Electrolyte and pH Responsive Surfactant Association in Ionic Semi-Interpenetrating Networks Containing Cellulose or Chitin Synthesized in Lithium Chloride–*N*,*N*-Dimethylacetamide

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ABSTRACT: Semi-interpenetrating networks (SIPNs) of N,N-dimethylacrylamide (DMAm)-N,N-dimethylamino-ethylacrylamide (DMAEAm), or N,N-dimethylacrylamide (DMAm)-2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) containing cellulose or chitin were synthesized in 9% LiCl-N,N-dimethylacetamide (DMAc). The SIPNs were formulated to contain (1, 2, or 5% w/w) cellulose or 0.8% w/w chitin. Control systems (without polysaccharide) were also synthesized in 9% LiCl-DMAc. An acrylamide (Am)-AMPS hydrogel was synthesized for comparison with the SIPN composites. The swelling behavior of these materials was investigated as a function of pH (DMAEAm-containing networks) or electrolyte concentration (AMPS-containing networks). The DMAm-AMPS materials were found to have higher equilibrium water content (EWC) values in deionized water than the DMAm–DMAEAm materials. The EWC of the DMAm–DMAEAm materials was largest between pH 4 and 5 due to the protonation of the tertiary amine, with the chitin-containing material exhibiting the largest EWC. The DMAm-AMPS materials exhibited a decrease in EWC values with an increase in electrolyte concentration. Polymersurfactant interactions were shown to exist for surfactants of opposite charge of the ionic mer units incorporated into the polymeric network. Surfactant sequestration by the polysaccharide-containing materials was greater than that of the control gels; however, the rates of surfactant binding were lower. Release of the bound surfactant was achieved by the disruption of the charge-charge interactions by changing the pH of the medium (DMAEAm-containing networks) or by the addition of electrolyte (AMPS-containing networks). The DMAm–DMAEAm SIPNs released only 4% of the surfactant originally sequestered. By contrast, the DMAm-AMPS SIPNs released approximately 80%. The control Am-AMPS hydrogel-surfactant complex collapsed in the presence of electrolyte, and no surfactant was released from the complex. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 989-998, 1999

Key words: semi-interpenetrating networks; polysaccharides; responsive surfactant association

INTRODUCTION

Semi-interpenetrating networks are characterized by having one (or more) linear polymers contained within one (or more) crosslinked polymer networks.¹ Cellulose derivatives and chitosan have been utilized to formulate semi-interpenetrating networks $(SIPNs)^{2-5}$; however, the use of unmodified cellulose and chitin in composites has been limited due to lack of solubility in common organic solvents. The discovery of the 9% lithium chloride (LiCl)–N,N-dimethylacetamide (DMAc)

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solvent system^{6,7} has allowed the synthesis of many cellulose and chitin derivatives as well as the characterization of unmodified cellulose and chitin. Recently, this solvent was employed to prepare SIPNs with N,N-dimethylacrylamide, (DMAm) resulting in materials with enhanced mechanical properties.⁸ By incorporating triggerable monomer units within DMAm networks, the final composite materials resemble typical responsive hydrogel systems that are characterized by abrupt changes in the degree of swelling of the polymer network with changes in external stimuli, such as temperature, pH, ionic strength, or dielectric constant.⁹⁻¹⁴ Significantly, the increased mechanical properties of SIPNs forecast future use in many technologies, such as controlled release of pharmaceuticals or remediation of foulants from waste streams.

