TRANSPORT IN GELS

MASAYUKI TOKITA

Department of Chemistry for Materials, Faculty of Engineering, Mie University, Tsu 514-8507, Japan
Fax: 81-059-231-9471, e-mail: tokita@chem.mie-u.ac.jp

We study the transport of substance across the gels by the time-lag method. The diffusion coefficient of potassium ion, which is used as a diffusing substance, slightly increases with temperature in poly(acrylamide) gel. On the other hand, an anomaly is found in the case of thermo-senisitive gel, that is, poly(N-isopropylacrylamide) gel. The diffusion coefficient of the probe substance drastically increases near the volume phase transition point of the gel. These results indicate that the transport process through the gel is markedly influenced by the critical density fluctuations of the polymer network.
Key words: thermo-sensitive gel, volume phase transition, diffusion, critical density fluctuation

1. INTRODUCTION

Gels are typical complex system that consists of three-dimensional polymer network and solvent. The volume fraction of the polymer network is usually much less than that of the solvent. The solvent in the gel, hence, forms the maze of pore. It has been well established that the gel shows the volume phase transition in response to the environmental change [1]. In the vicinity of the volume phase transition point, the polymer network of the gel fluctuates in time and space. Such a structural fluctuation may influence the transport properties of the gel [2]. Here, thus, we study the critical transport properties of the gel by the diffusion of probe molecule across the gel.

Recently, we have reported that the diffusion coefficient of substances through the gel can be determined by using the time-lag method [3]. The principle of time-lag method and typical experimental results are shown in Fig 1. The diffusion coefficient of substance, D, can be calculated by the time-lag, τ, which appears in the elution time course, $C(t)$, as follows

$$C(t) \approx K_c (t - \tau) \qquad (t \gg \tau) \qquad 1)$$

and

$$D = d^2/6\tau. \qquad 2)$$

Here, K_c and d are an apparatus constant and the thickness of the gel. Here, we report the temperature dependence of the diffusion coefficient of inorganic ion across poly(acrylamide) gel (AAM gel) and poly(N-isopropylacrylamide) gel (NIPA gel). The later gel is known as a thermo-sensitive gel which undergoes the discontinuous volume phase transition when heated in water [4].

2. EXPERIMENTAL

The sample gels were prepared by the radical copolymerization of the monomer and the cross-linker. Acrylamide, ammonium persulfate, N, N, N',

N'-tetramethylethylenediamine, and N, N'-methylene-bis-acrylamide were purchased from BioRad Japan and used without further purification. N-isopropylacrylamide was a gift from KOHJIN and used after re-crystalization.
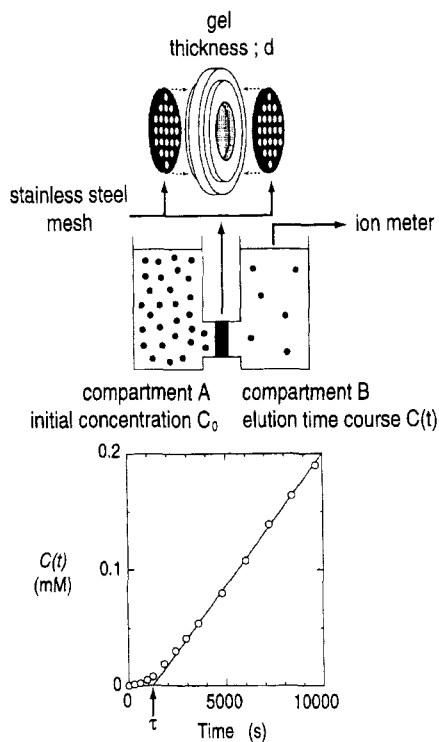

Fig.1 Schematic illustration of the time-lag apparatus (upper) and typical experimental results of the elution time course, $C(t)$, (bottom). The surface of the sample gel is fixed by the stainless steel mesh to prevent the swelling of the gel. The arrow in the bottom figure indicates the time-lag.

The concentration of the pre-gel solutions were fixed at 700 mM. The molar ratio of the main constituents and the cross-linker was also fixed at 100 : 1. The pre-determined amount of the main constituents and the cross-linker were dissolved into distilled and de-ionized water. The accelerator was added to the pre-gel solution at a concentration of 0.24 % (vol./vol.). Then the pre-gel solution was de-gassed for 20 min after immersing the gel mold that is illustrated in Fig 1. The initiator was added to the pre-gel solution at a concentration of 0.04 % to initiate gelation. The gelation reactions were made at room temperature in the case of AAM gel and at 4 °C in the case of NIPA gel. The gel mold, in which sample gel was contained, was taken out and washed in Tris-HCl buffer (200 mM, pH 7.0) that is also used as a solvent of measurements. The thickness of the gel was measured accurately after the diffusion experiments and was about 1.5 ,nm.

