

Network Parameters and Volume Phase Transition Behavior of Poly(*N*-isopropylacrylamide) Hydrogels

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ABSTRACT: Thermosensitive hydrogels were prepared by free radical polymerization in aqueous solution from *N*-isopropylacrylamide (NIPA) monomer and *N,N*-methylenebis(acrylamide) (MBAAm) crosslinker. The swelling equilibrium of the hydrogels in deionized water was investigated as a function of temperature and MBAAm content. The results indicated that the swelling behavior and temperature sensitivity of the hydrogels were affected by the amount of MBAAm content. The average molecular mass between crosslinks (\overline{M}_c) and polymer–solvent interaction parameter (χ) of the hydrogels were determined from equilibrium swelling values. The swelling variations were explained according to swelling theory based on the hydrogel chemical structure. The swelling equilibrium of the hydrogels was also investigated as a function of temperature in aqueous solutions of the anionic surfactant sodium dodecyl sulfate (SDS) and the cationic surfactant dodecyltrimethyl-

ammonium bromide (DTAB). In deionized water, the hydrogels showed a discontinuous volume phase transition at 32°C. In SDS and DTAB solutions, the equilibrium swelling ratio and the volume phase transition temperature (lower critical solution temperature) of the hydrogels increased, which is ascribed to the conversion of nonionic PNIPA hydrogel into polyelectrolyte hydrogels because of binding of surfactant molecules through the hydrophobic interaction. Additionally, the amount of free SDS and DTAB ions was measured at different temperatures by a conductometric method; it was found that the electric conductivity of the PNIPA–surfactant systems depended strongly on both the type and concentration of surfactant solutions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1756–1762, 2006

Key words: hydrogel; swelling; poly(*N*-isopropylacrylamide); surfactants

INTRODUCTION

Hydrogels exhibit unique properties such as the volume phase transition or critical phenomena.^{1,2} Among the volume phase transition hydrogels, it has been examined precisely that chemically crosslinked poly(*N*-isopropylacrylamide) [PNIPA] hydrogel in water undergoes a discontinuous volume phase transition in response to a change in temperature at critical point.³

The volume phase transition behavior of PNIPA across its lower critical solution temperature (LCST) is generally attributed to the reversible formation and breakage of the hydrogen bonding between the water and hydrophilic groups of PNIPA and the hydrophilic/hydrophobic groups within PNIPA chains.^{4–6} Therefore, the phase separation of the PNIPA hydrogel is the result of a balance between polymer–solvent interactions in the hydrophilic amide group of PNIPA and its the hydrophobic isopropyl pendant group. As the temperature increases, the pendant groups become

mobile, and the hydrophobic isopropyl groups also become more active, causing phase separation at LCST.^{7,8}

Hydrogel structure and elasticity depend on the nature of crosslinking agent as well as on the average molecular mass between crosslinks (\overline{M}_c). The \overline{M}_c is critical parameter that controls the volume phase transition behaviors and mechanical properties of hydrogel. Saito and coworkers⁶ examined the effect of the amount of the *N,N*-methylenebis(acrylamide) (MBAAm) crosslinking agent on the LCST and swelling properties of PNIPA. Recently, Huglin and coworkers⁹ reported the effect of the crosslinker content on the swelling ratio, polymer–water interaction parameter and so forth. However, to our knowledge the systematic investigations of the effect of the level of crosslinking on the properties, especially the LCST behavior and the responsive dynamics of the PNIPA hydrogels, have not been reported before.

On the other hand, the interaction between surfactants and hydrogels is of great importance in understanding the fundamentals of hydrogel volume transition because of the amphoteric property of surfactants. Mashelkar and coworkers¹⁰ investigated the swelling behavior of hydrophobically modified PNIPA copolymeric hydrogels in aqueous sodium dodecyl sulfate (SDS). The swelling ratios and LCST were found to be

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remarkably enhanced, which was interpreted on the basis of electrostatic repulsion due to binding of SDS to polymer chains. The change in the transition temperature was found to be influenced strongly by addition of small amounts of ionic surfactants.

