Hydrophobicity and Counterion Effects on the Binding of Ionic Surfactants to Uncharged Polymeric Hydrogels

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Gel swelling experiments have been used to study the binding of ionic surfactants to a series of nonionic alkylacrylamide hydrogels of increasing hydrophobicity. The binding of hexadecyl trimethylammonium ($C_{16}TA^+$) to uncharged gels is sensitive to both the hydrophobicity of the gel and the counterion to the surfactant. There is a minimum hydrophobicity threshold below which binding of the surfactant does not occur, and this is influenced by the counterion to the surfactant. The surfactant concentration at the onset of binding, the critical association concentration (cac), decreases with increasing gel hydrophobicity. The maximum swelling of the gel (at intermediate network hydrophobicity) increases in the order of the Hofmeister series of anions, bromide (Br^-) < chloride (Cl^-) < acetate (Ac^-). At higher gel hydrophobicity, differences in swelling are no longer observed on changing the counterion. A minimum hydrophobicity threshold was also found for the binding of the anionic surfactants sodium dodecyl sulfate (SDS) and sodium dodecyl-di(ethylene oxide)-sulfate ($SD-(EO)_2-S$). Differences in the swelling behavior with network hydrophobicity are explained in terms of the degree of saturation of the gel with surfactant at the cmc.

Introduction

The use of simple gel swelling experiments to study the interactions of ionic surfactants with uncharged[1] and polyelectrolyte[2] gels has been established recently. Such gel swelling experiments give direct indication of interactions between the gel and the surfactant. For an uncharged gel, the occurrence of binding is evidenced by the gel swelling at a surfactant concentration called the critical association concentration, or cac.[1,3] The cac is typically close to, but below, the cmc (critical micelle concentration). The existence of a critical aggregation concentration reflects the cooperative nature of the binding process, which is actually a micelle formation at the polymer.[4] The binding of surfactant to neutral gels is driven by an interaction between the hydrophobic part of the surfactant micelle and the polymer network of the gel, which implies a hydrophobic interaction. Thus we are interested in the effect of gel hydrophobicity on the binding of the cationic hexadecyl trimethylammonium ($C_{16}TA^+$) surfactants. Previous investigations of the effect of network hydrophobicity have involved introduction of long alkyl side-chains which bind the surfactant,[1,2,5] and thus interactions with the network backbone have not been investigated.

The generic features of the swelling isotherm of nonionic gels in solution with an associating ionic surfactant were presented previously.[1] For neutral gels, the gel volume is more or less constant until the cac. At the cac, an onset of gel swelling is observed as the bound surfactant effectively transforms the gel into an ionic gel. The swelling results from an increase in the osmotic pressure due to dissociation of the counterions to the surfactant. The swelling maximum, which occurs at a surfactant concentration close to the surfactant cmc, corresponds to the point at which the gel becomes saturated with surfactant.[6] At the cmc, free surfactant micelles form in the bulk solution, and thus the surfactant binding levels off, regardless of whether the gel is saturated with surfactant at this point.[1] The swelling behavior of gels is the macroscopic manifestation of the behavior of linear polymers,[7] where complexation has been shown to begin at the cac,[8] and saturation takes place at increasing surfactant concentration.[9]

C_nTA^+ surfactants, with various alkyl chain lengths, are by far the most studied cationic surfactants, particularly the bromide and chloride salts.[7] There have been many indications that cationic surfactants interact more weakly with polymers than anionic surfactants, and thus that the polymers need to be more hydrophobic in order for cationic surfactants to bind.[7] Several explanations have been proposed for the weakness of the interaction between cationic surfactants and polymers. One such explanation is that the bulkiness of the cationic headgroup effectively shields the hydrophobic micellar core and thus there is less to gain by forming polymer−surfactant micelles.[10,11] Another suggestion is that there are differences in the interaction of cations and anions with the hydration sheath of the polymer, with anions having a more pronounced effect than cations.[12,13]

In this work, gel swelling experiments have been used to determine the effects of polymer hydrophobicity and surfactant counterion on the binding of $C_{16}TA^+$ to a series of nonionic hydrogels of increasing hydrophobicity. The gels used are a series of alkylacrylamides of increasing hydrophobicity, namely, *N*,*N*-dimethylacrylamide (DAM), *N*-isopropylacrylamide (NIPA), and an 80:20 copolymer of NIPA and *N*-*tert*-butylacrylamide (BAM). A hydroxyethyl cellulose (HEC) gel is included for comparison. 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. This means that any binding that occurs is due to an interaction between the surfactant and the polymeric backbone, both for the homopolymers (DAM and

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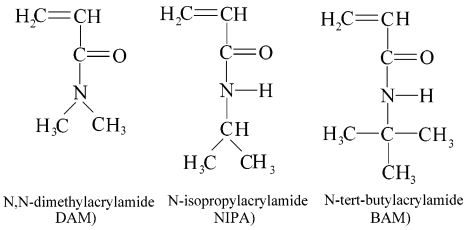

Figure 1. Structures of the alkylacrylamide monomers.

