Amphipathic Polymers with Stimuli-Responsive Microdomains for Water Remediation: Binding Studies with *p*-Cresol

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ABSTRACT: Amphipathic, stimuli-responsive water-soluble polymers have been investigated as potential remediation agents for micellar enhanced ultrafiltration (MEUF). The systems represent divergent architectural types, a triblock ABA copolymer of PEO-PPO-PEO, an *n*-octylamide modified poly(sodium maleate-*alt*-ethyl vinyl ether), and the transport protein, bovine serum albumin. Each type exhibits stimuli-dependent microphase separation or domain formation in response to temperature, pH, and/or ionic strength changes. Segmental associations result in hydrophobic clusters resembling those present in small molecule surfactant micelles. The effects of such segmental aggregation on sequestration of a model hydrophobic foulant, *p*-cresol, have been investigated using equilibrium dialysis. The favorable molar binding values, the large hydrodynamic dimensions of the stable polymer aggregates, and potential reversibility of foulant loading could have commercial utility in high flow rate, multiple-pass remediation processes. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2290–2300, 1999

Key words: micellar enhanced ultrafiltration; stimuli-responsive polymers; equilibrium dialysis

INTRODUCTION

Micellar enhanced ultrafiltration (MEUF) is a technique that has been developed for the removal of organic compounds from water. In MEUF, surfactant is added to an aqueous solution containing the hydrophobic contaminant to be recovered. At concentrations greater than the critical micelle concentration, the surfactant forms micelles, which solubilize the hydrophobic contaminant within the micellar domain. The solution is then processed by ultrafiltration through a porous membrane that allows passage of water, but prevents passage of the micelles and the sequestered contaminant. This process is typically modeled using equilibrium dialysis experiments to determine sequestration efficiency for a specific solubilization agent.

A limitation of small molecule surfactants in MEUF is the passage of individual surfactant molecules through the membrane into the permeate. Several studies show that polymer/surfactant complexes are capable of capturing hydrophobic foulants while, at the same time, reducing the loss of surfactant across the membrane.[1,2] However, the inevitable equilibrium created between the bound and free surfactant continues to present a problem in surfactant-based separations. Another limitation of MEUF is the small pore size (0.1–1 nm) needed to retain the surfactant micelles. Therefore, permeate flux is limited in typical MEUF applications that use small molecule surfactants.

Stimuli-responsive, amphipathic, water-soluble polymers are potential alternatives to small

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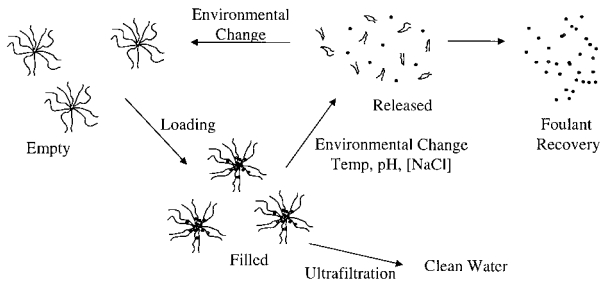

Figure 1 Idealized remediation cycle for stimuli-responsive polymeric surfactants.

molecule surfactants in MEUF since a number of these form discrete domains similar to those of small molecule surfactant micelles.[3–10] Such organized structures should allow capture of a hydrophobic contaminant and prevent passage through the membrane in an ultrafiltration process. The large size of the polymer domains would facilitate the use of larger pore membranes, extending the range of ultrafiltration and allowing greater flux across the membrane. Environmental stimuli (temperature, pH, and/or ionic strength) could trigger reversible association (Fig. 1), allowing foulant loading and unloading in repeatable cycles of remediation.

Despite the potential of amphipathic polymers as remediative agents, detailed studies of stimuli-controlled sequestration are limited. In this study, we report equilibrium dialysis and dynamic light scattering experiments that demonstrate the feasibility of stimuli-controlled (temperature, pH, electrolyte) sequestration of a model water foulant, *p*-cresol. Amphipathic water-soluble polymers representing three architectural designs—an ABA triblock; an *n*-octylamide-substituted polysoap; and the transport protein, bovine serum albumin—have been examined.

EXPERIMENTAL

Materials

p-Cresol was purchased from Aldrich Chemical Company (St. Louis, MO) and was purified by vacuum distillation. Pluronic™ F127 was obtained from BASF Corporation (Mount Olive, NJ) and was used as received. Hydrophobically modified copolymers of maleic anhydride-*alt*-ethyl vinyl ether were synthesized according to previously published procedures.[11] This polymer has a molecular weight of 3.5×10^5 g/mol and a molar incorporation of 30% octyl groups.[11] Bovine serum albumin (BSA, fraction V) was purchased from Sigma Chemical Company (St. Louis, MO) and used as received.