The interactions between polymer networks and surfactants have been extensively studied¹⁵⁻²⁷ and are reported to be governed by the following three effects: translational entropy of counterions, electrostatic forces, and hydrophobic interactions. The interactions between surfactants and water-soluble polysaccharide derivatives with varying degrees of hydrophobicity have also been investigated.²⁸⁻³⁵ It has been shown that hydrophobic regions along the polymer backbone serve as preferential binding sites for surfactant association and that the affinity of the polysaccharide for many surfactants increases upon the derivatization of the polysaccharide with hydrophobic moieties. However, surfactant association is also observed in unmodified polysaccharides since they exhibit high persistance lengths and often have crystalline/amorphous regions that are intricately networked by intra- and intermolecular hydrogen bonds. This complex hydrogen bonding results in hydrophilic/amorphous and hydrophobic/crystalline regions of the polysaccharide, which may serve to enhance surfactant associations with the polymer backbone.

It is the intent of this contribution to describe the synthesis of novel ionic SIPNs containing cellulose or chitin and the characterization of these materials with regard to the swelling behavior in various environments. As well, surfactant sequestration and release properties in the extremes of the environmental conditions are measured. It is our belief that the proper combination of charged monomers and hydrophobic monomers within a network can eventually result in an efficient system for the remediation and recovery of surfactants from waste streams.

EXPERIMENTAL

Materials

Reagent-grade cellulose (J. T. Baker) and chitin (Sigma) were used without purification. N,Ndimethylacrylamide (DMAm) (Aldrich) was vacuum-distilled prior to use. 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) (Aldrich) was recrystallized twice from methanol. N.N-methylenebisacrylamide (MBAm), and 2,2'-azobisisobutyronitrile (AIBN) were recrystallized twice from ethyl acetate and acetone, respectively. 9% (w/w) Lithium chloride (LiCl) solutions in N,N-dimethylacetamide (DMAc) were prepared at 100°C. The solvent was allowed to cool to room temperature before use. The cellulose and chitin were preswollen utilizing a technique reported by Mc-Cormick and Dawsey.³⁶ The lithium chloride was vacuum-dried to a constant weight. The DMAc was dried with barium oxide and stored over molecular sieves. All other reagents were obtained from Aldrich and used as received.

Preparation of *N,N*-Dimethylaminoethylacrylamide (DMAEAm)

This monomer was synthesized and purified as previously reported. $^{\rm 37}$

Polysaccharide Dissolution

Into a dry, 250-mL, three-necked flask fitted with nitrogen inlet/outlet and mechanical stirrer were added 100 mL 9% LiCl–DMAc and the appropriate amount of solvent-exchanged polysaccharide. The mixtures were stirred at room temperature for approximately 1 h for cellulose and 10 h for chitin. The chitin solutions were not completely dissolved, therefore filtration of solids was necessary.

DMAm-DMAEAm Control

The DMAEAm control system was formulated in a 100-mL round-bottom flask fitted with a septum, including inlet/outlet adapters. A 9% LiCl– DMAc solution (30 mL) was delivered into the flask, followed by 4.68 mL (4.5×10^{-2} mol) of DMAm, 0.666 g (4.0×10^{-2} mol) of DMAEAm, 0.225 g (1.0×10^{-3} mol) of MBAm, and 0.015 g (1.0×10^{-4} mol) of AIBN. The entire mixture was purged with nitrogen for approximately 10 min. The mixture was then transferred to 10 mm (i.d.) test tubes by syringe (approximately 10 mL for



Scheme 1 Proposed exchange/association site for sodium dodecylbenzyl sulfonate (NaDBS) with the protonated DMEAm-containing networks.

each test tube) with a nitrogen purge. The test tubes were then placed in a 60°C oil bath for 24 h. The samples were dialyzed in DMAc for 1 week to remove LiCl, then transferred into deionized water for continued dialysis for an additional week.

DMAm–DMAEAm Polysaccharide SIPNs

The SIPNs were prepared utilizing the same technique as the control system with one variation. The polysaccharide was dissolved in the solvent (9% LiCl-DMAc) to which the monomers, crosslinker, and initiator were added.