In this article, we have reported the findings of a systematic study of the effects of the crosslinker content on the properties of PNIPA hydrogels, especially the network structure, the LCST behavior, and the responsive dynamics. We have also studied the effects of the anionic surfactant SDS and the cationic surfactant dodecyltrimethylammonium bromide (DTAB) contents on the swelling behavior and volume phase transition temperature of PNIPA hydrogels.

EXPERIMENTAL

Materials

The monomer *N*-isopropylacrylamide (NIPA), the crosslinker *N,N*-methylenebis(acrylamide) (MBAAm), the initiator ammonium persulfate (APS), the accelerator *N,N,N',N'*-tetramethylethylenediamine (TEMED), and surfactants SDS and dodecyltrimethylammonium bromide (DTAB) were purchased from Aldrich Chemical (Milwaukee, WI). NIPA monomer was purified by crystallization from a toluene/*n*-hexane mixture before polymerization. The other chemicals were used as received. All aqueous solutions were prepared using deionized water.

Hydrogel synthesis

PNIPA hydrogels were synthesized by free-radical crosslinking polymerization of NIPA monomer in an aqueous solution at room temperature (22°C) for 24 h in the presence of predetermined concentrations of the MBAAm crosslinking agent. APS (0.056*M*) and TEMED (0.32*M*) were used as the redox initiators in the gelation process. The amount of MBAAm in the monomer mixture was varied from 0.25 to 1.25 wt %. The NIPA (1.0 g), APS (1.0 mL), and MBAAm (12.5 mg) 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(vinylchloride) straws of 4 mm diameters and about 20 cm long. The poly(vinylchloride) straws were sealed and immersed in a thermostated water bath at 20°C, and the copolymerization was conducted for 24 h. Upon completion of the reaction, the hydrogels were cut into specimens of ~10 mm in length and immersed in large excess of water to wash out any unreacted monomers and the initiator. The hydrogel samples were then dried at 50°C under vacuum to constant weight. The ratio between mass of dried polymer and calculated polymer mass for 100% conversion for these samples was found in the range

of 1.03–1.08. An analysis of these values shows both the presence of bound water and conversion of monomer to polymer to be close to 100%. The crosslinked *N*-substituted acrylamide hydrogels always contain about 10–20 wt % of bound water, even after several months of drying under vacuum.¹¹

The volume fraction of polymer network after preparation, ν_{2r} , was calculated as follows:

$$\nu_{2r} = \left[1 + \frac{\left(\frac{m_r}{m_d} - 1 \right) \rho_2}{\rho_1} \right]^{-1} \quad (1)$$

where m_r is the mass of the hydrogel after preparation, m_d is the mass of the hydrogel after drying, and ρ_2 and ρ_1 are densities of polymer network and solvent, respectively. The values ρ_2 and ρ_1 used were 1.35 and 1.0 g/mL, respectively. The density of polymer network was determined by a pycnometer using acetone as nonsolvent. On the other hand, ν_{2r} can also be calculated from initial monomer concentration of monomers C_0 (1.76×10^{-3} mol mL⁻¹) as¹²:

$$\nu_{2r} = C_0 \bar{V}_r \quad (2)$$

where \bar{V}_r is the molar volume of NIPA (83.8 mL mol⁻¹).

The experimental ν_{2r} values of the hydrogels with different MBAAm content were found larger than the theoretical ones because of the presence of bound water in the hydrogel. Hence, the theoretical ν_{2r} value was used for further calculations.

Determination of swelling kinetics

The swelling kinetic of the hydrogels was measured gravimetrically. The dried samples were placed in distilled water at 22°C and removed from water at regular time intervals. After the water on the surfaces of the hydrogels was wiped off with moistened filter paper, the weights of the hydrogels were recorded. The swelling ratio was defined as follows:

$$SR = \frac{m_t - m_d}{m_d} \quad (3)$$

where m_t is the mass of the swollen hydrogels at time t .

Determination of equilibrium swelling ratio

For the temperature–response studies, the hydrogels were equilibrated in distilled water at temperatures ranging from 5 to 60°C. The hydrogels were allowed to swell in distilled water for at least 24 h at each predetermined temperature, controlled up to $\pm 0.1^\circ\text{C}$

in a constant-temperature water bath (Thermo Haake K10). 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:

$$\text{ESR} = \frac{m_s - m_d}{m_d} \quad (4)$$

where m_s is the mass of the swollen hydrogel.

