Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Colloid-Enhanced Ultrafiltration of Chlorophenols in Wastewater: Part III. Effect of Added Salt on Solubilization in Surfactant Solutions and Surfactant-Polymer Mixtures

Napaporn Komesvarakul[a]; John F. Scamehorn[a]; Richard W. Taylor[b]
[a] Institute for Applied Surfactant Research and School of Chemical, Biological, and Materials Engineering, University of Oklahoma, Norman, Oklahoma, USA [b] Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma, USA

To cite this Article Komesvarakul, Napaporn , Scamehorn, John F. and Taylor, Richard W.(2004) 'Colloid-Enhanced Ultrafiltration of Chlorophenols in Wastewater: Part III. Effect of Added Salt on Solubilization in Surfactant Solutions and Surfactant-Polymer Mixtures', Separation Science and Technology, 39: 14, 3193 — 3214
To link to this Article: DOI: 10.1081/SS-200033166
URL: http://dx.doi.org/10.1081/SS-200033166

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 14, pp. 3193–3214, 2004

Colloid-Enhanced Ultrafiltration of Chlorophenols in Wastewater: Part III. Effect of Added Salt on Solubilization in Surfactant Solutions and Surfactant–Polymer Mixtures

Napaporn Komesvarakul,[1] **John F. Scamehorn,**[1,*]
and Richard W. Taylor[2]

[1]Institute for Applied Surfactant Research and School of Chemical,
Biological and Materials Engineering and [2]Department of Chemistry and
Biochemistry, University of Oklahoma, Norman, Oklahoma, USA

ABSTRACT

The solubilization of three phenolic solutes in micellar solutions and surfactant–polymer mixtures is studied: 2-monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP). The equilibrium dialysis (ED) technique is used to determine the solubilization equilibrium constant as a function of added NaCl concentration. The added salt enhances the solubilization ability of surfactant micelles, but

---

*Correspondence: John F. Scamehorn, Institute for Applied Surfactant Research and School of Chemical, Biological, and Materials Engineering, University of Oklahoma, Norman, OK 73019, USA; E-mail: scamehor@ou.edu.

DOI: 10.1081/SS-200033166
0149-6395 (Print); 1520-5754 (Online)
www.dekker.com

it only slightly affects the solubilization constant of surfactant–polymer aggregates. The solubilization constant for the surfactant–only systems is greater than that for the surfactant–polymer systems. In the micellar solution, the solute with a low water solubility shows a greater solubilization constant than the solute with a higher water solubility; the solubilization constants increase in the order MCP $<$ DCP $<$ TCP. However, in the surfactant–polymer mixtures, the solubilization constant of DCP can exceed that of TCP due to two opposing effects: ion-dipole interaction, and water solubility or hydrophobicity. Understanding and quantifying this solubilization phenomenon is crucial to optimization of the performance of colloid-enhanced ultrafiltration separation processes.

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

INTRODUCTION

Colloid-enhanced ultrafiltration (CEUF) is the class of separation methods which can be used to remove dissolved organic solutes and/or inorganic ionic species from water.[1–16] In micellar-enhanced ultrafiltration (MEUF), 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 as the colloid solution. Organic solutes solubilize in the micelles or surfactant–polymer complexes and charged solutes (e.g., heavy metal) 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. Chlorinated phenolics are important pollutants in wastewater from the pulp and paper industry,[17] so their removal is investigated in this study.

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.[18] Most of surfactants studied for use in MEUF are roughly spherical; however, surfactant configurations depend on such factors as surfactant concentration and salinity. For example, rod-like micelles for cetylpyridinium chloride (CPC) can occur at 0.3 M CPC.[19] Aqueous polymer-surfactant mixtures are of much interest from both fundamental and technological viewpoints. They are encountered in several industrial applications such as pharmaceuticals, personal care product formulations, enhanced oil recovery, and detergency. Surfactant binding to polymers in aqueous solution has been investigated extensively.[20–32] The overall picture for interaction in surfactant–polymer systems is that when the surfactant concentration exceeds a critical aggregation concentration (cac), surfactant bound to polymer begins to form micelle-like aggregates. Increasing surfactant concentration leads to increasing surfactant–polymer binding, until the polymer becomes saturated. This occurs at a surfactant concentration which is called c_{sat}. Free micelles do not appear until the unbound surfactant concentration reaches the CMC of the surfactant.[27]

In the presence of polymer, the surfactant is induced to form a micelle-like aggregate with a hydrophobic region in which solubilized organic can reside. The binding of ionic surfactants to polymer is a cooperative process due to strong electrostatic and hydrophobic interactions. As a result, forming micelle-like organized structures occurs even at concentrations more than 1 order of magnitude lower than the CMC of the surfactant.[28–31] The surfactant–polymer complex has been described as “micelles on a string” or “beads on a necklace” in which the polymer chain connects micelle-like surfactant aggregates by wrapping around them.[21,25,26,32] A few studies have been done to compare the solubilization ability of surfactant micelles and surfactant–polymer complexes,[15,16,27,33,34] primarily for phenolic solutes. It was found that ordinary micelles can solubilize an organic solute more efficiently than the surfactant–polymer complexes. This behavior may be attributed to a reduction in absolute value of the electrical potential at the surface of surfactant aggregates due to neutralization by the oppositely charged polymer.

The total amount of solubilization in different surfactant–polymer systems have been measured over the past few decades.[15,16,33–38] Ikeda and Maruyama defined the (macroscopic) solubilization power as the number of molecules solubilized per molecule of micellized surfactant.[38] The (microscopic) solubilization capacity is defined as the average number of molecules solubilized in a single micelle at saturation. However, we use the more commonly utilized solubilization constant (K_A) which is expressed as mole fraction of solubilized solute into micelles (X_A) divided by unsolubilized solute concentration (c).[15,16,33,34] Solubilization in micelles has been widely studied[39] whereas solubilization into surfactant–polymer complexes has received much less attention. In surfactant–polymer complexes, for surfactant concentrations between cac and c_{sat}, all solubilization occurs in polymer-bound aggregates, while at concentrations where the unbound surfactant concentration reaches the CMC, both polymer-bound aggregates and free micelles participate in solubilization.[27]

Organic solutes can solubilize at different locations in the micelle.[40] Polar solutes solubilize at the micellar surface or the palisade region whereas aliphatic hydrocarbons, such as hexane, solubilize primarily within the hydrocarbon core region of the micelles.[40,41] Because chlorine atoms are 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.[40] The solubilization ability of surfactant micelles and surfactant–polymer aggregates greatly depends on the solute characteristics such as hydrophobicity, water solubility and polarity. Ionizable solutes with a higher acidity (lower dissociation constant or pK_a) and lower water solubility can be solubilized more effectively than solutes with a low acidity and high water solubility, primarily with cationic surfactants[15,34,40,42,43].

