Diffusion of polymers through polyacrylamide gels

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The diffusion of rhodamine dye and poly(acrylic acids) (M_w=6000, 50000 and 150000) through polyacrylamide (PAM) gels has been studied. Diffusion coefficients were calculated by following the diffusion of the species out of PAM gel cylinders into the surrounding liquid. The effect of gel structure on diffusion was tested by making gels with varying monomer and crosslinker concentrations. The pore sizes in the gels were calculated from modulus measurements on the gels, and the effect of the ratio of diffusing species size to gel pore size was investigated. The diffusion coefficients decreased in a power-law fashion with increased molecular weight of the diffusing species, decreased with increased monomer concentration, and decreased with increased crosslinking. The partition coefficients of the species, as measured in the experiments, depend on competition between attractive hydrogen-bonding forces and repulsive entropic forces.

(Keywords: diffusion; polymer; polyacrylamide gel; gel; partition coefficient; polyacrylic acid; rhodamine)

INTRODUCTION

Aqueous polyacrylamide gels are used extensively in a variety of applications such as sorption, separations and biomaterials[1]. Central to their usefulness are their high permeability to water and relatively low permeability to larger molecules. For example, in polyacrylamide gel electrophoresis (PAGE), separation is achieved because mobilities of large molecules forced *through* the gel by an electrical field decrease with increasing molecular weight. In gel permeation chromatography, for which polyacrylamide gels are one type of column packing material, the separation is based on the relative ease with which polymer molecules diffuse *into* the gel. A newly proposed separation technique[2] makes use of the ability of the gels to imbibe large volumes of water without entraining large molecules. The extent and rate of diffusion of unreacted monomers, oligomers and unattached polymers out of gel particles are important safety parameters in the application of gels as absorbents in personal products, such as nappies (diapers) and surgical pads.

The rate of diffusion of large molecules through any gel is controlled by the size of the molecules, the size of the pore spaces in the gel matrix, and the interaction between the gel and the diffusing species. The gel pore size depends on the solids concentration and the extents of crosslinking and swelling. Rheinhart and Peppas[3] showed how these parameters affect the diffusion of bovine serum albumin (BSA) through crosslinked poly(vinyl alcohol) membranes.

Other recent work on diffusion through gels includes that of Nguyen and Luong[4], who studied κ-carrageenan gels, and that of Chen and Osterhoudt[5], who studied the diffusion of azo dyes in gelatin matrices. Brown and Johnsen[6] studied diffusion of polyhydric alcohols, oligosaccharides and low-molecular-weight poly(ethylene oxide) into polyacrylamide discs. They found that the logarithm of the diffusion coefficient decreased linearly with the logarithm of molecular weight. In similar experiments on polyacrylamide gels, the present paper extends the molecular-weight range of the diffusing species and shows the importance of gel pore size on polymer diffusion.

In this work, the diffusion of poly(acrylic acids) of three weight-average molecular weights (M_w=6000, 50000 and 150000) and a low-molecular-weight dye (rhodamine B, 479 g mol^{-1}) is studied by monitoring the concentration of these species in a spectrophotometer cuvette into which a cylindrical gel, previously saturated with the solutes, is suspended. Each of the four species is individually tested in gels of varying solids content and crosslink density. The crosslink density of each gel is independently determined by dynamic rheological testing, which allows the calculation of an effective gel pore size.

In addition to the diffusion coefficients of these species in the gels, the equilibrium partition coefficients are also determined. The equilibrium concentrations inside and outside of the gel are unequal because of attractive interactions between the solutes and the gel and 'repulsive' interactions resulting from the decrease in entropy of a polymer molecule that enters the gel (as in gel permeation or size exclusion chromatography). The partition coefficient, reflecting the relative strengths of the attractive and repulsive interactions, varies with molecular weight.

EXPERIMENTAL

Preparation and characterization of gel cylinders

The monomer, crosslinker and initiators for the polymerization were obtained from Kodak and used without further purification. A stock solution of 20% acrylamide was prepared in a buffered solvent of 0.1 M aqueous NaCl, 0.4 g l^{-1} sodium diacetate and 3 mM sodium azide (bactericide). A second stock solution containing these same components plus 1% bisacrylamide (crosslinker) was also prepared. Polymerization of mixtures of the two stock solutions and additional buffer

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provided a variety of gels with solids contents of 6–20% and crosslink ratios of 0.025–0.050, where the crosslink ratio is given by crosslinker/(crosslinker+monomer). The buffer, sodium diacetate, was added to maintain pH ≃ 4.7, preventing the undesirable hydrolysis of the polymer amide groups.

