Synthesis of Hydrophobically Modified Poly(acrylic acid) Gels and Interaction of the Gels with Cationic/Anionic Surfactants

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Poly(acrylic acid) (PAA) gel network with only chemical crosslinking and hydrophobically modified PAA (HM-PAA) gels with both chemical and physical crosslinking were synthesized by radical polymerization in *tert*-butanol, using ethylene glycol dimethacrylate (EGDMA) as crosslinker, and 2-(*N*-ethylperfluorooctanesulfoamido) ethyl methacrylate (FMA), stearyl acrylate (SA) or lauryl acrylate (LA) as hydrophobic comonomer respectively. The effect of the fractions and the species of the hydrophobes on swelling properties of HM-PAA gels and the interaction of gels and surfactants were studied. The results showed that the swelling ratio of HM-PAA gels exhibited a sharp decrease with increasing hydrophobic comonomer concentration, which could be ascribed to the formation of strong hydrophobic association among hydrophobic groups. It was proved that two kinds of binding mechanisms of surfactant/gel and different kinds of hydrophobic clusters existed in gels containing both physical and chemical networks.

Keywords hydrophobic association, acrylic acid, hydrogel, surfactant, equilibrium swelling ratio

Introduction

Accompanied with the prosperity of hydrophobically modified hydrogels (HM-gels), studies devoted to the hydrophobic interaction between HM-gels and surfactants have come out increasingly.[1-3] The experimental and theoretical results suggest that there are three main effects governing the interaction of the polymer gel and ionic surfactant,[4] that is, translational entropy of counterions, electrostatic force and hydrophobic associating force between polymers and surfactants. In surfactant/gel system, the surfactant molecules entering into the gel network need to gain considerable energy to compensate the loss of conformational entropy from confinement inside the network. The self-aggregation of the surfactant in the gel is very similar to the formation of polymer-bound micelles. According to the thermodynamic theory developed by Nagarajan,[5] irrespective of the polymer hydrophobicity, the free energy of the polymer-bound micelles is lower than that of the free micelles in solution. So the critical aggregation concentration (CAC) of the surfactant bound to polymers is usually much lower than its critical micelle concentration (CMC).[5-6] When CAC is reached, micelle-like aggregates form and serve as junctions to maintain viscoelastic network reversible.

Compared with hydrocarbon groups, fluorocarbon analogs have also been proved to lead to stronger hydrophobic association due to the lower cohesive energy density and surface energy.[7] However, most of the researches on HM-gels are focused on hydrocarbon-modified ones[6,8-10] and relatively little attention has been paid to the fluorocarbon-modified hydrogels.[11] In addition, studies of hydrogels containing both chemical crosslinking and physical crosslinking are few.[12]

In our previous works, the rheological properties,[13] the interactions with various surfactants,[14-15] and fluorescence study[14,16] of hydrophobically modified water-soluble

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polymers (HMWSP) were systematically studied. Results showed that fluorocarbon hydrophobes exhibited much stronger associations than the hydrogenated counterparts. By strong intermolecular association interaction of fluorocarbon groups, a gel-like solution could be obtained due to the formation of a 3D physically bridged network.[13] Therefore, it will be interesting to investigate HM-gels containing both chemical crosslinking and physical crosslinking, as well as the interaction of surfactant/HM-gels. In this study, a series of fluorocarbon and hydrocarbon-modified polyacrylic acid (PAA) gels were synthesized by solution polymerization. By studying on the interaction of HM-gels with anionic and cationic surfactants, hydrophobic association of hydrocarbon groups and fluorocarbon groups is compared.

Experimental

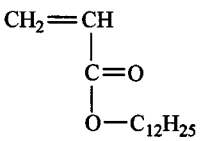
Materials

Acrylic acid (AA) was distilled under vacuum before use. 2-(*N*-Ethylperfluorooctanesulfoamido)ethyl methacrylate (FMA) was recrystallized from methanol twice and dried under vacuum before use. Stearyl acrylate (SA), Lauryl acrylate (LA), and ethylene glycol dimethacrylate (EGDMA) were purchased from the Aldrich Co.. Azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol. Cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS) were used as received.