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.[2,4–6] Therefore, equilibrium solubilization measurements obtained from semiequilibrium dialysis or SED[29–34] can be used to determine the process efficiency. Dialysis methods have been used to measure solubilization of organic solutes in surfactant micelles and surfactant–polymer mixtures.[15] In dialysis experiments with a surfactant–only system, the surfactant concentration in the permeate generally increases to the same concentration as the monomer in the retentate in about 18 hours. Then, the permeate surfactant concentration slowly increases as micelles form in the permeate. Because 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 equilibrium), or correction factors need to be applied to account for micellar solubilization in the permeate. As a result, the dialysis experiments in MEUF, where no polymer is present, are then called “semiequilibrium dialysis or SED” experiments. However, in polymer-surfactant systems, the surfactant concentration in the permeate is lower than the CMC of the surfactant under the conditions studied,[44] so there are no micelle. Analysis of the permeate shows that the polymer concentration in the permeate is less than 1% of that in the initial retentate; therefore, the solubilization of the solute by the surfactant–polymer aggregates is insignificant due to the small concentrations of surfactant and polymer. From these reasons, the dialysis experiments in PE-MEUF are called equilibrium dialysis (ED). As seen in previous work,[15] the concentration of the solute present in the permeate is much lower than that in the retentate; therefore, the presence of micelles in the permeate does not significantly influence the measured solubilization constant.

In surfactant–polymer systems, two driving forces may influence the solubilization constant of neutral species solutes that have high hydrophobicity or low water solubility such as dichlorophenol (DCP) and trichlorophenol (TCP): ion-dipole interaction and hydrophobicity or water solubility. It was found that the ion-dipole interaction is dominant at low solute loading. Therefore, the surfactant–polymer aggregates can solubilize DCP more strongly than TCP[15] due to the greater dipole moment of DCP than TCP.[45] At high solute concentration, the water solubility of solutes plays a more important role than the ion-dipole interaction; thus TCP has a higher solubilization constant than DCP.[15]

For ionizable polar organic solutes such as chlorophenols; pH influences solute charge. When the pH is much higher than the apparent pK_a of the solute, the phenolate anion predominantly exists in solution. It was found that the partition coefficient of the phenolate anion in a cationic surfactant micelle is higher than that of the neutral species because the interaction between the cationic surfactant head groups and the oppositely charged solute enhances the partition coefficients[46–49]. In contrast, the solubilization constant of the neutral species in surfactant–polymer aggregates is higher than that of the phenolate anion.[49]

The effect of added simple salt on micellar growth has been investigated by several research groups.[20,50–55] The large impact of salt concentration on micellar size is commonly known; the micellar size increases as salt concentration increases. It was also found that the addition of salt increases the solubilizing power of surfactants,[56,57] increases the surfactant aggregation number, and reduces the CMC.[27] In surfactant–polymer complexes, the added salt generally affects the surfactant binding to the polymer. An increase in the ionic strength of the solution shifts the onset of binding toward higher free surfactant concentrations and decreases the amount of bound surfactant.[20] These observations can be related to the screening influence of the simple salt, which acts to diminish the electrostatic interactions between surfactant cations and polyanions.[21,23] Kim et al. found that at a given ionic strength, the aggregation number of a polymer-bound aggregate is approximately 50–60% smaller than that of a free micelle, while its solubilization ability is within approximately 20% of a free micelle.[27]

To put this third paper in a series of five papers in perspective, in Part I, we compared the effectiveness of MEUF and PE-MEUF systems.[15] The effect of pH on solubilization of TCP was studied in Part II,[49] while the effect of added salt on solubilization of MCP (2-monochlorophenol), DCP, and TCP is discussed in this paper, Part III, in both surfactant micelles and surfactant–polymer complexes. In Part IV, the effect of added salt on surfactant leakage in MEUF and PE-MEUF is discussed.[44] In Part V, the ability of PE-MEUF to simultaneously remove DCP and magnesium from water is demonstrated,[58] and the flux behavior of PE-MEUF is shown as a function of salinity in a stirred cell ultrafiltration device. This series of papers allows prediction of the separation efficiency of both MEUF and PE-MEUF for three chlorinated phenolics, permitting comparison of the efficiency of the two techniques, and optimization of the separation processes for this paper industry application. Insight into the physical chemistry of solubilization into surfactant–polymer complexes is also gained, a phenomena about which little is published and compared to the better-known solubilization into micelles.

EXPERIMENTAL

A detailed description of the materials and methods used here is given in the first part in this series.[15] Briefly, the surfactant and the polymer used in this work were cetylpyridinium chloride or CPC and sodium poly(styrenesulfonate) or PSS. The repeating unit of the polymer is $CH_2CH(C_6H_4)SO_3Na$. Organic solutes with various degrees of chlorination studied here are 2-monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP). Sodium chloride (certified A.C.S.) from Fisher Scientific (Fair Lawn, NJ) is used as an added salt.

For the semiequilibrium dialysis experiments, in brief, 10,000 Da molecular weight cut-off (MWCO) regenerated cellulose membranes 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 mixture in the presence of salt was placed in the retentate compartment. A salt solution at a concentration identical to the salt concentration in the retentate was placed in the permeate compartment. The cells reached equilibrium within 24 hr at 25°C ± 0.1°C. Concentrations of the chlorophenols and CPC in the permeate were determined with a Hewlett–Packard HP 8452A diode array spectrometer. The concentrations of the chlorophenols and CPC remaining in the retentate at equilibrium were inferred by subtracting the loss of the species into permeate from the feed concentration using the analytical concentrations of these species in the permeate and volume changes due to osmotic pressure effects.

RESULTS AND DISCUSSION

Effect of Added Salt on Solubilization Constant

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

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

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

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. The values of C_A^{agg} and C_{CPC}^{agg} are obtained from the material balance equations

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

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

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.

Most solubilization experiments were done without pH adjustment unless it is mentioned otherwise (i.e., Figs. 3 and 5); though the pH of the initial and final retentate solutions was recorded also, as shown in Part II of this series.[49] This lack of exact control of final pH was dictated by degradation of CPC when base is added to the solution to control pH. Some experiments were carried out at pH 3 to make a comparison of the solubilization constants of TCP between two different systems, one of which is the system containing a mixture of neutral species and charged species (system without pH adjustment) and the other is the system predominantly containing only neutral species (system at pH 3) except the micellar system in the absence of salt which contains 11% phenolate anion.[49]

As shown in Figs. 1–6, the solubilization equilibrium constants (K_A) obtained by SED experiments for MCP, DCP, and TCP are plotted as a function of intramicellar mole fraction (X_A) of the solutes in CPC micelles and CPC-PSS complexes at different salinities. The pH range in the final retentate solutions is shown in parenthesis in the figures. In Figs. 1 and 2, it can be seen that the solubilization constants for MCP and DCP in CPC micelles in the presence of salt is higher than that in the absence of salt; the results for TCP are similar to the results for MCP and DCP. This behavior is also seen in the system at pH 3 for TCP (Fig. 3). In the presence of 50 mM PSS, the added salt does not significantly affect the solubilization ability of CPC-PSS complexes for MCP, as shown in Fig. 4, and for DCP (not shown here). However, K_{TCP} increases with increasing salinity for the system without pH adjustment in Fig. 5 and for the system at pH 3 in Fig. 6. The detailed results that are not shown in this paper are available in a dissertation.[59]

