Self-diffusion of water in gelatin gels: 1. Macroscopic measurements by tracer technique

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The one-dimensional diffusion of water from a reservoir into gelatin gels of different concentrations ϕ was investigated. In full agreement with calculations based on the concept of an effective medium, it is shown that the self-diffusion coefficient D of water in the asymptotic region, $kR < 1$ (k = screening constant, R = radius of diffusible particles), varies as D/D_0 $(\phi = 0) = 1 - 1.87\sqrt{\phi}$, if $D(\phi = 0) = 1.35 \times 10^{-5}$ cm^2 s^{-1}. The function $D(T)$ is of the Arrhenius type, with the value of the activation energy, $E_A = 4.1$ kcal mol^{-1}, close to that of bulk water.

(Keywords: self-diffusion; gels; gelatin)

INTRODUCTION

The past decade has been marked by continuous progress in theoretical and experimental investigations of cooperative processes in polymer gels[1–13]. It has been theoretically established that the transport of small particles through a gel may be described by the model of self-diffusion of Brownian particles through a system of randomly distributed fixed obstacles. The mobility of diffusible particles in such a model can be limited by the hydrodynamic interaction of the particle with itself due to the reflections of hydrodynamic perturbations from the obstacles or scattering centres and by the direct scattering of particles with these centres. It is shown that the interpretation of hydrodynamic interactions based on the concept of an effective medium results in the fundamental root-mean-square relation of the self-diffusion coefficient D of tracer particles to the volume fraction ϕ of obstacles.

In mobility experiments, spherical proteins, viruses, latices or micellae are usually added as tracer particles to a semidilute solution or gel. Recently rather contradictory data on the value of the index v in $D(\phi^v)$ have been obtained. In water–dextran and water–hyaluronic acid, Laurent and co-workers[14,15] used ultracentrifugation and boundary spreading to measure the drag coefficient of proteins and larger particles (with radii R = 2.5 nm–0.365 μm) and found $v = 1/2$. Langevin and Rondelez[12] made sedimentation studies of a series of probes with R = 1.7–46.0 nm in water–polyethylene oxide, and found $v = 2/3$. Phillies and co-workers[4,5,9] studied the diffusion of spherical probe particles in different systems using quasi-elastic light scattering spectroscopy, and found v in the range of 0.8–1.0. Probe motion in water–dextran was also studied by Brown and Stilbs[13], who used pulsed field gradient n.m.r. to measure the self-diffusion of a polyethylene oxide probe species, and by Turner and Hallett[11], who used light scattering spectroscopy to study D of polystyrene spheres; these two studies found $v = 1$.

Analysis of the above results shows that the observed discrepancy between experimental and theoretical v may be associated with the relatively large size of the tracers used, the smallest of which was of the order of nanometres. In this case an effective but not an asymptotic v is experimentally measured, since the conditions for which the theory is written in an explicit form are violated. Thus, the object of the present work is to determine the asymptotic index v within the region of validity of theoretical predictions, which is easily attained due to the small size of solvent molecules used as tracers. We developed a procedure for macroscopic determination of the self-diffusion coefficient of a solvent in polymer gels and studied the relation of the self-diffusion coefficient of water to the polymer concentration in gelatin hydrogels.

THEORETICAL BACKGROUND

The self-diffusion coefficient of a fluid in a polymer gel can be determined by the tracer technique, n.m.r. or quasi-elastic neutron scattering (QENS). In the tracer technique, some particles are labelled with isotopes which can be followed due to their specific properties; thus, labelling with radioactive isotopes enables their travel to be followed by radiation detectors[16,17]. Using isotope labelling, one can determine the number of diffused tracers in a sample by mass spectrometry[18]. It should be noted that there is a basic difference between the above methods, namely that they probe molecular motions at different observation times t_{obs}. In the tracer technique,

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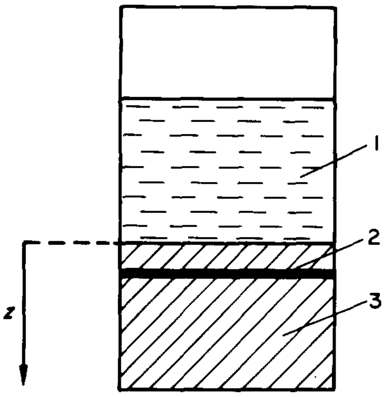

Figure 1 Diagram of cell for measuring the diffusion coefficient of a solvent in gels by the slow neutron transmission technique: 1, H_2O; 2, neutron beam (incident onto the figure plane);3, D_2O-saturated gelatin gel

n.m.r. and QENS, values of t_{obs} are $\sim 10^2$–10^4 s, 10^{-4}–10^{-6} s and 10^{-10}–10^{-13} s, respectively*.

