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Colloid-Enhanced Ultrafiltration of Chlorophenols in Wastewater: Part II. Apparent Acid Dissociation Constants of Chlorophenols in Colloid Solutions at Different Ionic Strengths and Effect of pH on Solubilization of Phenolic Compounds

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ABSTRACT

The effects of pH, ionic strength, and type of colloid on the efficiency of removal of an organic solute in colloid-enhanced ultrafiltration, as indicated by the tendency of the solute to solubilize into micelles and surfactant–polymer complexes, are investigated in this paper. The apparent acid dissociation constants ($K_{a,app}$) of 2-monochlorophenol (MCP),

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2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP) are determined in surfactant solutions and surfactant–polymer mixtures at different salinities using a spectrophotometric titration technique. The distribution coefficients of charged species and neutral species of MCP and the solubilization of TCP into micelles and into surfactant–polymer aggregates are measured using dialysis methods. Cetylpyridinium chloride (CPC) is the cationic surfactant and sodium polystyrenesulfonate (PSS) is the anionic polymer used. The apparent values of pK_a ($pK_{a,app}$) of the solutes in micellar solution are less than the corresponding values in aqueous solution ($pK_{a,aq}$), whereas the values of $pK_{a,app}$ for the solutes in the surfactant–polymer mixtures are slightly higher than those in the aqueous and micellar solutions. The $pK_{a,app}$ values increase as salt concentration increases in the micellar solution while remaining almost unchanged in the surfactant–polymer mixtures. In the micellar solutions, the distribution coefficient into the surfactant aggregate of the anionic species of MCP is greater than that of the neutral species, by factors of approximately 30 to 1.5 when salt concentration increases from zero to 0.10 M. However, in the surfactant–polymer mixtures, the distribution coefficient of the neutral species is higher than that of the charged species by factors of 5 to 8 when salt concentration increases from zero to 0.05 M. In the micellar solutions, the distribution coefficients of the neutral species are less dependent on salinity than those of the charged species. The solubilization and solute rejection are influenced by pH, primarily for solutes with low hydrophobicity.

Key Words: Distribution coefficient; Solubilization constant; Chlorophenols; Surfactant–polymer interaction.

INTRODUCTION

Colloid-enhanced ultrafiltration (CEUF) is a class of separation methods that can be used to remove dissolved organic solutes and/or inorganic ionic species from water. In CEUF, a colloid solution is added to a contaminated feed solution where the colloid can be surfactant micelles as in micellar-enhanced ultrafiltration (MEUF) or a surfactant–polymer mixture as in polyelectrolyte micellar-enhanced ultrafiltration (PE-MEUF).[1] Organic solutes solubilize in the micelles or surfactant–polymer complexes and charged solutes can electrostatically bind to these colloids. This solution is then passed through a membrane, which has pores small enough to block the passage of micelles or surfactant–polymer complexes, removing the surfactant aggregates and solubilized or bound solutes. It has been shown that the concentration of solute in the permeate (solution passing through the membrane) is approximately that expected if the system were at equilibrium.[2,3]

Therefore, equilibrium solubilization measurements obtained from dialysis experiments[1] can be used to determine the process efficiency. A detailed description of CEUF is available in a previous paper.[1]

Several studies have been done to investigate the ability of surfactant micelles[4–9] and surfactant–polymer complexes[10–12] to solubilize polar organic compounds. Using surfactant–polymer mixtures instead of surfactant micelles can substantially reduce surfactant monomer concentration or surfactant leakage.[1] It was found that ordinary cationic micelles can solubilize a polar ionizable organic solute to a greater extent per aggregated surfactant molecule than the cationic surfactant-anionic polymer complexes.[1,12] This was attributed to the reduction in electrostatic potential at the surface of surfactant aggregates through neutralization by the oppositely charged polymer. Not only does the solubilization equilibrium constant depend on the type of colloid, but it also relies on the solute characteristics such as hydrophobicity or water solubility, polarity, and the extent of ionization. For chlorophenols, increasing the number of chlorine atoms per molecule results in higher acidity, but lowers the dipole moment.[1] In micellar solution, solutes with a higher acidity (lower pK_a) or lower water solubility can be solubilized in a greater amount than solutes with a low acidity or high water solubility due to differing affinities of anionic (A^-) and neutral (HA) species for the colloid. This type of behavior has been demonstrated in studies using micellar-enhanced ultrafiltration or MEUF.[1,4,12–14] However, in surfactant–polymer systems, ion-dipole interactions may also play an important role in solubilization. For instance, although the water solubility of trichlorophenol (TCP) is less than dichlorophenol (DCP), the solubilization constant of DCP is higher than that of TCP at low solute concentration due to a higher dipole moment of DCP than TCP.[1]

In general, the solubilization constant of polar organic solutes decreases as the extent of solute loading increases.[1,4–7,9–12] This characteristic suggests that the solute is initially located at the micellar surface at low solute concentration. Once all the active sites are occupied, solubilization may occur in the palisade region. For ionizable solutes such as phenols, electrostatic interactions may occur between the negative charge on the solute oxygen atom and the cationic surfactant head groups, which should increase the partition of phenolate anion towards the micellar phase. In contrast, repulsive interactions would occur between phenolate anion and an anionic surfactant such as sodium dodecylsulfate (SDS). If the ionized organic solute has a charge opposite to that of the surfactant head groups, the solubilization ability and the removal efficiency can be further enhanced.

The acid dissociation reactions for solutes in micelles have been investigated by several groups[15–19] who found shifts of the apparent pK_a values for both charged and uncharged micelles. These shifts in apparent pK_a values are attributed partly to the low dielectric constant at the micellar surface and partly to the electrical potential at the surface of the charged micelles.[15] In addition, Underwood suggested that pK_a shifts are interpretable in terms of the influence of micelle charge on the work required for proton removal from the micellar surface to the bulk solution.[16] The $[H^+]$ at the colloid surface is different than in the bulk solution due to the electrical potential difference of the surface with respect to bulk solution.