DMAm–AMPS Control

The DAMPS control system was prepared in the same manner as the DMAEAm control. A 9% LiCl–DMAc solution (30 mL) was delivered into the flask, followed by 4.68 mL (4.5 × 10⁻² mol) of DMAm, 0.444 g (2.0 × 10⁻³ mol) of AMPS, 0.225 g (1.0 × 10⁻³ mol) of MBAm, and 0.015 g (1.0 × 10⁻⁴ mol) of AIBN.

DMAm-AMPS Polysaccharide SIPNs

The SIPNs were prepared utilizing the same methodology as the DMAEAm SIPNs.

Acrylamide (Am)-AMPS Hydrogel

For a 30-mL formulation, 3.366 g $(4.74 \times 10^{-2} \text{ mol})$ of Am, 1.092 g $(5.0 \times 10^{-3} \text{ mol})$ of AMPS, and 0.041 g $(3.0 \times 10^{-4} \text{ mol})$ of MBAm were dissolved in deionized water. N, N, N'N'-Tetramethylethyl-enediamine (TEMED) (0.039 g, $3.0 \times 10^{-4} \text{ mol})$ and 6N sodium hydroxide (NaOH) were added to obtain a pH of 9.0. Deionized water was added to adjust the total concentration of monomers to 13 wt %. The solution was purged with nitrogen for 15 min, and 0.039 g (0.33 mol %) of ammonium persulfate were added. The polymerizing solution was transferred to 1.0-cm (i.d.) test tubes, where the gelation occurred in approximately 10 min at

0°C. The hydrogel was allowed to react in the test tube for 24 h to assure complete crosslinking.

Equilibrium Swelling

After dialysis of the SIPNs, the samples were air-dried at room temperature for 1 week and subsequently vacuum-dried at 50° C for 48 h to obtain the weight of the dehydrated SIPN. The individual samples were then allowed to swell for 3 weeks to obtain the weight of the hydrated SIPN. The equilibrium water content was calculated for each sample utilizing equation (1), as follows:

$$EWC = \frac{wt(SIPN) - wt(xeroSIPN)}{wt(xeroSIPN)}$$
(1)

where wt(SIPN) represents the weight of the SIPN in its hydrated state and wt(xeroSIPN) represents the weight of the SIPN in its dehydrated state. The EWC values were calculated as a mean of three samples.

Surfactant Uptake

Model surfactants containing an ultraviolet (UV) active moiety were selected for polymer–surfactant binding studies. The anionic surfactant, sodium dodecylbenzyl sulfonate (NaDBS), was selected for binding studies with the protonated tertiary amine containing networks, (DMAEAm SIPNs) at pH 3 and 6.4 (Scheme 1). The cationic surfactant, benzyldimethylhexadecyl ammonium chloride (BAC), was selected for binding studies with the sulfonate-containing networks (AMPS SIPNs) in deionized water and in 1*M* NaCl aqueous solutions (Scheme 2).

Absorbance measurements were performed with a Hewlett Packard 8452A Diode Array Spectrophotometer. The molar absorbtivity at 223 nm



Scheme 2 Proposed exchange/association site for benzyldimethylhexadecyl ammonium chloride (BAC) with the AMPS-containing networks.

Sample	Polysaccharide	DMAm	Ionizable Monomer	MBAm
		94	19	4
		04	12	4
C5DMAEAm	5	79	12	4
C10DMAEAm	10	75	11	4
CT5DMAEAm	5	80	11	4
C21DMAEAm	21	66	10	3
DAMPS	_	77	19	4
C5DAMPS	5	74	17	4
C10DAMPS	10	69	17	4
CT5DAMPS	5	74	17	4
C23DAMPS	23	60	14	3
		75		
AMPS hydrogel	_	(Am)	24	1

Table I Composition of the Components in the Control Systems and the SIPNs in the Dry State (Wt %)

