

nectivity and degree of branching for a system of given molecular weight; (2) excluded volume, which will tend to delocalize the system. In the case of random-walk systems only the confinement process operates, and the reduction in the radius of gyration of a star polymer relative to its linear counterpart of identical molecular weight may be directly attributed to the structural reorganization alone.

If excluded-volume effects are now introduced, the expansion of the more weakly confined linear system may well exceed that of its more tightly confined star counterpart, in which case $g(\text{excluded volume}) < g(\text{random walk})$ at given (f, n) . This we find on the basis of our IC and MC analyses (Table I). Clearly, the behavior of these ratios depends on a subtle balance between these competing agencies: the effective interaction, explicit or implicit, adopted in the various theoretical approaches would seem to be largely responsible for the various ratios obtained.

The Daoud-Cotton predictions for the branching dependence of g appear unsubstantiated for stars of small-to-intermediate size on the basis of the present analyses, concurring with our earlier conclusions regarding the interior structure of uniform stars. (It should be said, however, that in the case of large stars, Whittington et al. support Daoud and Cotton's prediction for long branches in a good solvent (eq 8)). We therefore conclude that the packing and screening processes envisaged by Daoud and Cotton as operating in the core and intermediate regions of a uniform star are not supported by the present IC and MC analyses.

Finally, the mean square length of a branch appears to develop more strongly with n than its isolated counterpart for stars of small-to-intermediate molecular weight. This concurs with the lattice-based observations of Whittington et al. and reflects the high monomer concentration in the vicinity of the vertex. Only for $n > 30$ do these latter authors find that a branch regains the $n^{1.2}$ dependence characteristic of isolated linear self-avoiding sequences, and this appears to be the case regardless of branching number ($f \leq 6$).

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Kinetics of Swelling of Spherical and Cylindrical Gels

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ABSTRACT: The theory of kinetics of swelling of a gel previously developed by Tanaka and Fillmore for spherical samples has been generalized to the case of cylindrical samples. The effect of a nonnegligible shear modulus has been included in the derivation. The values of the cooperative diffusion coefficient obtained from macroscopic swelling experiments in spherical and cylindrical polyacrylamide and poly(dimethylsiloxane) gels show good agreement with results of quasielastic light-scattering experiments.

Introduction

The kinetics of swelling of spherical neutral gels have been studied both theoretically and experimentally by Tanaka and Fillmore, who showed that the macroscopic swelling behavior was described by a diffusion equation with a diffusion coefficient D given by¹

$$D = M_{os}/f = (K_{os} + 4\mu/3)/f \quad (1)$$

where M_{os} , K_{os} , and μ are the osmotic longitudinal modulus, the osmotic compressional modulus, and the shear modulus of the gel, respectively, and f is the friction

coefficient describing the viscous interaction between the polymer and the solvent. In their derivation, Tanaka and Fillmore have assumed that the shear modulus μ of the gel was negligible compared to the osmotic bulk modulus. Recently, we have extended the model of these authors to the case of spherical gels with a nonnegligible shear modulus.² The purpose of the present paper is to study the kinetics of swelling for cylindrical gels in the limit of infinite height or infinite diameter and to compare the theoretical predictions to swelling experiments performed in polyacrylamide gels swollen by water and in poly(di-

methyilsiloxane) (PDMS) gels swollen by toluene.

Theory

The equation of motion of a gel network as given by Tanaka et al.³ is

$$\frac{\partial \mathbf{u}}{\partial t} = \frac{K_{os} + \mu/3}{f} \text{grad}(\text{div } \mathbf{u}) + \frac{\mu}{f} \Delta \mathbf{u} \quad (2)$$

where Δ denotes the Laplacian and $\mathbf{u}(\mathbf{r}, t)$ is the displacement vector that represents the displacement of a point in the network from its final equilibrium location after the gel is fully swollen. Under this definition $\mathbf{u} \rightarrow 0$ if $t \rightarrow \infty$.

We solve eq 2 for a sphere, a cylinder of infinite height, and a cylinder of infinite diameter, respectively. We give successively the different steps of the derivation for the three cases considered.

