Poly(2-Hydroxyethyl methacrylate-*co*-Sulfobetaine) Hydrogels. II. Synthesis and Swelling Behaviors of the [2-Hydroxyethyl methacrylate-*co*-3-dimethyl(methacryloyloxyethyl)ammonium propane sulfonate] Hydrogels

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ABSTRACT: A series of the 2-hydroxyethyl methacrylate/3-dimethyl-(methacryloyloxyethyl)ammonium propane sulfonate (HEMA/DMAPS) copolymeric gels was prepared from various molar ratios of HEMA and the zwitterionic monomer DMAPS. The influence of the amount of the zwitterionic monomer in the copolymeric gels on the swelling behaviors in water, various saline solutions, and temperature was investigated. The results indicate that the PHEMA hydrogel (D0) and lower DMAPS content of the HEMA/DMAPS copolymeric gel (D1) exhibit overshooting phenomena in the dynamic swelling behavior. The maximum overshooting value decreases with increase in temperature. In the equilibrium swelling ratio, the PHEMA hydrogel exhibits a minimum swelling ratio at 55°C. Then, the minimum swelling ratio diminishes gradually with increasing of the DMAPS content in the HEMA/DMAPS copolymeric gels. In the saline solution, the swelling ratios of HEMA/DMAPS copolymeric gels increase rapidly with increasing of concentration of the salt with a smaller ratio of the charge/radius. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2021–2034, 1998

Key words: HEMA; DMAPS; hydrogel

INTRODUCTION

The general name "sulfobetaine-based polymers" refers to a type of macromolecule in which a zwitterion or "inner salt" has been incorporated in the side chain. The solution behavior of some polyzwitterions[1–3] discloses the following general features for these materials in aqueous systems: (1) They are mostly insoluble in water[4] or display an unusual phase behavior as a function of concentration,[5] and (2) the presence of salts enhances chain expansion (antipolyelectrolyte effect).

Hydrogels are a broad class of hydrophilic materials formed by a three-dimensional network held together by crosslinks of covalent bonds and weak cohesive forces in the form of hydrogen or ionic bonds. These crosslinked macromolecular structures are able to take up large quantities of water and biological fluids without dissolution. The biocompatibility of hydrogels is attributed to their ability to simulate material tissues due to their high water content and their special surface properties. As a result of the resemblance between the synthetic and natural materials, these gels which show a significant swelling change in response to external stimuli such as temperature,[6–9] pH,[10,11] ionic strength,[12] and electric potential[13,14]

have been investigated for applications ranging from solute separation[15,16] to controlled delivery of solutes.[7–9,17]

The dynamic swelling behavior of poly(2-hydroxyethyl methacrylate)(PHEMA) was reported by Peppas et al.[18,19] For example, Shieh and Peppas[18] reported the copolymers prepared from the copolymerization of 2-hydroxyethyl methacrylate with ethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TrEGDMA), tetraethylene glycol dimethacrylate (TeEGDMA), hexaethylene glycol dimethacrylate (HeEGDMA), or dodecaethylene glycol dimethacrylate (DoEG-DMA). The swelling dynamic of the P(HEMA-co-TeEGDMA) with 55 mol % HEMA exhibited a slight water uptake over the equilibrium value, a result similar to the one obtained by Franson and Peppas.[19] They reported the copolymers prepared from the copolymerization of HEMA with methyl methacrylate (MMA) or N-vinyl-2-pyrrolidone (NVP). Their result pointed that the swelling dynamics of the poly(HEMA-co-NVP) gel exhibited a slight water uptake over the equilibrium value. This can be attributed to molecular relaxation. The water diffuses into the network before the chains of the network have enough time to relax (diffusion is faster than relaxation), and the fractional uptake curve reaches a maximum: the overshoot value. When the chains do finally relax, water is forced out of the network and the water uptake eventually reaches its equilibrium value.

The hydrogels containing the zwitterionic monomer or sulfobetaine monomer are little reported in the literature.[20–24] However, Huglin and Rego[20–23] reported the copolymeric gels prepared from the copolymerization of HEMA and a zwitterionic monomer, N,N-dimethyl-N-methacryloyloxyethyl-N-(3-sulfopropyl)ammonium betaine (SPE), to survey their swelling behavior in the presence of the salt potassium thiocyanate (KSCN). In addition, Baker et al.[24] reported on the ampholytic hydrogels prepared from the copolymerization of acrylamide with a zwitterionic monomers, [N-(3-sulfopropyl)-N-methacrylamidopropyl-N,N-dimethylammonium betaine (SB1) (AAm/SB1) or [N-(3-sulfopropyl)-N-methacroyloxyethyl-N,N-dimethylammonium betaine (SB2) (AAm/SB2), and with a cationic monomer, [(methacrylamido)propyl]trimethylammonium chloride (MAPTAC), and an anionic monomer, sodium styrene sulfonate (SSS) (AAm/MAPTAC/SSS). They investigated the swelling behavior of these three xerogels in water and in the various concentrations (10^{-5} to $5M$) of the sodium chloride aqueous solution. Their results showed that antipolyelectrolyte behaviors were observed for the ampholytic hydrogels. The ampholytic hydrogel reswelled as the sodium chloride concentration increased to over $0.1M$.

The synthesis and aqueous solution properties of a series of polysulfobetaines were studied in our laboratory.[25–34] We found that the aqueous solution properties of polysulfobetaines in aqueous salt solutions were related to the kind of salts. Hence, a series of HEMA and sulfobetaine copolymeric gels were prepared to investigate their swelling behaviors in water or some saline solutions. The HEMA/2-vinyl-1-pyridium propane sulfonate (VPPS) copolymeric gels with some molar ratios were prepared and investigated.[35] Their results showed that the more the VPPS content the higher the swelling ratio and the swelling ratio increases rapidly with increasing concentration of the salt with a smaller ratio of charge/radius. The HEMA/DMAPS copolymeric gels were prepared at various molar ratios of HEMA and the zwitterionic monomer (DMAPS). The effect of DMAPS on the swelling ratios of HEMA hydrogels as well as the influence of the amount of the zwitterionic monomer in the copolymeric gels on the swelling behaviors in water, various saline solutions, and temperature were the aim of this article. The other purpose of this article was to check whether the zwitterionic component in the copolymeric gels still has the same solution behaviors as those of the polysulfobetaines in aqueous salt solutions.
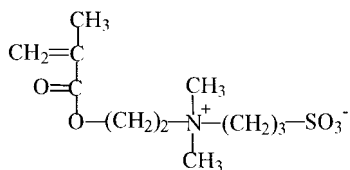
EXPERIMENTAL

Materials

2-Hydroxyethyl methacrylate (HEMA; TCI Co.) was further purified by vacuum distillation at 68°C/5 mmHg. N,N-Dimethylaminoethyl methacrylate (TCI Co.) was further purified by vacuum distillation at 160°C/60 mmHg. Propane sultone (TCI Co.), N,N′-methylene bisacrylamide (NMBA; Sigma Chemical Co.) as a crosslinker, and N,N,N′,N′-tetramethylethylenediamine (TEMED; Fluka Chemical Co.) as an accelerator were used as received. Ammonium persulfate (APS; Wako Pure Chemical Co.) as an initiator was further purified by recrystallization.