 (ϵ_{223nm}) for NaDBS has been reported to be 1.31 \times 10^4 L mol^{-1} cm^{-1} in deionized water, 38 and ε_{226nm} for NaDBS was determined to be 1.15 \times 10⁴ L mol⁻¹ cm⁻¹ at pH 3. The molar absorbtivity at 210 nm for BAC was determined to be 6.36×10^3 and $6.21\times10^3\,L\,mol^{-1}\,cm^{-1}$ in deionized water and 1M NaCl, respectively. The depletion of free surfactant in solution was monitored by UV absorbance after contact with the SIPN sample as a function of time. Control experiments were conducted to correct for deswelling of the sample at the various environmental conditions. The concentration of surfactant in the SIPN was calculated by subtraction of the surfactant in the external solution from the original concentration of surfactant with a correction for deionized water expelled from the SIPN during the course of the experiment. The moles of surfactant bound per mole of ionizable moiety within the polymeric network were then calculated. It was assumed that the molar incorporation of ionic monomer units was equivalent to that of the feed.

Surfactant Release

At the completion of the uptake experiment, the DMAEAm SIPN (pH 3) samples and the AMPS SIPN (deionized water) samples were weighed and placed into fresh deionized water and 1M NaCl, respectively. The external solution was monitored at designated intervals for the appearance of surfactant. The percentage of surfactant released was calculated from the absorbance measurements taken from the external solution.

RESULTS AND DISCUSSION

Network Formation

The pH-responsive networks and SIPNs were prepared by the free radical initiation of the monomers, DMAm and DMAEAm, and crosslinking agent, MBAm in 9% LiCl–DMAc. Compositions are shown in Table I for the control network (DMAEAm) and for the SIPNs containing cellulose and chitin. Scheme 3 presents a generalized model of a typical SIPN, illustrating the rigid polysaccharides within a network of ionized crosslinked hydrogel structure with pendent ionizable units. The nomenclature in this document



Scheme 3 Chemical structure of the components of the semi-interpenetrating networks.

Table IIEquilibrium Water Content of SIPNsand the Control Systems in Deionized Water

Sample	EWC	
DMAEAm	43.9 ± 6.0	
C5DMAEAm	38.2 ± 4.9	
C10DMAEAm	37.8 ± 3.8	
CT5DMAEAm	39.5 ± 2.1	
C21DMAEAm	43.5 ± 2.5	
DAMPS	202.1 ± 12.2	
C5DAMPS	$128.1\pm~6.3$	
C10DAMPS	127.3 ± 7.4	
CT5DAMPS	126.3 ± 4.5	
C23DAMPS	190.2 ± 9.1	
AMPS hydrogel	153.0 ± 4.0	

for the networks containing cellulose is derived from the weight percentage of polysaccharide incorporated within the network. For example, C21DMAEAm represents DMAEAm network containing 21 wt % cellulose in the dehydrated state. The single system incorporating chitin within the DMAEAm network is designated CT5DMAEAm.

Below pH 4, the DMAEAm moieties are protonated, yielding a polycationic character of the network and high degrees of swelling. When aqueous hydrochloric acid is utilized to lower pH, the resulting ammonium chloride moieties provide sites for interaction/exchange with the surfactant, sodium dodecylbenzyl sulfonate (NaDBS).

SIPNs were prepared by the free radical initiation of the monomers, DMAm and AMPS, and crosslinking agent, MBAm in 9% LiCl-DMAc. These AMPS containing SIPNs are not pH-responsive (due to the pKa value of the sulfonate group); however, these networks are electrolyteresponsive. Compositions and sample designations are shown in Table I for the control network (DAMPS) and for the SIPNs containing cellulose and chitin. In deionized water, the AMPS moieties are ionized providing sites for binding/ion exchange with the surfactant, benzyldimethylhexadecyl ammonium chloride (BAC). When external electrolyte is added, the AMPS moieties are shielded, and the polymer network collapses. This collapsed state is not conducive to interaction/exchange with the surfactant BAC.

The incorporation of the ionizable monomers (DMAEAm and AMPS) into the formulation of these SIPNs does not cause any precipitation of the polysaccharide, and the formulations remain homogeneous throughout the course of the polymerization.

