

Swelling of neutralized polyelectrolyte gels

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Abstract

Measurements are reported of the swelling pressure ω and of the collective diffusion coefficient D_c in two series of salt-free neutralized polyelectrolyte gels, one a poly(acrylamide–acrylic acid) copolymer, the other cross-linked potassium polyacrylic acid. The values of D_c measured by macroscopic deswelling are in reasonable agreement with those measured by dynamic light scattering. D_c increases as the degree of swelling of the gel increases, with similar behaviour being found for the elastic modulus G . The osmotic pressure, $\Pi = \omega + G$, displays a power law behaviour over the concentration range explored, the exponent σ depending on the counter-ion concentration: $\sigma \approx 1$ for the sample of lower charge density, while for the sample with a high charge density, $\sigma \approx 1.5$. The latter behaviour, unexpected at low polymer concentrations, is interpreted in terms of the inequivalence between static and dynamic concentration fluctuations. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The capacity of polymer gels to act as solvent storage systems is governed by two parameters, the osmotic swelling pressure $\omega(c)$ and the elastic modulus G , where c is the polymer concentration. The rate at which the solvent can be absorbed or released is defined by the mutual diffusion coefficient $D_c = (M_{os}/f)$, where the longitudinal osmotic modulus $M_{os} = c\partial\omega/\partial c + 4G/3$ and f is a friction coefficient. This mutual diffusion, which is a collective exchange (indicated by the suffix c) between polymer chains and the solvent molecules, is different from the translational diffusion of individual solvent molecules. The parameters ω and D_c , which have been investigated for a number of neutral gel systems [1–3], are of particular importance in the case of polyelectrolyte networks, since in addition to their use as the active constituent in super-absorbent applications and soil moisturizers, they are potential components of water storage devices in dry climates.

Measurements of D_c and of the shear modulus G have been reported for fully swollen weakly ionized polyelectrolyte gels [4–6]. It was shown by Schosseler et al. [4,5] for weak polyelectrolyte gels, that the degree of ionization is a crucial parameter in defining D_c . It was also found that in the

reaction bath (i.e. in the fully swollen state) G varies with concentration approximately as $c^{1.7}$, which is significantly more strongly than the power law generally observed for neutral gels after completion of cross-linking, namely $G \propto c^{1/3}$.

Given the importance of the fully neutralized gels, relatively few experimental investigations seem to have been made on their properties as a function of swelling. It is well known, however, that at high degrees of swelling the constituent polymer chains are stretched beyond the range where Gaussian statistics apply, and approximations using the inverse Langevin function become useful [7,8]. This condition causes the shear modulus G first to decrease, as for neutral gels, then, at high swelling, to increase again.

Measurements of the swelling kinetics of polyelectrolyte gels [9] have shown that the radius r of the spherical samples immersed in pure water increases with time t approximately as $t^{1/2}$, as expected in a diffusion controlled process. The corresponding diffusion coefficient D_c , however, increases with the degree of swelling. In a more recent observation [10] it was found that the parameter that governs the time variation of r , namely $D_c t/r^2$, is proportional to $t/r^{3/2}$. This last result suggests a simple scaling model in which D_c obeys a power law in concentration of the form $D_c \sim c^\alpha$. Since the concentration of the particle varies as $c \sim 1/r^3$, it follows from such a model that

$$D_c t/r^2 \sim c^\alpha r^{-2} t \sim (1/r^3)^\alpha r^{-2} t \sim r^{-3/2} t. \quad (1)$$

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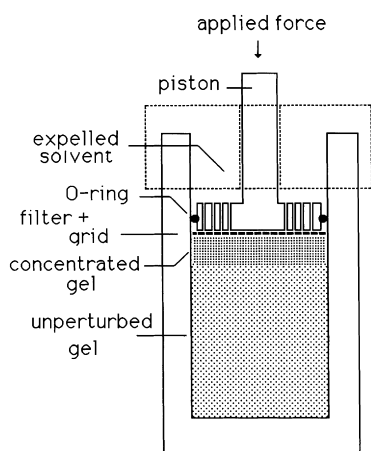


Fig. 1. Diagram of deswelling apparatus. The gel surface and porous piston are separated by a stainless steel grid and Millipore filter to prevent sample extrusion.

Equating the powers of r gives

$$3\alpha + 2 = 3/2 \quad (2)$$

thus yielding for the value of the exponent $\alpha = -1/6$. The two investigations [9] and [10] thus show that, over a certain concentration range, the diffusion coefficient in swollen polyelectrolyte gels indeed decreases with increasing concentration.