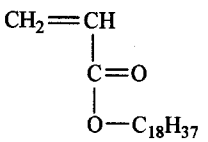
Gel synthesis

The macroscopic hydrogels were prepared in *tert*-butanol by radical copolymerization of acrylic acid (AA) with/without a certain amount of hydrophobic comonomer (FMA, SA and LA. respectively) (Scheme 1). In all cases, the concentration of AA ([AA]) remained constant at 2.2 mol/L and AIBN (as initiator) was kept at 0.001 mol/L (0.05 mol% of [AA]). The contents of the hydrophobic comonomer and the chemical crosslinker EGDMA ([EGDMA]) were varied from 0.1 to 2.5 mol% (relative to [AA]) respectively. The aqueous mixture before adding AIBN was bubbled with nitrogen gas for 10 min in an ice/water bath, and then AIBN was injected. The reaction was performed in a sealed cylindrical glass tube (inner diameter = 10 mm) equipped with a nitrogen inlet tube at (60 ± 0.5) ℃ for 24 h. Polymerizations were carried out to high fractional conversions (above 90%), as indicated by the weight ratio of the dry gel to the initial total monomer.

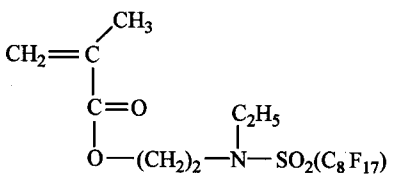
Scheme 1 Molecular structure of hydrophobic comonomer



Lauryl acrylate (LA)



Stearyl acrylate (SA)



2-(*N*-ethylperfluorooctanesulfoamido)ethyl methacrylate (FMA)

The resulting gels were cut into 10 mm disks, and then soaked in a large amount of absolute ethanol which was exchanged with fresh pure ethanol once every two days in order to remove all unreacted components. After one week, the gels were dried in a vacuum oven at 40 ℃ till their constant weights were obtained.

Anionic chromatography

Anionic chromatography is based on the anion-exchange process occurring between a mobile phase (eluent and anion) and a stationary phase (a cross-linked) polystyrene bead modified with quaternary ammonium groups). Separation of anions (fluorocarbon-modified copolymers were burned to produce F^-) is based on the affinity difference between F^- and quaternary ammonium. The concentration of F^- is detected by conductivity. With direct injection of a 50-mL sample, the detection limit is $\sim 10^{-9}$. Therefore, the concentration of F^- can be precisely determined with an error no more than ± 3% in our experiments. The fluorocarbon content determined by anionic chromatography (Dionex 2110I) is listed in Table 1.

Table 1 Monomer feed and F conversion in the syntheses of the gels[a]

Sample	Yield (wt%)	FMA (mol% of [AA])		F conversion[b]
		Feed	Actual	
FMA-0.2%-PAA	95	0.2	0.175	92
FMA-0.4%-PAA	92	0.4	0.351	95
FMA-0.5%-PAA	93	0.5	0.433	93
FMA-1.0%-PAA	95	1.0	0.874	92
FMA-1.5%-PAA	94	1.5	1.320	93
FMA-2%-PAA	93	2.0	1.752	94
LA-2%-PAA	91	2.0	—	—
SA-2%-PAA	90	2.0	—	—

[a] In gel samples, the feed amount of monomer AA, chemical crosslinker EGDMA and initiator AIBN were 2.2, 0.022 and 0.001 mol/L, respectively. [b] The F conversion was measured by anionic chromatography.

Swelling measurement

The dry gel samples were immersed in excess pure water or SDS/CTAB water solutions with different surfactant concentrations (based on the CMC of surfactant in water) for one week to attain equilibrium. When the constant weight was reached, gels were quickly taken out and weighted. The surface water was carefully wiped off before weighing. Swelling capacity was recorded gravimetrically as:

$$\text{Swelling ratio } (SR) = (M_t - M_0)/M_0$$

Where, M_t was weight of equilibrated gel; M_0 was weight of dry gel. All reported swelling ratios were averages of at least three trials.

