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Kinetics of water swelling and development of porous structure in ionic poly(acrylonitrile–acrylamide–acrylic acid) hydrogels

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The kinetics of water uptake into the dry form of, and benzoic acid diffusion through, swollen inhomogeneous poly(acrylonitrile–acrylamide–acrylic acid) gels were investigated with gravimetry and ultra-violet visible spectroscopy, respectively. The goal is to understand the effects of ionizable moieties and water–polymer affinity on the rate of water diffusion during the formation of hydrogels from glassy polymers and on the free-volume mechanism for solute transport through the resulting swollen networks. The xerogel with intermediate acid content or minimal affinity with water has the maximum water diffusion coefficient in the initial swelling stage and the maximum deviation from Fickian transport. The molecular diffusion of benzoic acid through hydrogels was found to be controlled by the swelling, and the size of voids for solute diffusion does not remain constant over all the range of compositions. This discrepancy from the simple free-volume theory is due to a wide range of molecular interactions for gels with amide/acid moieties. In conclusion, dynamic swelling is influenced by water–polymer affinity and subsequently causes various types of steady transport in hydrogels.

(Keywords: dynamic swelling; solute diffusion; ionic hydrogels)

INTRODUCTION

Unsteady water penetration into glassy xerogels (i.e. dry hydrogels) and diffusion of low-molecular-weight solutes through swollen hydrogels are elementary steps occurring during the controlled release of pharmaceuticals or cultivation of microorganisms/cells entrapped in gels. However, relatively little work has been concerned with the dynamic swelling of and solute diffusion through polyelectrolyte hydrogels with pH-, temperature- and current-sensitive characteristics.

Water sorption into glassy xerogels involves the Fickian or non-Fickian diffusion of water, depending on the relative magnitude of the rate of stress relaxation of polymers and that of molecular diffusion of water[1]. Higher crosslink concentration[2] and higher content of ionic comonomer in copolymer gels[3] affects the mode and rate of water diffusion through polymer matrices. The swelling of xerogels is controlled by three factors, namely, polymer–polymer affinity in solution, elastic retraction and electrostatic forces for ions[4]. Grimshaw *et al.* performed continuum modelling and swelling measurements on crosslinked poly(methacrylic acid) hydrogels to assess the influence of the ionization of acid moieties and the mechanical force of gels[5]. Shieh and Peppas[6] investigated the swelling kinetics of copolymer gels consisting of 2-hydroxyethyl methacrylate (HEMA) and tetraethylene glycol, and found that the time course of the fractional water uptake curve of gels with higher crosslink density exhibited a peak value due to the essentially longer relaxation time of the polymers themselves and the later disappearance of stress in gels.

In poly(hydroxyethyl methacrylate–methyl methacrylic acid) hydrogels, theophylline diffusion through hydrogel membranes is affected by the crosslink density or structural compactness and amount of acid comonomers. The copolymer gel with the most dense structure leads to the slowest theophylline diffusion[7,8]. With respect to the mechanistic aspects of solute diffusion through hydrogels, the free-volume theory has been used to present the logarithm of the diffusion coefficient of NaCl through copolymer gels consisting of HEMA and glycerol methacrylate as a linear function of the reciprocal of water content in gels[9]. This relationship is valid for data of solute (a drug, 9-beta-*arabino*-furanosyladenine) diffusion through poly(hydroxyethyl methacrylate–styrene) and poly(hydroxyethyl methacrylate–*N*-vinylpyrrolidone) hydrogels[10], in which the greater swelling favours solute diffusion. Murphy *et al.*[11] investigated the permeation of Li^+, Na^+ and K^+ through HEMA gels copolymerized with styrene and methyl methacrylate (MMA), and correlated the permeability of ions in the light of the free-volume formalism (i.e. linear plots of log (permeability) vs. the reciprocal of water content in gels). Both the amount of crosslinks and crystalline morphology influence the solute diffusion in glutaraldehyde-crosslinked poly(vinyl alcohol) hydrogels[12]. Other experimental studies on solute diffusion through hydrogels in conjunction with the transport model have also been documented[13].