The distribution of hydrophobic ionizable organic compounds between the aqueous and nonaqueous phases depends on the pH and ionic strength of the aqueous phase.[20–23] Previous studies with chlorophenols[1,4,12] have shown that increasing the number of chloro substituents leads to an increase in the hydrophobicity and an increase in partitioning of the solutes into the colloidal phase. Hence, phenols with more chloro constituents are more likely to be ionized at a given pH value and are also intrinsically more hydrophobic. However, although the introduction of a nitro substituent causes an increase in acidity of the phenols, the resulting compound is much less hydrophobic than the analogous chloro derivative.[20]

In the previous work (Part I)[1] of this paper series, we compared the effectiveness of MEUF and PE-MEUF systems. In this paper (Part II), we investigate the effects of surfactant micelles, surfactant–polymer complexes, and ionic strength on the apparent pK_a of chlorophenolic solutes with different degrees of chlorination, and measure the distribution coefficients of such solutes for both neutral and charged species. These results then help interpret the effect of pH level at a given ionic strength on the solubilization constant of a phenolic solute (TCP) obtained from dialysis experiments which dictate solute rejection in MEUF and PE-MEUF. Therefore, the removal efficiency can be quantified. The effect of salinity on the solubilization and surfactant leakage both in MEUF and PE-MEUF will be discussed in subsequent papers (Part III and Part IV).[24,25] In the final paper (Part V),[26] the use of PE-MEUF in simultaneous removal of an organic solute and a metal ion is demonstrated, and the flux behavior of PE-MEUF in a stirred cell ultrafiltration device is shown as a function of salinity.

EXPERIMENTAL

Materials

2-Monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP) (99+% pure) were obtained from Aldrich Co. (Milwaukee, WI) and used without further purification. High quality (99+% pure) *n*-hexadecylpyridinium chloride or cetylpyridinium chloride (CPC) from Zeeland Chemical (Zeeland, MI) does not exhibit a minimum in a plot of surface tension versus concentration, or show any impurities using HPLC chromatography and was used as received. Poly(styrenesulfonate) (PSS) (99+% pure), with an average molecular weight of approximately 70,000 daltons, was obtained from Alfa Aesar (Ward Hill, MA). Lower molecular weight fractions were removed by using a spiral wound ultrafiltration apparatus as described previously.[1] The final concentration of the purified polymer was measured by using a total organic carbon analyzer (Rosemount DC-180). Water was doubly deionized and treated with activated carbon. Sodium hydroxide and hydrochloric acid solutions from Fisher Scientific (Fair Lawn, NJ) were used to adjust the pH of the solutions. Sodium chloride (certified A.C.S.) from Fisher Scientific (Fair Lawn, NJ) was used as an added salt.

Methods

The concentration equilibrium constant (K_a^c) as shown in Eq. (1) was determined from spectrophotometic titration data[27–29] for the organic solutes at a concentration of 0.2 mM in micellar solutions and surfactant–polymer mixtures in both the presence and absence of added NaCl at room temperature (approximately 25°C). Spectra were obtained using a Hewlett-Packard HP 8452A diode array spectrometer with a 1.0 cm pathlength cuvet. Deionized water at several pHs was used to prepare solutions for the analysis. The pH of the solutions was recorded using an Accumet AR 20 pH/Conductivity meter (Fisher Scientific) before performing the UV analysis. Using measured absorbance values at different pHs, the value of K_a^m was determined by non-linear least-squares analysis using the following equations[30,31]

$$\mathrm{HL} \rightleftharpoons \mathrm{H}^+ + \mathrm{L}^-; \quad K_a^c = \frac{[H^+][L^-]}{[HL]} \tag{1}$$

$$Abs_i = \frac{Abs_L + Abs_{HL}\left(10^{-pH}/K_a^m\right)}{1 + \left(10^{-pH}/K_a^m\right)} \tag{2}$$

$$K_a^m = \frac{a_H[L^-]}{[HL]} = \frac{[H^+][L^-]\gamma_H}{[HL]} = K_a^c\gamma_H \tag{3}$$

$$-\log \gamma_H = 0.5Z_i^2\left(\frac{I^{1/2}}{1+I^{1/2}} - 0.3I\right) \tag{4}$$

where Abs_i is the measured absorbance at a given wavelength, Abs_L and Abs_{HL} are the limiting absorbances of the basic and acidic forms of the solute, respectively, K_a^m is the mixed-mode acid dissociation constant and pH is the observed pH of the solution, γ_H is activity coefficient of H^+, Z_i is the charge of the ions, and I is the ionic strength of the solution. The species distribution of the solutes was obtained using the pK_a^c values as described previously.[1]

The semiequilibrium dialysis (SED) method was used to measure solubilization as described previously.[1–7,11,12] Regenerated cellulose membranes (6000 daltons molecular weight cut-off) were soaked overnight in deionized water prior to mounting them between the two compartments of the SED cell. A known volume of a solution containing an organic solute, CPC or CPC–PSS mixtures, and any added NaCl was placed in the retentate compartment using a 10 mL syringe. A solution containing NaCl at a concentration identical to that in the retentate was placed in the permeate compartment. Preliminary runs showed that the cells reached equilibrium within twenty-four hours at 25°C ± 0.1°C. Each experiment was conducted with two separate SED cells for duplicate points. Osmotic pressure effects caused the water in the permeate to transfer to the retentate; up to a 40% increase in the volume of retentate was observed, especially, at high total colloid (i.e., surfactant, and polymer) concentration. The volume of solution in both compartments was measured using syringes. Concentrations of the chlorinated phenol and CPC in the permeate were determined with the UV/VIS spectrometer as described previously. A cuvet with 10-cm pathlength was used to determine solute and CPC concentrations providing a minimum detectability of 5×10^{-6} M. The pH of all samples, as well as calibration solutions, was adjusted to 10.5 before performing the UV analysis. At this pH, the surfactant can degrade; however, the analytical samples contain low CPC concentration (with the maximum concentration of 0.03 mM) and the spectrophotometric measurement was performed after adjusting the pH; therefore, the CPC degradation was minimal upon analysis.