Solution of the Equation of Motion. Sphere. The deformation $\mathbf{u}(\mathbf{r}, t)$ is radial with respect to the center of the sphere, and eq 2 becomes

$$\frac{\partial u}{\partial t} = D \frac{\partial}{\partial r} \left(\frac{\partial u}{\partial r} + 2 \frac{u}{r} \right) \quad (3)$$

with the condition¹

$$u(0, t) = 0 \quad \text{at all } t \quad (4)$$

The solution of the equation is

$$u(r, t) = \sum_n a_n e^{-t/\tau_n} N(X_n r/a) \quad (5)$$

where

$$X_n = a[\tau_n D]^{-1/2} \quad (6)$$

where a is the final radius of the gel spheres in equilibrium with the surrounding fluid.

The function $N(X)$ is

$$N(X) = \frac{\cos X}{X} - \frac{\sin X}{X^2} \quad (7)$$

Cylinder with Infinite Height. In this case, the deformation is radial with respect to the symmetry axis, and eq 2 becomes

$$\frac{\partial u}{\partial t} = D(1 + \mu/M_{os}) \left[-\frac{1}{\rho^2} u + \frac{1}{\rho} \frac{\partial u}{\partial \rho} + \frac{\partial^2 u}{\partial \rho^2} \right] \quad (8)$$

with the condition $u(0, t) = 0$ at all t .

The solution of this equation is

$$u(\rho, t) = \sum_n A_n e^{-t/\tau_n} J_1(X_n \rho/b) \quad (9)$$

where

$$X_n = b[\tau_n D(1 + \mu/M_{os})]^{-1/2} \quad (10)$$

b is the final radius of the cylindrical gel at the swelling equilibrium and $J_1(X)$ is the Bessel function of first order.

Disk with Infinite Diameter. The deformation of a disk of infinite diameter is along the axial direction. Equation 2 becomes

$$\frac{\partial u}{\partial t} = D(1 + \mu/M_{os}) \frac{\partial^2 u}{\partial z^2} \quad (11)$$

with $u(0, t) = 0$ at all t .

The origin $z = 0$ corresponds to the plane of symmetry of the disk. The solution of eq 11 has the form

$$u(z, t) = \sum_n A_n e^{-t/\tau_n} \sin(X_n z/h) \quad (12)$$

where

$$X_n = h[\tau_n D(1 + \mu/M_{os})]^{-1/2} \quad (13)$$

$H = 2h$ is the height of the disk at the swelling equilibrium.

Boundary Conditions. The boundary condition is obtained by canceling the normal stress on the free surface for $t \rightarrow \infty$. This condition can be written in the following ways for the three different shapes considered:

$$\text{sphere} \quad \sigma_{rr} = M_{os} \left[\frac{\partial u}{\partial r} + \left(1 - 2 \frac{\mu}{M_{os}} \right) \frac{2u}{r} \right] = 0 \quad t \rightarrow \infty, \quad r = a \quad (14)$$

$$\text{cylinder} \quad \sigma = M_{os} \left[\frac{\partial u}{\partial \rho} + \left(1 - 2 \frac{\mu}{M_{os}} \right) \frac{u}{\rho} \right] = 0 \quad t \rightarrow \infty, \quad \rho = b \quad (15)$$

$$\text{disk} \quad \sigma = M_{os} \frac{\partial u}{\partial z} = 0 \quad t \rightarrow \infty, \quad z = \pm h \quad (16)$$

Since in practice we are primarily interested in the later stage of the swelling process, that is, the range of large t , we assume that the above conditions are fulfilled at finite t .

Relaxation Equation. By writing that the boundary condition is fulfilled for each particular solution of the deformation vector, one obtains the following relaxation equations.

Sphere:

$$tgX_n = \frac{(4\mu/M_{os})X_n}{(4\mu/M_{os}) - X_n^2} \quad (17)$$

X_n is the n th root of the above equation. The variation of the two first roots as a function of μ/M_{os} is given in the Appendix (cf. Figure 6a).

