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Napaporn Komesvarakul[a]; John F. Scamehorn[a]; Hatice Gecol[b]
[a] Institute for Applied Surfactant Research and School of Chemical Engineering and Materials Science, University of Oklahoma, Norman, Oklahoma, USA [b] Chemical Engineering, University of Nevada, Reno, Nevada, USA

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Purification of Phenolic-Laden Wastewater from the Pulp and Paper Industry by Using Colloid-Enhanced Ultrafiltration

**Napaporn Komesvarakul,[1] John F. Scamehorn,[1,*]
and Hatice Gecol[2]**

[1]Institute for Applied Surfactant Research and School of Chemical
Engineering and Materials Science, University of Oklahoma, Norman,
Oklahoma, USA
[2]Chemical Engineering, University of Nevada, Reno, Nevada, USA

ABSTRACT

The removal of three phenolic pollutants with variable degrees of chlorination from water was investigated: 2-monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP). These compounds are often found in pulp and paper mill wastewater effluent. Colloid-enhanced ultrafiltration (CEUF) techniques were investigated for wastewater purification. Pollutants can associate with colloids: surfactant micelles or surfactant–polymer complexes solubilize nonionic compounds. In this application of CEUF, the micelles or

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[*] Correspondence: Dr. John F. Scamehorn, Director, Institute for Applied Surfactant Research, University of Oklahoma, Norman, Oklahoma 73019, USA; Fax: 405-3255813; E-mail: scamehor@ou.edu.

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surfactant–polymer complexes are ultrafiltered from solution with solubilized chlorinated phenol pollutant. An advantage of surfactant–polymer complexes, compared to only surfactants, is reduction of surfactant monomer (unaggregated surfactant) concentration. These surfactant monomers can pass through the ultrafiltration membrane, reducing the purity of the product water. Excellent solute rejections are observed for both micelles and surfactant–polymer complexes, generally exceeding 90% for DCP and TCP, even exceeding 99% in some cases. The ratio of the solubilization constant in micelles to that in surfactant–polymer complexes varied from approximately 1 to 5. In micelles, rejection increases in the order MCP $<$ DCP $<$ TCP, whereas in the surfactant–polymer system, rejection of the DCP and TCP can sometimes reverse order. The surfactant monomer leakage into the permeate for the surfactant–polymer system is only about 1 to 10% of that for the surfactant micelles, down to very low concentrations approaching 1 μM. Therefore, CEUF using surfactant-only or surfactant–polymer mixtures can be a very effective separation technique to remove chlorinated phenols from wastewater. Surfactant–polymer systems result in lower surfactant leakage, but somewhat poorer rejections of the pollutant. It is anticipated that it will be more difficult to recover the colloid for reuse compared to use of a pure surfactant.

Key Words: Colloid-enhanced ultrafiltration; Surfactant-polymer interaction; Phenolic solutes.

INTRODUCTION

Highly toxic and persistent chlorinated dibenzo-p-dioxins, dibenzofurans, and chlorinated phenolic compounds are formed during pulp bleaching when chlorine and chlorine derivatives are used and can be found in wastewater from pulp and paper mills. Chlorinated phenols are known as precursors of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), highly toxic and bioaccumulative matters.[1] In Canadian bleached pulp mill effluents,[2] 70 to 80% of dissolved matter consists of high-molecular weight chlorinated organic compounds (MW $\geq$ 1000). These compounds can be microbiologically transformed or degraded into low-molecular weight compounds that add to the total low-molecular weight loading. The low-molecular weight compounds simply pass through biological membranes[3,4] and accumulate in rivers and oceans, leading to aquatic toxicity. Generally, compared to compounds with a lower degree of chlorination, highly chlorinated compounds or meta-chlorinated compounds are more stable and more persistent in the aquatic environment.[5,6] A principal chlorinated phenol in bleached sulfite discharges is 2,4,6-trichlorophenol.[7] Also 2,4-dichlorophenol, together with a number of chlorinated phenolic compounds, are produced in significant quantity.[8]

Total chlorine free (TCF) and elemental chlorine free (ECF) bleaching can be used to reduce or eliminate the formation of wastewater pollutants; however, lower product quality[9] and heavy capital investment[10] are associated with these nonchlorine bleach technologies. Therefore, instead of "in-process technological changes" (i.e., TCF or ECF), end-of-pipe wastewater treatment can be used to remove pollutants formed during chlorine treatment. Ultrafiltration (UF) processes can be used to effectively treat the wastewater generated in the alkaline stage (E-stage) from bleach kraft pulp mills.[11] Nonetheless, the wastewater generated in the acid stage, which contains mostly low-molecular weight substances, cannot be efficiently treated with this technique.[12]

Colloid-enhanced ultrafiltration (CEUF) methods[13–27] are novel separation processes for removing organic solutes from aqueous streams. Micellar-enhanced ultrafiltration (MEUF)[13–27] is one technique in which a micellar solution is added to a contaminated feed solution. Polyelectrolyte micellar-enhanced ultrafiltration (PE-MEUF) is a modified MEUF technique where a surfactant–polymer mixture is used in the colloid solution.[28–30] This solution is then passed through a membrane, that has pores small enough to block the passage of micelles or surfactant–polymer complexes, removing the surfactant aggregates and solubilized organic solute. 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[16–20]; i.e., the permeate concentration is equal to the unsolubilized solute concentration in the retentate. Therefore, equilibrium solubilization measurements (for example using semiequilibrium dialysis or SED,[29–34] or vapor pressure techniques[28,35,36]) can predict rejection of solutes in MEUF. In this study, SED was utilized for this purpose.

Micelles are surfactant aggregates with the hydrophobic group of the surfactant molecules forming an oil-like interior and the hydrophilic part coating the surface of the micelle[37] (which are roughly spherical for most of the surfactants studied for use in MEUF). Organic solutes can solubilize in different locations in the micelle, as depicted in Fig. 1. Ionic surfactant micelles can interact electrostatically with highly polar solutes due to strong ion–dipole interaction,[38] whereas the hydrophobic core region of the surfactant micelle can interact strongly with hydrocarbon groups of solutes. As a result, aliphatic hydrocarbons, such as hexane, solubilize primarily within the hydrocarbon core region of micelles.[36,38] Since chlorine atoms are

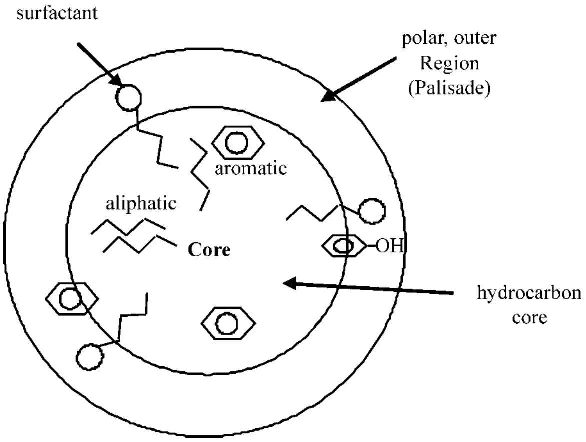


Figure 1. Schematic representation of the micellar structure and locus of solubilization of organic solutes in the micelle.

hydrophobic, for chlorinated phenols, the hydroxyl groups are located next to the cationic surfactant head groups due to ion–dipole interaction while the benzene ring is inserted into the hydrophobic interior of the micelles. In general, the greater the degree of chlorination, the more hydrophobic the solute is and the better it should solubilize.[30,31,38,39] If the solubilized organic molecule has an opposite charge to that of the surfactant head groups, solubilization is further enhanced.[40] This can be a factor in this work at pH levels where phenolics can be partially deprotonated and, thus, anionic.

Not all of the surfactant is present in micelles: the unaggregated individual surfactant is called monomer. The monomer concentration is equal to the critical micelle concentration (CMC) of the surfactant at the solution conditions present. Since the CMC depends on such factors as organic solute concentration, added electrolyte concentration, and temperature, this monomer concentration is not necessarily the same as the CMC value of the pure surfactant at room temperature. In MEUF, the concentration of surfactant in the permeate is approximately equal to the CMC.[19,20] Even for low-CMC surfactants, the monomer leakage can greatly hurt the economics of the separation[15] from the value of the lost surfactant, not even considering potential costs of downstream treatment of the permeate to reduce this surfactant concentration to environmentally acceptable levels.

Several approaches have been tried to address this surfactant leakage problem. The use of ultra-low CMC surfactants invariably involves nonionic surfactants. Unfortunately, fluxes tend to be low (low gel point concentration) with nonionic surfactants[15] due to the lack of electrostatic repulsion between the uncharged micelles in the gel layer. Polymeric surfactants[41,42] should exhibit no monomer leakage, but commercially available ones tend to be predominantly nonionic, with low flux. Another possibility is to treat the permeate with a downstream separation (like foam fractionation).[43,44]

Surfactant–polymer complexes, especially when the polymer and surfactant are oppositely charged, can be in equilibrium with much lower surfactant monomer concentrations than micelles,[45] with monomer concentration reductions of two orders of magnitude observed. The surfactant–polymer complex can solubilize organic solutes with approximately the same level as micelles, per surfactant molecule.[30] Use of these aggregated surfactant–polymer mixtures instead of surfactant alone in the ultrafiltration process is called polyelectrolyte micellar-enhanced ultrafiltration or PE-MEUF, depicted in Fig. 2. It has been shown that surfactant–polymer complexes retain the ability of the surfactant to solubilize hazardous organic solutes, with substantial reduction of surfactant loss through the ultrafiltration membrane.[28–30] Since a higher fraction of the surfactant is in aggregated form, lowering the monomer concentration results in more aggregated surfactant capable of solubilizing solute for surfactant–polymer complexes. However, since surfactant concentrations are generally high in PE-MEUF or MEUF (most of surfactant in aggregated form), this higher aggregate concentration is a minor factor.

