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Prediction of swelling behaviour of hydrogels containing diprotic acid moieties

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Prediction of swelling behaviour of hydrogels containing diprotic acid moieties, sensitive to pH and ionic strength changes of the swelling medium, was investigated. The equations derived for the prediction of the theoretical swelling curves are based on the phantom network theory of Erman *et al.* and the approaches of Peppas *et al.* For all predictions, a number of polymer-based parameters, solution property parameters and polymer–solvent combination type parameters were evaluated typical of dicarboxylated copolymers. The advantages of the derived equations for the determinations of average molecular weight between the cross-links and also a polymer–solvent interaction parameter have been exemplified. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Hydrogels are cross-linked hydrophilic polymers capable of imbibing large volumes of water, and yet are insoluble because of their network structures, crystalline regions or entanglements. The hydrophilicity of these materials is due to the presence of hydrophilic functional groups such as –OH, –COOH, –CONH$_2$, –CONH and –SO$_3$H along the polymer chains[1–3].

Much of the work on synthesis, characterization and swelling of hydrogels has been directed to the networks made of neutral polymeric chains. Increasing attention, however, has been directed in the past several years in hydrogels that display controllable changes in volume in response to small environmental conditions such as pH, temperature, ionic strength, etc.[4–7] Temperature and pH sensitive gels have been suggested for use in a number of new applications, including controlled drug delivery[8,9], immobilized enzyme systems[10,11] and separation processes[12,13].

One of the basic parameters that describes the structure of a hydrogel network is the molecular weight between cross-links, $\overline{M}_c$ for highly swollen networks. This describes the average molecular weight of polymer chains between two consecutive junctions. These junctions may be chemical cross-links, physical entanglements, crystalline regions, or even polymer complexes[14]. Several theories have been proposed to calculate the molecular weight between cross-links in a hydrogel. Probably the most widely used of these theories is that of Flory and Rehner[15,16]. This earliest theory describes the equilibrium swelling characteristics of a cross-linked polymer system where the polymer chains are reacted in the solid state and the chains exhibit a gaussian distribution. This theory deals with neutral polymer chains and tetrafunctional cross-linking within the polymer gel. From their swelling expression the average molecular weight between consecutive cross-links, $\overline{M}_c$ can be expressed by equations (1) and (2), these equations have been widely used to characterize a variety of networks.

Equations (1) and (2) were used when the networks were prepared from polymer and monomer or monomer mixtures, respectively[17–20].

$$\frac{1}{\overline{M}_c} = \frac{2}{\overline{M}_n} - \frac{(\bar{v}/V_1)\left[\ln(1 - v_{2m}) + v_{2m} + \chi v_{2m}^2\right]}{\left[v_{2m}^{1/3} - \dfrac{v_{2m}}{2}\right]} \quad (1)$$

$$\frac{1}{\overline{M}_c} = - \frac{(\bar{v}/V_1)\left[\ln(1 - v_{2m}) + v_{2m} + \chi v_{2m}^2\right]}{\left[v_{2m}^{1/3} - \dfrac{v_{2m}}{2}\right]} \quad (2)$$

Here $\overline{M}_c$ is the number average molecular weight of starting polymer, $\bar{v}$ is the specific volume of the polymer, V_1 is the molar volume of the swelling agent, v_{2m} is the polymer volume fraction in the equilibrium–swollen system and χ is the Flory polymer–solvent interaction parameter.

The Flory–Rehner model describes the situation in which cross-links are introduced in the dry stage. Peppas and Merrill[21] derived a model reported by Peppas and Barn-Howelll which accounts for the introduction of cross-links in the swollen state as in the case of solution polymerization. The final form of the Peppas–Merrill model for determining the molecular weight between cross-links is given in equation (3):

$$\frac{1}{\overline{M}_c} = \frac{2}{\overline{M}_n} - \frac{(\bar{v}/V_1)\left[\ln(1 - v_{2m}) + v_{2m} + \chi v_{2m}^2\right]}{v_{2r}\left[\left(\dfrac{v_{2m}}{v_{2r}}\right)^{1/3} - \left(\dfrac{v_{2m}}{2v_{2r}}\right)\right]} \quad (3)$$

Here, v_{2r} is the polymer volume fraction in the relaxed state, i.e. after cross-linking but before swelling.

The Flory–Rehner and Peppas–Merrill models describe the molecular weight between cross-links for neutral polymer networks, but hydrogels may be neutral or ionic in nature. If the polymer chains making up the network contain ionizable groups, the forces influencing swelling may be greatly increased due to localization of charges within the hydrogel[22,23]. Ionic polymer networks in aqueous salt solutions yield a far more complicated situation than that of neutral polymers. The equilibrium swelling ratios attained are often an order of magnitude larger than those of

neutral networks, as intermolecular interactions such as coulombic, hydrogen-bonding and polar forces are present. Brannon-Peppas and Peppas have derived equations to describe this ionic contribution term for both anionic and cationic hydrogels[24,25]. The expression for a monoprotic acid containing anionic homopolymeric network is given in equation (4), and theoretical swelling predictions based on this and other similar equations are well described by Brannon-Peppas and Peppas[24]:

$$\frac{V_1}{4I}\left(\frac{K_a}{10^{-pH}+K_a}\right)^2\left(\frac{v_{2m}}{\bar{v}}\right)^2 = \left[\ln(1-v_{2m})+v_{2m}+\chi v_{2m}^2\right]$$

$$+\left(\frac{V_1}{\bar{v}\bar{M}_c}\right)\left(1-\frac{2\bar{M}_c}{\bar{M}_n}\right)v_{2r}\left[\left(\frac{v_{2m}}{v_{2r}}\right)^{1/3}-\left(\frac{v_{2m}}{2v_{2r}}\right)\right] \quad (4)$$

During the last decade, the molecular treatment of rubber-like elasticity has been improved by Flory and Erman[26,27] including a detailed swelling–structure relationship[28-31]. These relationships, theories and the results are reviewed by Queslel and Mark[32,33] and Mark and Erman[34], for the characterization of model and randomly cross-linked networks. A brief description of these relationships emphasizing, the determination of molecular weight between cross-links of non-ionic networks by the gaussian models of networks i.e. affine and phantom are summarized below. A combined evaluation of the approaches of Peppas *et al.* and Erman *et al.* are later considered and predictive equations for the swelling of hydrogels containing diprotic acid moieties are derived in the present work.