Similarly, for the swelling measurements in aqueous surfactant solutions, the hydrogels were immersed in vials filled with aqueous surfactant solutions (SDS or DTAB). Aqueous surfactant solutions were prepared by dilution of the 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 that the concentration of the solution was practically unchanged. The hydrogels were equilibrated in aqueous surfactant solutions at temperatures ranging from 5 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 PNIPA hydrogel and surfactant (DTAB or SDS) systems was measured in the concentration range of 3.8–30 mM surfactant solutions at different temperatures by using a conductometer (Model WPA CM 35). The temperature was controlled with water circulation using a thermostatic circulator (Thermo Haake K10).

RESULTS AND DISCUSSION

Swelling kinetics

The swelling kinetic curves of the hydrogels with different MBAAm content are shown in Figure 1. The

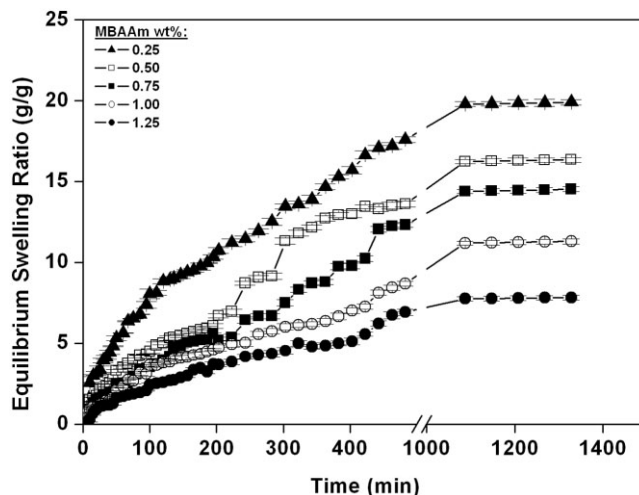


Figure 1 Swelling kinetics of the PNIPA hydrogels containing different MBAAm content. The crosslinker contents of the hydrogels are indicated as the insert.

data show that the swelling rate decreased with increasing MBAAm content from 0.25 to 1.25 wt %. The hydrogel with 0.25 wt % MBAAm has about 8.8 swelling ratio within 120 min or 15.7 within 400 min, whereas the hydrogel with 1.25 wt % MBAAm has about 2.5 and 5.1, respectively, within the same time frames. Before the swelling in the dry hydrogel, there are strong intermolecular or polymer–polymer interactions, such as hydrogen bonds and hydrophobic interactions, which remain in a glassy state.¹³ This suggests that a glassy inner core might exist in the dry hydrogel having a higher crosslinking level because the high crosslinking may lead to strong such interactions. In this case, the hydrogels having a high crosslinking level, such as the hydrogels with 1.00 and 1.25 wt % MBAAm, might have glassy cores, which would lead to a significant reduction in the rate of water absorb, and the rate of reduction in water absorb would depend on the disappearing rate of the core upon swelling.

To determine the nature of water diffusion into hydrogels, initial swelling data were fitted to following exponential equation¹⁴:

$$F = \frac{M_t}{M_\infty} = kt^n \quad (5)$$

where F denotes the amount of water fraction at time t , M_t and M_∞ represent the amount of water absorbed by the hydrogel at time t and at equilibrium, k is a characteristic constant of the hydrogel, and n is a characteristic exponent of the mode of transport of the penetrate. The constant n and k were calculated from the slopes and intercepts of the graph of $\log F$ against $\log t$ for hydrogels with various MBAAm content in water. These results are shown in Table I. In the eq.(5),