Results and discussion

Effect of chemical crosslinker content on the swelling capacities of gels

The dry gel samples with different chemical crosslinking degrees were swollen in pure water and attained equilibrium. The effects of the chemical cross-linking on the swelling of hydrophobically-modified hydrogels (HM-gels), FMA-1%-PAA, and unmodified PAA hydrogel are shown in Fig. 1. For these two kinds of gels, the swelling ratios decrease with the increase of the content of EGDMA ([EGDMA]). But the effect of crosslinker content on swelling properties of unmodified PAA gels is more obvious. The observed swelling ratios of HM-gels, in most cases, are much lower than that of unmodified PAA gel. It indicates that the hydrophobic aggregation acts as physical cross-linking points. When [EGDMA] varies from 1 to 1.5 mol%, there is little change in the swelling ratios of FMA-1%-PAA gels, indicating that the physical cross-linking from the hydrophobic association of 1 mol% FMA dominates and the effect of chemical cross-linking on swelling properties of gels can be neglected. With [EGDMA] above 2 mol%, the gel networks collapse, regardless of the absence of hydrophobe. In this case, the chemical cross-linking dominates. Therefore, we select the EGDMA content of 1 mol% to study HM-PAA gels because, in this case, the effect and difference of hydrophobic groups can be observed.

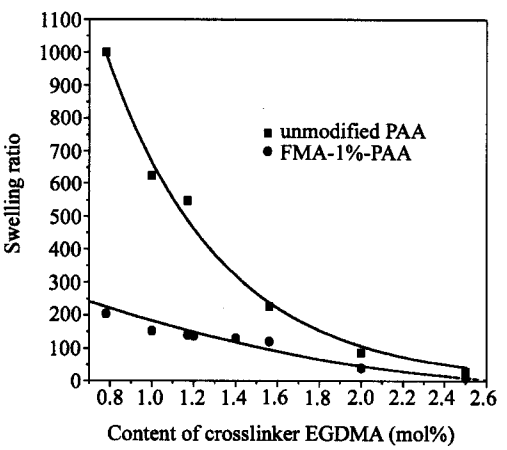


Fig. 1 Dependence of the swelling ratios of hydrogels on the content of crosslinker EGDMA.

Effect of hydrophobic modification on the swelling capacities of gels

The dry gel samples with different types and contents of hydrophobes were swollen in pure water and attained equilibium. The dependence of the swelling ratios of the HM-gels on the contents of hydrophobic comonomers is presented in Fig. 2. In gel samples, the content of EGDMA is fixed at 1 mol% and the feed ratios of hydrophobic comonomer (LA, FMA and SA, respectively) range between 0 and 2 mol%. As seen in Fig. 2, for these three kinds of HM-gels, the swelling ratio decreases with increasing the content of the hydrophobic

comonomer. It is proved that the hydrophobic aggregates acting as physical crosslinking points increase with the content of hydrophobic side groups in copolymer gels.

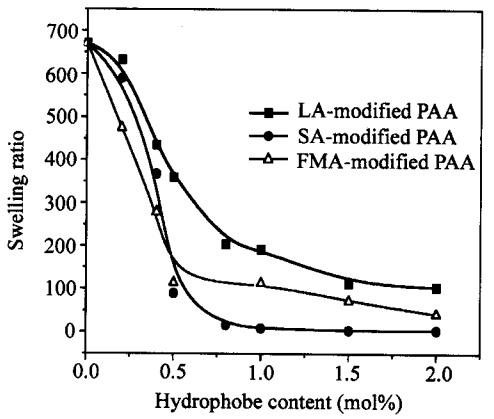


Fig. 2 Dependence of the swelling ratios of hydrogels on the hydrophobe content.