It seems clear that very little work has been reported

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*To whom correspondence should be addressed regarding the role of swollen microstructure in dynamic swelling and solute diffusion in physically crosslinked, multicomponent, ionic hydrogels. The diffusion coefficient of water in glassy xerogels, namely, poly(acrylonitrile–acrylamide–acrylic acid) (P(AN–AAm–AA)) and that of benzoic acid through swollen gels will be reported in this work. The solute is alternatively viewed as the probe to understand the influence of chemical composition on the microstructure of multicomponent gels.

EXPERIMENTAL

Sample preparation

Reagent-grade polyacrylonitrile (Aldrich, number-average molecular weight = 80 000) was heated in concentrated nitric acid (62 wt %) at 45°C for 8 to 22 h. Then the converted solution was stabilized at −10°C for seven days. The products were neutralized to pH 7 with 1 wt % $NaHCO_3$ solution.

One gram of dried samples was then dissolved in 10 ml dimethylsulfoxide (DMSO)/H_2O (vol. ratio = 1 : 1) mixture at 70°C. The solutions were subsequently cooled to room temperature, frozen at −10°C for 12 h and thawed at 10°C for 12 h. This sequence comprises gelation, resulting from liquid–liquid phase separation, microcrystallite formation and specific chemical interactions. The freezing–thawing cycle was repeated three times.

The contents of acrylamide and acrylic acid in gel polymers were analysed with proton n.m.r. (Bruker AC-200) and base titration, respectively. The above procedure is detailed elsewhere[14,15]. Briefly speaking, the mole percentage of amide to three functional groups is the ratio of the n.m.r. peak area at chemical shift equal to 6.7–6.8 ppm to that of methylene at 2.0 ppm (because each nitrile, carboxyl or amide corresponds to a methylene). The base titration was carried out by titrating the xerogels (i.e. the completely dry gels) in DMSO solvent with 0.0482 N aqueous KOH solution.

Dynamic swelling

The dry gel specimens with disc shape (20 to 30 mm diameter, 0.2 to 0.3 mm thick) are soaked in pH 7 deionized water. The water uptake was obtained by weighing the initial and swollen samples at various time intervals. The amount of water sorbed, M_t, was reported as a function of time, and the equilibrium sorption at infinitely long time was designated M_∞. The equilibrium water sorption was used to compute the hydrogel equilibrium water content (*HEWC*), which was defined as the weight percentage of water sorbed to that of hydrogels.

Permeation and diffusion of benzoic acid through swollen gels

The U-shaped diffusion cell consists of two cylinder sides (volume = 120 ml each) and a sample stand accommodating a 3 × 3 cm^2 gel piece in between. The gel piece is pinched in the sample stand. The donor side of the cell was filled with 0.025 wt % aqueous solution of benzoic acid (molecular weight = 122.16 g mol^{-1}, acid dissociation constant $K_a = 6.46 \times 10^{-5}$) and the donor side was filled with an equal amount of deionized water. The weak dissociation of benzoic acid in water and its use in pharmaceutical practice makes it a candidate for the permeation experiment. The concentration of benzoic acid in the solutions was determined with a u.v. spectrometer (Jasco 7800) with calibrated absorbance–concentration relationship at a wavelength of 206 nm. The accumulated mass of benzoic acid in the receptor side was plotted as a function of time. The lag time (t_l), defined as time from the mass data (a quasi-linear function of time) with steady-state mass flux extrapolated to zero accumulated mass, is related to the diffusion coefficient of benzoic acid (D) by the following expression[16]:

$$t_l = l^2/(6D) \qquad (1)$$

where l is the thickness of hydrogel membranes.

RESULTS AND DISCUSSION

Unsteady water diffusion

The chemical compositions and *HEWC* for eight gel samples with hydrolysis time ranging from 8 to 22 h are given in *Table 1*. It is seen that the amide and acid contents all increase with the hydrolysis time, and the *HEWC* (which has a maximum absolute deviation of 2%) exhibits a minimum at an intermediate content of amide or acid. This is caused by the phase behaviour of these multicomponent gels, and has been explained elsewhere[14]. For gels at amide content from 13 to 33.5 mol %, more amide causes a more inhomogeneous structure, and hence a more dense structure, leading to lower water absorption. At an amide content equal to 33.5%, the crosslink density or densification of gels reaches a maximum. As long as the mole percentage of AAm is greater than 33.5, increasing acrylic acid results in more network defects. The more network defects, the more water the gels can accommodate.