To polymerize, 100 ml of monomer/crosslinker solution was degassed under vacuum for 20 min to eliminate dissolved oxygen. To this, 62.5 μl freshly prepared ammonium persulphate solution (20 wt% in buffer) was added, followed by 62.5 μl tetramethylethylene diamine (TEMED). Using a pipette, the mixture was loaded into a mould containing 35 cylindrical cavities with a depth of 24 mm and a diameter of 1.5 mm. The mould was covered to exclude oxygen, and the reaction was allowed to proceed for 4 h. The gel cylinders were pushed out of the mould with a metal rod. Gel discs (50 mm diameter × 6 mm thick) were prepared for the rheological tests using the same procedure.

Since, for these experiments, diffusion *out* of the cylindrical gels was measured, it was necessary that the gels be 'filled' with the diffusing species of interest. This was done by soaking the gels in solutions containing the diffusing species. Soaking occurred over 5 days, which is sufficient time for the gels to imbibe the diffusing species and to swell to equilibrium volumes. The equilibrium concentration in the soaking bath, a quantity necessary for calculation of the equilibrium partition coefficient, was measured at the end of this period.

The size of a swollen gel cylinder was determined by measuring its diameter and length with calipers. To check the accuracy of these measurements, the gel volume was measured by displacement in a calibrated tube filled with buffer. The volume calculated from the measured dimensions agreed well (maximum error of 4%) with the displacement measurement.

The dynamic storage modulus of the gels, G', was measured using a Rheometrics System IV rheometer. The modulus was measured on the disc-shaped gels using a parallel-plate geometry with a strain amplitude of 3–5% and a frequency of 10 rad s^{-1}. By employing this low frequency in the dynamic measurement, the storage modulus G' can be assumed equal to the static shear modulus G, a parameter used in calculating the effective gel pore size. These measurements were performed on freshly polymerized, unswollen gels.

Preparation of diffusing species

The low-molecular-weight diffusing species to be studied was rhodamine B (DuPont), which was used as received. The polymeric diffusing species, poly(acrylic acid) (PAA), was covalently tagged with fluorescent dye to enhance the sensitivity of detection by u.v.-vis. absorption. Three PAA samples (Polysciences) of weight-average molecular weights 6000, 50 000 and 150 000 were lightly tagged using the following procedure.

First 100 ml of a 3 wt% polymer solution (in 2 mM NaCl) was brought to pH 6 using sodium hydroxide. To this solution, 40 ml dimethyl sulphoxide (DMSO) was added. After vigorous shaking for 15 s, the solution was cooled to below 20°C before proceeding. In a separate vial, 15 ml of a 1 g ml^{-1} fluoresceinamine (Aldrich) in DMSO was cooled until the solution began to freeze (18°C). To this vial was added 60 μl acetaldehyde (EM Science). After mixing, the fluoresceinamine/acetaldehyde mixture was poured into the cooled polymer solution. After vigorous shaking, 60 μl of cyclohexylisocyanide was added. The reaction mixture was shaken once more, after which the reaction was allowed to proceed for 4 h, unstirred.

To recover the tagged polymer from the reaction mixture, the reaction solutions (for the 50 000 and 150 000 M_w samples) were ultrafiltered using a Millipore Minitan system equipped with two 13 000–15 000 molecular-weight cut-off filter packs. Effluent from the ultrafiltration apparatus appeared clear after 8–10 h, indicating the removal of all unattached fluoresceinamine from the polymer solution. The 6000 M_w PAA was purified by dialysis against pure water in Spectrapor dialysis tubing (3500 molecular weight cut-off). The water was changed frequently over a period of 5 days.

