

Reswelling of Polyelectrolyte Hydrogels by Oppositely Charged Surfactants

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The interactions between charged alkylacrylamide gels of varying hydrophobicity and charge density and the oppositely charged surfactant hexadecyltrimethylammonium ($C_{16}TA^+$) have been investigated to determine the conditions necessary to induce excess surfactant binding (beyond charge neutralization) and resolubilization of the polymer–surfactant complex. In all cases, an initial gel collapse occurred due to neutralization of the charges in the gel, and the volume of the collapsed gel was smaller than that of the corresponding neutral gel at the same surfactant concentration, as a result of the formation of interchain micellar cross-links. For gels containing neutral repeating units that were found previously to bind $C_{16}TA^+$, a subsequent sharp reswelling of the gel network occurred, beginning at a critical surfactant concentration called the $cac(2)$. The reswelling is due to binding of excess surfactant, which results in the gels becoming recharged. For gels whose neutral repeating units do not bind $C_{16}TA^+$, there was no reswelling behavior (no $cac(2)$), but there was a gradual increase of the swelling back to that of the equivalent neutral gel with increasing surfactant concentration. The results are interpreted in terms of the expected surfactant binding isotherm.

Introduction

Polyelectrolytes (both natural and synthetic) interact very strongly via electrostatic attractions with oppositely charged surfactants,¹ with the onset of interaction occurring at the critical association concentration (cac), far below the cmc of the surfactant. Taking into account the strong tendency of surfactants to self-associate, polymer–surfactant complexation is essentially a surfactant micellization in the presence of polymer, and thus, the cac is the surfactant cmc in the polymer solution.²

The use of simple gel swelling experiments to study the interactions of ionic surfactants with neutral and polyelectrolyte gels has been established recently.^{3,4} Such swelling experiments can distinguish between associating and nonassociating polymer–surfactant pairs. It was found that binding is evidenced by a change in the gel volume at the cac .³ The general features of the swelling curve for polyelectrolyte gels, which exist as highly swollen networks in water due to the osmotic pressure of the counterions to the charged groups, is first a deswelling at low surfactant concentration, starting at the cac (which is typically very low), as the bound surfactant neutralizes the hydrogel charges, and then, for some polyelectrolyte gels, a reswelling at a surfactant concentration called the $cac(2)$, due to binding of excess surfactant which recharges the gel.⁴ It has been shown that this reswelling behavior is analogous to the resolubilization that occurs for the corresponding linear polymers at relatively low surfactant concentrations. The resolubilization is important, for example, in hair conditioner formulations, where the polymer must be soluble at high surfactant concentration and precipitate as the surfactant concentration is increased by dilution (rinsing).

A sharp reswelling (resolubilization) of polyelectrolyte gels, indicating the presence of a $cac(2)$ and due to cooperative binding of excess surfactant beyond charge neutralization, has been reported for both cationic gels^{4–9} and anionic gels^{10–14} in the presence of oppositely charged surfactants. The binding of

excess surfactant by the gel network is seen as the second step of the binding isotherm, where the first binding step starts at the normal cac of the oppositely charged gel–surfactant system. However, the requirements for obtaining a second binding step are not clear. Suggestions have been made in the literature that the charge density must be low or intermediate^{14,15} and the polymer network must not be too rigid.¹⁶