The fractional water uptake vs. the square root of time over the initial thickness of gel, $t^{1/2}/l$, for three samples with various equilibrium water uptakes is depicted in *Figure 1*, where samples with lower *HEWC* exhibit the faster initial uptake rate of water into dry gels, because on the initial part of this plot:

$$M_t/M_\infty = (4/\pi^{0.5})(Dt/l^2)^{0.5} \qquad (2)$$

The water uptake for four samples reaches equilibrium in 1050 min.

Table 1 Variation of chemical compositions and water uptake of terpolymers with various hydrolysis times

Code	TPH8	TPH10	TPH12	TPH13	TPH14	TPH16	TPH18	TPH20
Nitrile (mol %)	86.3	72.3	66.5	65.8	63.6	62.0	60.6	58.5
Amide (mol %)	13.2	27.1	32.7	33.3	35.5	36.8	37.9	39.2
Acid (mol %)	0.5	0.6	0.8	0.9	0.9	1.2	1.5	2.3
HEWC (%)	86.0	81.0	76.0	75.5	77.5	87.0	95.2	98.0

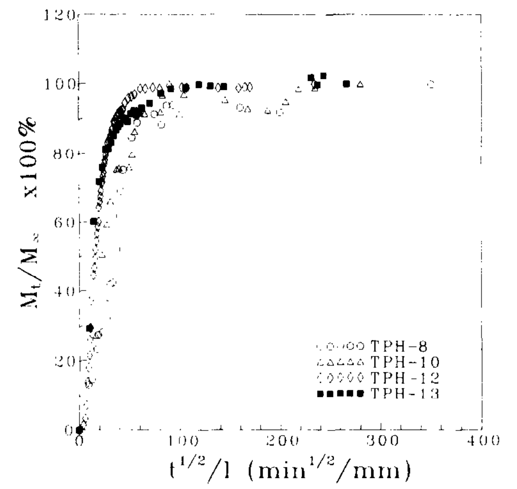

Figure 1 Plots of fractional water uptake vs. square root of time over initial thickness of four hydrogels with lower content of amide/acid at 30°C. Initial thickness = 0.2 to 0.3 mm

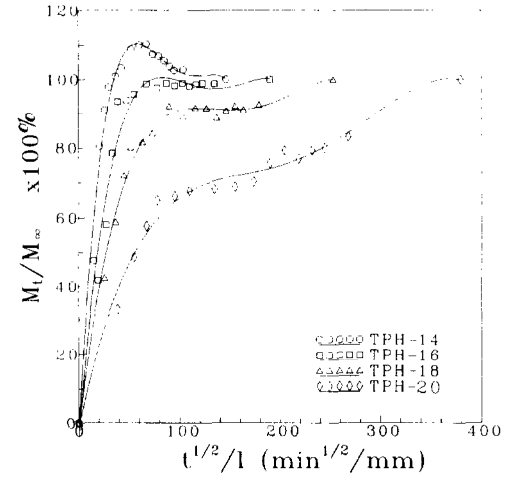

Figure 2 Plots of fractional water uptake vs. square root of time over initial thickness of four hydrogels with higher content of amide/acid at 30°C. Please note curves for two samples in non-equilibrium

Figure 2 shows the fractional uptake for four samples, showing the faster rate for samples with lower *HEWC*. Two distinct features are observable. First, the water uptake in to TPH14 experiences the 'overshooting' phenomenon, and the peak value appears at approximately 300 min or $t^{1/2}/l$ equal to 60 min$^{1/2}$ mm^{-1}. The most crosslinked or clustered structure, deformed under swelling pressure (a difference between osmotic pressure of crosslinked polymer/water mixture and the shear modulus of the network), has the most pronounced retarded mechanical response as exhibited by the lowest swellability among all samples. This sample has the highest relaxation time to reach the equilibrium volume. This implies that this sample has the largest Deborah number (a ratio of characteristic time of mechanical relaxation of polymer to that of molecular diffusion of water in polymer). Secondly, samples TPH18 and TPH22 are not equilibrated in 1100 h, and seem to have inflection points on S-shaped sorption curves at $t^{1/2}/l = 120$ and 160 min$^{1/2}$ min^{-1}, respectively. The S-shaped curves may indicate two interaction mechanisms sequentially in operation. In the first stage, we assume that water is sorbed into the bulk gel, and in the latter stage water penetrates into the pores that are gradually formed by the swelling. This situation is similar to gas adsorption onto a solid with dead-end pores. *Figures 1* and *2* indicate clearly the three modes for water penetration into polymers, due to the stress relaxation of and water penetration into pores of swollen structure.