Instrumentation

UV-vis measurements were made with a Hewlett–Packard 8452A diode array spectrophotometer. Dynamic light scattering experiments were performed with a Brookhaven Instruments 128-channel BI-2030 AT digital correlator (Holtsville, NY) using a Spectra Physics He–Ne laser (Mountain View, CA) operating at 632.8 nm. Hydrodynamic diameters were calculated by the cumulants method. Dust was removed from samples for light scattering measurements with an Eppendorf model 5415C microcentrifuge (Westbury, NY).

Equilibrium Dialysis Experiments

Equilibrium dialysis experiments were performed using equilibrium dialysis cells (5 ml) from Bel-Art Products (Pequannock, NJ) and regenerated cellulose membranes, which had a nominal molecular weight cutoff of 6000. Solutions containing the polymeric surfactant and *p*-cresol of known concentrations were placed in the retentate side of each dialysis cell and water of the appropriate pH or ionic strength was placed in the permeate side. The cells were thermostated at 25°C in a Napco incubator (Tualatin, OR) or at 5°C in a water bath regulated with a Lauda RM6 water circulator (Westbury, NY). The concentration of *p*-cresol in the retentate $[p\text{-cresol}]_{ret}$ and permeate $[p\text{-cresol}]_{per}$ were determined by UV spectroscopy. Dialysis experiments in the absence of polymer indicated that equilibrium concentrations of *p*-cresol were obtained in 24 h. Dynamic light scattering data indicated that the polymeric surfactant was quantitatively retained within the retentate compartment.

RESULTS AND DISCUSSION

Classical remediation models consider the micelle as a distinct pseudophase containing the hydrophobic foulant.[19] For small amphipathic molecules, micelles form only above a critical concentration, termed the critical micelle concentration (CMC). In some cases, the foulant is considered a guest within the micelle, whereas in others it participates in forming mixed micelles. If the

polymer domains are also treated as discrete solubilizing entities, then it is possible to propose a series of expressions that define the interaction between the foulant and the polymer domains. The concentration of the foulant in the domain is determined from the concentration of the foulant in the retentate ($[foulant]_{ret}$) and in the permeate ($[foulant]_{per}$) via eq. 1:

$$[foulant]_{bnd} = [foulantl]_{ret} - [foulant]_{per} \quad (1)$$

Equation 1 remains valid if the concentration of foulant in the permeate is equivalent to the concentration of unbound foulant in the retentate. With knowledge of the amount of foulant bound within the hydrophobic microdomains, the molar binding ratio r can be determined using eq. 2

$$r = \frac{[foulant]_{bnd}}{[polymer]} \quad (2)$$

in which [*polymer*] is the concentration of the polymer in the retentate. Binding isotherms may be constructed by plotting r as a function of the feed foulant concentration.

Knowledge of the concentration of the foulant in each compartment of the dialysis cell at the conclusion of the experiment, combined with knowledge of the polymer concentration in the retentate compartment, also allows calculation of the equilibrium constant k as illustrated in eq. 3.

$$k = \frac{[foulant]_{retentate} - [foulant]_{permeate}}{[foulant]_{permeate} \cdot [polymer]} \quad (3)$$

The term k is simply a mass action equilibrium constant for the transfer of the foulant from the aqueous bulk phase to the hydrophobic microdomain. This ratio has been used extensively in the literature, but it is more convenient to use an alternate equilibrium constant K, defined by eq. 4[12–18]

$$K = \frac{X}{c_0} \quad (4)$$

where X represents the mole fraction of the organic solute in the polymer domain and c_0 represents the concentration of free foulant present in a nonassociated state.[19] The two equilibrium constants k and K are easily determined from the experimental data and are related by eq. 5.[20]

$$K = k(1 - X) \quad (5)$$

An advantage of using the equilibrium constant K is that it has been shown to be closely related to the activity coefficient of the foulant in the domain.[20] This activity coefficient may be calculated using eq. 6

$$K = \frac{1}{\gamma_0 c_0^0} \quad (6)$$

where γ_0 is the activity coefficient of the foulant and c_0^0 is the saturation concentration of the foulant in water (0.18 *M*).[21] The value γ_0 is simply interpreted as a measure of the escaping tendency of the foulant from the domain. Information regarding the activity coefficient and the variance of γ_0 with X is useful in defining the environment of the foulant within the domain.

The overall efficiency of foulant sequestration may be evaluated from the rejection ratio. Whereas the binding isotherms and activity coefficients reflect the interaction of the polymer with the foulant on a molecular basis, the rejection ratio provides a practical means of determining effectiveness for remediation of the foulant from an aqueous wastewater stream. The value of the rejection ratio is calculated from the equilibrium dialysis data and is defined by eq. 7. Thus the rejection ratio is a measure of how well the polymer prevents passage of the foulant through the membrane. Low values indicate that the polymer has a low capacity for capture; high rejection ratios indicate that the polymer domain is capable of interacting with and retaining the foulant.

$$\text{Rejection ratio} = \left(1 - \frac{[Cresol]_{per}}{[Cresol]_{ret}}\right) \times 100 \quad (7)$$

