficient of TCE in CPC micelles and in the PSS/CPC complex at 25°C.

Discussion

It is well-known that homogeneous aqueous solutions of several types of polymers and surfactants can form aggregates that solubilize oil-soluble organic solutes; physicochemical studies have been made to determine parameters relating to interactions between polymers and surfactant molecules, and to infer possible structures and other properties of complexes formed by these species (Goddard and Leung, 1992; McQuigg et al., 1992; Carlsson et al., 1989; Brackman et al., 1992; Kido et al., 1991; Gao et al., 1990; Tokiwa et al., 1973). The polyelectrolyte ions of PSS and the CPC micelles have opposite charges, and with an excess of PSS monomer units (and charge) it is reasonable to expect that they will form complexes in which the negatively-charged polymer wraps around positively-charged CPC aggregates (Goddard et al., 1992; Uchiyama et al., 1994a; Kiefer et al., 1993).

The observation that CPC clusters in the polyelectrolyte/surfactant complex are somewhat less effective in solubilizing TCE than are ordinary CPC micelles is consistent with results obtained in studies of the solubilization of chlorinated aromatic solutes by complexes of negative polyelectrolytes and CPC (Lee et al., 1991b). As in these previous studies, however, it is observed that the solubilization equilibrium constants of the polyelectrolyte/cationic surfactant complexes do not greatly decrease with an increase in the concentration of solubilized organic. Thus, the effectiveness of solubilization of polar organic solutes is retained by the PSS/CPC complexes when the mole fraction of organic solutes solubilized in these aggregates increases.

Differences in solubilization behavior of TCE in pure CPC micelles and in the mixed PSS/CPC complexes may be related to changes in the electrostatic interactions of the dipolar solute with the ionic micelles. Micelles of pure CPC have a highly positive surface charge, but the cooperative attachment of surfactant to the negative PSS (to form the PSS/CPC complexes) should greatly reduce the charge density in the surfactant head-group region (Kiefer et al., 1993). Consequently, there should be a weakened electrostatic attraction between the PSS/CPC complex and any polar solute, tending to diminish the tendency of such a solute to solubilize in the CPC aggregates which are bound to the polymer. It is significant that the decreased extent of solubilization caused by the polymer is greatest at the lowest concentrations of TCE.

The results in Figures 2 and 3 show that the general quadratic equation,

$$K = K_0(1 - \alpha X_{\mathrm{TCE}} + \beta X_{\mathrm{TCE}}^2) \tag{3}$$

fits the experimental solubilization data for the PSS/CPC system quite well. The solubilization constant of TCE in PSS/CPC (2/1) mixtures decreases as the mole fraction of TCE in the complexes increases. The curves in Figure 2 show that K decreases monotonically as X increases, whereas the isotherms (K vs. X) for polar aromatic solutes, such as the chlorinated phenols (Lee et al., 1991b) and *p-tert*-butylphenol in CPC solution in the presence of added polyelectrolyte, are usually convex (Uchiyama et al., 1994a).

Polar organic solutes such as the aliphatic alcohols, carboxylic acids, phenols, and cresols tend to solubilize with a strong interaction between their polar groups and the polar/ionic head groups of surfactants. Solubilization results and other physical evidence imply that the head groups of these polar molecules are anchored in the surface region of surfactant micelles and that their aliphatic or aromatic moieties extend at least partly into the hydrocarbon core. Typically, when solubilized in the common ionic and nonionic micelles, these solute species have activity coefficient values on the order of 0.1 or less (based upon pure component standard states), and these values tend gradually to increase toward unity as X (the mole fraction of solubilizate in the micelle) increases (Christian and Scamehorn, 1989). As required by the reciprocal relationship between the solubilization equilibrium constant and activity coefficient, K values for the highly polar solutes decrease substantially as X increases.

In marked contrast, highly hydrophobic solutes such as the aliphatic hydrocarbons solubilize primarily within the hydrocarbon core region of typical aqueous micelles. Activity coefficients for these species tend to decrease from values of 3 to 5 or greater at infinite dilution to values nearer 1 as X increases. The aromatic hydrocarbons are intermediate in behavior between the highly polar solutes, which are anchored in the micelle surface region, and the aliphatic hydrocarbons (Christian and Scamehorn, 1989). Thus, solutes such as benzene and toluene have activity coefficients close to one in a variety of surfactant micelles, perhaps reflecting their tendency to solubilize both in the head group and hydrocarbon core regions of typical micelles. Moreover, the enthalpy and entropy changes for benzene, transferring from the pure solvent phase into typical ionic surfactant micelles (for pure component standard states), are small and usually positive (Christian et al., 1986; Smith et al., 1989).