Synthesis of Monomer

The monomer DMAPS was prepared as described previously.[25,26,29] Yield: 93.0%, mp: 280°C. The structure is given as follows:

CH₃ structure diagram:

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        CH₃
CH₂＝C
   O＝C
        O—(CH₂)₂—N⁺—(CH₂)₃—SO₃⁻
                 |
                CH₃
                |
                CH₃
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Preparation of Hydrogels

Various ratios of HEMA, DMAPS, and 3 mol % NMBA based on total monomers were dissolved in 10 mL of deionized water. To this solution, 1 wt % APS and 1 wt % TEMED as redox initiators were added, and the mixture was immediately injected into the space between two glass plates. The thickness of the gel membrane was adjusted with a silicone spacer between the two glass plates. Polymerization was carried out at room temperature (30°C) for 1 day. After the gelation was completed, the gel membrane was cut into disks and immersed in an excess amount of deionized water for 7 days to remove the residual unreacted monomers. Swollen polymer gels were dried at room temperature for 2 days, and these samples were further dried in a vacuum oven for 1 day at 60°C. The thickness of the dried gel was about 0.1–0.15 cm and the diameter was about 0.5–0.6 cm.

Measurement of Swelling Ratio

The dried gels were immersed in an excess amount of deionized water or various saline solutions with different concentrations at 25°C until swelling equilibrium was attained. The weight of the wet sample (Ww) was determined after removing the surface water by blotting with filter paper. The weight of the dry sample (Wd) was determined after drying the gel in a vacuum oven for 1 day. The swelling ratio (Q) based on Ww and Wd was then calculated by $Q = (Ww - Wd)/Wd$.

Dynamic Swelling

The dried gels were immersed in an excess amount of deionized water at different temperatures. Q was obtained by weighing the initial and swollen samples at various time intervals. The amount of water sorbed, Mt, was reported as a function of time, and the equilibrium sorption at an infinitely long time was designated $M\infty$. The following equation can be used to calculate the characteristic constant, k, and the characteristic exponent, n, for $Mt/M\infty \leqq 0.6$ (Ref. 36):

$$\frac{Mt}{M\infty} = kt^n \qquad (1)$$

where k is a characteristic constant of the gel, and n, a characteristic exponent of the mode transport of the penetrant.

The other equation can be used to calculate the diffusion coefficient D for $Mt/M\infty \leqq 0.8$ (Ref. 19):

$$\frac{Mt}{M\infty} = \left(\frac{4}{\Pi^{0.5}}\right)\left(\frac{Dt}{L^2}\right)^{0.5} \qquad (2)$$

where t is the time and L is the initial thickness of the dried sample.

RESULTS AND DISCUSSION

The swelling behavior of the hydrogels depends on the nature of the gel and the environmental conditions. The gel's nature involves the nature of the charge, ionic content, and extent of crosslinking. The environmental conditions include the pH, temperature, and various salt concentrations.

The swelling behavior of HEMA hydrogels has been studied by some researchers.[20–23] The effect of DMAPS on the swelling behavior of the HEMA/DMAPS copolymeric gels is studied here.

Characterization of the HEMA/DMAPS Copolymeric Gels

Some characteristics of the HEMA/DMAPS copolymeric gels at various feed compositions are shown in Table I. The results observed from Table I show that the appearance of the gels is opaque in the lower DMAPS content and is transparent in the higher DMAPS content of the HEMA/DMAPS copolymeric gels. The change of appearance may be caused by the phase separation during polymerization of HEMA or HEMA/DMAPS systems. This phenomenon is similar to our previous report on the HEMA/VPPS systems.[35] In the HEMA/DMAPS copolymeric gels, the DMAPS is a hydrophilic monomer: The more the DMAPS content in the copolymeric gel, the larger the affinity of the gel. In addition, the phase separation disappears in the higher DMAPS content of the said copolymeric gel. The equilibrium swelling ratios of the HEMA/DMAPS copolymeric gels increase with

Table I   Characterization of the HEMA/DMAPS Copolymeric Gels

Sample No.	Feed Composition (%)		Actual Composition (%)		Appearance of Gel Membrane	Equilibrium Swelling Ratio at 25°C (g/g)
	HEMA	DMAPS	HEMA	DMAPS		
D0	100.0	0.0	100.0	0.0	Opaque	1.53
D1	97.0	3.0	96.5	3.5	Opaque	1.80
D2	94.0	6.0	93.8	6.2	Transparent	1.74
D3	91.0	9.0	91.0	9.0	Transparent	2.94
D4	88.0	12.0	87.7	12.3	Transparent	3.22

increasing DMAPS content in the hydrogels, but when the gel exhibits an "overshoot," Q over its equilibrium swelling ratio, Q becomes larger (see Fig. 2). The elemental analysis is based on the assumption that the total NMBA is crosslinked with the copolymeric chain and the sulfur content of the xerogel is defined as the actual compositions. The results show that the actual compositions are almost equal to the feed compositions.

