

Poly(acrylamide-*co*-maleic acid) Hydrogels for Removal of Cr(VI) from Aqueous Solutions, Part 1: Synthesis and Swelling Characterization

S. K. Bajpai,¹ Susamma Johnson²

¹Polymer Research Laboratory, Department of Chemistry, Government Autonomous Science College, Jabalpur 482001, Madhya Pradesh, India

²Pt. L. S. J. Govt. Model Hr. Sec. School for Excellence, Jabalpur 482001, Madhya Pradesh, India

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ABSTRACT: The swelling behavior of poly (acrylamide-*co*-maleic acid) hydrogels has been investigated in distilled water at 30°C. The gels were characterized with respect to structural parameters, Fourier transform infrared, and thermogravimetric analysis. The gels showed fair pH-dependent swelling and exhibited double “s”-shaped curve between equilibrium water uptake and pH of the swelling media. The two pK_a values, as determined from the curve, were found to be 2.46 and 6.58. The activation energy of the water uptake process for plain and acid containing gels was found to be 7.93 and 3.26 kJ mol⁻¹ respectively. Similarly, the enthalpy of mixing between dry polymer and solvent showed positive values, thus indicating endothermic nature of the process, and the values increased from 10.06 to 16.29

kJ mol⁻¹ with increase in acid content from 2.1×10^{-1} to 4.7×10^{-1} mM respectively. There was an optimum initiator concentration 24.0×10^{-2} mM and reaction temperature 60°C at which gels synthesized showed maximum absorbency. The dilution of the reaction mixture resulted in the formation of hydrogels with enhanced absorbency. Finally, the gels with varying content of monomer acid in the feed mixture showed different swelling behavior when studied in the medium of pH 1.0 and 7.0. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2759–2769, 2006

Key words: hydrogels; adsorption; activation energy; swelling

INTRODUCTION

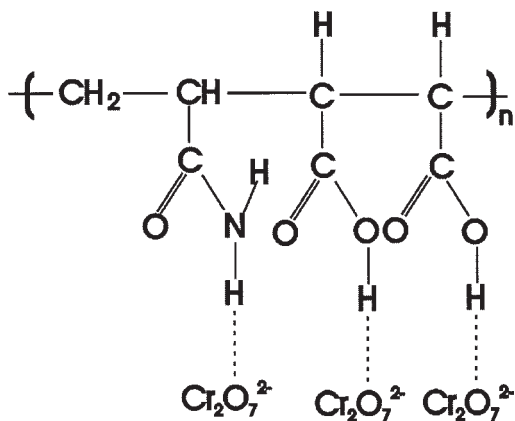
Hexavalent chromium, one of the inorganic pollutants with well-known toxicity,¹ is used extensively in industries such as electroplating, tanning, anodizing, and chrome mining. Strong exposure of chromium may cause cancer in the digestive tract and lungs.² Chromium compounds may cause epigastric pain, nausea, severe diarrhea, and hemorrhage.³ So it is essential to remove Cr(VI) from industrial effluents before it is mixed with drinking water sources.

Conventional methods for the removal of Cr(VI) from waste water include chemical precipitation, ion exchange, electrolysis, and reverse osmosis.^{4,5} However, owing to the operational difficulties and cost of the treatment, attempts have been made to develop new methods. In the recent past, in addition to conventional adsorbents, some nonconventional adsorbents such as fly ash,⁶ fire clay,⁷ chemically modified saw dust,⁸ heat-activated boxite,⁹ hydrous titanium oxide,¹⁰ and chitin¹¹ have been used. In addition to this, plant residues such as stalks, maize corn, and

sugar cane bagasse^{12,13} have also been used successfully for removal of Cr(VI). Apart from nonconventional adsorbents, polymeric hydrogels have also showed their ability to remove toxic metal ions from the aqueous solutions. For example, a number of hydrogels have been used successfully for the removal of heavy metal ions from the industrial effluents.^{14–16} However, to the best of our knowledge, the removal of Cr(VI) from aqueous solution by using synthetic hydrogel has not been reported. In an attempt to investigate the feasibility of the probable interaction between Cr(VI) and polymeric hydrogels, we found, in a preliminary study, that poly(acrylamide-*co*-maleic acid) hydrogels effectively removed Cr(VI) from aqueous solution. The possible reason for the adsorption of Cr₂O₇²⁻ ions onto the poly(acrylamide-*co*-maleic acid) hydrogels seems to be the H-bonded interactions between the electronegative oxygen atoms of dichromate ions and H atoms present in carboxylic groups of maleic acid and amide groups of acrylamide as shown in Scheme 1.

Since the absorption of metal ions into hydrogel system has been reported to be dependent upon crosslink density of the hydrogel, the pH of the swelling medium, and composition of gels,¹⁷ it becomes essential for us to carry out a detailed investigation of

Correspondence to: S. K. Bajpai (sciexcel@sancharnet.in).



Interactions between chromium (VI) and hydrogel

Scheme 1 Interactions between chromium (VI) and hydrogel.

the swelling behavior of this hydrogel system so that optimum conditions can be obtained under which the hydrogels may show maximum interaction with Cr(VI) to cause an efficient removal.

EXPERIMENTAL

Materials

The monomers acrylamide (AAM; purity, 99.8%) and maleic acid (MA; analytical reagent grade) were purchased from Hi Media, Mumbai, India. The crosslinking agent MB and initiator potassium persulfate (KPS; analytical reagent grade) were obtained from Research Lab, Mumbai, India, and used as received. The monomer AAM was recrystallized in methanol to remove the inhibitor. All other salts used were of analytical grade. The double-distilled water was used throughout the investigations.

Synthesis of cylindrical gels

The poly(acrylamide-co-maleic acid) hydrogels were synthesized by copolymerization of AAM and MA in aqueous medium, using MB as crosslinker and KPS as initiator. In brief, 23.90 mmol of AAM, 0.21 mmol of MA, and 0.097 mmol of crosslinker were dissolved in distilled water to give a total volume of 5.0 mL. After adding 0.074 mmol of initiator KPS, the resulting solution was transferred into PVC straws, each of diameter 0.30 cm, and kept in an electric oven (Tempstar, India) at 60°C for a period of 2 h. The resulting transparent gels were cut into small cylindrical pieces, each of area $2.54 \times 0.20 \text{ cm}^2$, washed with distilled water to remove the unreacted salts, and then dried in a dust-free chamber at 40°C till they attained constant weight. Here it is worth mentioning that in the preliminary

studies the compositions of the monomers and the amount of crosslinker were determined by gravimetry¹⁸ to attain the almost 100% gelation in the each hydrogel system studied. Moreover, the considerations for selecting the feed compositions in the present study were the solubility of the monomers and the shape stability of the swollen hydrogels in the equilibrium state.