Equilibrium Water Content

Table II presents the equilibrium water content (EWC) for all of the SIPNs and the control systems in deionized water at pH 6.4. In comparison with the initial SIPN system, DMAm,⁸ these systems are more hydrophilic due to the incorporation of the ionizable monomers. The AMPS systems have much higher EWCs than the DMAEAm systems because the sulfonic acid of the AMPS monomer is completely ionized in water, while the protonated tertiary amine is only partially ionized at pH 6.4. In both systems, there is an observable decrease in the EWC with increasing incorporation of polysaccharide (with the exception of the highest wt % cellulose SIPNs). The highest wt % cellulose SIPNs exhibit unique behavior since the volume fraction of polysaccharide allows synergistic intermolecular interactions between the extended cellulose chains within the network. This creates free volume within the network, which allows good solvation (high EWC) while providing superior mechanical properties.⁸

With the incorporation of the ionizable monomers, DMAEAm and AMPS, all SIPNs exhibit swelling responses to external stimuli. The swelling response of the DMAEAm systems as a function of pH is shown in Figure 1. At pH values greater than 7, the tertiary amine moieties are unprotonated; therefore, low EWCs are obtained. When the pH is lowered, the tertiary amine moieties become protonated, and the EWC values increase exhibiting a maximum between pH val-



Figure 1 Equilibrium water content of DMAEAm systems as a function of pH.



Figure 2 Equilibrium water content of DAMPS systems and the AMPS hydrogel as a function of added electrolyte.

ues of 4 and 5. When the pH is lowered to 3, the ionic strength of the aqueous medium is sufficient to collapse the networks, and decreasing EWC values are observed. The CT5DMAEAm SIPN exhibits the largest swelling response which maybe due to the additional protonated amine moieties (deacetylated mers) along the chitin backbone. The amine content in chitin may also contribute to the shift observed in the maximum pH response. By comparison, cellulose has no groups that can serve as additional ionizable sites and may be the rationale behind the dampened pH response exhibited by the C21DMAEAm SIPN.

As expected, all of the AMPS containing SIPNs and the AMPS hydrogels exhibit decreases in EWC as the concentration of added electrolyte increases (Fig. 2), a result of screening of charge– charge repulsions inherent within the polymer networks. The sensitivity to the external electrolyte is retarded as the concentration of the polysaccharide is increased, with the exception of C23DAMPS.

NaDBS Surfactant Uptake by DMAEAm Containing SIPNs

The DMAEAm polymer networks exhibit changes in EWCs as a function of pH; therefore, reversible binding of anionic surfactant is expected, provided the polymer networks maintain sufficient accessibility. The associations between the anionic surfactant sodium dodecylbenzyl sulfonate (NaDBS) and the DMAEAm-containing networks were investigated in aqueous HCl solution (pH 3) and in deionized water (pH 6.4).

The percentages of surfactant (NaDBS) bound within the DMAEAm-containing networks in



Figure 3 (A) Percentage of surfactant bound by the DMAEAm systems in aqueous HCl (pH 3) and DI H_2O (pH 6.4). (B) Moles of surfactant bound per mole of DMAEAm in aqueous HCl (pH 3) and DI H_2O (pH 6.4).

aqueous HCl (pH 3) and in deionized water (pH 6.4) are shown in Figure 3(A). At pH 3, the tertiary amine moiety of DMAEAm is protonated and exhibits an electrostatic affinity for the anionic surfactant (NaDBS), forming an ion pair (and releasing sodium chloride). Higher degrees of binding in aqueous HCl (pH 3) are observed for every DMAEAm-containing system than in deionized water (pH 6.4). At pH 3, the chitin containing DMAEAm SIPN (CT5DMAEAm) binds the highest percentage (60%) of surfactant due to the additional ionizable sites provided by the (deacetylated mers) free amine of chitin. In addition to electrostatic attraction, there is the possibility of hydrophobic associations of the surfactant to the polysaccharide-containing DMAEAm networks. It is likely that cellulose forms hydrophobic microdomains within the polymeric network due to the intra- and intermolecular hydrogen bonding of the hydroxyl moieties. Such postulated hydrophobic microdomains would enhance surfactant binding in the materials that contain polysaccharide compared to the control hydrogel. This is consistent with experimental results.