Diffusion experiments

After the gels had soaked in the rhodamine or PAA solutions for 5 days, their dimensions were measured, as described above. Each gel was suspended in a cuvette containing 3.5 ml of buffer, employing a wire basket shown schematically in *Figure 1*. The concentration in the cuvette was measured periodically using a Bausch and Lomb Spectronic 710 spectrophotometer, operated at 550 nm for rhodamine detection and at 450 nm for PAA/fluorescein detection. Before each concentration measurement, the cuvette was shaken in order to ensure uniform concentration throughout the cell. Previous calibration showed linearity of absorbance with

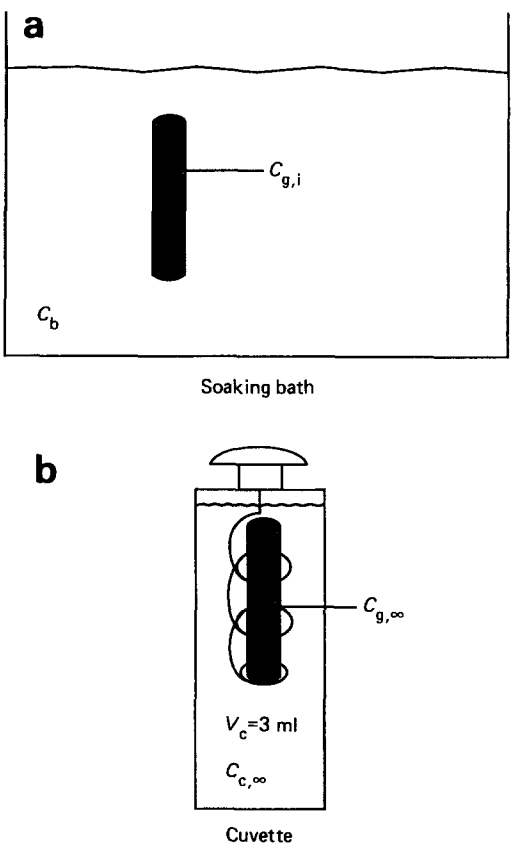

Figure 1 Schematic of the gel diffusion experiment. (a) The gels are soaked in a bath with concentration C_b of diffusing species. At the end of the soaking period, the concentration of species in the gel is $C_{g,i}$, the initial concentration of the diffusion experiment. (b) The gel is suspended in 3 ml of buffer in a cuvette. At the end of the diffusion experiment, the concentrations in the gel and the cuvette are $C_{g,\infty}$ and $C_{c,\infty}$, respectively

concentration of the solutes, allowing the use of the absorbance readings in the equation for determining the diffusion coefficients.

DATA ANALYSIS

Determination of the diffusion coefficients

The problem of diffusion of solute from an infinite circular cylinder to a well stirred solution of limited volume was treated by Carman and Haul[7] and Crank[8]. The following equation for the concentration in the external solution results:

$$\frac{C_c(t)}{C_{c,\infty}} = 1 - \sum_{n=1}^{\infty} \frac{4\alpha(1+\alpha)}{4+4\alpha+\alpha^2 q_n^2} \exp(-Dtq_n^2/a^2) \qquad (1)$$

where C_c is the concentration in the cuvette, $C_{c,\infty}$ is the final concentration in the cuvette,

$$\alpha = \frac{\text{cuvette solution volume}}{\text{gel volume}} \times K$$

(assuming end effects are negligible, i.e. long, thin gel cylinders), $K = C_{c,\infty}/C_{g,\infty}$ is the equilibrium partition coefficient of solute between the solution and the gel, q_n are the positive roots of the equation:

$$2J_1(q) + \alpha q J_0(q) = 0$$

D is the diffusion coefficient of the solute, t is time and a is the radius of the cylindrical gel.

A plot of $C_c/C_{c,\infty}$ vs. $(Dt/a^2)^{1/2}$ yields the full curve shown in *Figure 2*. In order to determine the unknown diffusion coefficient of a solute, the experimental concentration vs. time data are plotted in the manner of *Figure 2*, using a guess for the value of D. Iterations with D were continued until the root-mean-square error between the experimental data and the theoretical curve was minimized.