The initial slope of water-equilibrated samples in the above figures is equal to $(4/\pi^{1/2})D^{1/2}$, where D is the spatially averaged molecular diffusion coefficient of water into the dry polymers. However, for the unequilibrated samples TPH18 and TPH22, the M_∞ used to calculate the initial diffusion coefficient is the M at the inflection points in *Figure 2*. M_∞ is the maximum water uptake in to the polymer bulk in the first stage. Also, the empirical time dependence of the fractional water uptake in the initial stage:

$$M_t/M_\infty = Kt^n \tag{3}$$

is used to determine the parameters n and K with $M_t/M_\infty \leq 0.6$. *Table 2* shows the diffusion coefficient D and the index n, in which the gel with the lowest affinity with water, i.e. TPH13, leads to the highest uptake rate and the higher *HEWC* to lower diffusion rate. This 'diffusion' coefficient is not truly indicative of the relaxation motion due to the concentration gradient. Moreover, the exponents n of gels with lower *HEWC* such as TPH13, TPH14 and TPH16 exhibit greater departure from 0.5, which is characteristic of linear Fickian transport. The information from *Table 2* reveals that the coupling between molecular transport and stress relaxation during polymer swelling becomes more pronounced for samples of lower equilibrium water absorption. This implies that the gels with higher crosslink density warrant the more rubber elasticity while the dry gels are swollen and deformed. Nonetheless, the relaxation of swelling stress applied to dry polymers seems to be a positive factor for the rate of water penetration.

Biphasic sorption curves occur in a more pronounced way to samples TPH18 and TPH20. In all eight samples, a 'moving-front' mechanism is used to describe water uptake. It is postulated that a front separates a dry, glassy core from the swollen, rubbery zone in contact with water.

Steady diffusion, permeation and solubilization of solute in swollen gels

The accumulated mass of benzoic acid passing through the gel membrane vs. time is shown in *Figure 3*. The extrapolation on the abscissa is used to compute the molecular diffusion coefficient according to equation (1).

Table 2 Initial diffusion coefficient of water, D, and kinetic exponent, n, and correlation coefficient for kinetic exponent, γ, of water penetration through P(AN–AAm–AA) copolymers at 30°C

Sample code	D (cm^2 s^{-1}) × 10^9	n	γ
TPH8	0.66	0.52	0.9667
TPH10	1.57	0.53	0.9977
TPH12	4.95	0.50	0.9923
TPH13	5.27	0.55	0.9953
TPH14	2.89	0.61	0.9926
TPH16	1.85	0.58	0.9971
TPH18	0.81	0.53	0.9637
TPH20	0.24	0.52	0.9878

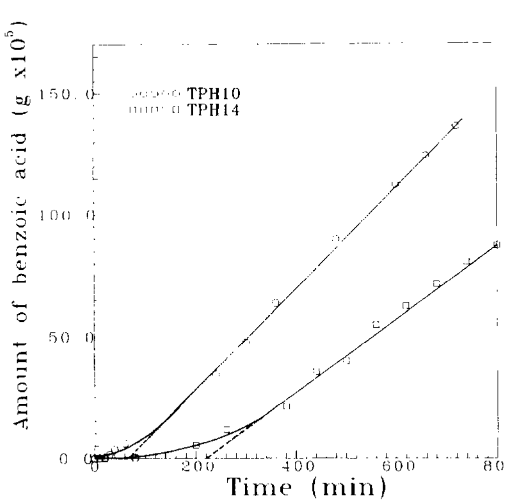

Figure 3 Permeation profiles of benzoic acid through swollen hydrogels at 30°C: (O) TPH10; (□) TPH14