There is a competitive balance between forces driving the side hydrophobic groups into aggregates and forces restraining the aggregation process. Since all the gels contain the same amount of AA units and are swollen in distilled water at the same pH value, it is reasonable to consider that the magnitude of the electrostatic repulsion is similar for different HM-gels. Therefore, the differences among HM-gels are mainly resulted from the hydrophobic forces that drive the hydrophobic groups into aggregates. As seen in Fig. 2, the swelling ratios of SA-modified gels are lower than the ones of LA-modified gels. It may be ascribed to the effect of chain length on hydrophobic association.[11] SA chain is longer than LA chain and owns the greater hydrophobic character. The stronger hydrophobic association of SA results in the more physical junctions in gel networks and the lower swelling ratios of the SA-modified gels. It is noticeable that the swelling ratios of FMA-modified PAA gels are lower than the ones of the LA series while the LA chain (12C) is longer than the FMA chain (8C). It shows that fluorocarbon groups have stronger hydrophobic association compared with hydrocarbon anolags.

With the hydrophobe contents lower than 0.5 mol%, the equilibrium swelling ratios of FMA-modified gels are lower than those of SA-modified gels. This is also explained by the stronger hydrophobicity of fluorocarbon group. With the contents of hydrophobes above 0.5 mol%, the aggregation of FMA and SA groups seems to attain saturation. Therefore, these two kinds of gel networks hardly collapse further. In this case, SA-modified gels show the lower swelling ability than FMA-modified ones, which may be related to the less steric volume of SA groups. FMA chains contain a spacer between the main chain and the perfluorooctyl group, which increases their steric volume. As a comparison, SA chains are more flexible. So when the physical association of SA- and FMA- modified gels obtains saturation, SA-aggregates take up the less volume than FMA-aggregates. While for LA-modified PAA gels, their gel networks collapse further with the content of LA above 0.5 mol%, which may be ascribed to the low hydrophobic character of LA, and the aggregation acting as physical crosslinking points will be saturated at the higher LA content.

Effect of pH *on the hydrophobic association*

The gel samples were swollen in buffer solutions with different pH for one day. The relevance of the pH of the elution medium to the swelling ratio of gels with different hydrophobes is showed in Fig. 3. As seen in Fig. 3, gels exhibit pH-sensitivity, swelling to high degree in basic solution and collapsing in acidic solutions. At the high pH value, HM-gels absorb less water than the unmodified PAA gel, which proves the presence of hydrophobic association. Gels' swelling ratios increase with the pH value due to changes in the balance between electrostatic interactions (which are affected by the pH value) and hydrophobic interactions. With increasing the pH value of elution medium, these collapsed hydrophobic coils divert into ones that are highly expanded and hydrated. From

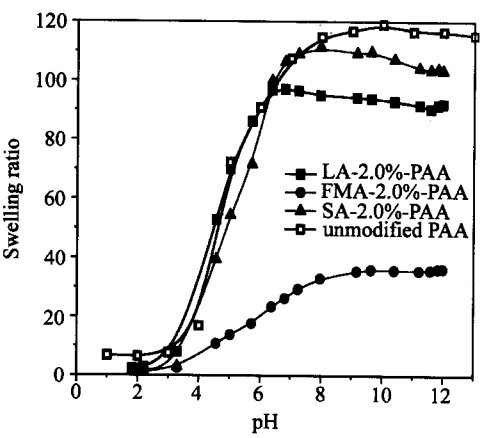


Fig. 3 Effect of pH value on the swelling properties of hydrogels with different types of hydrophobic groups.

Fig. 3, three kinds of gels without fluorin obtain the swelling ratio maximum at about the pH value of 6.5. However, for fluorin-containing gel, FMA-2.0%-PAA, at high pH value its swelling ratio is lowest and shows the maximum value at higher pH (about 8.5). It means that the electrostatic force must increase further in order to disentwine the hydrophobic clusters from FMA groups and the hydrophobic association of FMA groups is more stable than that of LA or SA groups.

Interaction of gels with surfactants

As mentioned in the introduction, in order to enter gel networks, surfactants need to gain considerable energy to compensate the loss in conformational entropy resulting from the confinement in the network. Two types of surfactants are investigated as models for the system of HM-gel/surfactant. As shown in Scheme 2, hydrophobic binding mechanism (a) and the electrostatic binding mechanism (b) are used to distinguish two kinds of interactions. According to these two kinds of binding mechanisms, two hypothetical models for the interaction of HM-gel/surfactant are depicted in Scheme 3 (for SDS) and Scheme 4 (for CTAB). In these models, the self-aggregates of hydrophobic side chains, and the mixing aggregates from hydrophobic side groups and surfactant-ions, are denoted by solid line circles and dotted line circles respectively. The surfactant micelles (denoted by double line circles) are surrounded by their counter ions in the outer solution or by the COO^- of polymer chains (Scheme 4).