TABLE I
The Parameters of Diffusion of Water into the PNIPA Hydrogels

| MBAAm (wt %) | k (10^2) | n | D (10^7 cm 2 s $^{-1}$) |
|--------------|----------------|-----------------|----------------------------------|
| 0.25 | 0.53 | 0.75 ± 0.02 | 3.05 |
| 0.50 | 1.10 | 0.61 ± 0.01 | 1.29 |
| 0.75 | 0.87 | 0.63 ± 0.02 | 1.27 |
| 1.00 | 1.48 | 0.55 ± 0.02 | 0.71 |
| 1.25 | 1.67 | 0.58 ± 0.02 | 0.17 |

the numerical value n provides information about the mechanism of swelling kinetics. For the first case, $n = 0.5$, corresponding to a Fickian diffusion, the rate of diffusion is much slower than the rate of relaxation and for the second, $n = 1$, the diffusion is very fast, contrary to the rate of relaxation, and the third case corresponds to an anomalous diffusion (or non-Fickian diffusion) with n values lying between 0.5 and 1.

A slight variation of diffusion exponent with MBAAm content is observed, and its value higher than 0.50 and it can be concluded that the overall process is anomalous diffusion, i.e. chain relaxation controlled process. The highly anomalous behavior of these hydrogels is due to the regularity of the chain and strong interchain interactions via the formation of hydrogen bonding, leading to a compact structure that would accentuate the anomalous aspects of diffusion even for a molecule as small as water.

For calculating diffusion coefficient of water moving through the PNIPA hydrogels, the following equation was employed.¹⁴

$$D = \pi r^2 \left(\frac{k}{4} \right)^{1/n} \quad (6)$$

where D is the diffusion coefficient of water (cm 2 s $^{-1}$) and r is the radius of the dry gel. The r was measured by a calibrated digital compass.

The D values are also presented in Table I. The diffusion coefficients D decreased with an increase of MBAAm content in the hydrogel. This is explained by the restriction of the expansion of the network structure resulting from the increase of the crosslinking density.

Network parameters

The molecular mass between crosslinks (\bar{M}_c) is one of the basic structural parameters of crosslinked polymeric networks that controls the volume phase transition temperature and mechanical properties of the hydrogels. It is well known that the increasing level of crosslinking, the \bar{M}_c of the hydrogel would be decreased, and the pore density in the network would be increased. In this study, the experimental \bar{M}_c values

were calculated from equilibrium swelling ratios of the hydrogels by using the following equation based the phantom network model^{15,16}:

$$\bar{M}_c(\text{Exp}) = - \frac{(1 - 2/\phi)V_1\rho_2v_{2r}^{2/3}v_{2m}^{1/3}}{(\ln(1 - V_{2m}) + V_{2m} + \chi V_{2m}^2)} \quad (7)$$

where ϕ is the functionality of the crosslinks ($\phi = 4$), V_1 is the molar volume of the solvent (18 mL/mol), v_{2m} is the volume fraction of the polymer network in the swollen gel at the equilibrium state, and χ is the polymer solvent interaction parameter. The v_{2m} values were calculated from the following expression valid at swelling equilibrium.

$$v_{2m} = \left[1 + \frac{(m_s/m_d - 1)\rho_2}{\rho_1} \right]^{-1} \quad (8)$$

The χ parameters of the hydrogels can be obtained experimentally via the following expression⁹:

$$\chi = \frac{1}{2} + \frac{v_{2m}}{3} \quad (9)$$

On the other hand, assuming that all MBAAm molecules used in the hydrogel synthesis participate in forming effective crosslinks, theoretical \bar{M}_c values of the hydrogels were calculated by the following equation¹²:

$$\bar{M}_c(\text{Theo}) = \frac{\rho_2 \bar{V}_r}{2X} \quad (10)$$

where X is the crosslinker ratio (mole ratio of MBAAm to NIPA). The relevant experimental and theoretical parameters of the hydrogels were collected in Table II. As can be seen from Table II, the slight increment in χ parameter with increasing crosslinker amount could be explained by the lower hydrophilic character of MBAAm. Because when a hydrophilic crosslinking agent is employed, the hydrogel shows a high affinity towards the aqueous solution owing to the presence of polar groups.¹⁷ As a result, the swelling ratio of the hydrogels increases with increasing the polarity of the polar group in the hydrophilic crosslinker.¹⁸ Xue and Hamley¹⁹ observed that replacing MBAAm with more hydrophilic glyoxal bis(diallylacetal) (GLY) as crosslinker, the swelling ratio of the crosslinked PNIPA hydrogel enhanced. In addition, at low crosslink density, increasing amounts of hydrophilic crosslinker may increase the swelling ratio. Poly (2-hydroxyethyl methacrylate) (PHEMA) hydrogels showed an exceptionally large increase in swelling ratio with the increasing amount of crosslinker tripropyleneglycol diacrylate.²⁰ The tripropyleneglycol dia-