In this work, gel swelling experiments have been used to determine the effect of network charge density and hydrophobicity on the resolubilization of the polymer–surfactant complex of the cationic surfactant hexadecyl trimethylammonium bromide ($C_{16}TABr$) with anionic hydrogels. The gels used are a series of alkylacrylamides, *N,N*-dimethylacrylamide (DAM), *N*-isopropylacrylamide (NIPA), and a copolymer of NIPA and *N*-*tert*-butylacrylamide (BAM), containing 20 mol % BAM. The alkylacrylamide gels were chosen because they have the most basic network structure possible, simply the backbone polymer and the cross linker, with no added side chains or other modifications. Thus, the increasing hydrophobicity comes from the polymeric backbone itself, as the NIPA monomer contains a bigger alkyl group than the DAM monomer, and hence is a little more hydrophobic, and similarly, the BAM monomer has a bigger alkyl group again. The swelling of the same series of neutral alkylacrylamide gels has been investigated in an accompanying paper,¹⁷ and the DAM gel was found not to interact with $C_{16}TA^+$ surfactants, while the more hydrophobic NIPA and BAM/NIPA (20:80) gels were found to interact with $C_{16}TA^+$ surfactants.¹⁷ Charges are introduced into the gels by copolymerization with sodium acrylate (NaA). For each of the gels, the effect of increasing charge density on the swelling behavior and the existence or not of a $cac(2)$ was investigated.

Experimental Section

Materials. *N*-Isopropylacrylamide (NiPAAm) monomer (purity >99%) from Phase Separations Ltd. (Clwyd, U.K.), was recrystallized twice from hexane. The following chemicals were

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used as supplied: *N*-*tert*-butylacrylamide (BAM) and *N,N*-dimethylacrylamide (DAM), from Fluka (Dorset, England); sodium acrylate (NaA) monomer (purity 97%), from Aldrich (Wisconsin, USA); *N,N'*-methylene-bisacrylamide (BisAM) cross-linker (purity 99%+) and ammonium peroxydisulfate (APS) initiator (purity 98%+), from Aldrich (Dorset, England); *N,N,N',N'*-tetramethylethylenediamine (TEMED) (promoter), from Sigma (Missouri, USA); hexadecyl trimethylammonium bromide (C_{16} TABr) (purity 98.5%, cmc 0.9 mM), from Merck (Germany). All water used was of Milli-Q (Millipore) quality and was degassed before use.

Synthetic hydrogels of increasing hydrophobicity were prepared by a standard method.^{19,20} An aqueous solution containing 700 mM monomer (C_0) (composed of neutral monomer and NaA in the required amounts) and 8.6 mM cross-linker (*N,N*-methylene bisacrylamide) was degassed under vacuum, and 15 μ L of TEMED was added. Initiator concentration was 40 mg in 1 mL water, of which 100 μ L was added. The gelation reaction proceeded over 24 h at 4 $^{\circ}$ C. Due to the hydrophobic nature of BAM, it was not possible to dissolve more than 140 mM of it in aqueous solution, and thus a copolymer of it and NIPA was prepared (the gel composition was thus NaA/BAM/NIPA 20:20:60 for the 20 mol % charged gel). Gels were formed in glass capillaries of 1.4-mm internal diameter (d_0), cut into approximately 1.4-mm rods after gelation and washed in a large excess of Millipore water for 1 week. The amount of leachable product (unreacted monomer and short chain polymer not incorporated into the gel network) was determined to be negligible (<0.1%) from weight determination measurements (weight of gel dried immediately after synthesis minus the weight of the same gel dried after washing in copious amounts of water for 1 week). Thus, we can assume that the actual concentrations in the gels are equivalent to the feed concentrations.

Gel Swelling Experiments. Gel swelling measurements were carried out as described previously.³ Washed gel rods were immersed in flat-bottomed vials, each containing one rod and 8 mL of surfactant solution. The gels rods were allowed to equilibrate at 25 $^{\circ}$ C for 1 week prior to measurement (also at 25 $^{\circ}$ C). The swelling is given as V/m , where V is the gel volume and m is the mass of monomer at synthesis. V/m was calculated as $(d/d_0)^3/C_0$, where d is the diameter of the gel in surfactant solution, determined using a video camera calibrated with a 0.1-mm scale and an image processing program.²¹

