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

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

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Abstract: The critical aggregation concentration (cac) in surfactant–polymer mixtures approximates a lower limit to the surfactant concentration in the permeate (surfactant leakage) in polyelectrolyte micellar-enhanced ultrafiltration. Here, the cac was measured at different salinities by using surface tension measurements. It was found that the cac increases slightly with the addition of simple salt, then the cac value decreases at higher salt concentration. The critical micelle concentration (CMC), which approximates surfactant leakage in micellar systems (no polymer), decreases monotonically with increasing salinity for ionic surfactants. The surfactant leakage in colloid-enhanced ultrafiltration (CEUF) processes is investigated by using a dialysis method in the presence of three phenolic solutes with various degrees of chlorination: 2-monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP). Cetylpyridinium chloride (CPC) or *n*-hexadecylpyridinium chloride is used as a cationic surfactant; and sodium poly(styrenesulfonate) (PSS) is used as an anionic polyelectrolyte. The effect of salinity and type of colloid is focused on here. In the absence of added salt, the cac can be over an order of magnitude less than the CMC, as can be surfactant leakage with added polymer. The added salt reduces the surfactant leakage in the micellar solution due to CMC reduction in the presence of

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electrolyte. In the surfactant–polymer mixture, the surfactant leakage is dramatically affected by salinity.

Keywords: Surfactant leakage, colloid-enhanced ultrafiltration, surfactant–polymer interaction

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 waste water. Micellar-enhanced ultrafiltration (MEUF) 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. Organic solutes solubilize in micelles or surfactant–polymer aggregates and charged solutes can electrostatically bind to these colloids. This solution is then passed through a membrane, which has pores small enough to block the passage of micelles or surfactant–polymer complexes, removing the surfactant aggregates and solubilized or bound solutes. The detailed description of MEUF and PE-MEUF processes was given in Part I of this paper series (1).

Surfactants are characterized by the presence of two moieties in the same molecule, one hydrophilic and the other hydrophobic. The hydrophilic group may carry a positive or negative charge, and/or may contain poly(ethylene oxide) chains. The hydrophobic group of the molecule is generally a hydrocarbon chain but may contain aromatic groups. The properties of surfactants in solutions are governed by their tendency to minimize the contact of their hydrophobic groups with water. This is accomplished by adsorbing at interfaces and association in solution (2). Surface tension vs. log concentration plot for surfactants generally exhibits a significant decrease with concentration, followed by a sharp break above which the surface tension remains almost constant. The break is due to the formation of surfactant clusters or micelles and the break point is called the critical micelle concentration or CMC. Above this concentration, almost all of the added surfactant molecules are used to form additional micelles and the monomer concentration does not change appreciably. Since only the surfactant monomers adsorb at the interface, the surface tension remains essentially constant above the CMC. Therefore, the surface tension can be directly related to the activity of monomers in the solution.

Surfactants and polymers are often used together in practical formulations. When present together, they can interact to provide beneficial properties. Owing to their industrial importance, aqueous surfactant–polymer mixtures are of much interest from both fundamental and technological viewpoints. Surfactant binding to polymers in aqueous solution has been investigated extensively (3–19). The interaction often observed between surfactants and oppositely charged polymers in aqueous solution is commonly known as being the result of one or both of two main driving forces (7, 19–21). The first is an electrostatic attraction generally accepted as an ion-exchange process where the electrostatic forces of interaction are reinforced by aggregation of alkyl chains of the bound surfactant molecules (21). The second is a force involving an interaction between hydrophobic groups on the polymer and those of surfactant molecules in their incipient aggregation process (19, 20). It was found that when dodecyltrimethylammonium ions ($C_{12}TA^+$) aggregate in solutions of hydrophobic polyelectrolyte, hydrophobic parts of the polyelectrolyte are taking part in the micellar structure (22). On the other hand, with a hydrophilic polyelectrolyte, the interaction with surfactant is expected to be mainly electrostatic (18).

