# Swelling Behavior of Poly{*N*-[3-(dimethylaminopropyl)] methacrylamide-*co*-acrylamide} Hydrogels in Aqueous Solutions of Surfactants

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*Received 16 December 2004; revised 22 August 2005; accepted 13 November 2005*
*DOI: 10.1002/polb.20835*

**ABSTRACT:** Temperature sensitive poly{*N*-[3-(dimethylaminopropyl)]methacrylamide-*co*-acrylamide} [P(DMAPMA-*co*-AAm)] hydrogels were prepared by the free-radical crosslinking copolymerization of corresponding monomers in water with *N,N*-methylenebisacrylamide as the crosslinker, ammonium persulfate as the initiator, and *N,N,N′,N′*-tetramethylethylenediamine as the activator. The swelling equilibrium of the P(DMAPMA-*co*-AAm) hydrogels was investigated as a function of temperature in aqueous solutions of the anionic surfactant sodium dodecyl sulfate and the cationic surfactant dodecyltrimethylammonium bromide. In pure water, regardless of the amount of *N,N*-methylenebisacrylamide, the P(DMAPMA-*co*-AAm) hydrogels showed a discontinuous phase transition between 30 and 36 °C. However, the transition temperature changed from discontinuous to continuous with the addition of surfactants; this was ascribed to the conversion of nonionic P(DMAPMA-*co*-AAm) hydrogels into polyelectrolyte hydrogels due to the binding of surfactants through hydrophobic interactions. Additionally, the concentrations of free sodium dodecyl sulfate and dodecyltrimethylammonium bromide ions were measured at different temperatures by conductometry, and it was found that the electric conductivity of the P(DMAPMA-*co*-AAm)–surfactant systems depended strongly on the swelling ratio; most notably, it changed drastically near the phase-transition temperature of the P(DMAPMA-*co*-AAm) hydrogel. ©2006 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 44: 1645–1652, 2006
**Keywords:** hydrogels; poly{N-[3-(dimethylaminopropyl)]methacrylamide-co-acrylamide}; surfactants; swelling; temperature-sensitive gels

## INTRODUCTION

The temperature sensitivity of hydrogels is associated with the temperature dependence of hydrogen bonding and hydrophobic interactions.[1] The phase-transition behavior of hydrogels is generally attributed to the reversible formation and breakage of hydrogen bonding between the water and hydrophilic groups of hydrogels and the hydrophilic/hydrophobic balance between hydrophilic and hydrophobic groups within polymer chains.[2,3] The effects of various additives on the swelling behavior and volume-phase-transition temperature of several N-substituted acrylamide (AAm) hydrogels have been investigated.[4–7] The swelling ratios and volume-phase-transition temperatures of these hydrogels are

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Journal of Polymer Science: Part B: Polymer Physics, Vol. 44, 1645–1652 (2006)

remarkably enhanced, and this has been interpreted on the basis of electrostatic repulsion due to the binding of ionic surfactants to polymer chains. The change in the transition temperature is influenced strongly by the addition of small amounts of ionic surfactants.[8–10] The phase-transition behavior of thermosensitive hydrogels is of interest as a model for understanding the folding and unfolding of biomolecular systems because the hydrogel contains both hydrophilic and hydrophobic units that play a vital role in determining the structures and functions of biopolymers. This type of study also provides important information on the nature of polymer–solvent interactions within hydrogels and helps us to understand the structures and functions of biopolymers.[11]

Surfactants are well suited for this purpose because they are composed of hydrophilic, ionic or nonionic groups bound to a nonpolar, hydrophobic group. In this study, the following two surfactants with dodecyl groups as hydrophobic chains were used: the anionic surfactant $CH_3(CH_2)_{11}SO_4Na$ [sodium dodecyl sulfate (SDS)] and the cationic surfactant $CH_3(CH_2)_{11}N(CH_3)_3Br$ [dodecyltrimethylammonium bromide (DTAB)].