PEO–PPO–PEO Block Copolymers—Pluronic™ F127

The first polymer selected for study in this work was Pluronic™ F127, a triblock copolymer of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO). PEO–PPO copolymers associate to form hydrophobic microdomains and have been widely studied as polymeric surfactants.[22–49] Pluronic™ F127 ($PEO_{99}PPO_{69}PEO_{99}$) is known to exhibit concentration- and temperature-dependent aggregation behavior in aqueous solution.[22–49] At 25°C, the copolymer has a critical aggregation concentration (CAC) of 0.6 g/dL. Below the CAC, the polymers are present as individually solvated

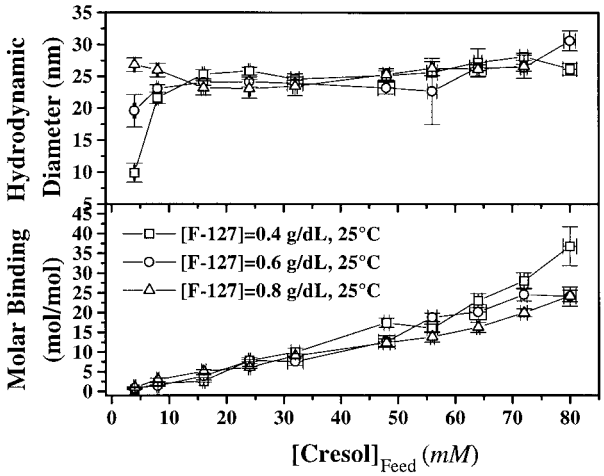

Figure 2 Binding isotherms for F127 and *p*-cresol at 25°C for [F127] = 0.4, 0.6, and 0.8 g/dL and the corresponding hydrodynamic diameter of the polymer–foulant complex as a function of *p*-cresol concentration.

unimers. At concentrations greater than 0.6 g/dL, the PPO blocks associate to form intermolecular multimers with an aggregation number of 5.[35] As the temperature is lowered to 15°C, the intermolecular aggregates dissociate due to increased solubility of the PPO blocks. At 5°C, the polymers are present predominantly as unimers in aqueous solution.

To study the temperature- and concentration-dependent sequestration of *p*-cresol by F127, equilibrium dialysis was performed for selected polymer concentrations at 25°C and 5°C. Binding isotherms for F127 with *p*-cresol and the corresponding hydrodynamic diameters for the F127/*p*-cresol complexes at 25°C for [F127] = 0.4, 0.6, and 0.8 g/dL are shown in Figure 2. The binding isotherms indicate that sequestration of *p*-cresol occurs throughout the range of *p*-cresol concentrations investigated. The hydrodynamic diameter, as determined from dynamic light scattering, agrees well with data shown previously for the multimer of F127. Therefore, the multimer of F127 acts as the solubilization agent for the organic solute. It is interesting to point out that even at [F127] = 0.4 g/dL (a concentration of F127 below the CAC at 25°C), a multimeric state exists for *p*-cresol concentrations greater than 5 m*M*. Therefore, the presence of the organic foulant facilitates the formation of multimers of F127 in solution, which thus leads to binding of the organic solute. The rejection ratios and activity coefficients summarized in Table I also indicate the similarity of the microphase-separated domains of the polymer for each polymer concentration.

The results of the experiments at 5°C are illustrated in Figure 3 and Table II. The data in Figure 3 confirm the expected result of minimal uptake of the foulant by the unimers at low concentrations of *p*-cresol. However, as the concentration of the foulant is increased, intermolecular polymer aggregation occurs at a critical concentration of 15 m*M* of *p*-cresol. Once the concentration of *p*-cresol surpasses 15 m*M*, aggregates with average hydrodynamic diameters of 25 nm are observed. The average size of the aggregates remains constant with further addition of *p*-cresol, whereas the binding increases linearly with addition. The rejection ratios and activity coefficients listed in Table II suggest that these aggregates

Table I Rejection Ratios and Activity Coefficients as a Function of [*p*-Cresol]$_{feed}$ and [F127] at 25°C

	[F127] = 0.4 g/dL (T = 25°C)		[F127] = 0.6 g/dL (T = 25°C)		[F127] = 0.8 g/dL (T = 25°C)	
[*p*-Cresol]$_{feed}$ (m*M*)	Rejection Ratio (%)	Activity Coefficient	Rejection Ratio (%)	Activity Coefficient	Rejection Ratio (%)	Activity Coefficient
7	8.1 ± 0.9	0.02	14 ± 4	0.02	15 ± 2	0.03
14	13 ± 2	0.03	13 ± 2	0.03	21 ± 3	0.04
21	9 ± 1	0.05	17 ± 2	0.05	22 ± 2	0.06
28	15 ± 1	0.07	22 ± 1	0.06	22 ± 1	0.07
35	15 ± 2	0.09	16 ± 2	0.09	25 ± 1	0.08
42	18 ± 1	0.12	18 ± 2	0.13	28 ± 2	0.09
49	14 ± 1	0.14	23 ± 1	0.14	27 ± 3	0.11
56	18 ± 1	0.16	22 ± 2	0.16	29 ± 2	0.12
63	18 ± 1	0.18	24 ± 2	0.17	31 ± 2	0.13
70	21 ± 3	0.19	23 ± 2	0.18	31 ± 2	0.16