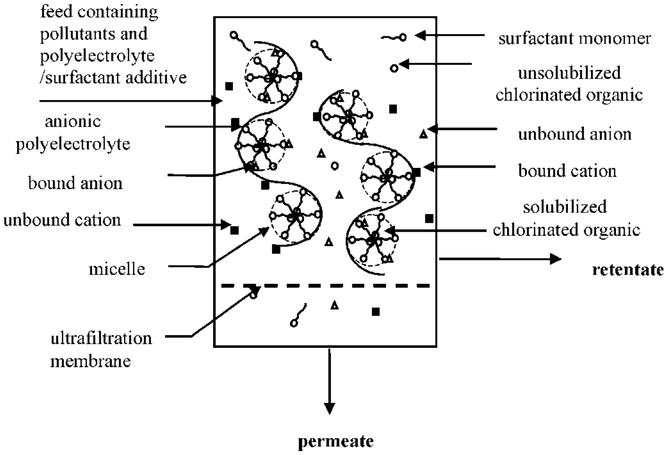


Figure 2. Schematic of polyelectrolyte micellar-enhanced ultrafiltration (PE-MEUF).

The interaction between ionic surfactants and oppositely charged polymers has been investigated using such techniques as surface tension, dye solubilization, and fluorescence spectroscopy.[46–54] There have been a few studies of solubilization of organic solutes in surfactant–polymer mixtures throughout wide ranges of relative concentrations of organic solutes in the polymer-bound surfactant aggregates, with a partially neutralized copolymer of maleic anhydride and vinyl methyl ether (Gantrez)–cetylpyridinium chloride (CPC) and sodium poly (styrenesulfonate) (PSS)–CPC complexes.[28–30] Since solubilization into the surfactant–polymer aggregate is reported to be similar to that into micelles composed of the same surfactant, the surfactant is deduced to be forming a micellar-like aggregate with a hydrophobic region in which solubilized organic can reside. One potential configuration is "micelles on a string," where the micelles are stabilized by the polymer chain to which they are electrostatically bound.[29,50,55–57]

In the present study, the removal of three chloro substitution phenolics [2-monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP)] from water using PE-MEUF are compared to removal using MEUF with the same surfactant. The optimum CEUF configuration for the pulp and paper industry wastewater containing chlorinated phenolics is discussed.

EXPERIMENTAL

Materials

MCP, DCP, and TCP (99+% pure) were obtained from Aldrich Co. (Mikwaukee, WI) and used without further purification. High quality (99+% pure) cetylpyridinium chloride (CPC) from Zeeland Chemical (Zeeland, MI) does not exhibit a minimum in a plot of surface tension vs concentration, or show any impurities in HPLC chromatograms and was used as received. Poly (styrenesulfonate) (PSS) (100% pure), which has an average molecular weight of approximately 70,000 Daltons, was obtained from Alfa Aesar (Ward Hill, MA). The repeating unit of the polymer is $CH_2CH(C_6H_4)SO_3Na$. Lower molecular weight fractions were removed by using a spiral wound ultrafiltration apparatus having 10,000 Daltons molecular weight cut-off and an area of 5 ft^2. The purification process was conducted five times. The final concentration of the purified polymer was measured by using a total organic carbon analyzer or TOC (Rosemount DC-180). Water was deionized twice 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.

Methods

The semiequilibrium dialysis (SED) method was used to measure solubilization. Regenerated cellulose membranes (6000 Da molecular weight cut-off) were soaked overnight in deionized water prior to mounting them between two compartments. A known volume of a solution containing an organic solute and CPC or CPC–PSS mixtures was placed in the retentate compartment using a 10-mL syringe. The water was placed in the permeate compartment. The cells reached equilibrium within 24 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., solute, surfactant, and polyelectrolyte) 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 a Hewlett-Packard HP 8452A diode array spectrometer. A cuvet with 10-cm pathlength was used to determine solute concentration with minimum detectability of 5×10^{-6} M. The concentrations of the chlorinated phenol and CPC remaining in the retentate at equilibrium were inferred by subtracting the analytical concentrations of these species in the permeate from the feed concentration. The pH level of samples was adjusted to 10.5 by using an AR 20 pH/Conductivity meter (Accumet Research, Fisher Scientific) before performing the UV analysis. It should be noted that the pH of calibration solutions was also adjusted to 10.5. Multiwavelength analysis was used to analyze both surfactant and solute concentrations simultaneously. Absorbance values were recorded at different wavelengths chosen near the absorption maxima of the surfactant and solute (260 nm for CPC, 300 nm for MCP, 314 nm for DCP, and 322 nm for TCP).

Spectrophotometric titrations were carried out to determine the protonation constant (K_H) for the organic solutes in micellar solutions and surfactant–polymer mixtures. Spectra were obtained using the spectrometer described previously with a 1-cm pathlength cuvet. Deionized water at several pHs was used to prepare solutions used for the analysis. The pH of the solutions was recorded before performing the UV analysis.

Surface tension measurements, by means of the Wilhelmy plate technique (Kruss Processor Tensiometer K12, Krüss, North Carolina, USA), were performed on solutions placed in a crystallizing dish held at constant temperature (25°C ± 0.1°C). Mixtures of PSS and CPC were prepared and kept at 25°C in a controlled temperature oven overnight. Precipitation was observed at the mole ratios of [CPC] to [PSS] $\geq$ 1 to 1; at mole ratios $\leq$ 1 to 2, no precipitation was observed and the solutions were isotropic. Only isotropic solutions were used in this study. At some high [CPC] to [PSS] ratio, the solutions would again become isotropic. However, this region was not considered because the beneficial effects of the polymer are not substantial at these surfactant-dominant compositions.

THEORY

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

$$K = \frac{X_A}{c_A} \tag{1}$$

$$X_A = \frac{C_A^{agg}}{C_A^{agg} + C_{CPC}^{agg}} \tag{2}$$

where c_A is the concentration of an unsolubilized organic solute, X_A is the mole fraction of the solute (MCP, DCP, or TCP) in the surfactant aggregate, C_A^{agg} is the concentration of solute in the aggregate, and C_{CPC}^{agg} is the concentration of CPC in aggregate form. From material balances:

$$C_A^{agg} = C_{A,tot} - c_A \tag{3}$$

$$C_{CPC}^{agg} = C_{CPC,total} - C_{CPC,monomer} \tag{4}$$

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. 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. Since the permeate micelles could solubilize the solute, the permeate solute concentration is 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 (although long enough to permit the unsolubilized solute to reach

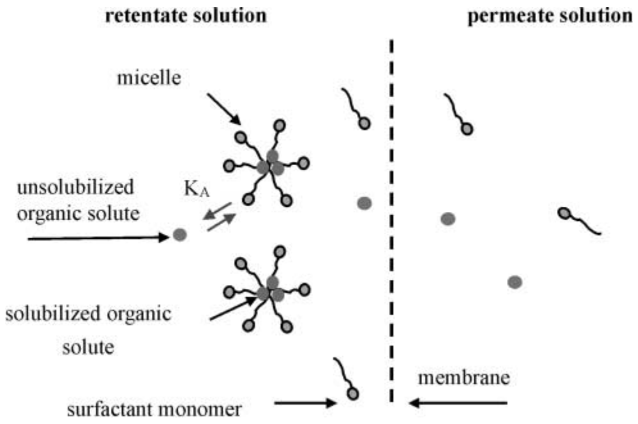


Figure 3. Distribution of surfactant and organic solute in SED compartments.

equilibrium), or correction factors used to account for solubilization in permeate micelles.[31–34,58] For PE-MEUF, the polymer is almost completely rejected by the membrane, so is present in insignificant concentration in the permeate,[59] therefore no surfactant–polymer aggregate forms in the permeate. In this study, for micellar systems, we observed 2 orders of magnitude lower concentration of solute and surfactant in the permeate than in the retentate, such that the presence of surfactant micelles in the permeate does not considerably influence the measured solubilization isotherm. Therefore, no correction for permeate micelle formation is made. The distribution of the organic solute and the surfactant in the SED compartments is illustrated in Fig. 3.

RESULTS AND DISCUSSION

Effective pK$_a$ Values

The phenolic solutes studied here are weak acids and can exist in two protonation states. The unprotonated compound is negatively charged while the protonated phenolics are uncharged. The charged species have higher water solubility than the neutral, protonated species. The equilibrium or dissociation constant (K$_a$) of the solutes has been reported in pure water[60]: pK$_a$ 8.52, 7.9, and 6.0 for MCP, DCP, and TCP, respectively. However, interaction between the phenolic group of the solute and the charged surfactant head groups and charged groups on the polyelectrolyte, when the solute is solubilized in micelles or surfactant–polymer complexes, can affect the K_a of solubilized species, and therefore, the apparent K_a of the phenolic in the colloid systems.