In this work a procedure is described for macroscopic measurements of the self-diffusion coefficient of a solvent in a gel by the slow neutron transmission technique[20], which is in fact analogous to the tracer method. Here protonated solvent molecules diffusing into the gel, originally saturated with the deuterated analogue of the same solvent, may be used as tracers (*Figure 1*). Since the bulk neutron cross-section of interaction between slow neutrons and hydrogen exceeds that of deuterium, the transmission, i.e. the ratio of transmitted to incident neutron beam intensities, is considerably dependent on the number of protonated molecules diffused into the gel. The narrow neutron beam formed by a collimation system and scanned vertically can measure the variation of transmission gradients in time or can investigate the kinetics of transmission variations in a chosen gel cross-section perpendicular to the direction of tracer flow.

As shown in ref. 21, the weight fraction C of diffused tracers is related to the transmission P by:

$$C(t,z) = b^{-1}[\ln(P,z) - a] \qquad (1)$$

where t is the time, z is the coordinate measured from the gel–reservoir interface along the direction normal to the flow, $a = \ln P_1 + [\ln(P_2/P_1)]^{-1}$ and $b = (\sigma_P/\sigma_D)[\ln(P_2/P_1)]^{-1}$ (a and b are experimental constants determined by calibration measurements), P_1 and P_2 are the transmissions of, respectively, an empty cell and a cell containing gel of a given concentration saturated with a deuterated solvent, σ_P and σ_D are the bulk cross-sections of slow neutron interactions with, respectively, the molecules of protonated and deuterated solvents. Therefore the variation of tracer concentrations in a local gel cross-section can effectively be followed by the slow neutron transmission technique, thus avoiding obvious inconveniences associated with the use of radioactive tracers or the complex sampling for mass spectrometry measurements.

To determine the self-diffusion coefficient D of tracers from the functions $C(t, z)$, it is necessary to solve Fick's equation describing the one-dimensional tracer diffusion in a polymer gel:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} \qquad (2)$$

Using the operator method and the Laplace transform $C(t,z) \rightarrow \xi(P,z)$, we have[22]:

$$P\xi(P,z) - C(0,z) = D\frac{d^2\xi(P,z)}{dz^2} \qquad (3)$$

where $C(0, z)$ is the initial distribution of diffusible particles in a gel. Under the boundary conditions:

$$\xi(P,0) = \xi_{\text{input}}(P) \qquad z = 0 \qquad (4)$$

$$\frac{d\xi}{dz} = 0 \qquad z = \delta \qquad (5)$$

where δ is the thickness of a gel sample, assuming $C(0, z) = 0$, we have:

$$\xi(P,z) = \xi_{\text{input}}(P)\frac{\cosh\left(\frac{\delta - z}{\sqrt{D}}P^{1/2}\right)}{\cosh\left(\frac{\delta}{\sqrt{D}}P^{1/2}\right)} \qquad (6)$$

Assuming the step input (concentration shock at the moment $t = 0$), the original function takes the form:

$$C(t,z) = \bar{C}\left\{1 - 2\sum_{n=0}^{\infty}(-1)^n\frac{\cos[(n+1/2)\pi(1-z\delta)]}{(n+1/2)\pi} \times \exp\left[-\frac{D\pi^2(n+1/2)}{\delta^2}t\right]\right\} \qquad (7)$$

where $\bar{C}$ is an average concentration of tracers in the gel–reservoir system. The obtained equation is indicative of the spectrum of relaxation times of diffusible particle concentrations. The detailed analysis shows that in the first approximation the first part of equation (7) can be presented as:

$$C(t,z) = \bar{C}[1 - \exp(-t/\tau)] \qquad (8)$$

where

$$\tau = \frac{4z^2}{\pi^2 D} \qquad (9)$$

is a certain characteristic relaxation time of C at a distance z from the gel–reservoir interface.