In the limit case

$$\mu/M_{os} = 0 \quad X_n = n\pi$$

If $\mu/M_{os} \neq 0$, the successive roots X_n are such that if n increases, the quantity $n\pi - X_n$ decreases and tends to 0. The roots X_n are determined if the parameter μ/M_{os} is known. The relaxation time of first-order τ_1 will be an experimental datum $\tau_1 = \tau_{\text{exptl}}$. Relation 6 allows one to express τ_n to τ_1 :

$$\mu/M_{os} \neq 0 \quad \tau_n = \tau_{\text{exptl}}(X_1/X_n)^2 \quad (18)$$

$$\mu/M_{os} = 0 \quad \tau_n = \tau_{\text{exptl}}/n^2 \quad (19)$$

Cylinder with Infinite Height:

$$X_n J_0(X_n) - 2(\mu/M_{os}) J_1(X_n) = 0 \quad (20)$$

where $J_0(X)$ is the Bessel function of zeroth order. The variation of the two first roots of eq 20 is given in the Appendix (cf. Figure 6b). In the limit $\mu/M_{os} = 0$ the successive roots X_n are the zero's λ_n of $J_0(X)$.

The relaxation times are

$$\mu/M_{os} \neq 0 \quad \tau_n = \tau_{\text{exptl}}(X_1/X_n)^2 \quad (21)$$

$$\mu/M_{os} = 0 \quad \tau'_n = \tau_{\text{exptl}}(\lambda_1/\lambda_n)^2 \quad (22)$$

Disk with Infinite Diameter:

$$\cos X_n = 0 \quad (23)$$

The roots of eq 23 are independent of the ratio μ/M_{os} :

$$X_{2n+1} = (2n+1)\pi/2 \quad (24)$$

The corresponding relaxation times are

$$\tau_{2n+1} = \tau_{\text{exptl}} \frac{1}{(2n+1)^2} \quad (25)$$

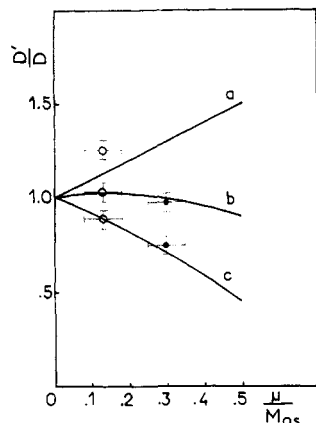


Figure 1. Theoretical variation of the ratio D'/D as a function of μ/M_{os} for a sphere (c), cylinder of infinite height (b), and a disk of infinite radius (a). The data correspond to measurements of D'/D_L for polyacrylamide gels (●) and PDMS gels (○).

Diffusion Coefficient. The diffusion coefficient D can be expressed as a function of the root X_1 and of the relaxation time $\tau_1 = \tau_{\text{exptl}}$. It is convenient to introduce the diffusion coefficient D' which is obtained if one assumes $\mu = 0$.

Sphere:

$$D = \frac{a^2}{\tau_{\text{exptl}} X_1^2} \quad D' = \frac{a^2}{\tau_{\text{exptl}} \pi^2} \quad \frac{D'}{D} = \left(\frac{X_1}{\pi} \right)^2 \quad (26)$$

Cylinder with Infinite Height:

$$D = \frac{b^2}{\tau_{\text{exptl}} X_1^2 (1 + \mu/M_{os})} \quad D' = \frac{b^2}{\tau_{\text{exptl}} \lambda_1^2} \quad \frac{D'}{D} = \left(\frac{X_1}{\lambda_1} \right)^2 (1 + \mu/M_{os}) \quad (27)$$

Disk with Infinite Diameter:

$$D = \frac{h^2}{\tau_{\text{exptl}} (\pi/2)^2 (1 + \mu/M_{os})} \quad D' = \frac{h^2}{\tau_{\text{exptl}} (\pi/2)^2} \quad \frac{D'}{D} = 1 + \mu/M_{os} \quad (28)$$

In the three cases, the ratio D'/D is function of the parameter μ/M_{os} , directly and/or through the root X_1 (cf. Appendix).

The curves calculated from eq 26–28 giving D'/D as a function of μ/M_{os} are reported in Figure 1. It can be seen that for a cylinder of infinite height, the effect of μ/M_{os} can be neglected in the determination of D from a kinetics of swelling. The values of X_n and D have a physical meaning only for $0 \leq \mu/M_{os} \leq 0.5$. The condition $\mu/M_{os} \leq 0.5$ is necessary to ensure that the internal stresses are negative. The resulting compression relaxes, thus producing the expansion of the gel in the surrounding solvent.