Effect of Temperature on Swelling Ratio for the HEMA/DMAPS Copolymeric Gels

The effect of temperature on Q for a series of the HEMA/DMAPS copolymeric gels is shown in Figure 1. The results show that the sample D0, PHEMA, exhibits a minimum swelling ratio at 55°C. This behavior conforms the result reported by Warren and Prins,[37] as follows: The binding water is caused by the hydrogen-bonding force between the water and the polymeric chain when it is below 55°C. The hydrogen-bonding force is reduced with increase in the temperature. Then, the binding water turns to the nonbinding water, free water that can be moved rapidly out of the polymeric networks. The Q of D0 will be decreased to the minimum value at 55°C. However, the entropy of the water and polymeric chain will be increased with increase in the temperature. When the temperature is over 55°C, the dispersion force of the water molecules is greater than the attraction force of the water and polymeric chain. A free water, the nonbinding water, will be moved from the surrounding into the hydrogels. Hence, the Q of D0 will be reincreased when the temperature is above 55°C. An interesting phenomenon is noticed: The minimum swelling ratio diminished gradually with the addition of the higher zwitterionic monomer content into the copolymeric gels. Because DMAPS is a hydrophilic monomer, the attraction force between water and the polymeric

chain will be increased when more hydrophilic groups are introduced into the HEMA/DMAPS copolymeric gels. Hence, the binding water will still be kept inside the hydrogels and be insignificantly affected by the change of the temperature. This phenomenon is more significant when more DMAPS contents are introduced into the HEMA/DMAPS copolymeric gels (D4). These results are similar to the HEMA/VPPS gel system in the previous article.[35] The Q value in the HEMA/VPPS hydrogel is larger than in the HEMA/DMAPS system. This can be explained by the structure effect of the copolymeric gel. The space of the pyridinium group in the HEMA/VPPS copolymeric gel is larger than that of the HEMA/DMAPS copolymeric gel. This larger space can be filled with the larger amount of water in the gel.

Effect of DMAPS Content on Swelling Ratio

The swelling ratios as a function of time for HEMA/DMAPS copolymeric gels in deionized water are shown in Figure 2. The results indicate that the equilibrium swelling ratio increases with increase of the DMAPS content. According to Flory's swelling theory,[38] the following equation is given:

$$Q^{5/3} = [(i/2V_u S^{1/2})^{1/2} + (1/2 - \chi_1)/\nu_1]/(\nu_e/V_0) \quad (3)$$

where i/V_u is the concentration of fixed charge referred to the unswollen network; S, the ionic concentration in the external solution; $(\frac{1}{2} - \chi_1)/\nu_1$, the affinity of the hydrogel with water; and ν_e/V_0, the crosslinked density of the hydrogel. Q has a relation to the ionic osmotic pressure, crosslinked density, and affinity of the hydrogel with water from the above equation. The total fixed charge was zero and the crosslinked density was
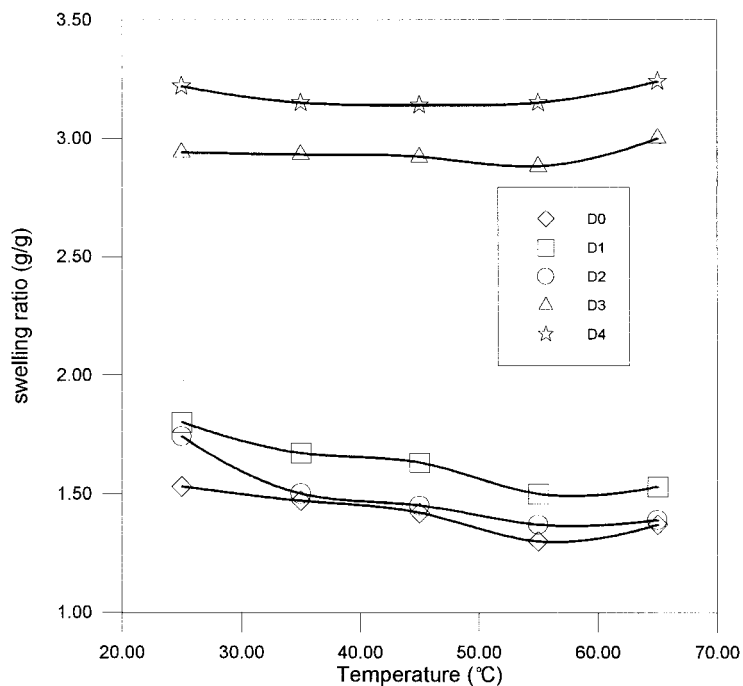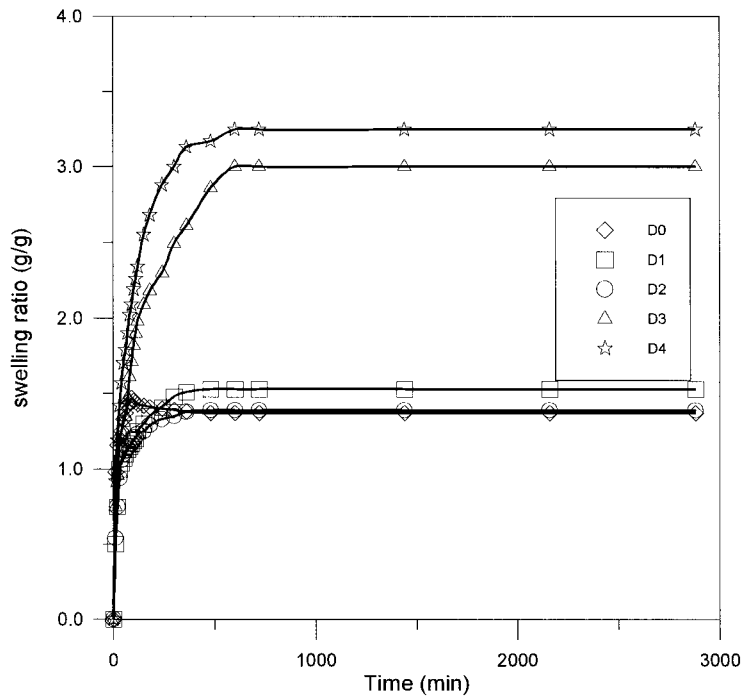
Figure 1   Swelling ratios as a function of temperature for HEMA/DMAPS copolymeric gels.