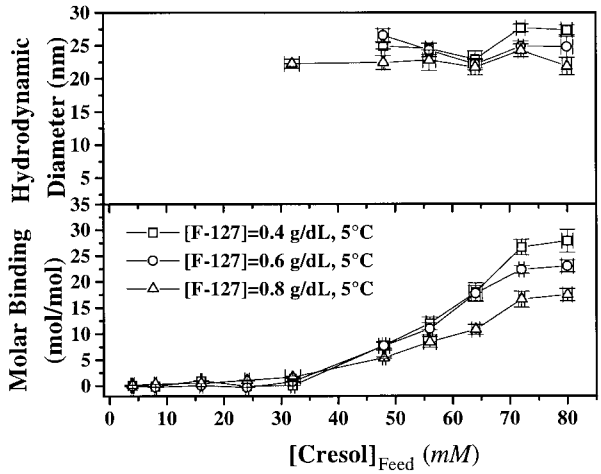

Figure 3 Binding isotherms for F127 and *p*-cresol at 5°C for [F127] = 0.4, 0.6, and 0.8 g/dL and the corresponding hydrodynamic diameter of the polymer–foulant complex as a function of *p*-cresol concentration.

have a strong interaction with *p*-cresol, similar to that observed at 25°C.

Overall, equilibrium dialysis indicates that F127 in the multimeric state is capable of interacting with and capturing *p*-cresol. A conceptual model of the interaction of F127 with *p*-cresol is illustrated in Figure 4. Sequestration of *p*-cresol is observed for each concentration of *p*-cresol at [F127] > 0.6 g/dL at 25°C. For [F127] = 0.4g/dL at 25°C, the presence of more than 2.0 m*M* *p*-cresol promotes a unimer-to-multimer transition that results in sequestration. At 5°C, unimers of F127 are observed at all concentrations in the absence of the foulant. With the addition of low amounts of *p*-cresol (<15 m*M*), no intermolecular associates are observed and therefore minimal binding of *p*-cresol is realized. At concentrations of *p*-cresol greater than 15 m*M*, multimers of F127 are observed for all F127 concentrations, and sequestration occurs with linear uptake of added *p*-cresol. Although the above-mentioned studies indicate that F127 will associate with *p*-cresol, the temperature-responsiveness of the system is compromised by the *p*-cresol-induced unimer-to-multimer transition. Therefore, other polymer architectures must be used to achieve more control over foulant sequestration.

n-Octylamide-Substituted Poly (sodium maleate-*alt*-ethyl vinyl ether) (C8–MA–EVE)

The second polymer examined in this work was an *n*-octylamide-substituted poly (sodium maleate-*alt*-ethyl vinyl ether), C8–MA–EVE. This polymer represents a class of hydrophobically modified polyelectrolytes that form intramolecular associates termed *polysoaps,* first investigated by Strauss and coworkers.[50–59] Previous research in our laboratories with the C8–MA–EVE has shown that the polymer exhibits a pH responsive, polysoap-to-polyelectrolyte transition.[60,61] This transition has a direct impact on the solution properties, depending on concentration. At low pH and low concentration, the polymer behaves as a compact coil with little intermolecular interaction. At pH 8.0, the polymer behaves as an extended chain polyelectrolyte but does not show intermolecular chain entanglements below a polymer concentration 1 g/dL.

Table II Rejection Ratios and Activity Coefficients as a Function of [*p*-Cresol]$_{feed}$ and [F127] at 5°C

	[F127] = 0.4 g/dL (T = 5°C)		[F127] = 0.6 g/dL (T = 5°C)		[F127] = 0.8 g/dL (T = 5°C)	
[*p*-Cresol]$_{feed}$ (m*M*)	Rejection Ratio (%)	Activity Coefficient	Rejection Ratio (%)	Activity Coefficient	Rejection Ratio (%)	Activity Coefficient
7	<1	—	<1	—	2.4 ± 0.4	0.16
14	<1	—	<1	—	2.7 ± 0.2	0.15
21	<1	—	<1	—	2.5 ± 0.1	0.18
28	<1	—	<1	—	4.3 ± 0.3	0.14
35	<1	0.09	1.9 ± 0.1	0.22	4.9 ± 0.7	0.15
42	8 ± 1	0.14	12 ± 1	0.14	14 ± 1	0.11
49	11 ± 1	0.15	14 ± 2	0.15	18 ± 2	0.12
56	14 ± 1	0.16	19 ± 2	0.16	19 ± 2	0.13
63	18 ± 1	0.17	22 ± 1	0.17	25 ± 2	0.14
70	17 ± 1	0.19	22 ± 1	0.18	24 ± 2	0.16