Multiwavelength analysis was used to analyze both surfactant and solute concentrations simultaneously. Absorbance values were recorded at six different wavelengths chosen to be near the absorption maxima of the surfactant and the anionic form of the solutes (260 nm, CPC; 300 nm, MCP; 314 nm, DCP; 322 nm, TCP). The concentrations of the chlorinated phenol and CPC remaining in the retentate at equilibrium were determined by subtracting the analytical concentrations of these species in the permeate from the feed concentration after taking into account the final volumes of the permeate and retentate.

To study the effect of pH on the solubilization value of a solute (TCP), two initial pH levels were chosen in order to obtain different charge distributions. To avoid membrane degradation, a pH value of 3.0 was chosen as the lower limit for these studies. At this pH, the solutions predominantly contain the neutral species. The initial pH of the permeate and retentate solutions was set at 3.0. Preparation of colloid solutions at higher pH is difficult because the colloid solutions turn yellow as NaOH is added, presumably due to CPC degradation. Therefore, the solutions at higher pH were obtained without pH adjustment. The pH values of initial and final retentate solutions were measured and are available in a dissertation.[32]

THEORY

The solubilization equilibrium constant (K) of a solute A in CPC micelles or CPC–PSS aggregates is defined as:

$$K = \frac{X_A}{c_A} \tag{5}$$

$$X_A = \frac{C_A^{agg}}{C_A^{agg} + C_{CPC}^{agg}} \tag{6}$$

where c_A is the concentration (mol/L) of an unsolubilized organic solute, X_A is the mole fraction of solute TCP in the surfactant or surfactant–polymer aggregates, C_A^{agg} is the concentration (mol/L) of solute in the surfactant or surfactant–polymer aggregates, and C_{CPC}^{agg} is the concentration (mol/L) of CPC in surfactant or surfactant–polymer aggregates. These concentrations are obtained from the material balance relationships for this system,

$$C_A^{agg} = C_{A,tot} - c_A \tag{7}$$

$$C_{CPC}^{agg} = C_{CPC,total} - C_{CPC,monomer} \tag{8}$$

where $C_{A,tot}$ is the total concentration of the solute in the retentate, c_A is the unsolubilized solute concentration in the retentate (which is essentially the concentration of solute in the permeate compartment), $C_{CPC,total}$ is the total concentration of surfactant in the retentate, and $C_{CPC,monomer}$ is the concentration of monomeric surfactant in the retentate. During the dialysis runs, the surfactant concentration in the permeate generally increases to the same concentration as the monomer in the retentate. Then, the permeate surfactant concentration slowly increases as micelles form in the permeate. Because the permeate micelles could solubilize the solute, the total solute concentration in the permeate would be greater than the unsolubilized concentration in the retentate. Therefore, either the equilibration time must be chosen to be short enough so that an insignificant concentration of micelles is formed (but long enough to permit the unsolubilized solute to reach equilibrium), or correction factors must be used to account for solubilization in permeate micelles.[4,6,7,12,33] Hence, the dialysis experiments in MEUF are called semiequilibrium dialysis (SED). For PE-MEUF, analysis of the permeate shows that the permeate polymer concentration was less than 1% of that in the initial retentate. The concentration of surfactant in the permeate is lower than the CMC of the surfactant under the conditions studied,[25] so there are no micelles for solubilization. The solubilization of the solute by the surfactant–polymer aggregates is insignificant due to the small concentrations of surfactant and polymer; therefore, the dialysis experiments in PE-MEUF are called equilibrium dialysis (ED). In this study, for both MEUF and PE-MEUF, we observed that the concentration of solute and surfactant in the permeate was more than an order of magnitude lower than in the retentate, such that the presence of surfactant micelles or surfactant–polymer aggregates in the permeate does not considerably influence the measured solubilization isotherm. Therefore, no correction for permeate micelle or surfactant–polymer aggregate formation is made.

RESULTS AND DISCUSSION

Apparent pK_a Values

For system containing colloid, the apparent pK_a ($pK_{a,app}$) is defined by the following equation

$$pK_{a,app} = pK_a^m + \log \gamma_H \tag{9}$$

where pK_a^m is obtained from spectrometric titration data and γ_H is calculated using the Davies equation (Eq. (4)). Plots of absorbance versus pH for MCP are shown in Figure 1, for the wavelength at which the maximum absorbance

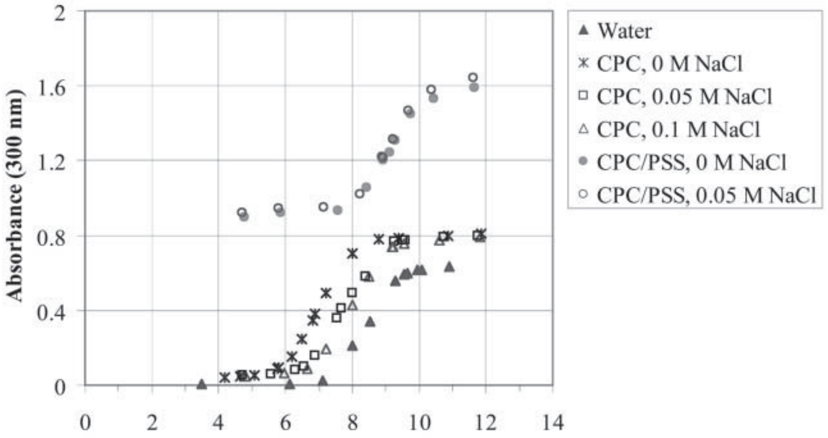

Figure 1. Plots of absorbance vs. pH at 300 nm for MCP in water, in 25 mM CPC solutions in the presence of 0, 0.05, and 0.1 M added NaCl, and in the mixture of 25 mM CPC and 50 mM PSS in the presence of 0 and 0.05 M added NaCl.