The gel samples shall be designated as HG (X), where the number X in parenthesis is the percent mole fraction of the monomer MA in the feed mixture. For example, the hydrogel system synthesized earlier may be designated as HG (0.9).

Fourier transform infrared spectral analysis

The hydrogel sample prepared as described earlier was characterized by recording Fourier transform infrared (FTIR) spectra on a Bio-Rad WIN Fourier Transformed Infrared Spectrophotometer (Bio-Rad, Hercules, CA) in the Indian Institute of Technology, (IIT), Mumbai, India.

Thermogravimetric analysis

Thermal analysis of the polymer was carried out using a thermogravimetric analyzer (Mettler, Toledo GmbH, Switzerland). About 9.5 mg of powdered sample was placed in ceramic crucibles and analyzed over the temperature range of 25–1000°C at the rate of 20°C min⁻¹ under the dry flow of N₂ at the rate of 30 mL min⁻¹.

Swelling studies

Completely dried pre-weighed hydrogel samples were placed in 500 mL of distilled water with an ionic strength of 0.01M at 30°C. The swollen gels were taken out at regular time intervals, wiped superficially with filter paper to remove the surface water, weighed, and then put in the same bath. The mass measurements were continued until constant weight was attained for each sample. The percent mass swelling was determined using the following expression¹⁹

$$\% S_M = (m_t - m_0 / m_0) \times 100 \quad (1)$$

where m_t and m_0 are the initial mass and mass at different time intervals, respectively. All the experiments were carried out with five samples and the average values have been reported in the data. It is worth mentioning here that the reason for using large volume of swelling media was to avoid any possible pH change during the whole swelling process.

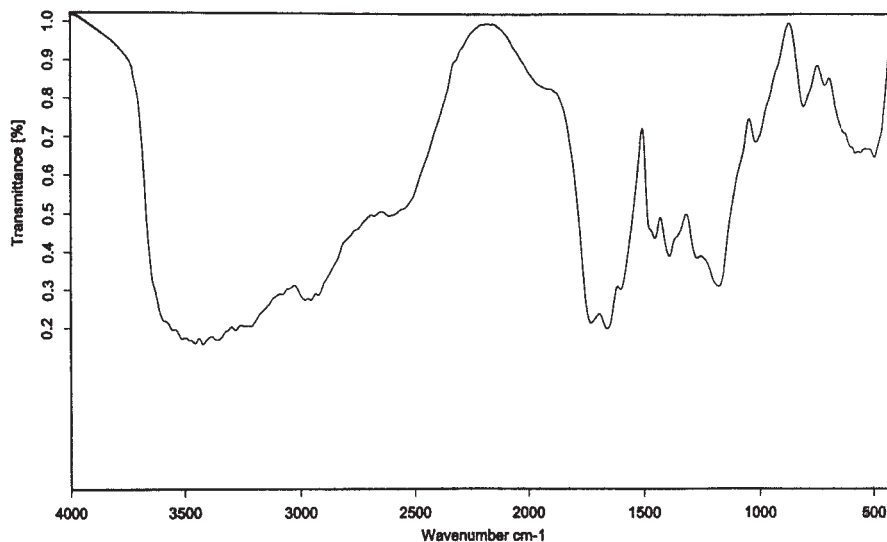


Figure 1 FTIR spectrum of synthesized poly(acrylamide-co-maleic acid) hydrogel.

RESULTS AND DISCUSSION

Ftir spectral analysis of polymer

The IR spectra (See Fig. 1) clearly shows a broad band in (3350–3550) cm^{-1} , which is due to hydrogen bonded ν OH from carboxylic group and ν NH from amide group. The $\text{C}=\text{O}$ stretching vibration at 1650 cm^{-1} is due to the carboxylic group of MA and the $-\text{CONH}_2$ group of AAm. Symmetrical and asymmetrical stretching of $\text{C}-\text{H}$ is found at 2613 and 2954 cm^{-1} , respectively. The IR spectra also shows a broad band at 2162 cm^{-1} , which is due to presence of $-\text{CN}$

group of crosslinking agent (N,N'-methylenebisacrylamide) and polyacrylamide.

Thermogravimetric analysis

Figure 2 depicts the thermogram obtained for the control sample HG (0.9). The values of T_{id} (initial decomposition temperature), T_{fd} (final decomposition temperature), and T_{max} (temperature of maximum rate of weight loss) were found to be 220 , 500 , and 380°C , respectively. It is also clear that the polymer is highly stable up to 100°C . Since the proposed polymer is to be

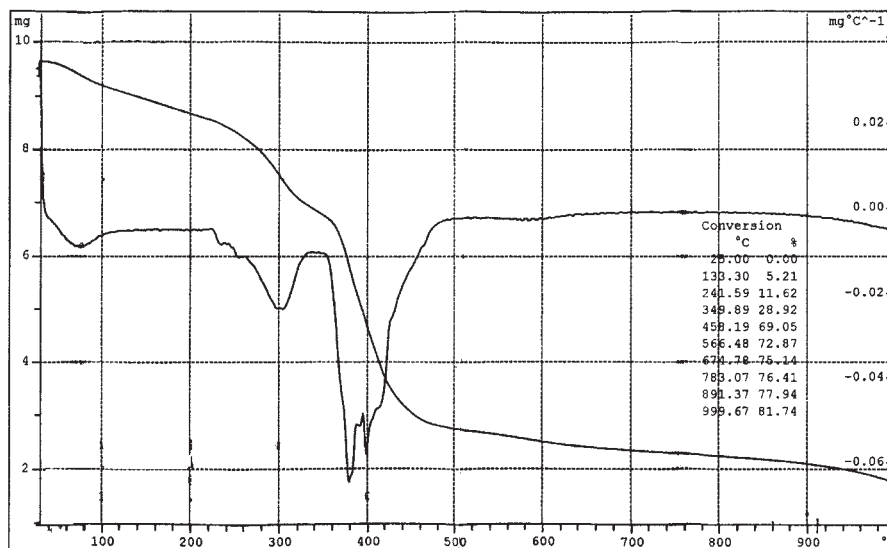


Figure 2 Thermogram of the copolymeric hydrogel.

used for the removal of Cr(VI) at room temperature (i.e., in the range 25–30°C), the stability of the polymer is beyond any doubt.