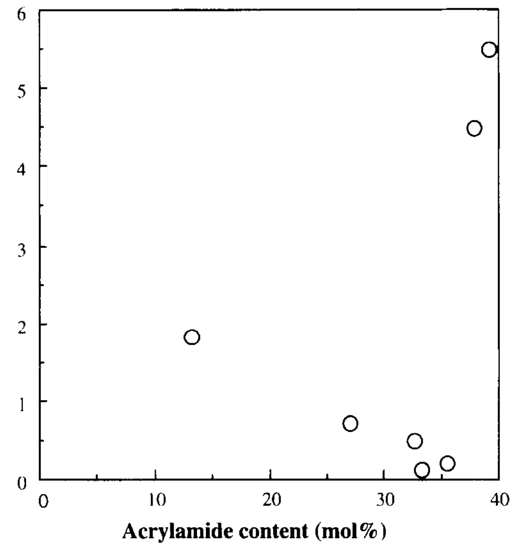

Figure 4 The diffusion coefficient of benzoic acid through swollen gels vs. mole percentage of acrylamide over overall functional groups in gels

The plot of the logarithm of the diffusion coefficient of benzoic acid through gels against the mole percentage of acrylamide is shown in *Figure 4*, indicating the minimum point at a composition (i.e. TPH13) corresponding to the lowest swelling. It is clear that the phase behaviour, in addition to the abundance of acrylamide/acrylic acid, plays a role in affecting the diffusion rate.

In diffusion experiments, if the cumulative amount of diffusant in the receptor side becomes a linear function of time, then the mass flux of diffusant through a gel membrane becomes constant:

$$\text{mass flux through membrane} = (\mathrm{d}M/\mathrm{d}t)/A = C_0P/l \tag{4}$$

where P = permeability of solute through water-filled gels (cm^2 s^{-1}); $C_0 = 2.5 \times 10^{-4}$ g solute cm^{-3} H_2O is the initial concentration difference between the donor and receptor sides; A = area of gel membranes; M = accumulated mass in the receptor side of diffusion cell; t = time; and l = membrane thickness. As a consequence:

$$P = l(\mathrm{d}M/\mathrm{d}t)/(AC_0) \tag{5}$$

Table 3 Permeability (or permeation coefficient) of benzoic acid through hydrogel membranes at 30°C and membrane thickness[a]

Sample code	Permeation coefficient P (cm^2 s^{-1}) × 10^7	Thickness of membrane (mm)
TPH8	3.15	0.49
TPH10	3.87	0.43
TPH12	2.23	0.31
TPH13	2.41	0.21
TPH14	2.95	0.42
TPH18	3.78	0.40
TPH20	4.53	0.22

[a] Membrane thickness was measured with a micrometer caliper with a contact needle

The water permeability (or hydraulic permeability) P through hydrogels is given in *Table 3*. It clearly indicates that the higher *HEWC* corresponds to the greater water permeability. According to Silberberg's proposal, water permeability is related to the number and distribution of polymer segments blocking the path of water travelling through a gel matrix[17]. Kedem and Katchalsky[18] performed a thermodynamic analysis on the permeability of membranes, and pointed out the difficulty for the measurement of solute permeability. Permeability of heterogeneous gels has been reported by Weiss *et al.*[19]. The minimum permeability for sample TPH12 or TPH13 implies that either gel has the minimum voidage or maximum chain crosslinking. Permeability is clearly an indication of the reciprocal of hydraulic resistance of gels, and this perfectly matches the water absorption data.

The solubility S of a gel is related to P and D:

$$S = P/D \tag{6}$$

S is also called the solute partition coefficient, describing the ratio of the saturation concentration of benzoic acid in the hydrogel to that in the phase of dilute benzoic acid solution. This is a thermodynamic property, with a dimensionless unit of g solute cm^{-3} hydrogel over g solute cm^{-3} water. *Figure 5* shows the relationship of solubility vs. hydrolysis condition. Interestingly, this implies that the benzoic acid in aqueous solution has the maximum affinity to the gel with minimum water content (i.e. TPH13). The thermodynamic driving force (a negative