changes occur during the spectrophotometric titrations. Analogous plots for DCP and TCP are not shown here, but are available.[32] In the micellar solutions, the inflection points of the titration curves shift to a higher pH as the NaCl concentration increases. However, the added salt has a negligible effect on the titration curves of the solutes in the surfactant–polymer mixtures. The apparent pK_a values of the solutes in the micellar solutions and the surfactant–polymer mixtures are listed in Table 1. In water, the $pK_{a,app}$ values increase in the order TCP < DCP < MCP. In the CPC solutions with no added salt, the values of $pK_{a,app}$ follow the same order. Likewise, in the presence of 0.05 M and 0.1 M NaCl, the $pK_{a,app}$ values of the solutes maintain the same order found in the water and micellar systems. In contrast to the behavior found in the CPC systems, the order of the $pK_{a,app}$ values for MCP and DCP in the CPC–PSS systems is reversed, and the pK_a of the solutes in the CPC–PSS mixtures increase in the order TCP < MCP < DCP, both in the absence and presence of the added salt.

In the CPC solutions with no added salt, the $pK_{a,app}$ of a given solute is lower than the corresponding value in water. In the presence of 0.05 M and 0.1 M salt, the $pK_{a,app}$ values in the CPC solutions increase but remain lower than the value in the aqueous system without CPC. The presence of 0.1 M NaCl increases the $pK_{a,app}$ value of the solutes by almost 1 unit in the micellar solutions. However, at the same concentration, the added salt does not affect the $pK_{a,app}$ of the solutes in the CPC–PSS mixtures. It should be noted that the $pK_{a,app}$ values of the solutes in the CPC–PSS mixtures are higher than those in the water system and the micellar solutions. For a given solute, the $pK_{a,app}$ values follow the order $pK_{a,micelle} < pK_{a,water} < pK_{a,surfactant-polymer}$.

Table 1. The apparent pK_a values of MCP, DCP, and TCP in water, in 25 mM CPC solutions, and in a mixture of 25 mM CPC and 50 mM PSS at different salinities at 25°C.

Water/colloid solution	[NaCl] (M)	$pK_{a,aq}$ and $pK_{a,app}$		
		MCP	DCP	TCP
Water	0	8.40	7.84	6.14
CPC	0	6.98	6.22	3.91
CPC	0.05	7.84	6.98	4.68
CPC	0.1	8.10	7.19	5.01
CPC-PSS	0	9.09	9.54	7.52
CPC-PSS	0.05	9.23	9.66	7.47

Note: $pK_{a,aq}$ and $pK_{a,app}$ refer to the pK_a obtained in water and in colloid solutions, respectively.

In the CPC–PSS systems, both in the absence and the presence of the added salt, the $pK_{a,app}$ values of MCP and DCP are relatively high (>9). At pHs of 9 or higher, the solution turns yellowish due to CPC degradation; therefore the determination of the $pK_{a,app}$ value is unreliable. This unreliability makes it difficult to distinguish the order of MCP and DCP because their $pK_{a,app}$ values are close to each other (the difference between the $pK_{a,app}$ values of MCP and DCP in water is 0.56 whereas the difference between MCP and TCP is 2.26). In micellar solutions without salt, the cationic surfactant head groups should interact preferentially with the phenolate anion. Therefore, at a given bulk pH, a greater fraction of the solute is likely to be ionized compared to the case in water, thus reducing the apparent pK_a. In contrast, ion expulsion between the negatively charged surfactant–polymer aggregates and the phenolate anion occurs in the surfactant–polymer mixtures. As a result, a smaller fraction of the solute is ionized at a given bulk pH, thus increasing the $pK_{a,app}$. For example, the $pK_{a,app}$ values of TCP in micellar solution, water, and surfactant–polymer mixtures are 3.91, 6.14, and 7.52, respectively.

The apparent pK_a of a weak acid or weak base residing in the vicinity of a charged interface is generally composed of an electrostatic component due to the surface potential and an inherent interfacial non-electrostatic component. This relationship is often expressed,[18,19] as

$$pK_a = pK_a^0 - \frac{F\psi}{2.303RT} \tag{10}$$

where pK_a^0 is the apparent pK_a of the molecule in the absence of any potential (i.e., the intrinsic pK_a), ψ is the mean field potential (in V) at the average interface site of residence for the prototropic moiety, F and R are the Faraday and gas constants, respectively, and T is the absolute temperature.

Underwood has also observed large $pK_{a,app}$ shifts for a number of acids and bases in ionic micelles.[16,17] He found that $pK_{a,app}$ is increased by anionic micelles but it is decreased by cationic micelles. Soto and Fernandez found a similar trend where the $pK_{a,app}$ values of a given organic solute in hexadecyltrimethyammonium bromide or CTAB (cationic surfactant), octylphenol ethylene oxide or Triton X-100 (nonionic surfactant), and sodium dodecyl sulfate or SDS (anionic surfactant) are 6.88, 7.58, and 9.92, respectively.[19] Such shifts can be attributed to the effect of surface polarity and electrical potential on the dissociation of the solutes bound to micelles and surfactant–polymer aggregates. It was found that the surface potentials of CTAB and SDS micelles are $+155$ mV and -125 mM, respectively;[19] and according to Eq. (10), the pK_a value for a given solute in a cationic micelle is smaller than that in an anionic micelle. This corresponds with the observed values of chlorophenols in CPC–PSS mixtures, where the $pK_{a,app}$ values in aggregates having a net negative charge are larger than the corresponding values in cationic micelles. The addition of electrolyte has been found to influence the partition coefficients, acid dissociation constants, and activity coefficients.[22,28] The latter can be estimated using the Davies equation (Eq. (4)).