Further information may be found in small angle neutron scattering measurements that have been reported on polyelectrolyte gels as a function of concentration [11–13]. The results from the poly(acrylamide–acrylic acid) copolymer system studied show that the intensity $I_d(0)$ of the dynamic concentration fluctuations decreases with increasing swelling. Such scattering is governed by the relation [1] $I_d(0) \propto c^2/M_{os}$. From the data of Ref. [13] it can be inferred that as the gel swells the longitudinal osmotic modulus M_{os} varies as

$$M_{os} \propto c^{1.6}. \quad (3)$$

Few direct measurements of the swelling pressure of polyelectrolyte gels seem to have been reported in the literature. Lagutina and Dubrovskii [14] used a membrane osmometer to measure swelling pressures of hydrolysed polyacrylamide gels as a function of concentration. As these measurements were made in saline solutions, the chain extension was moderate, and the elastic modulus could be described by the Gaussian approximation [15]. Measurements of the swelling pressure ω as a function of concentration have also been reported by Silberberg-Bouhnik et al. [16]. It was found that far from swelling equilibrium with the pure solvent, the swelling pressure varied as

$$\omega \propto c^\beta. \quad (4)$$

where $\beta = 1.66$. Insofar as the osmotic pressure in these systems is expected to be dominated by the pressure of

the ions, results 3 and 4 are somewhat unexpected, as the ionic concentration should be linear in c , i.e.

$$\beta = 1 \quad (5)$$

A number of swelling pressure observations have also been reported on polyelectrolyte systems using analytical ultracentrifugation (cf. [17] and references therein). This technique, however, is generally confined to modest pressures (<1 bar), a range in which other deswelling techniques can equally well be used in combination with simple optical detection methods [18].

In this paper we report measurements by osmotic deswelling of ω and of D_c in two fully neutralized polyelectrolyte systems in the absence of added salt. Owing to the strong ionic contribution to the osmotic pressure in these systems, pressures in excess of one atmosphere are necessary in order to obtain appreciable changes in concentration. Differences in the charge density in the two gel systems investigated reveals the existence of different regimes of concentration dependence for the osmotic pressure.

2. Experimental

2.1. Sample preparation

Two different samples were investigated. Type I was a commercial acrylamide–acrylic acid co-polymer manufactured by JRM Chemical Inc., OH, in the form of irregular grains of size less than or equal to 1 mm, having a swelling ratio in pure water of approximately 300. These samples are neutralized with potassium hydroxide. Further details on this sample are proprietary. Chemical analysis indicated that the acrylamide–acrylic acid ratio of this co-polymer is approximately 2:1 and that the acid is fully neutralized. The second sample (Type II) was a polyacrylic acid (PAA) network cross-linked with *N*-acryloxy-succinimide with the water-soluble 1-(3-dimethylaminopropyl) 3-ethylcarbodiimide hydrochloride, and fully neutralized with potassium hydroxide. These latter samples were prepared at PAA concentration 10%, with a molar ratio of cross-link molecules to PAA monomers equal to 8%; this high cross-link density limited the swelling ratio in pure water to about 100. To enable shear modulus measurements to be made, the latter samples were moulded as isometric cylinders.

2.2. Deswelling

Osmotic compression measurements were made using the device shown in Fig. 1. A sliding piston with a porous head moves with low friction inside a cylinder in contact with the gel being studied. A rubber O-ring prevents extrusion of the gel between the cylinder and piston head, which is pierced with holes and has its lower surface channelled to allow the solvent to pass freely into the upper chamber of the cylinder. A fine stainless steel grid supporting a 0.4 μm Millipore filter of the same diameter is placed between the piston

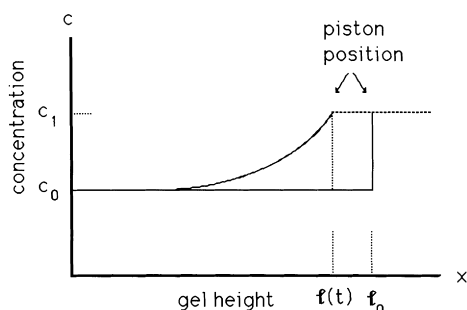


Fig. 2. Diagram of the concentration profile inside sample during deswelling.

and the gel so that the gel can be compressed osmotically, releasing the solvent through the piston when pressure is applied to the top. During the whole experiment, therefore, the gel is in contact with excess solvent.