NIPA) and the copoplymer BAM/NIPA (20:80). The latter was prepared as a copolymer due to the insolubility of BAM in water at the concentration necessary to prepare a gel. The structures of the monomers used are given in Figure 1. The HEC gels, which have a more complex structure, are used for comparison purposes, as their swelling behavior has already been well characterized.[1]

Previous studies of the interaction between NIPA gels and cationic surfactants have, to date, been confined to C_{12}-surfactants, and the main emphasis has been on the effect of surfactants on the lower critical solution temperature (LCST) of the polymer.[14−17] In all studies, the binding of surfactant was found to increase the LCST, by making the polymer water-soluble at higher temperatures. In the case of HEC gels, several studies with cationic surfactants have been conducted, such as varying the surfactant tail length,[1] and the effect of various hydrophobic modifications, such as HMHEC,[1] EHEC,[18] and *cat*-HMHEC[18] (HM = hydrophobically modified, EHEC = ethyl hydroxyethyl cellulose, *cat*-HMHEC = cationic hydrophobically modified HEC). It was found that in contrast to the unmodified HEC gels, HMHEC, EHEC, and *cat*-HMHEC gels interact with cationic surfactants.

The surfactant used in the present study was $C_{16}TA^+$ with bromide (Br^-), chloride (Cl^-), or acetate (Ac^-) counterions. The cmc values of the counterions increase in the order $Br^- < Cl^- < Ac^-$. We report here that the binding of $C_{16}TA^+$ to neutral gels (both alkylacrylamide and HEC) is sensitive to both the hydrophobicity of the gel and the counterion to the surfactant. For comparative purposes, the interaction of the same series of gels with the anionic surfactants sodium dodecyl sulfate (SDS) and sodium dodecyl-di(ethylene oxide)-sulfate (SD−$(EO)_2$−S) was also studied. These two surfactants differ only by the presence of ethylene oxide spacer groups between the alkyl chain and the sulfate moiety in SD−$(EO)_2$−S.

Experimental Section

Materials. *N*-Isopropylacrylamide (NIPA) monomer (purity >99%), from Phase Separations Ltd. (Clwyd, U.K.), was recrystallized twice from hexane. The following chemicals were used as supplied: *N*-*tert*-butylacrylamide (BAM) and *N*,*N*-dimethylacrylamide (DAM), from Fluka (Dorset, England); *N*,*N*^{1}-methylene-bisacrylamide (BisAM) cross-linker (purity 99%+), from Aldrich (Dorset, U.K.); ammonium peroxydisulfate (APS) initiator (purity 98%+) and *N*,*N*,*N*^{1},*N*^{1}-tetramethylethylenediamine (TEMED) promotor, from Sigma (Missouri, USA); HEC (commercial name Natrosol 250 GR), from Aqualon; divinyl sulfone (DVS), from Sigma; NaOH, from Eka Nobel; hexadecyl trimethylammonium bromide (C_{16}TABr) (purity 98.5%), from Merck (Germany); hexadecyl trimethylammonium chloride (C_{16}TACl), from TCI-EP (Japan); and especially pure sodium dodecyl sulfate (SDS), from BDH. C_{16}TAAc was prepared from C_{16}TABr by an ion-exchange process according to the method of Svensson et al.[19] Dowex 1 ion-exchange resin (Sigma, USA) was activated by stirring in 1 M NaOH solution, followed by rinsing with copious amounts of deionized water immediately prior to use. Acetic acid (1 M) was prepared from a standard solution kit. Sodium dodecyl-di(ethylene oxide)-sulfate (SD−$(EO)_2$−S) from Kao Chemicals GmbH was a gift from Chematex AB in Täby, Sweden. It is a technical grade (28% aqueous solution), used without further purification, and the impurities were estimated from the molecular weight to be about 25% sodium tetradecyl-di(ethylene oxide)-sulfate (ST−$(EO)_2$−S). Cylindrical molds were Duron Ring caps from Hirschumann Laborgoräte (Germany), with a 1.4-mm internal diameter. All water used was of Milli-Q (Millipore) quality.