TABLE II
The Characteristic Data of the PNIPA Hydrogels

| MBAAm (wt %) | $X (10^3)$ | $v_{2m} (10^2)$ | χ | \bar{M}_c (Theo) (10^{-3} g/mol) | \bar{M}_c (Exp) (10^{-5} g/mol) |
|--------------|------------|-----------------|--------|---------------------------------------|--------------------------------------|
| 0.25 | 1.8 | 3.6 | 0.512 | 31.4 | 25.0 |
| 0.50 | 3.7 | 4.3 | 0.514 | 15.3 | 15.0 |
| 0.75 | 5.5 | 4.9 | 0.516 | 10.3 | 8.9 |
| 1.00 | 7.3 | 6.2 | 0.521 | 7.8 | 4.0 |
| 1.25 | 9.2 | 8.6 | 0.529 | 6.1 | 1.3 |

crylate in the highly crosslinked PHEMA is supposed to contribute to the enhanced swelling.

On the other hand, the experimental \bar{M}_c values of the hydrogels decreased from 25.0×10^5 to 1.3×10^5 g/mol with increasing amount of MBAAm, ranging 0.25–1.25 wt %. The experimentally found \bar{M}_c values of the hydrogel with 0.25 wt % MBAAm is 80-fold higher than its theoretically calculated counterpart. This value decreased to 51 and 21 when 1.00 and 1.25 wt % MBAAm was used in the hydrogel preparation, respectively. The difference between the theoretical and experimental \bar{M}_c values of the hydrogels indicates that a significant fraction of the crosslinker MBAAm is wasted during the crosslinking copolymerization, probably due to the cyclization and multiple crosslinking reactions. The high degree of dilution during the hydrogel preparation as well as the higher crosslinker reactivity is mainly responsible for these reactions.

Effect of crosslinker content on equilibrium swelling ratio

Figure 2 shows the temperature dependence of the equilibrium swelling ratio and LCST of the PNIPA hydrogels with different amount of crosslinker in wa-

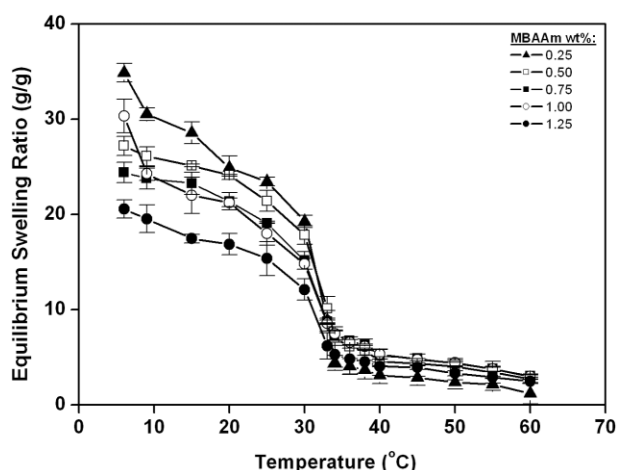


Figure 2 Equilibrium swelling ratios of the PNIPA hydrogels in water shown as a function of temperature. The crosslinker contents of the hydrogels are indicated as the insert.

ter when the temperature increased from 5 to 60°C. The data show that all the PNIPA hydrogels, regardless of the amount of the MBAAm, had similar swelling behaviors as a function of temperature and the volume phase transition temperature or LCST of these hydrogels is at about 32°C. It is also shown that all PNIPA hydrogels exhibit a negative temperature-sensitive, which is swelling at lower temperature and shrinking at higher temperature. Under equilibrium swelling conditions, all PNIPA hydrogels showed increasing swelling at lower temperatures, but they deswelled at high temperatures because of the aggregation of the network chains. When the external temperature was increased from 5 to 60°C, the volume or water content inside PNIPA hydrogels decreased slowly during the shrinkage, and the water release rate is controlled mainly by collective diffusion of the hydrogel.²¹