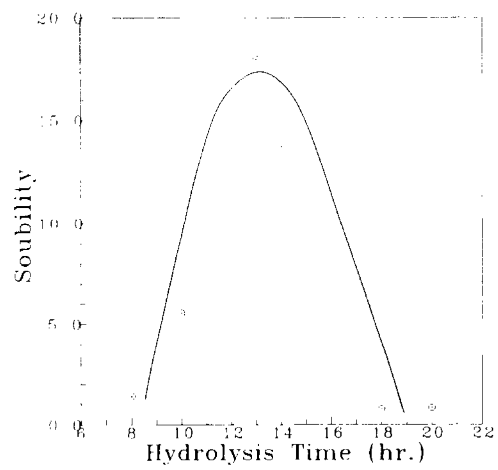

Figure 5 Solubility constant (dimensionless) of benzoic acid into hydrogels vs. hydrolysis time of hydrogels

value), or the absolute value of the molar change of Gibbs free energy for the partitioning of a small amount of benzoic acid from aqueous solution to the swollen hydrogel, has the maximum value for a gel with intermediate composition, because the change of Gibbs free energy (ΔG) for 1 mol of benzoic acid in water (at concentration = $2.5 \times 10^{-4}\,\mathrm{g\,cm^{-3}}$) dissolved into hydrogels is related to S by this expression:

$$\Delta G = -RT \ln S \tag{7}$$

In conjunction with *Figures 4* and *5*, it is concluded that the rate of solute transport through and the driving force of solute partitioning into swollen hydrogels are influenced by the structure in an opposite way. The gel with the lowest content of water is demonstrated to have the highest solubility of benzoic acid within it.

Interpretation of hydrogel structure as probed by solute diffusion

Free-volume approach. Free-volume theory for the diffusion of small molecule in polymers postulates that the diffusant jumps from one void to the neighbouring one, without resort to thermal motion. The jump rate is controlled by the fraction of unoccupied (or void) space. Fujita[20] and Vrentas and Duda[21] dealt with this theory for mutual diffusion in polymer–solvent systems and tracer diffusion of solute through amorphous rubbery polymers. Yasuda *et al.*[9] considered the free-volume theory for swollen gels, and Reinhart and Peppas[22] extended the theory to incorporate the effect of cross-linking. The free-volume theory was first proposed by Yasuda and Lamaze[23] to find the relationship between the degree of hydration (=1 – swelling ratio) and diffusion coefficient (D) in swollen membranes. The free volume is the matrix volume that is not occupied by polymer matrix and water molecules, and is generated by the density fluctuation with time, which does not imply any fixed pore structure. The two-parameter expression relating D with water content H is:

$$\ln(D/D_0) = -k(1/H - 1) \tag{8}$$

in which D_0 = constant, usually taken as the diffusion coefficient of solute in water; H = approximately the degree of hydration, while dry gel and water have equal density; and k = characteristic constant. The generalized free-volume theory for the self-diffusion of infinite-dilution solute through a polymer was proposed by Vrentas and Duda[21]:

$$\ln(D/D_0) = -(\gamma V_1^*/V_{\mathrm{FH}}) \tag{9}$$

where γ = a factor ($0 \leqslant \gamma \leqslant 1$) accounting for the overlap of free volume associated with two or more polymer molecules; V_1^* = the minimum volume of the 'hole' required for the solute to undergo the jump motion in gels; and V_{FH} = free volume contributed by 1 mol of hydrogel $\cong$ [(hydration factor)$^{-1}$ – 1] × (molar volume of dry gel). The above two equations, therefore, lead to:

$$k = V_1^*/(\text{molar volume of dry gel}) \propto V_1^* \tag{10}$$

The relationship between the diffusion coefficient and the swelling is presented in *Figure 6* in terms of the free-volume theory for molecular diffusion. *Figure 6* appears to indicate two separate lines, with the relative deviation of diffusion coefficient within 13%. This means that the error bars for diffusion data have magnitude = 0.45 on these plots. This figure illustrates $\ln D$ vs. the reciprocal of water content ($1/H$) minus 1, exhibiting the lower line (slope = –12.05) for gels with hydrolysis time greater than or equal to 13 h and the upper line (slope = –9.01) for gels with hydrolysis time less than 13 h. Two correlation lines are established on this figure, suggesting that gels with hydrolysis time greater than or equal to 13 h have a larger critical 'hole' volume of hydrogels for solute transport than other gels. This reduction of critical hole volume for a hydrolysis time less than 13 h (the upper line on *Figure 6*) may be caused by the less abundant polar functional groups of gels in the immediate neighbourhood of water (which is influenced by the phase behaviour of hydrogels), leading to weaker intermolecular interactions with benzoate ions. Such weaker intermolecular interactions facilitate the jump of diffusant through gels. This phenomenon in terms of the free-volume formalism has been found in the diffusion of polar organic vapour through either non-polar or weakly polar rubbery polymers[24]. (This situation is similar to the upper line on this plot.)