For a monovalent ion at an ionic strength of 0.1 M, the activity coefficient is 0.785, resulting in a decrease in $pK^c_{a,aq}$ of 0.21 compared to the thermodynamic value or $pK^T_a (pK^T_a = (a_H a_L)/a_{HL},\ I \rightarrow 0)$. However, as mentioned previously, the $pK_{a,app}$ value observed in the micellar solution increases by one log unit in the presence of 0.1 M salt. This contradiction can be associated with the presence of the ionic micelle. The presence of both salt and an ionic micelle may affect the apparent pK_a value for the system shown by the following equilibria,

$$HCP_{(aq)} \overset{K^c_{a,aq}}{\rightleftharpoons} H^+_{(aq)} + CP^-_{(aq)} \tag{11}$$

$$HCP_{(aq)} \overset{K_{D,HCP}}{\rightleftharpoons} HCP_{coll} \tag{12}$$

$$CP^-_{(aq)} \overset{K_{D,CP^-}}{\rightleftharpoons} CP^-_{coll} \tag{13}$$

where $K_{a,aq}$ is concentration equilibrium constant at a given ionic strength in aqueous solution, and $K_{D,HCP}$ and K_{D,CP^-} are distribution coefficients (vol/vol) between colloid and aqueous phases for the protonated (neutral) form (HCP) and unprotonated (anionic) form (CP^-) of the solute, respectively. From the equilibria above, we obtain,

$$K_{D,HCP} = \frac{[HCP]_{coll}\left(V_{aq}/V_{coll}\right)}{[HCP]_{aq}} \tag{14}$$

$$K_{D,CP^-} = \frac{[CP^-]_{coll}\left(V_{aq}/V_{coll}\right)}{[CP^-]_{aq}} \tag{15}$$

where V_{aq} is the volume of the aqueous phase and V_{coll} is the volume of the colloid phase (or organic phase). The apparent acid dissociation constant, $K_{a,app}$, can be written as follows[34]

$$K_{a,app} = \frac{[H^+]([CP^-]_{aq} + [CP^-]_{coll})}{([HCP]_{aq} + [HCP]_{coll})} \tag{16}$$

Combining Eqs. (14) and (15) with Eq. (16) gives

$$\frac{K_{a,app}}{K^C_{a,aq}} = \frac{1 + K_{D,CP^-}(V_{aq}/V_{coll})}{1 + K_{D,HCP}(V_{aq}/V_{coll})} \tag{17}$$

As shown in Eq. (17), $K_{a,app}$ is primarily affected by the distribution coefficients of the neutral and charged species and these coefficients are dependent on the ionic strength. For the CPC micelles, K_{D,CP^-} is expected to be larger than $K_{D,HCP}$ due to the electrostatic interaction between the cationic surfactant head groups and the phenolate anion. Therefore, the apparent pK_a in micellar solution is smaller than that in water. Increasing ionic strength is expected to have only a slight effect on $K_{D,HCP}$. It is reasonable to expect a decrease in K_{D,CP^-} as the salt concentration increases because of a reduction in the electrostatic interaction between the surfactant head groups and the negatively charged phenolate ion, thus increasing the pK_a value. This behavior was also seen with indicator dyes solubilized by CTAB[29] where increasing salt concentration causes a decrease in the absolute value of ψ, resulting in an increase in the pK_a value. For the CPC–PSS complexes, the aggregates have a net negative charge; therefore, it is plausible that the K_{D,CP^-} value is lower than the $K_{D,HCP}$ value due to the ion-ion expulsion between the negatively charged surfactant–polymer aggregate and the phenolate anion, resulting in $pK_{a,app}$ being greater than $pK_{a,aq}$ (as previously noted). In addition, the effect of ionic strength is diminished by the counterions present in the CPC–PSS mixtures. As a result, the addition of salt does not significantly influence the apparent pK_a.

Distribution Coefficients

The distribution coefficient of the neutral species ($K_{D,HCP}$) can be obtained from dialysis experiments, as shown in following equation, using data at low solute concentrations and at a pH low enough to minimize the concentration of the anionic form (CP^-)

$$K_{D,HCP} = \left(\frac{[HCP]_{ret} - [HCP]_{perm}}{[HCP]_{perm}}\right)\left(\frac{V_{aq}}{V_{org}}\right) \tag{18}$$

where $[HCP]_{ret}$ and $[HCP]_{perm}$ are solute concentrations in the retentate and the permeate obtained from dialysis experiments described previously. Table 2 shows the percentage of the phenolate anion present in the solution at the lowest concentration (corresponding to the highest pH as shown in the parentheses) for the system without pH adjustment and for the system at pH 3. As shown in Table 2, the lowest concentration of the phenolate anion in both micellar solutions and surfactant–polymer mixtures without pH adjustment is observed in the system studied with MCP; therefore, MCP is chosen as a model solute to investigate the distribution coefficients. Moreover, the partitioning of DCP and TCP in the colloids is very strong,[1] leading to very high distribution coefficients; for example, the K_{D,CP^-} values for DCP and TCP are of the magnitude of 10^5 and 10^6, respectively. As a result,

Table 2. The percentage of the phenolate anion in the final retentate solutions at the highest pH value (the lowest solute concentration) for MCP, DCP, and TCP and at pH 3 for TCP.