The equilibrium constant may be evaluated from the protonation step following:

$$\mathrm{L^- + H^+ \overset{K_H}{\rightleftharpoons} HL} \tag{5}$$

$$K_H = \frac{[HL]}{[L^-][H^+]} \tag{6}$$

where:

$[\mathrm{H^+}] = 10^{-\mathrm{pH}}$

$\mathrm{K_H}$ = the protonation constant of the protonation equilibrium, Eq. (5)

Values of $\mathrm{K_H}$ were obtained by using nonlinear least squares program to fit the absorbance-pH data to the following expression[61]:

$$Abs(\lambda) = \frac{Abs_L + Abs_{HL}K_H(10^{-pH})}{1 + K_H(10^{-pH})} \tag{7}$$

where:

$\mathrm{Abs_L}$ = limiting absorbance of basic form of the solute at λ

$\mathrm{Abs_{HL}}$ = limiting absorbance of acid form of the solute at λ

$\mathrm{K_H = 1/K_a}$

$\mathrm{\log K_H = \log(1/K_a) = pK_a}$

All solutions contain the solute of interest at a concentration of 0.2 mM although the actual solute concentration in the SED experiments ranges from 0.5 mM to 25 mM. This is due to the limited range of solute concentration over which the UV spectrum obeys Beer's law when the colloids are also present. Plots of absorbance as a function of pH are shown in Figs. 4–6 for water, 25 mM [CPC], and 25 mM/50 mM [CPC]–[PSS], respectively. The wavelength selected for each plot is the wavelength where the maximum absorbance (λ_{max}) changes as the pH of the solutions is changed in the presence of 25 mM [CPC]. For example, in the CPC solution at 25 mM, the λ_{max} of MCP, DCP, and TCP is 300, 314, 322 nm, respectively. These values are different from the values observed in pure water; the λ_{max} of the solutes in

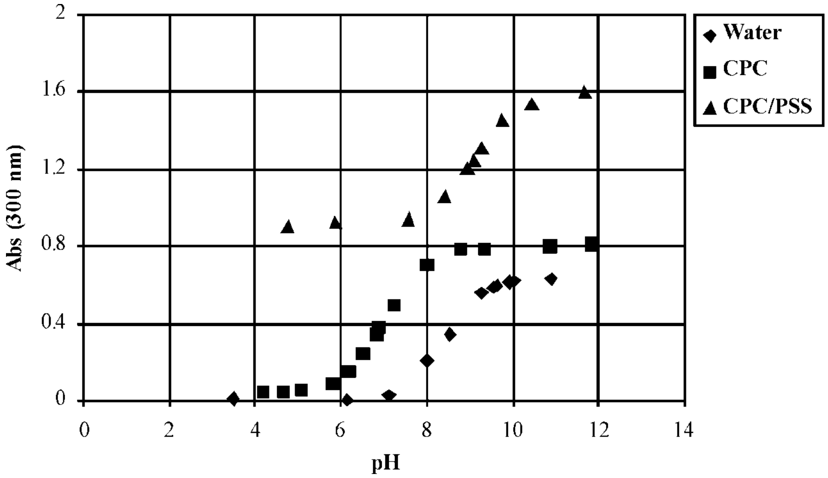


Figure 4. Plots of pH vs. absorbance at 300 nm for MCP in water, CPC solution (25 mM), and CPC–PSS mixture (25 mM/50 mM of [CPC]–[PSS]).

pure water is 294, 306, and, 312 nm for MCP, DCP, and TCP, respectively. This contributes to the difference in the $\mathrm{Abs_L}$ value shown in Figs. 4 through 6. A relatively high $\mathrm{Abs_L}$ in the CPC–PSS mixtures is associated with the absorbance of the PSS itself at the chosen wavelength.

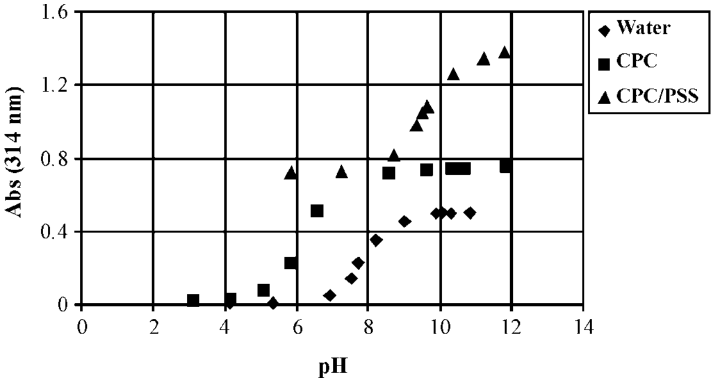


Figure 5. Plots of pH vs. absorbance at 314 nm for DCP in water, CPC solution (25 mM), and CPC–PSS mixture (25 mM/50 mM of [CPC]–[PSS]).

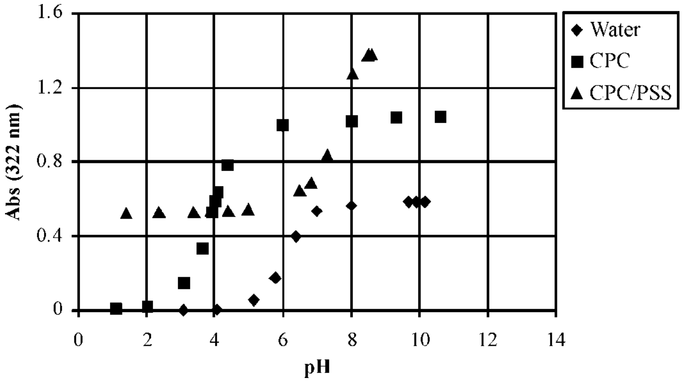


Figure 6. Plots of pH vs. absorbance at 322 nm for TCP in water, CPC solution (25 mM), and CPC–PSS mixture (25 mM/50 mM of [CPC]–[PSS]).

Table 1 shows the apparent pK_a values obtained from the spectrophotometric titration. The pK_a values in water are close to published research values[60]: 3.28%, 1.1%, and 2.6% different for MCP, DCP, and TCP, respectively. In the micellar solutions, due to the electrostatic interaction between the cationic surfactant and the negatively charged solute, the equilibrium shown in Eq. (5) favorably shifts toward the unprotonated form, therefore, lowering the apparent pK_a of the solute. On the other hand, in the presence of PSS, the net charge of surfactant–polymer aggregates is negative; the solute is shifted toward the protonated form, resulting in an increase in the apparent pK_a compared to the pK_a in pure water. By knowing the pK_a values, distribution of species with different charges can be obtained by using software called Comics,[62] which are shown in Figs. 7 through 9. In micellar solution, the pH of the initial retentate solutions ranges from 4.6 to 6 for MCP, 4 to 5 for DCP, and 2.9 to 3.3 for TCP. However, it was observed in the SED experiment, for TCP in the micellar solution, that the pH value in the retentate

Table 1. The pK_a values of MCP, DCP, and TCP in water, CPC solutions, and CPC–PSS mixtures.

Solute	MCP	DCP	TCP
Water	8.80	7.99	6.16
CPC (25 mM)	6.98	6.22	3.91
CPC–PSS (25 mM/50 mM)	9.09	9.54	7.52

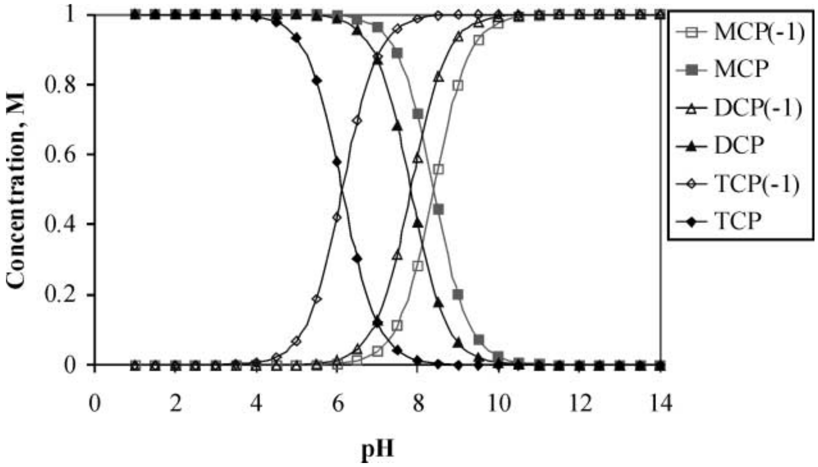


Figure 7. Charge distribution of MCP, DCP, and TCP in water. (− 1) represents the negatively charged species.

can increase by a maximum of 0.6 units at the lowest solute concentration and that the increase becomes less at higher solute concentrations. As shown in Fig. 8, the solute is comprised of both neutral form and the negatively charged form, depending on the initial solute concentration. For example, in Fig. 8, at the lowest solute concentration for TCP, corresponding to an initial solution

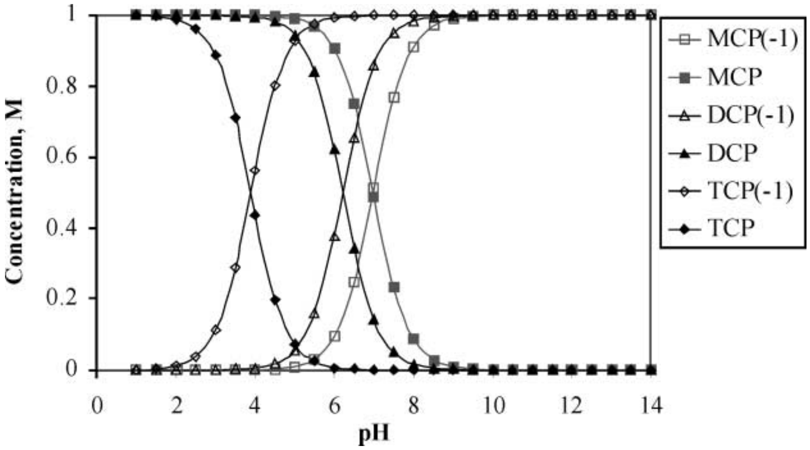


Figure 8. Charge distribution of MCP, DCP, and TCP in CPC solution (25 mM).