DETERMINATION OF $\bar{M}_c$ FOR NON-IONIC HYDROGELS

When a non-ionic polymeric network is placed in a swelling agent, there are two contributions to the free energy of the system, mixing and elastic-retractive free energies as expressed as ΔG_{mix} and ΔG_{el}, respectively. It is assumed that the change in the total free energy is the sum of ΔG_{mix} and ΔG_{el}, thus

$$\Delta G = \Delta G_{mix} + \Delta G_{el} \quad (5)$$

By taking the derivative of each term in equation (5) with respect to the number of molecules of swelling agent in the system, a relationship between the chemical potential contributions and total chemical potential can be derived for equilibrium conditions:

$$\mu_1 - \mu_1^0 = (\Delta\mu_1)_{mix} + (\Delta\mu_1)_{el} = 0 \quad (6)$$

where μ_1 is the chemical potential of the swelling agent in the polymer–swelling agent mixture, and μ_1^0 is the chemical potential of the pure swelling agent. The first term in the right-hand side of equation (5), for the mixing of polymer chains with the solvent can be given in terms of the Flory–Huggins relationship:

$$(\Delta G)_{mix} = kT[n_1\ln v_1 + n_2\ln v_{2m} + \chi n_1 v_{2m}] \quad (7)$$

In this equation n_1 is the number of swelling agent molecules in the solution, v_1 is the volume fraction of solvent, n_2 is the number of polymer molecules in the solution and v_{2m} is the polymer volume fraction of the swollen chains (swollen state). For any cross-linked polymeric system, the number of 'free' polymer molecules, in the solution n_2 is zero. Therefore equation (7) may be differentiated to give equation (8):

$$(\Delta\mu 1)_{mix} = RT[\ln(1-v_{2m})+v_{2m}+\chi v_{2m}^2] \quad (8)$$

Expressions of $(\Delta G)_{el}$ for a phantom and an affine network to the state of isotropic dilation are given in equations (9) and (10) below, respectively[34]:

$$(\Delta G)_{el} = \frac{3\nu kT}{2}\left[\left(\frac{v_{2r}}{v_{2m}}\right)^{2/3}-1\right]-\mu kT\ln\frac{v_{2r}}{v_{2m}} \quad (9)$$

$$(\Delta G)_{el} = \frac{3\xi kT}{2}\left[\left(\frac{v_{2r}}{v_{2m}}\right)^{2/3}-1\right] \quad (10)$$

where ν is the number of network chains, μ is the number of junctions, and ξ is the cycle rank which denotes the number of chains that have to be cut in order to reduce the network to a tree with no closed cycles. The polymer volume fractions in the gels immediately after preparation (relaxed state), v_{2r}, and the polymer volume fraction of the swollen gels (swollen state), v_{2m}, can be determined by equations (11) and (12).

$$V_{2r} = V_d/V_o \quad (11)$$

$$V_{2m} = V_d/V_s \quad (12)$$

Here, V_d is the volume of the dry polymer sample and V_o and V_s the gel sample volumes before and after equilibrium swelling, respectively.

Differentiation of equations (9) and (10) with respect to the number of moles of solvent and substitution in equation (6) together with equation (8), one obtains for an affine network[34]:

$$\ln(1-v_{2m})+v_{2m}+\chi v_{2m}^2+B\left(1-\frac{2}{\phi}\right)\left[\left(\frac{v_{2m}}{v_{2r}}\right)^{1/3}-1\right]$$

$$-\frac{\mu}{\nu}\left(\frac{v_{2r}}{v_{2r}}\right)=0 \quad (13)$$

and for a phantom network,

$$\ln(1-v_{2m})+v_{2m}+\chi v_{2m}^2+B\left(\frac{v_{2m}}{v_{2r}}\right)^{1/3}=0 \quad (14)$$

where

$$B=\left(\frac{V_1\xi kT}{RTV_0}\right)=\left(1-\frac{2}{\phi}\right)\frac{V_1}{\bar{v}\bar{M}_c} \quad (15)$$

and ϕ is the functionality at the cross-linking site.

In the highly swollen state, the constrained junction theory indicates that a real network exhibits properties closer to those of the phantom network model. Consequently equation (14) is a more realistic representation for equilibrium swelling. equation (14) may thus be used to estimate the average chain length between cross-links, especially at the high degrees of expansion obtained in the swelling experiments[34]. Using equation (15) and solving equation (14) for $\bar{M}_c$ leads to

$$\bar{M}_c = -\frac{(1-2/\phi)V_1 v_{2r}^{2/3}v_{2m}^{1/3}}{\bar{v}\left[\ln(1-v_{2m})+v_{2m}+\chi v_{2m}^2\right]} \quad (16)$$

This derived equation using the phantom network model is valid for neutral or non-ionic structures and Bahar *et al.*[35] using several network samples with different cross-link densities had proved that equation (16) leads to an estimate of χ as a function of v_{2m} as well.

In the following discussion we have attempted to derive similar equations for the case of ionically charged and diprotic acid containing copolymeric hydrogels. The derivation given below is a combination of the approaches of Peppas *et al.* and Erinan *et al.* presented so far.

DETERMINATION OF $\overline{M}_c$ IN IONIC COPOLYMERIC HYDROGELS

When an ionic polymer is placed in swelling agent there is an extra contribution to the free energy of the system which is expressed with ΔG_{ion}. Thus the following equation can be written for the total free energy change of the system.

$$\Delta G = \Delta G_{mix} + \Delta G_{el} + \Delta G_{ion} \qquad (17)$$

This can be rewritten in terms of chemical potentials by taking the derivative of each term in equation (17) with respect to the number of molecules of swelling agent in the system:

$$\mu_1 - \mu_1^0 = (\Delta\mu_1)_{mix} + (\Delta\mu_1)_{el} + (\Delta\mu_1)_{ion} = 0 \qquad (18)$$

The μ_1 and μ_0^1 are already defined above. At swelling equilibrium, the chemical potential of the swelling agent, μ_1, is equal to the chemical potential of the swelling agent in the solution surrounding the polymer, μ_1^*, i.e.

$$(\Delta\mu_1^*)_{ion} - (\Delta\mu_1)_{ion} = (\Delta\mu_1)_{mix} + (\Delta\mu_1)_{el} \qquad (19)$$

