

Effects of inhomogeneities in polyacrylamide gels on thermodynamic and transport properties

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The difference in swelling of polyacrylamide gels of various polymer concentrations and the nuclear magnetic resonance self-diffusion measurements of water in these gels suggest that inherent inhomogeneities in dilute gels play an important role in the thermodynamic and transport properties of these gels.

Keywords Polyacrylamide; gels; inhomogeneities; swelling; nuclear magnetic resonance; diffusion

INTRODUCTION

In a series of papers published in 1958 on dilute gelling systems¹, it was demonstrated that there is a definite dilution limit below which no gelation occurs. It was presumed that reactive groups became buried within independent microscopic crosslinked macromolecular clusters in the solution which were not able to link together to form a gel. At a concentration just above the critical dilution concentration at which gelation does occur, one would expect that due to the increase in reactive groups the small crosslinked clusters of relatively high polymer and crosslink concentrations that are formed in the solution become crosslinked to one another by a weak network of relatively low polymer concentration. The idea of crosslink clustering at low monomer concentration was successfully invoked by Richards and Temple² to explain qualitatively the swelling behaviour in water of polyacrylamide gels of a wide range of composition. More recently, essentially the same idea was used by Silberberg and his group³ to develop a model for the interpretation of the results of water permeation studies through dilute polyacrylamide gels. That model was also used to analyse the thermodynamic swelling behaviour of these gels⁴. Recent mechanical measurements⁴, dynamic light-scattering measurements⁵, and transmission electron micrographs⁶ lend further support to the original hypothesis of crosslink clustering and confirm the presence of heterogeneities in these gels.

We investigate in this paper the effects of these inhomogeneities on the swelling of dilute polyacrylamide gels and on the self-diffusion of water in these gels and show that the thermodynamic properties and transport properties are appreciably affected by the inhomogeneities. Before proceeding with the preparation and experimental results obtained, we must first briefly digress to discuss a complication exhibited by polyacrylamide gels: a phenomenon of ageing which occurs while the gels are left in their moulds under seal at room temperature.

Polyacrylamide gels prepared by a standard redox procedure (from solutions of pH \sim 8) were shown to exhibit a continuous transition from a swollen state to a collapse state when the acetone-water mixture in which the gels are equilibrated goes over \sim 40% in volume of acetone^{4,7} (close to the θ -condition). The time the gels were left in their moulds (which we shall call ageing or curing time) had an important effect on the swelling curve (acetone concentration *versus* polymer volume fraction in the gel). A large difference occurs in swelling with ageing where the different swelling curves all go through a smooth transition that occurred at approximately the same acetone concentration. The original postulate for ageing as due to an extensive increase in crosslinking was not substantiated by mechanical measurements⁴ and a new hypothesis associating ageing to the degree of hydrolysis of the macromolecular chains was proposed⁸. Although the swelling results of polyacrylamide gels aged in high pH solutions (pH \sim 12) clearly confirm that hydrolysis lead to different swelling curves, they also show that, as hydrolysis proceeds and the net charge concentration along the macromolecular chains increases, the collapse transition clearly shifts to higher acetone concentration of the equilibrating bath⁸. Similar results are predicted theoretically when the effect of electrostatic interactions on the swelling of polymeric networks is taken into account⁹ and confirmed experimentally by the swelling behaviour of ionized networks of copolymers of acrylamide and sodium methacrylate: higher charge concentrations in the network lead to a collapse transition at higher acetone concentration¹⁰. The polyacrylamide gels prepared from solutions of pH \sim 8 and aged in their moulds do not show, however, a shift in the collapse transition to higher acetone concentration with ageing (see *Figure 4*) as would have been expected if hydrolysis was the only effect considered. The failure of classical swelling theories^{8,9} to provide an interpretation for these results is at least in part due to: (a) the existence of heterogeneities in the polyacrylamide gels which are probably enhanced by the strong