It is well known that micellar growth occurs as the electrolyte concentration increases.[52–55] This is attributed to the fact that the initial added salt reduces the electrostatic repulsion between surfactant head groups, and

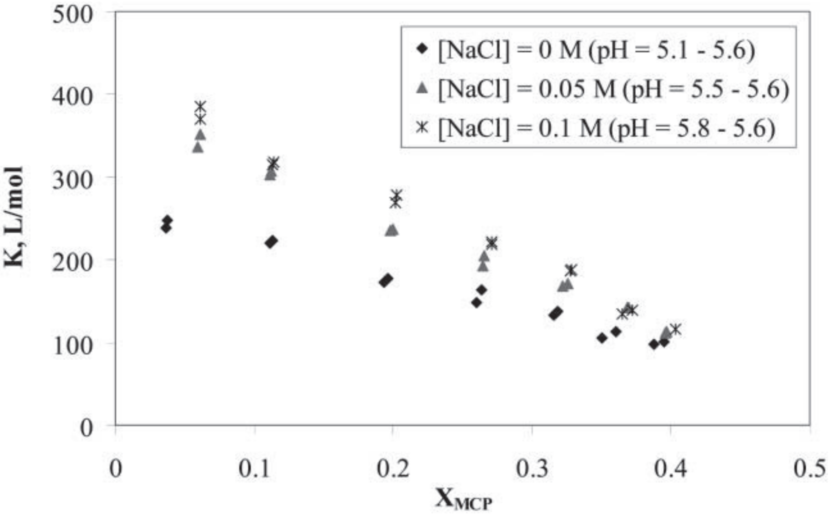

Figure 1. Solubilization equilibrium constant of MCP vs. mole fraction of MCP at different NaCl concentrations in CPC micelles. Initial [CPC] is 25 mM.

therefore increases the micellar size and the surfactant aggregation number. The increase in the micellar size could cause the increase in the solubilization ability of the micelle as salt concentration increases, as seen in Figs. 1 and 2. However, the further addition of salt may not significantly change the micellar

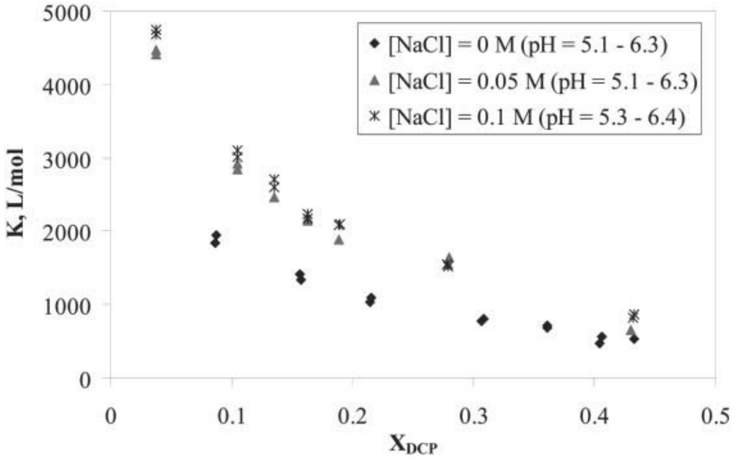

Figure 2. Solubilization equilibrium constant of DCP vs. mole fraction of DCP at different NaCl concentrations in CPC micelles. Initial [CPC] is 25 mM.

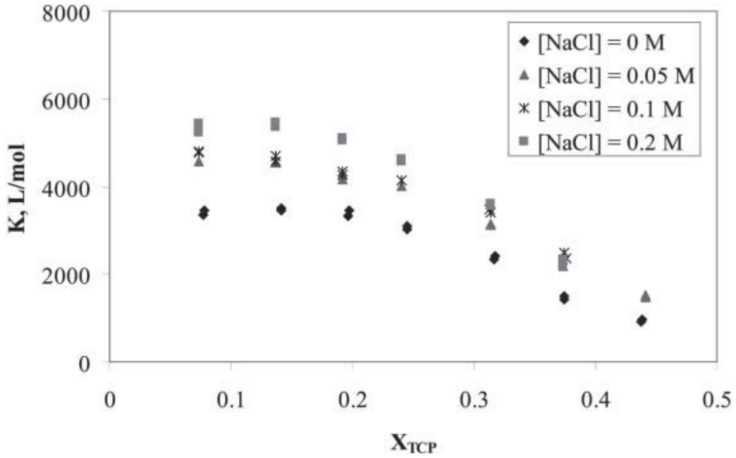

Figure 3. Solubilization equilibrium constant of TCP vs. mole fraction of TCP at different NaCl concentrations in CPC micelles at pH of 3. Initial [CPC] is 25 mM.

size, resulting in only a slight or negligible increase in the solubilization constant when the salt concentration is increased from 0.05 M to 0.1 M, primarily for DCP. The increase in the solubilization constant also may be due, in part, to a salting-out effect which causes a reduction in water solubility of the organic solutes in the aqueous solution,[53] and therefore enhances the

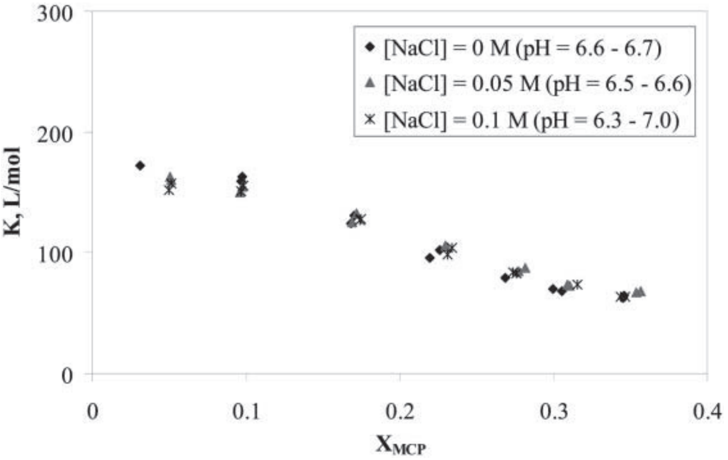

Figure 4. Solubilization equilibrium constant of MCP vs. mole fraction of MCP at different NaCl concentrations in CPC-PSS complexes. Initial [CPC] to [PSS] is 25 to 50 mM.