Micelle-like organized structures can occur even at concentrations several orders of magnitude lower than the CMC of the surfactant (23–26). The concentration at which the micelle-like organized structure occurs is called critical aggregation concentration or cac. The CMC of surfactant and cac of surfactant–polymer complexes are very important factors in CEUF in that they dictate the surfactant leakage into the permeate of ultrafiltration processes. It has been shown that the surfactant monomer passing through the membrane (or surfactant leakage) in MEUF is 10–20% greater than the CMC of the surfactant. The surfactant leakage in PE-MEUF was observed to be around the cac of the surfactant–polymer system (1).

Semiequilibrium dialysis (SED) or equilibrium dialysis (ED) methods have been used to measure solubilization of organic solutes and surfactant leakage into the permeate in surfactant micelles and surfactant–polymer mixtures (1, 27, 28). In micellar solutions, the surfactant concentration in the permeate gradually increases to the CMC of the surfactant, resulting in micelle formation. That means the solubilization can occur not only in the retentate but also in the permeate. Therefore, dialysis experiments with micellar solutions or MEUF are called SED because permeate samples are extracted for analysis before equilibrium is attained. In surfactant–polymer mixtures or PE-MEUF, the dialysis experiments are ED because an insignificant amount of surfactant–polymer complexes is present in the permeate, resulting in negligible solubilization. As shown in Part I, the surfactant leakage in PE-MEUF in the absence of salt is in between 0.005 to 0.1 mM. The cac is 0.006 mM in the absence of organic solute and the CMC is 0.09 mM under these conditions. This indicates the almost complete absence of micelle formation, and therefore insignificant solubilization in the permeate in these ED experiments.

The overall picture for interaction within oppositely charged surfactant–polymer systems is described as follows: at low surfactant concentration, the ionic surfactant head groups individually bind to the oppositely charged polymer due to electrostatic attraction. When the surfactant concentration exceeds the cac, the polymer-bound surfactant aggregate forms, resulting in the formation of surfactant–polymer complexes (21). Increasing surfactant concentration leads to an increase in surfactant–polymer binding, until the polymer becomes saturated with the surfactant (29). 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 (4, 8, 13).

Surface tension measurements afford a simple and informative method of studying mixtures of two components, one of which is highly active and the other is relatively inactive at the air-water interface. The surface tension results are used to interpret the surfactant–polymer interaction as well as to determine the cac (1, 7, 15, 17, 30–35). A schematic representation of the surface tension curve with generally accepted aggregate structures in each surfactant concentration regime is shown in Fig. 1 (1, 20, 33). The general features of the surface tension trends are as follows: (i) a synergistic lowering of surface tension at very low surfactant concentration regime or region a–b–c, implying the formation of a highly surface-active complex and also indicating the beginning of cooperative adsorption of the polymer and the surfactant (33), (ii) the surface tension reaches a plateau at region c–d where the addition of the surfactant above point c contributes to the formation of the surfactant–polymer complexes, (iii) eventually, the surface tension curve plateaus again at point e where micelles form. In some cases, the concentration at point e can coincide with CMC of the surfactant (20). It is commonly known that the cac can be deduced from the surface tension vs. surfactant concentration plot as shown in Fig. 1, as point c (32).

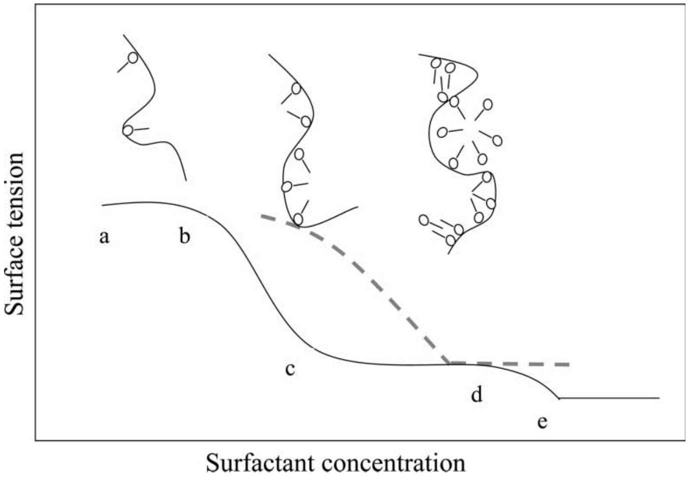

Figure 1. A schematic of surfactant–polymer aggregation. Dashed line is for the surfactant (CPC) alone. Full line is for CPC-PSS mixture. Counterions are not depicted here.