The diffusing substance used in this study was potassium ion that was used in a form of potassium chloride. The pre-determined amount of potassium chloride solution was poured into the compartment A in Fig 1. The initial concentration of potassium chloride in the compartment A was fixed at 50 mM. Then the elution time course of the sodium ion, $C(t)$, in the compartment B in Fig 1 was measured using an ion meter(HORIBA, F-23, Japan) that was equipped with the potassium ion selective electrode. Temperature was controlled by a circulating bath system within an accuracy of 0.1 °C.

3. RESULTS

Figure 2 shows the temperature dependence of the diffusion coefficient of potassium ion in AAM gel and in NIPA gel. The swelling curves of NIPA gel are also shown in this figure. The diffusion coefficient of potassium ion in AAM gel monotonously increases with temperature. The values of the diffusion coefficient are about one third of that in water. It is also clear from Fig 2 that the diffusion coefficients of potassium ion in NIPA gel are almost the same value with that in AAM gel at lower temperature region. The diffusion coefficient of potassium ion, however, suddenly increases with temperature in the vicinity of the volume phase transition point and it seems to approach to the value in the simple fluid.

These results are intuitively explained as follows. When a probe substance is diffusing in a simple fluid, the diffusion coefficient is determined by the ratio of the thermal fluctuation, kT, and the hydrodynamic resistance of surrounding fluid, $6\pi\eta R$ [5].

$$D_0 = kT / 6\pi\eta R \qquad 3)$$

Here, D_0, η, and R are the diffusion coefficient of substance in a simple fluid, the viscosity of the fluid, and the hydrodynamic radius of the substance. On the other hand, the additional resistance due to the

polymer network is superposed onto the hydrodynamic resistance of fluid when the substance is diffusing in the gel. The diffusion coefficient, therefore, becomes smaller in the gel than in simple fluid.

In the case of AAM gel, the volume phase transition does not occur in the temperature range studied here. The resistance due to the polymer network of AAM gel is, thus, almost constant in this temperature region. On the other hand, NIPA gel is a typical LCST system. This gel shows the volume phase transition at about 33°C above which the gel collapses into a compact state. The anomalous behavior of the diffusion coefficient of potassium ion suggests the reduction of the resistance near the phase transition point.
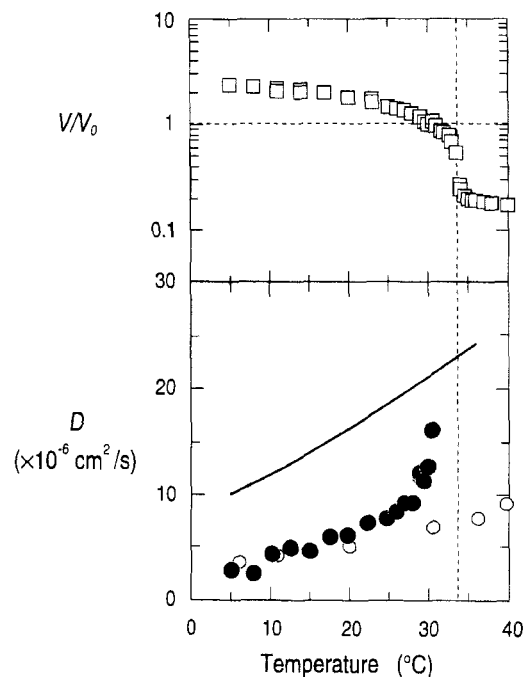

Fig.2 The swelling curve of NIPA gel (upper) and the temperature dependence of the diffusion coefficient of potassium ion in AAM (open symbols) and NIPA (closed symbols) gels (bottom). The solid line in the bottom figure indicates the temperature dependence of the diffusion coefficient of potassium ion in water that calculated by Stokes-Einstein relationship.

4. DISCUSSION

4.1 General Discussion

The diffusion process of substance in the gel has been extensively studied so far [6]. Many theoretical studies as well as experimental studies have been reported. These studies suggest that the measure of the resistance due to the porous medium can be estimated by the ratio of the diffusion coefficient of substance in the porous media and that in the simple fluid.

$$D/D_0 = f(x) \qquad\qquad 4)$$

Here, x represents the scaling variable and is a function of the sizes of the pore and the diffusing substance. Hence, the normalyzed diffusion coefficient of substance depends on the porous structure of the medium, the size of the substance used, and so forth [7]. Many functional forms have been proposed but unified functional form has yet to be obtained. Here, therefore, we qualitatively discuss the experimental results by using the normalyzed diffusion coefficient, D/D_0. The value of the diffusion coefficient of potassium ion in water is taken from table [8]. Then the values of D_0 at each temperature are calculated by eq 3. The results are also given in Fig 2.