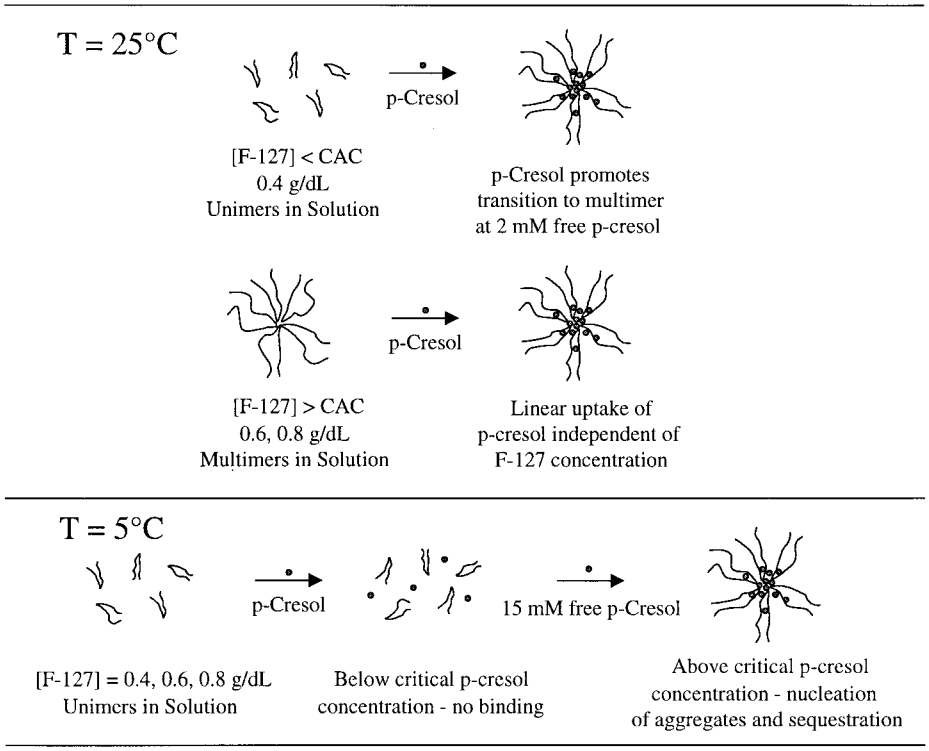

Figure 4 Conceptual model for the sequestration of *p*-cresol as a function of F127 concentration and temperature.

To study the pH-dependent sequestration of *p*-cresol by C8–MA–EVE, equilibrium dialysis experiments were conducted at a polymer concentration of 0.05 g/dL and respective pH values of 4.0 and 8.0. It should be noted that the *p*-cresol (pKa = 10.5) should remain in the phenolic form during sequestration studies. The binding isotherms and light scattering results are illustrated in Figure 5. At low concentrations of *p*-cresol, the binding is similar at both pH values and the molar binding increases in a linear fashion. However, at a concentration of feed *p*-cresol of 4.5 m*M*, a large increase in the molar binding occurs for the solution at pH 4.0. It appears that the *p*-cresol in the solution promotes a change in the domain organization such that significantly higher loadings of *p*-cresol can be accommodated. Whereas the binding increases linearly with free *p*-cresol at pH 8.0, the values of the molar binding at pH 4.0 increase to greater than 6000 molecules of *p*-cresol per polymer chain. Such a large change in the binding isotherm might suggest a change in aggregation number and polymer conformation. However, light scattering measurements do not indicate any significant changes in hydrodynamic dimensions with addition of *p*-cresol.

The presence of the hydrophobic microdomains is substantiated by the values of the activity coefficients and the rejection ratios listed in Table III. As illustrated in Figure 6, the polymer has less ionic charge at pH 4.0 and the reduced in-

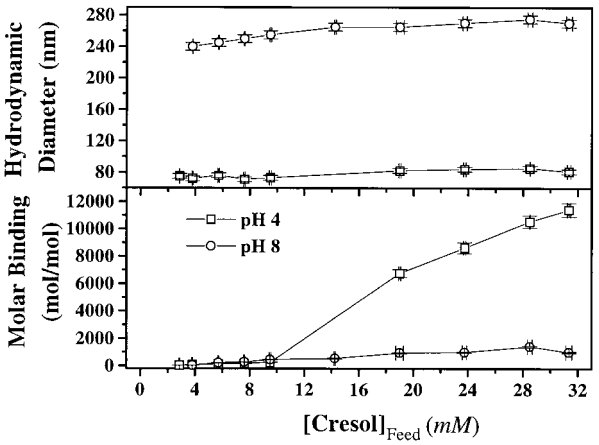

Figure 5 Binding isotherms for C8–MA–EVE copolymers and p-cresol at 25°C at pH 4.0 and pH 8.0 and the corresponding hydrodynamic diameter of the polymer–foulant complex as a function of *p*-cresol concentration (C_p = 0.05 g/dL).