fixed in a series of different compositions of HEMA/DMAPS copolymeric gels, so the major effect on Q for the hydrogel is only the affinity with water. Because the DMAPS is a hydrophilic monomer, the more the DMAPS content, the larger the affinity of the hydrogels with water and the higher
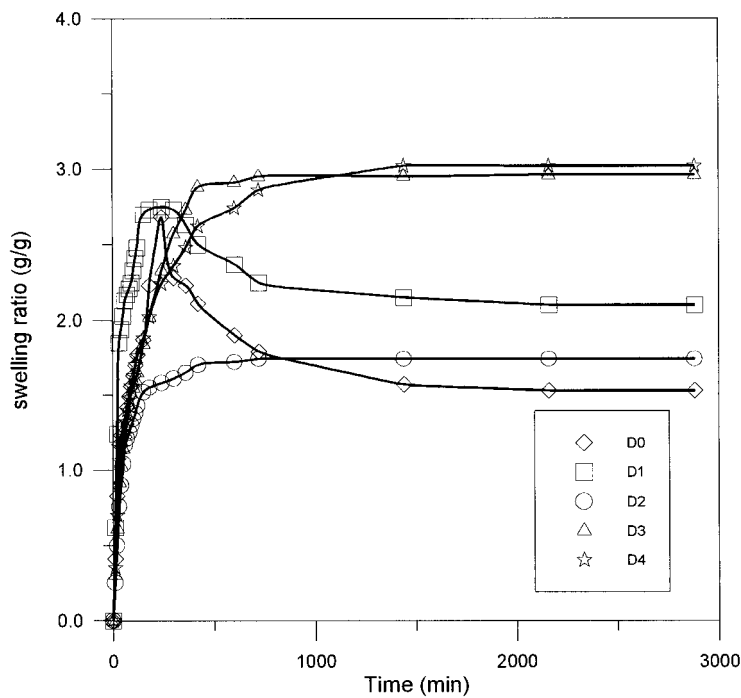
Figure 2   Swelling ratios as a function of time for HEMA/DMAPS copolymeric gels at 25°C.

Figure 3 Swelling ratios as a function of time for HEMA/DMAPS copolymeric gels at 65°C.

Q of the hydrogels. Figure 2 also shows that the dynamic swelling ratio of the low DMAPS content of HEMA/DMAPS copolymeric gel (D1) exhibits a swelling ratio over the equilibrium value. This phenomenon is called "overshooting." This overshooting phenomenon disappears at a higher DMAPS content and at a higher temperature (65°C; see Fig. 3). Hence, the "overshoot" effect may influence the equilibrium swelling ratio of the copolymeric gel, such as that D1 has a larger swelling ratio than that of D2, and the overshooting phenomenon may also be affected by the temperature. Thus, we will discuss the effect of the temperature on the overshooting phenomenon for the said copolymeric gel in the next section.

Effect of Temperature on Overshooting Phenomenon

The fractional Q's of the D0 as a function of time at various temperatures are shown in Figure 4. The fractional Q, $Mt/M\infty$, the ratio of penetrant uptake at any time, Mt, to the mass of penetrant uptake at equilibrium, $M\infty$, was also analyzed as a function of time. The dynamic swelling ratio of the PHEMA hydrogel exhibits a water "overshoot" over the equilibrium value, which is a result similar to that obtained by Shieh and Peppas.[18] This

can be attributed to molecular relaxation. Water diffuses into the network before the chains of the molecule have enough time to relax (diffusion is faster than relaxation), and the fractional Q reaches a maximum: the overshoot value. When the chains do finally relax, water is forced out of the network, and Q eventually reaches its equilibrium value. This overshoot value decreases with increase in the temperature, and the equilibrium time shortens with increase in the temperature. These results are shown in Table II. The dimensionless time is defined as $(\sqrt{t}/l)^2 \times D$, where t is the time of maximum overshoot value; l, the thickness of the dried gel; and D, the diffusion coefficient of the water penetrant to the gels. The results show that the dimensionless time shortens with increase in the temperature, implying that the dimensionless time of the hydrogel, which is transformed from the glassy state to the rubbery state, decreases at a higher temperature. This is because the entropy of the polymeric chain will increase and the relaxation motion of the polymeric chain will be quickened at higher temperature. Thus, the equilibrium time of the polymeric chain shortens as temperature increases. This behavior has a resemblance to the HEMA/VPPS gel system.[35]

Figure 5 shows the fractional Q of D1 as a func-
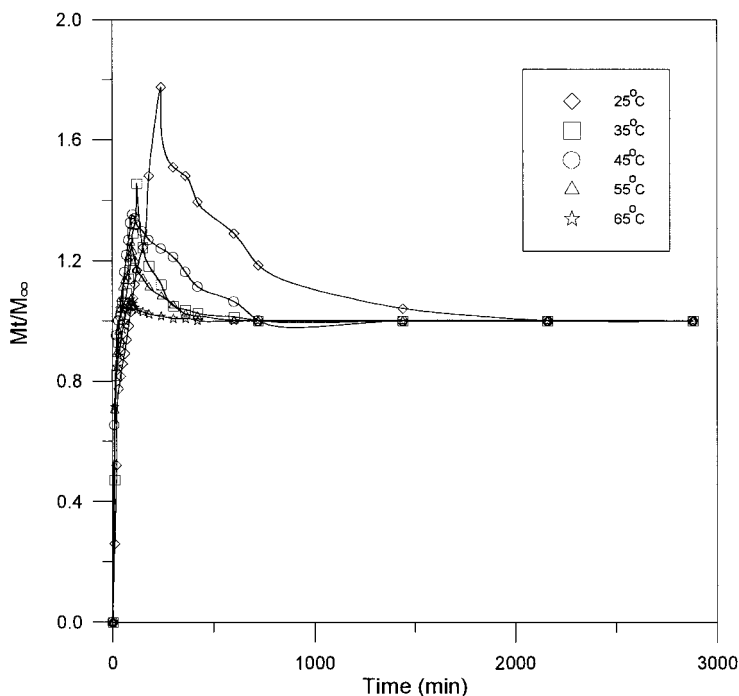
Figure 4 Fractional swelling ratio of the PHEMA (D0) gel as a function of time at various temperatures.

tion of time at various temperatures. The overshooting phenomenon disappears at 65°C. This result implies that the hydrophilic zwitterionic component, DMAPS, in the HEMA gel could suppress its overshooting temperature. From the above results, the overshooting phenomenon for a hydrogel is controlled by the amount of a strong hydrophilic component and temperature, aside from the nature of hydrogel itself. The dynamic analysis of the transport mechanism for the D1 copolymeric gel shown in Table II indicates that the overshooting phenomenon causes the larger n value at higher temperature, and the diffusion mode is closed to the Case II diffusion. The n value

Table II   Analysis of Transport Mechanism of Water Transport in Glassy HEMA/DMAPS Copolymeric Gels for Various Temperatures

Sample	Temperature (°C)	Kinetic Exponent (*n*)	Overshoot (%)	Time[a] (min)	Dimensionless Time[b] at Maximum Overshoot ($\times 10^2$)
D0	25	0.86	77.5	240	1.53
	35	0.90	45.5	120	0.83
	45	0.96	35.2	100	0.74
	55	0.97	25.9	90	0.70
	65	0.99	7.3	90	0.65
D1	25	0.85	30.9	240	2.52
	35	0.90	28.9	150	1.73
	45	0.92	20.8	110	1.32
	55	0.99	11.7	100	1.20
	65	0.92	N.O.[c]	N.O.	N.O.