When the sample is in place a weight is set on the piston. As the gel is compressed the concentration of polymer inside the sample develops a profile similar to that illustrated in Fig. 2, governed by Fick's equation of diffusion for the local concentration c ,

$$\partial c / \partial t = D_c \nabla^2 c. \quad (6)$$

The initial concentration of the gel is c_0 , while the concentration at equilibrium with the applied pressure is c_1 . As a first approximation the diffusion coefficient D_c may be assumed to be independent of concentration. As stated in the introduction, however, this assumption is incorrect, but the approximation is likely to be unsatisfactory only in the most swollen state, where results are uncertain anyway owing to the presence of free water between the irregular gel granules. This water is expelled in the initial deswelling stage when the granules are squeezed together. It is also assumed that at $x=0$ the cell wall is impermeable. The following boundary conditions then apply.

$$\begin{aligned} \frac{\partial c}{\partial x} &= 0 & \text{at } x &= 0 \\ c &= c_1 & \text{at } x &= \ell \end{aligned} \quad (7)$$

$$c = c_0 \quad \text{at } x = 0, t = 0.$$

$$c = c_1 \quad \text{everywhere at } t = \infty.$$

Eq. (6) is then solved for the concentration c at any point x . This gives

$$\begin{aligned} c(x, t) &= (c_1 - c_0) \left\{ 1 - \frac{4}{\pi} \sum_0^{\infty} \frac{(-1)^n}{(2n+1)} \right. \\ &\quad \times \exp \left[- \frac{D_c (2n+1)^2 \pi^2 t}{4\ell^2} \right] \cos \left(\frac{(2n+1)\pi x}{2\ell} \right) \left. \right\} + c_0 \end{aligned} \quad (8)$$

Eq. (8) is assumed to apply also to the system in movement.

As solvent is expelled, the position of the piston $\ell(t)$ is then determined by the condition of conservation of polymer within the sample chamber, i.e.

$$\int_0^{\ell(t)} c \, dx = \text{constant} = c_0 \ell_0, \quad (9)$$

which yields [19]

$$\begin{aligned} (c_1 - c_0) \ell(t) \left\{ 1 - \sum_0^{\infty} \frac{8}{(2n+1)^2 \pi^2} \right. \\ \left. \times \exp \left[- \frac{D_c (2n+1)^2 \pi^2 t}{4\ell^2} \right] \right\} + c_0 \ell(t) = c_0 \ell_0 \end{aligned} \quad (10)$$

The experiment proceeds by observing the displacement of the piston under a given load from an initial to a final position. When equilibrium is reached, an extra weight is added to the piston and the next deswelling step is begun. In each set of deswelling observations the ratio c_1/c_0 of the final to the initial concentration is calculated from the final and initial positions of the piston, the current height of the piston, $\ell(t)$, being measured as a function of time by means of a cathetometer. The value of D_c in Eq. (10) is then fitted for each data set $\ell(t)$ corresponding to a given applied pressure, using a nonlinear least squares procedure. For the first step, the absolute value of the concentration c_0 is found by weighing the dry network and the gel swollen to equilibrium with pure water. At the conclusion of a complete set of deswelling steps, the cell was opened for cleaning. No sign of adherence of the gel to the membrane or the cell walls could be detected.

The main potential source of error in these deswelling measurements comes from friction forces encountered as the piston slides inside the cylinder. To overcome the static friction between the piston and cylinder, an applied force of 15 N was found to be required; to obtain the value of ω , this threshold value was subtracted from the applied force. Under dynamic friction with water in place of the sample, the velocity of the piston with a force of 15 N was close to $5 \times 10^{-5} \text{ cm s}^{-1}$, which is at least an order of magnitude faster than the maximum rate of displacement observed with a gel sample in position. For this reason, in the measurements of D_c , dynamic friction could be discounted.

2.3. Light scattering

In swollen networks light is scattered by concentration fluctuations involving local swelling and deswelling of the polymer in its thermal interaction with the solvent [1]. This mutual diffusion establishes concentration uniformity throughout the sample. The decay rate Γ of the fluctuations is proportional to q^2 , where q is the transfer wave vector ($q = (4\pi n/\lambda) \sin(\theta/2)$, λ being the incident wavelength, n the refractive index of the sample and θ the scattering angle). The q^2 dependence indicates that the motion is translational [2–4]. The proportionality constant is $D_c =$

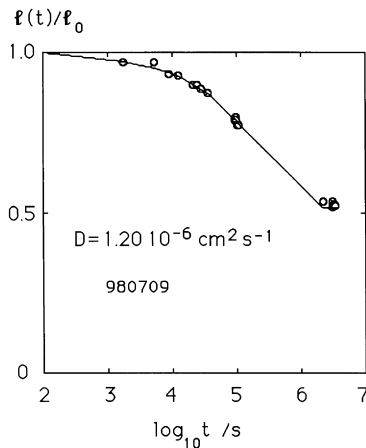


Fig. 3. Deswelling of sample I under applied pressure of 95 kPa. Continuous lines are least square fit of the data to Eq. (10). Duration of experiment is approximately 4×10^6 s.