Gels/anionic surfactant

Typical dependence of the gel's swelling ratios on the initial SDS concentration ([SDS]) in the outer solution is shown in Fig. 4. The plots of HM-gels show a turn at about the SDS concentration of 0.8×10^{-3} mol/L, which is regarded as the critical self-aggregate concentration (CAC). It shows that CAC from different HM-gel networks is similar (the dotted-line region in Fig. 4) but much lower than CMC of SDS in water (8×10^{-3} mol/L)[17] and CAC (5×10^{-3} mol/L) from Philippova's report.[18] It may be ascribed to that the hydrophobic association among the hydrophobic side-groups in the HM-gels with SDS molecules promotes SDS molecules to enter gel networks.

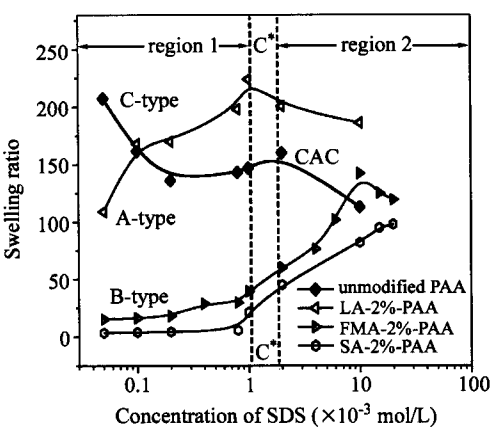
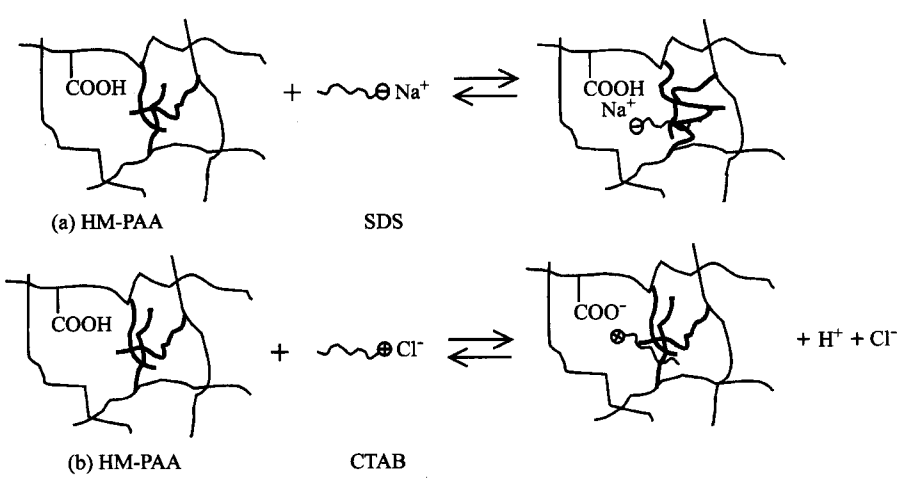
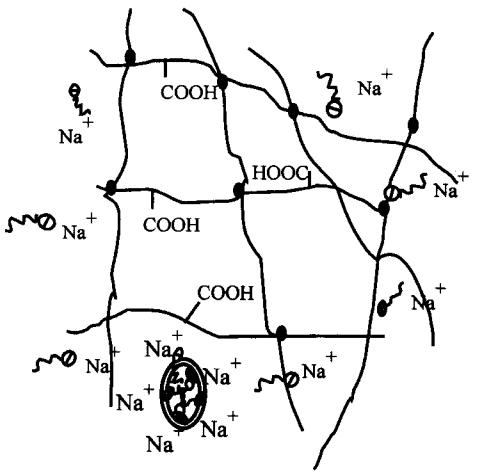


Fig. 4 Dependence of the swelling ratios of gels on the concentration of SDS.