[a] Time of maximum overshoot.
[b] Dimensionless time $(\sqrt{t}/1)^2 \times D$.
[c] N.O., nonobservable.
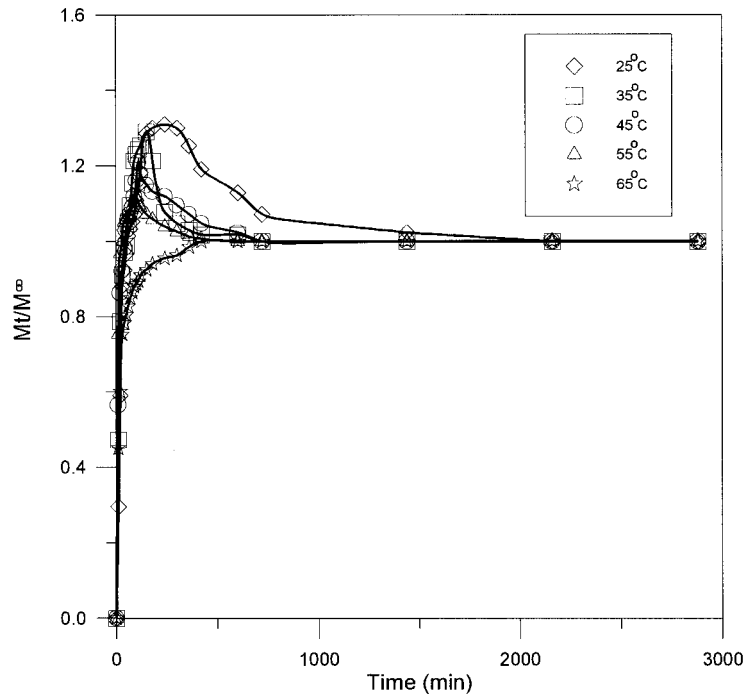
Figure 5 Fractional swelling ratio of the HEMA/DMAPS copolymeric gel (D1) as a function of time at various temperatures.

of the D1 sample is smaller at higher temperature (65°C), because the overshooting phenomenon disappears at higher temperature (65°C). Table II also indicates that the characteristic exponent, n, increases with decrease of the dimensionless time, but increases with increase in the temperature.

Investigation of Water Diffusion in Xerogels

Alfrey et al.[39] distinguished three classes of diffusion, based on the rate of diffusion, relative to the rate of polymer relaxation: 1) case I, or Fickian diffusion, in which the rate of diffusion is low relative to the rate of relaxation; 2) case II, or relaxation-balanced diffusion, in which the diffusion rate is very fast relative to the relaxation rate; and 3) non-Fickian, or anomalous diffusion, which occurs when the diffusion and relaxation rates are comparable. The characteristic constant of the gel, k, and the characteristic exponent of the mode transport of the penetrant, n, are calculated through eq. (1). Then, D can be calculated from eq. (2). The typical plot of $Mt/M\infty$ versus $t^{0.5}$ is shown in Figure 6. A straight line is drawn using the linear regression method. From this line, D is determined. Table III shows D, n, and k for a

series of HEMA/DMAPS copolymeric gels at various temperatures.

The results shown in Table III indicate that the swelling exponents, n, for the HEMA/DMAPS copolymeric gels (D0 and D1) at various temperatures are between 0.85 and 0.99. This evidence indicates that the swelling transport mechanisms for the HEMA/DMAPS copolymeric gels (D0 and D1) are non-Fickian transport near to the Case II transport. Additionally, the swelling exponents, n, for D2 copolymeric gels at various temperatures are between 0.64 and 0.73. These findings indicate that the swelling transport mechanisms for D2 gels belong to non-Fickian transport. On the other hand, the swelling exponents, n, for the said copolymeric gels (D3 and D4) at various temperatures are between 0.52 and 0.59. These results indicate that the swelling transport mechanism for D3 and D4 gels are near to Fickian transport. From the above results, it is implied that the swelling transport mechanism will be transformed from non-Fickian transport to Fickian diffusion transport as the HEMA/DMAPS copolymeric gel contains a hydrophilic or water-soluble polymer, that is, the DMAPS segment in the HEMA/DMAPS copolymeric gel would affect the transport mode of the HEMA/DMAPS copoly-
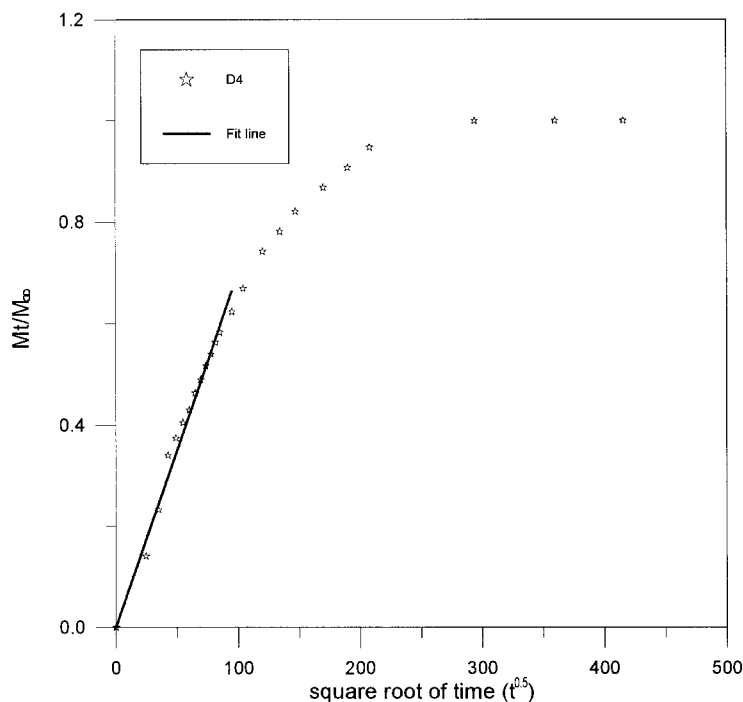
Figure 6 Mt/M_∞ versus $t^{0.5}$ for HEMA/DMAPS copolymeric gel (D4) at 25°C.

meric gel. These phenomena are similar to the HEMA/VPPS gel system, but the transport modes are different,[35] showing that the transport mode may be affected by the various sulfobetaine comonomers, so we will discuss the other sulfobetaine comonomers in our laboratory. In addition, n and D increase with increase of the temperature, that is, the diffusion rate is faster and the equilibrium time is shorter at higher temperature.