Spatial and Temporal Variation of the Displacement Vector. To obtain the spatial variation of the displacement vector, one introduces the following initial conditions:

$$\text{sphere} \quad u(r,0)/u(a,0) = r/a \quad (29)$$

$$\text{cylinder } (h \rightarrow \infty) \quad u(\rho,0)/u(b,0) = \rho/b \quad (30)$$

$$\text{disk } (b \rightarrow \infty) \quad u(z,0)/u(\pm h,0) = z/\pm h \quad (31)$$

In the limit case $\mu/M_{os} = 0$ the spatial and temporal variation of the displacement vector, satisfying eq 2 and conditions 14–16 and 29–31, is

$$\text{sphere} \quad \frac{u(r,t)}{u(a,0)} = 6 \sum_{n=1}^{\infty} e^{-t/\tau_n} N(n\pi) N(n\pi r/a) \quad (32)$$

$$\text{cylinder } (h \rightarrow \infty) \quad \frac{u(\rho,t)}{u(b,0)} = 4 \sum_{n=1}^{\infty} e^{-t/\tau_n} \frac{1}{\lambda_n^2 J_1(\lambda_n)} J_1(\lambda_n \rho/a) \quad (33)$$

$$\text{disk } (b \rightarrow \infty) \quad \frac{u(z,t)}{u(h,0)} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} e^{-t/\tau_{2n+1}} \frac{(-1)^n}{(2n+1)^2} \sin \left[\frac{z}{h} (2n+1) \frac{\pi}{2} \right] \quad (34)$$

The generalization of these solutions to the case $\mu/M_{os} \neq 0$ leads to

$$\text{sphere} \quad \frac{u(r,t)}{u(a,0)} = \frac{1}{\sum_{n=1}^{\infty} (N(X_n))^2} \sum_{n=1}^{\infty} e^{-t/\tau_n} N(X_n) N\left(X_n \frac{r}{a}\right) \quad (35)$$

$$\text{cylinder } (h \rightarrow \infty) \quad \frac{u(\rho,t)}{u(b,0)} = \frac{1}{\sum_{n=1}^{\infty} \frac{1}{X_n^2}} \sum_{n=1}^{\infty} e^{-t/\tau_n} \frac{J_1\left(X_n \frac{\rho}{b}\right)}{X_n^2 J_1(X_n)} \quad (36)$$

$$\text{disk } (b \rightarrow \infty) \quad \frac{u(z,t)}{u(h,0)} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} e^{-t/\tau_n} \frac{(-1)^n}{(2n+1)^2} \sin \left[\frac{z}{h} (2n+1) \frac{\pi}{2} \right] \quad (37)$$

The displacement at the free surface of the gel is obtained by letting respectively

$$r = a \quad \rho = b \quad z = h$$

The first term of the series (35–37) becomes predominant at large t and is given by respectively

$$\text{sphere} \quad -\ln \frac{u(a,t)}{u(a,0)} \simeq \frac{t}{\tau_1} + B_1 \quad (38)$$

with

$$B_1 = -\ln \frac{[N(X_1)]^2}{[N(X_1)]^2 + \sum_{n=2}^{\infty} [N(n\pi)]^2}$$

$$\sum_{n=2}^{\infty} [N(n\pi)]^2 = \frac{1}{6} - \frac{1}{\pi^2}$$

where we have used the approximation $X_n \simeq n\pi$ for $n > 1$.

$$\text{cylinder } (h \rightarrow \infty) \quad -\ln \frac{u(b,t)}{u(b,0)} \simeq \frac{t}{\tau_1} + B_2 \quad (39)$$

with

$$B_2 = -\ln \frac{1/X_1^2}{1/X_1^2 + \sum_{n=2}^{\infty} 1/\lambda_n^2}$$

$$\sum_{n=2}^{\infty} 1/\lambda_n^2 = \frac{1}{4} - \frac{1}{\lambda_1^2} = 0.077$$

within the approximation $X_n \simeq \lambda_n$ for $n > 1$.

$$\text{disk } (b \rightarrow \infty) \quad -\ln \frac{u(h,t)}{u(h,0)} \simeq \frac{t}{\tau_1} - \ln \frac{8}{\pi^2} \quad (40)$$

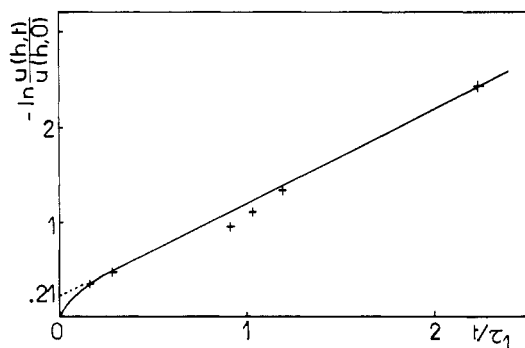


Figure 2. Variation of $-\ln [u(h,t)/u(h,0)]$ with the scaled time calculated from eq 37 relative to a disk with infinite radius. Crosses represent experimental data for a PDMS disk with $H/b = 1.14$.