Swelling and network parameters

The swelling behavior of a pH-sensitive copolymer network depends upon a number of factors, such as crosslink density of network, hydrophilic–hydrophobic interactions, extent of chain-relaxation process,²⁰ etc. Therefore, it is important to determine various structural parameters, such as crosslink density, q ; average molecular mass between crosslinks, M_c ; number of elastically effective chains, V_e ; etc, so that the swelling behavior of polymer can be predicted in more realistic manner. The molar mass, M_c , between the crosslinks was calculated using the well-known Florry–Rehner equation,²¹ given as

$$M_c = -d_p V_s \phi^{1/3} [\ln(1 - \phi) + \chi \phi^2]^{-1} \quad (2)$$

The volume fraction, ϕ , of the swollen polymer was calculated using the equation

$$\phi = [1 + d_p/d_s(M_a/M_b) - d_p/d_s]^{-1} \quad (3)$$

In this equation d_p and d_s represent the densities of polymer and solvent, respectively, M_a and M_b are the mass of hydrogels after and before swelling, V_s is the molar volume of solvent used for swelling studies, and χ is the Florry–Huggins interaction parameter between polymer and solvent, which was calculated by a method described elsewhere.²²

The crosslink density ' q ' was calculated as

$$q = M_0/M_c \quad (4)$$

where M_0 is the molar mass of repeating unit, given as

$$M_0 = m_{AAm}M_{AAm} + m_{MA}M_{MA}/m_{AAm} + m_{MA} \quad (5)$$

Here, m_{AAm} and m_{MA} are the amounts (in grams) of monomers AAm and MA; M_{AAm} and M_{MA} their molar mass, respectively.

It is also reasonable to define a crosslink density as the number of elastically effective chains induced in a perfect network per unit volume, V_e , being given as

$$V_e = d_p N_A/M_c \quad (6)$$

where N_A is the Avogadro's number.

The diffusion of a solute into or from the hydrogel depends upon a number of parameters, such as partition coefficient of solute between the gel phase and solution phase,²³ mesh size of the network,²⁴ etc. The mesh size, ξ , was calculated as stated here.

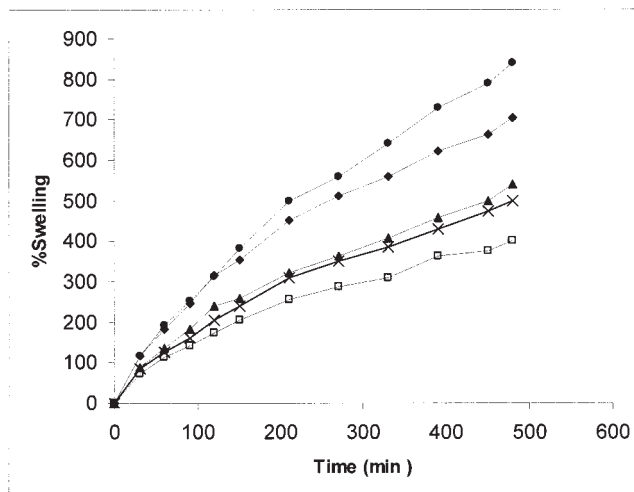


Figure 3 Dynamic uptake of water as a function of time for the hydrogel samples. HG (0.9) with various amounts of crosslinker in distilled water at 30°C. 0.357 mmol (□); 0.259 mmol (×); 0.194 mmol (▲); 0.097 mmol (◆); and 0.064 mmol (●).

From the molecular weight between crosslinks (i.e., M_c), the number of links between two crosslinks, n , was calculated as

$$n = 2M_c/M_0 \quad (7)$$

After evaluating n , the value of root mean squared end-to-end distance of the polymer chain in the freely jointed state was calculated using eq. (8)

$$(\bar{r}^2)^{1/2} = l n^{0.5} \quad (8)$$

where l is the carbon–carbon single bond length (1.54 Å). The root mean squared end-to-end distance of the polymer chain in the unperturbed state was

$$(\bar{r}_0^2)^{1/2} = C_n^{0.5} (\bar{r}^2)^{1/2} \quad (9)$$

where C_n is the rigidity factor of the polymer. Finally, the mesh size of the network, ξ , was determined as

$$\xi = \phi^{-1/3} (\bar{r}_0^2)^{1/2} \quad (10)$$

To evaluate the above-mentioned parameters, hydrogel samples HG (0.9) with various amounts of crosslinker, in the range of 0.064–0.357 mM, were synthesized, and their swelling behavior was studied in the distilled water at 30°C, with ionic strength maintained at 0.01M. The results, as depicted in the Figure 3, clearly indicate that as the amount of crosslinker in the polymer network increases, the dynamic uptake of water at different time intervals decreases. This may simply be attributed to the fact that with the increase

TABLE I
Network Parameters of Hydrogel Samples HG (0.9) with
VariouS Amounts of Crosslinker

| Amount of crosslinker (mM) | Average molar mass between crosslinks ($M_c; 10^{-4}$) | Crosslink density ($q; 10^4$) | Elastically effective chains ($V_e; 10^{-18}$) | Mesh size ($\xi; \text{\AA}$) |
|----------------------------|--|---------------------------------|--|---------------------------------|
| 0.064 | 12.68 | 5.61 | 5.69 | 751.96 |
| 0.097 | 10.28 | 6.93 | 7.38 | 562.06 |
| 0.194 | 3.70 | 19.22 | 21.10 | 346.85 |
| 0.259 | 2.71 | 26.21 | 29.21 | 284.74 |
| 0.357 | 1.58 | 44.91 | 51.64 | 203.31 |

in the amount of crosslinker, the number of crosslinkers per unit volume also increases, which finally causes a decrease in the free space available between the crosslinks, thus providing less space for accommodation of water molecules in the network.