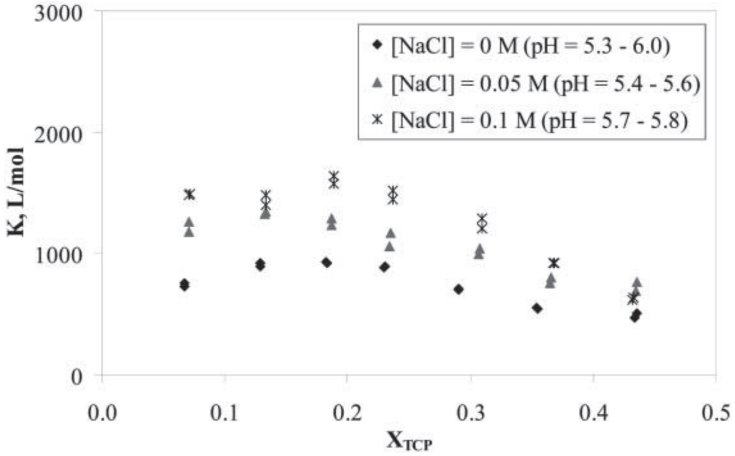

Figure 5. Solubilization equilibrium constant of TCP vs. mole fraction of TCP at different NaCl concentrations in CPC-PSS complexes. Initial [CPC] to [PSS] is 25 to 50 mM.

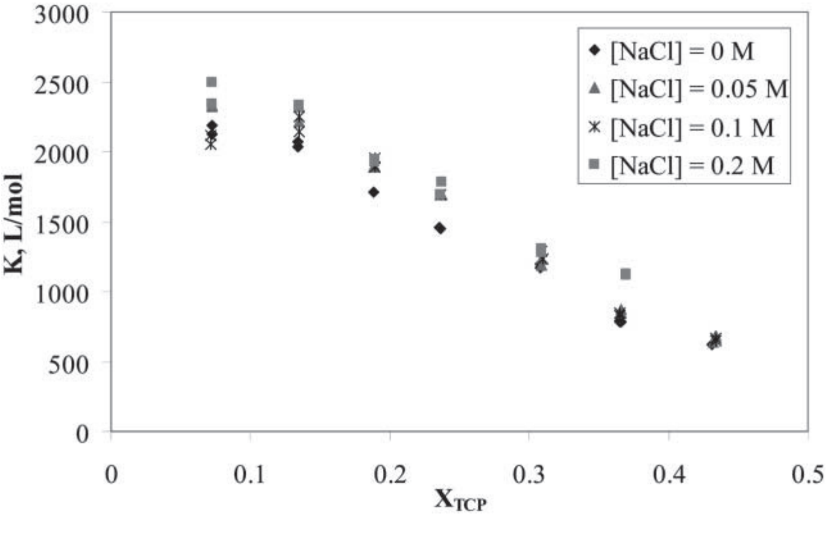

Figure 6. Solubilization equilibrium constant of TCP vs. mole fraction of TCP at different NaCl concentrations in CPC-PSS complexes at pH of 3. [CPC] to [PSS] is 25 to 50 mM.

solubilization of the solute into the CPC micelle. In addition to the effect of added salt, a synergistic effect of organic solute on the micellar growth has been observed.[53,55]

In the surfactant–polymer mixtures, it is commonly known that the size and the aggregation number of surfactant–polymer aggregates are smaller than those of ordinary micelles.[22,28,60] Kogej and coworkers reported the characteristic size of the ordered element ($\bar{a}$) of CPC-PSS;[32] the $\bar{a}$ value is the center-to-center distance between micelles consecutively bound to the polyion, which comprises one micellar diameter and the thickness of the polymer chain wrapped around it. They found that the $\bar{a}$ value is approximately 35.2–38.0 Å which is less than the largest possible extension of two C_{16} hydrocarbon chains incorporated in a liquid hydrocarbon-like environment which would be 43.5 Å.[61] Hansson and Almgren found that the aggregation numbers of surfactant–polymer aggregates are not significantly affected by the presence of salt.[22] This suggests that the aggregate size may not be drastically influenced by the added salt, which may explain that the solubilization ability of the surfactant–polymer aggregates is not dramatically affected by the added salt for MCP, DCP, and TCP at pH 3. It should also be noted that there are only negligible concentrations of charged species present for MCP, DCP and TCP at pH 3. Another possible reason is that the counterions present in the surfactant–polymer mixtures, at a relatively higher concentration than in the surfactant solutions, have already diminished the electrostatic repulsion between surfactant head groups. Therefore, additional salt may no longer affect the electrostatic repulsion, and consequently the size or the aggregation number of the surfactant–polymer aggregates. In addition, the polymer-bound micelles are partly neutralized by the polyanion and have therefore lower charge density than the corresponding free micelles.

In the surfactant–polymer system, the increase in the solubilization constant for TCP as the salt concentration increases in the system without pH adjustment, as shown by Fig. 5, is somewhat difficult to understand. We speculate that the presence of the phenolate anion could be a reason for such phenomena. Although the presence of the phenolate species can be negligible, the values of phenolate anion fraction were obtained at a low solute concentration of 0.2 or 0.3 mM in some cases.[49] Unfortunately, the fraction of the phenolate anion at solute concentrations greater than 0.3 mM is not measurable due to the high absorbance (≥ 1.0) at these higher solute concentrations. The presence of the phenolate anion, where the fraction can be different at higher solute concentrations, influences the solubilization of TCP by the surfactant–polymer complexes. In the previous work, it was observed a slight shift of the apparent pK_a of TCP in CPC solution as the solute concentration increases from 0.2 to 0.3 mM.[15] It should be noted that the effect of the solute concentration on the apparent pK_a in CPC-PSS mixture can not be measured due to the high absorbance.

Effect of Types of Colloid on Solubilization Constant

Figure 7 shows plots of the solubilization constant versus intramicellar mole fraction of MCP in CPC and CPC-PSS mixtures containing 0.05 M NaCl, illustrating the effect of the type of colloid. Similar results were obtained for DCP and TCP and are not shown here.[59] It is observed that the solubilization constant in the micellar solution monotonically decreases as the solute concentration increases and is higher than the solubilization constant of surfactant–polymer aggregates. This behavior was also seen in a system without salt.[15] The increase in polymer concentration from 50 to 75 mM does not significantly influence the solubilization constant in the surfactant–polymer system. Results for the system with 0.1 M NaCl (not shown) are approximately the same as the system with 0.05 M NaCl.[59]

The solubilization of polar solutes in neutral form generally occurs at the micellar surface and palisade region with significant ion–dipole

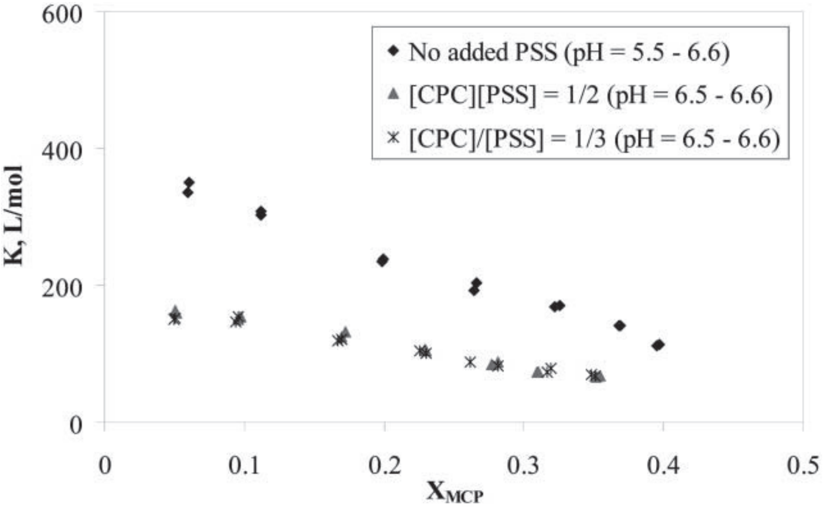

Figure 7. Solubilization equilibrium constant of MCP vs. mole fraction of MCP in different types of colloids. Initial [CPC] to [PSS] are 25 to 0 mM (no added PSS), 25 to 50 mM (mole ratio 1 : 2), and 25 to 75 mM (mole ratio 1 : 3). Initial [NaCl] is 0.05 mM.