The solubilization results reported here for trichloroethylene in PSS/CPC complexes are in many respects analogous to those for benzene or toluene in ionic surfactant micelles. Values of the activity coefficient for TCE are somewhat greater than unity at each temperature, approaching a maximum at approximately $X = 0.3$; correspondingly, K values decrease from about 67 M^{-1} to 58 M^{-1} in the same intramicellar composition range. The fact that K does decrease, initially, as X increases suggests that a Langmuir-type adsorption model (Mukerjee, 1971; Lee et al., 1990, 1991a) may be useful in correlating the solubilization results. Thus, it could be argued that the observed decrease in K with increasing X implies that adsorption "sites" are being used up as TCE solubilizes in micelles at small values of X. On the other hand, the tendency of K to increase again at the larger values of X (or for the solute activity coefficient to decrease) cannot be reconciled with the Langmuir equation, and may indicate that as X becomes larger, solubilization within the micellar interior tends to predominate. In any event, it appears that TCE, unlike solubilizates such as the chlorinated phenols and other polar derivatives of phenol (Lee et al., 1989), is not strongly or specifically attached to surface sites.

The magnitudes of activity coefficient values, plotted in Figures 4 and 5, and their dependence on intramicellar composition and temperature indicate that the transfer of TCE molecules from the pure liquid state into the micelle occurs with very little deviation from Raoult's law (implying that the excess Gibbs free energy of transfer is quite small), and it is reasonable to expect that the excess entropies and enthalpies of transfer are also small. All in all, the thermodynamic effects for the TCE/CPC system (Uchiyama et al., 1994b) and for the TCE/PSS/CPC system are quite analogous to those for the benzene/CPC system (Smith et al., 1989), for which benzene activity coefficients are also in the range 1 to 1.6.

Finally, it should be noted that the results of solubilization studies utilizing the PSS/CPC complex imply that the concentrations of TCE solubilized by the polyelectrolyte/surfactant mixed solution are nearly as great as those solubilized by pure CPC micelles at the same total surfactant concentration. The extent of solubilization is large enough so that it should be feasible to use PSS/CPC complexes in colloid-enhanced ultrafiltration to remove TCE from contaminated aqueous streams. Previously, it was shown that dissolved TCE can be effectively removed from an aqueous stream by using MEUF (Roberts, 1993). However, an important advantage of adding the oppositely-charged polyelectrolyte is that this substance significantly reduces the activity (or monomer concentration) of CPC, so that very low concentrations of surfactant are transferred into the permeate in CEUF separations (Uchiyama et al., 1994a). Previous SED and MEUF studies (using CPC with no added polyelectrolyte) indicated that the concentrations of CPC in the permeate are approximately equal to or somewhat greater than the critical micelle concentration (0.88 mM) (Scamehorn et al., 1986, 1990; Dunn et al., 1985, 1987). But use of the 2:1 PSS/CPC mixtures in CEUF should cause the concentration of CPC in the permeate to be reduced below the normal critical micelle concentration by at least a factor of ten, so that more than 99.6% of the added CPC molecules should remain in the retentate solution throughout wide ranges of CPC concentrations.

Acknowledgment

The authors appreciate the financial support of the Center for Waste Reduction Technologies of AIChE, Agreement No. N12-N10.

Notation

C_{CPC} = molar concentration of CPC in micelle or PSS/CPC complex
C_{TCE}^{agg} = molar concentration of solubilized TCE
G^E = excess Gibbs free energy of transfer of TCE from the pure liquid state into micelle
H^E = excess enthalpy of transfer of TCE from the pure liquid state into micelle
R = gas constant
S^E = excess entropy of transfer of TCE from the pure liquid state into micelle
T = absolute temperature
TBP = *p-tert*-butylphenol
X_{TCE} = mole fraction of TCE in micelle or PSS/CPC complex

Greek letters

α = empirical parameter
β = empirical parameter
γ = activity coefficient of TCE

Superscript

agg = PSS/CPC complex and CPC micelle

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Manuscript received Nov. 1, 1993, and revision received Jan. 14, 1994.