Table I describes various structural parameters mentioned earlier. It is clear from the data that with the increase in the crosslink density, the molar mass between the crosslinks M_c decreases. Moreover, the number of elastically effective chains increases as it varies inversely with M_c . Similar results have also been reported elsewhere.²⁵

Analysis of dynamic uptake of water

When immersed in a compatible solvent, a glassy polymer network swells. If the gel is clear, then a distinct boundary between the swollen and dry regions can be observed during the penetration of the solvent into the polymer. The solvent invades the dry network until the transition from glassy state to the rubbery state is complete.²⁶ The swelling of the hydrogel involves larger scale segmental motion, ultimately resulting in an increased distance of separation between the macromolecular chains.²⁷

The following equation was used to determine the nature of the diffusion process:

$$F = M_t/M_\infty = kt^n \quad (11)$$

where M_t and M_∞ are the mass of the hydrogel at time t and at equilibrium respectively, k is the gel characteristic constant, and the swelling exponent, n , describes the type of diffusion. For cylindrical-shaped gels, $n = 0.45$ – 0.50 corresponds to the Fickian type of diffusion, while $n = 1.0$ indicates anomalous or case II transport. However, if n lies between 0.50 and 1.0 , the swelling process may be regarded as a non-Fickian one.

The swelling data, displayed in the Figure 3, was applied to the logarithmic form of the eq. (11) to

evaluate the swelling exponent n and constant k . The swelling exponent n was found to be in the range 0.62 – 0.71 , thus indicating that the non-Fickian type of swelling pattern was demonstrated by the samples with various amounts of crosslinker. The reason for this is that at the experimental pH of the swelling medium (i.e. 7.0), the almost complete ionization of the $-\text{COOH}$ groups present in the polymer matrix not only increases the osmotic swelling pressure but also causes the macromolecular chains to get relaxed because of electrostatic repulsion among similarly charged $-\text{COO}^-$ groups. These two factors, namely, osmotic swelling pressure and chain relaxation process, being comparable, are thus responsible for the non-Fickian swelling behavior of the gels.

Linear regression of swelling data

Swelling can also be described in terms of rate and maximum uptake at equilibrium, W_∞ . An earlier investigation indicated that the rate of swelling of hydrophilic polymers can be described by a second-order rate equation.²⁸ In light of this, the swelling rate at any time is directly proportional to the quadratic of the swelling capacity before reaching the equilibrium uptake. Therefore, a second-order equation²⁹ can be given as

$$dw/dt = k(W_\infty - W)^2 \quad (12)$$

where W_∞ is the equilibrium water uptake, W the water uptake at time t , and k is the rate constant. On integration, followed by rearrangement

$$t/W = A + Bt \quad (13)$$

where A and B are two coefficients, whose physical sense is interpreted as follows. At a long treatment time, Bt [tmt] A and therefore $B = 1/W_\infty$, that is, B is reciprocal of the maximum water uptake. In contrast, at a very short time treatment, A [tmt] Bt and therefore

$$Lt(dw/dt) = 1/A \quad t \rightarrow 0 \quad (14)$$

So, the intercept a is reciprocal of initial swelling rate.

Figure 4 reproduces the swelling data in Figure 3, calculated according to Eq. (13). The straight lines are obtained by linear regression. The agreement between the experimental points and the regression lines is satisfactory, thus confirming the validity of eq. (13).

Fick's first and second laws of diffusion (1855) adequately describe most diffusion processes. For cylindrical-shaped hydrogels, the integral diffusion at short times, the main result is

$$F = 4[(Dt/1^2)^{1/2}]/\pi^{1/2} \quad (15)$$

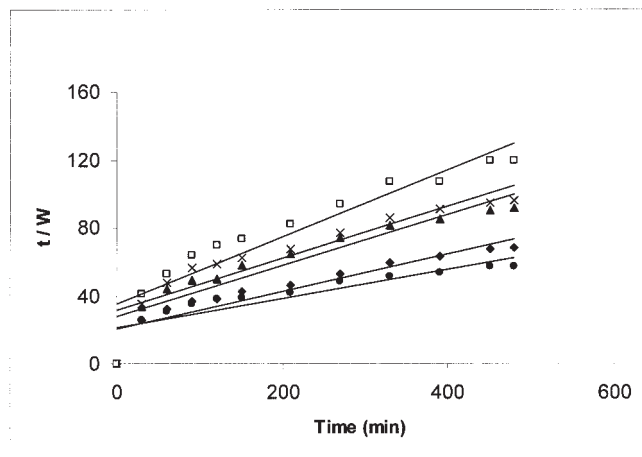


Figure 4 Variation of reciprocal of swelling as a function of time for the hydrogel sample. HG (0.9) with various amounts of crosslinker in distilled water at 30°C. 0.357 mmol (\square); 0.259 mmol (\times); 0.194 mmol (\blacktriangle); 0.097 mmol (\blacklozenge); and 0.064 mmol (\bullet).

where F is the fractional water uptake (M_t/M_∞) and D is diffusion coefficient. In eq. (15), the slope of the linear plot between F and $t^{1/2}$ yields diffusion coefficient D . However, it is not unusual to observe that F is nonlinear³⁰ with $t^{1/2}$. This non-Fickian behavior is often found for diffusion into glassy polymers below their T_g . Therefore, initial diffusion coefficient, D_i , was also evaluated from the initial linear portion of the plots.