Results

Charge Density—DAM Gels. Figure 1 shows swelling isotherms for NaA/DAM gels of increasing charge density in C_{16} TABr solutions. It was established in the accompanying paper that neutral DAM gels do not bind C_{16} TABr, as there was no evidence of a swelling behavior or a cac.¹⁷ From Figure 1, it is clear that in the case of charged NaA/DAM gels, there is an immediate (starting at a very low cac) binding of the surfactant, resulting in a gradual gel deswelling as the osmotic pressure within the gel is reduced as a result of the release of the small counterions. The deswelling is monotonic with surfactant concentration, and for the 100% poly(sodium acrylate) gel, we were unable to observe a cac, as shown in Figure 2, where the data from Figure 1 is shown on a linear scale. It can also be seen in Figure 1 that the charged gels collapsed to a smaller volume than that of the corresponding neutral gel, indicating the presence of an attractive force, due to the polymer-bound micelles forming cross-links between nonadjacent network segments. There is no evidence of a cac(2) in Figure 1,

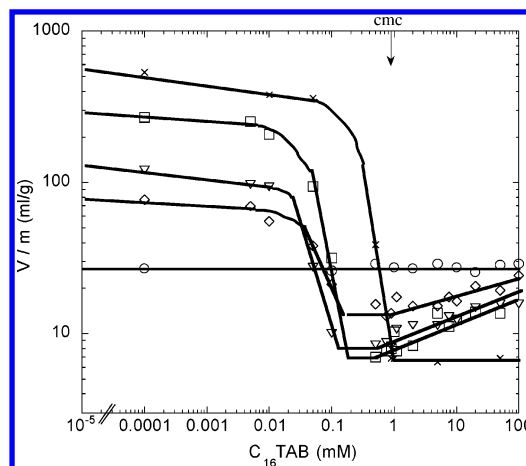


Figure 1. Equilibrium swelling isotherms for NaA/DAM gels of increasing charge density immersed in solutions of C_{16} TABr. (○) uncharged; (◇) 5 mol % NaA; (▽) 10 mol % NaA; (□) 20 mol % NaA; (X) 100% NaA. The arrow denotes the cmc. Lines are guides to the eye only.

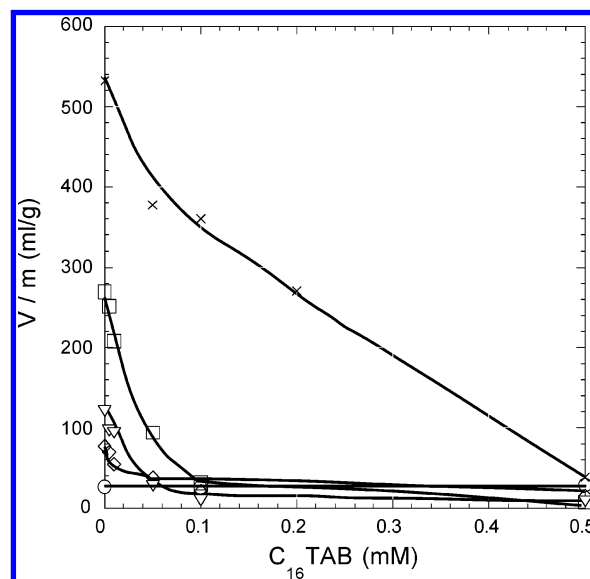


Figure 2. Equilibrium swelling isotherms for NaA/DAM gels of increasing charge density immersed in solutions of C_{16} TABr represented on a linear scale, and showing only the first few points at very low C_{16} TAB concentrations. (○) uncharged; (◇) 5 mol % NaA; (▽) 10 mol % NaA; (□) 20 mol % NaA; (X) 100% NaA.

and no reswelling (resolubilization) of the gel—surfactant complex, regardless of the charge density; however, there is a significant but gradual reswelling of the gel—surfactant complex at high surfactant concentration.

The effect of increasing charge density on the swelling of anionic DAM gels in pure water is shown in Figure 3(a). The gel volume increases approximately linearly with increasing charge density, due to the increased internal osmotic pressure introduced by the freely mobile counterions associated with the charged groups. At higher charge densities, the gel volume in pure water levels off, probably due to counterion condensation, although it could also be argued that the leveling off is due to limiting extensibility of the network subchains. For a 100 mol % NaA gel, the swelling degree in pure water was 532 mL/g.