B_1 and B_2 are decreasing functions of μ/M_{os} through the parameter X_1 . Their limit values are

$$\begin{aligned} \mu/M_{os} = 0.5 & \quad B_1 = 0.29 \quad B_2 = 0.23 \\ \mu/M_{os} = 0 & \quad B_1 = 0.5 \quad B_2 = 0.37 \end{aligned}$$

In a semi-log representation the theoretical curves representing eq 35–37 coincides closely for $t/\tau_1 > 0.25$ with the straight lines corresponding to eq 38–40. In Figure 2 is reported the theoretical variation of $-\ln [u(h,t)/u(h,0)]$ as a function of t/τ_1 .

Experimental Section

Swelling Experiments. The PDMS networks were prepared by end-linking α - ω functional precursor chains. Their synthesis, which is based on the classical addition reaction of a hydrogenosilane group onto a vinyl or allyl double bond, has already been described elsewhere.^{4,5} The precursor polymer with end-standing hydrogenosilane functions had a molecular weight $M_n \sim 9700$ daltons. Commercial (tetraallyloxy)ethane, used as a tetrafunctional cross-linker, was treated first with sodium and then distilled over sodium wire under vacuum. The networks used for the present investigation were prepared in toluene at 75 °C at a volume fraction 0.56.

The polyacrylamide gels were prepared by a standard redox reaction employing ammonium persulfate and tetramethylethylenediamine (TEMED). The concentrations used were 5 g of recrystallized acrylamide monomer, 0.133 g of N,N' -methylenebis(acrylamide), 40 mg of ammonium persulfate, and 400 μ L of TEMED dissolved in water to make a total volume of 100 mL. After thorough mixing, the preparations are poured through a small aperture in spherical or cylindrical glass molds. Once the gelation is performed, the molds are broken, and the gel spheres are transferred into a cell containing an excess of water. This time is taken to be zero ($t = 0$). At the swelling equilibrium the concentration of polymer in the polyacrylamide gel is 0.033 g cm⁻³, and it is 0.135 g cm⁻³ in the PDMS gel. The diameter of the gel sphere or the diameter and height of the gel cylinder are measured as a function of time on the screen of a profile projector by using a calibrated scale. All the experiments were carried out at room temperature.

Quasielastic Light-Scattering Experiments. To obtain an independent determination of the cooperative diffusion coefficient D , we measured the average decay rate $\bar{\Gamma} = DK^2$ of the auto-correlation function of light scattered from a polyacrylamide gel with the same composition as in the swelling experiments; K is the scattering wave vector. The dynamic light-scattering spectrophotometer operated in a photon-counting mode by using a Spectra Physics argon ion laser ($\lambda = 488$ nm) and a Brookhaven correlator.

Results

Sphere. Figure 3 shows the variation of $-\ln [u(a,t)/u(a,0)]$ for a PDMS spherical sample with final radius $a = 1.485$ cm. From the straight part of the curve one ob-

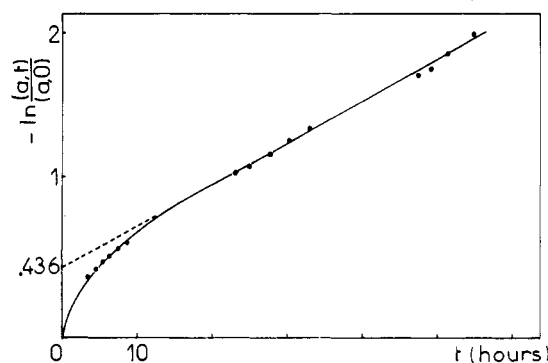


Figure 3. Experimental variation of $-\ln [u(a,t)/u(a,0)]$ versus time for a PDMS sphere with final radius $a = 1.485$ cm. From the slope of the linear part of the experimental curve one obtains $\tau_1 = 39.12$ h.