Values of cmc for C_{16}TAAc and SD−$(EO)_2$−S were determined by conductance measurements using a Metrohm 712 Conductometer, with a cell constant of 0.83 cm^{-1}. The cmc of C_{16}TAAc was determined to be 1.8 mM, and that of SD−$(EO)_2$−S was 2.2 mM, both at 23 °C.

Synthetic hydrogels of increasing hydrophobicity were prepared by a standard method.[20,21] An aqueous solution containing 700 mM monomer (C_0) and 8.6 mM cross-linker (BisAM) was degassed under vacuum, and 15 μL of TEMED was added. The initiator concentration was 40 mg in 1 mL of water, of which 100 μL was added. The gelation reaction proceeded over 24 h at 4 °C. Due to the hydrophobic nature of *N*-*tert*-butylacrylamide, 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 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 weight of the same gel dried after washing in copious amounts of water for 1 week).

HEC gels, from a batch of gels prepared previously, were prepared by cross-linking HEC with divinyl sulfone (DVS) in alkaline solution.[1] Concentrations used in the synthesis were HEC 20 g/L (C_0) and DVS 0.3 mL/g polymer, and 20 mM NaOH was added to the polymer solution. DVS was added under stirring, and the gelation reaction proceeded over 24 h at 50 °C.

All gels (alkylacrylamide and HEC) 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 HEC gels, which had been stored in Millipore water since their synthesis, had a higher swelling degree now than previously reported,[1] due to a moderate swelling with time. The HEC gels had swollen about 40% after 2.5 years in pure water.

Gel Swelling Measurements. Gel swelling measurements were carried out as described previously.[1] 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 °C for 1 week prior to measurement (also at 25 °C). The swelling is given as V/m, where V is the gel volume and m is the mass of monomer in the case of the alkylacrylamide gels, and the mass of linear polymer in the HEC gels, 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.[22] Using the initial monomer or polymer mass is an appropriate way to compare the swelling degree of gels prepared by different methods.

Results and Discussion

Cationic Surfactants. Figure 2 (a−d) shows the equilibrium swelling isotherms of DAM, HEC, NIPA, and BAM/NIPA