$kT/6\pi\eta\xi$, where kT is the Boltzmann coefficient and η is the viscosity of the solvent [20]. Since the polymer–polymer correlation length ξ in these systems is of the order of 10 \AA , the condition for Rayleigh scattering, $q\xi \ll 1$, applies. It follows that D_c should display no angular dependence. Generally, the values of D_c measured by dynamic light scattering are in agreement with those found by deswelling techniques [21–23].

Measurements of the diffusion coefficient D_c were accordingly made using dynamic light scattering. The light source was a Spectra Physics SP1161 laser, working at wavelength $\lambda = 488 \text{ nm}$, together with a Malvern 7032 correlator. The operating conditions were such that the intensity of light scattered by the concentration fluctuations in the gels I_f was much smaller than that scattered by permanent static structural inhomogeneities of the sample, I_s . This situation produces strong optical heterodyning and is treated as described in Ref. [24]. Briefly, the field correlation function $g(\tau)$ is calculated from the intensity correlation function $G(\tau)$ using the expression

$$G(\tau) - 1 = \beta[2X(1 - X)g(\tau) + X^2g^2(\tau)], \quad (11)$$

where $X = I_f / \langle I_f + I_s \rangle$ is the ratio of the fluctuating to the total scattered intensity $I = I_f + I_s$ and β ($= 0.9$) is the optical coherence factor of the light collection system. The quantities in angular brackets are time averages. Since β is known for the apparatus and $g(0) = 1$, the ratio X can be calculated from $G(0)$ and the quadratic Eq. (11) solved to obtain the field correlation function $g(\tau)$ [25]. Since both deswelling and light scattering are governed by changes in concentration, $g(\tau)$ is defined by the same Eq. (6). The spatial Fourier transform of Eq. (6) yields

$$g(\tau) = \exp(-D_c q^2 \tau), \quad (12)$$

Experimentally, the decay rate $\Gamma = D_c q^2$ is found to vary as

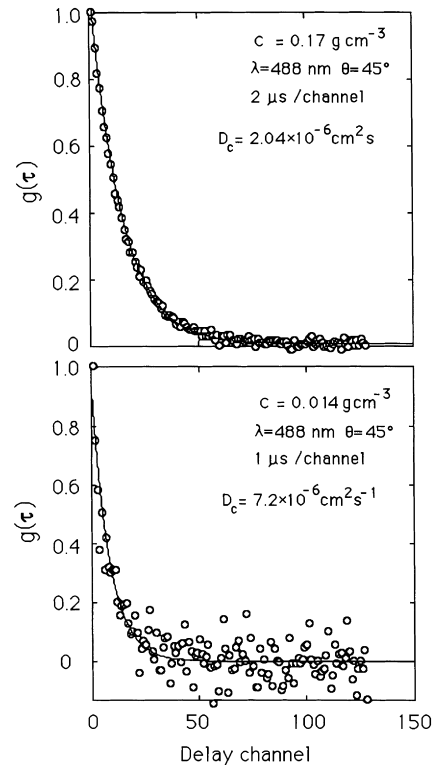


Fig. 4. Field correlation function, $g(\tau)$, of light scattered at 45° by a PAA gel at two different concentrations, 0.17 and 0.014 g cm^{-3} . Acquisition time 1 h in both cases, the detection being heterodyned by the signal scattered from heterogeneities in the gel. Wavelength of incident light 488 nm .

q^2 and therefore D_c is indeed independent of angle as discussed above.

3. Results and discussion

Fig. 3 shows a deswelling sequence of sample I as a function of time, where the scale of the horizontal axis is logarithmic. The least squares fit (continuous line) is in reasonable agreement with the observed data, indicating that the use of a single value for D_c is satisfactory in this case. In this sequence, the applied pressure is 30 N , with $c_0 = 0.027 \text{ g cm}^{-3}$ and $c_1 = 0.053 \text{ g cm}^{-3}$.

For the light scattering measurements, owing to the granular form of the type I samples, optical continuity between the grains was difficult to achieve except in the most swollen state, where excess water fills the space between the swollen grains in the cylindrical optical cell. At lower degrees of swelling, lack of a well-defined optical path through the sample made it impractical to make dynamic light scattering measurements. In contrast, for the type II samples, their cylindrical shape ensured correct mating with the wall of the optical cells.