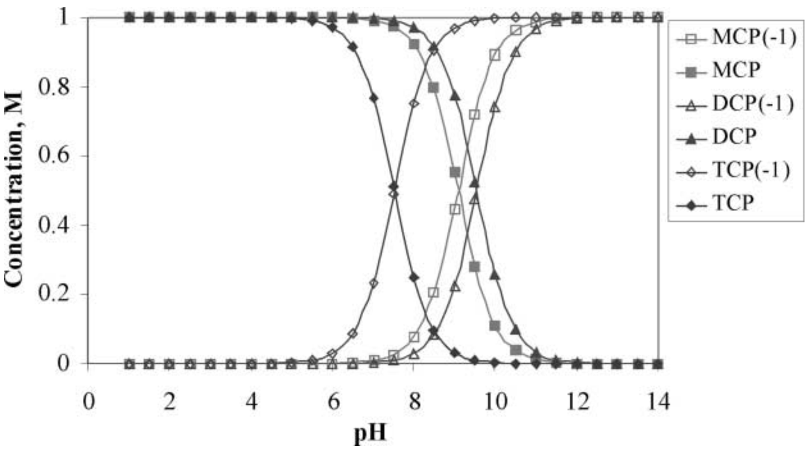


Figure 9. Charge distribution of MCP, DCP, and TCP in CPC/PSS mixtures (25 mM/50 mM of [CPC]–[PSS].

pH of 3.3, the pH of the final retentate is expected to be 3.9. As a result, the solution contains 50% neutral form and 50% negatively charged form of TCP. In a similar manner for DCP, at the final pH of 5.6, the solution contains 85% neutral form and 15% negatively charged solute. At the final pH of 6 for MCP, the solution contains 90% neutral form and 10% negatively charged solute. It should be noted that the pH in the final retentate for MCP does not significantly change from the initial pH because the initial pH is close to the pH of the initial permeate, which is between 6 and 7. However, since the charge distribution was done at a solute concentration of 0.2 mM, with higher solute concentrations, the pK_a can be changed. A series of experiments was carried out at a higher TCP concentration to investigate the effect of solute concentration on the pK_a. At 0.3 mM TCP under the same condition (25 mM CPC), the pK_a slightly shifts to a lower pH (from 3.91 at 0.2 mM TCP to 3.80 at 0.3 mM TCP). The experiment cannot be done at higher solute concentration or in the CPC/PSS mixtures due to the violation of Beer's law that can occur. From this result, it indicates that the percentage of the negatively charged TCP present in the CPC solution can be slightly higher than 50%. In the presence of PSS, the pH of the initial retentate solutions ranges from 6.3 to 7 for MCP, 6.3 to 6.9 for DCP, and 4.9 to 6 for TCP. The pH of the final retentate is expected to be almost the same for MCP and DCP because the initial retentate pH is close to the pH of the initial permeate. As shown in Fig. 9, the solutes are almost completely protonated or have a slight net negative charge at the pH values studied. For example, in the CPC–PSS mixtures at a pH of 6, TCP consists of 97% neutral form and 3% negatively charged solute. As mentioned previously, the percentage of the negatively charged solute can be higher than 3% due to the higher solute concentration in the SED experiment higher than in the charge distribution experiment.

Surfactant–Polymer Interaction

The PSS concentrations are based on the repeating units, not the total molecular weight. So, for example, 206 g/L of PSS is reported as 1 M based on a repeating unit molecular weight of 206 Daltons even though the total molecular weight is 70,000 Daltons. Figure 10 shows surface tension as a function of CPC concentration at different concentrations of PSS, and Fig. 11 is a schematic representation of the curve with generally accepted aggregate structures in each concentration regime.[48] The general features of the surface tension trends in Fig. 10 are that there is synergistic lowering of surface tension with increasing PSS concentration below the CPC concentration at which the surface tension reaches a plateau. This plateau surface tension is only mildly dependent on PSS concentration, but is attained at a lower CPC

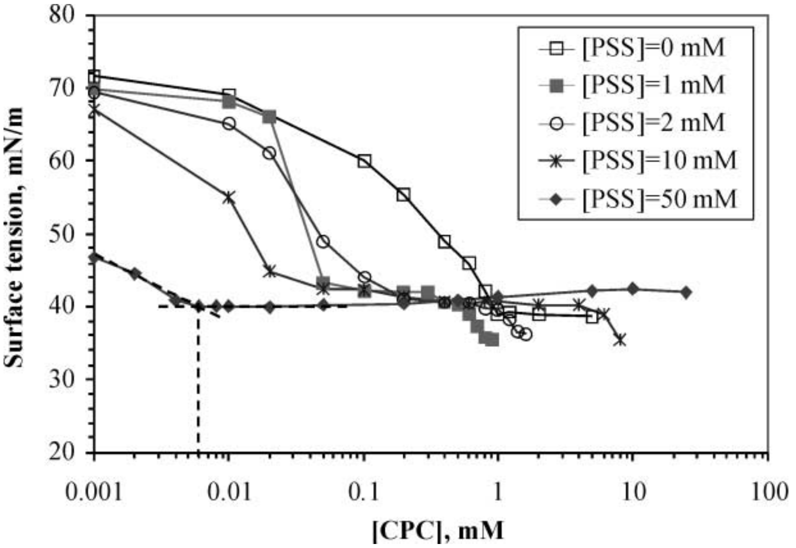


Figure 10. Surface tension of surfactant and surfactant–polymer systems.

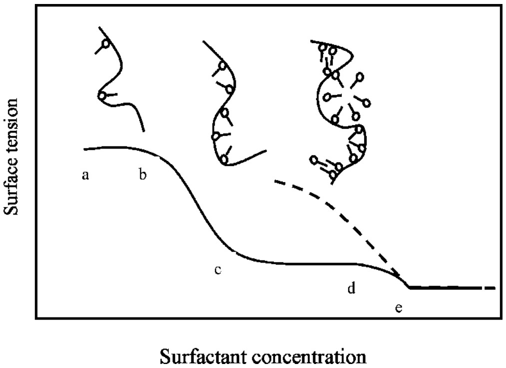


Figure 11. A schematic of surfactant–polymer aggregation. Dashed line is for the surfactant (CPC) alone. Full line is for CPC–PSS mixture. Counterions are not depicted here.

concentration as PSS concentration increases. The PSS can have a massive effect on surface tension lowering. For example, the concentration of CPC required to attain a surface tension of 45 mN/m is approximately 0.7 mM with no PSS, but only less than 0.002 mM in the presence of 50 mM PSS, over 2 orders of magnitude reduction. This clearly implies that the PSS is contributing to surface tension lowering and is surface active even in

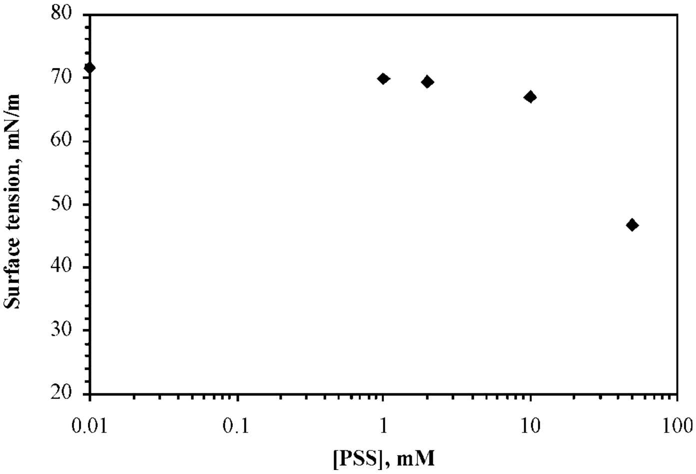


Figure 12. Surface tension for PSS-only solutions.

the absence of surfactant, as shown in Fig. 12. Surfactant–polymer complexes can adsorb at the air–water interface,[48] causing the synergistic surface tension lowering observed for the CPC–PSS mixture. However, for purposes of this article, we are interested in the solution aggregate structure and what these surface tension curves allow us to deduce about the CPC–PSS complex in solution.