The average diffusion coefficient D_{ave} may also be calculated for 50% of the equilibrium swelling by putting $M_t/M_\infty = 0.5$ in the above expression, which finally yields

$$D_{ave} = 0.049 \text{ l}^2/\text{t}^{1/2} \quad (16)$$

Diffusion coefficients were also calculated using the late time approximation, as described by Peppas and Brazel.³¹

$$M_t/M_\infty = 1 - [8/\pi^2 \{ \exp(-\pi^2 D t / 4l^2) \}] \quad (17)$$

On plotting $\ln(1M_t/M_\infty)$ against t , linear plots with distinct break in slopes were obtained. Similar type of observations have also been reported previously.³² Finally the late-time diffusion coefficient D_L was calculated from the slope of the lines after the break, using the simplified form of eq. (17):

$$D_L = -(\text{Slope} \times \text{l}^2/\pi^2) \quad (18)$$

All the three types of diffusion coefficients mentioned earlier have been listed in the Table II. The data displayed reveal one interesting fact. The late time diffusion coefficients are nearly the same as the initial diffusion coefficients for all the hydrogel samples. This is just opposite to our previous findings,³³ where late time diffusion was nearly 5 times greater than the initial diffusion for poly(*N*-vinyl-2-pyrrolidone-co-acrylic acid) hydrogel system. The observed unusual finding in the present system may be explained as follows:

When a —COOH-groups-containing pH-sensitive hydrogel network swells in the medium of almost neutral or slightly alkaline pH, the later part of the swelling process is usually dominated by the chain relaxation process, thus resulting in faster diffusion of solvent molecules into the swelling network. This makes the late time diffusion coefficients much greater than the initial one. However, in the present investigation, the gels have been synthesized with very small quantity of acidic monomer MA (nearly 0.9% mole fraction in control set) as compared with the nonionic monomer AAm. Therefore, even the almost complete ionization of —COOH groups does not result in greater extent of chain-relaxation process. Therefore, even in the fully relaxed state (which is achieved in the later part of the swelling process) the solvent molecules diffuse into the swollen network with almost the same rate as in the initial phase of the swelling process. This accounts for the almost same values of diffusion coefficients in the initial and later stages of swelling.

TABLE II
Swelling Parameters and Various Diffusion Coefficients for the Hydrogel Sample HG (0.9) Containing Varying Amounts of Crosslinker, in the Distilled Water with Ionic Strength 0.01M at 30°C

| Amount of crosslinker (mM) | Swelling exponent (n) | Gel characteristic constant ($k; 10^2$) | Diffusion coefficients ($\text{cm}^2 \text{min}^{-1}$) | | |
|----------------------------|---------------------------|---|--|-----------------------------|---------------------------|
| | | | Initial ($D_i; 10^2$) | Average ($D_{ave}; 10^5$) | Late time ($D_L; 10^6$) |
| 0.064 | 0.71 | 0.76 | 5.11 | 1.39 | 4.67 |
| 0.097 | 0.64 | 1.10 | 4.22 | 1.42 | 4.15 |
| 0.194 | 0.64 | 1.35 | 5.97 | 1.79 | 5.97 |
| 0.259 | 0.64 | 1.43 | 7.56 | 2.21 | 7.27 |
| 0.357 | 0.62 | 1.71 | 7.87 | 2.35 | 8.04 |

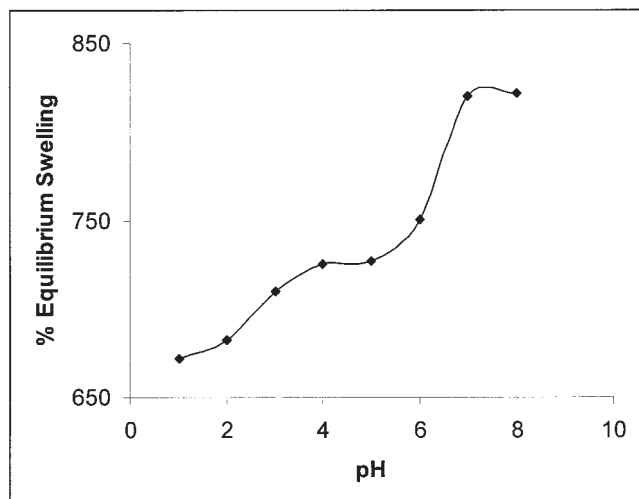


Figure 5 Variation in equilibrium water uptake of sample HG (0.9) with pH of the swelling medium at 30°C.

Effect of pH on equilibrium swelling

If the hydrogel contains some functional groups that can get protonated³⁴ or ionized³⁵ at a suitable pH, then variation in the pH of the swelling medium causes an appreciable change in the water uptake properties of the hydrogel. The effect of the pH of the swelling media on the equilibrium water uptake of the sample HG (0.9) was investigated in swelling media of various pH^{1–8} with the ionic strength maintained at 0.1M at 30°C. The results, as depicted in the Figure 5, clearly indicate that the equilibrium water uptake increases with the pH of the swelling media. It is also interesting to see that the observed increase in equilibrium water uptake is much more pronounced in the pH range 2–3 and 6–7. The observed findings may be explained on the basis of the two pK_a values of the MA.³⁶ When the pH of the external medium increases beyond 2.0, the ionization of first carboxylic groups takes place because pK_a value of MA is 1.85. The ionization of —COOH groups causes a sudden increase in the number of counter/free ions within the gel phase. At the same time, the mutual repulsion among similarly charged —COO[−] groups along the macromolecular chains results in extensive chain relaxation. These two factors, ultimately, cause an appreciable water uptake. Similarly when the pH of the swelling medium exceeds the value 6.0, the second carboxylic group also starts to ionize as pK_{a2} of MA is 6.06. Therefore, again there occurs an appreciable enhancement in the water uptake. The two pK_a values, as determined from the Figure 7, were found to be 2.46 and 6.58, respectively. These values are slightly greater than the actual values 1.85 and 6.06. This may probably be due to the hindrance offered in the ionization of carboxylic groups within the network due to crosslinked structure. In this way, two inflations are observed in the water

uptake versus pH curve because of the occurrence of two pK_a values of MA. Here it is also worth mentioning that for biprotic acids whose two pK_a values do not differ by more than 2 units, the two inflations usually overlap each other, thus giving a broad single “s-shaped” curve,³⁷ as has been observed for poly(acrylamide-co-itaconic acid) hydrogels³⁸. However, in the present study, as the difference between the two pK_a values is nearly 4.2, the chances of overlapping of two dissociations are almost nil.