An example of the light scattering results is illustrated in Fig. 4, showing the field correlation functions $g(\tau)$ obtained from sample II in the deswollen state and in the fully

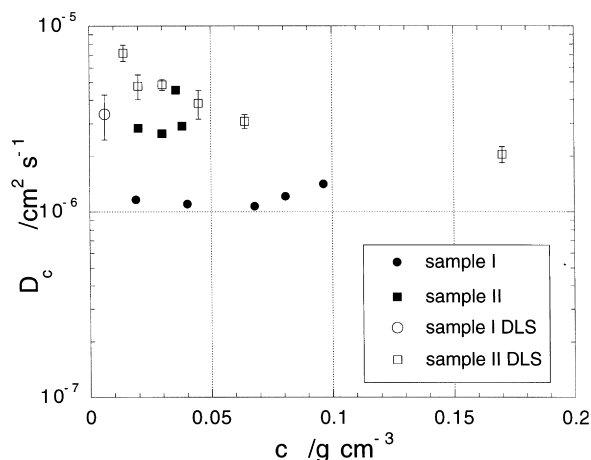


Fig. 5. Concentration dependence of the diffusion coefficient D_c for gels undergoing deswelling; filled circles: sample I, filled squares: sample II. Open symbols: measurements of D_c in same samples by dynamic light scattering.

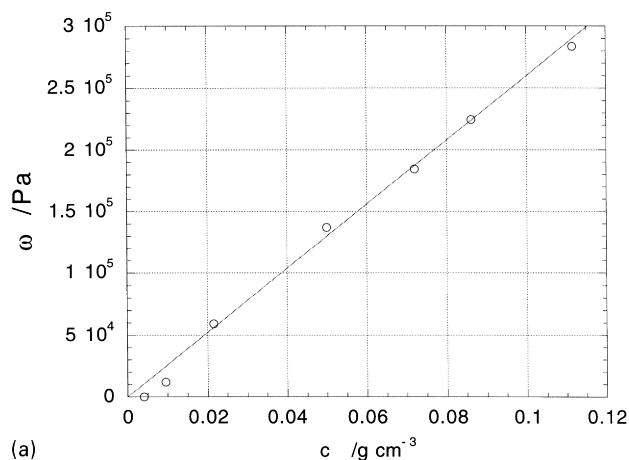
swollen state. Both these measurements were made at $\theta = 45^\circ$ to enhance signal-to-noise-ratio. At low polymer concentration the scattered intensity is weak, which explains the poorer signal-to-noise-ratio in the fully swollen gel. To describe the decay of $g(\tau)$, it was found that a single exponential is insufficient, a two-exponential decay yielding better agreement with the data. The value of the diffusion coefficient was then obtained from the first cumulant,

$$D_c = - \frac{1}{q^2} \left. \frac{d \ln g(\tau)}{d \tau} \right|_{\tau=0} \quad (13)$$

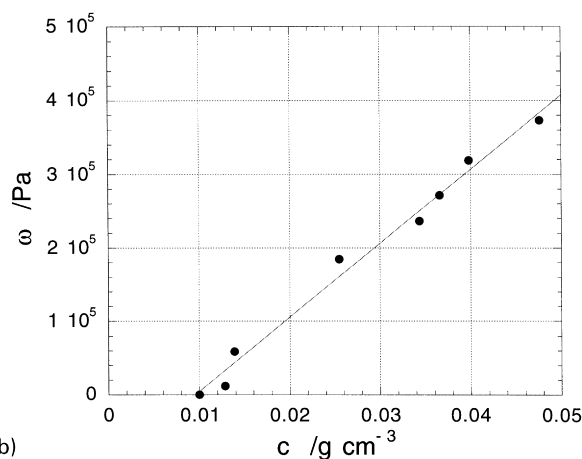
Fig. 5 shows a comparison between the values of D_c measured by the two techniques. Since the deswelling method does not yield reliable results for the initial deswelling stage, these measurements are omitted from the figure. The value of D_c from light scattering for the fully swollen sample I is about three times greater than the results from mechanical measurements at higher concentrations. This difference cannot be entirely attributed to the difference in technique, since an increase in D_c is expected in the fully swollen state (see Section 1). Moreover, an increase, albeit more gradual, is also observed at low concentrations in sample II. The values of D_c are about three times greater for sample II (square symbols) than for sample I; it can also be seen that for sample II there is relatively good agreement between the results from the two methods. We may conclude therefore, for both samples, that the present results confirm the increase in D_c at low concentration in polyelectrolyte gels.

Fig. 6a shows the swelling pressure ω (as measured by the pressure exerted on the piston) as a function of polymer concentration for the Type I samples. At all but the lowest concentrations, ω varies linearly with concentration,

$$\omega = 2.6 \times 10^6 c \text{ Pa}. \quad (14)$$



(a)



(b)

Fig. 6. (a) Swelling pressure of Sample I swollen in distilled water. The slope of the straight line drawn through the origin is $2.6 \times 10^6 \text{ Pa cm}^3 \text{ g}^{-1}$ and (b) Swelling pressure of gel sample II as a function of concentration.