Brandon-Peppas and Peppas[24] have obtained the following equations for $(\Delta\mu_1^*)_{ion} - (\Delta\mu_1)_{ion}$ for the cases where external electrolyte concentration is small [equation (20)], and large [equation (21)], as compared to the concentration of counterions belonging to the polymer and the concentration difference of the mobile electrolyte between the inside and outside of the gel is non-comparable and comparable in magnitude to the concentration of counterions for equations (20) and (21), respectively:

$$(\Delta\mu_1^*)_{ion} - (\Delta\mu_1)_{ion} = V_1 RT \left(\frac{ic_2}{z_-} \right) \qquad (20)$$

$$(\Delta\mu_1^*)_{ion} - (\Delta\mu_1)_{ion} = V_1 RT \left(\frac{i^2 c_2}{4I} \right) \qquad (21)$$

In the above equations, i is the degree of ionization, I is the ionic strength of the swelling medium, c_2 is the concentration of ionizable polymer(g dry gel cm^{-3}). c_2 can be written in terms of polymer structural parameters for copolymeric hydrogels, using the polymer volume fraction(v_{2m}) and weight fraction (X) of ionizable polymer in the gel system, equation (22):

$$c_2 = \frac{v_{2m}X}{\bar{v}} \qquad (22)$$

The degree of ionization i, can be expressed in terms of other analytical variables of the polymer–solvent system. For gels with diprotic acid moieties there are two equilibria:

$$K_{a1} = \frac{[HA^-][H^+]}{[H_2A]} \qquad (23)$$

$$K_{a2} = \frac{[A^{2-}][H^+]}{[HA^-]} \qquad (24)$$

where $[H_2A]$ is the concentration of undissociated anionic repeating units on the chain, $[HA^-]$ and $[A^{2-}]$ are the concentration of dissociated polymer chains and $[H^+]$ is the concentration of hydrogen ions. The ionization i is defined as shown in equation (25):

$$i = 2 - \bar{n}/2 = (2\alpha_0 + \alpha_1)/2 \qquad (25)$$

where $\bar{n}$ represents the average number of protons bound to carboxyl groups in the diprotic acid and α_0, α_1 and α_2 are the ratio of the concentration of species $[A^{2-}]$, $[HA^-]$ and

$[H_2A]$ to the analytical concentration (C) of diprotic acid, respectively[36]. The α values can be defined by the following equations in terms of the dissociation constants K_{a1} and K_{a2} of the ionizable polymer[36]:

$$\alpha_0 = \frac{[A^{2-}]}{C} = \alpha_2 \left(\frac{K_{a1}K_{a2}}{[H^+]^2} \right) \qquad (26)$$

$$\alpha_1 = \frac{[HA^-]}{C} = \alpha_2 \left(\frac{K_{a1}}{[H^+]} \right) \qquad (27)$$

$$\alpha_2 = \frac{[H_2A]}{C} = \left[1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2} \right]^{-1} \qquad (28)$$

Combining equations (26)–(28) into equation (25) and substituting in equations (20) and (21), the following equations can be obtained for $(\Delta\mu_1^*)_{ion} - (\Delta\mu_1)_{ion}$:

$$(\Delta\mu_1^*)_{ion} - (\Delta\mu_1)_{ion}$$

$$= \left[\frac{[2K_{a1}K_{a2} + 10^{-pH}K_{a1}]}{2[(10^{-pH})^2 + 10^{-pH}K_{a1} + K_{a1}K_{a2}]} \right] \frac{V_1 RTc_2}{z_-} \qquad (29)$$

$$(\Delta\mu_1^*)_{ion} - (\Delta\mu_1)_{ion}$$

$$= \left[\frac{[2K_{a1}K_{a2} + 10^{-pH}K_{a1}]}{2[(10^{-pH})^2 + 10^{-pH}K_{a1} + K_{a1}K_{a2}]} \right]^2 \frac{V_1 RTc_2^2}{4I} \qquad (30)$$

Using the phantom network model, as proposed by Erman[37] the complete equilibrium expression accounting for the mixing, elastic-retractive and ionic contributions to the chemical potential of diprotic copolymeric networks satisfying the conditions for equations (20) and (21) are given below in equation (31)eq. equation (32).

$$\left(\frac{[2K_{a1}K_{a2} + 10^{-pH}K_{a1}]}{2[(10^{-pH})^2 + 10^{-pH}K_{a1} + K_{a1}K_{a2}]} \right) \left(\frac{V_1 v_{2m}X}{z_- \bar{v}} \right)$$

$$= \ln(1 - v_{2m}) + v_{2m} + \chi v_{2m}^2 + \frac{(1 - 2/\phi)V_1 v_{2r}^{2/3} v_{2m}^{1/3}}{\bar{v}\overline{M}c} \qquad (31)$$

$$\left(\frac{[2K_{a1}K_{a2} + 10^{-pH}K_{a1}]}{2[(10^{-pH})^2 + 10^{-pH}K_{a1} + K_{a1}K_{a2}]} \right)^2 \left(\frac{V_1 v_{2m}^2 X^2}{4I\bar{v}^2} \right)$$

$$= \ln(1 - v_{2m}) + v_{2m} + \qquad (32)$$

$$\chi v_{2m}^2 + \frac{(1 - 2/\phi)V_1 v_{2r}^{2/3} v_{2m}^{1/3}}{\bar{v}\overline{M}_c}$$