In region a-b-c in Fig. 10, surfactant is adsorbing on the polymer chain as unassociated CPC molecules. Lateral interactions between surfactants are negligible since they are at a low adsorption density on the polymer chain. In region c-d, surfactant aggregates that are stabilized by the polymer molecule form "micelles on a string." The concentration of these polymer-stabilized surfactant aggregates in solution increases from c to d. At CPC concentrations above point d, the monomeric CPC concentration increases as the polymer becomes saturated with the surfactant aggregates. At yet higher CPC concentration, eventually ordinary micelles form (point e) and the surface tension tends to plateau again. Goddard also observed this kind of behavior.[48] Compared to the polymer-free system, this CPC concentration required to form micelles is much higher because a vast majority of surfactant is present in surfactant–polymer complexes instead of monomer when this micelle formation concentration is attained. This CPC concentration was not reached for any of the PSS concentrations studied in Fig. 10, primarily because the polymer and surfactant form a precipitate prior to this concentration. It should be noted that this type of behavior has also been observed in a turbidity plot vs concentration of a surfactant.[63]

It is the surfactant aggregate, stabilized by polymer, which is solubilizing the organic pollutant in PE-MEUF, so the CPC concentration needs to be above point c. However, in the PE-MEUF, at a total CPC concentration above point e, the CPC monomer concentration would be equal to the CMC, and the surfactant permeate concentration reduction advantage of the PE-MEUF would be lost. The higher the PSS concentration, the lower the CPC concentration at which the polymer-stabilized surfactant aggregate forms (point c). It was observed that the gel point (colloid concentration in retentate where flux becomes zero) in the 1:2 surfactant–polymer complex solution is approximately 0.4 M in CPC concentration,[29] corresponding to 0.8 M in PSS concentration. In the case of the surfactant-only solution, the gel point is 0.53 M,[19] whereas the gel point is approximately 0.7 M in the polymer-only system.[64] The total colloid (surfactant plus polymer) concentration in the PE-MEUF is higher than the colloid concentration when either the surfactant or polyelectrolyte is present alone, but the surfactant concentration at the gel point is less for PE-MEUF than for MEUF. At lower [CPC] to [PSS] ratios, a lower surfactant concentration is present at the gel point. Therefore, [CPC] to [PSS] ratio in the retentate is a compromise between a higher fraction of surfactant in aggregated form at a low [CPC] to [PSS] ratio, but a reduced ability to increase the retentate surfactant concentration until unacceptably low fluxes are observed. The latter translates to lower permeate to feed or water recycle ratios. So the information in Fig. 10 can help to determine the optimum polymer and surfactant feed concentrations in PE-MEUF. It is important to note that since the PSS concentration affects the surface tension at a given CPC monomer concentration, one cannot deduce CPC monomer concentration from the value of surface tension. Therefore, we will show permeate CPC concentrations that approximate this CPC monomer concentration in the retentate.

From the data in Fig. 10, and referring to Fig. 11, point d corresponds approximately to a CPC to PSS molar ratio of 1, so two anionic sulfonate PSS groups stabilize one aggregated cationic surfactant molecule. Previous studies[29] indicate that at a [CPC] to [PSS] ratio of 1 to 2 or less, there is no precipitation of the surfactant–polymer mixture. At a [CPC] to [PSS] ratio greater than about 1 to 2, some precipitation will occur and redissolution may be slow. Thus, [CPC] to [PSS] ratios of 1 to 3 and 1 to 2 were used in SED experiments in this work.

Solubilization Isotherms

As shown in Figs. 13 through 18, the solubilization equilibrium constants obtained by SED experiments for 2-monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6- trichlorophenol (TCP) are plotted as a function of intramicellar mole fraction (X_A) in CPC micelles and CPC–PSS complexes. From Figs. 13 through 15, solubilization capacity in a surfactant-polymer system is lower than that in a polymer-free system. Depending on the solute type and concentration, as the solute concentration increases, the ratio of the solubilization constant in micelles to that in surfactant–polymer complexes varies from 1.5 to 2.5 for MCP, from 1 to 1.6 for DCP, and from 2.2 to 4.9 for TCP. The solubilization constant decreases monotonically with increasing X_A for CPC-only, and for CPC–PSS complexes at higher values of X_A. Unlike the micellar systems, K exhibits a slight maximum with X_A for MCP and TCP in surfactant–polymer systems. The polyelectrolyte causes the greatest reduction in K for TCP, compared to MCP and DCP. The reduction in K caused by the polymer is the greatest at low solute concentrations. In addition, compared to CPC system, the solubilization ability of CPC–PSS complexes is less dependent on the solute concentration (or X_A), particularly for MCP.

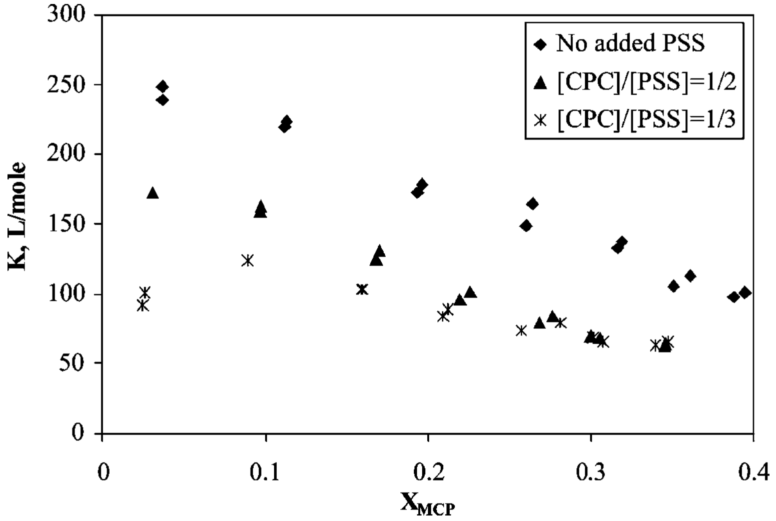


Figure 13. Solubilization equilibrium constant of MCP vs. mole fraction of MCP in the micelle, with and without PSS. Initial [CPC] to [PSS] are 25 mM to 0 mM (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3).

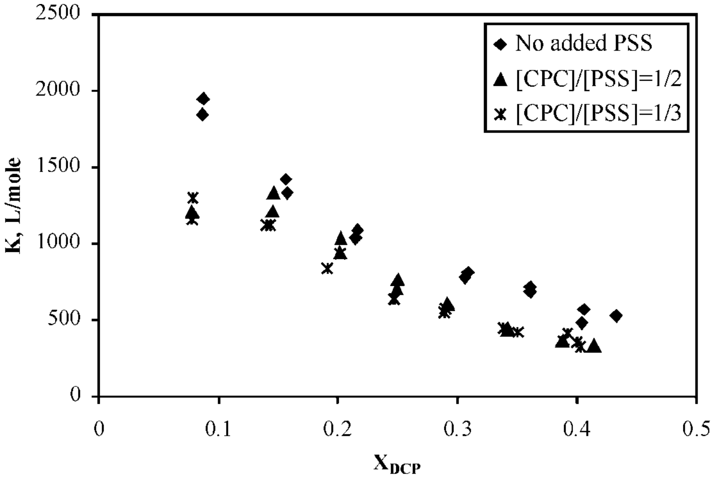


Figure 14. Solubilization equilibrium constant of DCP vs. mole fraction of DCP in the micelle, with and without PSS. Initial [CPC] to [PSS] are 25 mM to 0 mM (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3).

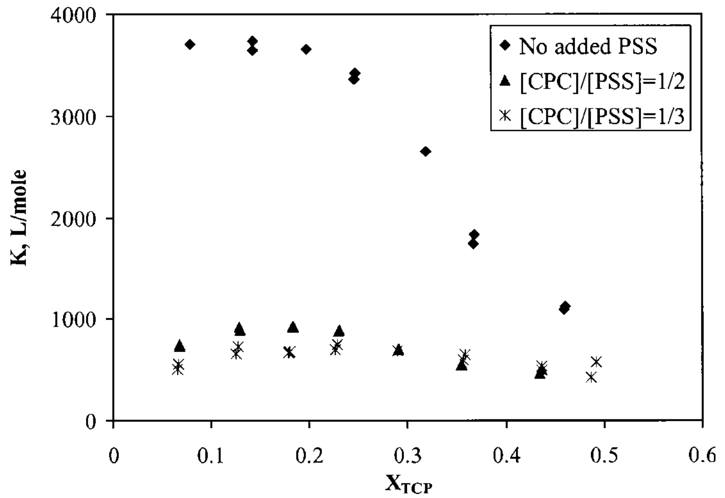


Figure 15. Solubilization equilibrium constant of TCP vs. mole fraction of TCP in micelle, with and without PSS. Initial [CPC] to [PSS] are 25 mM to 0 mM (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3).