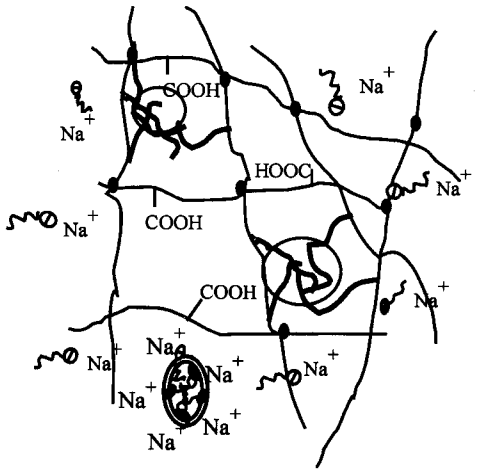
Scheme 2 Schematic representation of the two binding mechanism in gel/surfactant system. (a) Hydrophobic interactions leading to the absorption of surfactant together with counterions. (b) Electrostatic interactions through ion exchange reaction



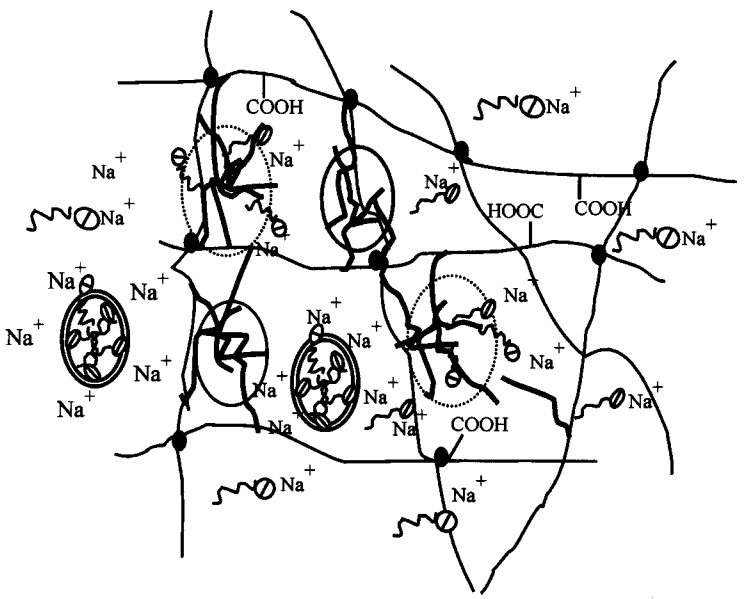
Scheme 3 Schematic representation of the interaction of gels with SDS (solid point denotes chemical cross-linking point, solid line circle denotes hydrophobic aggregates of hydrophobic side chain; dotted line circle denotes mixed clusters between hydrophobic side chain and SDS, double line circle denotes SDS micelle).



(a) PAA gel without SDS inside gel network



(b) HM-PAA gel without SDS inside gel network



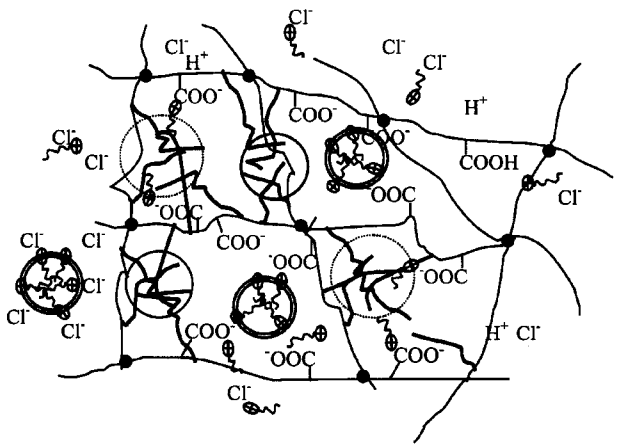
(c) HM-PAA gels with SDS inside gel network

In this HM-gels/SDS surfactant system, the hydrophobic interaction and gel's conformation determine whether SDS will enter into gel network or not. If SDS molecules enter gel networks, hydrophobic binding mechanism (a) (Scheme 2) will dominate. According to this binding mechanism,[18] gels absorb the hydrophobic tail ions of SDS together with its counter ions Na^+ due to electroneutrality (Scheme 3c). As a result, the concentration of ions in gels increases and gels swell.