The previous analysis is formally applicable only to monodisperse solutes with a single diffusion coefficient. For polydisperse samples, such as the poly(acrylic acid) samples, the theoretical concentration–time curve described by equation (1) is modified to represent a sum of many contributions from each molecular weight in the sample. This is done by integrating (numerically) equation (1) with each molecular-weight contribution weighted by a factor equal to its mass fraction, $W(x)$:

$$\frac{C_c(t)}{C_{c,\infty}} = \int_x \frac{C_c(t,x)}{C_{c,\infty}} W(x)\,dx \qquad (2)$$

The Schultz–Flory distribution is chosen to represent $W(x)$ with the polydispersity (M_w/M_n) set equal to 2—the value expected for a polymer prepared by free-radical polymerization:

$$W(x) = x(1-p)^2 p^{x-1}$$

where x is degree of polymerization, i.e. the number of monomer units in the chain, and

$$p = \frac{x_{\text{average}} - 1}{x_{\text{average}} + 1}$$

is the extent of polymerization, $0 < p < 1$.

Note that for this calculation to be made, each molecular weight must be assigned a value for its diffusion coefficient. This is done by using the Stokes–Einstein relation to relate diffusivity to the degree of polymerization:

$$D_x = \frac{kT}{6\pi\eta R_{Hx}} = \frac{kTC_1}{6\pi\eta R_{gx}} = \frac{kTC_1}{4.54\pi\eta(M_0 x)^{1/2}} \qquad (3)$$

where D_x is the diffusion coefficient of species with degree of polymerization x, k is Boltzmann's constant, T is temperature, η is the solvent viscosity, R_{Hx} is the hydrodynamic radius of the species, R_{gx} is the radius of gyration of the species, given by

$$R_{gx} = 0.756(M_0 x)^{1/2}$$

from light scattering, where M_0 is monomer molecular weight, and C_1 = constant of order 1. The constant C_1 is introduced since the radius of gyration (which is available from light scattering data[1]) is similar to, but not identical to, the hydrodynamic radius[9]. Equation (3) is substituted into (1) and the resulting equation is integrated over the molecular-weight distribution according to (2). The result is the calculated solution concentration as a function of time with the single constant C_1 as a parameter. The calculation is performed for various values of C_1 until the predicted and experimental curves match. The value of C_1 obtained by this fitting procedure is used to calculate the sample's average diffusion coefficient by using equation (3) and the known weight-average molecular weight of the sample. The result of this procedure for incorporating the effect of polydispersity is slightly to improve the fit of the predicted and experimental curves at short times, as shown in *Figure 3*.

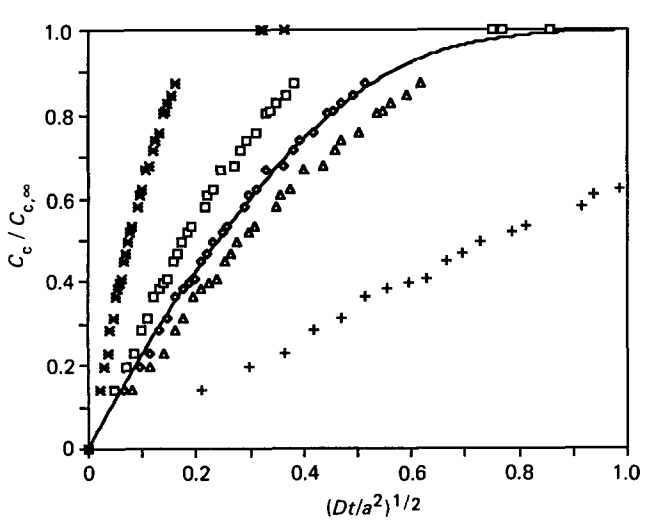

Figure 2 Determination of diffusion coefficient. The diffusion data are plotted in this manner, using various values of the diffusion coefficient D. The final D is one that matches the experimental data to the theoretical curve (———). The values of D are: 0.225×10^{-6} (*), 1.25×10^{-6} (□), 2.25×10^{-6} (◇), 3.25×10^{-6} (△) and 22.5×10^{-6} (+)

Calculation of the partition coefficient

The partition coefficient K is required for the above calculation. The value of K can be calculated for each diffusing species using the equilibrium concentrations of

