Pressure-induced deswelling of gels

A. M. Hecht
Laboratoire de Spectroscopie Optique, Université de Savoie, BP 143, 73011 *Chambéry-Cédex, France*

and E. Geissler
Laboratoire de Spectrométrie Physique[*], *Université I de Grenoble, BP* 53, 38041 *Grenoble Cédex, France*

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When a sufficiently large hydrostatic pressure, P, is applied to a swollen polymeric gel in contact with a semipermeable membrane, reverse osmosis occurs and the gel deswells. The rate of deswelling depends on the time elapsed, t, the difference between P and the longitudinal elastic modulus, E, of the gel network, and the friction coefficient, f, between the solvent and the polymer. In certain circumstances the deswelling process takes a simple form[1].

To measure the rate of deswelling, polyacrylamide gels were formed in a cylindrical glass tube in such a way that the top and bottom surfaces were flat. The lower surface was placed in contact with a Millipore MF (cellulose) filter of pore diameter 1.2 μm, which presented a negligible resistance to solvent flow. The upper end of the glass tube was connected by a watertight joint to a manometer containing water in the high pressure arm, by which a steady hydrostatic pressure could be applied to the top of the gel. The height of the top meniscus of the gel was read as a function of time, using a cathetometer, starting from the time when the connecting tap to the manometer was opened. Provided the gel is sufficiently thick (i.e. greater than a few mm), the deswelling at small times takes place only at the lower end, and the upper surface, being held laterally at the glass walls, falls, forming a spherical cap of decreasing radius of curvature. For small displacements Δh of the meniscus, the volume change of the gel is equal to $\Delta hA/2$, where A is the cross-sectional area of the tube.

For a given initial concentration of the gel c_1 (measured in g cm^{-3}) and a fixed applied pressure, the displacement Δh is proportional to $\sqrt{t}$, indicating a diffusion process[1]. Also, the rate of diffusion $\Delta h^2/t$ is proportional to the applied pressure for $P > E$, where E is the longitudinal elastic modulus of the gel. This linearity can be observed in *Figure* 1.

We explained these observations using the following simplified model. At times $t \geqslant 0$, the layer of gel in immediate contact with the membrane must be in thermodynamic equilibrium, that is, it must have a concentration c_0 such that $\Pi(c_0) = P$, where Π is the osmotic pressure. It is assumed that at any time t this layer has a thickness q, which increases as more polymeric material accumulates at the membrane. For simplicity it is supposed that the polymer concentration is c_0 in the boundary layer, or plug, and c_1 elsewhere beyond it. All the resistance to the motion arises in the plug, which has a friction coefficient f with respect to the solvent flow. If the rate of displacement of the free end is denoted v, then conservation of matter gives[*]:

$$c_1 v = (c_0 - c_1)\frac{dq}{dt} \qquad (1)$$

The flow through the plug has two components. The first, due to the pressure gradient across the plug, is simply P/fq. The second component opposes the collapse of the gel by the collective diffusion mechanism[2], the diffusion constant of which, D_c, is equal to E/f. Here E is the longitudinal elastic modulus of that part of the gel undergoing deswelling (i.e. at concentration c_1); the frictional resistance to this reverse flow, however, is encountered in the plug itself, and hence the restoring counterflow is $-E/fq$. The total flow therefore is:

$$v = (P - E)/fq \qquad (2)$$

Since q is taken to be zero at $t = 0$, we find on combining equations (1) and (2):