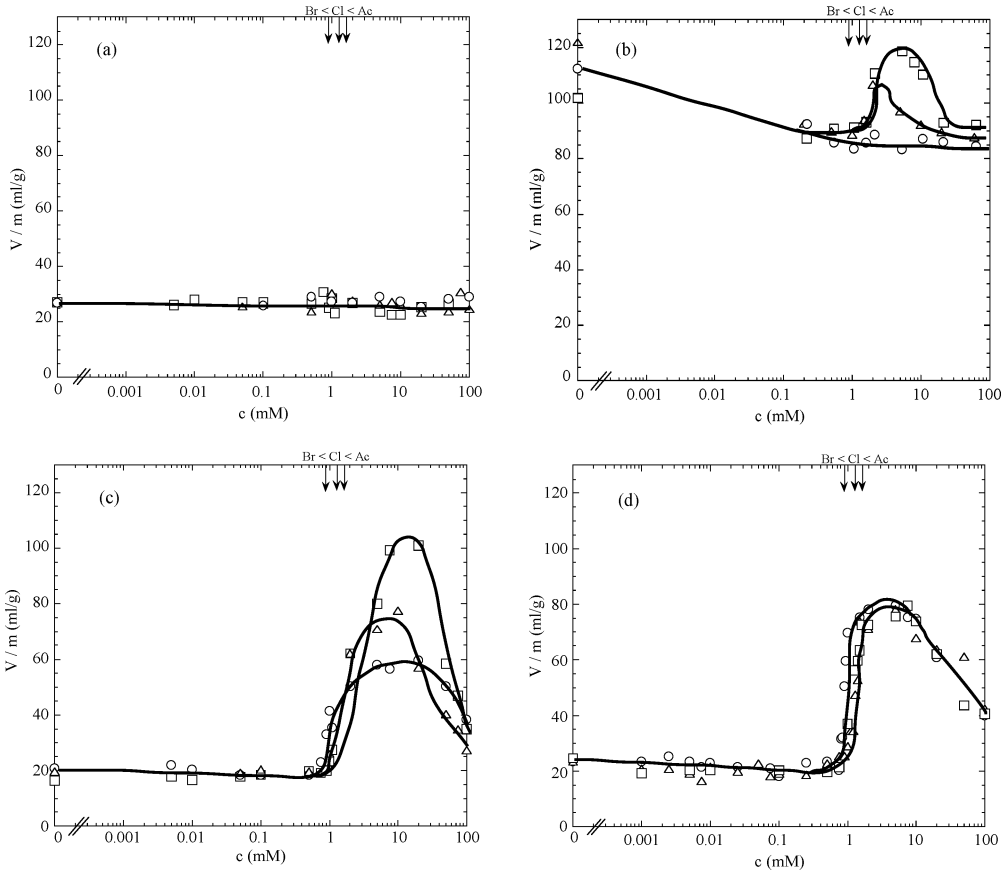

Figure 2. Interaction of neutral gels with $C_{16}TA^+$ surfactants: (a) DAM gels, (b) HEC gels, (c) NIPA gels, and (d) BAM/NIPA (20:80) gels. (○) $C_{16}TAB$, (△) $C_{16}TACl$, and (□) $C_{16}TAAc$. Arrows indicate the cmc values. Lines are guides for the eye only.

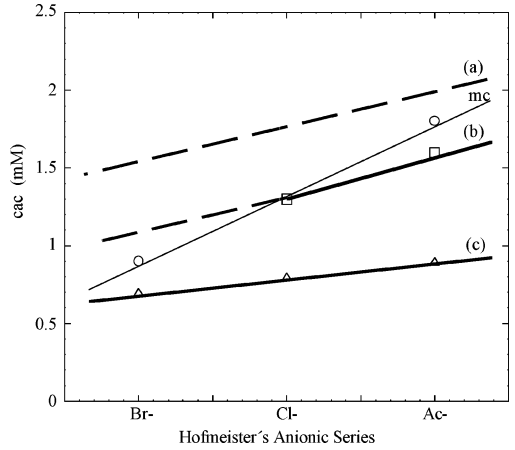

Figure 3. Schematic representation of the cmc:s and cac:s as a function of the Hofmeister's series of inorganic ions. (○) cmc of $C_{16}TAX$, (□) cac with HEC gel, and (△) cac with NIPA gel. The ions of the Hofmeister series have been placed in the known order, but the distance between the ions is schematic. The cac values come from Figure 2(a−c). Dashed lines are hypothetical and indicate where no cac was observed.

(20:80) gels in solutions with $C_{16}TA^+$. $C_{16}TA^+$ did not bind to DAM gels, regardless of which counterion was present in the surfactant, as shown in Figure 3(a), where there is clearly no swelling of the gels. NIPA gels were found to interact strongly with all $C_{16}TA^+$ surfactants, with the degree of swelling increasing in the order $Br^- < Cl^- < Ac^-$, as shown in Figure 3(c). Introduction of 20 mol % BAM groups into NIPA gels resulted in very hydrophobic gels, all of which interacted strongly with $C_{16}TA^+$, and without any dependence of the degree of swelling on which counterion was present, as shown in Figure 3(d). HEC gels do not interact with $C_{16}TA^+$ when bromide is the counterion, which has been reported previously,[1] but interact weakly when acetate is the counterion, as shown in Figure 3(b). Since the only change between the systems in Figure 3 (a,c,d) is the hydrophobicity of the gel network, it seems clear that the binding of $C_{16}TA^+$ to neutral alkyl acrylamide gels is hydrophobically driven. It is interesting to note that the chemically unrelated HEC gel appears to have a hydrophobicity intermediate between that of the DAM and NIPA gels, on the basis of its interaction with the $C_{16}TA^+$ surfactant—the extremely hydrophilic DAM gel does not bind $C_{16}TA^+$ with any of the counterions, HEC gels do not bind $C_{16}TA^+$ with Br^- as the counterion, but bind significantly with Ac^- as the counterion, while the more hydrophobic NIPA gel binds $C_{16}TA^+$ with all three counterions. Thus, we can conclude that the order of hydrophobicity of the gels is as follows: BAM/NIPA (20:80) > NIPA > HEC > DAM, and that there is a minimum hydrophobicity threshold necessary in order for $C_{16}TA^+$ surfactants to bind to gels, and that the threshold is sensitive to the counterion to the surfactant.