For this study, poly{*N*-[3-(dimethylaminopropyl)]methacrylamide-*co*-acrylamide} [P(DMAPMA-*co*-AAm)] copolymeric hydrogels were synthesized from *N*-[3-(dimethylaminopropyl)]methacrylamide (DMAPMA) and AAm monomers. These monomers were chosen for two reasons. First, a poly{*N*-[3-(dimethylaminopropyl)]methacrylamide} (PDMAPMA) hydrogel swollen in water is a typical temperature-sensitive hydrogel that exhibits a volume phase transition in response to temperature changes around 34 °C.[12] However, it has very low mechanical strength. Second, AAm is a versatile hydrophilic comonomer, but its homopolymer does not show a volume-phase-transition temperature in water.[13] The introduction of the AAm component improves the mechanical strength of PDMAPMA hydrogels. In this case, P(DMAPMA-*co*-AAm) hydrogels should have both good mechanical strength and temperature sensitivity. The effects of ionic surfactants on the equilibrium swelling ratio of P(DMAPMA-*co*-AAm) hydrogels were studied in an aqueous system as a function of the surfactant type and their respective concentrations. The association of ionic surfactants with the P(DMAPMA-*co*-AAm) chains was further investigated by conductometric measurements for aqueous solutions including both the surfactant and hydrogel.

## EXPERIMENTAL

### Materials

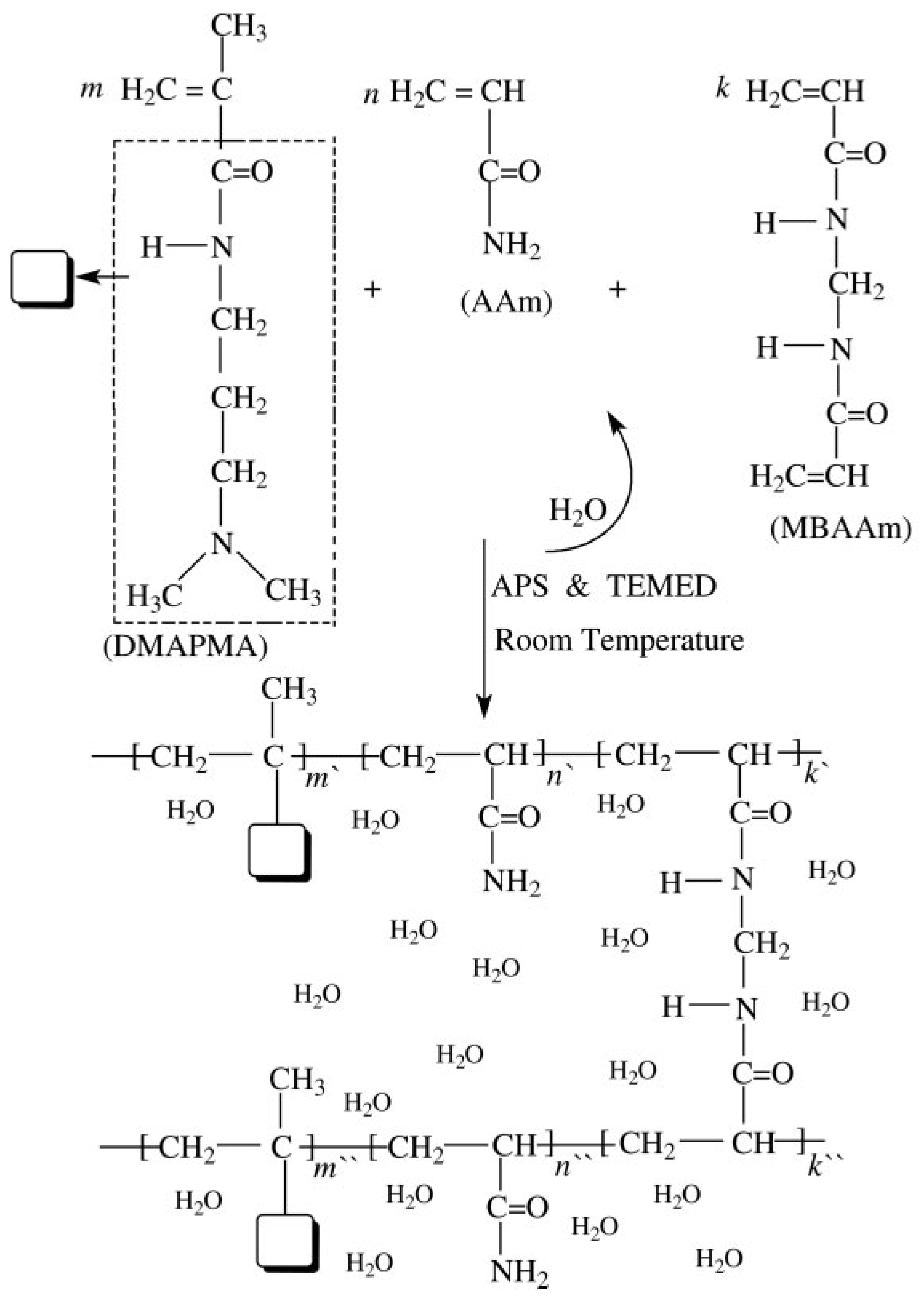
Monomers DMAPMA and AAm, crosslinker *N,N*-methylenebisacrylamide (MBAAm), initiator ammonium persulfate (APS), accelerator *N,N,N′,N′*-tetramethylethylenediamine (TEMED), and surfactants SDS and DTAB were purchased from Aldrich Chemical Co. The chemicals were used as received. All aqueous solutions were prepared with deionized water.