Table III Rejection Ratios and Activity Coefficients of MA-EVE Copolymers as a Function of pH

	pH 4.0 ([Polymer] = 0.05 g/dL)		pH 8.0 ([Polymer] = 0.05 g/dL)	
$[p\text{-Cresol}]_{feed}$ (m*M*)	Rejection Ratio (%)	Activity Coefficient	Rejection Ratio (%)	Activity Coefficient
2.8	3.7 ± 0.1	8.0E-03	2.0 ± 0.2	0.01
3.8	5.4 ± 0.1	0.01	2.2 ± 0.7	0.01
5.7	6.3 ± 0.2	0.02	10.1 ± 0.3	0.02
7.6	6.0 ± 0.3	0.02	9.8 ± 0.5	0.02
9.5	7.3 ± 0.4	0.03	12.7 ± 0.7	0.03
14.2	25 ± 1	0.03	10.2 ± 0.8	0.04
19.0	67 ± 2	0.03	13.1 ± 0.6	0.04
23.8	68 ± 3	0.03	11.2 ± 0.5	0.06
28.5	69 ± 3	0.04	13.1 ± 0.5	0.07
31.3	68 ± 3	0.04	8.6 ± 0.3	0.08

tramolecular repulsions and enhanced hydrogen bonding of carboxylic acid groups allow the formation of polymeric micelles (hydrophobic microdomains). These micelles are characterized by extremely low activity coefficients, high molar binding, and high rejection ratio. At pH 8.0, the polymer behaves as a highly charged polyelectrolyte and chain expansion (due to ionic repulsions) prevents the formation of hydrophobic microdomains. However, the values of the activity coefficients indicate that the polymer interacts favorably with the *p*-cresol despite the absence of the hydrophobic microdomains. In this case, it is likely that the interaction of the *p*-cresol with the polymer occurs at the individual *n*-octyl sites along the polymer chain.

Bovine Serum Albumin

The third polymer studied in this work was a naturally occurring protein, bovine serum albumin (BSA). BSA represents a family of proteins that are key to the transport of fatty acids and other amphiphiles.[62–64] The serum albumins are structurally similar and have approximately ten binding sites within the protein tertiary structure.[65] The protein has been extensively studied and has been found to interact with a number of hydrophobic molecules and surfactants.[66–70]

To determine the dilute solution behavior of the protein, dynamic light scattering and fluorescence experiments were performed in our laboratories at a range of pH values and ionic strengths.[71] These experiments reveal an electrolyte-dependent aggregation at pH 2.0. Light scattering, summarized in Table IV, shows the change in the aggregation number of the protein with addition of electrolyte. The results indicate that the protein has a hydrodynamic diameter of 7 nm at pH 2.0 in aqueous media. The addition of 0.5 *M* NaCl promotes the aggregation of the protein to form multimers with average hydrody-

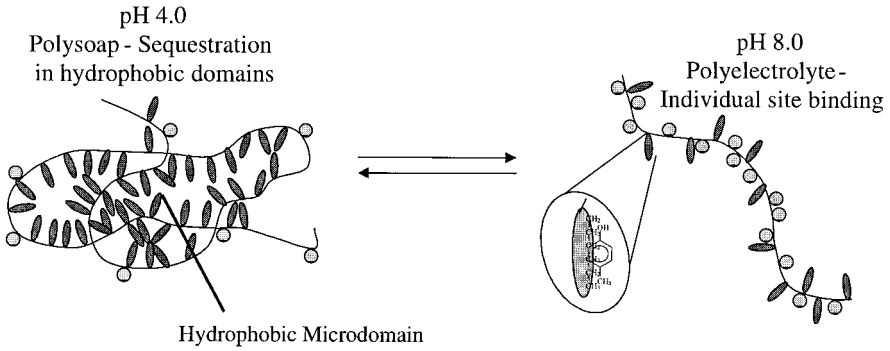

Figure 6 Mechanism of binding by C8–MA–EVE copolymers in the polysoap form at pH 4.0 and the polyelectrolyte form at pH 8.0.

Table IV Light Scattering Results Reflecting Electrolyte-Dependent Aggregation of BSA at pH 2.0

	Hydrodynamic Diameter (nm)	Molecular Weight (g/mol)	Aggregation Number
pH 2.0, 0*M* NaCl	7	2.4×10^5	3
pH 2.0, 0.5*M* NaCl	28	4.0×10^5	6

namic diameters of 28 nm and aggregation numbers of 6. The aggregation appears to occur through the association of exposed hydrophobic patches along the surface of BSA.