interaction.[40,62] The solubilization behavior has been observed to obey the Langmuir adsorption isotherm. This suggests that the adsorption initially occurs at the micellar surface. The adsorption or the solubilization of the solutes decreases once all active site are occupied as solute concentration increases as seen in the Fig. 7. This type of behavior was also observed in previous work.[15,34,40,43] The reduction of the solubilization constant in the presence of polymer may be attributed to the decrease in the charge density at the micellar surface due to partial neutralization of the cationic surfactant by the anionic polymer. In addition, as noted previously, the size of surfactant–polymer aggregate is smaller than the size of the ordinary micelle. As a result, the volume in the palisade layer is reduced, causing steric hindrance for penetration of the hydroxyl groups, therefore decreasing the solubilization constant.

Effect of Types of Solute on Solubilization Constant

The data is replotted in Figs. 8–13 to illustrate the effect of type of solute on the solubilization constant of the surfactant micelle and the surfactant–polymer aggregates in the presence of 0.05 and 0.1 M NaCl. In the micellar solutions at both salt concentrations, the solubilization constant of the solutes increases in the order MCP < DCP < TCP, as shown in Figs. 8 and 9. In the surfactant–polymer mixtures at 50 mM PSS, the relative order of

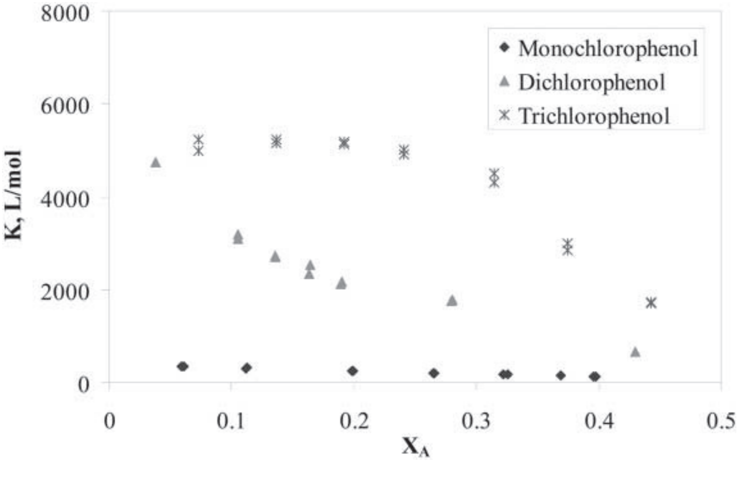

Figure 8. Solubilization equilibrium constant vs. mole fraction for different solutes in CPC micelle. Initial [CPC] is 25 mM. Initial [NaCl] is 0.05 M.

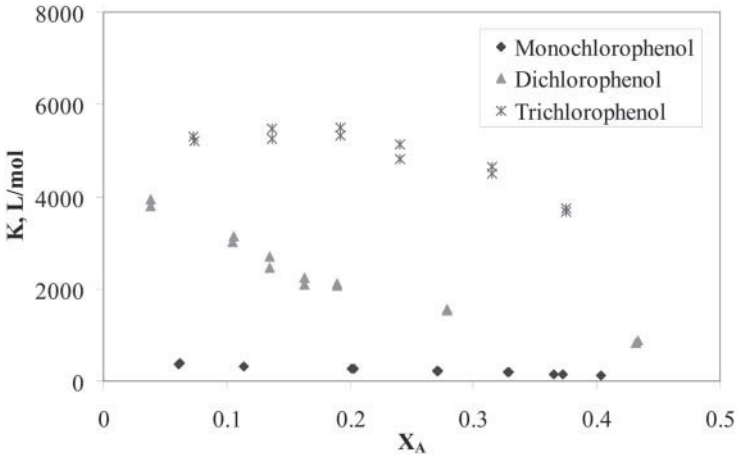

Figure 9. Solubilization equilibrium constant vs. mole fraction for different solutes in CPC micelle. Initial [CPC] is 25 mM. Initial [NaCl] is 0.1 M.

the solubilization constant of DCP and TCP is reversed at low solute concentration for both salt concentrations, as shown in Figs. 10 and 11. The solubilization of DCP is higher than that of TCP at low solute loading whereas the opposite trend is observed at high solute loading as seen by the intersection between the solubilization isotherm for DCP and TCP. In the presence of

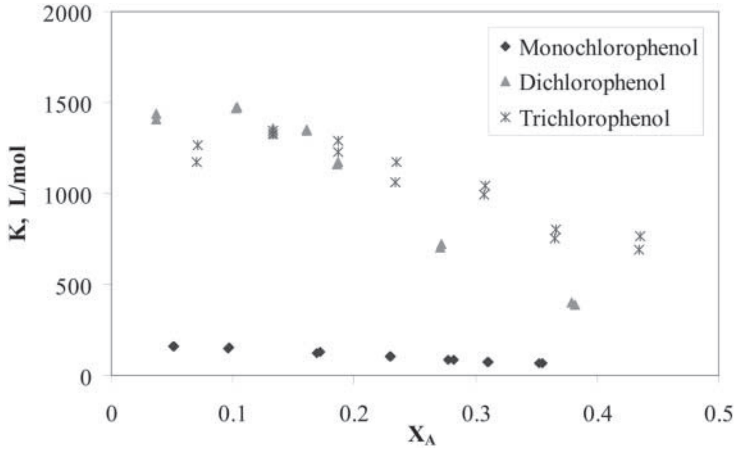

Figure 10. Solubilization equilibrium constant vs. mole fraction for different solutes in CPC/PSS complexes. Initial [CPC] to [PSS] is 25 to 50 mM. Initial [NaCl] is 0.05 M.

