Probe diffusion in gels

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The diffusion constant of probe molecules in the poly(acrylamide) gel is measured at various concentrations of the acrylamide using probe molecules that have different molecular weights. It is found that the normalized diffusion coefficients of the probe molecules are superposed onto a single master curve when the results are plotted as a function of a variable $M^{1/3}\phi^{3/4}$. The results indicate the scaling function of the form $D/D_0=f(x)$, where $x=R/\xi$.

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INTRODUCTION

Transport phenomena in and through gels have attracted much experimental and theoretical attention in recent years because of the significance of such phenomena in a wide variety of contexts in complex fluids, biological transport, and separation technologies. One of the physical quantities, which characterizes the transport properties of gel, is the diffusion coefficient of substances (probe molecules) in the gel. The probe molecule, when dissolved in a simple fluid, thermally fluctuates in time and space. The fluctuation and the friction ζ between the probe molecule and the fluid determine the diffusion coefficient of the probe molecule in the solution.

$$D=\frac{k_B T}{\zeta} . \tag{1}$$

Here, k_B and T are Boltzmann's constant and the absolute temperature, respectively. The hydrodynamic friction of the fluid of the viscosity η that is experienced by a probe molecule of the hydrodynamic radius R_h is given by the following equation:

$$\zeta=6\pi\eta R_h . \tag{2}$$

The combination of Eqs. (1) and (2) yields the Stokes-Einstein relationship [1]. The probe molecules, when introduced into the gel, however, experience additional friction by the polymer network of the gel as well as the friction of the fluid. Thus the diffusion of the probe molecule slows down because of the presence of the polymer network of the gel. Extensive studies of the diffusion in the gel have been done in various systems of the gels and the probe molecules [2–4]. The experimental results obtained so far are, however, still a matter for discussion. From today's knowledge about the physical properties of gels, the previous studies of the probe diffusion in gels have been made under not ideal experimental conditions.

The purpose of this paper is to describe detailed studies on the probe diffusion in the poly(acrylamide) gel. The diffusion coefficients of the probe molecules are measured under various experimental conditions of the concentration of the gel and the molecular weight of the probe molecules by a pulsed field gradient NMR technique. Then the results are discussed on the basis of the scaling theory.

EXPERIMENT

The sample gels were prepared by the standard radical copolymerization of the acrylamide (main constituent) and the *N,N*-methylenebisacrylamide (cross-linker). All the reagents used here were of the electrophoresis grade obtained from BioRad and used without further purification. The predetermined amount of acrylamide *N,N'*-methylenebisacrylamide and ammonium persulfate (initiator; final concentration is 0.04 wt% in the pregel solution) were dissolved into 2 ml of solvent (H_2O:D_2O=9:1) which contains a probe molecule at a concentration of 10 wt%. The pregel solution was then degassed and polymerized in a nuclear magnetic resonance tube of diameter 10 mm at a temperature of 60°C for 1 h. The concentration of the gel was changed from 0.02 to 0.5 g/ml while the concentration of the cross-linker was fixed at 2 mol%.

The probe molecules used in this study were water, ethanol, glycerin, low molecular weight poly(ethyleneglychol), and sucrose. The molecular weights of these probe molecules are 18, 46, 92, 200, and 342, respectively.

The diffusion experiments were made on a JEOL FX-60Q nuclear magnetic resonance spectrometer, which was equipped with a pulsed field gradient apparatus NMPL-502, at a frequency of 60 MHz. The temperature was controlled to 30.0±0.5°C.

RESULTS

The diffusion coefficients of the probe molecules are determined from the intensity of the spin echo signal. The principles of the pulsed field gradient nuclear magnetic resonance technique have already been reported in detail so that we only glance at the background [5–7].

The intensity of the spin echo signal A in the presence

of the field gradient pulses is expressed as follows:

$$A = A_0 \exp\left[-\gamma^2\delta^2G^2\left[\Delta-\frac{\delta}{3}\right]D\right]$$
$$= A_0\exp[-DK(\delta)] \,. \quad (3)$$

Here, A_0 is the echo amplitude in the absence of the field gradient pulses. D, δ, G, γ, and Δ denote the diffusion coefficient of the probe molecule, the duration of the field gradient pulse, the intensity of pulse field gradient, the magnetogyric ratio of the observed nucleus, and the time interval between the leading edges of the field gradient pulses, respectively. It is therefore clear that the intensity of the spin echo signal decreases upon increasing the duration of the field gradient pulse δ when G and Δ are fixed at certain values. Typical results thus obtained are shown in Fig. 1. Although the poly(acrylamide) gel is present, the spectra of the polymer network are not observed in the entire concentration region of acrylamide at this resolution because of the short spin-lattice relaxation time of protons of the gel network. The intensities of the spin echo signal are determined from the height of these spectra. Then the ratio A/A_0 is plotted in Fig. 2 as a function of $K(\delta)$ in a semilogarithmic manner. The diffusion coefficient of the probe molecule can be determined from the slope of the straight line in Fig. 2.