To study the electrolyte-dependent sequestration of *p*-cresol by BSA, equilibrium dialysis experiments were conducted at pH 2.0 in the presence of and absence of 0.5 *M* NaCl. The binding isotherms and the measured hydrodynamic diameters are illustrated in Figure 7. The measured hydrodynamic diameters at pH 2.0 in the absence of NaCl remain constant at 7.0 nm for all concentrations of *p*-cresol studied, indicating retention of the trimer conformation. The binding isotherm for this conformation reveals a binding of approximately 19 molecules of *p*-cresol per protein chain. In contrast, the addition of 0.5 *M* NaCl drastically increases the molar binding of *p*-cresol. At concentrations of *p*-cresol less than 4 m*M*, the hydrodynamic diameter of the BSA-*p*-cresol aggregate is 30 nm, which corresponds to the size of protein aggregate in the absence of *p*-cresol at pH 2.0 in the presence of 0.5 *M* NaCl. However, as the concentration of *p*-cresol is increased above 4 m*M*, larger aggregates with average hydrodynamic diameters of 65 nm are observed. The formation of these larger aggregates does not seem to alter the binding mechanism as evidenced by the linearity in the binding isotherm.

The equilibrium dialysis experiments with BSA demonstrate a remarkable dependence on NaCl concentration for efficiency of sequestration of *p*-cresol. Although the values of the activity coefficients are similar (Table V), the rejection ratios indicate that the multimer at pH 2.0 in the absence of added NaCl has a low overall effectiveness in capturing *p*-cresol. A conceptual model illustrating the differences in the associative state of the protein and the corresponding uptake of *p*-cresol is depicted in Figure 8. This model is directly related to the unimer-to-multimer transition initially described by Strauss[72] and discussed more recently by our laboratories.[3,6]

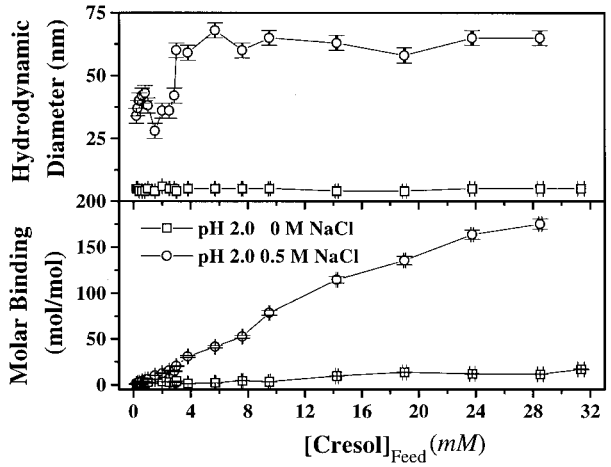

Figure 7 Binding isotherm for bovine serum albumin (BSA) and p-cresol at 25°C and the corresponding hydrodynamic diameter of the polymer–foulant complex as a function of *p*-cresol concentration ($C_{\text{protein}} = 1 \times 10^{-4M}$).

Modeling of the Sequestration of *p*-Cresol in a Remediation System

The rejection ratios calculated for each of the polymers reflect their respective abilities to capture *p*-cresol in a remediation process. Each polymer type exhibits considerable differences in binding isotherms and rejection ratios with changes in temperature, pH, or ionic strength of the system. These polymeric amphipaths compare very well with small molecule surfactants as potential remediative agents. Although the small molecule surfactants, such as hexadecylpyridinium chloride, have been shown to have rejection ratios of greater than 97%, these systems are plagued by the loss of surfactant across the filtration membrane.[21] The polymeric systems studied in this work are quantitatively retained by the filtration membrane and pose no threat as a potential pollutant in the cleaned water (permeate)

Table V Rejection Ratios and Activity Coefficients for BSA as a Function of pH and NaCl Concentration

	pH 2.0, 0*M* NaCl [Protein] $= 1 \times 10^{-4}M$		pH 2.0, 0.5*M* NaCl [Protein] $= 1 \times 10^{-4}M$	
$[p\text{-Cresol}]_{feed}$ (m*M*)	Rejection Ratio	Activity Coefficient	Rejection Ratio	Activity Coefficient
0.2	47 ± 3	9.8E-04	82 ± .3	2.8E-04
0.3	40 ± 2	1.4E-03	83 ± .3	3.3E-04
0.4	14 ± 1	4.2E-03	80 ± 2	5.0E-04
0.6	54 ± 2	1.5E-03	82 ± .2	6.0E-04
0.8	36 ± 1	2.7E-03	82 ± 2	8.0E-04
1.0	46 ± 1	2.7E-03	76 ± 2	1.2E-03
1.5	59 ± 2	5.7E-03	80 ± 2	1.5E-03
2.0	31 ± 1	8.2E-03	77 ± 2	2.2E-03
2.5	20.8 ± 0.6	0.01	77 ± 2	2.7E-03
2.8	2.5 ± 0.1	0.03	70 ± 3	3.4E-04
3.0	7.0 ± 0.2	0.02	70 ± 2	5.1E-03
5.7	8.0 ± 0.2	0.02	70 ± 2	7.5E-03
7.6	11.0 ± 0.3	0.02	70 ± 2	9.8E-03
9.5	6.7 ± 0.2	0.03	70 ± 2	0.01
14.2	12.6 ± 0.4	0.04	71 ± 2	0.02
19.0	13.5 ± 0.4	0.05	75 ± 2	0.02
23.7	9.5 ± 0.3	0.07	72 ± 2	0.03
28.5	7.8 ± 0.2	0.08	73 ± 2	0.03
31.3	10.2 ± 0.3	0.08	71 ± 2	0.03

stream. Although the rejection ratios for some of the systems are low, multiple passes through ultrafiltration devices may be utilized to achieve high removal of water foulants. In addition, the stimuli-responsive nature of the polymer microdomains offers an advantage over small molecule surfactants in that they may allow separation of the foulant from the polymer.