From equation (8), it follows that τ is the inverse slope of the linear function $\ln[1 - C(t,z)/\bar{C}]$ against time. If τ is known, the self-diffusion coefficient D can easily be found for the corresponding z by equation (9).

EXPERIMENTAL AND RESULTS

Samples

Gelatin, of photographic grade, was used to prepare gels. The viscosity of a 10% aqueous solution at 40°C was 2×10^{-2} N m^{-2} s, its isoelectric point was 4.7 and pH was 6.2. Dry gelatin was first swollen in the appropriate amount of D_2O (with 11% residual water contained in the gelatin itself) for 2 h. Then the mixture was warmed up to 45°C and stirred thoroughly until dissolution was complete. The volume fraction of gelatin ϕ was calculated by assuming the additivity of gelatin and solvent volumes, taking the gelatin density as

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*Using backscattering and spin-echo spectrometers[19], the time scale probed by QENS can be increased to 10^{-7}–10^{-9} s

1.465 g cm^{-3}. The solution was poured into a thin-walled aluminium cell and quenched to 16°C, at which temperature the gel solution was aged for 12 h. The values for gelation temperature and ageing time were chosen on the basis of data[23] on the kinetics of gelation relative to the quenching temperature. These conditions enabled completion of the initial rapid gelation stage, thus these gels can be considered as quasi-equilibrium systems during the times of observation used in the experiment.

Procedure and results

The investigations were performed on a research water–water reactor at the Nuclear Research Institute, Academy of Sciences, Kiev; the reactor is described in ref. 20. The system of collimators formed a neutron beam with a wavelength of 0.154 nm and a width of 0.5 mm. The cell was placed in a temperature-controlled container on a lift, which enabled it to be moved vertically relative to the neutron beam with a minimal spacing of 0.1 mm. A two-stage thermostatting system controlled to ± 3 mK was used to maintain samples at constant temperature. The cell temperature was measured with a platinum resistance thermometer. Thermodiffusion was absent from the system because of an infinitely small gradient (of the order of several mK along the height of the cell). The absolute error of concentration measurements did not exceed $\Delta C = 4 \times 10^{-4}$ at a cell thickness of 10 mm and exposure time of 5 min. At the same time the absolute error of self-diffusion coefficient measurements was $\Delta D = 3 \times 10^{-7}$ cm^2 s^{-1}.

At the moment $t = 0$, distilled water was added to the cell containing the D_2O-saturated gel. The total height of the gel sample and water column was 30 mm. The kinetics of variation of cell transmissions as a function of height is shown in *Figure 2*; it can be seen that the shape of the curves $P(z)$ changes with time due to diffusion of water.

The water concentration at a given height z at a moment of time t was calculated by equation (1). To verify the consistency of the obtained data, we determined the self-diffusion coefficient of water in the gelatin gel with $\phi = 0.0338$ by the functions $C(t)$ derived for different z values. For this purpose $\ln[1 - C(t, z)/\bar{C}]$ was plotted against t (*Figure 3*); the slope of the lines (values of τ^{-1}) was determined by the least-squares method and corresponding D values were found by using equation (9). The difference between these self-diffusion coefficients did not exceed the above absolute error of their measurement.

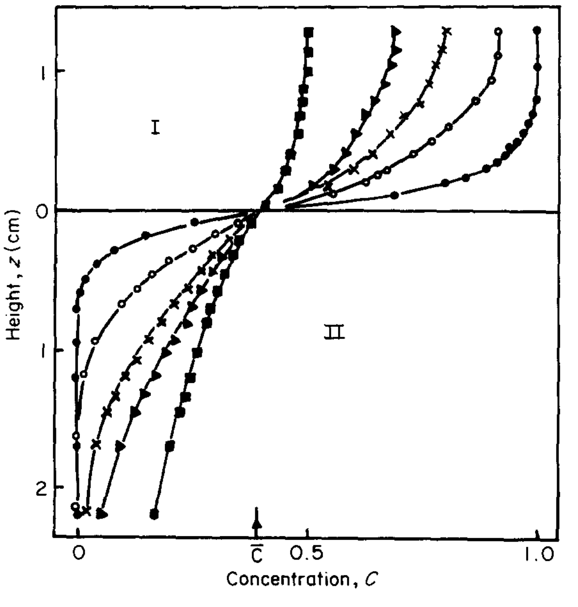

Figure 2 Kinetics of variation of H_2O concentration in reservoir (I) and gel (II) as a function of height. ●, 0.3 h; ○, 2.4 h; ×, 8 h; ▼, 25 h; ■, 37 h. The value of $\bar{C}$ corresponds to the average H_2O concentration in the cell