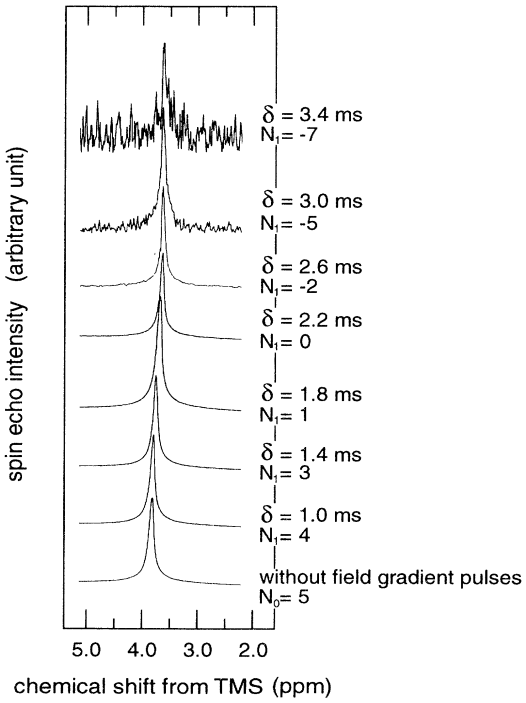

FIG. 1. Spin echo signals of water protons in poly(acrylamide) gel. The concentration of the gel is 20%. Signals are obtained at different values of δ and the gain N_1 given in this figure. The gain is changed, so that the height of the signals becomes almost the same, to obtain the maximum accuracy. The actual intensity of the signal is calculated by $A(\delta) = A \times 2^{-N}$, where A and N are the maximum height of the signal of the spectra and $N = N_0 - N_1$. The height of the signal that is taken without field gradient pulses corresponds to A_0. The intensity of the pulse field gradient G and the time interval between the leading edges of the field gradient pulses Δ are fixed to 25.34 G/cm and 100 ms in these measurements.

The diffusion coefficients of the probe molecules in the gel thus obtained are shown in Fig. 3 as a function of the concentration of acrylamide. It is clear from Fig. 3 that the diffusion coefficients of the probe molecules decrease with increasing concentration of the gel. It is also clear that the diffusion coefficients of the probe molecules decrease with increasing molecular weight of the probe molecules at a constant concentration of the gel.

These results are intuitively explained as follows. The diffusion coefficients of the probe molecules depend on the mesh size of the polymer network as well as the size of the probe molecule. The diffusion coefficient of the probe molecule decreases with increasing size of the probe molecule when the mesh size, and hence the concentration of acrylamide, is fixed at a certain value. This indicates that the friction of the polymer network becomes dominant if the sizes of the probe molecule approach the mesh size of the polymer network. On the other hand, the diffusion coefficient of a probe molecule decreases with the concentration of the polymer network. These results also indicate that the friction of the polymer network becomes dominant when the mesh size of the polymer network approaches the size of the probe molecule. It is, therefore, expected that it is the ratio of the sizes of the probe molecules and the polymer mesh that determines the diffusion coefficient of the probe molecules in the gel.

DISCUSSION

It is well established that the polymer network of the gel fluctuates in time and space. The fluctuation of the polymer network of the gel is well described by the

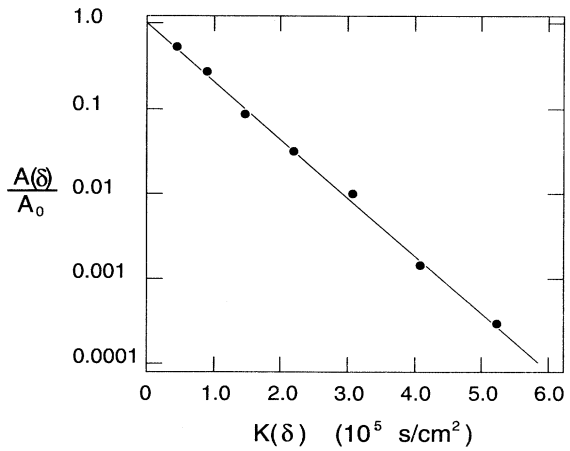

FIG. 2. The relationship between the normalized intensity of the spin echo signal, which was obtained from the results shown in Fig. 1, and $K(\delta)$. The straight line in this figure is the result of the least-squares fitting. The diffusion coefficient of water molecules, which was calculated from the slope of the straight line, in a 20% poly(acrylamide) gel yields $D = 1.5_8 \times 10^{-5}$ cm^2/s.