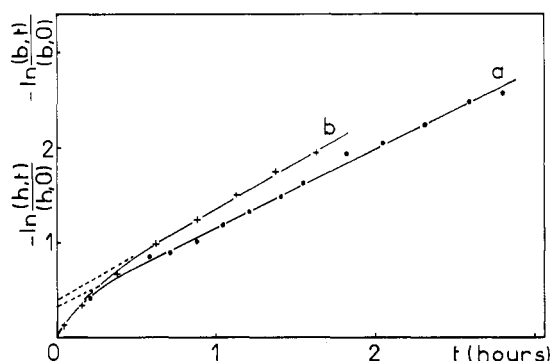


Figure 4. Experimental time dependences of $-\ln [u(b,t)/u(b,0)]$ (a) and of $-\ln [u(h,t)/u(h,0)]$ (b) for a PDMS cylinder (final diameter $2b = 0.431$ cm, final height $H = 2h = 1.0775$ cm). From the slopes of the linear parts of the curves one obtains $\tau_1 = 1.21$ h (a) and $\tau_1 = 1.04$ h (b).

tains $\tau_{\text{exptl}} = \tau_1 = 39.12$ h and $B_1 = 0.436$. This latter value corresponds to $X_1 = 2.98$.

From eq 17 and 26 one obtains the following for PDMS: $\mu/M_{os} \approx 0.12 \pm 0.05$; $D' = 15.9 \times 10^{-7}$ cm² s⁻¹; $D = 17.6 \times 10^{-7}$ cm² s⁻¹. Quasielastic light scattering experiments give

$$D_L = 18.0 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$$

The following results obtained from kinetics of swelling in polyacrylamide gels have already been reported.²

$$\begin{aligned} \mu/M_{os} &\approx 0.3 \pm 0.05 & D' &= (3 \pm 0.3) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1} \\ D &= (4.1 \pm 0.3) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1} \\ D_L &= (4 \pm 0.1) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1} \end{aligned}$$

One observes a good agreement between the values D_L and D obtained respectively by quasielastic light scattering and kinetics of swelling when taking into account the effect of a nonnegligible shear modulus. This is also illustrated in Figure 1, where the experimental values of D'/D_L are compared to the theoretical predictions for D'/D . The value obtained for μ/M_{os} is also in reasonable agreement with that obtained from combined use of light-scattering and stress-strain experiments.⁶

Cylinders. Figure 4 shows the variations of $-\ln [u(b,t)/u(b,0)]$ and $-\ln [u(h,t)/u(h,0)]$ as a function of time for a PDMS cylinder with final diameter $2b = 0.431$ cm and final height $H = 2h = 1.0775$ cm. From the slopes of the straight portions of the curves one obtains the following values of the relaxation time:

$$\tau_1(b) = 1.21 \text{ h} \quad \tau_1(H) = 1.04 \text{ h}$$

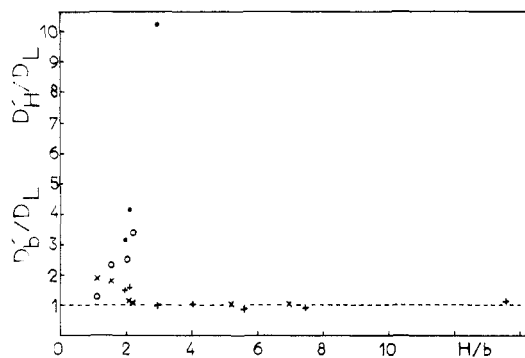


Figure 5. Variations of the apparent relative diffusion coefficients D'_b/D_L and D'_H/D_L as a function of the ratio H/b of cylindrical samples: PDMS (O, x); polyacrylamide (●, +).

From the value of $\tau_1(b)$ and with use of eq 27, strictly valid for a cylinder of infinite height, one can determine an apparent value of D' ; $D'_b = 18.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which gives

$$D'_b/D_L \simeq 1.03$$

The value $\tau_1 = 1.04 \text{ h}$ obtained from the time dependence of the height of the cylinder would lead, if inserted into eq 28, valid for a disk with infinite radius, to an apparent value $D'_H = 314 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which gives $D'_H/D_L = 17.4$.