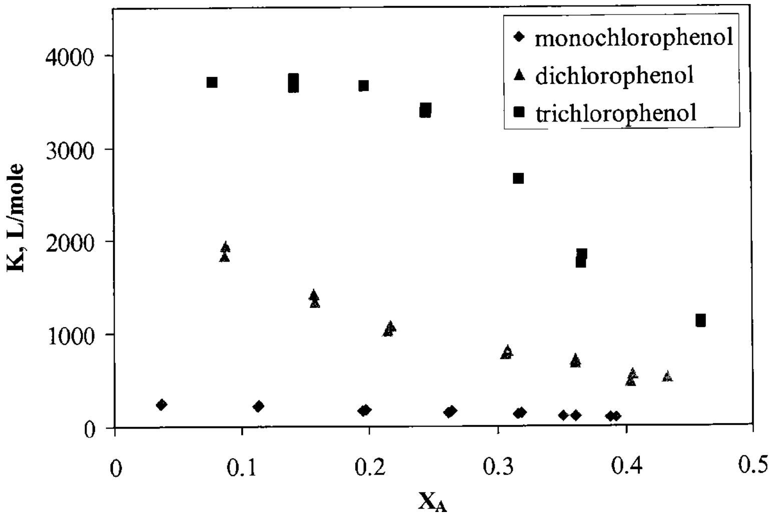


Figure 16. Solubilization equilibrium constant vs. mole fraction of solute in the surfactant micelle. Initial [CPC] is 25 mM (no added PSS).

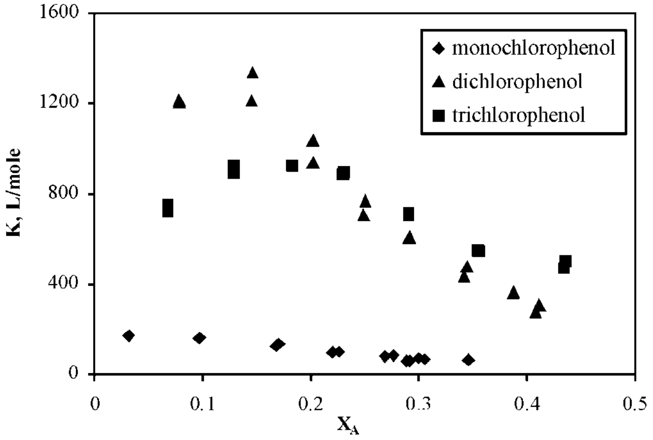


Figure 17. Solubilization equilibrium constant vs. mole fraction of solute in the surfactant–polymer complex. Initial [CPC] to [PSS] is 25 mM to 50 mM.

The data is replotted in Figs. 16 through 18 to show the effect of solute structure. In the polymer-free system, shown in Fig. 16, the solubilization constant (K) has the order $K_{MCP} < K_{DCP} < K_{TCP}$, and K monotonically decreases as X_A increases for MCP, DCP, and TCP. In the surfactant–polymer systems, shown in Figs. 17 and 18, $K_{TCP} < K_{DCP}$

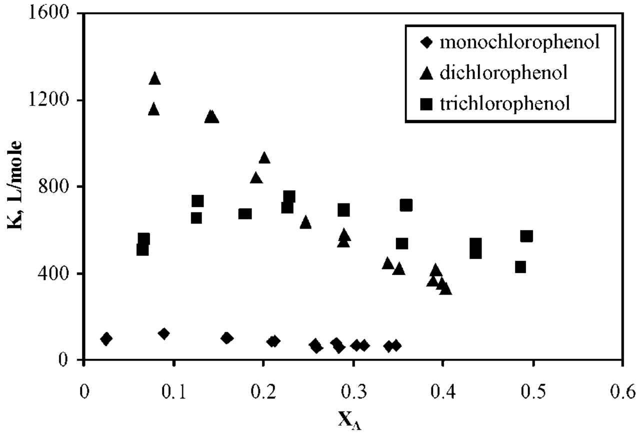


Figure 18. Solubilization equilibrium constant vs. mole fraction of solute in the surfactant–polymer complex. Initial [CPC] to [PSS] is 25 mM to 75 mM.

at $X_A < 0.25$; but $K_{DCP} < K_{TCP}$ at $X_A > 0.25$; whereas K_{MCP} is less than K_{DCP} or K_{TCP} over the entire concentration range. At both [CPC] to [PSS] ratios of 1 to 2 and 1 to 3, K_{TCP} has a maxima near $X_A = 0.2$.

Differences in solubilization behavior of the solutes in CPC micelles and in CPC–PSS complexes may be attributed to a reduction in electrostatic interheadgroup interaction upon the formation of the smaller polymer-stabilized micelles, resulting in a reduction in both CMC and surfactant aggregation number[52] and, presumably, electrical potential at the surface of surfactant aggregates. Therefore, solutes partition more strongly into the ordinary micelles compared to the surfactant–polymer aggregates for all three solutes, probably due to increased ion–dipole interaction between the cationic surfactant headgroup and the phenolic solute hydroxyl group. The neutralization or partial neutralization of surfactant aggregates by the oppositely charged polyelectrolyte would be expected to have a greater effect on solubilization of more acidic solutes than the less acidic solutes. It should be noted that the pK_a of DCP is higher than MCP in the CPC–PSS mixtures (at 1 to 2 mole ratio), as shown in Table 1 although the pK_a of DCP is more than MCP in both water and CPC solutions. As predicted from pK_a values, the highest ratio of K for CPC to K for CPC–PSS is observed for TCP, and the lowest ratio of the K values is found for DCP. However, as the solute concentration approaches zero, the effect of polyelectrolyte is relatively large; a greater reduction in K is observed for DCP than for MCP. This behavior was also observed in CPC–Gantrez mixtures.[30] It should also be noted here that the [CPC] to [PSS] ratio does not significantly influence the solubilization of the solutes at the same surfactant concentration for the 1 to 2 and 1 to 3 ratios studied here.

Hydrophobicity of the solute has been considered to be a key factor in dictating solubilization behavior, although other factors, such as polarizability and substitution site, are also important. In general, the more hydrophobic the solute, or the lower the water solubility, the higher the solubilization constant. It should be noted that the water solubility of 2-MCP, 2,4-DCP, and 2,4,6-TCP are 2, 0.4, and 0.04 wt% (or 0.173, 0.034, and 0.002 M), respectively.[65] The value of K for the three solutes is in inverse order compared to water solubility for the surfactant-only system, as seen in Fig. 16. For instance, K_{TCP} to K_{DCP} ratio is ranging from 2.1 to 3.4, while the water solubility ratio for DCP to TCP is 17. In addition, as mentioned previously, a higher percentage of the negatively charged solute was observed in TCP than MCP or DCP at low solute concentration, therefore increasing the K value of TCP as compared to the K value of DCP or MCP.

In general, a decrease in the solubilization equilibrium with an increasing mole fraction has been observed in micelles for alcohols and other polar solutes[66]; as shown in Fig. 16, we observed this trend here for CPC with all three solutes. At low concentrations, K can vary linearly with solute concentration in the micelles, so that

$$K = K_0(1 - bX_A) \tag{8}$$

where K_0 is the value of the solubilization constant in the limit as X_A approaches zero. Dougherty and Berg have been found a linear dependence of K vs $X_A$at low solute concentration for several surfactant–polar organic solute systems.[67] By inserting the definition of K [Eq. (1)] and rearranging Eq. (8), the resultant equation yields a Langmuir adsorption isotherm:

$$X_A = \frac{K_0 c_A}{1 + K_0 b c_A} \tag{9}$$

This behavior suggests that the solute is initially located at the micellar surface at low X_A. Once all active sites are occupied, the solubilization may occur deeper into the palisade region or into the hydrocarbon interior of the micelles as supported by an upward curvature in the plot of K vs X observed in both MCP and DCP, which implies an increase in micellar solubility at high occupation number. This means that the Langmuir isotherm fails at higher MCP, DCP, and TCP concentrations. It is plausible that the solutes penetrate deeper into the palisade layer or are incorporated into the hydrocarbon interior of micelles by hydrophobic interaction between the chloro group of the solute and the hydrocarbon core of the micelle.

Previous studies[31,32] showed the linear correlation of $\sqrt{K}$ against X_A over the entire range of solute concentration. Our solubilization results also fit the correlation of $\sqrt{K}$ vs. X_A better than a linear plot of K vs X_A. However, $\sqrt{K}$ vs. X_A did not produce an excellent correlation and does not have a strong theoretical basis, so is not used here.

Since the solutes are almost completely protonated under the conditions in the presence of polymer, ion–dipole interaction can affect the solubilization of the solute in the surfactant aggregate. The dipole moment (μ) of MCP, DCP, and TCP is reported as 2.93, 2.25, and 1.08 D, respectively,[68] which has an opposite order to hydrophobicity of the solute (e.g., TCP shows the greatest hydrophobicity). As a result, two opposing effects for a given solute are viewed here; a solute with higher degree of chlorination like TCP with the highest hydrophobicity is speculated to have the lowest ion–dipole interaction. This effect can presumably explain the results for DCP and TCP, shown in Figs. 17 and 18. At low solute concentrations, the ion–dipole interaction between the solute and the surfactant–polymer aggregate plays a greater role than the effect of hydrophobicity; therefore, at a given solute concentration, a higher K value is observed in DCP than TCP. However, at higher solute concentration, besides the effect of the hydrophobicity, TCP may be solubilized more deeply into the core of the micelle as mentioned previously; as a result, the solubilization constant of TCP is higher than that of DCP. The solubilization of MCP in both figures are smallest over an entire range of concentration because of its lower hydrophobicity, and higher water solubility, compared to DCP and TCP, although its dipole moment is the highest.