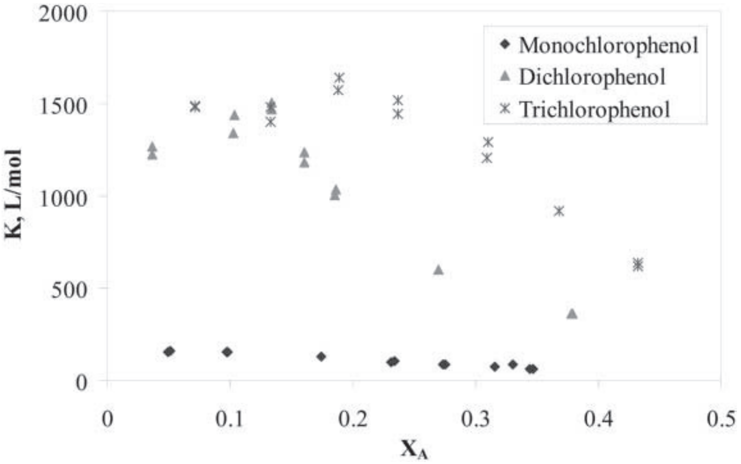

Figure 11. Solubilization equilibrium constant vs. mole fraction for different solutes in CPC/PSS complexes. Initial [CPC] to [PSS] is 25 to 50 mM. Initial [NaCl] is 0.1 M.

50 mM PSS, the intersection occurs at a lower solute loading when the salt concentration is 0.05 M NaCl (Fig. 10) than the case for 0.1 M NaCl (Fig. 11). At 75 mM PSS, the intersection no longer exists at 0.1 M NaCl (Figure 13); the solubilization of the solutes at 0.1 M NaCl follows the same order found in the micellar systems.

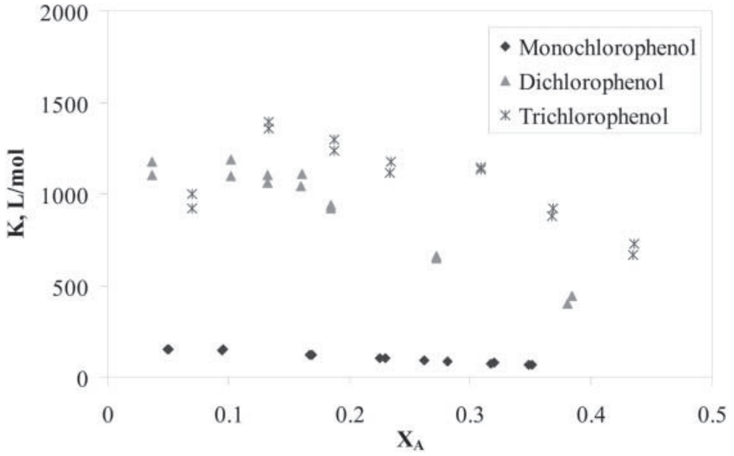

Figure 12. Solubilization equilibrium constant vs. mole fraction for different solutes in CPC/PSS complexes. Initial [CPC] to [PSS] is 25 to 75 mM. Initial [NaCl] is 0.05 M.

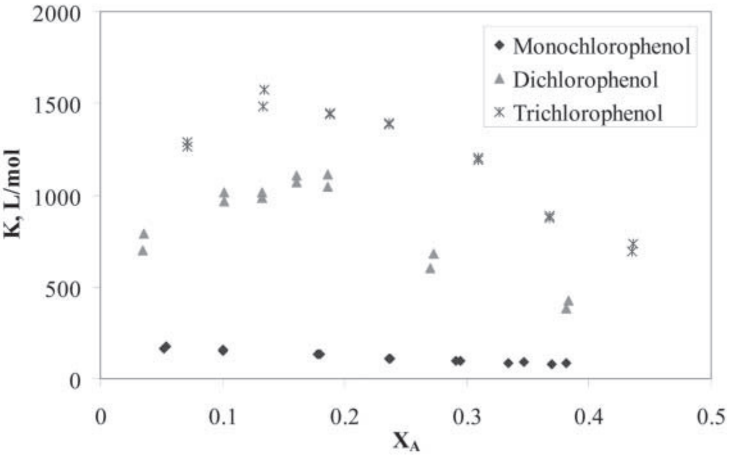

Figure 13. Solubilization equilibrium constant vs. mole fraction for different solutes in CPC/PSS complexes. Initial [CPC] to [PSS] is 25 to 75 mM. Initial [NaCl] is 0.1 M.

In general, the lower the water solubility, the greater the solubilization constant because the solute with low water solubility tends to partition into surfactant micelle more effectively than the solute with high water solubility. It should be noted that the water solubility increases in the order TCP $<$ DCP $<$ MCP.[63] As seen in Figs. 8 and 9, the values of K_A for the solutes in the micellar systems are in inverse order compared to their water solubility.

In the surfactant–polymer systems, the previous study showed that DCP and TCP were almost completely protonated under the conditions used here.[49] Therefore, ion-dipole interaction can affect the solubilization of the neutral solute in the surfactant aggregate. The dipole moments (μ) of MCP, DCP, and TCP are 2.93, 2.25, and 1.08 D, respectively,[45] which is the same as the order of water solubility and opposite to the order of the hydrophobicity of the solutes (e.g., TCP shows the greatest hydrophobicity and the lowest water solubility). As a result, the two opposing effects of ion–dipole interaction and water solubility for a given solute are present as also seen in previous work[15] for the system without salt. As salt concentration increases from 0.05 to 0.1 M, the effect of ion-dipole interaction on the solubilization constant may be diminished; therefore the intersection between the solubilization isotherm of DCP and TCP occurs at a lower solute concentration. Likewise, at the highest salt concentration (0.1 M), the ion-dipole interaction may be reduced as polymer concentration increases from 50 to 75 mM, resulting in the disappearance of the intersection point in Fig. 13 as compared to Fig. 11. In the presence of 75 mM PSS and 0.1 M NaCl, it is plausible that solubilization constant is predominantly affected by the water solubility or hydrophobicity (the ion–dipole interaction effect is diminished; therefore the order of the solubilization constants is the same as the order observed in the micellar solution. It should be noted that the solubilization of MCP is smallest (Figs. 8–13) over an entire range of concentration because of its lower hydrophobicity or higher water solubility, compared to DCP and TCP, although its dipole moment is the greatest.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Edwin E. Tucker for valuable discussions. We acknowledge the financial support of the TAPPI Foundation as well as the industrial sponsors of the Institute for Applied Surfactant Research at the University of Oklahoma including Akzo Nobel Chemicals, Albemarle, Church and Dwight, Clorox, Colgate-Palmolive, Dial, Dow, Halliburton Services, Huntsman, ICI Americas, Kerr-McGee, Lubrizol, Phillips Petroleum, Pilot Chemicals, Procter & Gamble, Reckitt Benckiser North America, Schlumberger Technology, Shell Chemical, and Unilever. Dr. Scamehorn holds the Asahi Glass Chair in Chemical Engineering at the University of Oklahoma.

REFERENCES

1. Harwell, J.H.; Scamehorn, J.F. Treatment of hazardous and toxic wastes using surfactant-based separations processes. In *Management of Hazardous and Toxic Wastes in the Process Industries*; Kolaczkowski, S.T., Crittenden, B.D., Eds.; Elsevier: London, 1987; 352–361.
2. Scamehorn, J.F.; Harwell, J.H. An overview of surfactant-based separation processes. In *Surfactant in Emerging Technologies*; Rosen, M.J., Ed.; Marcel Dekker: New York, 1987; 169–185.
3. Scamehorn, J.F.; Harwell, J.H. Surfactant-based treatment of aqueous process streams. In *Surfactant in Chemical/Process Engineering*; Wasan, D.T., Shah, D.O., Ginn, M.E., Eds.; Marcel Dekker: New York, 1988; 77–125.
4. Christian, S.D.; Scamehorn, J.F. Use of micellar-enhanced ultrafiltration to remove dissolved organics from aqueous streams. In *Surfactant-Based Separation Processes*; Scamehorn, J.F., Harwell, J.H., Eds.; Marcel Dekker: New York, 1989; 3–28.