The data in Figure 2 clearly showed also that at 5 and 30°C temperature intervals, the equilibrium swelling ratios of the hydrogels increased with decreasing amount of MBAAm. Especially at 5°C, the equilibrium swelling ratio increased 75% with decreasing amount of MBAAm from 1.25 to 0.25 wt %. This is presumably due to the increasing mesh size or \bar{M}_c value of the network with decreasing crosslinker content, which enhances the diffusion of water molecules into the hydrogel. However, Figure 2 shows that the LCST values for these hydrogels are unaffected by the crosslinker content. This result is in accord with those reported by Xue and Hamley¹⁹ for hydrogels of NIPA with a hydrophobic comonomer. In addition, as can be shown in Figure 2, there was no obvious effect of the crosslinker content on the equilibrium swelling ratio of the PNIPA hydrogels at temperatures above the LCST. This suggests that regardless of the amount of crosslinker, all the PNIPA hydrogels may collapse into similar collapsed structure at above LCST.

Effects of surfactants on swelling equilibrium

Figures 3 and 4 show the temperature dependence of the equilibrium swelling ratio of the PNIPA hydrogel with 1.0 wt % MBAAm in the presence of two different ionic surfactants with various concentrations. The

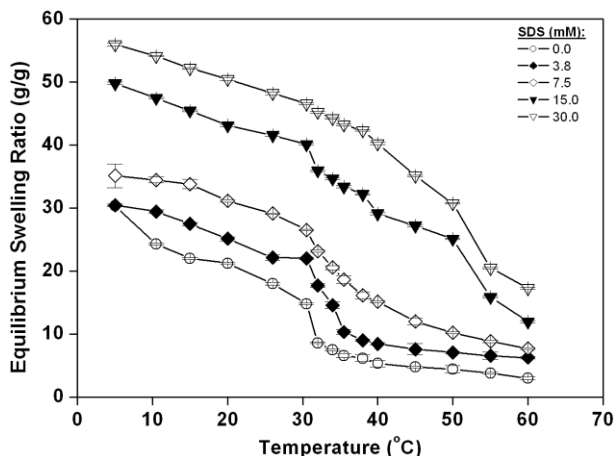


Figure 3 Equilibrium swelling ratio of the PNIPA hydrogel with 1.0 wt % MBAAM in SDS solutions shown as a function of temperature. The concentrations of SDS solutions are indicated as the insert.

overall effect observed is an increase in the equilibrium swelling ratio of the hydrogel in surfactant solutions for the whole temperature range investigated when compared with that in pure water. When DTAB or SDS molecules diffuse into the hydrogel strong association should take place through the hydrophobic interaction between the hydrophobic groups of the PNIPA and long chain alkyl groups of the DTAB or SDS, thereby increasing the surface charge density of the hydrogels as the neutral polymer chains assume a degree of polyelectrolyte character. These acquired network charges and the counterions associated with them exert an extra osmotic pressure on the network. As a result, the polymer conformation will become more like that of an expanded coil than a globule, and

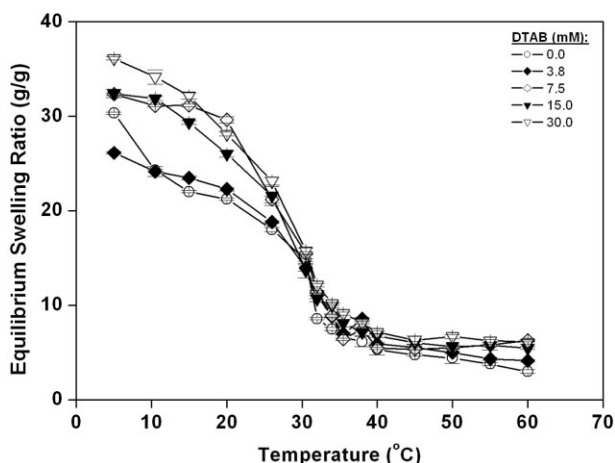


Figure 4 Equilibrium swelling ratio of the PNIPA hydrogel with 1.0 wt % MBAAM in DTAB solutions shown as a function of temperature. The concentrations of DTAB solutions are indicated as the insert.