Solute Rejection

Solute rejection is a more convenient parameter than the solubilization equilibrium constant to use in process design for the UF processes. A retentate-based rejection (in %) is defined as[19]:

$$\text{Solute rejection}\,(\%) = \left(1 - \frac{C_{A,perm}}{C_{A,ret}}\right) * 100 \tag{10}$$

where $C_{A,perm}$ and $C_{A,ret}$ are the concentration of solute A in the permeate and the retentate solution, respectively. High solubilization equilibrium constants correlate to high solute rejection.

At high rejections (as rejection approaches 100%), rejection values are not sensitive to separation efficiency. Permeate to retentate solute concentration ratios of 1 to 10, 1 to 100, and 1 to 1000 correspond to rejection of 90%, 99%, and 99.9%, respectively. A typical retentate solute to colloid concentration ratio in CEUF is 1 to 10: Table 2 shows the rejection values at this condition for MCP, DCP, and TCP for MEUF and PE-MEUF. The experiments were performed at constant colloid concentrations of 25 mM, 75 mM, and 100 mM for the CPC only system, a [CPC] to [PSS] ratio of 1 to 2, and a [CPC] to [PSS] ratio of 1 to 3, respectively, while retentate solute concentration was varied. Therefore, corresponding to the ([solute] to

Table 2. Rejection of solute at [solute] to [colloid] = 1 to 10 (%).

[CPC to PSS]	25 mM to 0 mM	25 mM to 50 mM	25 mM to 75 mM
MCP	85.0	76.0	70.0
DCP	97.3	95.5	95.0
TCP	99.0	96.3	95.5

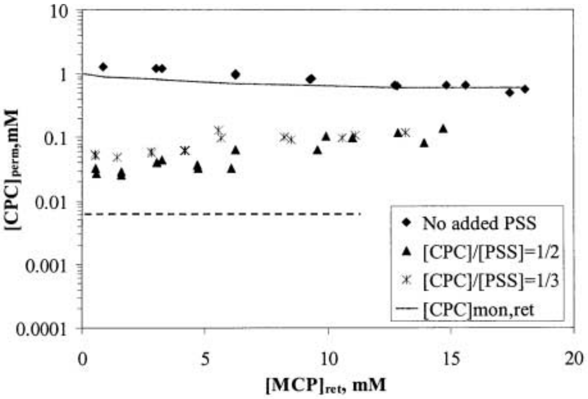
[colloid])$_{ret}$ ratio of 1 to 10, [solute]$_{ret}$ for the colloid concentrations of 25 mM, 75 mM, and 100 mM are 2.5 mM, 7.5 mM, and 10 mM, respectively.

If a pollutant permeate concentration is unacceptably high, the feed colloid concentration can be increased and/or the process can be staged. For example, in a previous study, about four stages were found to be optimum for removal of 99% of trichloroethylene from groundwater.[15] Rejections below 80% could be considered not very efficient, above 95% good, and above 98% excellent, as rough guides. So, from Table 2, use of MEUF for removal of MCP is feasible, but use of PE-MEUF for MCP does not appear promising if substantial concentration reductions are required. Nonetheless, the removal of DCP and TCP can be accomplished by use of both MEUF and PE-MEUF; the rejections of DCP and TCP exceed 95%. In, PE-MEUF systems, an increased colloid concentration from 75 mM to 100 mM does not significantly influence the DCP and TCP rejections because, although, the colloid concentration is increased, the retentate solute concentration is increased as well.

Surfactant Leakage

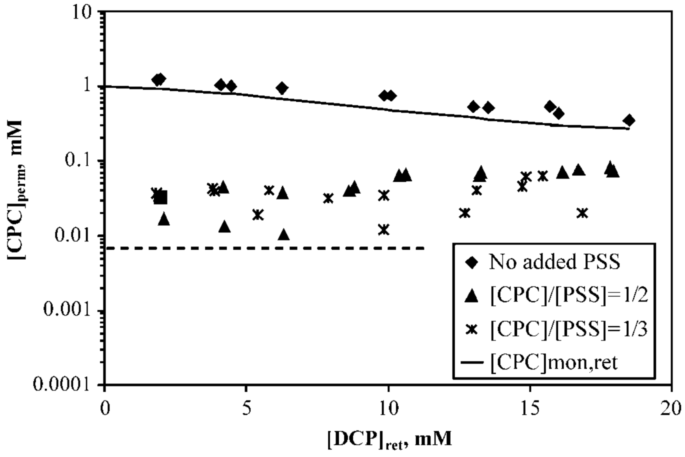
As shown in Figs. 19 through 24, the surfactant (CPC) concentration in the permeate or "surfactant leakage," studied with MCP, DCP, and TCP, in the MEUF and PE-MEUF systems, are plotted as a function of retentate solute concentration. As seen in Figs. 19 through 21, the extent of surfactant leakage can be reduced by as much as approximately 2 orders of magnitude due to the presence of PSS; the retentate [CPC] to [PSS] ratio of 1 to 2 gives a slightly lower extent of the surfactant leakage than does a ratio of 1 to 3. The data is replotted in Figs. 22 through 25 to show the effect of solute structure.

For PSS-free systems, the CMC can be deduced from the surface tension data (see Fig. 10). With varying the solute type and concentration, the CMC results for MCP and DCP are shown in Fig. 26. The effect of TCP is not shown here because of its very limited solubility below the CMC. A significant reduction in the CMC due to solubilization of solutes is observed (approaching an order of magnitude) with a greater CMC depression at higher unsolubilized solute concentrations. This effect is due to reduction in repulsion between the positively charged surfactant head groups upon insertion of the phenolic hydroxyl groups between them (reduction in electrical potential at micelle surface). Ion–dipole interactions between surfactant head groups and solute hydroxyl groups also help stabilize micelles and reduce the CMC. At a given unsolubilized solute concentration (c_A), DCP has a higher K value and so, higher X_A [Eq. (1)], so the greater effect of DCP than MCP on CMC



- - - $[\mathrm{CPC}]_{\mathrm{monomer}}$ in the CPC/PSS mixture (50 mM PSS) at zero solute concentration

Figure 19. CPC concentration in the permeate vs. MCP concentration in the retentate. Initial [CPC] to [PSS] are 25 mM to 0 mM (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3).



- - - - $[\mathrm{CPC}]_{\mathrm{monomer}}$ in the CPC/PSS mixture (50 mM PSS) at zero solute concentration

Figure 20. CPC concentration in the permeate vs. DCP concentration in the retentate. Initial [CPC] to [PSS] are 25 mM to 0 mM (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3). Curve is CPC monomer concentration in retentate (from surface tension data) for no added PSS.

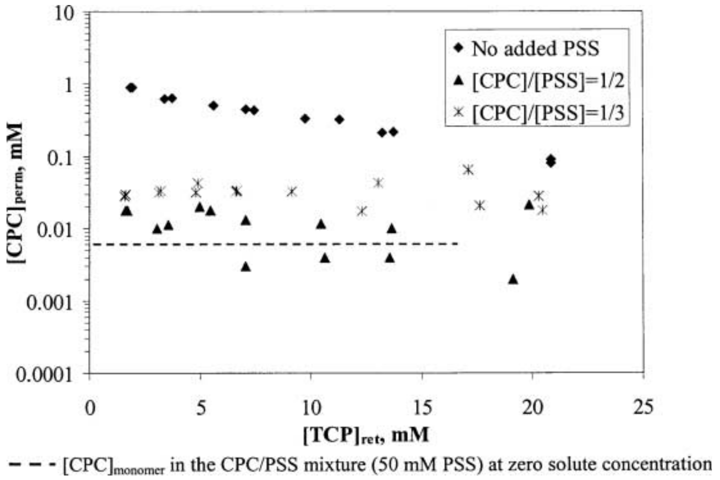


Figure 21. CPC concentration in the permeate vs. TCP concentration in the retentate. Initial [CPC] to [PSS] are 25 mM to 0 mM (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3).

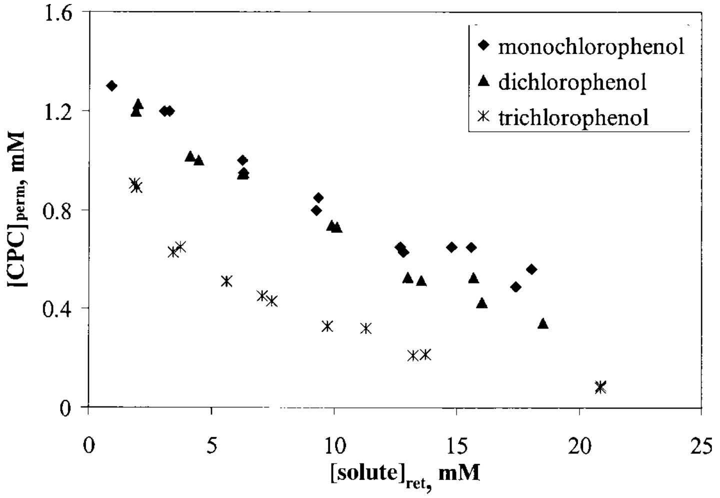


Figure 22. CPC concentration in the permeate vs. solute concentration in the retentate. Initial [CPC] is 25 mM (no added PSS).