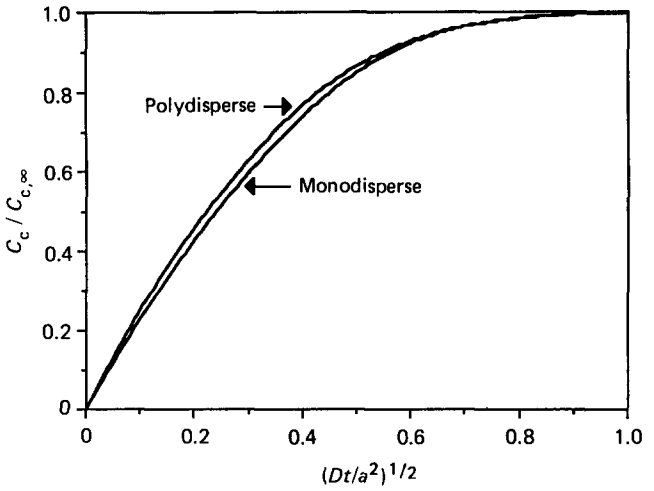

Figure 3 Comparison of the theoretical diffusion curves for a polydisperse and monodisperse sample. Note that these curves are essentially the same

solute in the soaking bath (C_b) and the cuvette ($C_{c,\infty}$), provided that the volumes of the gel and the cuvette solution are known. The concentration in the gel itself, which is never measured, is not required for the calculation. Thus partition coefficient:

$$K = C_b/C_{g,i} = C_{c,\infty}/C_{g,\infty} \tag{4}$$

By conservation of solute:

$$C_{g,i}V_g = C_{g,\infty}V_g + C_{c,\infty}V_c \tag{5}$$

Combining (4) and (5):

$$K = \frac{(C_b - C_{c,\infty})V_g}{C_{c,\infty}V_c} \tag{6}$$

Calculation of the gel pore size

Knowing the elastic modulus of the gels, an effective gel pore size can be calculated from rubber-elasticity theory[10]:

$$G = \frac{gvRT}{N_A} \tag{7}$$

where G is the elastic modulus, v is the number concentration of crosslinks, g is a constant of order 1 for a tetrafunctional crosslinker, R is the gas constant and N_A is Avogadro's number.

The effective gel pore size ξ is given by $v^{-1/3}$; thus:

$$\xi = \left(\frac{G_0 N_A}{RT} V_0/V_g\right)^{-1/3} \tag{8}$$

The factor V_0/V_g has been introduced to correct the measured modulus G_0 of the unswollen gels (with volume V_0) to the value of the modulus of the swollen gel (with greater volume V_g). That this correction is appropriate is evident from (7), where the modulus is linearly proportional to the concentration of crosslinks. Swelling of a gel increases its volume without altering the number of crosslinks; thus, the concentration of crosslinks and the modulus are effectively reduced during swelling by the factor V_0/V_g.

RESULTS AND DISCUSSION

Effect of monomer and crosslinker concentration on diffusion

In *Figure 4*, the diffusion coefficients for the four solutes are plotted as a function of the initial monomer concentration in the gel (constant crosslink ratio of 0.035). Note that the effect of increasing monomer concentration is to reduce the diffusivity of all of the solutes. This behaviour is to be expected as diminishing amounts of gel chains provide less and less resistance to molecular diffusion. In addition, each of the solutes is affected to the same degree over the monomer concentration range. The rhodamine diffusivity decreases 39% over this range, and the 150000 M_w PAA diffusivity decreases 30%. This suggests that the mode of diffusion is the same for the large and small molecules alike.

In *Figure 5*, the diffusion coefficients are again plotted, this time as a function of crosslinker concentration (crosslink ratio multiplied by monomer concentration).