Colloid solutions	[NaCl] (M)	Phenolate anion, (%)			
		MCP	DCP	TCP	TCP (pH = 3)
CPC	0	30 (6.6)	54 (6.3)	56 (4.0)	11
CPC-PSS (1/2)	0	0 (6.7)	0 (6.6)	3 (6.0)	0
CPC	0.05	7 (6.6)	21 (6.3)	94.4 (5.9)	2
CPC-PSS (1/2)	0.05	0 (6.6)	0 (6.8)	1 (5.6)	0
CPC	0.1	4 (6.6)	17 (6.4)	87.5 (5.8)	1

Note: The value in the parenthesis is the value of experimental pH used to calculate the fraction of phenolate.

$[HCP]_{perm}$ can be very low, leading to greater relative error in the calculated value of $K_{D,HCP}$.

The value of K_{D,CP^-} could be determined from Eq. (17) with the known values of $K_{D,HCP}$, $K_{a,app}$, $K_{a,aq}$, and V_{aq}/V_{coll}. It was found that the partial molar volume for CPC in the presence of 0.03 M salt is 380 cm^3/mole; in addition, the added salt had no significant effect on the molar volume.[35] In the CPC–PSS mixtures, Škerjanc and Kogej found that the molar volume of the CPC–PSS mixtures at 1/2 mole ratio is approximately 224.5 cm^3/mole.[36] Because the product of the distribution coefficient (K_D) and (V_{aq}/V_{coll}) is much greater than unity;[27,29,34–38] Eq. (17) may be simplified to give

$$\frac{K_{a,app}}{K_{a,aq}} \cong \frac{K_{D,CP^-}}{K_{D,HCP}} \tag{19}$$

From the SED experiments for MCP at the lowest solute concentration, based on the partial molar volumes of CPC micelles and CPC–PSS complexes, we obtain the distribution coefficient of the neutral species ($K_{D,HCP}$) using Eq. (18) and the distribution coefficient of the charged species (K_{D,CP^-}), by using Eq. (19). The results are listed in Table 3.

As seen in Table 3, in the micellar solutions, the distribution coefficient for the phenolate anion is higher than that of the neutral species at all salt concentrations. In contrast, the distribution coefficient for the phenolate anion is lower than that of the neutral species in the CPC–PSS mixtures. In the micellar solutions, the phenolate ion tends to partition more strongly than the neutral form due to the electrostatic interaction between the cationic surfactant head groups and the phenolate anion. However, the ion-ion repulsion between the phenolate anion and the negatively charged

Table 3. Distribution coefficients of the neutral and anionic forms of MCP in 25 mM CPC solutions and in mixtures of 25 mM CPC and 50 mM PSS at different salinities.

Colloid solutions	[NaCl] (M)	pH_{feed}	$[MCP]_r$ (mM)	$[MCP]_p$ (mM)	$K_{D,HCP}$	$K_{D,CP}$
CPC	0	6.00	0.916	0.150	563	14,821
CPC	0.05	6.05	1.786	0.173	1029	3,027
CPC	0.1	6.45	1.715	0.165	1037	1,626
CPC-PSS (1/2)	0	6.30	0.928	0.180	241	49.2
CPC-PSS (1/2)	0.05	6.30	1.628	0.320	237	28.4

Note: Subscripts "r" and "p" indicate retentate and permeate, respectively.

surfactant–polymer aggregates contributes to the lower partition coefficient of the phenolate anion than the neutral species.

In the absence of salt, the $K_{D,HCP}$ value for MCP is reduced by a factor of two in the CPC–PSS mixture as compared to the value in the CPC solution; however, the reduction of the K_{D,CP^-} caused by the presence of PSS is more pronounced. This is due to fact that the charged species more strongly influence partition coefficients in the surfactant–polymer mixtures than the neutral species. In the micellar solutions, the value of $K_{D,HCP}$ increases from 563 to 1029 when the salt concentration increases from 0 M to 0.05 M. However, the $K_{D,HCP}$ value does not significantly increase as salt concentration increases from 0.05 M to 0.1 M. On the other hand, the distribution coefficient of the charged species (K_{D,CP^-}) decreases by almost a factor of 5 in the presence of 0.05 M salt. The increase in salt concentration from 0.05 M to 0.1 M further decreases the K_{D,CP^-} value, approximately by a factor of two. In the surfactant–polymer mixtures, the added salt does not significantly change the $K_{D,HCP}$ value, but it does decrease the K_{D,CP^-} value by about a factor of 2.

In the micellar solution, the initial addition of salt can increase the micelle size,[39–43] therefore increasing the distribution coefficient of the neutral species. The further addition of salt may not significantly enhance the micelle size, and thus the $K_{D,HCP}$ value does not significantly increase. The salting out effect can contribute to the increase in the distribution coefficient of the neutral species; however, this effect will play an important role only at high salt concentration (greater than 1 M).[44] Westall also found that the distribution coefficient of pentachlorophenol between octanol and water is independent of salt concentration between 0.05 to 0.2 M salt.[20] For the anionic species, the addition of salt affects the partition of the anionic solute into the cationic micelles in two ways: (1) the electrostatic interaction between the phenolate ion and cationic surfactant head groups is diminished as salt concentration increases; (2) the anion of the added salt competes for "sites" on the micellar surface in an ion exchange type of phenomenon.[45] Similar behavior was also seen in previous studies with ligand-modified polyelectrolyte-enhanced ultrafiltration (LM-PEUF).[46,47] For the surfactant–polymer systems, the effect of salt on the partitioning of the phenolate anion in the polymer bound micelles is expected to be similar to that in the micellar system although ion-ion expulsion between the negatively charged surfactant–polymer complexes and the phenolate anion can be reduced by the addition of salt.