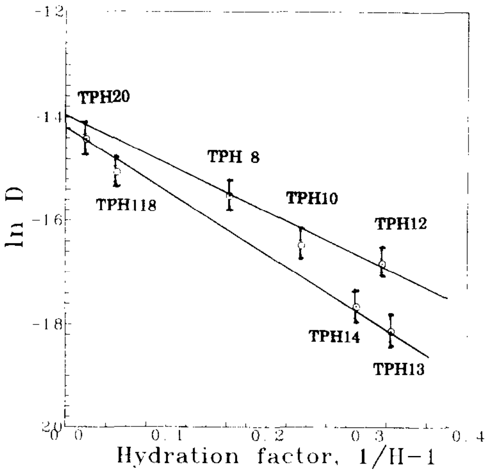

Figure 6 The logarithm of diffusion coefficient vs. hydration factor ($1/H - 1$). H is the *HEWC*. Please note two separate families of lines within experimental error

The structure of this series of gels has been discussed in the previous paper[13]. At intermediate amide content, sample TPH13 has the maximum densification. Below this level of amide, more amide leads to a more inhomogeneous structure or cluster. While the mole percentage of AAm is greater than this value, increasing AA results in more network defects between the AN-rich phase and the AAm-rich one. As seen from the lower line on *Figure 6*, such network defects lead to a higher value of slope. The data may signify the existence of two kinds of transport mechanisms. First, the solute molecule goes through a void space filled with water, caused by swelling of dry polymers by water at the uptake stage. This is the typical hole-controlled process. Secondly, simultaneous diffusion in the former mode and partial partitioning of solute into the polymer phase occur during solute transport. The molecular mechanisms may explain the slower diffusion due to the diffusion–partitioning coupling in TPH14, TPH18 and TPH20 (the lower line on *Figure 6*) than the purely void-controlled diffusion process in TPH8, TPH10 and TPH12. It is visualized that the network defects or interphase zones are responsible for the solute partitioning.

At this juncture, it should be mentioned that the log D vs. $(1/H - 1)$ approach was used by Miyajima *et al.*[10] to analyse drug diffusion through poly(HEMA) and copolymers of styrene of *N*-vinylpyrrolidone with HEMA at 37–60°C. In this treatment, H is percentage volume increase of swelling based on volume of swollen gel. The data show the slight decrease of slope on the free-volume-type plots at higher temperature.

The diffusant, benzoic acid, is a weak acid. In such a dilute solution (concentration = 0.002 M) as that under study, approximately 18% of benzoic acid exists in the ionized form. Some 0.5–2.3% of total functional groups are acrylic acid (a weak acid). The K_a of polyacrylic acid is 1.74×10^{-5}. The corresponding water absorption is 86–98 wt%. Under such conditions, the concentration of H^+ released in hydrogels prior to the contact with benzoic acid solution is approximately 0.01 M. Considering the relatively high ratio of concentration of ionic species in gels to that of benzoate in overall diffusing species, the molecular interactions between diffusants and gel matrix are ion–ion (predominantly) and dipole–dipole (relatively minor).

Parameter estimation of void structure of gels. Solute diffusion in hydrogels involves the small molecule travelling through the pores (with size ranging from 50 to 200 Å) in a restricted manner. The hindered diffusion in pores differentiates solute transport through gels from solute transport in water. The diffusion coefficients of benzoic acid in gels (*Figure 3*) range from 0.13×10^{-7} to 5.46×10^{-7} cm^2 s^{-1}, which is far below the diffusion coefficient of benzoic acid in free water at 25°C, 1.05×10^{-5} cm^2 s^{-1} (ref. 25). The ratio is 0.5 to 0.01. The maximum and minimum have a fifty-fold difference.