The swelling of DAM gels of increasing charge density in C_{16} TABr solutions is shown in Figure 3(b). Two trends are apparent from the plot. First, at constant surfactant concentration, increasing the charge density reduces the degree of swelling; however, the effect appears to level off at about 20 mol %

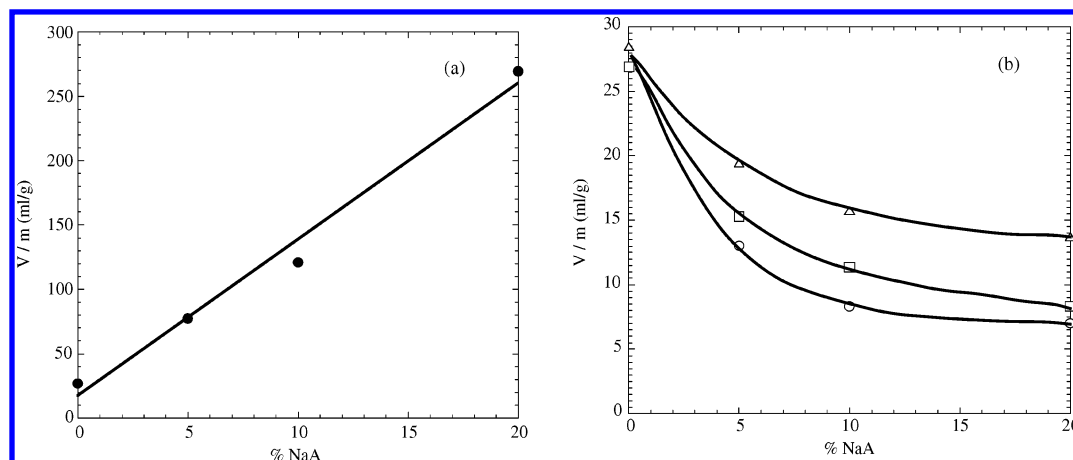


Figure 3. Equilibrium swelling of NaA/DAM gels as a function of the charge density (mol % NaA). (a) In pure water, and (b) in solutions of $C_{16}TABr$: (○) minimum swelling (0.5–0.9 mM); (□) 2 mM; (△) 50 mM. Lines are guides to the eye only.

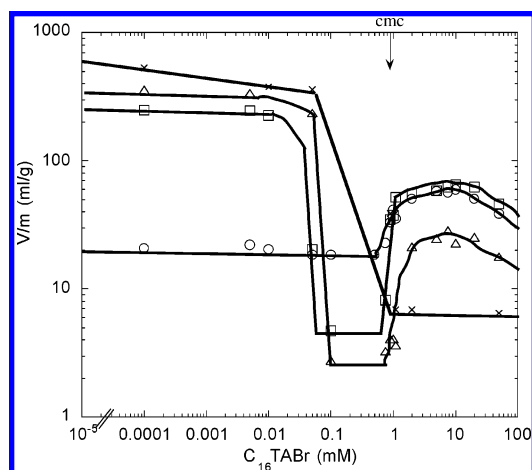


Figure 4. Equilibrium swelling isotherms for NaA/NIPA gels of increasing charge density immersed in solutions of $C_{16}TABr$. (○) uncharged; (□) 20 mol % NaA; (△) 50 mol % NaA; (X) 100 mol % NaA. The arrow denotes the cmc. Lines are guides to the eye only.

charges. Second, at a particular charge density, e.g., 20 mol % NaA, the gel volume increases with increasing $C_{16}TABr$ concentration, indicating a weak reswelling behavior. At $C_{16}TABr$ concentrations below the cmc (0.5–0.9 mM), the 20 mol % NaA gel is completely collapsed and its volume is significantly smaller than that of the neutral gel in water, as a result of the gel-bound micelles linking nonadjacent parts of the gel network (i.e., the micelles act as cross linkers).