Several investigators have studied the effect of salt in dilute systems of polyelectrolyte and oppositely charged surfactant (4, 15, 17, 36–39). It was found that the cac increases when simple salt is added. This suggests that the attractive interaction between polyelectrolyte and surfactant is reduced by the addition of salt. A study of the effect of simple salt on the surfactant binding by Kogej and Škerjanc shows that an increase in the ionic strength of solution shifts the onset of binding toward higher free surfactant concentrations and decreases the amount of bound surfactant (3). Hayakawa and Kwak observed that a higher added salt valency results in a larger increase in the cac (37). Mattai and Kwak found that the binding of inorganic counterions on the polyions shows anticooperatively, presumably due to the reduction of electrostatic force as the binding takes place (39). The effect of added salt is thus opposite to the influence of salt in micellar systems, where stabilization occurs, manifested by a lowering of the CMC (40, 41).

As mentioned previously, the binding of surfactant ions on polyions takes place not only by coulombic attractive force but also by hydrophobic interaction between bound surfactant ions or surfactants and polymers. Wang et al. have studied the interaction mechanism within oppositely charged polymer-surfactant systems by using isothermal titration calorimetry (ICT) (11). They found that in the presence of salt, the binding isotherm has three stages corresponding to the electrostatic binding, the micellization of bound surfactant molecules, and the formation of free surfactant micelles. In the presence of excess salt, the binding isotherm follows a similar trend to the curve in a polymer-free system, representing the formation of free micelles. This is due to the fact that the coulombic attractive force between polymer and surfactant is considerably screened, resulting in the electrostatic binding of surfactant onto polymer being significantly weakened; and consequently the polymer-induced micellization cannot occur since negligible amounts of surfactant are electrostatically bound to the polymer backbone. On the other hand, the coulombic repulsion between the surfactant head groups is also shielded by the addition of salt, which favors the formation of free micelles.

In Part I, we compared the effectiveness of MEUF and PE-MEUF systems, then the effect of pH on solubilization of TCP was investigated in Part II. The effect of salinity on solute solubilization was discussed in Part III. Continuing in Part IV, the effect of salinity on the surfactant leakage is discussed for both MEUF and PE-MEUF. In Part V in this series of five papers, the ability of PE-MEUF to simultaneously remove a chlorinated phenolic solute and magnesium from wastewater is investigated. This series of papers demonstrates and compares separation efficiency for three chlorinated phenolic between MEUF and PE-MEUF, indicating the possibility of the use of either type of process to remove organic solutes. These studies also aid in understanding physical properties of surfactant micelles and surfactant–polymer complexes in CEUF processes, and help estimate the removal efficiency of CEUF processes for other chlorinated organic solutes.

EXPERIMENTAL

As seen in our previous work (1), the surfactant leakage in CEUF can be determined by using the semiequilibrium dialysis technique (SED). Each experiment was conducted with two separate SED cells for duplicate measurements, so each point was the average value of those two data points. A detailed description of the materials and methods for determining the surfactant leakage used here is given in previous papers (1, 27, 28). In brief, a surfactant and a polyelectrolyte used in this work were cetylpyridinium chloride or CPC and sodium poly(styrenesulfonate) or PSS, respectively. The PSS has an average molecular weight of approximately 70,000 Daltons; the repeating unit of the polymer is $CH_2CH(C_6H_4)SO_3Na$. Organic solutes with various degree of chlorination studied here are 2-monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP). The only difference in the concentration analysis procedure in this paper from the previous papers is that PSS concentration is not set at zero when multiwavelength analysis is conducted. Less than 1% of PSS was found in the permeate; this small amount of PSS is probably low molecular weight components left in the solutions after the purification using ultrafiltration. Nonetheless, the slight presence of PSS does not affect the qualitative analysis in the previous papers.