PREDICTION OF SWELLING BEHAVIOUR

Swelling in solutions with low ionic strength

In order to predict the swelling behaviour of copolymeric hydrogels with diprotic acid moieties, the equations derived in the previous section were analysed under various conditions with a number of parameters. The parameters in the construction of theoretical equilibrium swelling curves were chosen to be very close to typical experimental parameters. Thus in all analyses the specific volume of the polymer was $\bar{v} = 0.8 \ cm^3 \ g^{-1}$, the Flory interaction parameter was $\chi = 0.5$. All simulations were made for aqueous solutions, and therefore the molar volume of the solvent $V_1 = 18 \ g \ cm^{-3}$. It was assumed that cross-linking occurred in the presence of solvent and with a polymeric volume fraction after cross-link but before swelling of $v_{2r} = 0.6$. The weight fraction of ionizable polymer in the gel
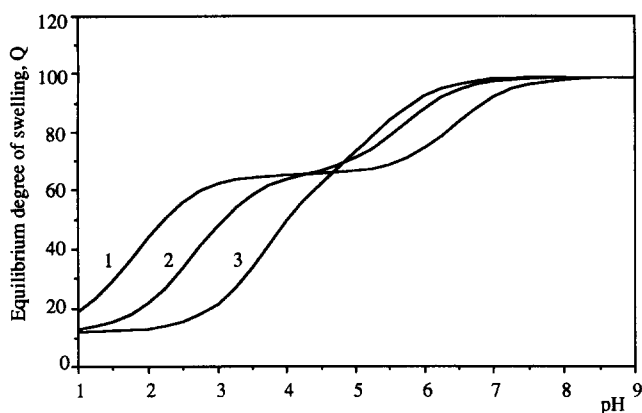
Figure 1 Theoretical swelling curves at low ionic strength for a diprotic anionic network, where $\overline{M}_c = 10000$ and $X = 0.05$ with: $pK_{a1} = 2.0$ and $pK_{a2} = 6.50$ for curve 1, $pK_{a1} = 2.85$ and $pK_{a2} = 5.75$ for curve 2, $pK_{a1} = 3.85$ and $pK_{a2} = 5.45$ for curve 3
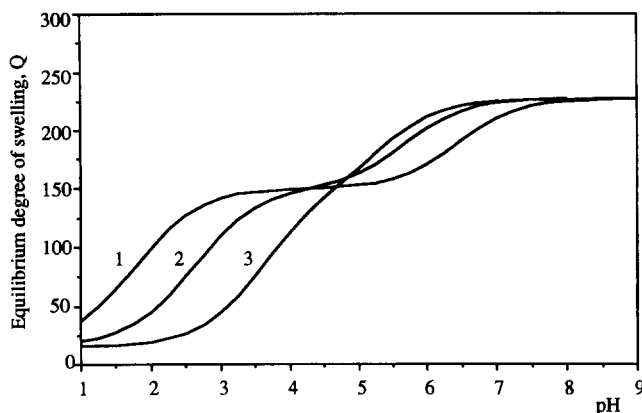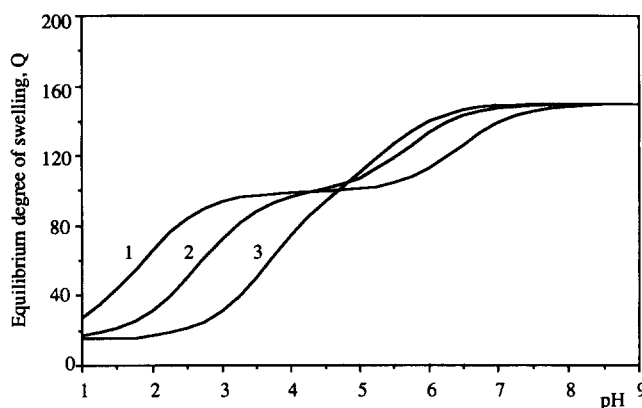

Figure 3 Theoretical swelling curves at low ionic strength for a diprotic anionic network, where $\overline{M}_c = 20000$ and $X = 0.1$ with $pK_{a1} = 2.0$ and $pK_{a2} = 6.50$ for curve 1, $pK_{a1} = 2.85$ and $pK_{a2} = 5.75$ for curve 2, $pK_{a1} = 3.85$ and $pK_{a2} = 5.45$ for curve 3
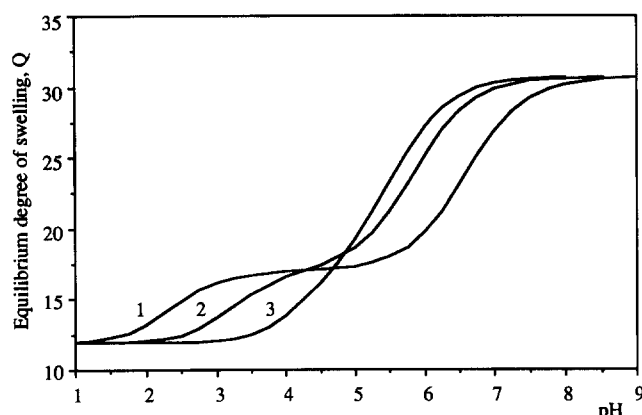

Figure 2 Theoretical swelling curves at low ionic strength for a diprotic anionic network, where $\overline{M}_c = 20000$ and $X = 0.05$ with $pK_{a1} = 2.0$ and $pK_{a2} = 6.50$ for curve 1, $pK_{a1} = 2.85$ and $pK_{a2} = 5.75$ for curve 2, $pK_{a1} = 3.85$ and $pK_{a2} = 5.45$ for curve 3

Figure 4 Theoretical swelling curves at 0.1 M ionic strength for a diprotic anionic network, where $\overline{M}_c = 10000$ and $X = 0.05$ with: $pK_{a1} = 2.0$ and $pK_{a2} = 6.50$ for curve 1, $pK_{a1} = 2.85$ and $pK_{a2} = 5.75$ for curve 2, $pK_{a1} = 3.85$ and $pK_{a2} = 5.45$ for curve 3

system between $X = 0.02{-}0.05$. The K_{a1} and K_{a2} values are taken to be close to the dissociation constants of itaconic and maleic acids whose copolymeric hydrogels have already been prepared with acrylamide[3,12,13,38].

A comparative study of theoretical and experimental swelling behaviours of these hydrogel systems has recently been undertaken and will be published separately[39].

Influence of the K_{a1} and K_{a2} on the equilibrium degree of swelling (EDS) in the low ionic strength solution, i.e. external electrolyte concentration being small as compared to the concentration of counterions belonging to the polymer, is given in *Figure 1*.

The EDS is defined as $Q = 1/v_{2m}$. As the difference between the K_a values increased the shape of the swelling curves changed from an S-shape to a double S-shape. The maximum equilibrium swelling, however, is not changed. When this difference, ΔpK_a, is 4.5, two steps were observed in the theoretical swelling curves. First and second steps indicating the dissociation of the first and second acidic groups of the ionic repeating unit in the gel system. When the difference is 1.6 the swelling curve has almost had one step with a broadened S-shape which can be compared to the swelling curves of monoprotic acid containing systems[24].

EDS can be increased by increasing the molecular weight

between the cross-links as well as by increasing the fraction of ionizable groups within the polymer chains. *Figure 2* shows that when $\overline{M}_c$ is doubled EDS increased by 50%.