Charge Density—NIPA Gels. Typical swelling curves for a copolymer gel whose neutral comonomer binds $C_{16}TABr$ are shown in Figure 4, where the swelling of NaA/NIPA gels of increasing charge density (mol % NaA) is plotted as a function of the surfactant concentration. The swelling of pure NaA is also shown for comparison. Neutral NIPA gels were shown in the accompanying paper to bind $C_{16}TABr$ and to swell at a surfactant concentration just below the cmc.¹⁷ As was the case for DAM gels, introduction of anionic charges into NIPA gel resulted in the gel deswelling dramatically upon initial addition of $C_{16}TABr$, as shown in Figure 4 where the NaA/NIPA gel with 20 mol % NaA units is fully deswollen at 0.1 mM $C_{16}TABr$. In contrast to the DAM gels, however, there is a subsequent strong reswelling of the charged NaA/NIPA gels at a surfactant concentration called the second cac or cac(2). This cac(2) corresponds to the cac of the neutral NIPA gel and is evidence that binding of excess surfactant occurs, resulting in the gel becoming recharged. Thus, as can be seen in Figure 4,

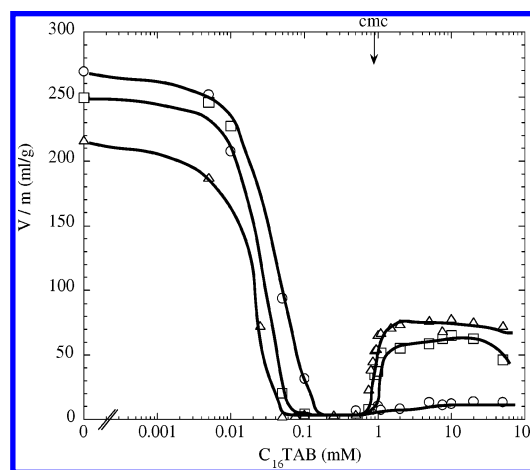


Figure 5. Equilibrium swelling isotherms for 20 mol % NaA gels with different hydrophobicity immersed in solutions of $C_{16}TABr$: (○) DAM gels; (□) NIPA gels; (△) BAM/NIPA (actual composition 20:20:60 NaA/BAM/NIPA). The arrow denotes the cmc. Lines are guides to the eye only.

increasing the $C_{16}TABr$ concentration to concentrations above cac(2) (1.0–10 mM) results in the gel volume increasing again, as a result of binding of excess surfactant. The same trend is apparent for the 50 mol % NaA gel, except that the cac(2) is higher and the degree of reswelling is less, which suggests that less excess surfactant is bound, and the reswelling behavior disappears at higher charge densities (pure 100 mol % NaA does not show any reswelling).

A further difference between the NIPA and the DAM copolymer gels was that the NaA/NIPA copolymers were more collapsed than the NaA gel at the swelling minimum, again pointing to an additional attraction between the polymer and the surfactant, which is missing in the NaA/DAM case.

Network Hydrophobicity. The requirement for a minimum amount of hydrophobicity in the gel network in order to induce excess binding of $C_{16}TABr$ is further illustrated in Figure 5, where the swelling behavior of the increasingly hydrophobic alkylacrylamide gels containing 20 mol % of the anionic monomer NaA in $C_{16}TABr$ solutions is plotted. For both NaA/NIPA and NaA/BAM/NIPA gels, in contrast to the NaA/DAM gels, the initial deswelling is followed by a dramatic reswelling. It can also be seen from Figure 5 that the degree of reswelling increases with increasing hydrophobicity of the network. Additionally, the cac(2) decreases slightly with increasing hydrophobicity of the network, as did the cac for the equivalent neutral gels,¹⁷ and the gel swelling in pure water, which increases with

increasing charge density as seen in Figure 3(a), decreases with increasing hydrophobicity of the network. Both of these swelling trends are well-known.