Surface tension measurements, by means of the Wilhelmy plate technique using a Krüss Processor Tensiometer K12 (Krüss USA, North Corolina), were performed on solutions (at pH 3) 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 in the presence of added salt. Precipitation was observed at the mole ratios of [CPC] : [PSS] 1 : 1; at mole ratios $\leq$ 1:2, no precipitation was observed and the solutions were isotropic. Only isotropic solutions were used in this study. Repeated surface tension measurements were made until readings were within 0.02 mN/m. The equilibrium time was found to depend on the type of solution, and all measurements were made at equilibrium.

RESULTS AND DISCUSSION

The concentration of PSS is based on the concentration of repeating units ($CH_2CH(C_6H_4)SO_3Na$), not on total molecular weight of the polymer. So, if a solution contains 1 mM of PSS and 1 mM of CPC, the concentration of cations (from CPC) and anions (from PSS) are equal.

Surface Tension

The surface tension of 50 mM PSS solutions in the presence and absence of salt was measured as a function of CPC concentration in the absence of

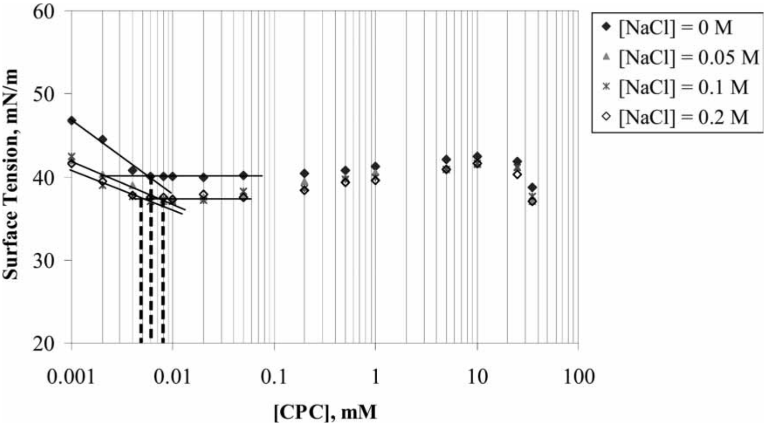

Figure 2. Surface tension of surfactant–polymer system in the absence and presence of salt.

solute. As shown in Fig. 2, a synergistic lowering of surface tension at low CPC concentrations due to the PSS is observed. As also found in the previous study (1), the PSS can have a massive effect on surface tension lowering; therefore, a dramatic reduction in surface tension is observed even at 0.002 mM CPC in the presence of PSS. This results in the absence of region a–b, or point b is buried in region a–b–c. The cac is determined by the intersection between two straight lines drawn on region a–b–c and c–d. An apparent step is observed before the surface tension reaches the plateau region. Previous work found that this plateau surface tension is mildly dependent on PSS concentration, but it is attained at a lower CPC concentration as PSS concentration increases over the range of PSS concentrations studied (1). At higher surfactant concentration in the plateau region, the surface tension slightly increases as the surfactant concentration increases. Then, the surface tension decreases as the surfactant–polymer concentration ratio increases up to the ratio at which precipitation is observed at a surfactant-to-polymer concentration ratio of 1 to 1. It should be noted that the repeating unit of the PSS is $CH_2CH(C_6H_4)SO_3Na$ and the CPC structure is $C_{21}H_{38}NCl$. As the surfactant and polymer stoichiometrically associate, precipitation is often observed for oppositely charged surfactants and polymers. Kogej et al. also observed precipitation when the [CPC] to [PSS] ratio becomes unity (42). As shown in Fig. 2, the cac corresponding to the point where the surface tension reaches the plateau region and is approximately equal to a CPC concentration of 0.006 mM in the absence of salt. In the presence of 0.05 M NaCl, the cac increases to 0.0075 mM CPC. However, at higher salt concentration, the cac is observed to decrease; the cac in the presence of 0.1 M and 0.2 M NaCl is approximately 0.005 mM CPC. It should be noted that the lines drawn for the systems in the presence of 0.1 M and 0.2 M NaCl coincide, resulting in the same cac value.