In Fig. 4 the swelling behaviors are divided into two regions according to CAC (region 1 denotes [SDS] below CAC and region 2 denotes [SDS] above CAC).

We consider that in region 1, SDS can enter into LA-modified gel but can not enter into other gels (including unmodified, SA- and FMA-modified gels) and there are no self-aggregates (double line circles) of SDS in all gels. According to the degree of hydrophobic association, A-, B- and C-type gels are divided and discussed in the following.

Scheme 4 Schematic representation of the interaction of gels with CTAB (solid point denotes chemical cross-linking point, solid line circle denotes hydrophobic aggregates of hydrophobic side chain; dotted line circle denotes mixed clusters between hydrophobic side chain and CTAB, double line circle denotes CTAB micelle).



A-type gel is the unmodified PAA gel. SDS can not enter into A-type gel (Scheme 3a), mainly because there are no hydrophobic interactions between gel and SDS molecules and then SDS in the outer solution can not obtain energy to enter gel networks. The concentration of anionic surfactant in the exterior solution is higher than in the gel phase. As a result similar to salt effect, water inside gels goes into the outer solution. The osmotic pressure attains a balance with [SDS] from 0.2×10^{-3} to 0.8×10^{-3} mol/L.

B-type gels denote the gels with strong hydrophobic association, for example, FMA-2%-PAA and SA-2%-PAA. In this case, although there exists hydrophobic association (solid line circles in Scheme 3b) between HM-PAA gels and SDS molecules, the strong self-aggregation of hydrophobic side-groups (FMA and SA) induces so compact gel surface that SDS can not enter into gels (Scheme 3b). As a result, the swelling ratios change little with [SDS]. The swelling behavior of gels mainly depends on the hydrophobic self-aggregate of hydrophobic side-groups.

C-type gel is the gel with hydrophobic side groups which result in weaker hydrophobic association and the loose network structure, for example, LA-2%-PAA. In this case, hydrophobic associating force between SDS and hydrophobic side group of copolymer urges SDS to enter gels with the loose surface (Scheme 3c) and to form aggregates (including solid and dotted line circles). The hydrophobic association of LA groups with SDS molecules can provide energy for SDS to enter gel networks. The absorption of SDS molecules results in the increase of ion concentration of inside gel.

In region 2, SDS concentration is higher than CAC. In this case, for all type of gels, SDS can gain considerable energy by self-aggregation (double line circles in the inner of gels, in Scheme 3c). From Fig. 4, once SDS entering the inner of HM-gels, at first electrostatic force from SDS ions dominates and the increase of Na^+ ion (from SDS) concentration in HM-gels results in the increase of HM-gel's swelling ratios. And then, when SDS concentration is too high and HM-gels have swollen to some extend, the effect of hydrophobic self-aggregates of SDS dominates. The swelling ratios of gels decrease instead. Noticeably, the increase of swelling ratios of the LA-modified gel starts at [SDS] lower than CAC, while the swelling ratios of FMA- and SA-modified gels increase at [SDS] higher than CAC. It can be related to the tighter network of FMA- and SA-modified gel resulted from the stronger hydrophobic association of FMA and SA groups.

Gels / cationic surfactant

Typical plots of the swelling ratio of the gel networks as a function of the concentration of CTAB ([CTAB]) are presented in Fig. 5. It shows that the absorption of CTAB surfactant leads to gels' shrinkage. This result complies with electrostatic binding mechanism,[18] according to which (Scheme 2b) the surfactant ions penetrate into the gel via ion exchange reaction with network counterions H^+, giving rise to the release of the latter to the external solution (Scheme 4). This ion-exchange process is extremely favorable from the viewpoint of translation entropy of the counterions.[19] First, the volume charge density of the network is much higher than that of the external solution, and the substitution of the surfactant ions for H^+ ions will decrease the volume charge density efficiently. Second, the hydrophobic association forces and the electrostatic interaction forces promote the surfactant ions to penetrate the gel networks.