### Hydrogel Synthesis

P(DMAPMA-*co*-AAm) hydrogels were synthesized by the free-radical crosslinking copolymerization of DMAPMA and AAm in aqueous solutions (see Scheme 1). APS (0.056 M) and TEMED (0.32 M) were used as the redox initiator system. The MBAAm/DMAPMA–AAm feed ratios were 11.1/88.9, 12.9/87.1, 14.3/85.7, 15.8/84.2, and 17.3/82.7 mol/mol. DMAPMA (0.7 mL), AAm (0.3 g) APS (1.0 mL), and MBAAm (0.12 g) were dissolved in distilled water (4 mL), and the solution was purged with nitrogen gas for 10 min. After the addition of TEMED (0.5 mL), the solution was placed in poly(vinyl chloride) straws 4 mm in diameter and about 20 cm long. The poly(vinyl chloride) straws were sealed and immersed in a thermostated water bath at 20 °C, and the copolymerization was conducted for 1 day. Upon the completion of the reaction, the hydrogels were cut into specimens approximately 10 mm long and immersed in a large excess of water to wash out any unreacted monomers and the initiator. The hydrogel samples were then dried at room temperature *in vacuo* to a constant weight. The conversion of the monomers to the copolymer, determined by a gravimetric method, was higher than 100% because of the presence of residual water in the dried copolymers. Crosslinked, *N*-substituted AAm copolymers always contain about 10–20 wt % water, even after several months of drying *in vacuo*.[14]

### Determination of the Equilibrium Swelling Ratio

For the temperature-response studies, the hydrogels were equilibrated in distilled water at temperatures ranging from 10 to 60 °C. The hydrogels were allowed to swell in distilled water for at least 24 h at each predetermined temperature, which was controlled up to ±0.1 °C in a Thermo



**Scheme 1**

Haake K10 constant-temperature water bath. The gravimetric method was employed to study the hydrogel swelling ratio. After immersion in distilled water at a predetermined temperature, the hydrogels were removed from the water and blotted with wet filter paper for the removal of excess water on the hydrogel surface; they were then weighed. After this weight measurement, the hydrogels were re-equilibrated in distilled water at another predetermined temperature, and their swollen weight was determined. The average values of three measurements were taken for each hydrogel, and the equilibrium swelling ratio was calculated as follows:

$$\text{Equilibrium swelling ratio} = \frac{m_s - m_d}{m_d} \qquad (1)$$

where $m_d$ and $m_s$ are the masses of the dry and swollen hydrogels, respectively.