Owing to their high cross-linking density, Type II gels have a higher elastic modulus than Type I, which also accounts for their higher equilibrium swelling concentration in distilled water, $c_0 = 0.014 \text{ g cm}^{-3}$. Over the same pressure range (Fig. 6b), the swelling pressure of the Type II gels approximately obeys a relation of the form

$$\omega = 1.0 \times 10^7 (c - c_0) \text{ Pa}, \quad (15)$$

where c_0 is the concentration at equilibrium swelling. The difference in response between these samples reflects the lower charge density in Type I associated with the co-polymerization with acrylamide. The above results may be illustrated as follows: application of a pressure difference of 1 atm to a fully swollen Type I gel causes it to deswell from $c = 0.004$ to 0.04 g cm^{-3} ; i.e. 90% of the absorbed water is released. Sample II requires a greater applied pressure to achieve the same release.

Owing to the irregular shape of the granules, it was impractical to measure the elastic modulus of sample I.

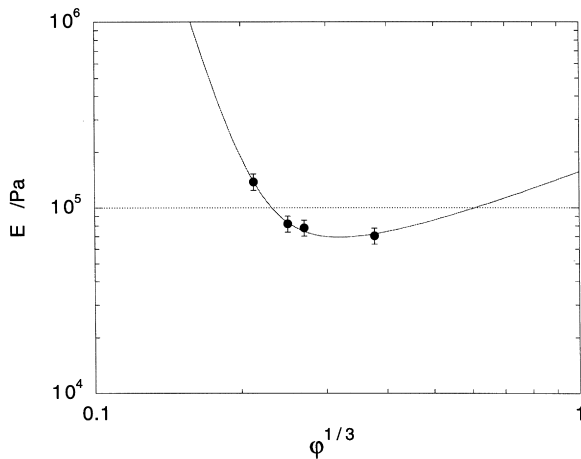


Fig. 7. Young's modulus of sample II measured as a function of concentration. Continuous line is the interpolation used to calculate $G = E/3$ in Eq. (19).

For sample II, however, the cylindrical shape allowed measurements to be made of Young's modulus

$$E = 3G. \quad (16)$$

Fig. 7 shows the results of these measurements, found from the stress–strain curves under compression at constant volume. The measurements were made with an Instron 4301 instrument over a time period short enough for the samples not to deswell. In the concentration range explored E is clearly a decreasing function of gel concentration, indicating that the constituent polymer coils are strongly extended in this concentration range.

The swelling pressure ω exerted by a gel is the difference between the osmotic pressure Π , which causes the polymer chains to expand, and the elastic pressure from the chains, which tends to make them contract. In the following, we make the assumption, valid for neutral gels, that the elastic pressure is equal to $-G$. The osmotic pressure is thus

$$\Pi = \omega + G \quad (17)$$

To calculate the value of Π for each measurement of ω in Fig. 6, it is necessary to interpolate the Young's modulus data of Fig. 7. For this, the inverse Langevin function approximation [7,8,15] may be used, according to which the uniaxial stress Σ at constant volume is given by

$$\Sigma = G_0 q^{-2/3} n^{1/2} [\lambda \mathcal{L}^{-1}(\lambda q^{1/3} n^{-1/2}) - \lambda^{-1/2} \mathcal{L}^{-1}(\lambda^{-1/2} q^{1/3} n^{-1/2})] \quad (18)$$

where q is the volume swelling ratio with respect to the equilibrium coil size, λ the uniaxial strain and n the number of monomers in a network chain. $\mathcal{L}^{-1}(x)$ is the inverse Langevin function. Since the mechanical measurements are performed at deformations $\lambda = 1 + \epsilon$ such that ϵ is

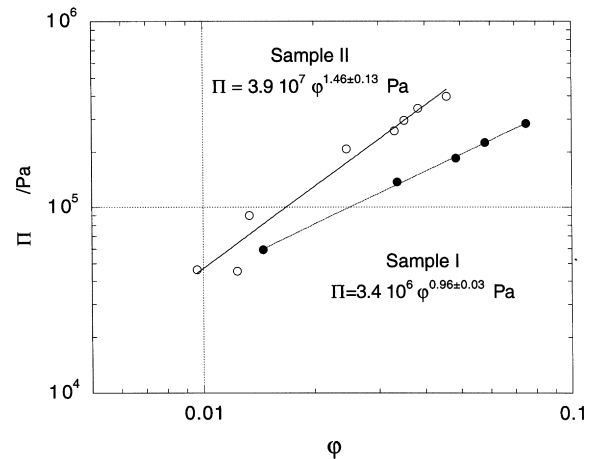


Fig. 8. Osmotic pressure $\Pi = \omega + G$ for sample II (open circles), where G is calculated from Eq. (19). For sample I (filled circles), the approximation $G \ll \Pi$ is used, where only the five highest concentrations are retained for the power law fit.