molecular interactions in this system¹¹; and (b) the neglect of higher-order virial terms in the expression for the mixing term contribution to the free energy of the system. We investigate in this paper the effects of factor (a); the importance of factor (b) on the thermodynamics of gels will be examined separately¹². We show that the swelling of networks of higher polymer concentrations show much smaller swelling differences in water with ageing time. At these higher polymer concentrations one may assume a more uniform segment distribution and thus a more homogeneous gel such that one is indeed looking at the small effect of hydrolysis alone. The effect of water-acrylamide interaction is indirectly examined by a systematic study of n.m.r. self-diffusion of water in polyacrylamide solutions, and in polyacrylamide gels with polymer concentration in the range of 3 to 30% and a wide range of crosslinking density in the gels. For polymer solutions and gels with concentration lower than the concentration at which uniform segment density is achieved¹³ ($C^+ \sim 8\%$), inhomogeneities affect both the self-diffusion of water and the swelling of the gels. In fact we observe that the self-diffusion of water in these dilute systems is not different from that expected for an acrylamide monomer solution at the same concentration.

PREPARATION AND PROCEDURE

The mode of preparation of polyacrylamide gels by a redox reaction employing ammonium persulphate and tetramethyl-ethylene-diamine is well established. For the swelling experiments two sets of gels were prepared using the following two variations of the recipe.

(1) The ratio C of crosslinking agent to monomer concentration was kept constant at 2.66%. In general 5 g acrylamide, 0.133 g N,N' -methylene bisacrylamide, 40 mg ammonium persulphate, and 160 μ l tetramethyl-ethylene-diamine (TEMED) were dissolved in water. The amount of water was varied so as to vary the initial monomer concentration M from 2.5 g dl⁻¹ to 15 g dl⁻¹. For example, when the ingredients of the above recipe are dissolved in water to make 100 ml of solution, the gel formed is characterized by a total concentration $T = 5.133$ g dl⁻¹ and a crosslink concentration $C = 2.66\%$.

(2) To vary C , the amount of bisacrylamide was changed; once doubling it ($C = 5.32\%$), and once reducing it by a half ($C = 1.33\%$) while keeping the rest of the ingredients unchanged and the total volume of the solution as 100 ml.

The solutions were thoroughly mixed and poured into separate test tubes and pendulum moulds for use in the various experiments. The gels, after gelation and curing at room temperature, were removed from the test tube and cut into approximately 0.5 cm thick cylindrical samples of ~ 1.5 cm diameter. The samples were immersed in water-acetone mixtures for several days to allow for equilibration and their size subsequently measured. The crosslink densities of the prepared gels were measured as a function of ageing time by using simple test-tube torsional pendulums⁴.

The n.m.r. measurements were performed on samples prepared in standard n.m.r. micro-cells. Precautions were taken to avoid trapping bubbles in the solutions. During polymerization or gelation, the micro-cell was placed in an ice-water bath to control the temperature and to minimize the risks of breaking the cell due to the

appreciable exothermic heat of reaction of samples of high polymer concentration. The micro-cell was then capped with a Teflon chuck and transferred into a 5 mm n.m.r. tube which contained D₂O as a lock solvent. The self-diffusion coefficient D of water in solutions and gels was measured by using n.m.r. pulse techniques on a Varian CFT 20 spectrometer at 79.5 MHz. Corrections to small deviations from the temperature at which the data are reported here were made using the activation energy of self-diffusion in pure water¹³. The Carr-Purcell pulse sequence was used for observing n.m.r. spin echoes and values of D were obtained by standard procedure using $D_0 = 2.26 \times 10^{-5}$ cm² s⁻¹ for the self-diffusion in pure water at 27°C.

All the samples were prepared with high-purity ingredients and with distilled and sterilized water. The solutions were filtered through Metricel membrane filters, and the filtrates were freed from dissolved oxygen (an inhibitor) by bubbling nitrogen through them.