Solubilization Constants

Figures 2 through 5 show plots of the solubilization constants (K) of TCP as a function of mole fraction of TCP (X_{TCP}) in the micelles and surfactant–polymer aggregates for micellar solutions and surfactant–polymer mixtures at a given salinity. As justified previously, the results at high pH range are obtained in the experimental series without pH adjustment whereas the results at low pH range are carried out at a constant initial pH of 3. Trichlorophenol is chosen as a model solute because it has the highest percentage of the phenolate anion at high pH (without pH adjustment). This makes it possible to compare the solubilization constants between two different systems; one without pH adjustment where the phenolate anion is predominantly

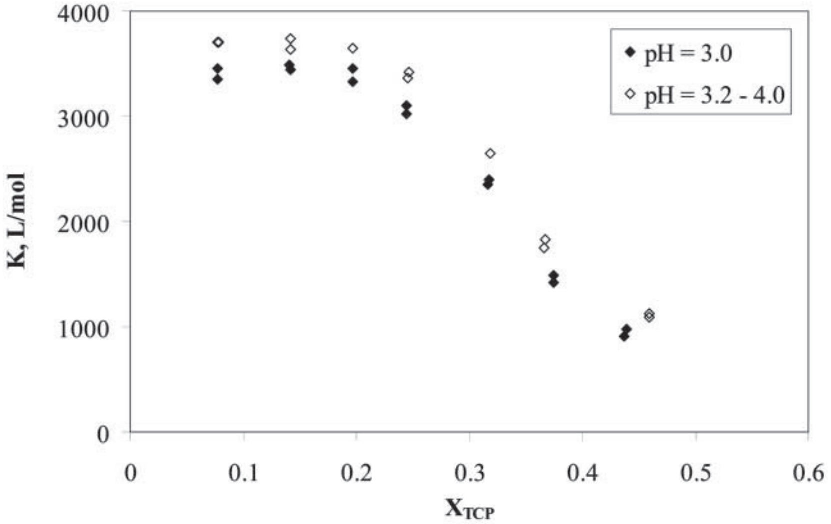

Figure 2. Solubilization equilibrium constant of TCP vs. mole fraction of TCP in CPC micelles in the absence of added salt. Initial [CPC] is 25 mM.

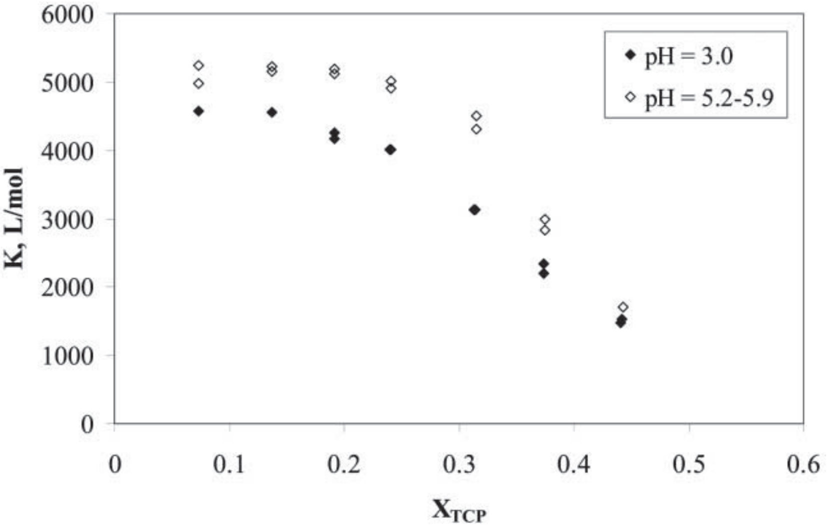

Figure 3. Solubilization equilibrium constant of TCP vs. mole fraction of TCP in CPC micelles in the presence of 0.05 M NaCl. Initial [CPC] is 25 mM.

present, and another at pH 3 where the neutral species is the predominant form. The open symbols are the results obtained from the system without initial pH adjustment where the pH value varies with the solute concentration; the lower the solute concentration, the higher the pH. The closed symbols are the results obtained from the systems where both the retentate and permeate solutions are initially at pH 3. The pH values listed in Figures 2 through 5 are the pHs of the final rentenate solutions. In the micellar solutions, for both the absence and the presence of the added salt, the solubilization constants obtained without pH adjustment or at high pH range (open symbols) are greater than the solubilization constants at pH 3 or at low pH range (closed symbols), as shown in Figures 2 and 3. In contrast, for CPC–PSS mixtures, the K values for the high pH range are lower than the corresponding values for the series at pH 3, as shown in Figures 4 and 5. As the solute concentration increases, the K values of those two series tend to converge for both micellar solutions and surfactant–polymer mixtures.

The difference in the solubilization constants for a given system can be qualitatively interpreted by considering the distribution coefficients and the species distribution. Although the individual distribution coefficients of TCP are not evaluated here, the effect of added salt on the distribution coefficients for TCP as well as DCP follow the same trend as for MCP. In the micellar systems, the solutions at higher pH contain a higher percentage of the

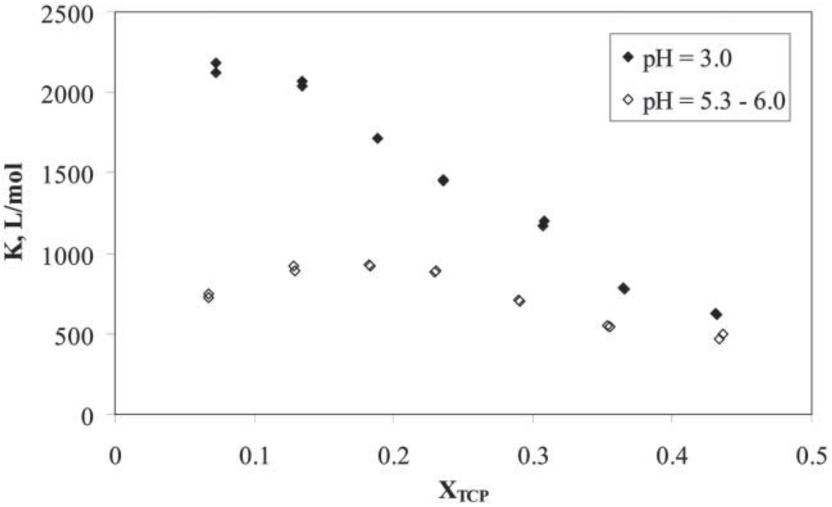

Figure 4. Solubilization equilibrium constant of TCP vs. mole fraction of TCP in CPC–PSS mixtures in the absence of added salt. Initial [CPC] and [PSS] are 25 mM and 50 mM, respectively.

charged species than the solutions at lower pH. According to the species distribution results, the micellar systems without pH adjustment (open symbols) at the lowest solution concentration contain approximately 56% and 94.4% of the phenolate anion for the systems shown in Figures 2 and 3, respectively, as shown in Table 2. For the systems at pH 3 (closed symbols), the solutions contain approximately 11% and 2%, of the phenolate anion for the systems in Figures 2 and 3, respectively.