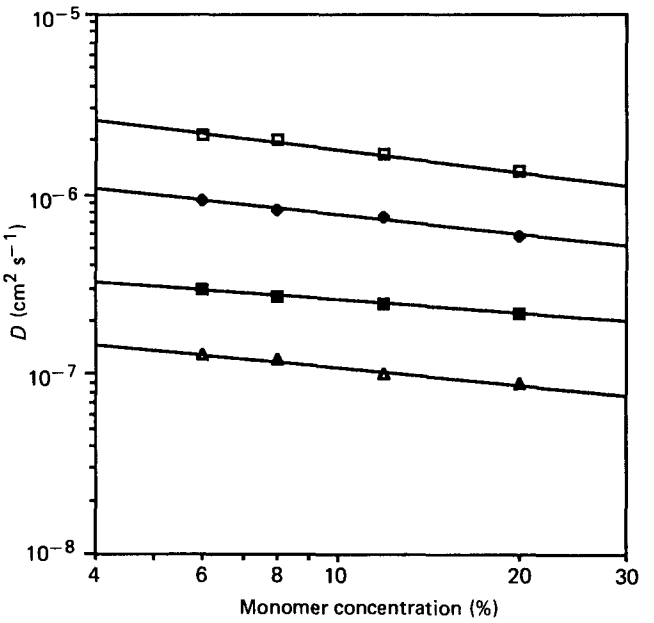

Figure 4 Effect of gel monomer concentration on diffusion coefficients. Each of the species' diffusion coefficients decrease a similar amount (35%) when the monomer concentration is changed from 6% to 20%. Data shown are for experiments at a constant crosslink ratio of 0.035

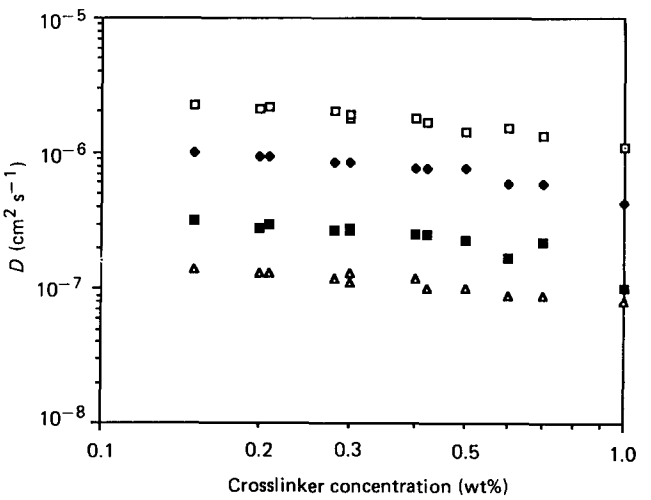

Figure 5 Effect of crosslinker concentration on diffusion coefficients. Independent of the monomer concentrations of the gels (total solids content), the diffusion coefficients decrease as the crosslinker concentration increases. The diffusing species are: rhodamine dye (□), 6000 M_w PAA (◆), 50000 M_w PAA (■) and 150000 M_w PAA (△)

As expected, the diffusivities decrease as the crosslinker concentration increases. Crosslinker concentration, the amount of bisacrylamide used in the polymerization, is not identical to the crosslink concentration in the final gel. The incorporation of bisacrylamide as crosslinks may depend on the total monomer concentration. For example, the modulus, which reflects the elastically effective crosslink concentration, is lower for the 20 wt% monomer gel than for the 12 wt% monomer gel at equal crosslink ratio, as is shown later in *Table 2*. The decrease in crosslinking efficiency is caused by the formation of dangling chain ends and small cyclic rings during polymerization at high monomer concentrations. The relationship between polymerization conditions and network morphology has been investigated in the context of elastomer formation[11,12]. The polymerized chain ends and rings occupy volume in the gel and 'hinder' diffusion of species through the gel; however, they do not contribute to the modulus. Diffusivities are similar in gels with the same crosslinker concentration, even though these gels have different monomer concentrations and crosslink ratios.

Effect of molecular weight of the diffusing species

The effect of molecular weight on the diffusivity through the gels is shown in *Figure 6*. The data for the two smallest PAA samples lie on a line with slope of $-1/2$ on this log–log plot, suggesting that the diffusivity depends on molecular weight according to $D \sim M_w^{-1/2}$ over this range of molecular weights. The data for the highest M_w sample lie below this line. As described below, for this molecular weight (150000) the molecular size is significantly larger than the average pore size. The diffusion of this high-molecular-weight sample, therefore, requires that the molecules be significantly perturbed from their equilibrium conformation, and the diffusion coefficient is accordingly reduced. Also shown in *Figure 6* is a line representing data from Brown and Johnsen[6], which parallels our data, but is slightly lower. The gel used by Brown and Johnsen in this example differs from those used in our study; theirs contained 17.6 wt% monomer, with a crosslink ratio of 0.04.