The value of the equilibrium swelling of an ionic network very much depends on the concentration of ionizable polymer in the network. *Figure 3* shows the influence of the weight fraction of the anionic polymer segments and pH of the surrounding solution on the equilibrium degree of swelling. *Figure 3* indicates that the contribution of ionizable component in the swelling gel is quite significant.

Swelling in solutions with moderate and high ionic strength

Theoretical swelling prediction at moderate ionic strength condition $I = 0.1$ for an ionic network described in previous section is given in *Figure 4*. The experimental variables considered in *Figures 1* and *4* are the same except for the ionic strength. It is clear from a comparison of these two figures that there are some significant changes in the shape of the swelling curves and equilibrium swelling values. Increasing ionic strength of the solution causes a decrease in EDS. The effect of ionic strength on the swelling of ionized gels has been explained by Donnan-equilibrium arguments[40]. As ionic strength rises, the difference in concentration of mobile ions between the gel and solution is
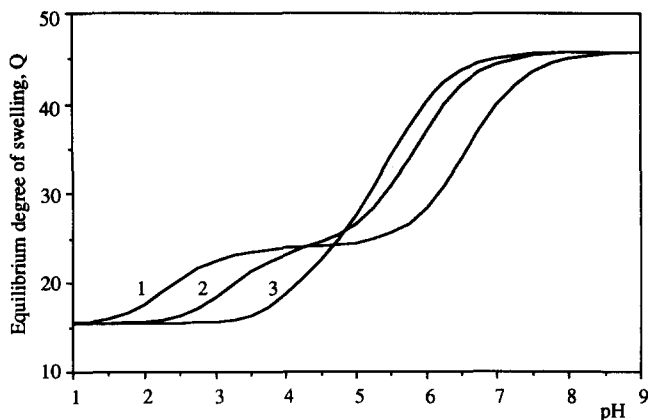
Figure 5 Theoretical swelling curves at 0.1 M ionic strength for a diprotic anionic network, where $\overline{M}_c = 20000$ and $X = 0.05$ with: $pK_{a1} = 2.0$ and $pK_{a2} = 6.50$ for curve 1, $pK_{a1} = 2.85$ and $pK_{a2} = 5.75$ for curve 2, $pK_{a1} = 3.85$ and $pK_{a2} = 5.45$ for curve 3
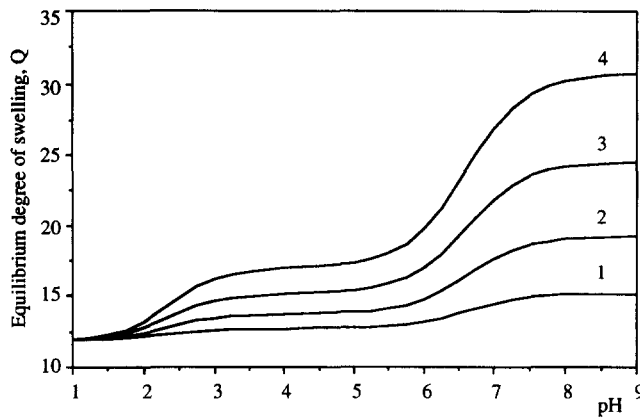

Figure 7 Theoretical swelling curves at 0.1 M ionic strength for a diprotic anionic network, where $\overline{M}_c = 10000$ and $pK_{a1} = 2.00$, $pK_{a2} = 6.50$ with: (1) $X = 0.02$, (2) $X = 0.03$, (3) $X = 0.04$, (4) $X = 0.05$
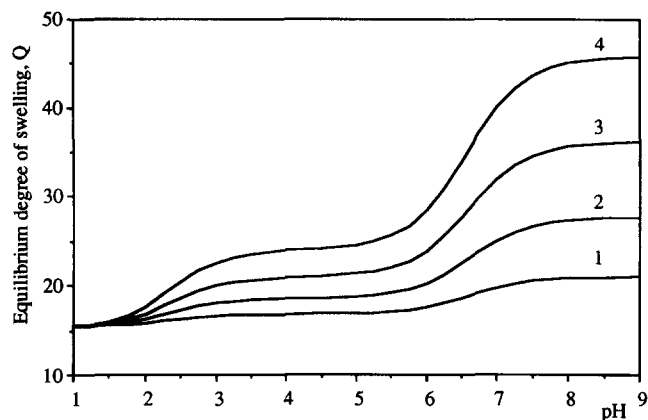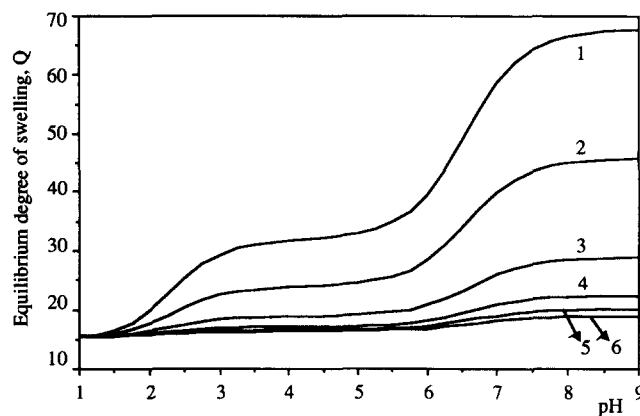

Figure 6 Theoretical swelling curves at 0.1 M ionic strength for a diprotic anionic network, where $\overline{M}_c = 20000$ and $pK_{a1} = 2.00$, $pK_{a2} = 6.50$ with: (1) $X = 0.02$, (2) $X = 0.03$, (3) $X = 0.04$, (4) $X = 0.05$

Figure 8 Theoretical swelling curves for a diprotic anionic network, where $\overline{M}_c = 20000$, $X = 0.05$ and $pK_{a1} = 2.00$, $pK_{a2} = 6.50$ with: (1) $I = 0.05$, (2) $I = 0.1$, (3) $I = 0.25$, (4) $I = 0.5$, (5) $I = 0.75$, (6) $I = 1.0$

reduced, thereby decreasing the osmotic swelling pressure of these mobile ions inside the gel. This low EDS may be increased by increasing the molecular weight between cross-links as depicted in *Figure 5*. The effect of other parameters used in equation (30) onto EDS are given below for two extreme cases of $\Delta pK_a = 4.5$ and $\Delta pK_a = 1.6$.