Figure 3 shows a representation of the information obtained from Figure 2 regarding the cac values of the gels with the different surfactant−counterion solutions. It is clear from Figure 3 that the cac line for the HEC gels intersects the cmc line when chloride is the counterion. Thus, the binding of $C_{16}TA^+$ to HEC gels is dependent on which counterion is present. The observation that there is no binding of $C_{16}TA^+$ to DAM gels for any of the counterions is obtained from Figure 3 by a dashed hypothetical line above the cmc line. It is evident from the figure that in order for there to be an interaction between a gel and $C_{16}TA^+$, the cac must be lower than the surfactant's cmc, and that the association between the gel and the surfactant disappears

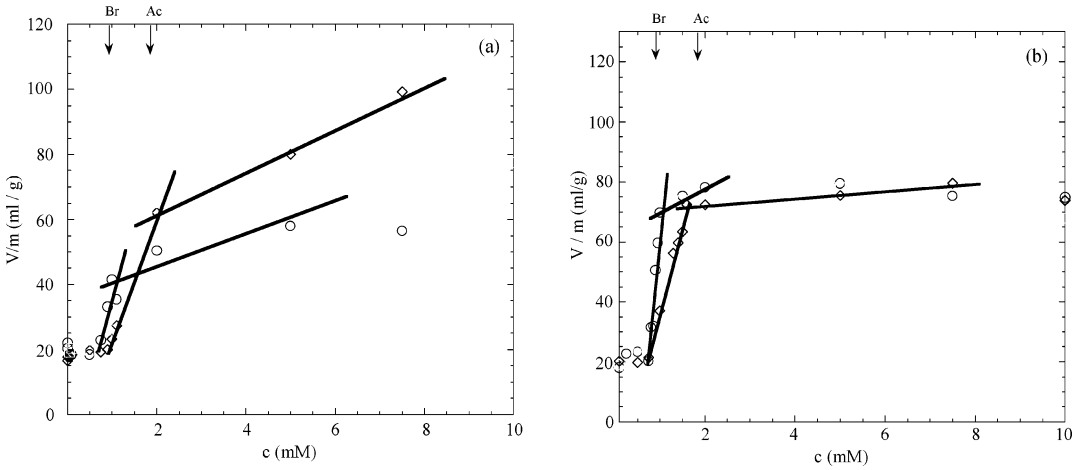

Figure 4. Data from Figure 2(c,d) replotted on a linear scale from 0.1 to 10 mM surfactant. (a) NIPA gels, and (b) BAM/NIPA (20:80) gels. (○) C_{16}TAB, (◇) C_{16}TAAc. Arrows indicate the cmc values. Lines are guides for the eye only.

when cac ≈ cmc. A similar effect was observed for HEC gels with sodium alkyl sulfate surfactants; when the surfactant tail length was decreased, the ratio cmc/cac decreased, and eventually became unity, at which point no interaction between the gel and the surfactant occurred.[1] It is possible to speculate that a cac for DAM gels would be seen with a counterion even higher in the Hofmeister's anionic series, e.g., fluoride. Conversely, for the more hydrophobic NIPA gels, it is probable that the cac would disappear with a counterion lower in the Hofmeister's anionic series, e.g., iodine. However, in the latter case, Krafft point problems are expected. The cac values for HEC and for NIPA gels with $C_{16}TA^+$ surfactants follow the same order as the cmc of the pure surfactant ($Br^- < Cl^- < Ac^-$), as shown in Figure 3. However, the ratio cmc/cac increases when going from Br^- to Ac^-, which indicates that the association tendency between the surfactant and the polymer gels increases in this order. This is in contrast to results found by Sakai et al. who observed that changing the counterion to the surfactant did not alter the transition temperature of NIPA gels, and thus they concluded that changing the surfactant counterion did not change the amount of surfactant bound.[16] The differences in the cac values shown in Figure 3 also support the order of the gel hydrophobicities inferred above.