The surface tension behavior is different from that normally observed for surfactant solutions without polymer. For polymer-free surfactant solutions, a single sharp break in variation of surface tension with surfactant concentration occurs at the CMC. For surfactant–polymer mixtures, the classical pattern of surface tension variation corresponds to two abrupt changes in surface tension at the cac and the CMC (20, 21, 32–35). In region a–b–c in Fig. 2, surfactant is adsorbing on the polyelectrolyte chain as unassociated CPC molecules. In addition, the presence of PSS (even in the absence of surfactant) showed a massive effect on surface tension lowering (1). In region c-d, the concentration of surfactant aggregates stabilized by the polymer-bound surfactant aggregates in solution increases from c to d. The slight increase in the surface tension in the plateau region as CPC concentration increases may be due to a conformational change in the aggregate occurring in the region c-d as also observed by Park and coworkers (17); they proposed that more surfactant can bind to such surfactant–polymer aggregates, resulting in a decrease in free surfactant concentration in the bulk solution and at the air/water interface, and therefore increasing the surfactant tension.

At CPC concentrations above point d, the monomeric CPC concentration increases as the polymer becomes saturated with the surfactant aggregates. At yet higher CPC concentrations, eventually ordinary micelles form (point e) and the surface tension tends to plateau again above the CMC of the surfactant as also observed in previous work (20, 21, 32–35). It should be noted that this CPC concentration (at point e) was not reached for conditions studied here, primarily because the polymer and surfactant form a precipitate prior to this concentration. It was explained that the binding of surfactant to the polyelectrolyte makes the complex more hydrophobic (18). When their net charge becomes sufficiently low, the complexes will start to attract each other, and, due to hydrophobic nature of the interaction, the water content will be low in the concentrated phase; i.e., a precipitate will be formed. Our previous work showed that the higher the PSS concentration, the higher the CPC concentration obtainable prior to the precipitation. In other words, if the phase separation does not occur, the CMC tends to occur at higher CPC concentration as the PSS concentration increases (1). In addition, the CPC concentration required to form micelles in the presence of PSS is higher than the CMC because a vast majority of surfactant is present in surfactant–polymer complexes instead of monomer when this micelle formation concentration is attained, compared to the polymer-free surfactant system. The drastic decrease in surface tension of PSS solutions when the concentration of surfactant exceeds about 50% of that of PSS is of particular interest. A previous study has measured the surface tension at different PSS concentrations and it was also found that point d corresponds approximately to a CPC/PSS molar ratio of 1/2; this implies that two anionic sulfonate PSS groups stabilize one aggregated cationic surfactant molecule (1). The addition of surfactant exceeding the binding capacity of PSS would increase the concentration of free surfactant, and thus decrease surface tension.

The coulombic interaction between surfactant and polymer is screened by the presence of salt. Therefore, the polymer-bound micellization does not occur as favorably, resulting in an increase in the cac. However at yet higher salt concentration, the added salt tends to stabilize the polymer-bound micelle, resulting in a decrease in the cac. This corresponds to a mechanism proposed by Lindman and Thalberg that the effect of salt is two-fold (43): (i) reduction of the electrostatic interaction between polymer and surfactant, and (ii) stabilization of the surfactant aggregates (reduction of repulsion between surfactant head groups). They projected that the first mechanism will dominate at low ionic strength while the second mechanism will play a more important role at higher ionic strength. Similar to the CMC behavior, the decrease in the cac at high salt concentration can be expected as seen in the present work.

The addition of salt does not change the cac dramatically, probably due to the strong hydrophobic interaction between CPC and PSS. It was found that for systems with a higher degree of binding, the free and bound surfactant is approximately constant with the addition of salt whereas the concentration of free surfactant increases with increasing salt concentration for systems with a lower degree of binding (5). For systems where the polyelectrolyte contains hydrophobic moieties (such as PSS), the interaction with surfactant is stronger, and the effect of salt on the cac is smaller (4) than for hydrophilic polyelectrolytes (e.g., sodium polyacrylate or PA). This indicates that there is a hydrophobic interaction not only between the surfactants but also between the surfactant and polymer. We emphasize that the purpose of the cac determination is not to precisely estimate the surfactant monomer concentration but to illustrate how the salt affects the surface activity, and therefore the surfactant monomer concentration which approximates the surfactant leakage.