Effect of Salt Concentration on the Swelling Ratio

The effect of salt concentration on the swelling ratios (Q's) for a series of the HEMA/DMAPS copolymeric gels are discussed here. Figure 7 shows the Q's as a function of KI aqueous solution for the HEMA/DMAPS copolymeric gels (D0–D4) at 25°C. The results shown in Figure 7 exhibit that the swelling ratios remain constant in the dilute KI aqueous solution at $< 10^{-3}M$ and $0.1M$ and those increase at a high ionic concentration of $10^{-2}M$ and $1M$ for D1–D4 and D0 gels, respectively. The Q for the D0 gel was reported by Refojo.[40] The iodine, or more likely I_3^- ions, combine with HEMA, producing various degrees of a yellow color in the gel, depending on the solution concentration. The swelling behavior for D1–D4 can be explained by the nature of poly(DMAPS).

The poly(DMAPS) is a polyzwitterionic polymer and displays a so-called antipolyelectrolyte behavior, that is, the polymeric chain expands with increase of the ionic strength, resulting in a better water solubility and higher intrinic viscosity.[26] Hence, the swelling ratios of the HEMA/DMAPS polymeric gels increase with increase of the DMAPS content in the gels. This increasing tendency is more significant in D3 and D4 samples. These results are the same with the HEMA/SPE system reported by Huglin and Rego.[23] The more sulfobetaine content in the copolymeric gel, the larger the swelling ratio of the copolymeric gel. They only reported the effect of the KSCN solution on the swelling ratio of the HEMA/SPE copolymeric gels. We will discuss more of the salt effect on the swelling ratio and check whether the DMAPS component in the copolymeric gel still has the same aqueous solution behavior as does poly(DMAPS) in various aqueous salt solutions.

Influence of Different Halide Ions with a Common Cation (K⁺) on the Swelling Ratio

Figure 8 shows the Q's of samples D4 and D0 as a function of the salt concentration for the KF, KCl, KBr, and KI solutions. The results shown in Figure 8 indicate that the curves of Q have a significant difference for these four salt concentra-

Table III   Initial Diffusion Coefficient of Water, *D*, and Kinetic Exponent, *n*, and Characteristic Constant, *K*, of Water Penetrated Through HEMA/DMAPS Copolymeric Gels at Various Temperatures

| Sample No.	Temperature (°C)	Kinetic Exponent *n*	Characteristic Constant *K*	$D \times 10^8$ (cm^2/s)	Equilibrium Swelling Time (min)
D0	25	0.86	0.02	1.07	2160
	35	0.90	0.05	1.15	720
	45	0.96	0.07	1.37	720
	55	0.97	0.08	1.57	600
	65	0.99	0.10	2.02	480
D1	25	0.85	0.01	1.05	2160
	35	0.90	0.05	1.15	720
	45	0.92	0.06	1.20	720
	55	0.99	0.10	2.02	600
	65	0.92	0.06	1.20	480
D2	25	0.64	0.04	0.13	720
	35	0.66	0.06	0.15	720
	45	0.67	0.07	0.22	720
	55	0.70	0.08	0.25	600
	65	0.73	0.09	0.28	480
D3	25	0.52	0.02	0.13	720
	35	0.53	0.02	0.15	720
	45	0.55	0.03	0.22	720
	55	0.56	0.03	0.25	720
	65	0.58	0.03	0.28	600
D4	25	0.53	0.02	0.15	1440
	35	0.54	0.02	0.20	720
	45	0.56	0.03	0.23	720
	55	0.57	0.03	0.27	720
	65	0.59	0.03	0.30	480

tions. For potassium salts, the swelling ratios for D0 are approximately constant in these four kinds of salts except the concentration of KBr and KI above $0.1 M$. However, the swelling behavior for the D4 gel shows an increase in the swelling ratio of the hydrogels in the order of $F^- < Cl^- < Br^- < I^-$ for KF, KCl, KBr, and KI, respectively. This tendency is similar to the aqueous salt solution behavior of polysulfobetaines in our previous reports.[25–34] Hence, the swelling behavior of the D4 gel can be explained by the small charge/radius ratio of the anion which is found to be easily bound to the quaternary ammonium group of DMAPS. This is because the ion with the smaller charge density is easily polarized when the ion of the salt neared and then bound on quaternary ammonium group of DMAPS. The larger anion, therefore, easily infiltrates into the ionically crosslinked network and expands the molecular chain. Hence, as the anion size of the external salt solution is

larger, the antipolyelectrolyte's swelling behavior of the hydrogels are more obvious. On the other hand, Figure 8 significantly shows that the sample D4 exhibits a "salting-in" behavior in KBr and KI salt solutions, but exhibits a "salting-out" behavior in the KF salt solution.

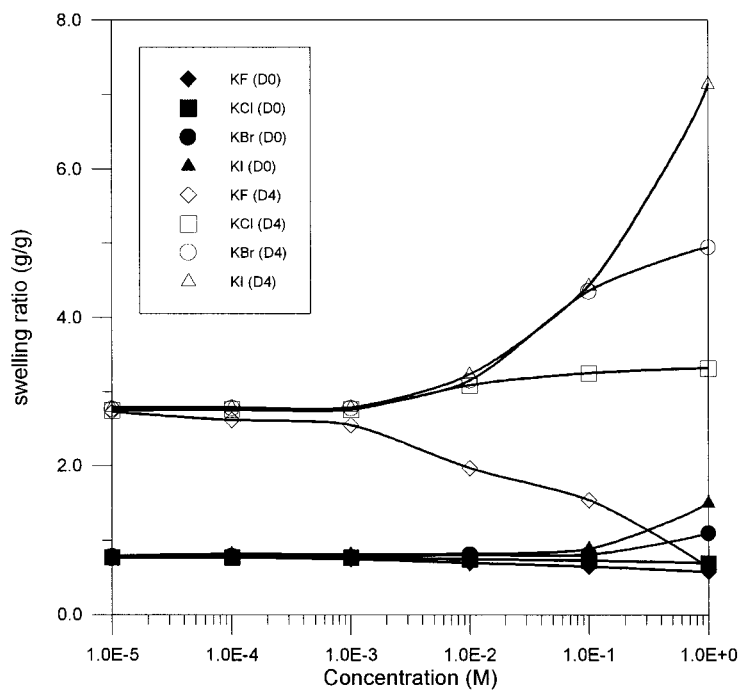## Influence of Different Monovalent Cations with a Common Anion (Cl^-) on the Swelling Ratio