Thus far we have shown that the binding of $C_{16}TA^+$ surfactants to alkylacrylamide gels is hydrophobically driven and that there is a minimum hydrophobicity threshold below which the surfactant will not bind to the gel. Rosén et al. have shown, by direct measurements, that the swelling of slightly hydrophobic nonionic gels immersed in solutions with ionic surfactants is due to binding of the surfactants to the gels; the gels swell due to the dissociated counterions of the bound surfactant ions.[6] The question then arises as to the origin of the rather striking differences between the NIPA and the BAM/NIPA (20:80) gels in their swelling behavior with the various $C_{16}TA^+$ surfactants (compare Figure 2(c and d)). For the more hydrophobic BAM/NIPA (20:80) gels, the maximum swelling is independent of the counterion to the surfactant, and the swelling levels off close to the surfactant cmc. By contrast, the NIPA gels continue to swell significantly well after the respective surfactant cmc, and the maximum degree of swelling varies strongly with the surfactant counterion. A closer examination of the swelling data plotted on a linear concentration scale provides important clues (Figure 4). Figure 4 reveals that in all cases there is a clear break point in the gel swelling isotherm at the surfactant cmc, as expected. For the BAM/NIPA (20:80) gels, the level of swelling at this point is the same for all $C_{16}TA^+$ surfactants, and no further swelling occurs beyond cmc. This implies that the interaction in this case is so strong that the surfactant binding has reached saturation at the cmc, regardless of the counterion. For the NIPA gels, on the other hand, the degree of swelling at the cmc is much less, and it also varies with the counterion in the order $Br^- < Cl^- < Ac^-$. This suggests that, owing to the lower hydrophobicity of NIPA, the surfactant has not reached saturation binding at the surfactant cmc, and the affinity of the surfactant to the polymer varies with the counterion in the same way as it does for the HEC gels in Figure 2(b). Hence, the binding and swelling can continue for the NIPA gels—although with significantly reduced slopes—even beyond the surfactant cmc.

The mechanism behind the ion specificity is not clear, but it appears that the adsorption free energy for a slightly hydrophobic polymer on the micellar surface is less favorable the larger the counterion. Possibly, one may view this in terms of a competition between the counterions and the polymer to reside at the micellar surface, since larger counterions bind more strongly. Interestingly, it seems that the general trend of a stronger binding of anionic surfactants, compared to cationics, to nonionic polymers fits into this pattern, since the (positive) counterions to anionic surfactants generally are smaller than the (negative) counterions to cationic surfactants.

On the basis of these observations, we make the following postulates regarding surfactant binding and gel swelling.

(1) For each gel/surfactant pair, there exists a saturation level of binding; once this has been reached, no further surfactant binding occurs. The saturation binding is insensitive to the nature of the counterion. Moreover, the degree of swelling at saturation is also insensitive to the nature of the counterion.

(2) At the cmc, the surfactant binding may or may not have reached the saturation level. Presumably, this depends on the free energy difference between the free and the polymer-bound micelles. In the present case, the free energy difference increases with polymer hydrophobicity and decreases with increasing level of counterion binding to the micelle (see Figure 2).

The above postulates lead to the following explanation for the differences between the NIPA and BAM/NIPA (20:80) swelling isotherms (Figures 2 and 4) with $C_{16}TA^+$ surfactants. The BAM/NIPA (20:80) gel is sufficiently hydrophobic so that saturation binding is essentially reached at the cmc, regardless of the surfactant counterion. Therefore, no further swelling is seen beyond the cmc, and no differences are observed upon changing the surfactant counterion. The NIPA gel, on the other hand, is not so hydrophobic. Hence, saturation of the gel with