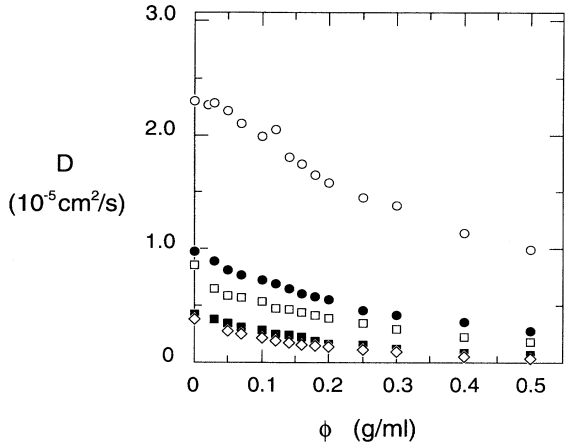

FIG. 3. The concentration dependence of the diffusion coefficients of the probe molecules. The symbols represent the following: ○, water; ●, ethanol; □, glycerin; ■, poly(ethyleneglychol) and ◇, sucrose. The data points at $\phi=0$ indicate the diffusion coefficient of the probe molecules in the aqueous solution. These values are also determined by the pulsed field gradient NMR measurements.

cooperative diffusion coefficient of the polymer network of the gel that is determined from the spectrum of light scattered from the polymer network of the gel [8]. Since the cooperative diffusion coefficient of the gel is much smaller than that of the probe molecules, the polymer network of the gel behaves as fixed obstacles for the diffusion of the small molecules in the gel. If the specific interactions between the polymer chain of the poly(acrylamide) gel and the probe molecules are negligible, the diffusion coefficients of the probe molecules are determined only by the mesh size of the polymer network and the sizes of the probe molecules. The mesh size of the polymer network is reasonably assumed to be proportional to the correlation length ξ that represents the average distance between two neighboring contact points of the polymers in a good solvent.

In the modern statistical theory of the polymer systems, many physical quantities are expressed as a function of the relevant length of the system [9]. The relevant length scales of the probe diffusion processes in the gel are the correlation length of the polymer network of the gel and the size of the probe molecule. It is, therefore, natural to expect the following scaling function $f(x)$ for the diffusion coefficient of the probe molecule in the gel:

$$\frac{D}{D_0}=f(x), \tag{4}$$

where D_0 is the diffusion coefficient of the probe molecule in the simple fluid and x denotes the relevant scaling variable of the form

$$x=\frac{R_h}{\xi}. \tag{5}$$

It is expected that the correlation length of the polymer network depends on the concentration as well as the swelling ratio of the gel [9]. In the present study, however, the volume of the gel is fixed when gels are prepared so that the measurements are carried out under isochoric conditions. The correlation length of the polymer network is, therefore, determined only by the predetermined concentration ϕ of acrylamide in the pregel solution. It has been reported that the concentration dependence of the correlation length is well explained by the following power law relationship when the cross-linking density is low enough [9,10]:

$$\xi \propto \phi^{-3/4}. \tag{6}$$

Since the probe molecules used in this study are rather compact molecules, we assume a power law relationship for the size of the probe molecule R_h and the molecular weight of the probe molecule M.

$$R_h \propto M^{1/3}. \tag{7}$$

Substitution of Eqs. (6) and (7) into Eq. (5) yields the scaling variable of the form

$$x=\frac{R_h}{\xi} \propto M^{1/3}\phi^{3/4}. \tag{8}$$

The results shown in Fig. 3 are thus plotted in Fig. 4 according to the scaling variable x given in Eq. (8). It is found from Fig. 4 that all the reduced diffusion coefficients of the probe molecules in the gel D/D_0 that were obtained at different concentrations of the acrylamide are well expressed by a single master curve. Furthermore, these results strongly suggest, though there is a scattering of data, the scaling function of the form

$$\frac{D}{D_0} \propto \exp(-M^{1/3}\phi^{3/4}). \tag{9}$$

According to the calculation by hydrodynamic theory, the scaling function of the diffusion coefficient is expected to be [11,12]

$$f(x)=\exp(-x). \tag{10}$$

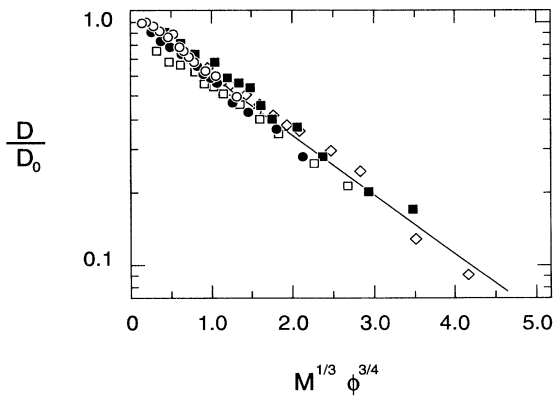

FIG. 4. The relationship between the normalized diffusion coefficients of the probe molecules in the gel D/D_0 and the scaling variable $M^{1/2}\phi^{3/4}$. Symbols are the same as in Fig. 3. The straight line in this figure represents the result of the least-squares analysis.