Surfactant Leakage

The surfactant concentration in the permeate is indirectly determined by using the mathematical analysis of multiwavelength UV spectra as mentioned earlier and the surfactant leakage is very low due to the presence of salt and polyelectrolyte. Using this mathematical technique, it was found that the surfactant leakage results for some systems are unreliable (e.g., the surfactant concentration is unacceptably low and within the magnitude of their standard deviations). Therefore, the surfactant leakage results for some systems are not shown here. Like the solubilization measurements in the previous part of this series (Part III) (28), most surfactant leakage measurements were done without pH adjustment (unless it is mentioned otherwise) due to CPC degradation (which occurs at high pH) as the NaOH is added to solution, though the pH of the initial and final solutions was recorded (27). The experiments at pH 3 were carried out for the system with TCP to minimize the concentration of phenolate anion. The percentage of phenolate anion in colloid solutions is shown in Part II in this series (27). In brief, the percentage of phenolate

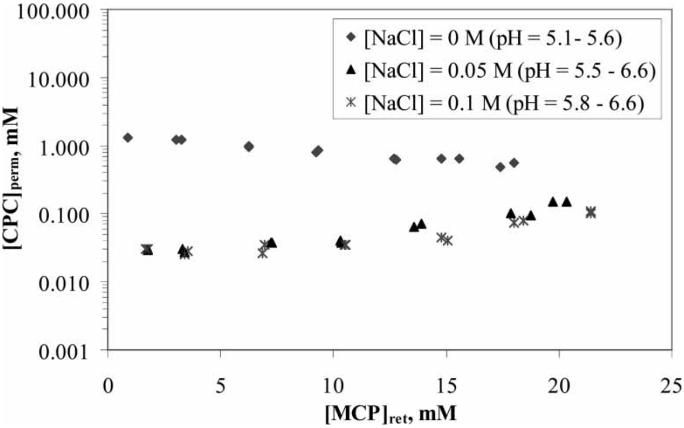

Figure 3. Surfactant leakage in the permeate vs. concentration of MCP in the retentate at different NaCl concentrations in CPC micelles. Initial [CPC] is 25 mM.

anion in the micellar solution in both the absence and presence of added salt has order MCP < DCP < TCP; however, the percentage of phenolate anion is negligible in the surfactant–polymer mixtures at all salt concentrations. In the micellar solutions, the percentage of phenolate anion for all solutes decreases as the salt concentration increases.

Without pH adjustment, the surfactant concentration in the permeate or surfactant leakage is plotted as a function of solute concentration in the retentate in the micellar solutions as shown in Fig. 3 for MCP; the surfactant leakage result for DCP and TCP are the same as that for MCP. The experiments at pH 3 were carried out for TCP in micellar solutions, as shown in Fig. 4. In the surfactant–polymer mixtures, the surfactant leakage in the

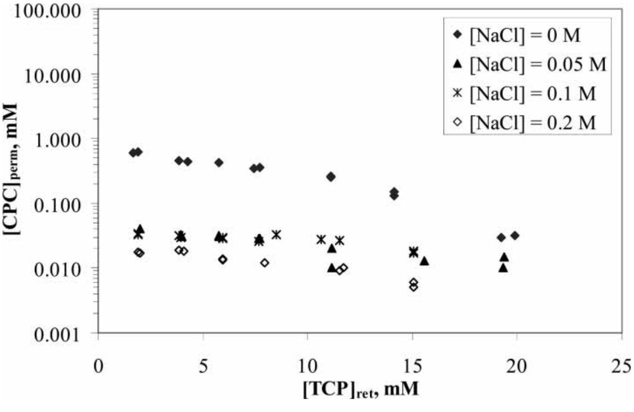

Figure 4. Surfactant leakage in the permeate vs. concentration of TCP in the retentate at different NaCl concentrations in CPC micelles at pH of 3. Initial [CPC] is 25 mM.

absence and the presence of 0.05 M NaCl as a function of MCP concentration without pH adjustment is shown in Fig. 5. Surfactant leakage results at pH 3 are not shown here due to unreliable results caused by the aforementioned data analysis constraint.