EXPERIMENTAL RESULTS

Degree of swelling versus initial monomer concentration

We define the degree of swelling, V/V_0 , as the ratio of the volume of the equilibrium swollen gel (immersed in large excess of solvent) to the volume of prepared gel. The effects of initial monomer concentration on the degree of swelling in water for samples with $C = 2.66\%$ aged for 6 h, 3 days and 15 days are shown in *Figure 1*. Large swelling and great variations in swelling with age occur at low values of T (or M) but decrease as T (or M) increases. Variations in swelling with age level off at monomer concentrations around 8 g dl⁻¹. In *Figure 2* the degrees of swelling for a constant total concentration ($T = 5.133$ g dl⁻¹) are plotted versus crosslink concentration for three different curing times. Here again, low concentration of crosslinks leads to larger ageing effects indicating that *hydrolysis alone* (which should be cross-linking independent) *cannot account for the much larger swellings at low values of C .*

Effective crosslink density

The effective crosslink densities were measured via the storage modulus by using simple torsional pendulums. Effective crosslink densities as a function of ageing for three different initial crosslinking concentrations ($C = 1.33\%$, 2.66% and 5.32%) are reported in *Figure 3*. As previously reported¹⁴, there is practically no change in the storage modulus during ageing. The effective crosslink density N was calculated using¹⁵:

$$G = 2NkT$$

where G is the measured shear storage modulus, k is Boltzmann's constant, and T is the absolute temperature. Values of N obtained account for only about 5% of the theoretical crosslink densities calculated by assuming that each bisacrylamide molecule forms one crosslink. This is another indirect indication that inhomogeneities due to clustering of bisacrylamide and cyclizations must be occurring.

Swelling and collapse curves

Swelling curves representing the variation of acetone-water mixture concentration versus the swelling ratio

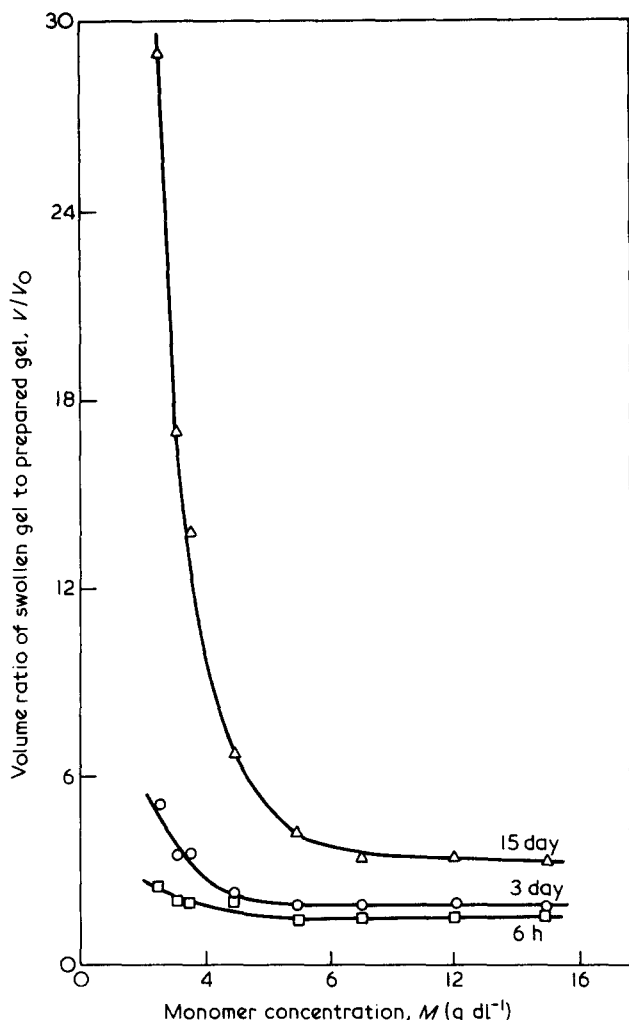


Figure 1 Degree of swelling in water, V/V_0 , versus initial monomer concentration M for 6 h, 3 day and 15 day old gels with $C=2.66\%$ (temp.=25°C)