Similarly, for the swelling measurements in aqueous surfactant solutions, the P(DMAPMA-

*co*-AAm) hydrogels were immersed in vials filled with aqueous surfactant solutions (SDS or DTAB). Aqueous surfactant solutions were prepared by the dilution of 30 mM surfactant stock solutions with required volumes of water. The volume of the surfactant solutions in the vials was much larger than the hydrogel volume, so the concentration of the solution was practically unchanged. The hydrogels were equilibrated in aqueous surfactant solutions at temperatures ranging from 10 to 60 °C. The hydrogels were allowed to swell in aqueous surfactant solutions for at least 24 h at each predetermined temperature. After immersion in aqueous surfactant solutions at a predetermined temperature, the hydrogels were removed from the aqueous surfactant solutions and blotted with wet filter paper for the removal of excess water on the hydrogel surface; they were then weighed. After a particular measurement, the hydrogels were re-equilibrated in aqueous surfactant solutions at another predetermined temperature, and their swollen weight was also determined.

### Conductivity Measurements

The conductivity of the P(DMAPMA-*co*-AAm) hydrogel and surfactant (DTAB or SDS) systems was measured in 3.8–30 mM surfactant solutions at different temperatures with a model WPA CM 35 conductometer. The temperature was controlled with water circulation with a Thermo Haake K10 thermostatic circulator.

## RESULTS AND DISCUSSION

### Effect of the Crosslinker Content on the Swelling Equilibrium

Figure 1 demonstrates the temperature dependence of the equilibrium swelling ratio of P(DMAPMA-*co*-AAm) hydrogels with different amounts of crosslinker in water when the temperature was increased from 10 to 60 °C. The data show that all the P(DMAPMA-*co*-AAm) hydrogels, regardless of the level of crosslinking, had similar swelling behaviors as a function of temperature, and the phase-transition temperatures of these hydrogels lay in the range of 32–36 °C. Moreover, all the P(DMAPMA-*co*-AAm) hydrogels exhibited a negative temperature coefficient, that is, swelling at lower temperatures and shrinking at higher temperatures, which is briefly explained in the introduction. Under equilibrium swelling conditions, all the P(DMAPMA-*co*-AAm) hydrogels showed increasing swelling at lower temperatures, but they deswelled above their phase-transition temperatures because of the aggregation of the network chains. When the external temperature was increased from 10 °C toward the phase-transition temperature, the volume or water content inside the P(DMAPMA-*co*-AAm) hydrogels decreased slowly, and the water release rate was controlled mainly by collective diffusion of the hydrogels. Even though the phase-transition temperatures of the P(DMAPMA-*co*-AAm) hydrogels were virtually not affected by the amount of MBAAm within the ranges studied in this work, the data in Figure 1 clearly show also that, at all temperatures, the equilibrium swelling ratios of these hydrogels were significantly reduced with increasing amounts of MBAAm. This behavior can be attributed to dense, three-dimensional structure formed at the high crosslinker concentration.

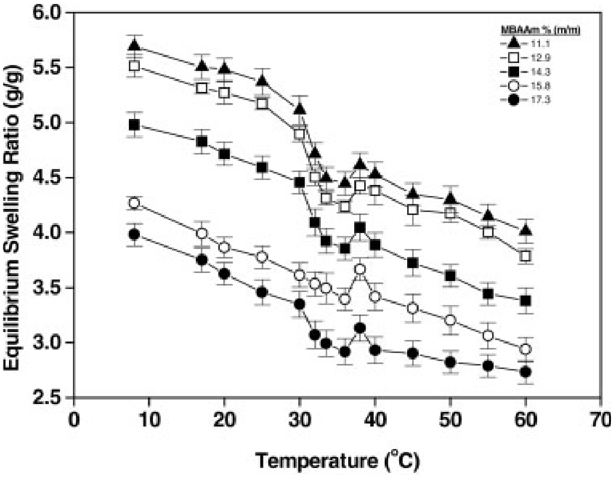


**Figure 1.** Equilibrium swelling ratios of the P (DMAPMA-*co*-AAm) hydrogels in water shown as a function of temperature. The crosslinker contents of the hydrogels are indicated.