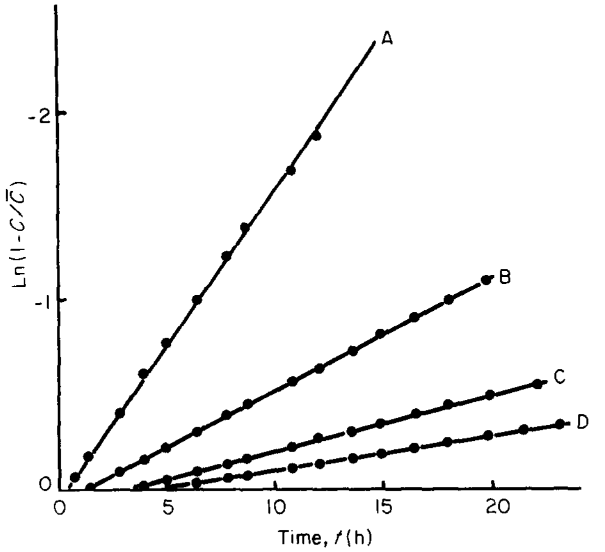

Figure 3 Processing of the functions $C(t, z)$ by equation (8) for the gelatin gel with $\phi = 0.0338$ and different distances z from the gel–reservoir interface; A, 7.2 mm; B, 12.2 mm; C, 17.2 mm; D, 22.2 mm

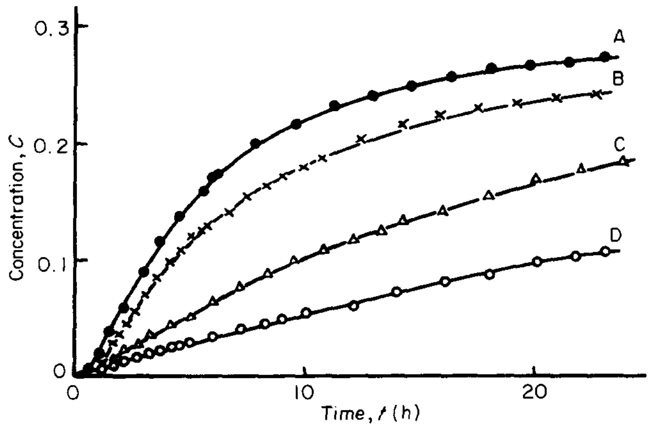

Figure 4 Kinetic function C for $z = 7.2$ mm and volume fractions of gelatin ϕ: A, 0.0338; B, 0.0683; C, 0.1769; D, 0.2536

Henceforth the functions $C(t)$ were measured for gels of different concentrations at a fixed distance from the gel–reservoir interface ($z = 7.2$ mm). Several kinetic curves are given in *Figure 4*. Processing of the data by the described procedure enabled the self-diffusion coefficient of water to be related to the concentration of the gelatin gel (*Figure 5*). The values of D at a fixed gel concentration ($\phi = 0.0475$) as a function of temperature are given in *Figure 6*.

DISCUSSION

Within the concept of an effective medium, it is shown[2] that in the limit of infinitesimal concentration of

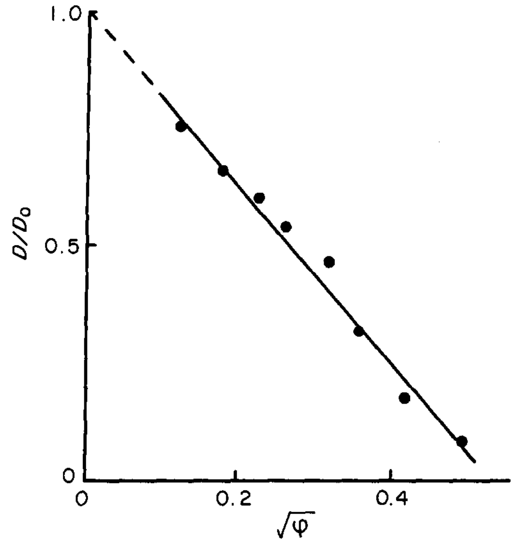

Figure 5 Self-diffusion coefficient of water as a function of $\sqrt{\phi}$ at 16°C