Effect of temperature

Many polymers having *N*-substituted AAmS have been observed to undergo a thermally induced reversible transition in aqueous media³⁹ at a temperature known as lower critical solution temperature (LCST) or “cloud point”. If the polymer constituent present in the hydrogel possesses a LCST, then a sharp volume phase transition is expected to occur across it.⁴⁰ Otherwise, an increase in temperature of the swelling media results in an enhancement in the diffusion rate of solvent into the polymer matrix. In the present investigation, the effect of temperature of the swelling media on the equilibrium water uptake of samples HG (0) and HG (0.9) was studied in the range of 12–50°C in the distilled water. The results, as depicted in the Table III, clearly indicate that an increase in temperature causes an increase in the diffusion coefficients, which may simply be attributed to the fact that rise in temperature results in faster diffusion of solvent molecules into the polymer matrix. However, the data also indicate that the equilibrium water uptake of both hydrogel samples also increases with increase in temperature. This finding is rather interesting because the monomers used to synthesize hydrogels are not temperature-sensitive or do not possess LCST. However, the observed increase in equilibrium water uptake with temperature may simply be attributed to the fact that in addition to chemical or covalent crosslinking due to *N,N'*-methylenebisacrylamide, the hydrogen bondings existing among oxygen atoms of amide groups of one macromolecular chain and H atom of

TABLE III
Diffusion Coefficients and Equilibrium Water Uptake of the Hydrogel Samples HG(0.9) at Various Temperatures of the Swelling Media

| Temperature (°C) | HG (0) | | HG (0.9) | |
|------------------|--|----------------|--|----------------|
| | D ($10^5 \text{ cm}^2 \text{ min}^{-1}$) | M_∞ (%) | D ($10^5 \text{ cm}^2 \text{ min}^{-1}$) | M_∞ (%) |
| 12 | 1.67 | 912 | 1.85 | 1337 |
| 27 | 2.04 | 887 | 1.73 | 1243 |
| 37 | 2.38 | 850 | 1.64 | 1094 |
| 50 | 2.64 | 631 | 1.30 | 770 |

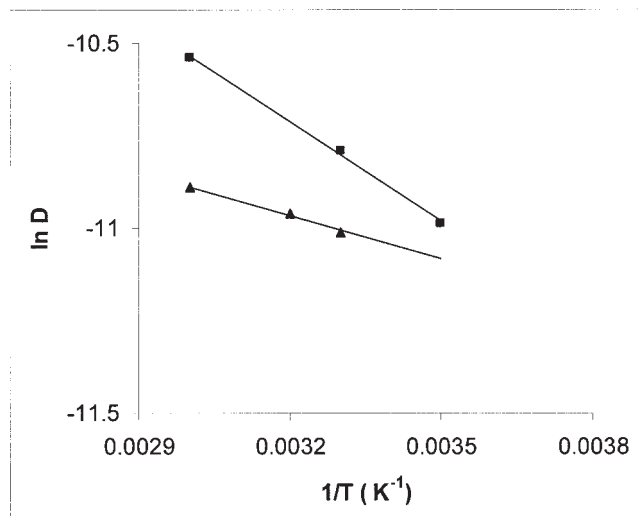


Figure 6 Evaluation of activation energy of the diffusion process for the sample HG (0) (□) and HG (0.9) (▲) in distilled water.

amide groups of other polymeric chains also serve as physical crosslinks within the swelling polymer network. With the rise in temperature, these H bondings become weak or are broken up, thus permitting a greater unfolding of macromolecular chains. This finally results in higher water uptake.

The activation energy of the swelling process was also determined by fitting experimental data to Arrhenius equation:

$$D = D_0 \exp(-E_a/RT) \quad (19)$$

where E_a is the apparent activation energy for the diffusion process. The values of E_a for the samples HG(0) and HG (0.9), as determined from the slope of the linear plots between $\ln D$ and $1/T$ (see Fig. 6), were found to 7.93 and 3.26 kJ mol^{-1} , respectively. The value 7.93 for sample HG (0) (i.e., without acid monomer) is quite in agreement with the value 8.30 kJ mol^{-1} determined by Vasquez et al.⁴¹ for nonionic hydrogel film. The lower activation energy for the sample Hg (0.9) (acid-containing gel) may simply be attributed to the fact that the sample HG (0.9) shows faster swelling because of the presence of driving forces, namely, osmotic swelling pressure and chain relaxation.

Finally, the enthalpy of mixing between the dry polymer and infinite amount of water was determined for the samples HG (0.9), HG (1.4), and HG (1.9) by measuring their equilibrium water uptake in the temperature range 25–55°C, using the well-known Gibbs–Helmholtz equation.

$$d \ln M_\infty / d(1/T) = -\Delta H_{\text{mix}} / R \quad (20)$$

where R is the gas constant, M_∞ is equilibrium water uptake, and T is the temperature on absolute scale. On plotting $\ln M_\infty$ values against $1/T$, straight lines with negative slopes were obtained, as shown in the Figure 7. The values of ΔH_{mix} , as calculated from the slopes of the linear plots, were found to be 10.06, 14.13, and 16.29 kJ mol^{-1} for the samples with percent mole fraction of MA 0.9, 1.42, and 1.94, respectively. It is clear that the values obtained are indicative of endothermic mixing process. Moreover, the absolute values of ΔH_{mix} increase with MA content within the hydrogels. In other words, it can be concluded that the values of enthalpy of mixing increase with increase in hydrophilic character of the gels. However, these results are just opposite to those from the work of Gan and coworkers,⁴² who reported exothermic mixing process for pH-responsive poly(*N*-acryloyl-*N'*-methyl piperazine-*co*-methylmethacrylate) hydrogels and also observed a decrease in absolute values of ΔH_{mix} with increase in hydrophilic character of hydrogels.