As shown in Figs. 3 and 4, the surfactant leakage in the micellar solution is reduced by more than an order of magnitude by addition of only 0.05 M NaCl. When the solute concentration increases, the surfactant leakage in the micellar solution in the absence of salt decreases, while the surfactant leakage in the presence of salt remains almost constant or slightly increases. It is commonly known that in aqueous solution, the presence of electrolytes causes a decrease in the CMC for ionic surfactants (41). The quantitative effect of electrolyte concentration on the CMC of ionic surfactants is given by Corrin and Harkins (44); for a single monovalent counterion, the log of the CMC is a linear function of log of the free concentration of the counterion as follows

$$\log CMC = -\mathrm{a} \log C_i + \mathrm{b} \tag{1}$$

where a and b are constants for a given ionic head at a particular temperature and C_i is the free counterion concentration. For CPC with added NaCl, chloride anions are the counterion. The depression of the CMC is due mainly to the decrease in thickness of the ionic atmosphere (or electrical diffuse double layer) surrounding the ionic head groups in the presence of electrolyte, resulting in a decreased electrical repulsion between the surfactant head groups. Previous work showed that the surfactant leakage in micellar solutions is within about 20% of the CMC values (1). Therefore, the surfactant leakage is reduced due to the CMC depression in the presence of added salt as seen in Figs. 3 and 4. Our previous work found that in the absence of salt, the

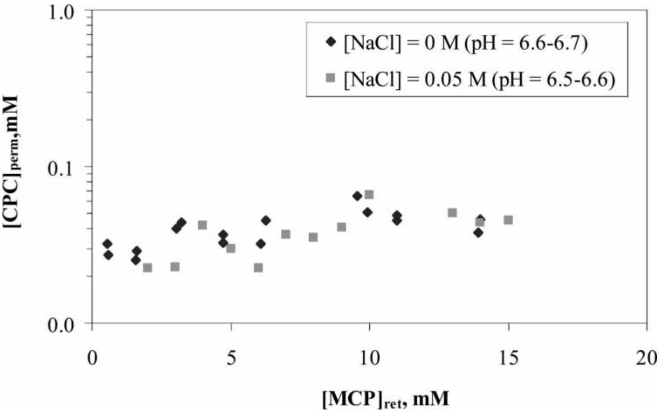

Figure 5. Surfactant leakage in the permeate vs. concentration of MCP in the retentate in the absence and presence of 0.05 M NaCl in CPC–PSS complexes. [CPC] to [PSS] is 25 mM to 50 mM.

solute also causes a CMC depression in micellar solutions (1), resulting in the reduction of the surfactant leakage as the solute concentration increases. The solutes studied here are chlorinated phenols, so the reduction in the CMC of the cationic surfactant is due to a reduction in repulsion between the charged surfactant head groups; the solute hydroxyl groups insert themselves into the micellar palisade layer and increase the distance between the charged surfactant head groups. If the solute is ionized to a phenolate anion, the CMC depression due to the presence of solute will be even greater due to electrostatic attraction between solute and surfactant. As seen in Fig. 3, the effect of solute concentration on decreasing the surfactant leakage is more pronounced in the micellar solutions without salt, as compared to the systems with salt. This could be due to the presence of the phenolate anion as just mentioned. For example, 30% of the phenolics is present as the anion for MCP in the absence of salt, whereas the fraction of MCP present in anionic form is 7% and 4% in the micellar solution with 0.05 M and 0.1 M NaCl, respectively (27). Since the anionic form of the solute decreases the CMC of the cationic surfactant more than the neutral form of the solute, the reduction of the surfactant leakage due to the solute is stronger in the absence of salt than in the presence of salt. In fact, the surfactant leakage slightly increases with increasing the solute concentration in the presence of salt.