Figure 9 shows the *Q*'s of samples D4 and D0 as a function of the salt concentrations for LiCl, NaCl, and KCl solutions. The results show that the D0 hydrogel exhibits a constant *Q* for LiCl, NaCl, and KCl solutions, but the *Q* for sample D4 exhibits an increase with the salt concentration and in the order of $Li^+ \leqq Na^+ < K^+$ for LiCl, NaCl, and KCl, respectively. This behavior is also similar to the aqueous salt solution behavior of polysulfobetaines in the presence of these salts.[25–34]
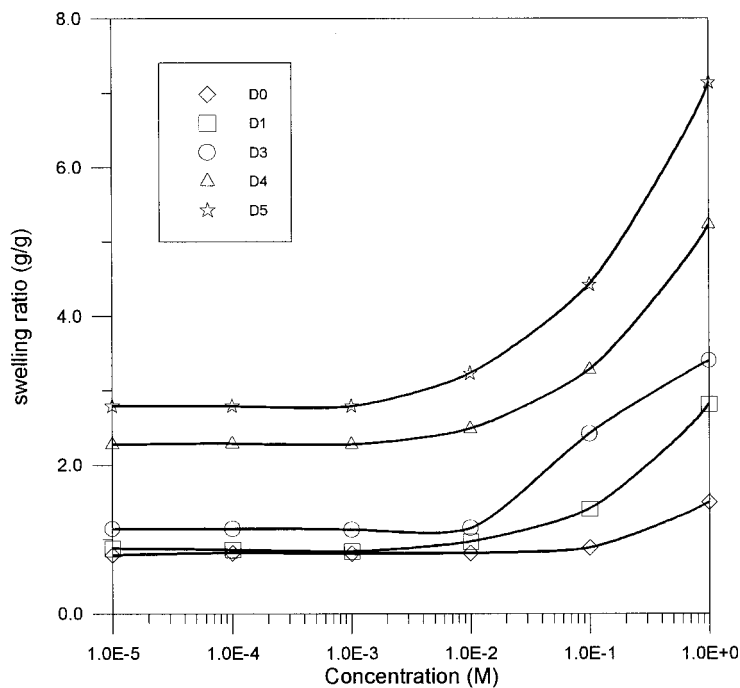
Figure 7 Swelling ratios as a function of $KI_{(aq)}$ for HEMA/DMAPS copolymeric gels at 25°C.

Compare Figures 8 and 9: The Q for the D4 gel is profoundly affected by the kind and concentration of the salts, and the anionic effect is larger than the cationic effect at higher salt concentration. There is an interesting phenomenon in Figure 9 for the D0 gel. We found that the Q for sample

Figure 8 Swelling ratios of samples D4 and D0 in different halide ion salt aqueous solutions of various concentrations at 25°C.
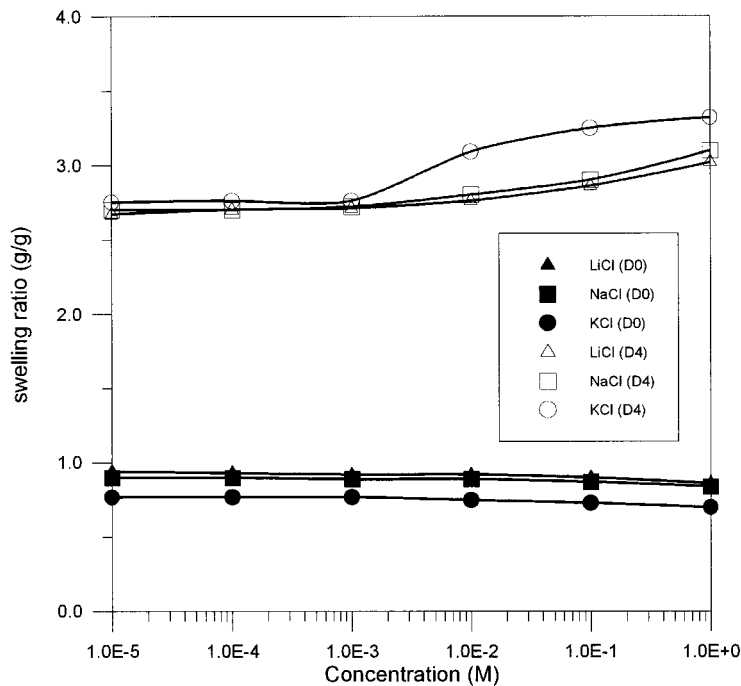
Figure 9 Swelling ratios of samples D4 and D0 in different monovalent cation salt aqueous solutions of various concentrations at 25°C.

D0 is higher in the LiCl solution than that in the NaCl and KCl solutions, that is, $Li^+ \geqq Na^+ > K^+$. This is due to their cationic radius or their hydration forces. The hydration radius grows as a result of the small cation (Li^+) surrounded with a large amount of water. Therefore, the Q for sample D0 is higher in the LiCl solution than that in the NaCl and KCl solutions. This behavior is also observed in the HEMA/VPPS gel system.[35]

Influence of Different Divalent Cations with a Common Anion (Cl^-) on the Swelling Ratio

Figure 10 shows the Q's of samples D4 and D0 as a function of the salt concentrations for $MgCl_2$, $CaCl_2$, and $SrCl_2$ solutions. Based on the above-mentioned reason, the Q's for the D0 gels in $MgCl_2$, $CaCl_2$, and $SrCl_2$ have the same tendency as those gels in LiCl, NaCl, and KCl salt solutions, respectively. The sample D0 keeps Q constant in the $MgCl_2$, $CaCl_2$, and $SrCl_2$ solutions. But the sample D4 exhibited an antipolyelectrolyte swelling behavior, which is also observed in $MgCl_2$, $CaCl_2$, and $SrCl_2$ solutions. The Q's also show a tendency in the order of $Mg^{2+} < Ca^{2+} < Sr^{2+}$ for $MgCl_2$, $CaCl_2$, and $SrCl_2$, respectively. This

tendency conforms to the aqueous solution properties of poly(DMAPS) in these salt solutions.[25]