5. Gibbs, L.L.; Scamehorn, J.F.; Christian, S.D. Removal of *n*-alcohols from aqueous streams using micellar-enhanced ultrafiltration. J. Membr. Sci. **1987**, *30* (1), 67–74.
6. Dunn, R.O.; Scamehorn, J.F.; Christian, S.D. Concentration polarization effects in the use of micellar-enhanced ultrafiltration to remove dissolved organic pollutants from wastewater. Sep. Sci. Technol. **1987**, *22* (2&3), 763–789.
7. Dunn, R.O.; Scamehorn, J.F.; Christian, S.D. Use of micellar-enhanced ultrafiltration to remove dissolved organics from aqueous streams. Sep. Sci. Technol. **1985**, *20* (4), 257–284.
8. Fillipi, B.R.; Brant, L.W.; Scamehorn, J.F.; Christian, S.D. Use of micellar-enhanced ultrafiltration at low surfactant concentrations and with anionic-nonionic surfactant mixtures. J. Colloid Interface Sci. **1999**, *213* (1), 68–80.
9. Dunn, R.O.; Scamehorn, J.F.; Christian, S.D. Simultaneous removal of dissolved organics and divalent metal cations from water using micellar-enhanced ultrafiltration. Colloids Surf. **1989**, *35* (1), 49–56.
10. Roberts, B.L.; Scamehorn, J.F.; Christian, S.D. Micellar-enhanced ultrafiltration in a spiral wound ultrafiltration module and comparison with stirred cell performance. In *Surfactant-Based Separations: Science and Technology*; Scamehorn, J.F., Harwell, J.H., Eds.; American Chemical Society: Washington DC, 2000; 158–174.
11. Tounissou, P.; Hebrant, M.; Rodehuser, L.; Tondre, C. Ultrafiltration of micellar solutions in the presence of electrolytes. J. Colloid Interface Sci. **1996**, *183* (2), 484–490.
12. Tounissou, P.; Hebrant, M.; Tondre, C. On the behavior of micellar solutions on tangential ultrafiltration using mineral membranes. J. Colloid Interface Sci. **1996**, *183* (2), 491–497.
13. Gelinas, S.; Weber, M.E. Micellar-enhanced ultrafiltration using a twin-head cationic surfactant. Sep. Sci. Technol. **1998**, *33* (9), 1241–1245.
14. Kandori, K.; Schechter, R.S. Selection of surfactants for micellar-enhanced ultrafiltration. Sep. Sci. Technol. **1990**, *25* (1&2), 83–108.
15. Komesvarakul, N.; Scamehorn, J.F.; Gecol, H. Purification of phenolic-laden wastewater from the pulp and paper industry by using colloid-enhanced ultrafiltration. Sep. Sci. Technol. **2003**, *38* (11), 2465–2501.
16. Uchiyama, H.; Christian, S.D.; Tucker, E.E.; Scamehorn, J.F. Solubilization and separation of *p*-tert-butylphenol using polymer/surfactant complexes in colloid-enhanced ultrafiltration. J. Colloid Interface Sci. **1994**, *163* (2), 493–499.
17. Canadian Environmental Protection Act. *Effluents from Pulp Mills Using Bleaching*, Priority Substances List Assessment Report 2, Minister of Supply and Services: Canada, 1991; 37.

18. Rosen, M.J. *Surfactants and Interfacial Phenomena*, 2nd Ed.; John Wiley & Sons: New York, 1988; 108–169.
19. Cappelaere, E.; Cressely, R. Influence of $NaClO_3$ on the rhelogical behavior of a micellar solution of CPCl. Rheol. Acta **2000**, *39* (4), 346–353.
20. Kogej, K.; Škerjanc, J. Surfactant binding to polymers. In *Physical Chemistry of Polymers*; Radeva, T., Ed.; Marcel Dekker: New York, 1999; Vol. 99; 793–827.
21. Hayakawa, K.; Kwak, J.C.T. Surfactant-polymer interactions. 1. Binding of dodecyltrimethylammonium ions by sodium dextran sulfate and sodium poly(styrenesulfonate) in aqueous solution in the presence of sodium chloride. J. Phys. Chem. **1982**, *86* (19), 3866–3870.
22. Hansson, P.; Almgren, M. Polymer-induced micelle formation of ionic surfactants and binary surfactant mixtures studied by time-resolved fluorescence quenching. J. Phys. Chem. **1995**, *99* (45), 16684–16693.
23. Malovikova, A.; Hayakawa, K.; Kwak, J.C.T. Surfactant–polymer interactions. 4. Surfactant chain length dependence of the binding of alkylpyridinium cations to dextran sulfate. J. Phys. Chem. **1984**, *88* (10), 1930–1933.
24. Goddard, E.D.; Leung, P.S. Interaction of cationic surfactants with a hydrophobically modified cationic cellulose polymer. Langmuir **1992**, *8* (5), 1499–1500.
25. Tokiwa, F.; Tsujii, K. Solubilization behavior of the surfactant-polyethylene glycol complex in relation to the degree of polymerization. Bull. Chem. Soc. Jpn. **1973**, *46* (9), 2684–2686.
26. Kiefer, J.J.; Somasundaran, P.; Ananthapadmanabhan, K.P. Interaction of tetradecyltrimethylammonium bromide with poly(acrylic acid) and poly(methacrylic acid). Effect of charge density. Langmuir **1993**, *9* (5), 1187–1192.
27. Kim, J.H.; Domach, M.M.; Tilton, R.D. Pyrene micropartitioning and solubilization by sodium dodecyl sulfate complexes with poly(ethylene glycol). J. Phys. Chem. B. **1999**, *103* (48), 10582–10590.
28. Okuzaki, H.; Osada, Y. Effect of hydrophobic interaction on the cooperative binding of a surfactant to a polymer network. Macromolecules **1994**, *27* (2), 502–506.
29. Okuzaki, H.; Osada, Y. Ordered-aggregate formation by surfactant-charged gel interaction. Macromolecules **1995**, *28* (1), 380–382.
30. Okuzaki, H.; Osada, Y. Role and effects of cross-linkage on the polyelectrolyte-surfactant interactions. Macromolecules **1995**, *28* (13), 4554–4557.
31. Hansson, P. Self-assembly of ionic surfactant in cross-linked polymer gel of opposite charge. A physical model for highly charged systems. Langmuir **1998**, *14* (9), 2269–2277.