small, the elastic modulus may be written

$$\Sigma/(\lambda - 1/\lambda^2) = G = (G_0/2)q^{2/3}n^{-1/2}[\mathcal{L}^{-1}(q^{1/3}n^{-1/2}) + q^{1/3}n^{-1/2}\mathcal{L}^{-1}'(q^{1/3}n^{-1/2})] \quad (19)$$

where $\mathcal{L}^{-1}'(x) \equiv d\mathcal{L}^{-1}(x)/dx$ is the first derivative of the inverse Langevin function. The continuous curve in Fig. 7 shows the least squares fit of Eq. (19) through the data points, yielding $G_0 = 50.7$ kPa and $n = 42.0$. This corresponds to a value of the shear modulus in the fully swollen state

$$G(c_0) = 46 \text{ kPa}. \quad (20)$$

As stated earlier, for sample I, Young's modulus could not be measured directly owing to the irregular shape of the grains. However, at high concentrations where $\Pi \gg G$, Eq. (14) provides a good approximation for $\Pi(c)$, since on account of Eq. (19) the effect of G is substantial only close to the fully swollen state. Fig. 6a shows that deviations from linearity occur only at the two lowest concentrations: in the fully swollen state where $\omega = 0$, the value of G is about 10 kPa. Given the additional requirement that $\Pi(0) = 0$, it may be concluded that

$$\Pi(c) = 2.6 \times 10^6 c \text{ Pa}. \quad (21)$$

applies over the whole concentration range.

The resulting curves of $\Pi = \omega + G (\propto \varphi^\sigma)$ are shown in Fig. 8 as a function of polymer volume fraction $\varphi = c/\rho_0$, where $\rho_0 = 1.486 \text{ g cm}^{-3}$ is the density of the pure polymer [26]. In the double logarithmic representation, it can be seen that both samples display power law behaviour. The slope corresponding to sample I, $\sigma = 0.96 \pm 0.03$, consistent with the linear behaviour expected of polyelectrolytes [27], is characteristic of counter-ions. This result is also consistent with the findings of Ref. [16] for polyelectrolyte solutions over a wide range of degree of neutralization. For sample II,

however, the power law exponent, $\sigma = 1.46 \pm 0.13$, is significantly higher and agrees better with the value found by Silberberg-Bouhnik et al. [16] for their gel system. It may be added that for many applications of these gels, low values of σ are an advantage, since the useful range of swelling pressure is extended to lower concentrations, thereby increasing the solvent absorbing capacity of the gel.

The higher exponent in sample II calls for comment. In the scaling approach of de Gennes, the exponent σ describing the concentration dependence of the osmotic pressure in neutral polymer solutions is given by Ref. [20]

$$\sigma = 3\nu/(3\nu - 1), \quad (22)$$

where the excluded volume exponent ν describes the relation between the size of a polymer coil and its mass. For linear polymers in a good solvent, where van de Waals forces prevail and excluded volume statistics apply, $\nu \approx 0.6$, yielding $\sigma = 9/4$. The osmotic pressure generated by the excluded volume interaction in neutral polymers, however, is too weak to generate the swelling pressures observed here. For example, for polyvinyl acetate gels swollen in the excellent solvent acetone [28], the osmotic pressure generated at polymer volume fraction $\varphi = 0.05$ is equal to 4.6 kPa, whereas the data for sample II indicate a value some two orders of magnitude greater at the same concentration. The excess osmotic pressure observed here therefore cannot be associated with a cross-over to an excluded volume regime, but must come from the electrostatic charge distribution.

As noted in the experimental section, network I is a copolymer in which the acrylamide/potassium acrylate ratio is 2:1: the average distance between ions on the polymer backbone (ca. $3 \times 2.5 \text{ \AA}$) therefore exceeds the Bjerrum length ($l_B = 7.1 \text{ \AA}$). For the Type II network, in contrast, owing to its higher charge density, the opposite is true and the condition for Manning condensation is in principle satisfied [29,30]. In either case, for salt-free solutions the osmotic pressure is expected theoretically to have the form [27]

$$\Pi/kT = c/A + (l_B/A^2 b)^{3m/2} (cb)^{3/2} \quad (23)$$

where A is the number of monomers between effective charges on the polymer chain and b is the length of the monomer. The first term on the right hand side of Eq. (23), is the contribution of the counter-ions, while the second term, due to the polymer, is equal to $1/\xi^3$, where ξ is the correlation length. For theta conditions $m = 1/3$, while for excluded volume conditions $m = 2/7$. According to Eq. (23), the concentration c_t at which the osmotic pressure changes from a linear dependence in c to one in $c^{3/2}$ is

$$c_t = (b^2 l_B)^{-1} \quad (\text{theta condition}) \quad (24)$$

$$c_t = (A^{2/7} l_B^{6/7} b^{15/7})^{-1} \quad (\text{good solvent}).$$

In both cases the calculated values of c_t are comparable to that of the bulk polymer, with, at best, a weak dependence on the charge spacing parameter A . The present observa-

tions on sample II, however, demonstrate that in practice the $c^{3/2}$ behaviour starts at a concentration much lower than predicted theoretically.