Effect of MA content

The variation in concentration of MA within the feed mixture is expected to cause a change in swelling behavior of the resulting polymer matrix. To investigate this, the hydrogels having various amounts of monomer acid in the range 8.6×10^{-2} to 51.6×10^{-2} mM were synthesized, and their equilibrium water uptake was measured in the swelling media of pH 1.0 and 7.0 at 30°C. The results, as depicted in the Figure 8, clearly indicate that the hydrogels, containing various amounts of MA, demonstrate different behaviors at two experimental pH values. At pH 1.0, the equilibrium water uptake decreases slightly with the increase in the amount of MA. The observed decrease in

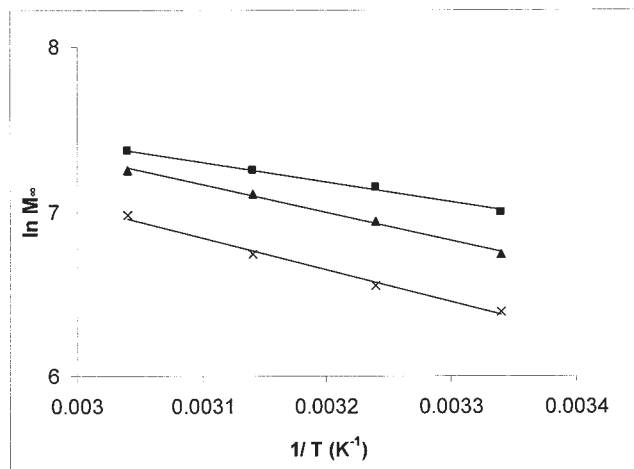


Figure 7 $\ln M_\infty$ versus $1/T$ plots to evaluate ΔH_{mix} for the hydrogel samples. HG (0.9) (■); HG (1.42) (▲); and HG (1.94) (×) in distilled water at 30°C.

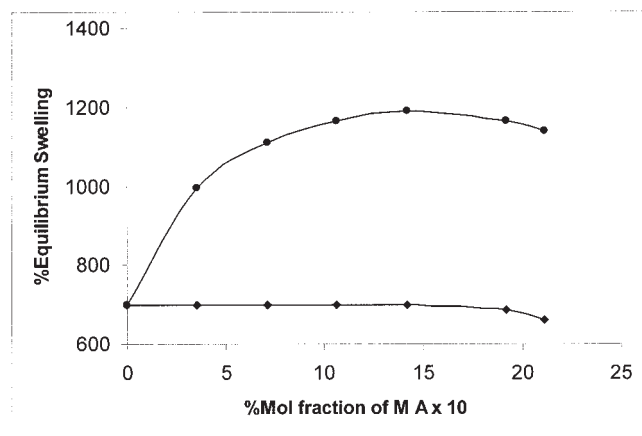


Figure 8 Variation in percent equilibrium swelling with MA content in the hydrogel samples in the swelling medium of pH 1.0 (◆) and 7.0 (●) at 30°C.

the water uptake may be attributed to the fact that at pH 1.0, the carboxylic groups present within the polymer matrix are almost in the undissociated form, as the pK_a values are above the pH of the swelling medium. This imparts nonionic character to the hydrogels. In other words, gels behave as if they were composed of nonionic constituents. Now, when the content of MA is increased, the hydrophobicity provided by unionized MA in the gel discourages the solvent entry into the gel. This causes a slight decrease in the water uptake of gels. Here it is also worth mentioning that in the medium of lower pH, the H-bonding interaction between unionized $-\text{COOH}$ groups and $-\text{CONH}_2$ groups may also increase the crosslink density of the polymer networks, thus resulting in lower water uptake. With the increase in acid content, the H-bonding interactions become more prominent and provide compact structure to the gel.⁴³

However, when the same effect was studied in the swelling medium of pH 7.0, the results obtained were quite different, and rather surprising. The water uptake is found to increase with the MA content up to 25.8×10^{-2} mM and then it begins to decrease slightly with further rise of acid content. For the lower concentrations of MA in the polymer matrix, the observed increase in equilibrium water uptake may simply be attributed to the fact that as the pH of the swelling medium (i.e., 7.0) is above the two pK_a values of the MA, the almost complete ionization of acid monomer causes an enhancement in the water uptake because of increased osmotic swelling pressure as well as chain relaxation. However, when the acid content exceeds beyond 25.8×10^{-2} mM, a slight decrease in water uptake is observed. This may probably be due to the predominant role of undissociated MA. Here the H-bonding interactions between unionized $-\text{COOH}$ groups of MA and $-\text{CONH}_2$ groups of AAm seem to work effectively.

This finally caused a slight decrease in the water uptake of hydrogels.

Effect of reaction temperature

The structural parameters such as crosslink density and molecular weight of the resulting polymer play a significant role in deciding the swelling behavior of hydrogels. This suggests that reaction temperature (i.e., the temperature at which hydrogels were synthesized) should also influence the swelling capacity of hydrogels. To investigate this, the reaction temperature was varied in the range 35–70°C and the equilibrium water uptake values of resulting hydrogels were determined in the distilled water at 30°C. It was observed that water absorbency increased as the reaction temperature increased from 35 to 60°C and then started to decrease with further increase in the reaction temperature. It is clear that 60°C seems to be the optimum reaction temperature for obtaining maximum absorbency. When the reaction temperature is decreased below 60°C, the rate of polymerization decreases, which results in the enhancement of crosslink density.⁴⁴ This causes the equilibrium water uptake to decrease according to Flory network theory.⁴⁵ However, when the temperature is increased beyond 60°C, the equilibrium water uptake value begins to decrease again. This may be attributed to the fact that with the rise in temperature, the rate of polymerization increases, thus resulting in the formation of macromolecular chains of low molecular weight. This causes the water absorbency to decrease. Similar results have also been reported elsewhere.⁴⁶ Therefore, it is concluded that to obtain maximum water uptake of hy-

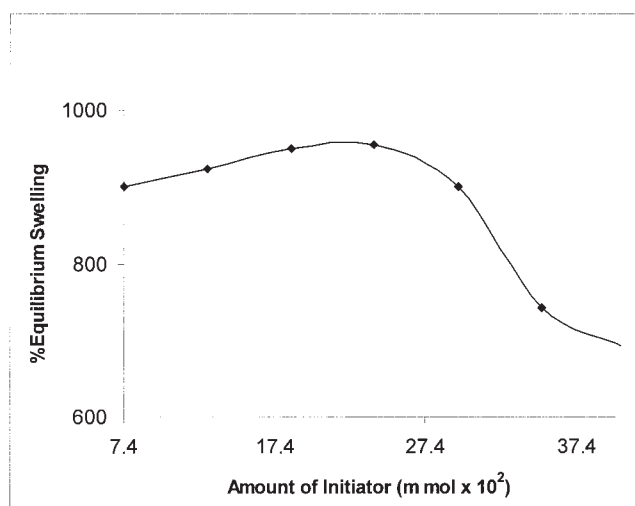


Figure 9 Effect of variation in the amount of initiator in the reaction mixture on the equilibrium water uptake of resulting hydrogel samples HG (0.9) in distilled water at 30°C.

drogels, the synthesis must be carried out at an optimum temperature, which was 60°C in the present case.