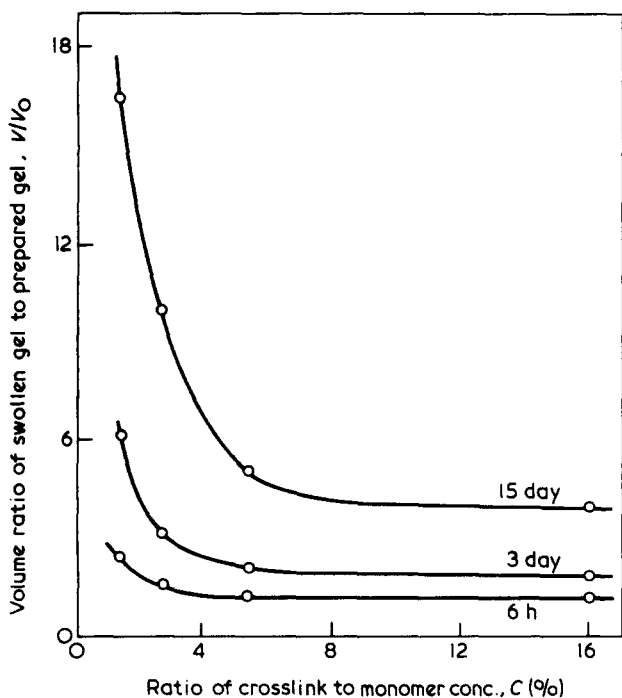


Figure 2 Degree of swelling in water, V/V_0 , versus the ratio C of crosslink to monomer concentration for 6 h, 3 day and 15 day old gels with $T=5.133 \text{ g dl}^{-1}$ (temp.=25°C)

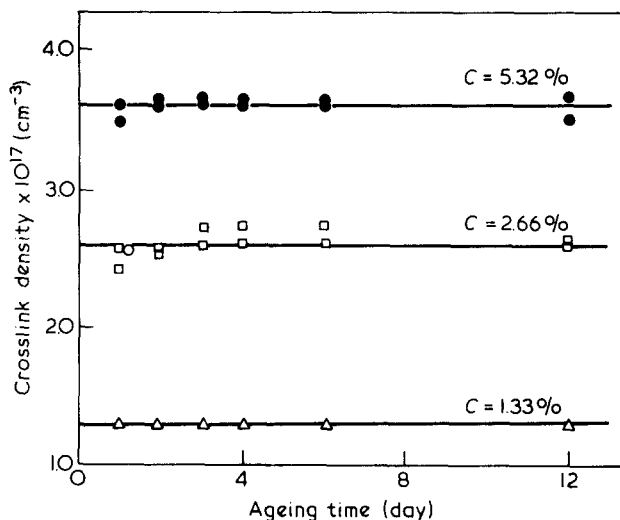


Figure 3 Crosslink density versus ageing time for gels with $M=5 \text{ g dl}^{-1}$ and difference C . The data point (O) for $C=2.66\%$ was obtained with a more sophisticated gas-bearing torsion pendulum⁴

ϕ/ϕ_0 , defined as the ratio of the volume fraction ϕ of the polymer in the gel network after equilibration to the volume fraction ϕ_0 of the polymer in the prepared gel, have been used to study the ageing and thermodynamics of these gels^{4,7}:

$$\phi/\phi_0 = V_0/V$$

In Figure 4 we show the effect of ageing at room temperature on the equilibrium swelling of a specific gel with $M=5 \text{ g dl}^{-1}$ and $C=2.66\%$. As has previously been reported⁴, swelling increases with ageing and a gel collapse occurs at approximately 40% acetone. In Figure 5 the effect of crosslink concentration on the swelling curves, keeping the monomer concentration M constant at 5 g dl^{-1} , is reported for 3 day old gels with $C=5.32\%$, 2.66% and 1.33% . Larger swelling and sharper transition