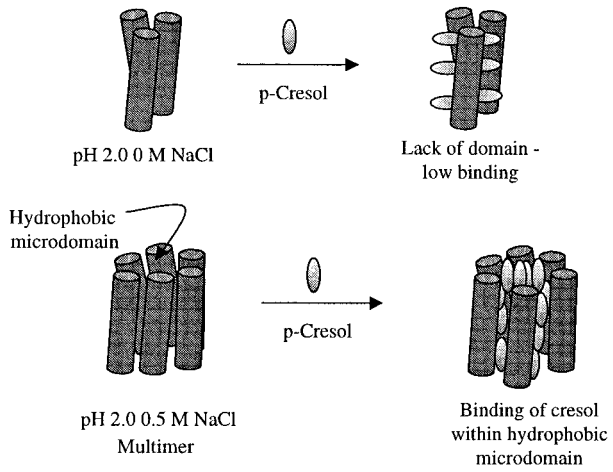

Figure 8 Conceptual model of the binding of p-cresol by BSA.

Using data from equilibrium dialysis experiments, the recovery of *p*-cresol with a multiple-pass filtration system connected in series may be projected (Table VI). The rejection ratios of the synthetic polymers allow a maximum recovery of 65% to 75% of the total *p*-cresol with five steps or passes. BSA shows a projected recovery rate with 98% recovered after only two filtration steps. As the concentration of the *p*-cresol drops, the rejection ratios remain high, with BSA yielding 99% recovery after five process steps.

In our studies, the average hydrodynamic diameters of the polymer aggregates are considerably large (25–100 nm). Therefore, in order to efficiently use these amphipathic polymers in a remediative process, one could select membrane pore sizes sufficiently large (~20–75 nm) such that high permeate flux could be obtained while still retaining the stabilized, foulant-filled polymeric micelles. Larger pore-size membranes would extend the current range of microfiltration, which would therefore decrease the transmem-

Table VI Calculated Recovery Percentages for Domain-Forming Water-Soluble Polymers with Multiple Pass Filtration[a]

	F127 (0.8 g/dL, 25°C)		MA-EVE (pH 4.0)		BSA (pH 2.0, 0.5*M* NaCl)	
Number of Passes	[*p*-Cresol] (m*M*)	% Recd	[*p*-Cresol] (m*M*)	% Recd	[*p*-Cresol] (m*M*)	% Recd
0	20.0	0	20.0	0	20.0	0.0
1	15.6	22	6.6	67	3.0	75.0
2	12.3	38	6.2	69	0.30	98.5
3	9.6	51	5.8	70	0.05	99.7
4	8.2	59	5.8	71	0.01	99.9
5	6.9	65	5.4	73	0.01	99.9

[a] Based on rejection ratios at the corresponding concentration of *p*-cresol.

brane pressure and fouling of the membrane surface.

CONCLUSIONS

The interaction of naturally occurring biopolymers and synthetic polymeric surfactants with *p*-cresol has been studied. By utilizing equilibrium dialysis and dynamic light scattering, we have examined the formation of polymer microdomains and the uptake of *p*-cresol as a function of pH, ionic strength, or temperature. The Pluronic™ F127 block copolymers form polymeric micelles and exhibit a unimer-to-multimer transition as a function of temperature. In the unimer state at low temperature and/or low polymer concentration, the uptake of *p*-cresol is limited. The addition of larger amounts of *p*-cresol to these systems nucleates the formation of polymeric microdomains and the binding of large amounts of *p*-cresol is realized. The hydrophobically modified C8–MA–EVE copolymers exhibit a pH-dependent, polysoap-to-polyelectrolyte transition. The C8–MA–EVE copolymers form polymeric micelles at low pH values and undergo a chain expansion with an increase in pH. At low pH, in the polysoap form, the C8–MA–EVE copolymers bind over 10,000 molecules of *p*-cresol per polymer chain. In the expanded polyelectrolyte form, lower binding is observed due to the disruption of the polymeric micelles. Bovine serum albumin undergoes an electrolyte-dependent aggregation at pH 2.0. It appears that the protein aggregate at pH 2.0 with 0.5 *M* NaCl forms a hydrophobic microdomain similar to those of small molecule surfactants. The domains formed within the aggregate have a high affinity for the *p*-cresol and retain greater than 83% of the *p*-cresol in a dialysis experiment. From these investigations, it has been demonstrated that stimuli-responsive polymeric surfactants may serve as alternatives to small molecule surfactants in wastewater remediative processes.

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