### Effects of the Surfactants on the Swelling Equilibrium

The effect of each ionic surfactant on the swelling process of the P(DMAPMA-*co*-AAm) hydrogel with 11.1% MBAAm, which had the highest equilibrium swelling ratio in water of the hydrogels prepared and studied in this work, was investigated in detail. Figures 2 (DTAB) and 3 (SDS) show the temperature dependence of the equilib-

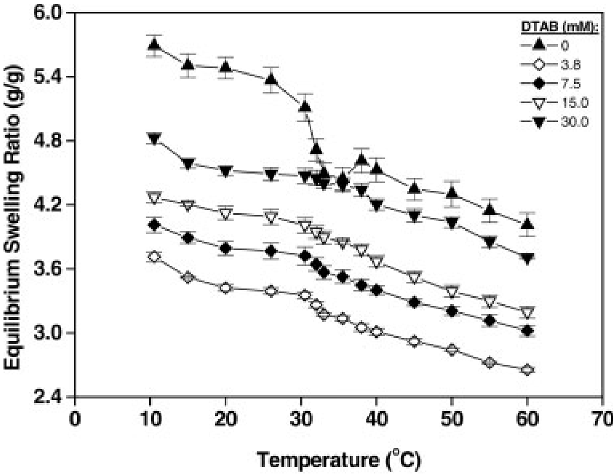


**Figure 2.** Equilibrium swelling ratios of the P(DMAPMA-*co*-AAm) hydrogel with 11.1% MBAAm in DTAB solutions shown as a function of temperature. The concentrations of the DTAB solutions are indicated.

rium swelling ratio of the P(DMAPMA-*co*-AAm) hydrogel with 11.1% MBAAm in the presence of two oppositely charged ionic surfactants with various concentrations. The overall effect observed is a reduction in the equilibrium swelling ratio of the hydrogel in surfactant solutions for the whole temperature range investigated in comparison with pure water. DTAB and SDS molecules consist of a long, aliphatic hydrocarbon chain, and P(DMAPMA-*co*-AAm) has hydrophobic dimethylaminopropyl moieties $[(CH_3)_2N(CH_2)_3]$ as side groups and $—CH_2CCH_3R—$ of DMAPMA and $—CH_2CHR—$ of AAm in the backbone of its hydrogel. When DTAB or SDS molecules diffuse into the gel network of P(DMAPMA-*co*-AAm), strong association takes place through the hydrophobic interaction between the dimethylaminopropyl groups of DMAPMA units and long-chain alkyl groups of DTAB or SDS, resulting in a decrease in the equilibrium swelling ratio of the hydrogel. However, the increase in the surfactant concentration in the external solution increases the counterion concentration ($Na^+$ or $Br^-$) inside the hydrogel, and the neutral polymer chains become polyelectrolytes. These acquired network charges and counterions associated with the charges exert extra osmotic pressure on the network. As a result, increased binding of charged surfactants increases the charge density of polyelectrolyte chains and thus leads to an enhanced swelling ratio.

In the absence of surfactants, this hydrogel underwent a discontinuous phase transition (chain collapse) at 32–36 °C with a swelling ratio change at this temperature range defined by the following ratio: swelling ratio of the swollen phase/swelling ratio of the collapsed phase $\sim 1.2$. In solutions containing DTAB (Fig. 2), a sharp discontinuity in the phase transition of the P(DMAPMA-*co*-AAm) hydrogel was converted into a smoother change with increasing surfactant concentration while a break in the curves corresponding to the onset of transition was maintained. On the other hand, in the presence of SDS (Fig. 3), even though the continuous phase transition was exhibited, the data in Figure 3 clearly show also that the equilibrium swelling ratio of the P(DMAPMA-*co*-AAm) hydrogel first drastically decreased with an increase in the temperature from 10 to 36 °C and then remained less sensitive toward a temperature increase from 36 to 60 °C for all SDS surfactant concentrations studied.