In deionized water (pH 6.4), the percentage of NaDBS bound to the DMAEAm-containing polymer networks is much lower than at pH 3 [Fig. 3(A)]. At pH 6.4, the number of potential binding sites is diminished, and a decrease in binding is evidenced. Even in this unfavorable environment, the 21 wt % cellulose containing DMAEAm SIPN is able to bind more surfactant (NaDBS) than the control through hydrophobic interactions.

Figure 3(A) also shows that the DMAEAm control system binds NaDBS at a faster rate than the polysaccharide containing SIPNs. The presence of the polysaccharide in the latter retards the kinetics of the surfactant uptake by decreasing the diffusion of the surfactant into the SIPN materials.

In Figure 3(A), the accessible binding sites of the DMAEAm polymeric networks become saturated since substantial amounts of surfactant remain free in solution. The determination of the moles of surfactant bound per binding site (ionizable moiety) provides a means of evaluating the efficiency of sequestration. The moles of surfactant bound per protonated tertiary amine within the DMAEAm materials in aqueous HCl (pH 3) and in deionized water (DI H₂O) (pH 6.4) are shown in Figure 3(B). In an aqueous environment (pH 3), both the 21 wt % cellulose and 5 wt % chitin containing DMAEAm SIPNs have higher quantities of NaDBS per tertiary amine site than the control hydrogel (DMAEAm). As stated previously, the hydrophobicity and/or additional site accessibility of the polysaccharide containing DMAEAm SIPNs contributes to the binding of additional surfactant; therefore, larger ratios are observed. In deionized water (pH 6.4), the moles of NaDBS bound per mole of protonated tertiary amine moieties are substantially lower for all three systems than at pH 3. This is expected due to the lower degree of ionization of the polymer network [Fig. 3(B)]. The ratio of bound surfactant to moles of ionic site approaches but does not exceed one. This is indicative of an equilibrium exchange mechanism dominating the surfactant binding process and seems to preclude hemimicelle formation around the binding site.

BAC Surfactant Uptake by AMPS Containing SIPNs

The AMPS containing polymer networks exhibit changes in EWC as a function of externally added electrolyte; therefore, reversible binding of cationic surfactant should also be possible, provided the polymer networks maintain sufficient accessibility for diffusion of surfactant to the anionic binding sites. The association of a cationic surfactant benzyldimethylhexadecyl ammonium chloride (BAC) with the AMPS containing networks was monitored in aqueous NaCl solution (1*M*) and in deionized water.

The percentage of surfactant sequestered by the AMPS systems is shown in Figure 4(A) as a function of time in 1*M* NaCl and deionized water. In deionized water, all of the AMPS-containing materials sequester the cationic surfactant BAC at the same rate. The high ionic content of these crosslinked polymer networks allows for high water content within the network; this does not appear to hinder diffusion of the surfactant. The two polysaccharide-containing AMPS SIPNs sequester more than the control DAMPS material, again due to morphology, allowing increased hydrophobicity and/or access to more sites. In 1M NaCl, the AMPS systems are in a collapsed state as all of the ionized sites within the systems are shielded. This 1M NaCl environment neutralizes the electrostatic forces and eliminates the primary driving force for surfactant penetration into the network.