Effect of initiator content

The effect of variation in the amount of KPS (i.e., initiator) in the feed mixture on the water absorbency was studied by varying the initiator content in the range 7.4×10^{-2} to 37.4×10^{-2} mM and measuring the equilibrium water uptake of the resulting hydrogels in the distilled water at 30°C. The results, as depicted in the Figure 9, are rather interesting. The hydrogels synthesized with initiator content 24.0×10^{-2} mM exhibited maximum water uptake, while at lower and higher concentrations of KPS, the water absorbency is found to decrease. The water absorbency increases as the KPS content increases from 7.4×10^{-2} to 24.0×10^{-2} mM and then decreases with further increase in the content of initiator. The relation between the average kinetic chain length ($\bar{\phi}$) and the concentration of the initiator in free radical polymerization is given by the following equation⁴⁷:

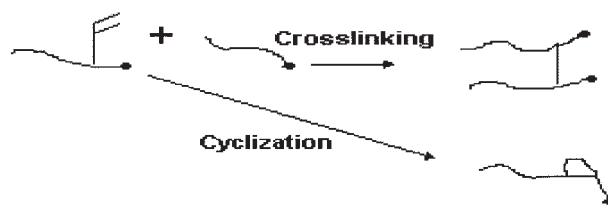
$$\bar{\phi} = \frac{1}{2} k_p (fk_i k_t)^{-1/2} [I]^{-1/2} [M] \quad (21)$$

where k_p , k_i , and k_t are the rate constants for propagation, initiation, and termination respectively; f is the efficiency of initiation by the initiator; and $[I]$ and $[M]$ are the initial concentration of the initiator and monomer respectively. According to the above equation, the molecular weight in free radical polymerization will decrease with an increase in initiator concentration. With the decrease in the molecular weight, the relative amount of polymer chain ends increases. However, with it has been reported earlier⁴⁸ that polymer chain ends do not contribute to the water absorbency. Therefore, the increase of initiator is responsible for the decrease in the equilibrium water uptake of hydrogels. However, further decrease in KPS content below 24.0×10^{-2} mM, the optimum value, the water uptake decreases. This may be attributed to the decrease in the number of radicals produced due to decrease in KPS content. So, the network can not be formed efficiently with small number of radicals in the free radical polymerization, thus causing a decrease in the water uptake.

Effect of dilution of feed mixture on water uptake

The degree of crosslinking in a polymer network structure is a significant property because it affects mechanical strength, water uptake, and many other properties of the polymer matrix by influencing the molecular weight between crosslinks (M_c). Now, the degree of crosslinking is mainly controlled by the fraction of crosslinking agent present in the feed mixture

and the extent to which double bonds are consumed during the polymerization. Smaller quantities of crosslinking agent and diminished final conversion both lead to a less densely crosslinked material. The most important fact is that not all of the double bonds present in the crosslinker are consumed in the formation of crosslinks. In fact, potential crosslinking is also lost because of intramolecular cyclization reactions wherein both ends of the crosslinker molecule react into the same growing polymer chain, forming a loop structure as shown below:



Although, the equivalent amount of crosslinking agent may be present and incorporated into the network, when cyclization is occurring, the polymer produced is less crosslinked and demonstrates higher water uptake.

In the present study, the reaction mixture was diluted by adding 3.5 to 6.0 mL of water, and the water absorbency of resulting hydrogels was determined in distilled water at 30°C. The results thus obtained indicate that the equilibrium water uptake increases with dilution of the feed mixture. The reason behind this effect may be explained on the basis of the concept of cyclization mentioned earlier. In a higher monomer concentration case, when little water is present during the polymerization, the propagating macroradical is surrounded by unreacted double bonds and reacts quickly away from the pendant double bond. There is only limited opportunity to react in a primary cyclization reaction with a pendant double bond. Hence, less cyclization and more crosslinking occur, which cause less water uptake by hydrogels. However, on dilution, the propagating radicals are surrounded by many water molecules, the double bonds concentration is lower, and the radical reacts away from the pendant double bond more slowly. Thus, the pendant double bonds are still in close proximity, and there will be more time available to radical for the react with the pendant double bond. As a result, more cyclization and less crosslinking will occur within the polymer matrix. This finally results in higher water uptake of hydrogels. It was also found that further dilution of the reaction mixture beyond 5.0 mL did not enhance the degree of cyclization, as it might have reached saturation. Therefore, the resulting hydrogels did not show any tendency to further exhibit higher water uptake. That is why, nearly same water absorbency was observed in the volume range 5–6 mL of the

reaction mixture. However, on further dilution, the gels did not form.

CONCLUSIONS

The above study reveals that poly(acrylamide-co-maleic acid) hydrogels demonstrate pH-dependent swelling behavior, with non-Fickian swelling pattern. The equilibrium water uptake versus pH –of the medium plot exhibits two inflations (i.e., a double s-shaped curve), thus confirming the ionization of two carboxylic acid groups at two different pH (namely, 2.46 and 6.58) respectively. The hydrogels, when swollen in water, demonstrate second-order kinetics, which was confirmed by fitting the experimental data to Schott equation. The values of activation energy for the monomer-acid-containing and plain hydrogel samples reveal that MA containing hydrogel has relatively lower activation energy, which is indicative of the fact that it demonstrates faster swelling in distilled water at room temperature because of the presence of driving forces, namely, ion osmotic swelling pressure and chain relaxation. The plots between $1/T$ and $\ln M_{\infty}$ exhibit a negative slope, thus yielding positive enthalpy of mixing, which indicates the mixing of dry polymer with solvent being endothermic. The gels with various amounts of MA demonstrated different swelling behavior in the medium of pH 1.0 and 7.0. In the former case, the equilibrium water uptake decreases with acid content, while in latter case it increases continuously and attains maximum value. The dilution of feed mixture also enhances the absorbency of the resulting hydrogels which was explained on the basis of cyclization. For an optimum initiator concentration, maximum water uptake is observed, while it decreases on either side of the concentration axis of initiator. Finally, the temperature of the reaction system also influences the absorbency of the resulting hydrogels. The optimum reaction temperature was found to be nearly 60°C.

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