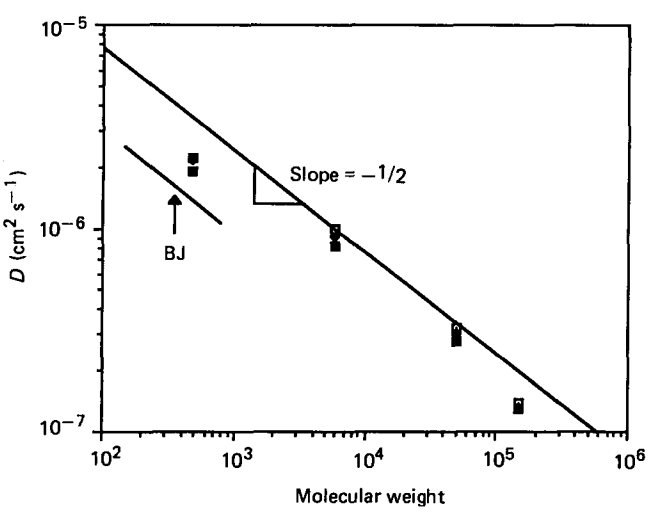

Figure 6 Effect of molecular weight on diffusion coefficients. The two PAA samples of lowest molecular weight lie on a line of slope $-1/2$, the same dependence on molecular weight predicted for free diffusion. The lower diffusion coefficient of the PAA of highest molecular weight suggests that a transition to a different mode of diffusion may be occurring. Brown and Johnsen's data[6] (BJ) (17.6 wt% gels) show the $-1/2$ slope as well. Our data are for a 6 wt% monomer gel. The crosslink ratios are: 0.025 (□), 0.035 (◆) and 0.050 (■)

Table 1 Gel characterization. The gel pore sizes, calculated from the moduli, can be compared to the radii of gyration of the polymers: 5.86, 16.9 and 29.3 nm for the 6000, 50000 and 150000 molecular-weight samples, respectively

Monomer conc. (wt%)	Crosslink ratio	$\frac{V_{swollen}}{V_{initial}}$	Modulus, $G \times 10^{-4}$ (dyn cm^{-2})	Pore size (nm)
6	0.025	1.6	2.321	14.12
	0.035	1.4	2.326	13.69
	0.050	1.2	2.729	12.25
8	0.025	1.6	3.993	11.85
	0.035	1.5	3.937	11.60
	0.050	1.2	6.199	9.36
12	0.025	1.7	11.80	8.44
	0.035	1.6	12.87	7.98
	0.050	1.3	13.67	7.38
20	0.025	2.1	10.54	9.25
	0.035	1.9	11.44	8.78
	0.050	1.6	13.02	8.01

Swelling of gels

The degree of swelling of the gels, as calculated from measurements of the gel dimensions before and after soaking, is tabulated in *Table 1*. Two trends are important to note. First, the amount of swelling decreases with increases in the crosslink ratio, since the gels become more rigid. Secondly, the amount of swelling increases with increases in the initial gel concentration. The cause of this arises from the low osmotic pressure in the high-concentration gels, providing a strong driving force for water entry into the gel. These results are necessary for the calculation of the true elastic modulus of the gels and the effective gel pore size.

Effect of gel pore size on diffusion and partitioning

Using the elastic moduli tabulated in *Table 1* along with the swelling ratios allows the calculation of an effective pore size in the gel. These pore sizes can then be compared to the radii of gyration R_g of the polymers calculated from (3). The radii of gyration of the 6000, 50000 and 150000 M_w samples are 5.86, 15.9 and 29.3 nm, respectively.

Note that, for the polymer of lowest molecular weight, all of the gel pore sizes are larger than R_g. For the two higher-molecular-weight PAA samples, R_g is larger than the pore sizes of all the gels. For the highest gel concentration, the pore size is smaller than R_g of the 150000 M_w PAA by a factor of 4. Though this is a significant difference, the polymer can diffuse through the gel by deforming only slightly. Diffusion by reptation (the mode of polymer motion through a concentrated network or melt), which has a diffusivity dependence of $D \sim M_w^{-3}$, is not the mode of diffusion observed.