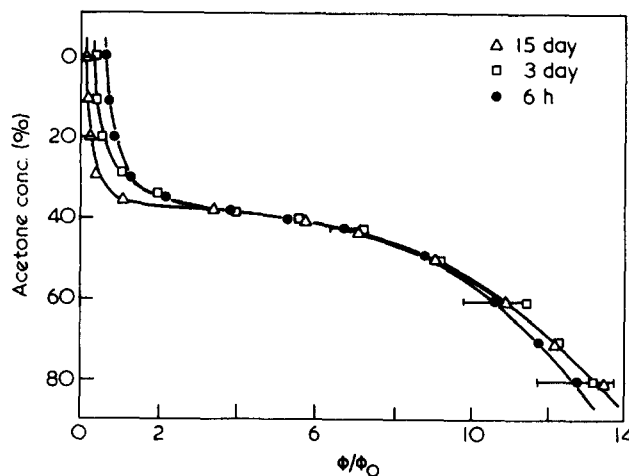


Figure 4 Acetone concentration versus swelling ratio, ϕ/ϕ_0 , for gels of $M=5 \text{ g dl}^{-1}$, $C=2.66\%$ and different curing time (temp.=25°C). Below 40% acetone, the error bars lie within the indicated data points

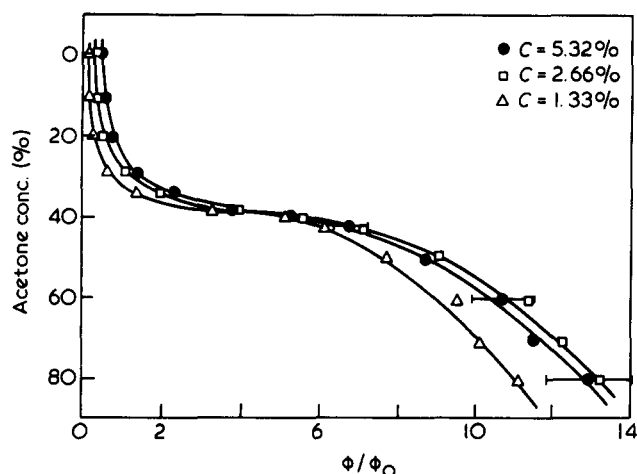


Figure 5 Acetone concentration versus swelling ratio, ϕ/ϕ_0 , for 3 day old gels with $M=5 \text{ g dl}^{-1}$ and $C=1.33\%$, 2.66% and 5.32% (temp.= 25°C). Below 40% acetone, the error bars lie within the indicated data points

are observed for gels having lower crosslink concentrations but the smooth transition from swollen to collapsed state occurs always at around 40% concentration irrespective of the crosslinking density.

Self-diffusion of water

The self-diffusion coefficient of water was measured at 27°C in the following systems: (i) linear polyacrylamide-water solution with initial monomer concentration (prior to polymerization) in the range of 5 to 30%; and (ii) polyacrylamide gels with a wide range of initial monomer concentrations and crosslink densities ($3 < T < 30$ and $2 < C < 8$). The experimental results are summarized in Table 1. Values of D reported in the third column of Table 1 were obtained for fresh gels (i.e. measured in the first day

of preparation). We have made, however, several measurements on gels aged for various lengths of time (up to a maximum of 33 days) and found no detectable effect on D . The results in the third column of Table 1 indicate that within our experimental error the value of D is independent of crosslink density C ; we have therefore averaged in column 4 of the table the values of D for a given T with a given $C > 0$. The self-diffusion of water in polymer solutions ($C=0$) also had the same value as in crosslinked gels within our experimental error. The results are shown in Figure 6 in the form of a plot of $\ln(D/D_0)$ versus ϕ where D_0 is the self-diffusion in pure water and ϕ is the polymer volume fraction in the polyacrylamide solution or gel assuming complete polymerization. The volume fraction ϕ may be expressed as

$$\phi = (T/100)v$$

where v is the specific volume of the polymer which we have taken as 0.74 ml g^{-1} . The broken curve in Figure 6 represents the function $[(1-\phi)/(1+\phi)]^2$ which is predicted on the basis of a simple obstruction theory¹⁶.