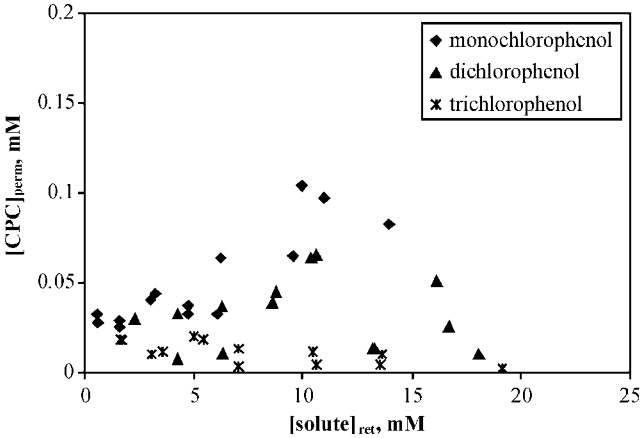


Figure 23. CPC concentration in the permeate vs. solute concentration in the retentate. Initial [CPC] to [PSS] is 25 mM to 50 mM.

depression, shown in Fig. 26, at a given unsolubilized solute concentration is expected.

When the surfactant concentration is at the CMC, all of solute in solution is unsolubilized and the monomer concentration equals the CMC. When the total surfactant concentration is above the CMC and some of the solute is

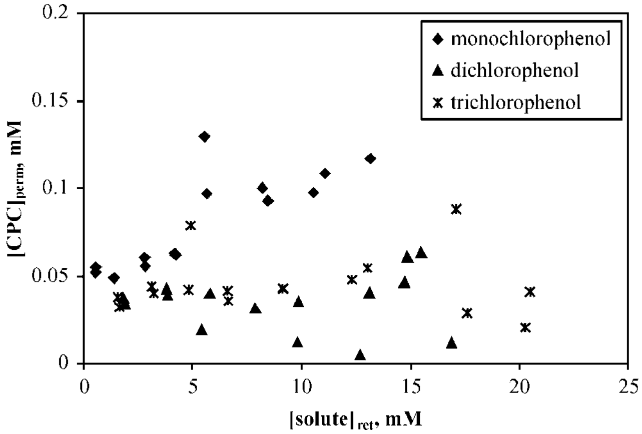


Figure 24. CPC concentration in the permeate vs. solute concentration in the retentate. Initial [CPC] to [PSS] is 25 mM to 75 mM.

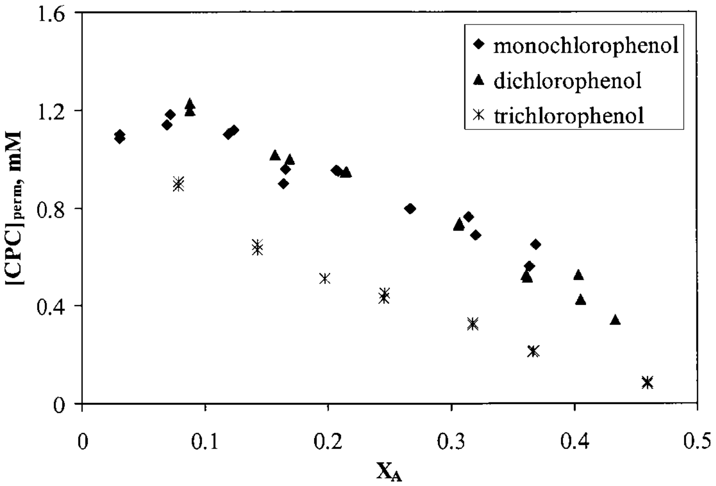


Figure 25. CPC concentration in the permeate vs. mole fraction of the solute in the micelle. Initial [CPC] is 25 mM (no added PSS).

solubilized, the surfactant monomer concentration is equal to the CMC at a solute concentration (from Fig. 26), which is equal to the unsolubilized solute concentration (c_A) in the retentate solution, not the total solute concentration in the retentate. Therefore, when permeate surfactant concentrations are compared to that of the monomer in the retentate (for PSS-free systems), it is

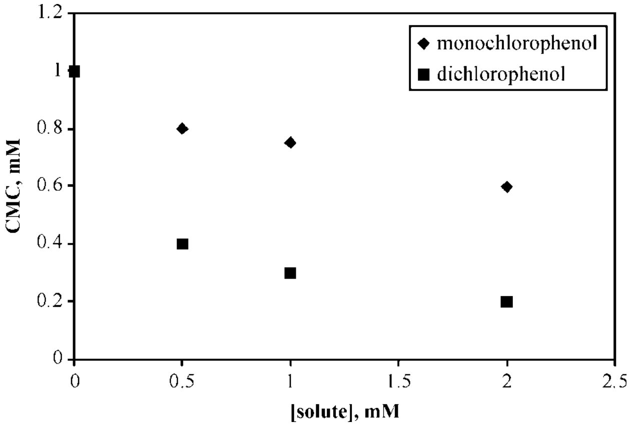


Figure 26. CMC value of CPC vs. solute concentration.

this CMC that is used to estimate the equilibrium monomer concentration. The retentate monomer concentration [deduced from its CMC values (Fig. 26) at a given unsolubilized solute concentration] is shown as an additional curve in Figs. 19 and 20 for MCP and DCP, respectively.

As shown in Figs. 19 and 20, for MEUF, the surfactant leakage (CPC concentration in permeate) for MCP and DCP is approximately 20% higher than its CMC values. In the micellar systems studied here, it is observed that the equilibrium $[CPC]_{ret}$ is approximately 5% different from initial $[CPC]_{ret}$. Therefore, the assumption that solubilization is insignificant in the permeate is justified. At a given solute concentration, the surfactant leakage is in the order of TCP $<$ DCP $<$ MCP. This effect is due to the increased solubilization and decreased monomer concentration with increasing hydrophobicity of the solute (Figs. 16 and 26). In Fig. 25, the surfactant leakage is shown as a function of X_A and, in general, minimum surfactant leakage is seen for TCP, followed by DCP, then MCP. This indicates that at a given degree of solubilization (X_A), the greater reduction of head group repulsion for the more hydrophobic solute results in a slightly lower surfactant monomer concentration in the retentate and lower surfactant leakage. However, it is the dramatic effect of solute structure on K (Fig. 16) that is the main cause of degree of chlorination of the solute on surfactant leakage.

As shown in Figs. 19 through 21, the surfactant leakage in MEUF systems relative to that in PE-MEUF systems ($[CPC]_{perm,MEUF}/[CPC]_{perm,PE\text{-}MEUF}$), decreases with increasing retentate solute concentration; the ratio ranges from 4 to 46.7 for MCP, 5.5 to 86.7 for DCP, and 2.5 to 120 for TCP. In other words, in the PE-MEUF systems, the surfactant leakage increases with increasing solute concentration in the retentate. This effect is presumably due to further solubilization of the solute reducing surfactant–polymer interaction or stabilization, resulting in an increase in surfactant monomer concentration. An increased PSS concentration (or increased colloid concentration) slightly enhances the surfactant leakage; as is obvious in the system studied with TCP. This is probably due to an increased ionic strength, resulting in an increase in the critical aggregate concentration,[48] thus an increase in surfactant monomer concentration in the retentate.

Comparing the surfactant leakage to that at equilibrium, as seen in Fig. 10, at a [PSS] of 50 mM, surface tension reaches the plateau region at point c, which approximately corresponds to a [CPC] of 0.006 mM. An increase in [CPC] up to point d in Fig. 11 does not significantly change the unaggregated surfactant concentration because the additional surfactant forms aggregates with the polymer. As a result, at a given [PSS], surfactant monomer concentration can be estimated from the surfactant concentration at point c, which is approximately 0.006 mM for 50 mM PSS concentration. However, there is no organic solute present in this case. In the presence of solute, the solubilization of solute in the surfactant–polymer aggregates can increase the surfactant leakage, as just discussed. The extent of the surfactant leakage, in the presence of 50 mM PSS, increases from about 0.05 to 0.13 mM for MCP, 0.01 to 0.1 mM for MCP, and 0.005 to 0.02 mM for TCP mM with increasing retentate solute concentration. The lower range of this surfactant leakage (when the solute is infinitely dilute) is relatively close to the monomeric CPC concentration at equilibrium from Fig. 10. Therefore, the permeate surfactant concentrations can be approximated by the equilibrium surfactant monomer concentration in the retentate for both MEUF and PE-MEUF. However, it is important to note that the cac cannot be correctly interpreted as the concentration of free surfactant at the onset of surfactant–polymer aggregate formation since a fraction of the surfactant molecules would be bound to the polyions when the cac is attained.

As shown in Figs. 23 and 24, maximum surfactant leakage is observed for MCP, compared to DCP and TCP. In the absence of PSS, the higher degree of chlorination causes greater CMC depression, as shown in Fig. 26. Although the CMC values in the presence of TCP are not available, we presume that TCP would cause even greater depression at a given solute concentration. Like the polymer-free system, it is reasonable to expect the same qualitative effect of the type of solute on the surfactant–polymer systems (see Fig. 23); for example, MCP shows greater surfactant leakage than DCP and TCP.

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