Prediction for a diprotic acid with $\Delta pK_a = 4.5$

In the simulation of swelling behaviour of hydrogels the choice of dissociation constants greatly affects the ultimate swelling. These constants, in other words pK_a values are not, however, arbitrarily selected, $pK_{a1} = 2.0$ and $pK_{a2} = 6.50$ values used in the following discussion are considered for being very close to the dissociation constants of maleic acid, one of the comonomers used in our previous works[3,12,13].

The role of the concentration of ionizable polymer in the network has already been discussed for low ionic strength above. *Figure 6* shows the influence of the weight fraction of the anionic gel and pH of the surrounding solution on the equilibrium degree of swelling in moderate ionic strength conditions. *Figure 6* predicts that as the amount of ionizable component in the gel increased large equilibrium swelling ratios are achieved. This value can be tempered by decreasing the molecular weight between cross-links (*Figure 7*).
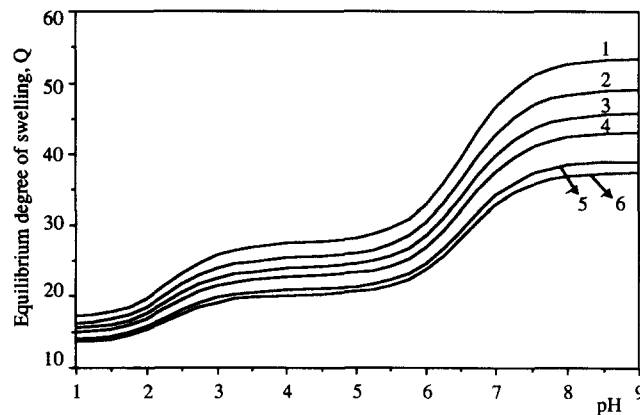

Figure 9 Theoretical swelling curves at 0.1 M ionic strength for a diprotic anionic network, where $\overline{M}_c = 20000$, $X = 0.05$ and $pK_{a1} = 2.00$, $pK_{a2} = 6.50$ with: (1) $v_{2r} = 0.4$, (2) $v_{2r} = 0.5$, (3) $v_{2r} = 0.6$, (4) $v_{2r} = 0.7$, (5) $v_{2r} = 0.9$, (6) $v_{2r} = 1.0$

The effect of ionic strength of the swelling medium on the equilibrium degree of swelling is shown in *Figure 8*. As expected an increase in the ionic strength decreased the extent of swelling. The drastic changes in the swelling, however, occured in the same pH regions for all ionic strength values. This behaviour is very similar to the predictive curves of monoprotic acid containing polymeric gels[24].
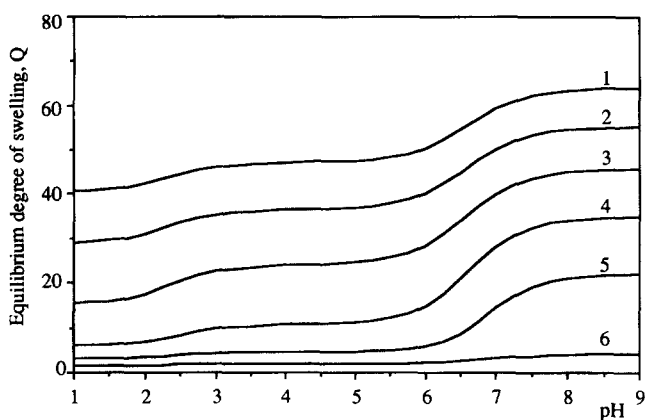
Figure 10 Theoretical swelling curves at 0.1 M ionic strength for a diprotic anionic network, where $\bar{M}_c = 20\,000$, $X = 0.05$ and $pK_{a1} = 2.00$, $pK_{a2} = 6.50$ with: (1) $\chi = 0.40$, (2) $\chi = 0.45$, (3) $\chi = 0.50$, (4) $\chi = 0.55$, (5) $\chi = 0.60$, (6) $\chi = 0.70$
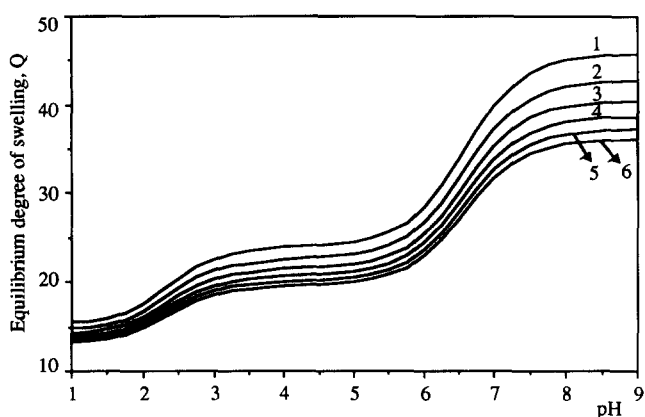

Figure 11 Theoretical swelling curves at 0.1 M ionic strength for a diprotic anionic network, where $\bar{M}_c = 20\,000$, $pK_{a1} = 2.00$, $pK_{a2} = 6.50$ and $X = 0.05$ with: (1) $\phi = 3.0$, (2) $\phi = 3.2$, (3) $\phi = 3.4$, (4) $\phi = 3.6$, (5) $\phi = 3.8$, (6) $\phi = 4.0$

Another parameter to be considered is the volume fraction of polymer in the cross-linking medium. The mobility of the polymer chains in the final cross-linked system may be increased as the amount of solvent present during the cross-linking is increased, i.e. as the volume fraction v_{2r} increases (*Figure 9*). This variation becomes more significant at higher pH values when the polymer fully ionized.

The polymer solvent interaction parameter, χ, is another important factor affecting the swelling of gels. As shown in *Figure 10* in poor solvents $\chi \geq 0.7$ and the equilibrium degree of swelling is not affected at all with variations in pH. In such solutions one can hardly expect any swelling. For good solvents i.e. $\chi < 0.5$, however, because of increasing polymer–solvent interactions equilibrium swelling is shifted to higher values at every pH.

The influence of the functionality at the cross-linking site, ϕ, on the equilibrium degree of swelling is given in *Figure 11*. Network structure formed by the simultaneous random copolymerization and cross-linking of monomers, at least one type of which has a functionality ϕ of 3 or greater where ϕ is the number of sites from which chains grow has an influence on the density of cross-links. An increase in ϕ decreases the swelling of the polymer in both the nonionized and fully ionized states.