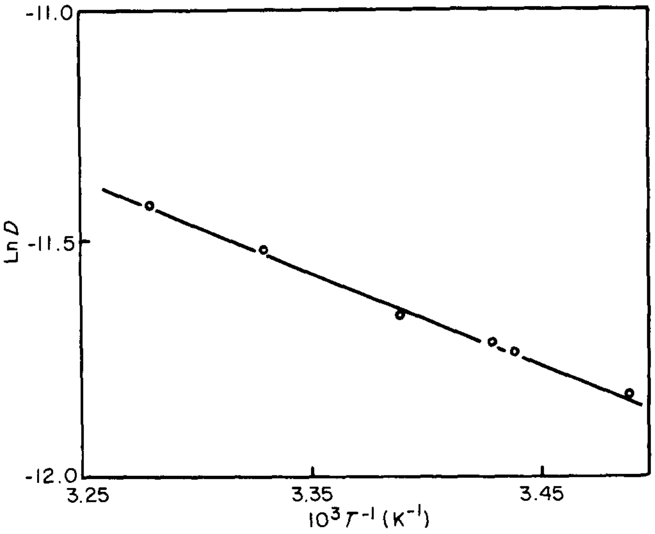

Figure 6 Self-diffusion coefficient of water as a function of temperature with $\phi = 0.0475$

obstacles, the self-diffusion coefficient should vary according to the law:

$$D/D_0 = 1 - A\sqrt{\phi} - B\phi, \qquad \phi \to 0 \qquad (10)$$

where $D_0 = D(\phi = 0)$, A and B are the positive constants depending on diffusible particle sizes and repulsive interaction range of scattering centres. In equation (10) the root-mean-square dependence on ϕ corresponds to the contribution from the hydrodynamic self-interaction, and the substantial linear dependence corresponds to the scattering mechanism. In ref. 3 the following equation was obtained for systems with purely hydrodynamic interactions of Brownian particles with obstacles:

$$D/D_0 = \exp(-kR) \approx 1 - kR \qquad \text{if } kR < 1 \quad (11)$$

Here k is the screening constant which characterizes the resistance of a polymer network to a fluid flow (for random coil polymers with the Debye–Bueche screening $k \sim \sqrt{\phi}$) and R is the radius of diffusible particles. It follows from equation (11) that if R is small enough, kR may remain in the asymptotic region of <1 when the concentration of obstacles varies over rather wide ranges. The function $D(\phi)$ in the $D/D_0 = \sqrt{\phi}$ plane is given in *Figure 6*. Within the experimental error, this function is a straight line described by:

$$D/D_0 = 1 - 1.87\sqrt{\phi}, \qquad D_0 = 1.35 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1} \qquad (12)$$

over a wide range of gelatin concentrations of $0.0168 \leqslant \phi \leqslant 0.2536$. At the same time $kR = 1.87\sqrt{\phi}$ varies in the range of $0.24 \leqslant kR \leqslant 0.94$. As can be seen in *Figure 5*, the function $D(T)$ measured in the temperature range of $14°\text{C} \leqslant T \leqslant 33°\text{C}$ is satisfactorily described by the Arrhenius law, with the activation energy $E_A = 4.1$ kcal mol^{-1} being close to that of bulk water[24].

Thus, the experimental data confirm the theoretical predictions[2,3] that the self-diffusion coefficient of small tracers in a polymer gel related to a volume fraction of obstacles is described by an asymptotic index $v = 0.5$. The undistorted root-mean-square relation valid for the whole range of polymer concentrations investigated is indicative of the purely hydrodynamic nature of self-diffusion of water in gelatin gels*. This procedure will also be useful for measuring the interdiffusion of low-molecular-weight solvents in polymer gels or the self-diffusion of macromolecules in porous media of different nature.

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*It is now established that water molecules in gelatin gels may stay in 'free' and 'bound' states characterized by considerably different mobility[25]. In the experiment described the mass transfer of water in gel pores, which can be identified with the self-diffusion of free water, was investigated (this is confirmed by the similar value of measured activation energy to that of bulk water). The measurements of the total self-diffusion coefficient and its components corresponding to the contributions from free and bound water in gelatin gels have already been performed by QENS[26]

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