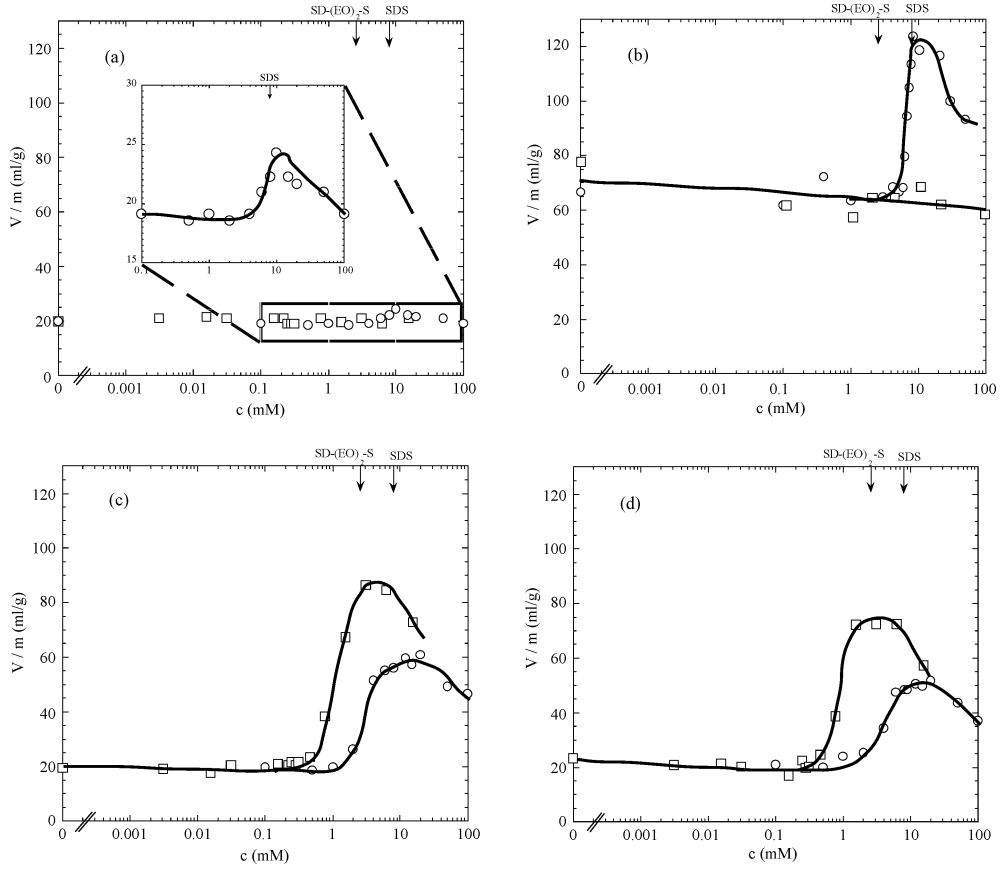

Figure 5. Interaction of neutral gels with the anionic surfactants SDS (○) and SD−(EO)2−S (□). (a) DAM gels, (b) HEC gels, (c) NIPA gels, (d) BAM/NIPA (20:80) gels. Arrows indicate the cmc values. Lines are guides for the eye only.

surfactant is not reached at the cmc, and the degree of surfactant binding at the cmc depends on the counterion. Significant swelling occurs after the cmc, for all counterions tested, but the extent of this additional swelling seems to depend on the counterion. The much lower maximum swelling with the bromide and chloride counterions, as compared to acetate, suggests that saturation binding may not be reached in all cases.

Anionic Surfactants. We have also investigated the interaction of the same series of alkylacrylamide gels with the anionic surfactants SDS and SD−$(EO)_2$−S (Figure 5). SD−$(EO)_2$−S is similar to SDS, but it contains an additional short ethylene oxide spacer inserted between the alkyl chain and the sulfate moiety. It was shown recently that HEC gels do not bind SD−$(EO)_2$−S but that HMHEC gels do,[1] and therefore this interaction must also be hydrophobically driven, since introduction of hydrophobic side chains results in binding. From Figure 5(a) it is clear that there is a slight interaction between DAM and SDS, but no interaction between DAM and SD−$(EO)_2$−S. HEC gels interact strongly with SDS, but not with SD−$(EO)_2$−S (Figure 5(b)). As shown in Figure 5(c,d), NIPA and BAM/NIPA (20:80) gels bind both SDS and SD−$(EO)_2$−S. Again, there is a hydrophobicity threshold to induce binding of the anionic surfactants, with the threshold for SDS being DAM gel, and that for SD−$(EO)_2$−S being somewhere between HEC and NIPA. From Figure 5(c,d) it can be seen that the degree of swelling is greater with SD−$(EO)_2$−S than with SDS with both NIPA and BAM/NIPA (20:80) gels.

This reverse of the swelling trend compared to the DAM and HEC gels is surprising, especially in view of the fact that the cationic surfactants gave the same trends for HEC and NIPA gels, see Figure 2 (b,c). We find no reason to suspect a stronger binding of SD−$(EO)_2$−S, compared to SDS, to NIPA. Instead, we tentatively ascribe the increased swelling with SD−$(EO)_2$−S compared to that with SDS to the fact that the surfactant counterions, which give rise to the swelling, are less tightly bound to SD−$(EO)_2$−S micelles than to SDS micelles. This is because the sulfate charges of an SD−$(EO)_2$−S micelle, due to the EO "spacers", are located at a significant distance above the surface of the hydrophobic core.