DISCUSSION

Our results for the swelling of fresh gels (6 h ageing) presented in Figure 1 are in good qualitative and quantitative agreement with the measurements previously reported by Richards and Temple² indicating that, for a given crosslink concentration ($C=2.66$ in our case), the swelling ratio V/V_0 becomes insensitive to initial monomer concentration above a certain value of M ($\sim 6 \text{ g dl}^{-1}$ for $C=2.66$); below that concentration, crosslink cluster formation is enhanced leading to inhomogeneous gels. The swelling results for $T=5.133 \text{ g dl}^{-1}$ as a function of C for the 6 h gels (Figure 2) are also in agreement with the previously reported values² which show a levelling off of the swelling ratio to an approximate value of 1.2 for $C > 6$.

Table 1 Self-diffusion coefficients of water in polyacrylamide solutions and gels at 27°C

T	C	$D \times 10^5 \text{ (cm}^2 \text{ s}^{-1}\text{)}$	Average value of $D \times 10^5 \text{ (cm}^2 \text{ s}^{-1}\text{)}$	D/D_0	$\ln(D/D_0)$	ϕ
3	4	2.12	2.12	0.938	-0.064	0.022
5.1	2.6	2.06	2.06	0.912	-0.092	0.038
5	0	2.09	2.09	0.925	-0.078	0.037
7	2	1.97	2.02	0.894	-0.112	0.052
	6	1.97				
	2	2.04				
	4	2.11				
7	6	2.02	2.01 (average)	0.889	-0.117	0.052
	0	2.01 (average)				
	4	1.96				
8.5	4	1.96	1.96	0.867	-0.143	0.063
10	2	1.71	1.74	0.770	-0.261	0.074
	4	1.77				
	6	1.73				
	8	1.76				
10	0	1.73	1.73	0.765	-0.268	0.074
	4	1.54	1.56	0.690	-0.371	0.104
14	8	1.57	1.55	0.686	-0.377	0.104
	0	1.55				
18.7	4	1.44	1.44	0.637	-0.451	0.138
18.7	0	1.44	1.44	0.637	-0.451	0.138
25	4	1.18	1.18	0.522	-0.650	0.185
25	0	1.14	1.14	0.504	-0.685	0.185
30	4	1.06	1.06	0.469	-0.757	0.222
30	0	1.05	1.05	0.465	-0.766	0.222

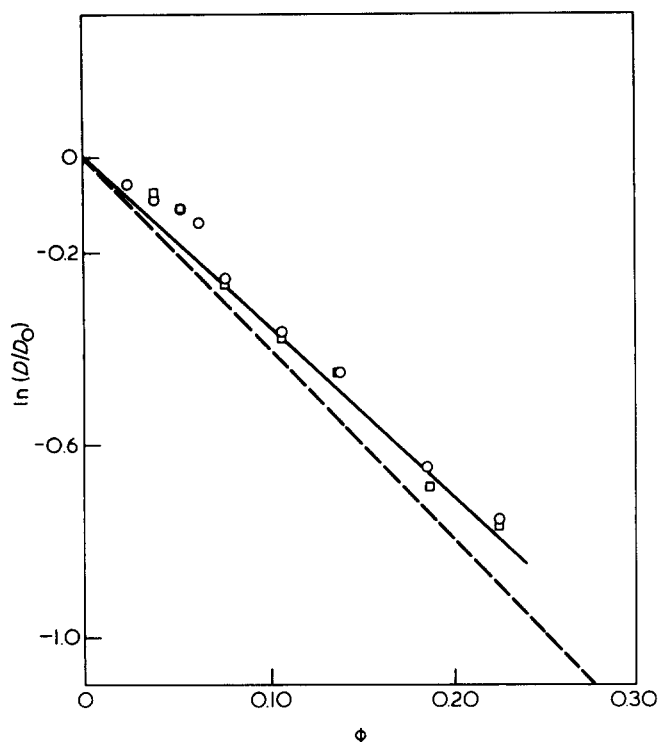


Figure 6 Plot of $\ln(D/D_0)$ versus ϕ for polyacrylamide solutions (\square) and gels (\circ). The full line indicates the trend of the results at high concentrations; the broken line represents the function $[(1-\phi)/(1+\phi)]^2$