The moles of BAC bound per mole of sulfonate moieties are shown in Figure 4(B) as function of time in 1M NaCl and deionized water. As expected, the AMPS materials exposed to the 1M NaCl environment have low ratios of BAC per site



Figure 4 (A) Percentage of surfactant bound by the DAMPS systems in aqueous NaCl (1M) and DI H₂O. (B) Moles of surfactant bound per mole of AMPS in aqueous NaCl (1M) and DI H₂O.

due to the screening of charge-charge attraction. In deionized water, the control and the chitincontaining AMPS materials have similar profiles with equilibrium values of 0.7 mol BAC per mole of binding sites. The 5 wt % chitin AMPS SIPN (CT5DAMPS) has a higher equilibrium value approaching 1.0 mol BAC per binding site in 25 h, suggesting a morphology conducive to efficient migration and binding via an ion exchange mechanism.

Surfactant Release

Since it has been shown that these novel, ionic SIPNs exhibit the capacity to bind surfactants of opposite charge, the next phase of this investigation probed the ability of these materials to reversibly release the captured surfactant. The surfactant-loaded (pH 3) DMAEAm and deionized water AMPS samples were placed in 50 mL of surfactant-free, deionized water and 1*M* NaCl, respectively, and the external water was monitored for the appearance of free surfactant.

Figure 5(A) illustrates the percentage of NaDBS released from the pH 3 DMAEAm materials in deionized water. When the protonated DMAEAm samples (fully loaded with surfactant) are placed in deionized water, the osmotic swelling forces are small due to strong ion pairing and hydrophobicity of the local network. Therefore, each of the DMAEAm systems released only 4% of the surfactant originally sequestered.

The AMPS composite materials released approximately 80% of the initially bound surfactant when placed in 1M NaCl, as illustrated in Figure 5(B). Surfactant release is proposed to occur through a reversible ion exchange mechanism between the sodium cation and the surfactant cation. However, in the case of the AMPS hydrogel, the sulfonate group complexes strongly with BAC. Addition of 1M NaCl causes total network collapse and retention of surfactant. The morphology of the AMPS composite materials allows reversible accessibility of surfactant to binding sites. The increased crosslinking density (more MBAm) and the network reinforcement by polysaccharide chains are likely to be responsible for preventing the collapse.

CONCLUSIONS

Novel ionic SIPNs have been prepared with DMAm–DMAEAm or DMAm–AMPS and unmod-



Figure 5 Percentage of surfactant released from (A) DMAEAm samples in deionized water and (B) DAMPS samples in 1*M* NaCl.

ified cellulose or chitin utilizing a 9% LiCl–DMAc solvent system. The AMPS materials have higher EWC values than the DMAEAm materials, reflecting higher hydrophilicity. The pH swelling properties of the DMAEAm materials show maximum EWC values between pH 4 and 5. All of the AMPS materials exhibit a decrease in EWC values with an increase in the concentration of added electrolyte.

The surfactant sequestration behavior of polysaccharide-containing DMAEAm SIPNs is better than that of the control material; however, the rates of surfactant uptake are lower due to the hindered diffusion of the surfactant through the SIPNs. The chitin-containing DMAEAm system exhibits enhanced surfactant uptake with very little addition of polysaccharide due to the additional free amine (deacetylated mers) moieties. The polysaccharide-containing AMPS materials are able to sequester surfactant to a higher extent than the control DAMPS hydrogel in deionized water. The control AMPS hydrogel is able to sequester more surfactant than any of the composite materials due to the lower crosslinker density. The ratio of moles of surfactant bound per moles of binding site remain less than one indicating an ion exchange mechanism of binding, with no formation of hemimicelles along the polymer backbone.

Release of captured surfactant in the DMAEAm materials is diminished due to the hydrophobicity of the systems, thus limiting the recyclable nature of these materials in a water remediation application. By contrast, the AMPS composite materials release nearly 80% of the surfactant that they originally sequestered. Further work is in progress to optimize the AMPS SIPN systems in order to produce a mechanically robust hydrogel system capable of reversible capture/release of cationic surfactants.

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