Another important characteristic of surfactant effects on the phase transition of the P(DMAPMA-*co*-AAm) hydrogel is the large difference in the values for the equilibrium swelling ratio observed between DTAB and SDS (Figs. 2 and 3). This behavior can be attributed to the differences in the counterions, the ionizable groups, and the bound amounts of the surfactants. In addition, the equilibrium swelling ratios of the hydrogels with binding surfactant molecules depend on the types and nature of the water-binding sites, such as $—O—SO_3^-$ and $—N^+(CH_3)_3$ of the surfactant molecules. Their high electric

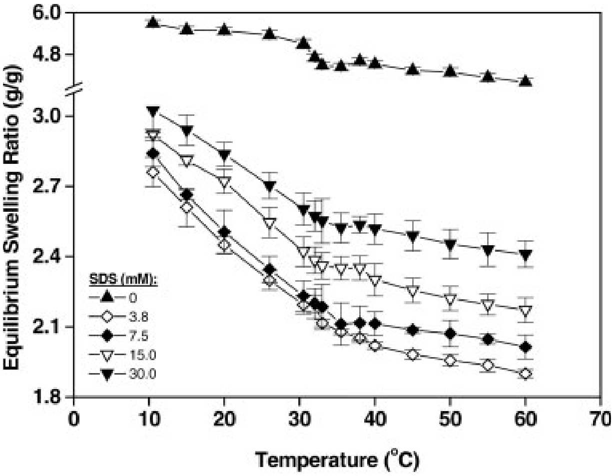


**Figure 3.** Equilibrium swelling ratios of the P(DMAPMA-*co*-AAm) hydrogel with 11.1% MBAAm in SDS solutions shown as a function of temperature. The concentrations of the SDS solutions are indicated.

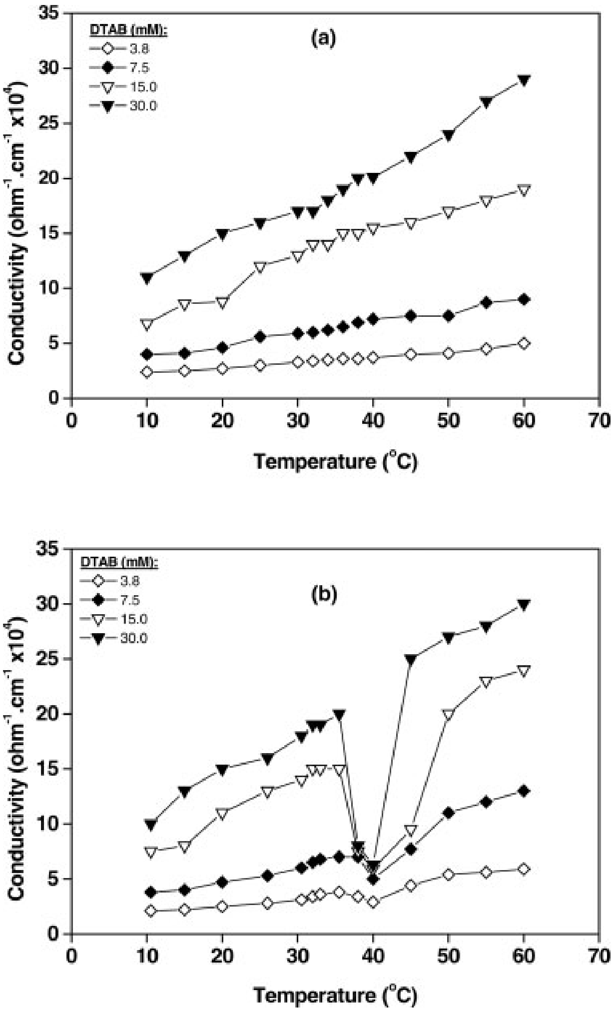


**Figure 4.** Temperature dependence of the conductivity of DTAB solutions (a) in the absence and (b) in the presence of the P(DMAPMA-*co*-AAm) hydrogel with 11.1% MBAAm.

fields not only polarize, immobilize, and electrostrict nearest neighbor molecules but also induce additional order beyond the first layer of water molecules. Ions such as —O—$SO_3^-$, however, can immobilize the water molecules of only the first layer.[15] The higher attractive field that can be felt to several layers in the case of —$N^+(CH_3)_3$ probably causes many more layers of water to be associated with the first layer, which is in the immediate vicinity of the polymer in comparison with the —O—$SO_3^-$ group, and hence more water uptake can be seen in a hydrogel with the binding of DTAB containing —$N^+(CH_3)_3$ groups.