In a recent study of salt-free polyelectrolyte solutions [31,32] an analogous result has been found: above a certain polymer concentration the osmotic pressure undergoes a change in power law from c^1 to $c^{3/2}$. The value of c_t observed in Ref. [31] is approximately the same as the point in Fig. 8 at which the two values of Π are equal (ca. 0.1 monomer mol/l). The present results are not expected to be identical to the solutions, however, in that the elastic constraints of the cross-links in a gel modify the polymer distribution and thereby the effective concentration. Nonetheless, the chief effect of cross-linking in these measurements is to limit the lowest observable concentration of the sample; the upper concentration range is limited by the pressure at which the gel extrudes past the membrane. These technical constraints on the measurable concentration range seem to be the reason that the crossover is not observed directly in these gels. The similarity between the behaviour of the present gels and the uncross-linked solutions [31,32], however, indicates that differences in cross-linking are not the underlying cause of the different power laws observed in samples I and II.

Likewise, it is legitimate to examine the ionic contribution to the osmotic pressure (first term of Eq. (23)). From the data of sample I this term may be expressed as the dimensionless number $\Pi A M / R T c \approx 0.26$, where $M = 85 \text{ g/mol}$ is the effective molar mass per monomer, R the gas constant, T the temperature and $A \approx 3$. In view of the uncertainty in composition of this specimen and the fact that it is cross-linked, this result appears to be in reasonable agreement with that calculated [29,33] from the first term on the right hand side of Eq. (23) for uncross-linked solutions, namely $\Pi A M / R T c \approx 0.18$. It would therefore seem that the ionic contribution is of the correct order of magnitude.

To elucidate the discrepancy in behaviour between the two gel samples, we turn our attention to the second term on the right hand side of Eq. (23). It is assumed in Dobrynin et al. [27] that the relevant correlation length ξ in this contribution to the osmotic pressure (kT/ξ^3) corresponds to the characteristic distance detected by small angle X-ray or neutron scattering experiments (SAXS or SANS). Indeed, such experiments [31,34] show that ξ (i.e. the inverse of the position of the maximum in intensity) varies with concentration as

$$\xi \sim c^{\nu(3\nu-1)} \sim c^{-1/2}, \quad (25)$$

corresponding to $\nu = 1$. It follows therefore from Eq. (22) that $\sigma = 3/2$, in agreement with the present observation for sample II.

The second term in Eq. (23) thus appears to have the correct form. Its amplitude, however, is underestimated. This discrepancy arises from the fact that, unlike neutral polymer solutions, where different polymer coils interpenetrate and static and dynamic concentration fluctuations are

therefore equivalent, the polyelectrolyte system is not fully ergodic. The value of ξ measured in scattering experiments defines the mean separation between adjacent polymer segments, whereas, owing to electrostatic repulsion between these segments, their dynamic fluctuations explore only a fraction of this distance, say $f\xi$. Because the osmotic properties relate to dynamic fluctuations, the second term of Eq. (23) thus represents a severe underestimate of the osmotic contribution from the polymer. When the effect of the amplitude reduction factor f is incorporated into Eq. (23), the estimate of c_t in Eq. (24) is reduced by a factor f^6 . On the basis of the measurements on Sample II, where the $c^{3/2}$ behaviour extends to a concentration approximately a hundred fold smaller than indicated by Eq. (24), we therefore conclude that $f \approx (100)^{-1/6}$, or $f \approx 0.5$.

4. Conclusions

The measurements described here on the osmotic properties of polyacrylic acid gels show, first, that the diffusion coefficients deduced from the rate of deswelling are, within the experimental uncertainty, in agreement with those measured by dynamic light scattering. The diffusion coefficients increase as the gel approaches maximum swelling. Second, the dependence on concentration of the mixing pressure $\Pi(c) = \omega + G$, where ω is the swelling pressure and G the elastic modulus, depends upon the concentration range explored. In gels for which the effective concentration of charges c/A is low, Π depends linearly on c . Above a certain threshold concentration c_0 , Π displays a power law dependence on concentration with an exponent close to $3/2$. Owing to the electrostatic repulsion effects the amplitude of the dynamic concentration fluctuations is smaller than the mean separation between neighbouring polymer chains, with the result that the value of c_t is significantly lower than predicted by the model of Dobrynin et al. [27]. The data presented here suggest that the amplitude reduction factor is of the order of 50%.

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