TABLE 1: The cac Values (in mM) of Different Ionic Surfactant/Nonionic Gel Pairs[a]

	C_{16}TAB	C_{16}TAAc	SD−$(EO)_2$−S	SDS
cmc[b]	0.9	1.8[c]	2.2[d]	8.1
cac with AM	—[e]	—[e]	—[e]	—[f]
cac with DAM	—[g]	—[g]	—[h]	≈6[h]
cac with HEC	—[g]	1.6[g]	—[i]	6.0[i]
cac with EHEC	≈0.7[j]	1[k]	0.6[k]	2[l]
cac with NIPA	0.7[g]	0.9[g]	0.4[h]	1[m]
cac with BAM	≈0.7[g]	0.8[g]	0.35[h]	≈0.8[h]

[a] The gel hydrophobicity increases in the following order: AM (= acrylamide) < DAM < HEC < EHEC < NIPA < BAM/NIPA (20:80). A line denotes the absence of a cac. The cmc values (in mM) of the pure surfactants are also included in the table. [b] Values from ref 23, unless otherwise specified [c] Determined using conductivity measurements. [d] The cmc of SD−$(EO)_2$−S is 3 mM.[23] However, our product contains, according to the product description, some impurities of sodium tetradecyl-di(ethylene oxide)-sulfate. The cmc was determined to be 2.2 mM. [e] Not studied, but a cac is not expected [f] Refs 24,25. [g] See Figure 2. [h] See Figure 5. [i] Refs 1,26. [j] Ref 18. [k] Unpublished swelling isotherms. [l] Refs 18,27,28. [m] Ref 28.

Summary of cac Values. Table 1 summarizes the cac values for the cationic (C_{16}TABr and C_{16}TAAc) and anionic (SD−$(EO)_2$−S and SDS) surfactants studied here with six polymer gels of increasing hydrophobicity. Some cac values are from Figures 2 and 5, some are from previously published work, and

some are from unpublished work. The general trend seen for all of the ionic surfactants is that there is a minimum hydrophobicity threshold, below which no cooperative hydrophobic association between the polymer and the ionic surfactant is seen. The EHEC gel shown in the table is ethyl hydroxyethyl cellulose, which is more hydrophobic than HEC due to the additional alkyl groups. For C_{16}TABr and SD−$(EO)_2$−S, the hydrophobicity threshold seems to be EHEC; for C_{16}TAAc, it is HEC; and for SDS it is DAM. For temperature-sensitive gels, e.g., NIPA and EHEC gels, increased temperature is expected to increase the strength of the gel−surfactant interaction due to the increased hydrophobicity of the gels. From Table 1, it is also clear that the cationic surfactant C_{16}TAAc interacts with HEC, but the anionic surfactant SD−$(EO)_2$−S does not. This is the case, despite the fact that the cmc values of these two surfactants are approximately the same and the fact that it is generally believed that anionic surfactants interact more strongly with polymers than cationic surfactants. For C_{16}TAAc, there is a gain in free energy for the micelles to bind to HEC, but for SD−$(EO)_2$−S there is not.

Conclusion

The results presented in this article provide evidence that there is a minimum hydrophobicity threshold below which ionic surfactants ($C_{16}TA^+$, SDS, SD−$(EO)_2$−S) will not interact with (bind to) uncharged gels, either alkylacrylamide- or HEC-based. Additionally, the onset of interaction occurs at different hydrophobicities, depending on both the nature of the surfactant headgroup and the counterion to the surfactant. Three different swelling behaviors have been observed for the uncharged gel/ionic surfactant systems.

(1) The gel swelling continues to increase even above the cmc of the surfactant (e.g., NIPA and HEC gels with $C_{16}TA^+$ surfactants), and changing the surfactant counterion influences the degree of swelling.

(2) The gel swelling increases up to the cmc and then levels off very rapidly (e.g., BAM/NIPA (20:80) gels with $C_{16}TA^+$ surfactants, NIPA gels with SDS and SD−$(EO)_2$−S), and changing the surfactant counterion does not influence the swelling.

(3) The gel swelling levels off even before the surfactant cmc is reached (e.g., BAM/NIPA (20:80) gels with SDS and SD−$(EO)_2$−S.

Thus, we postulate that ionic surfactants continue to bind to neutral gels until saturation of the network with surfactant and that this is independent of the micellization in the bulk. Thus, in case 1, the gel does not become saturated with surfactant until much after the cmc, and so continues to swell even after the cmc; in case 2, saturation approximately coincides with the cmc, and thus the gel reaches its maximum swelling around the cmc; and in case 3, saturation of the gel with surfactant actually occurs before the cmc, and thus no further increase in gel swelling is observed, even before the cmc. While it was well-known that these three possibilities existed, here we show evidence of the occurrence of each of the three binding scenarios.

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