Figure 5 shows the variations of the apparent relative diffusion coefficients D'_b/D_L and D'_H/D_L as a function of the ratio H/b for both PDMS and polyacrylamide gel samples. It can be seen that for $H/b \geq 3$ the apparent values of D'_b are in good agreement with the values obtained by quasielastic light scattering (cf. Figure 1). When H/b decreases to values smaller than 2, then the apparent values D'_H obtained from the theoretical expression derived for a disk with infinite radius approach the values obtained by quasielastic light scattering.

The ratio $D'_H/D_L = 1.25$ found for the PDMS cylinder with the smallest value of H/b (1.14) approaches the theoretical prediction of Figure 1 ($D'_H/D \simeq 1$) if one takes the value 0.12 ± 0.05 obtained for μ/M_{os} from intercept of Figure 3.

It must be noted that the measurement of the height of a disk in the course of swelling is more difficult to perform than that of the radius of a cylinder. Furthermore, eq 28 shows that D'_H/D for a disk is strongly dependent on μ/M_{os} .

Conclusion

The results presented in this paper show that the kinetics of swelling of neutral polymeric gels having the shape of a sphere, an elongated cylinder, or a flat disk are satisfactorily described by the model of Tanaka and Fillmore generalized to account for the nonnegligible value of the shear modulus. An important conclusion is that the diffusion coefficient obtained from the kinetics of swelling of an elongated cylinder is almost independent of the ratio μ/M_{os} . This is of practical relevance since it is often easier to prepare cylindrical samples than spherical ones. Furthermore, the comparison between the apparent diffusion coefficients measured from the kinetics of swelling of differently shaped samples of the same gel should provide

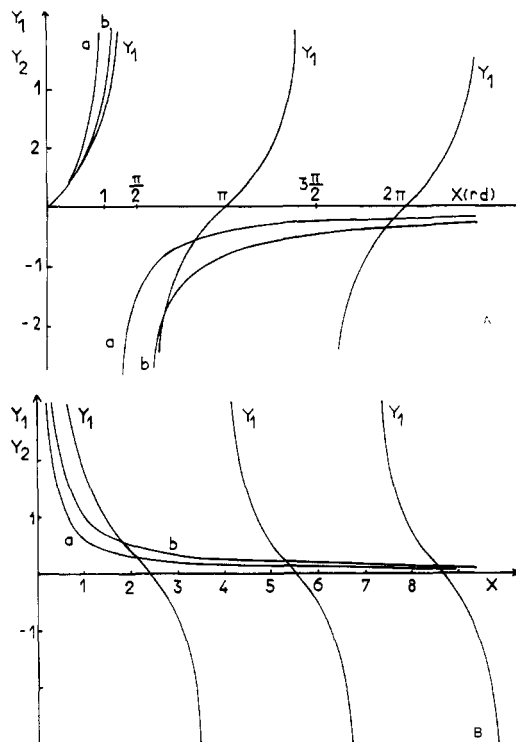


Figure 6. (A) Variation of $Y_1 = \tan X$ and $Y_2 = 4(\mu/M_{os})X / [(4\mu/M_{os}) - X^2]$ for $\mu/M_{os} = 0.3$ (a) and $\mu/M_{os} = 0.5$ (b). (B) Variation of $Y_1 = J_0(X)/J_1(X)$ and $Y_2 = 2(\mu/M_{os})X^{-1}$ for $\mu/M_{os} = 0.3$ (a) and $\mu/M_{os} = 0.5$ (b).

measurements of the ratio of μ/M_{os} . As an example, for a ratio $\mu/M_{os} \simeq 0.3$, the apparent diffusion coefficient measured from the time dependence of the height of a flat disk is almost twice that obtained from the time dependence of the radius of a sphere of same gel.

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Appendix

The roots of the relaxation equations (eq 17 and 20) are the abscissa of the intercepts of the curves representing (Figure 6, parts A and B) respectively the following functions:

$$Y_1 = \tan X \quad Y_2 = \frac{(4\mu/M_{os})X}{(4\mu/M_{os}) - X^2} \quad (\text{A1})$$

$$Y_1 = \frac{J_0(X)}{J_1(X)} \quad Y_2 = 2(\mu/M_{os})X^{-1} \quad (\text{A2})$$

Registry No. (Acrylamide)(N,N' -methylenebis(acrylamide)) (copolymer), 25034-58-6.

References and Notes

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