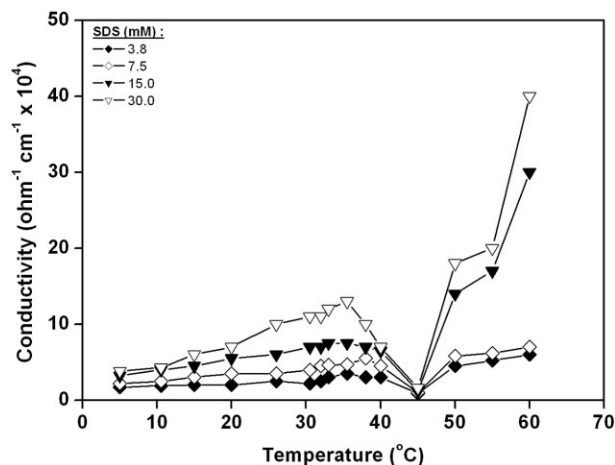


Figure 5 Temperature dependence of conductivity of SDS solutions in presence of the PNIPA hydrogel with 1.0 wt % MBAAM. The concentrations of SDS solutions are indicated as the insert.

therefore the equilibrium swelling ratio of the hydrogels will be increased.¹⁹

In solutions containing SDS (Fig. 3), the value of LCST not only increased but also a single LCST was not displayed for SDS concentrations above 7.5 mM; instead two LCST were observed, one at about 32–40°C and another one at about 50–55°C. A similar observation was reported by Mashelkar and coworkers¹⁰ for their hydrophobically modified PNIPA hydrogels. They have attributed this behavior to the presence of heterogeneous phases as a result of uneven binding of SDS molecules. However, in the DTAB solutions (Fig. 4), the PNIPA hydrogels had almost the same LCST value irrespective of the concentration of DTAB solutions. This difference observed in SDS and in DTAB solutions was attributed to the differences in the counterions, the ionizable groups, and the binding amounts of the surfactants.

Figures 5 and 6 show the temperature dependence of conductivity in the presence of this hydrogel in the respective surfactant solutions. The conductivity was linearly dependent with respect to temperature variation for the temperature range investigated, except in the temperature range of 36 and 45°C, where a significant sudden decrease in conductivity was observed, and this did not change with the type of surfactant. This temperature range can be thus referred to as the binding temperature.^{22,23} The magnitude of the decrease in the free DTAB or SDS concentrations, indicated by the decrease in conductivity, was found to increase with the surfactant concentration. However, after 45°C, the conductivity of the hydrogel–surfactant systems increased again linearly with increasing temperature. This conductivity behavior must be the result of the desorption of the DTAB and SDS molecules at around the surface of hydrogel. Because the hydro-

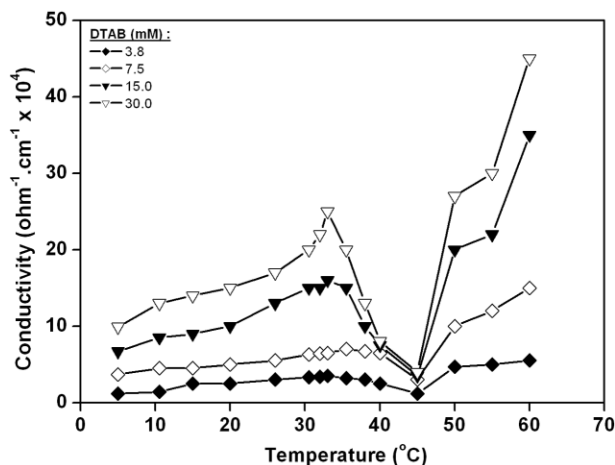


Figure 6 Temperature dependence of conductivity of DTAB solutions in presence of the PNIPA hydrogel with 1.0 wt % MBAAM. The concentrations of DTAB solutions are indicated as the insert.

phobic interactions between the hydrogel and the surfactant molecules having a low energy would be overcome with increasing temperature, in this case, the conductivity of the hydrogel–surfactant systems increases.

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