Conductivity measurements were used to determine the amounts of free DTAB and SDS in their aqueous solutions in the presence of the P(DMAPMA-*co*-AAm) hydrogel. This hydrogel was expected to adsorb some of the DTAB and SDS molecules, and because the polymers within the hydrogel structure are nonionic, the conductivity should be proportional to the concentration of free ionic surfactant molecules. Figures 4 and 5 show the temperature dependence of conductivity in the absence [Fig. 4(a) for DTAB and Fig. 5(a) for SDS] and presence [Fig. 4(b) for DTAB and Fig. 5(b) for SDS] of this hydrogel in the respective surfactant solutions. The conductivity of the solutions without the hydrogel increased almost linearly with both the DTAB and SDS concentrations and the temperature. In the presence of the P(DMAPMA-*co*-AAm) hydrogel, the conductivity was also linearly changed with respect to the temperature variation for the temperature range investigated, except in the temperature range of 34–40 °C, in

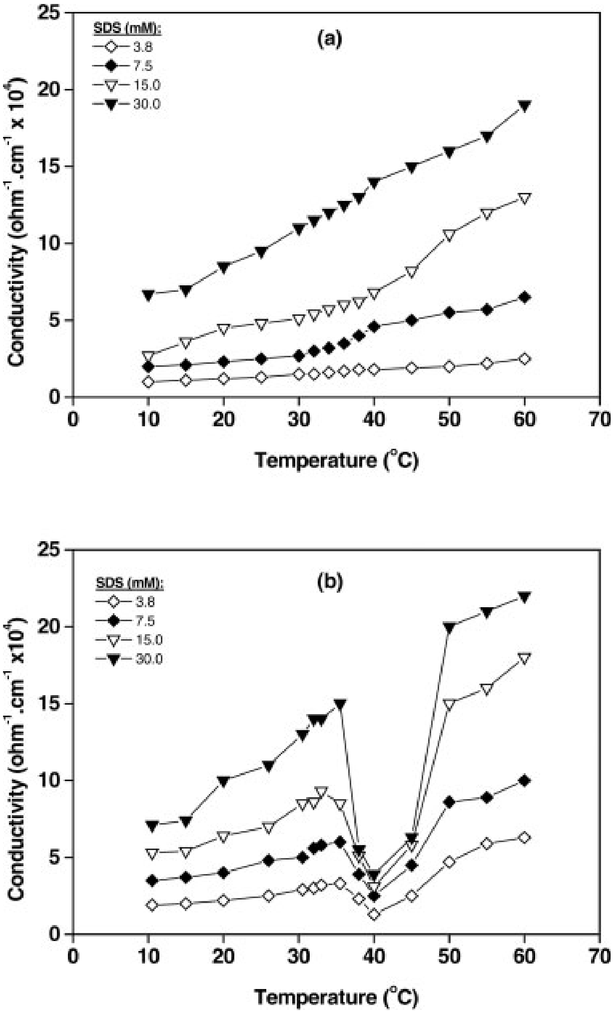


**Figure 5.** Temperature dependence of the conductivity of SDS solutions (a) in the absence and (b) in the presence of the P(DMAPMA-*co*-AAm) hydrogel with 11.1% MBAAm.