In surfactant–polymer system with 50 mM PSS, as shown in Fig. 5, the surfactant leakage in the absence and presence of 0.05 M NaCl is not significantly different over the entire range of MCP concentrations. This suggests that the presence of salt does not dramatically affect the surfactant monomer concentration. In other words, the effect of salinity on the surfactant leakage in the presence of the polymer is not as strong as that in the absence of polymer. An interesting observation is that the surfactant leakage in the surfactant–polymer mixtures in the presence of salt is of the same magnitude as the CMC of the surfactant in the presence of salt (around 0.05 M NaCl).

In the system containing polyelectrolyte and oppositely charged surfactant, where the polymer acts as an electrolyte, the complexes formed are stabilized by both electrostatic attraction and cooperative hydrophobic effects, thus leading to a CAC which is lower than the CMC by several orders of magnitude, resulting in reduction in surfactant monomer concentration. The presence of additional salts like NaCl therefore might not show a significant impact on further reduction in the surfactant leakage since the surfactant leakage has been much reduced by the presence of the polymer. Furthermore, the surface tension results show that the cac is not very sensitive to salt concentrations. It should also be noted that the surfactant leakage results found in the SED experiment are greater than that found from surface tension results. This can be attributed to the presence of the chlorophenols in the SED experiments (the surface tension experiments were carried out in the absence of the solutes); the chlorophenols may reduce the surfactant–polymer interaction due to hydrophobic interaction between the solute and the polymer backbone, resulting in the increase in the surfactant leakage.

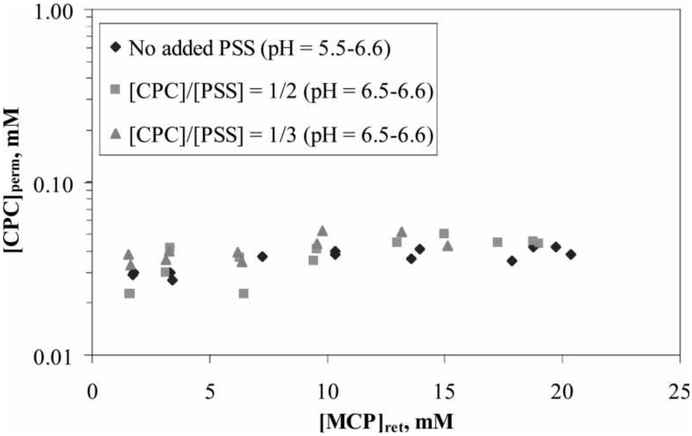

Figure 6. Surfactant leakage in the permeate vs. concentration of MCP in the retentate in different types of colloid. Initial [CPC] to [PSS] are 25 mM to 0 mM (no added PSS), 25 mM to 50 mM (mole ratio 1 to 2), and 25 mM to 75 mM (mole ratio 1 to 3). Initial [NaCl] is 0.05 mM.

The data is replotted in Fig. 6 to show the effect of type of colloid for the system studied with MCP in the presence of 0.05 M NaCl. It is observed that the surfactant leakage in the micellar system and in the surfactant–polymer mixture are not significantly different. A previous study showed that, in the absence of salt, the surfactant leakage is significantly reduced by the presence of polymer (1) because the surfactant–polymer aggregates form at several orders of magnitude below the CMC of the surfactant. However, the surfactant leakage results in Fig. 6 show that for high ionic strength water, the use of polymer/surfactant mixtures shows comparable surfactant leakage to the system without polymer. This due to the fact that the surfactant monomer concentration has been already significantly reduced by the presence of salt (CMC at 0.05 M NaCl is around 0.05 M CPC); therefore, the effect of the presence of PSS does not play a significant role. In conclusion, in PE-MEUF, the ionic strength does not play a strong role in surfactant leakage due to the fact that the cac or the surfactant monomer concentration is suppressed by the presence of polymer. At high ionic strength, the use of MEUF and PE-MEUF shows a comparable surfactant leakage. Since solute solubilization constants tend to be lower in PE-MEUF than MEUF (1), resulting in lower solute rejections in PE-MEUF, these leakage results would imply that MEUF would be a superior separation technique at high ionic strength, while either MEUF or PE-MEUF may be superior at low ionic strength water. Other considerations include ability to regenerate separating agents (where MEUF is better in some cases) and flux through the membrane (to be discussed in Part V of this series).

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