The partition coefficients, calculated using (6), are shown in *Table 2*. As mentioned in the introduction, the two competing effects causing partitioning of the solutes between the gel and solution phases are: an attractive interaction between the solute and gel matrix and a 'repulsive' interaction due to pore size exclusion of large molecules. The partition coefficients of rhodamine dye in all of the gels is less than unity, i.e. it shows an affinity for the gel matrix. Because this dye is an organic (though water-soluble) molecule, it prefers to reside in the somewhat hydrophobic gel matrix.

Table 2 Equilibrium partition coefficients. Increasing molecular weight and gel concentration cause the polymers to prefer free solution to the gels. At low molecular weight and gel concentration, however, the polymers prefer residing in the gel because of energetically favourable interactions

		Partition coefficient, K			
Monomer conc. (wt%)	Crosslink ratio	Rhodamine dye	6000 M_w polymer	50000 M_w polymer	150000 M_w polymer
6	0.025	0.750	0.555	1.01	1.32
	0.035	0.843	0.598	0.974	1.39
	0.050	0.835	0.507	0.918	1.46
8	0.025	0.754	0.648	1.09	1.36
	0.035	0.800	0.610	1.21	1.65
	0.050	0.837	1.01	1.14	1.56
12	0.025	0.768	1.16	1.20	1.84
	0.035	0.855	1.09	1.28	2.13
	0.050	0.805	1.27	0.970	2.23
20	0.025	0.879	1.37	1.12	3.25
	0.035	0.831	1.24	1.21	3.59
	0.050	0.979	1.37	1.53	4.85

Similar behaviour is observed for the 6000 M_w PAA in the dilute gels, where the pore sizes are significantly larger than the radius of gyration. For this polymer, as the gel concentration increases (and the pore size decreases), the partition coefficients rise to above unity, showing that the entropic effect becomes more important than the hydrogen-bonding attraction of the PAA for the polyacrylamide gel. The partition coefficients of the higher-molecular-weight PAA samples are similarly above unity, rising to a value of 4.85 for the 150000 M_w polymer in the most concentrated and crosslinked gel. This is an excellent example of the 'exclusion' that takes place during size exclusion chromatography separations.

CONCLUSIONS

The diffusion of rhodamine dye and poly(acrylic acid) polymers through polyacrylamide gels has been studied. The molecular weights of the diffusing species varied from 479 to 150000. Combinations of 6%, 8%, 12% and 20% acrylamide initial monomer concentrations and 0.025, 0.035 and 0.05 crosslink ratios were used to make the gels. The major results are as follows.

The diffusivities showed a power-law dependence on monomer concentration. The per cent decrease was similar for all species, e.g. D decreased by 39% for the rhodamine and 30% for the 150000 M_w PAA between the 6% and 20% monomer gels at a crosslink ratio of 0.035.

For the low-molecular-weight PAA samples, the diffusivity in the gel scales as $D \sim M_w^{-1/2}$ in the same fashion as the calculated free solution diffusivity $D_0 \sim M_w^{-1/2}$.

Diffusivities are constant for gels with equal crosslinker concentration.

Swelling of the gels increases with increasing monomer concentration and decreasing crosslink ratio.

From modulus measurements on the gels and swelling data, the sizes of the pores in the gel were calculated. The ratios of PAA diffusing species size R_g to pore size R_p varied over approximately an order of magnitude ($R_g/R_p = 0.42$ to 3.7). Over this size range the mode of diffusion appears to remain the same—hindered diffusion[13]. The deviation for the polymer of highest molecular weight ($M_w = 150000$) suggests that a transition to diffusion by reptation might occur at even higher molecular weights or smaller pore sizes.

The partition coefficient K, defined as the ratio of the equilibrium concentration of diffusing species in the gel to the concentration of the diffusing species in free solution, has been determined. When the polymer size/gel pore size ratio R_g/R_p is smaller than unity, then $K > 1$; and for $R_g/R_p > 1$, then $K < 1$. This behaviour results from negative free-energy contributions from attractive interactions between the diffusing species and the gel (hydrophobic interactions for rhodamine and carboxyl:amide hydrogen bonding for PAA) balanced with positive free-energy contributions from loss in configurational entropy when large molecules are constrained in small pores.

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