As shown in Table 3, the distribution coefficients of the charged species are higher those that of the neutral species in the micellar solutions, resulting in a greater contribution of the charged species than the neutral species to the solubilization constant. This results in a higher solubilization constant in the system containing the higher percentage of the charged species.

In the surfactant–polymer mixtures, for the systems without pH adjustment (open symbols) at the lowest solution concentration, the mixtures contain 3% and 1% of the phenolate anion for the systems shown in Figures 4 and 5, respectively. At pH 3 (closed symbols), the concentration of charged species approaches zero. As shown in Table 3, the distribution coefficient of the neutral species is higher than that of the charged species in the surfactant–polymer mixture. As a result, the apparent solubilization constants are higher for the systems containing a greater percentage of the neutral species. It should be noted that the fraction of the phenolate anion can change at higher

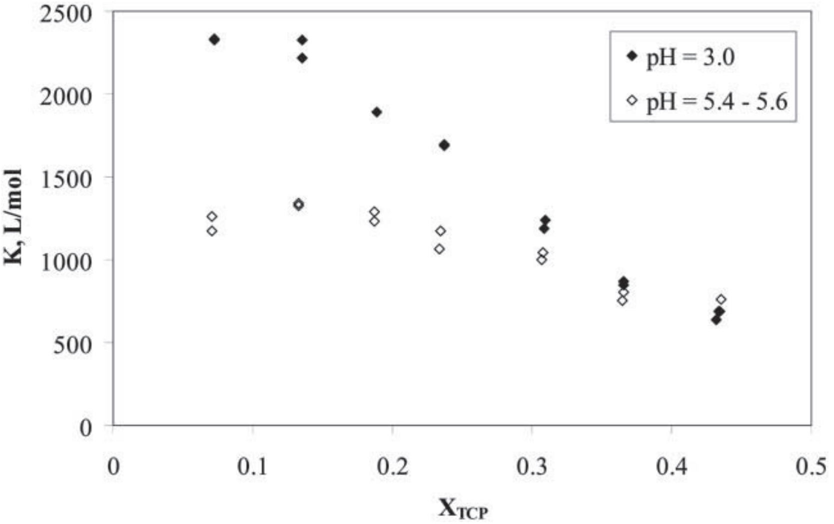

Figure 5. Solubilization equilibrium constant of TCP vs. mole fraction of TCP in the CPC–PSS mixtures in the presence of 0.05 M NaCl. Initial [CPC] and [PSS] are 25 mM and 50 mM, respectively.

solute concentrations. Unfortunately, the fraction of the phenolate anion at solute concentrations greater than 0.2 mM is not measurable due to the high absorbance (>1) limit of spectrophotometer at these solute concentrations.[1] For both the micellar and the surfactant–polymer systems, without initial pH adjustment, the measured pH decreases, as the solute concentration increases, approaching pH ~3.0. Therefore, as the solute concentration increases, the solubilization constants become closer to the values obtained where the initial pH was set at 3.

Rejection of TCP

Solute rejection is a parameter used to determine process efficiency. A retentate-based rejection (%) is defined as:

$$\text{Solute rejection } (\%) = \left(1 - \frac{C_{A,perm}}{C_{A,ret}}\right) * 100 \qquad (20)$$

Where $C_{A,perm}$ and $C_{A,ret}$ are the concentrations of solute A in the permeate and the retentate solutions, respectively. High solubilization constants correlate to high solute rejection. A typical solute to colloid concentration ratio in CEUF is 1 to 10: Table 4 shows the rejection value of TCP for MEUF

Table 4. Comparison of TCP rejection in MEUF and PE-MEUF for [TCP]/[colloid] of 1 : 10. The values in parenthesis are pH values corresponding to the rejection value.

		Rejection of TCP (%)	
Colloid solutions	[NaCl] (M)	Without pH adjustment	pH = 3
CPC	0	99.0 (4.0)	99.0
CPC	0.05	99.2 (5.9)	99.2
CPC	0.1	99.3 (5.8)	99.2
CPC-PSS (1/2)	0	96.3 (5.5)	97.9
CPC-PSS (1/2)	0.05	97.0 (5.6)	98.0

and PE-MEUF at different pH values (low and high pH). In micellar solution, the rejection of TCP without pH adjustment is not significantly different from the rejection at pH 3 at all salinities. However, in the surfactant–polymer mixtures, the rejection of TCP at pH 3 is higher than TCP rejection at higher pH. The addition of salt does not significantly influence the rejection of TCP.

The solubilization for TCP is relatively high as seen in this work and the previous work,[1] resulting in very high rejection ($\geq$99%), primarily in micellar solutions. Therefore, the reduced solubilization constant in the micellar solutions at low pH (pH 3) does not significantly affect the solute rejection. Unlike the micellar solutions, the effect of pH can be seen in the surfactant–polymer mixtures. A higher rejection is observed at lower pH (pH 3) due to the higher solubilization of the neutral species of TCP. It should be noted that the effect of pH can be more pronounced for systems studied with solutes that have higher water solubility such as MCP.

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