The observation that softer gels (lower monomer concentrations) have higher degree of swelling and more pronounced ageing effects on equilibrium swelling (Figure 1) suggests that inherent inhomogeneities (crosslink clusters and other non-ideal network structures), which are more likely to occur in dilute gels, play an important role in the swelling of aged gels. The swelling curves of these gels shown in Figure 4 indicate that the extent of hydrolysis during ageing (i.e. the formation of charges on the chains) is not particularly extensive since all the curves exhibit a smooth transition from a swollen state to a collapse state that always occur around 40% acetone in water. The large variations of swelling in pure water with gel age that occur in dilute gels are probably due to structural changes (possibly expansion of the dilute regions of the network at the expense of the cluster regions⁴) driven by the limited extent of hydrolysis occurring. At high polymer concentrations ($M > 8 \text{ g dl}^{-1}$), the variation of swelling with age becomes constant (Figure 1). This latter variation should then be a better representation of purely hydrolysis effects since these higher-density gels are expected to be more homogeneous. For a given monomer concentration ($M = 5 \text{ g dl}^{-1}$), the effective crosslink densities experimentally measured via the shear modulus appear to be proportional to C at low C (see Figure 3 for $C = 1.33$ and 2.66). At higher C values ($C = 5.32$), this simple linear proportionality breaks down presumably due to a larger degree of clustering and inhomogeneities². Weiss and Silberberg³ have in fact shown that the storage modulus reaches a maximum around $C = 5$ and then decreases.

The values of the self-diffusion of water in polyacrylamide solutions and gels examined here cover a wide

range of polymer concentrations. Our value for D/D_0 of 0.64 at $\phi = 0.138$ is in good agreement with the single experimental value of 0.63 reported by Brown and coworkers¹³ for $\phi = 0.131$. The variation of D with polymer concentration presents some interesting features, the most notable of which is the large deviations at low ϕ from the simple obstruction theory represented by the broken curve in Figure 6. At high polymer concentration ($T > 10$ or equivalently $\phi > 0.074$), the very simple obstruction model^{16,17}, based on the fact that the segments of the polymer chains are less mobile and therefore impede the translational motion of the small diffusing water molecules which will thus have to go around them, gives a reasonable trend. At low polymer concentrations, however, deviations from the obstruction model predictions are quite noticeable (Figure 7). These deviations occur for both polymer solutions and gels which give practically identical results. We attribute this breakdown of the simple obstruction model to the more heterogeneous nature of dilute gels and polymer solutions. The latter are known to achieve uniform segment density only at a fairly high concentration¹³. The self-diffusion coefficient of water in these systems will thus be dominated by the fast diffusion occurring through the less dense regions.

The values of $\ln(\eta_0/\eta)$, where η_0 is the viscosity of water and η is the viscosity of acrylamide monomer solutions, have been measured and plotted in Figure 7 as a function of monomer volume fraction (calculated with $v = 0.891 \text{ ml g}^{-1}$). For the sake of clarity we have presented only the curve $\ln(\eta_0/\eta)$ (full line) which was drawn through experimental points that are not shown in the Figure. The self-diffusion of water in the dilute macromolecular systems (polymer solutions and gels below $\phi \approx 0.07$) can be seen to lie surprisingly close to the predicted self-diffusion of water in the acrylamide monomer solutions assuming that some form of Stokes' law applies. Water molecules in the dilute macromolecular systems must therefore be primarily diffusing in regions where the large frictional effects of the polymer are not present. Obviously the simple obstruction theory is not entirely satisfactory even at high polymer concentrations where deviations do