Discussion

Charged gels in the presence of oppositely charged surfactants undergo electrostatically driven surfactant binding, which results in the formation of polymer-bound surfactant micelles, where the micelles act as cross-linkers between parts of the network that would otherwise be far apart, resulting in the collapse of the gel. In some cases, additional cooperative surfactant binding, beyond charge neutralization, occurs at the $\text{cac}(2)$ and results in the disruption of the micellar cross-links and a subsequent resolubilization of the gel–surfactant complex, seen as a reswelling of the gel network.

The approximately linear initial decrease of the gel volume with increasing surfactant concentrations, observed in both the NaA/DAM and NaA/NIPA gels, and which proceeds until a stoichiometric polyion–surfactant complex has been formed at the swelling minimum, has been described in detail by other authors²² and is not our major concern here. Rather, we will focus on the effects of chain hydrophobicity for the swelling behavior.

One interesting result from Figures 1 and 4 is the effect of the neutral comonomers on the gel volume at the swelling minimum in comparison to the swelling minimum for the 100% charged NaA gel. Starting with the gel volume at the swelling minimum, we noted that this volume increased monotonically with an increasing content of the neutral DAM comonomer, which does not bind the surfactant (Figures 1–3). It is well-known that the structure of the stoichiometric CTA–polyacrylate complexes is a liquid crystal of surfactant aggregates, connected by the binding polyions.^{18,22,23} At high fractions of neutral comonomers, we expect that these will form neutral loops on the polyion. These loops will protrude into the solvent and give rise to an additional repulsion between the surfactant aggregates. Hence, an increased swelling of the stoichiometric polyion–surfactant complex is expected. The situation is different when the neutral comonomer also binds to the surfactant aggregate, as is the case for NIPA. In this case, the comonomer loops should not protrude into the solvent, but rather bind to the aggregate surface by short-range hydrophobic attractions. This, we believe, is the reason an additional shrinking, rather than a swelling, is observed for the NaA/NIPA gels compared to the NaA gel at the swelling minimum (see Figure 4).

Another striking difference between Figures 1 and 4 is the lack of a $\text{cac}(2)$ with the NaA/DAM gels (Figure 1) and the presence of a $\text{cac}(2)$ with the NaA/NIPA gels (Figure 4). Clearly, the requirement for a $\text{cac}(2)$ is that the surfactant interacts with the polymer backbone, and in order for this to happen the backbone polymer must be sufficiently hydrophobic. Thus, the key effect of gel hydrophobicity observed here is obviously that the degree of hydrophobicity can determine the presence or absence of a sharp reswelling at $\text{cac}(2)$. To obtain a molecular understanding of this observation, we should consider the expected binding isotherm of surfactant to the oppositely charged polyion in the two cases. This is schematically illustrated in Figure 6. Figure 6a shows the expected binding isotherm for a hydrophilic polyion, such as NaA or NaA/DAM copolymers. Initially, there is a high affinity binding that commences at the cac (very close to zero surfactant concentration) and proceeds until charge stoichiometry, where the ratio between bound surfactant ions and polyion charges, β , equals