$$v = \{(P - E)(c_0 - c_1)/2c_1 ft\}^{1/2} \qquad (3)$$

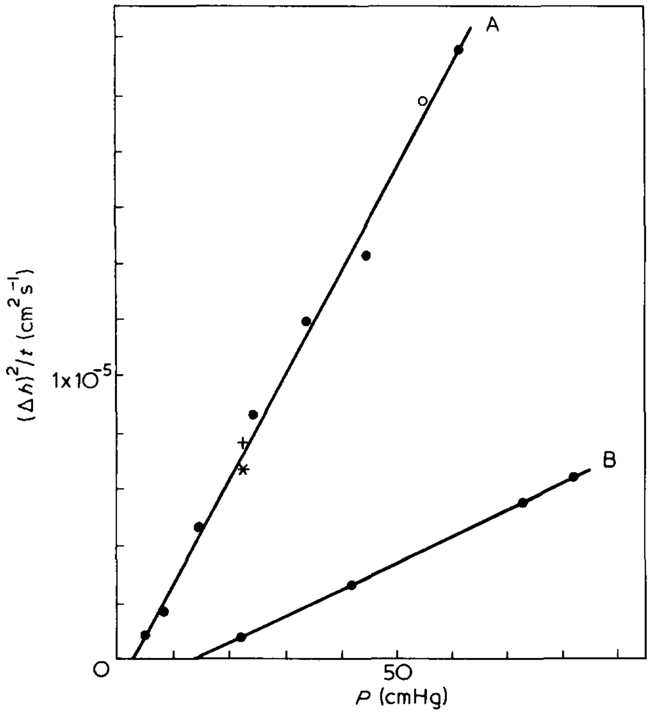

Figure 1 Variation of $\Delta h^2/t$ with applied pressure. A, For c_1 = 0.033 g cm^{-3}; each point corresponds to a different sample, all of which were prepared with a ratio of acrylamide to crosslinking agent (*N,N'* methylene bisacrylamide) *A/B* = 37.5 by wt, apart from the points marked +(*A/B* = 20) and *(*A/B* = 75). The point denoted by an open circle was obtained using ordinary coarse laboratory filter paper. All other measurements were performed using Millipore MF grade filters. B, For c_1 = 0.065 g cm^{-3}, with *A/B* = 37.5 and using Millipore filters

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[*] Laboratoire associe au CNRS.

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The factor 1/2 appearing under the root sign is a consequence of the rectangular concentration profile chosen to describe the plug, and has no special significance here. We leave this geometrical factor undetermined and replace it by a constant α.

When there is a strong attractive potential between the polymer and the filter material, then $c_0 \gg c_1$ and is independent of applied pressure, so that:

$$\Delta h^2/t = 16v^2 t = 16\alpha(P-E)c_0/c_1 f \qquad (4)$$

The above relation is found to be valid for gels consisting of polyacrylamide with pure water, in contact with cellulose filters (the rate of deswelling is unaltered when the Millipore MF grade filter is replaced by ordinary laboratory filter paper). When, however, methanol is added to the gel solvent or the filter material is replaced by PTFE, the observed relation becomes non-linear.

The values of E found in this way for two PA–water gel concentrations were in good agreement with those obtained by inelastic light scattering[1,3]. For the 0.033 g cm^{-3} sample of *Figure* 1, we obtain $E = (3.2 \pm 1.2) \times 10^4$ dynes cm^{-2}, while the intercept for the 0.065 g cm^{-3} sample gives $E = (1.70 \pm 0.14) \times 10^4$ dynes cm^{-2}.

The above results were obtained from essentially dynamic experiments. Additional evidence can be adduced from static measurements of the osmotic pressure Π. In the deswelling experiment the hydrostatic pressure head was replaced by a vertically sliding piston on top of which were placed suitable weights. The piston transmits the resulting pressure directly to the gel. With a knowledge of the initial concentration of the gel, the osmotic pressure of any given sample may be obtained as a function of concentration by measuring for each applied weight the equilibrium height of the piston above the lower end of the gel. In this arrangement the top of the gel is flat and moves with the piston. The longest equilibration time found was of the order of 2 months. The results of these measurements are shown in *Figure* 2, plotted on a double logarithmic scale. The slope of the line through the experimental points is 2.26 ± 0.15, or approximately 9/4, which is the result expected for solutions of non-crosslinked polymers in a good solvent[4].