In contrast with H^+, the cationic hydrophobic tails of CTAB form hydrophobic self-aggregate or aggregate with hydrophobic side-groups of gels (Scheme 4). Therefore the concentration of the mobile counterions decreases and gels collapse. For different gels, the slopes of curves in

Fig. 5 increase in the order: SA-2%-PAA < FMA-2%-PAA < LA-2%-PAA. It shows that for HM-PAA gels, the tighter the gel networks (decided by the kind of hydrophobic modification) are, the slower the ion-exchange reaction is. The ion-exchange reaction is the strongest for the LA-2%-PAA gel due to its weakest hydrophobic attracting force for CTAB, and is the weakest for the SA-2%-PAA gel due to its most compact networks.

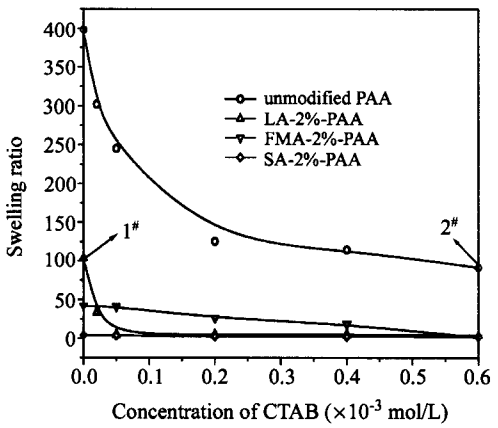


Fig. 5 Dependence of the swelling ratios of gels on the concentration of CTAB.

For the LA-2%-PAA gel filled in pure water without CTAB, 1 # in Fig. 5, its swelling property is affected mainly by the aggregation of polymer hydrophobic side-groups. This kind of cluster is covalently bound to gel networks. While for the unmodified PAA gel in the CTAB solution ([CTAB] = 2×10^{-4} mol/L), 2 # in Fig. 5, gel's swelling property is affected mainly by the aggregation of surfactant cationic ions. This kind of charged CTAB cluster is bound to the oppositely charged network by the electrostatic attracting force. As seen in Fig. 5, these two kinds of gels have a similar swelling ratio (about 100). It demonstrates that the contraction of gels is mainly related to the association of hydrophobes, whether these hydrophobes are bound to gels by covalent bond or by electrostatic force.

Conclusions

The hydrophobic association ability of hydrophobic comonomers increases by the following order: LA < SA < FMA. The hydrophobic association acts as physical cross-linking in HM-gels. Therefore the stronger the hydrophobicity of the hydrophobic comonomer is, the lower the swelling ratio of HM-PAA gels is. The hydrophobic aggregates of FMA are more stable than those of LA or SA, and are more difficult to be disentwined by electrostatic force.

In the gel/anionic surfactant systems, hydrophobic binding mechanism dominates. In gels there exists the critical aggregation concentration (CAC), about 0.8×10^{-3} mol/L for SDS. The hydrophobic interaction and gel's conformation determine whether SDS can enter into the gel network. Above CAC, SDS molecules enter into all gels by energy obtained by the aggregation of SDS in gels. Below CAC, SDS molecules only enter into LA-modified gel that owns both hydrophobic side group and loose gel structure. For HM-gels, once SDS entering into gels, their swelling ratios increase with SDS concentration ([SDS]) at first due to the dominance of the electrostatic repulsive interaction and then decrease due to the dominance of hydrophobic interaction of SDS. In addition, SDS molecules enter into LA-modified gel at the lower [SDS] than into FMA- and SA-modified gels. While for unmodified gel, the swelling ratio decreases with [SDS] mainly due to the salt effect with [SDS] lower than CAC and mainly due to self-aggregation of SDS with [SDS] higher than CAC.

In the anionic gel/cationic surfactant systems, the surfactant ions enter the gel networks by ion exchange mechanism. The hydrophobic clusters arising from the surfactant or from hydrophobic side groups make a similar effect on gels' collapse. The ion-exchange reaction is the weakest for gels with tightest network structure.

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