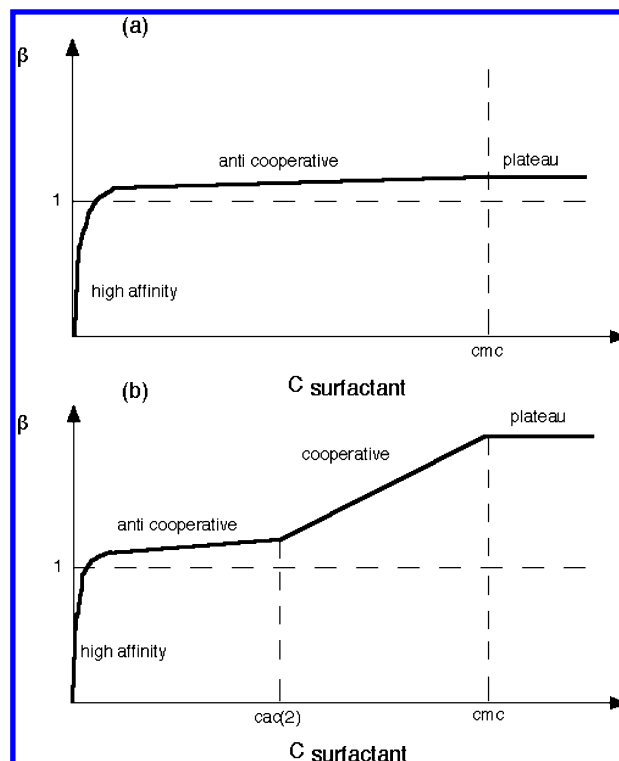


Figure 6. Schematic representations of the expected binding isotherms for (a) a hydrophilic polyion and an oppositely charged surfactant; and (b) for a hydrophobic polyion and an oppositely charged surfactant.

unity. From this point, further binding of surfactant will again increase the charge density of the aggregate. The binding thus becomes anti-cooperative; the affinity will be low initially and will decrease as more surfactant is added to the aggregate. This region of the isotherm will persist until a further leveling off occurs at the cmc of the surfactant. Beyond this point, free micelles are formed, and the chemical potential of the surfactant increases only very slowly with increasing surfactant concentration. Thus, not only is the affinity of the surfactant ion to the complex low, but also the driving force for further binding—the chemical potential of the surfactant—increases very slowly. This general picture—which is independent of details such as the charge density of the polyion—seems to explain why it should be difficult to obtain a charge reversal of the complex.

For a polyion that also binds surfactant by hydrophobic association, the situation is different, as depicted in Figure 6(b). The initial regions of the binding isotherm are unchanged, as is the plateau beyond the cmc , but a new cooperative binding occurs here at the $\text{cac}(2)$, which is the point at which interactions with the hydrophobic functionalities on the polymer give rise to additional surfactant binding. Depending on the cooperativity of this binding, saturation of the polymer hydrophobic groups with surfactant may or may not occur before the surfactant has reached the cmc . (In either case, there should be a leveling off of the binding beyond the cmc , as explained above.) It seems clear that the extent of binding above $\beta = 1$ should increase with an increasing amount of hydrophobic “binding sites”, i.e., in our case, the fraction of hydrophobic comonomers.

Conclusions

Introduction of charged groups into alkylacrylamide gels resulted in the gels undergoing a deswelling until charge neutralization, and then either no further changes with increasing surfactant concentration or a reswelling at the $\text{cac}(2)$. The cac -

(2) of an oppositely charged polyelectrolyte–surfactant complex is related to the cac of the corresponding nonionic polymer–ionic surfactant system. Thus, we can conclude that an interaction with the backbone polymer of the gel network is necessary in order to get a reswelling/resolubilization of the gel–surfactant complex, and that the presence of ionic groups alone is not sufficient to induce a second cooperative binding of C₁₆TABr and a resolubilization of the gel–surfactant complex.

The cac(2), at which resolubilization of the gel–surfactant complex occurs, was found to decrease slightly with increasing hydrophobicity, as did the corresponding cac in the equivalent neutral gels. The cac(2) increased slightly with increasing charge density at constant network hydrophobicity.

The swelling isotherms obtained for the NaA/NIPA gels with a cationic surfactant in this study closely resemble the sharp collapse, followed by a sharp reswelling that was previously observed for cat-HEC gels with anionic surfactants.⁴ These two gel types represent polymers that differ widely in stiffness. Thus, it seems that polymer flexibility is not an important factor to determine whether a second cooperative binding step occurs. Neither is charge density per se. A physical picture based on the expected binding isotherms can rationalize these observations.

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