Prediction for a diprotic acid with $\Delta pK_a = 1.6$

The shape of the swelling curves would be quite different if the dissociation constants of the diprotic acid part are relatively close to each other. For this purpose a ΔpK_a value of 1.6 has been considered in the following analysis. The selection of this value is not arbitrary since it corresponds to the difference in the dissociation constants of acidic groups in itaconic acid, another comonomer that we used in our previous works[38,41]. Theoretical swelling curves predicted for a copolymeric anionic gel having ionizable groups with $\Delta pK_a = 1.6$ are collected in *Figures 12–16*.

The influence of weight fraction of ionizable groups, X, the ionic strength, I, the mobility of the polymer chains in the final cross-linked system, v_{2r}, the χ parameter and functionality of cross-linking, ϕ, on the equilibrium swelling of hydrogel are given in *Figures 12–16*, respectively.

The comparison of theoretical swelling curves shown in *Figures 6–11* with those in *Figures 12–16* indicates two main points. Instead of having double S-shaped curves, single S-shapes are observed when the ΔpK_a value is as small as 1.6. The overlap of dissociation ranges of two acidic groups gives rise to a single broad S-shape. When ΔpK_a value is small, the swelling curves become very much like the curves of hydrogels containing monoprotic acid moieties[24].
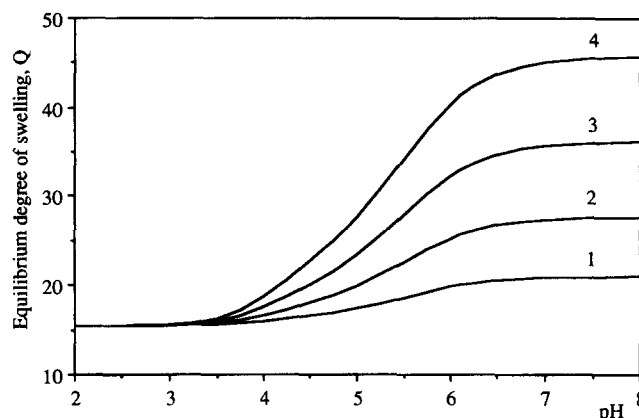

Figure 12 Theoretical swelling curves at 0.1 M ionic strength for a diprotic anionic network, where $\bar{M}_c = 20\,000$ and $pK_{a1} = 3.85$, $pK_{a2} = 5.45$ with (1) $X = 0.02$, (2) $X = 0.03$ (3) $X = 0.04$, (4) $X = 0.05$
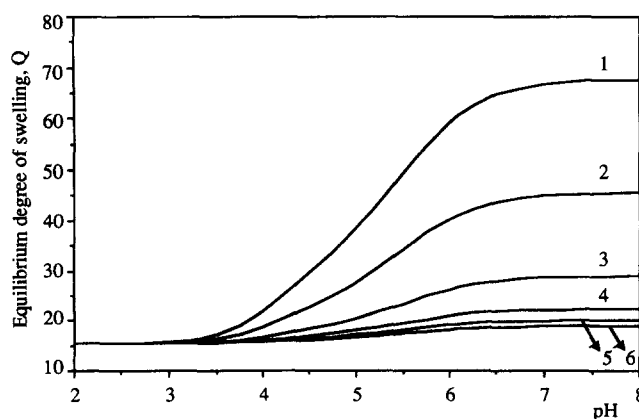

Figure 13 Theoretical swelling curves at 0.1 M ionic strength for a diprotic anionic network, where $\bar{M}_c = 20\,000$, $pK_{a1} = 3.85$, $pK_{a2} = 5.45$ and $X = 0.05$ with: (1) $I = 0.05$, (2) $I = 0.1$, (3) $I = 0.25$, (4) $I = 0.5$, (5) $I = 0.75$, (6) $I = 1.0$
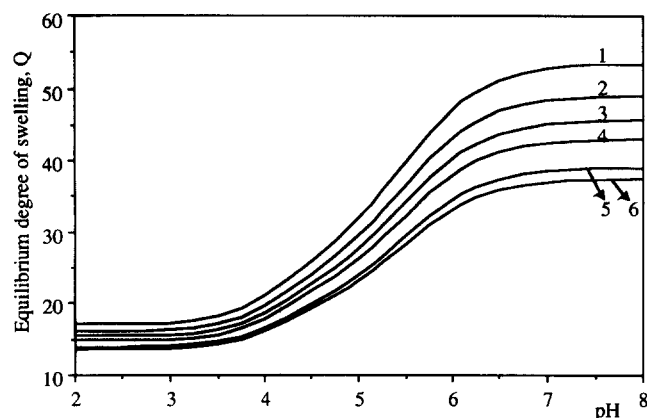
Figure 14 Theoretical swelling curves at 0.1 M ionic strength for a diprotic anionic network, where $\overline{M}_c = 20\,000$, $pK_{a1} = 3.85$, $pK_{a2} = 5.45$ and $X = 0.05$ with: (1) $v_{2r} = 0.4$, (2) $v_{2r} = 0.5$, (3) $v_{2r} = 0.6$, (4) $v_{2r} = 0.8$, (5) $v_{2r} = 0.9$, (6) $v_{2r} = 1.0$
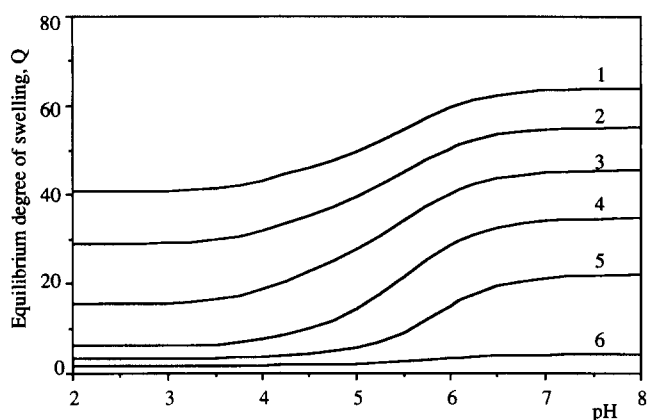

Figure 17 Graphical representation of equation (34) for the determination of $\overline{M}_c$ and χ values