**Influence of Different Acidic Ions with a Common Cation (Na^+) on the Swelling Ratio**

Figure 11 shows the Q's of samples D4 and D0 as a function of the salt concentration for the $NaClO_4$, $NaNO_3$, and CH_3COONa solutions. The results indicate that the swelling behaviors of these two hydrogels are similar to those found in Figure 8. Similar tendencies shown in Figure 11 have been observed for the different acidic groups and in the order of $CH_3COO^- < NO_3^- < ClO_4^-$ for $NaClO_4$, $NaNO_3$, and CH_3COONa solutions, respectively. The Q value for sample D0 remains constant at low concentration $(<0.01M)$, but increases rapidly at high concentration for the $NaClO_4$ and $NaNO_3$ salt solutions. Sample D4 also exhibits the "salting-in" swelling behavior in $NaClO_4$ and $NaNO_3$ but the "salting-in" swelling behavior in CH_3COONa. The acetate ion (CH_3COO^-) is a weak acid group easily associated to form an acetic acid in the aqueous solution, so the ionic intensity is very small. Therefore, the Q of the hydrogels is the lower than that of the other anions.
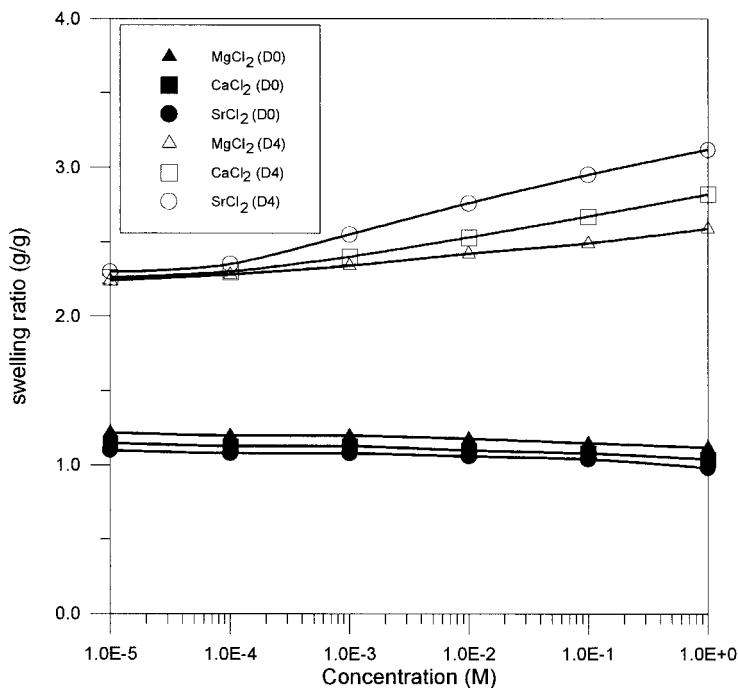
Figure 10 Swelling ratios of samples D4 and D0 in different divalent cation salt aqueous solutions of various concentrations at 25°C.

From the above results, we can find that when the gels contain a zwitterionic monomer, DMAPS, the swelling ratios of the gels in different salt solutions show the same result similar to the aqueous solution properties of poly(DMAPS) in different salt solutions.
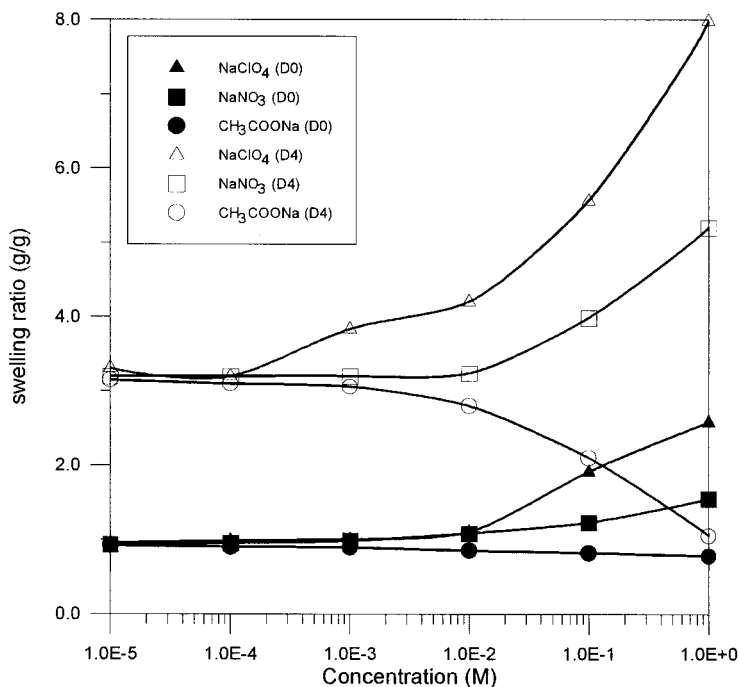
Figure 11 Swelling ratios of samples D4 and D0 in different acidic ion salt aqueous solutions of various concentrations at 25°C.

CONCLUSIONS

The swelling ratios of the HEMA/DMAPS copolymeric gels increase with increase of the DMAPS content, and the equilibrium absorption time of the hydrogel is shortened. The equilibrium absorption time is shortened at high temperature. The minimum swelling ratio diminishes gradually with the introduction of the higher zwitterionic monomer content into the HEMA/DMAPS copolymeric gels.

In dynamic swelling behavior, the overshooting phenomenon has been observed from the low DMAPS contents in the copolymeric gels. The overshooting phenomenon disappears at high temperature, and the overshooting maximum value decreases with increase in temperature. The transport diffusion mechanism shows a Case II mode, non-Fickian diffusion, and Fickian diffusion mode for the HEMA/DMAPS copolymeric gel containing a lower, medium, and higher DMAPS content, respectively.

The effect of the salt solution on the Q for this series of gels shows a special behavior. When the salts own a small charge density, such as I^-, Br^-, Sr^{2+}, Ca^{2+}, ClO_4^-, and NO_3^-, the Q's of the HEMA/DMAPS copolymeric gels increase with increase in the DMAPS content and in the salt concentration. Conversely, when the salts own a large charge density, such as F^- and CH_3COO^-, the Q's of the HEMA/DMAPS copolymeric gels decrease with increasing salt concentration.

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