The experimental results obtained here are in good agreement with these theories [13].

Poly(acrylamide) gel is widely used as a matrix in separation technologies. One of the reasons is that poly(acrylamide) gel is noninteractive with many substances such as proteins. This is a main reason why the simple scaling relationship is realized in this system. If the gel strongly interacts with the probe molecule, for instance through the selective adsorption of the probe molecule, the diffusion process of the probe molecule in the gel is significantly modified from the simple picture so that such effects should be explicitly taken into account in the theory. Besides this, the choice of the probe molecules is also important. In this study, nonionic and hydrophilic substances are chosen as the probe molecules by which we can avoid complications due to the interactions between the polymer network and the probe molecules. Furthermore, these probe molecules are rather compact. We can, therefore, expect a simple power law relationship between the radius and the molecular weight of the probe molecule. If, for instance, flexible polymers of large molecular weight are chosen for the probe molecules, the diffusion process of the polymer chain due to the reptation becomes effective. In such a case the probe diffusion process in the gel is expected to be quite different from the diffusion process of small molecules.

Finally, it is worth noting the effects of the density fluctuations of the gel. It has been shown that the poly(acrylamide) gel becomes opaque at the onset of gelation under certain gelation conditions [14,15]. This opacification of the gel is caused by the inhomogeneous spatial density distribution of the polymer network. The opalescence which appears in the gel is static in time so that such a fluctuation is called the static fluctuation. It is shown by frictional measurements of the poly(acrylamide) gel that the static fluctuation of the polymer network of the gel appears in the region even though the gel looks completely transparent [16]. Hence, it is generally expected that some regions of the gel are more dilute and other regions are denser even in transparent gels. This static density fluctuation of the polymer network creates nonuniform frictional resistance to the diffusion of probe molecules in the gel. The friction of the polymer network is small in the dilute region so that it serves as an open path for the diffusion of the probe molecules. Hence, small molecules easily permeate through the open path. In contrast, the dense regions block the diffusion of the probe molecules behaving as a closed path for the probe diffusion process. Hence, in this case, the relevant length scale of the gel for the probe diffusion process is determined by the static density fluctuations of the polymer network of the gel rather than the correlation length. The simple scaling relationship for the correlation length, therefore, cannot be applied for such a static density fluctuation of the polymer network of the gel. This is, presumably, a reason for the discrepancy between the theoretical results and the experimental results so far reported. Recently, it was reported that the static density fluctuation of the gel is determined by the relative location of the gelation point and the phase diagram of the polymer solution [17]. The static density fluctuation of the polymer network becomes dominant when the reaction system is close to the phase boundary. Since acrylamide-water is a typical upper critical solution temperature system, the effects of the density fluctuation becomes less effective as the reaction temperature is raised. In this study, the sample gels are, therefore, prepared at a temperature of 60 °C to avoid the complications that arise from the static density fluctuation of the polymer network.

Further detailed studies of the probe diffusion in various gels are necessary for the full understanding of the transport phenomena in gels. It would be of interest to study a gel near its critical point since the correlation length of the dynamic density fluctuation diverges at this point. The diffusion coefficient of the probe molecules may increase at the critical point of the gel according to the results of frictional measurements of the gel [18]. Recently such anomalous behaviors have indeed been observed and will be reported elsewhere.

CONCLUSIONS

It is found that the diffusion coefficients of the probe molecules in poly(acrylamide) gel are well explained by a simple scaling theory. This fact indicates that the diffusion of the probe molecules in poly(acrylamide) gel is mainly determined by the geometrical futures of the polymer network and that of the probe molecules, namely, the correlation length of the polymer network and the hydrodynamic radii of the probe molecules.

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[13] The mesh size of poly(acrylamide) gel can be estimated from the slope of the straight line in Fig. 4, slope $=-0.243$, by a simple calculation. The prefactor of the scaling variable x is assumed to be $-(4/3\pi\rho N_A)^{-1/3}\xi_0^{-1}\log_{10}(e)$ for the spherical probe molecule of density ρ. Here, N_A represents Avogadro's number. Assuming $\rho\approx 0.7$, the correlation length ξ_0 is obtained to be 1.5 Å. The mesh size of 2.5% poly(acrylamide) gel is then calculated to be about 23 Å from Eq. (6), which is comparable to 11 Å found in the dynamic light scattering studies by T. Tanaka, Phys. Rev. A **17**, 763 (1978).
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