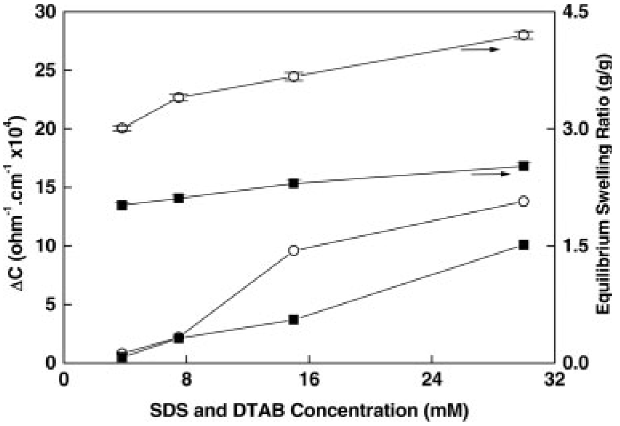


**Figure 6.** Surfactant concentration dependence of the equilibrium swelling ratio and difference in the conductivity ($\Delta C$) at 40 °C between hydrogel-containing and hydrogel-free surfactant solutions: (○) DTAB and (■) SDS.

which a significant sudden decrease in conductivity was observed that did not change with the type of surfactant. This temperature range can thus be called the binding temperature of the surfactant onto the polymer.[11,16] The magnitude of the decrease in the free DTAB or SDS concentrations, indicated by the decrease in the conductivity, increased with the surfactant concentration. To see this effect more clearly, the differences in the conductivities at 40 °C for each surfactant with and without hydrogels were plotted as a function of surfactant concentrations (Fig. 6). As shown, the values increased linearly with increasing surfactant concentration. These results indicate that the association of DTAB and SDS with the hydrogel became stronger in the vicinity of the phase-transition temperature and increased the binding amounts of these surfactants. In addition, at a temperature slightly higher than the phase-transition temperature, a strong uptake of DTAB and SDS molecules by the P(DMAPMA-*co*-AAm) hydrogel occurs primarily because of hydrophobic interactions. The observed effects of both the cationic surfactant DTAB and anionic surfactant SDS on the P(DMAPMA-*co*-AAm) hydrogel can thus be readily understood if we assume that the hydrogel acquires a partially ionic character upon the binding of DTAB or SDS molecules onto the polymer network. It is reasonable to suppose that DTAB or SDS binds to the hydrogel within the gel phase though hydrophobic interactions. The strong hydrophobic interactions between DTAB or SDS molecules and the P(DMAPMA-*co*-AAm) hydrogel enables the surfactants to bind to polymer networks not only from free DTAB or SDS molecules but also from micelles of these, through the destruction or breakdown of the latter.[17] The critical micelle concentrations of DTAB and SDS are 15.6 and 8.3 mM at room temperature, respectively.[11,17] At surfactant concentrations beyond this characteristic concentration, the excess free surfactant is in a dual equilibrium with micelle formation and binding to the hydrogel. Both cases would result in a saturation value for the amount of the surfactant bound to the hydrogel. On the other hand, the conductivity of the surfactant solutions in the absence and presence of the hydrogel should be different in the whole range of temperatures studied if there is a hydrophobic interaction between the surfactant molecules and hydrogel or the hydrogel becomes a polyelectrolyte. However, as mentioned previously, the conductivity of the surfactant solutions in the absence and presence of the hydrogel is about the same, except that there is a sudden decrease in the conductivity around 40 °C when the hydrogel is present. This behavior shows that the surfactant molecules bind a majority to the near vicinity of the hydrogel surfaces, not to the internal part.

Beyond 40 °C, however, the conductivity of the hydrogel–surfactant systems increased again linearly with increasing temperature. When the hydrogel shrank around 40 °C, the salting out of the surfactant molecules from the hydrogel matrix occurred, and surfactant molecules hydrophobically bound to the hydrogel were released and, because of collapse, were pumped out of the matrix into the contacting medium. This conductivity behavior must be the result of the desorption of the DTAB and SDS molecules around the surface of the hydrogel. Because the hydrophobic interactions between the hydrogel and the surfactant molecules involve very low energies, these could be overcome with increasing temperature easily, and this would cause the conductivity of the hydrogel–surfactant systems to increase beyond the binding temperature of the surfactant.

O. Güven acknowledges the support of the Academy of Sciences of Turkey. This work was supported by the State Planning Organization of Turkey (2003 K 120 470-31 DPT).

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