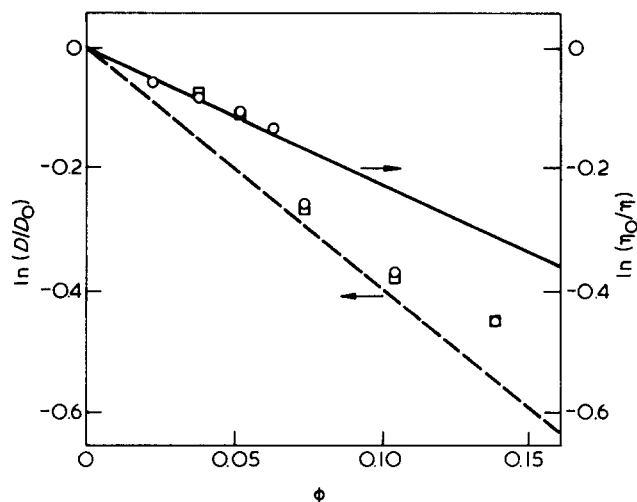


Figure 7 Plot of experimental $\ln(\eta_0/\eta)$ versus ϕ for acrylamide monomer solutions (full line) compared to experimental $\ln(D/D_0)$ values for polyacrylamide solutions (\square) and gels (\circ) at low concentrations. The broken line represents the function $[(1-\phi)/(1+\phi)]^2$

occur due to the thermodynamic interactions that affect D (van der Waals forces, hydrogen bonding, etc.); but our purpose here is just to point out the quite different behaviour of D in polymer gels and solutions at low concentrations from that at high concentrations where it follows more closely the obstruction model. It is also interesting to note that the concentration at which the obstruction theory (which assumes a homogeneous system) starts to be qualitatively obeyed occurs at approximately the same concentration at which the swelling behaviour goes over from the region dominated by heterogeneities to the more constant swelling of more homogeneous systems (Figure 1).

The fact that the degree of crosslinking has little effect on the self-diffusion of water (Table 1) is readily understood by considering the smallness of the water molecule; the diffusion of small solutes has been reported by several investigators to be independent of crosslink concentration¹⁷. This is not the case for large solutes where the effect of crosslink concentration is significant and cannot be simply predicted from an assumption of homogeneity where an increase of crosslinks would lead to a decrease in permeability in the gel. The fact that the permeability of these solutes decreases but goes through a minimum (at $C \sim 5$) and then increases as a function of C in dilute gels^{2,18} is another indication of crosslink cluster formation and heterogeneities. Attempts to interpret the thermodynamics of swelling of dilute polyacrylamide gels on the basis of theories for homogeneous systems should be regarded with caution particularly when electrostatic effects are not large.

SUMMARY AND CONCLUSION

We have examined the swelling behaviour of polyacrylamide gels in acetone-water mixtures when hydrolysis effects are not dominant. The swelling curves exhibit a continuous transition from a swollen state to a collapse state when the acetone-water mixture goes over $\sim 40\%$ in volume of acetone. Although swelling increases appreciably with gel curing, the collapse transition does not shift to higher acetone concentration as in the case of strongly hydrolysed gels. By studying the swelling of gels of different polymer concentrations and crosslink concentrations, we demonstrate that inherent inhomogeneities suspected by previous investigators to be due to crosslink clustering drastically affect the swelling behaviour of these gels. Large variations of swelling in pure water with gel age occur at low crosslink concentrations and cannot be accounted for by hydrolysis alone; they

may be due to structural changes driven by the limited extent of hydrolysis occurring in the inhomogeneous network.

The n.m.r. self-diffusion measurements of water in polyacrylamide gels of different concentrations appear to corroborate the presence of inhomogeneities in dilute gels. For the gels with high polymer concentrations, the obstruction theory gives a reasonable trend for the behaviour of the self-diffusion of water. At lower polymer concentrations, where the anomalously larger swelling with ageing time occurs, the self-diffusion of water is higher than expected; this may be taken to indicate that the water molecules are diffusing primarily in regions of lower polymer density than the average polymer density in the gel.

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