32. Kogej, K.; Theunissen, E.; Reynaer, H. Formation of organized structure in systems containing alkylpyridinium surfactant and sodium poly(styrenesulfonate). Acta Chim. Slov. **2001**, *48* (3), 353–362.
33. Uchiyama, H.; Christian, S.D.; Tucker, E.E.; Scamehorn, J.F. Solubilization of trichloroethylene by polymer-surfactant complexes. AIChE J. **1994**, *40* (12), 1969–1975.
34. Lee, B.H.; Christian, S.D.; Tucker, E.E.; Scamehorn, J.F. Effect of an anionic polymer on the solubilization of mono- and dichlorophenols by aqueous solutions of *n*-hexadecylpyridinium chloride. Langmuir **1991**, *7* (7), 1332–1335.
35. Horin, S.; Arai, H.J. The effect of added salt on the interaction between polymer and detergent in aqueous solution. J. Colloid Interface Sci. **1970**, *32* (3), 547–550.
36. Abuin, E.B.; Scaiano, J.C. Exploratory study of the effect of polymer-surfactant aggregates on photochemical behavior. J. Am. Chem. Soc. **1984**, *106* (21), 6274–6283.
37. Sudbeck, E.A.; Dubin, P.L.; Curran, M.E.; Skelton, J. Dye solubilization in polymer-micelle complexes. J. Colloid Interface Sci. **1991**, *142* (2), 512–517.
38. Ikeda, S.; Maruyama, Y. Solubilization of a water-insoluble dye in aqueous sodium halide solutions of dodecylpyridinium halides: effects of counterion species of ionic micelles. J. Colloid Interface Sci. **1994**, *166* (1), 1–5.
39. Christian, S.D.; Scamehorn, J.F. *Solubilization in Surfactant Aggregates*; Surfactant Science Series 55, Marcel Dekker: New York; 1995.
40. Sepulveda, L.; Lissi, E.; Quina, F. Interactions of neutral molecules with ionic micelles. Adv. Colloid Interface Sci. **1986**, *25* (1), 1–57.
41. Tucker, E.E. Vapor pressure studies of solubilization. In *Solubilization in Surfactant Aggregates*; Christian, S.D., Scamehorn, J.F., Eds.; Marcel Dekker: New York, 1995; 429–453.
42. Sakulwongyai, S.; Trakultamupatam, P.; Scamehorn, J.F.; Osuwan, S.; Christian, S.D. Use of a surfactant coacervate phase to extract chlorinated aliphatic compounds from water: extraction of chlorinated ethanes and quantitative comparison to solubilization in micelles. Langmuir **2000**, *16* (22), 8226–8230.
43. Lee, B.H.; Christian, S.D.; Tucker, E.E.; Scamehorn, J.F. Solubilization of mono- and dichlorophenols by hexadecylpyridinium chloride micelles. Effects of substituent groups. Langmuir **1990**, *6* (1), 230–235.
44. Komesvarakul, N.; Scamehorn, J.F. Colloid-enhanced ultrafiltration of chlorophenols in wastewater: Part IV. Effect of added salt on surfactant leakage in surfactant solutions and surfactant-polymer mixtures. Sep. Sci. Technol. *in preparation*.

45. http://www.chemistrymag.org/cji/2001/037034pe.htm (accessed Jul 2001).
46. Westall, J.C. Influence of pH and ionic strength on the aqueous–nonaqueous distribution of chlorinated phenols. Environ. Sci. Technol. **1985**, *19* (2), 193–198.
47. Johnson, C.A.; Westall, J.C. Effect of pH and KCl concentration on the octanol–water distribution of methylanilines. Environ. Sci. Technol. **1990**, *24* (12), 1869–1875.
48. Bunton, C.A.; Sepulveda, L. Hydrophobic and coulombic interactions in the micellar binding of phenols and phenoxide ions. J. Phys. Chem. **1979**, *83* (6), 680–683.
49. Komesvarakul, N.; Scamehorn, J.F.; Taylor, R.W. 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. Sep. Sci. Technol. **2004**, *39* (14), 3169–3191.
50. Sommer, C.; Pederson, J.S.; Egelhaaf, S.U.; Cannavacciuolo, L.; Kohlbrecher, J.; Schurtenberger, P. Wormlike micelles as "equilibrium polymers": light and neutron scattering experiments. Langmuir **2002**, *18* (7), 2495–2505.
51. Magid, L.J.; Li, Z. Flexibility of elongated sodium dodecyl sulfate micelles in aqueous sodium chloride: a small-angle neutron scattering study. Langmuir **2000**, *16* (26), 10028–10036.
52. Mazer, N.A.; Benedek, G.B. An investigation of the micellar phase of sodium dodecyl sulfate in aqueous sodium chloride solutions using quasielastic light scattering spectroscopy. J. Phys. Chem. **1976**, *80* (10), 1075–1085.
53. Ud-Din, K.; Bansal, D.; Kumar, S. Synergistic effect of salts and organic additives on the micellar association of cetylpyridinium chloride Langmuir **1997**, *13* (19), 5071–5075.
54. Gilányi, T.; Varga, I. Aggregation number of ionic surfactants in complex with polymer via measurements of trace probe electrolyte. Langmuir **1998**, *14* (26), 7397–7402.
55. Kumar, S.; Naqvi, A.Z.; Ud-Din, K. Solubilization-site dependent micellar morphology: Effect of organic additives and quaternary ammonium bromides. Langmuir **2001**, *17* (16), 4787–4792.
56. Tucker, E.E.; Christian, S.D. Solubilization of benzene by aqueous sodium octylsulfate: effect of added sodium chloride. J. Colloid Interface Sci. **1985**, *104* (2), 562–568.
57. Mahmoud, F.Z.; Higazy, W.S.; Christian, S.D.; Tucker, E.E.; Taha, A.A. Solubilization of hydrocarbons by surfactant micelles and effect of added salt. J. Colloid Interface Sci. **1989**, *131* (1), 96–102.

58. Komesvarakul, N.; Scamehorn, J.F.; Nguyen, T.T.; Do, L.D.; Gecol, H. Colloid-enhanced ultrafiltration of chlorophenols in wastewater: Part V. simultaneous removal of a chlorophenol and a metal ion. Sep. Sci. Technol. *in preparation*.
59. Komesvarakul, N. The use of colloid-enhanced ultrafiltration to remove organic pollutants and metal ions from wastewater generated from the pulp and paper industry. University of Oklahoma: Norman, OK, 2003; Ph. D. Dissertation.
60. Brackman, J.C.; Engberts, J.B.F.N. Influence of polymers on the micellization of cetyltrimetylammonium salts. Langmuir **1991**, *7* (10), 2097–2102.
61. Tanford, C. Micelle shape and size. J. Phys. Chem. **1972**, *76* (21), 3020–3024.
62. Dougherty, S.J.; Berg, J.C. Distribution equilibria in micelle solutions. J. Colloid Interface Sci. **1974**, *48* (1), 110–121.
63. Lide, D.R. Ed. *CRC Handbook of Chemistry and Physics*, 81st Ed.; New York, 2000–2001; 8–91.

Received December 2003
Accepted July 2004