Figure 15 Theoretical swelling curves at 0.1 M ionic strength for a diprotic anionic network, where $\overline{M}_c = 20\,000$, $pK_{a1} = 3.85$, $pK_{a2} = 5.45$ and $X = 0.05$ with: (1) $\chi = 0.40$, (2) $\chi = 0.45$, (3) $\chi = 0.50$, (4) $\chi = 0.55$, (5) $\chi = 0.60$, (6) $\chi = 0.70$
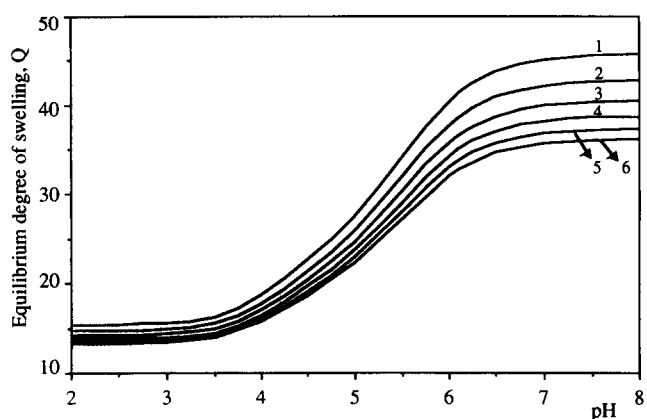
physico-chemical and analytical parameters have been utilized. These can be grouped as polymer-based parameters, solution property parameters and polymer–solvent combination type parameters. By recasting equations (31) and (32) it is therefore possible to find some relations which can be used for the determination of some of these parameters from swelling data. One of the most important properties to be characterized of a network is the average chain length between consequetive cross-linking points, that means $\overline{M}_c$. The other parameter that would be of great interest is the polymer–solvent (swelling agent) interaction parameter, χ. When equations (31) and (32) are rearranged for low and moderate ionic strength conditions, equations (33) and (34) are obtained, respectively:

$$\left(\frac{[2K_{a1}K_{a2} + 10^{-pH}K_{a1}]}{2[(10^{-pH})^2 + 10^{-pH}K_{a1} + K_{a1}K_{a2}]}\right)\left(\frac{V_1 X v_{2m}^{-1}}{z_- \bar{v}}\right)$$

$$- \ln(1 - v_{2m})v_{2m}^{-2} - v_{2m}^{-1} = \chi + \left(\frac{(1 - 2/\phi)V_1 v_{2r}^{2/3} v_{2m}^{-5/3}}{\bar{v}\overline{M}_c}\right)$$

(33)

$$\left(\frac{[2K_{a1}K_{a2} + 10^{-pH}K_{a1}]}{2[(10^{-pH})^2 + 10^{-pH}K_{a1} + K_{a1}K_{a2}]}\right)^2\left(\frac{V_1 X^2}{4I\bar{v}^2}\right)$$

$$- \ln(1 - v_{2m})v_{2m}^{-2} - v_{2m}^{-1} = \chi + \left(\frac{(1 - 2/\phi)V_1 v_{2r}^{2/3} v_{2m}^{5/3}}{\bar{v}\overline{M}_c}\right)$$ (34)

Figure 16 Theoretical swelling curves at 0.1 M ionic strength for a diprotic anionic network, where $\overline{M}_c = 20\,000$, $pK_{a1} = 3.85$, $pK_{a2} = 5.45$ and $X = 0.05$ with: (1) $\phi = 3.0$, (2) $\phi = 3.2$, (3) $\phi = 3.4$, (4) $\phi = 3.6$, (5) $\phi = 3.8$, (6) $\phi = 4.0$

The other observation is related with the ultimate degree of swelling of hydrogels. Since the individual pK_a values in these two cases are rather close, the equilibrium degree of swelling are almost the same at high pH values under various conditions.

Determination of $\overline{M}_c$ and χ parameter from equilibrium swelling behaviours
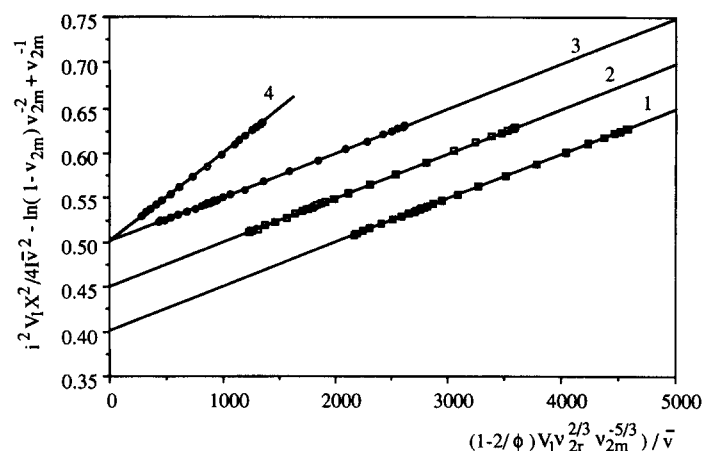
In the derivation of equations (31) and (32) a number of

A plot of the left-hand side of these equations *versus* $(1 - 2/\phi)V_1 v_{2r}^{2/3} v_{2m}^{-5/3}/\bar{v}$ should give a straight line with $1/\overline{M}_c$ and χ as the slope and intercept of the horizontal axis, respectively. Thus equation (34) is checked by using the swelling data of the curves 1–3 in *Figure 10* and curve 1 in *Figure 4*. The predictive linear curves are collected in *Figure 17*.

The χ values determined from the intercept are 0.40, 0.45 and 0.50 for the curves 1, 2 and 3, and 4. The three parallel lines obtained for the data of curves 1, 2 and 3 give the identical $\overline{M}_c$ value of 20 000 whereas 10 000 is found for curve 4.

In the construction of experimental curves based on equations (33) and (34), polymer related properties such as ρ, X and ϕ must be known or determined as accurately as possible.

CONCLUSION

Within the context of this paper it has been tried to derive some equations for the prediction of swelling behaviours of hydrogels containing diprotic acid moieties. In the derivation of predictive equations the Flory–Rehner equation was modified by incorporating the previous approachs of Peppas *et al.* and Erman *et al.* It has become possible to include the effect of various extents of dissociation of diprotic acids, dissociation constants on the swelling of hydrogels under varying pH, ionic strength, relaxed state, volume fraction of ionizable polymer, functionality of cross-links and polymer–solvent interaction parameter. The theory satisfactorily predicts the equilibrium swelling of hydrogels with mono and diprotic acid containing systems under different experimental conditions.

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