The ratio D/D_0 is influenced by the obstruction of molecular motion by the microporous structure in the following way:

$$D/D_0 = K\varepsilon/\tau \tag{11}$$

where K = partition coefficient of pores; ε = porosity (void fraction); and τ = tortuosity. If we assume furthermore that there is a linear relationship between pore and bulk partition coefficients:

$$K \cong S \tag{12}$$

the Carman–Kozeny equation for slow flow through porous media gives the relationship between permeability and porosity[26]:

$$\varepsilon^3/(1 - \varepsilon) \cong P \tag{13}$$

The relative porosity and tortuosity of materials (with assigned value of TPH13 = 1) are given in *Table 4*. It is notable that sample TPH12 has the minimum void space, and that sample TPH13 with minimum water uptake has the longest pathway for solute molecules to travel through. This implies that the solute motion in sample TPH13 is the most obstructed of all. Since the gel with minimum swelling has maximum crosslink density, the maximum crosslink density corresponds to the maximum diffusive tortuosity. The length of the diffusion path for the diffusant through hydrogels therefore can be viewed as an indicator of crosslink density of hydrogels.

Table 4 Relative values of porosity (ε) and tortuosity (τ) for samples at 30°C

Sample code	ε	τ
TPH8	0.926	4.162
TPH10	0.916	39.275
TPH12	0.882	167.019
TPH13	0.892	674.301
TPH14	0.918	334.016
TPH18	0.947	1.152
TPH20	1.000 (basis)	1.000 (basis)

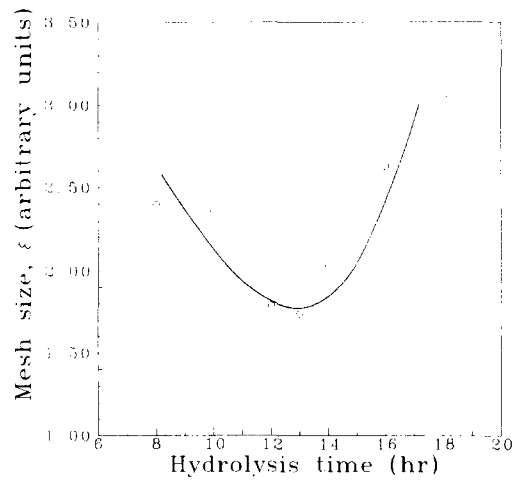

Figure 7 Relative mesh size vs. hydrolysis time of gels

Scaling-law approach. Another way to relate the rate of solute diffusion with the extent of swelling is to consider the swelling parameter, namely, the mesh size of swollen networks (ξ), in a semi-dilute polymer solution, as a function of concentration of polymer, C_2 (ref. 27):

$$\xi = aC_2^{0.75}L^3 \tag{14}$$

where L is the length of repeat units[12] at the experimental temperature and a is a constant for this scaling relationship. The solute, with a molecular size relatively smaller than the average length between crosslinks in the polymer gel, passes through gel via the sieving mechanism.

The volume fraction of polymer in polymer (V_2) can be related to the swelling ratio Q, which is the ratio of the volume of swollen gels to that of dry gels:

$$V_2 = 1/Q = C_2V_m = bC_2 \tag{15}$$

where V_m = molar volume of gels, approximately independent of water content; and b = proportionality constant. Therefore, we have:

$$\xi = (\text{const.})Q^{0.75} \tag{16}$$

The mesh size is inversely proportional to the volume fraction of polymer in solution to the power 3/4, or increases rapidly with the swelling volume. It should be commented that the absolute mesh size, or correlation length, is experimentally obtainable from dynamic light scattering, which is not depicted in this work. *Figure 7* shows the relative mesh size vs. the hydrolysis time of gels, indicating a minimum. In combination with *Figures 4* and *7*, a qualitative correlation is obtained that the lower the swelling of gels, the lower the rate of diffusion of solute through swollen gels.

It may be recalled that water is a very good solvent for P(AN–AAm–AA) copolymers, and the polymer coils in water mutually interpenetrate with each other, which is the sufficient condition for the above scaling law to be valid.

CONCLUSIONS

The stress relaxation during dynamic swelling of hydrogels, as manifested by the non-Fickian water diffusion through dry gels, is influenced by the water affinity of the initially dry gels. The physical crosslinking, in addition to chemical compositions, of gels significantly enhances the swelling rate. The influence of swellability of gels on solute diffusion is understandable in terms of free-volume theory and the scaling law for 'sieving' of solute in hydrogels. However, for gels with a complex phase structure, solute transport through water-filled voids and partitioning into polymers deviate from the simple hole mechanism for the diffusion rate. The minimum hole size for transport in this study is apparently higher for gels with more polarity. This makes the one-parameter free-volume theory fail to describe the diffusion of all samples under study. The structural parameters of resulting porous gels have been shown to be correlated with the swelling property.

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