Using the relation:

$$E = c\frac{\partial \Pi}{\partial c} \qquad (5)$$

we can deduce from the osmotic pressure measurements the value of E at the original gel concentration c_1. On the basis of the analogy between the crosslinked gel and the equivalent polymer solution, it follows from equation (5) that $E = 9\Pi/4$. The value of E measured for the 3.3% samples by deswelling compared with the osmotic pressure, obtained by extrapolation to the initial concentration in *Figure* 2, gives:

$$E = (2.27 \pm 0.14)\Pi \qquad (6)$$

This result is an independent confirmation of the dynamic deswelling and the quasi-elastic light scattering results mentioned above.

From *Figure* 1 it appears that the friction coefficient f of the gel depends strongly on the initial gel concentration. In order to obtain equation (4) we have assumed that the concentration c_0 at the plug is independent of applied pressure, and that α is a constant geometrical factor. The ratio of the slopes of the two straight lines of *Figure* 1 indicates that the slope varies as $c_1^{-2.0}$. It follows from equation (4) that:

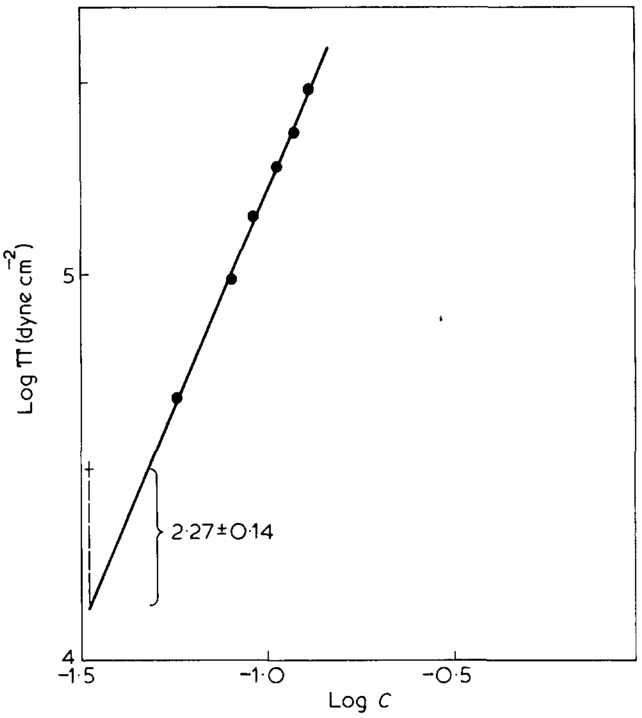

Figure 2 Variation of the osmotic pressure π as a function of concentration (in g cm^{-3}) for a polyacrylamide–water gel of initial concentration 0.033 g cm^{-3}. For each pressure applied to a piston in contact with the gel the equilibrium volume of the gel was calculated by measuring the height of the psiton above the base of the gel. The average straight line through the experimental points in the double logarithmic plot is 2.26 ± 0.15. The point marked + represents the value of the longitudinal elastic modulus measured in the original unperturbed state from the measurements of the rate of deswelling. The height of this point above the extrapolated straight line given by $\Pi(c)$ is represented by the factor 2.27 ± 0.14 shown by the curly bracket

$$f \propto c_0 c_1 \qquad (7)$$

This result is not inconsistent with observations of the collective diffusion coefficient[5], where it is found that on deswelling D_c varies approximately as $c^{0.3}$, provided we make the further assumption that:

$$c_0 \propto c_1 \qquad (8)$$

i.e. that the effective concentration in the plug depends linearly on the initial concentration of the gel. According to the data presented above, $E \propto c^{2.26}$, so that $D_c = E/f$ can be expected to vary as $c^{0.26}$ on deswelling.

References

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* Strictly speaking, the concentration in equation (1) should be the polymer weight fraction. The difference here is small, and the distinction is not justified by the experimental accuracy.