4.2 Poly(acrylamide) gel

First of all, we discuss the results of AAM gel. The normalized diffusion coefficient of potassium ion, D/D_0, in AAM gel is plotted in Fig 3 as a function of temperature. It is clear from Fig 3 that the normalized diffusion coefficient of potassium ion in AAM gel is independent of the temperature.

The normalized diffusion coefficient directly reflects the information on the mesh size of the gel. It becomes larger when the mesh size becomes larger. Here, the hydrodynamic radius of potassium ion can be assumed as constant of order 0.2 nm. Thus, the mesh size of AAM gel is totally independent of the temperature in entire temperature range studied here.

It is, however, worth noting that the average value of the normalized diffusion coefficient is found to be about one third of that in water. This value is, if one taking into account that the radius of potassium ion is about 0.2 nm, too small. This implies that many elementary processes are included in the whole transport process across the gel. Among others, the adsorption and the absorption processes influence the transport through the gel. These effects should be taken into account to analyze the results quantitatively. Such studies are now under way and will be reported elsewhere.

4.2 Poly(N-isopropylacrylamide) gel

The temperature dependence of the normalized diffusion coefficient of potassium ion in NIPA gel is also illustrated in Fig 3. The normalized diffusion coefficient of potassium ion in NIPA gel slowly increases at lower temperature region. Then it suddenly increases at about 30 °C. This temperature is almost 4 degrees lower than the volume phase transition temperature. It is found that the swelling ratio of NIPA gel becomes unity at this temperature.

These results indicate that the mesh size of NIPA gel increases with temperature and seems to diverge at the phase transition temperature. Since the surface of the sample gel is fixed by the stainless steel mesh, as shown in Fig 1, the volume of the gel is constant until the swelling ratio of the gel becomes lower than unity. This indicates that the mesh size of NIPA gel

increases under the constant volume conditions of the gel. Besides, such increase of the mesh size can be observed in the temperature region below the phase transition temperature.
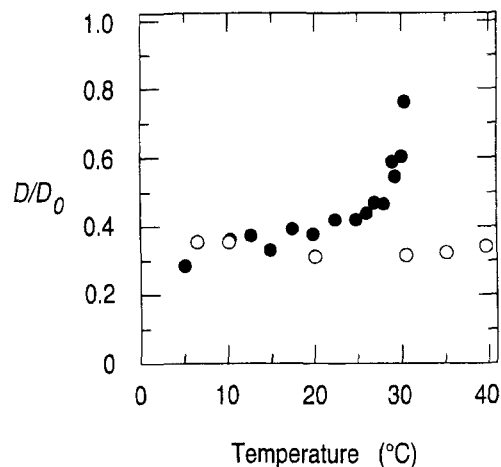

Fig.3 The temperature dependence of the normalized diffusion coefficient of potassium ion in AAM gel (open symbols) and NIPA gel (closed symbols).

The driving force of the volume phase transition in NIPA gel is the hydrophobic interaction between the side chains of the polymer. The hydrophobic interaction becomes dominant at about 33 °C above which the gel collapses into a compact state. This swelling behavior indicates that the hydrophobic interaction between polymer chains causes the attractive force between them. According to the attractive force, the density of polymer network in some portion of the gel becomes dense while other portion of the gel becomes dilute at a cost of dense regions. Thus, the distribution of the polymer network in the gel becomes inhomogeneous in the pre-transition state. The diffusion of substance is expected to be easier in such an inhomogeneous gel since the probe substance diffuses choosing mainly the dilute regions, that serve as a more open and free path, while avoiding the denser regions, that block the diffusion. The gel behaves as a porous sponge for the diffusing substance in the vicinity of the transition temperature, and the closer to the transition temperature, the larger the pore size.

It is noteworthy that the critical density fluctuations of the polymer network begin to increase above 25 °C which is relatively far from the phase transition temperature. Furthermore, the fluctuations of mesh size can be observed even below 25 °C where the normalized diffusion coefficient of potassium ion gradually increases with temperature. In this region, the gel looks completely transparent suggesting the homogeneous spatial distribution of the polymer network in the sense of the optical measurements. Thus, the diffusion measurements through the gel

reveal, in an extremely sensitive manner, the spatial distribution of the polymer network.

5. CONCLUSION

The diffusion coefficient of potassium ion through the poly(acrylamide) gel and poly(N-isopropylacrylamide) gel is measured as a function of temperature. It is found that the diffusion coefficient of potassium ion, when normalized by the diffusion coefficient in water, is independent of the temperature in poly(acrylamide) gel. On the other hand, the normalized diffusion coefficient of potassium shows a singular behavior near the phase transition point of poly(N-isopropylacrylamide) gel. The singular behavior may be caused by the critical density fluctuations of the polymer network.

ACKNOWLEDGEMENTS

6. REFERENCES

[1] T. Tanaka, *Sci. Am.*, **249**, 124 (1981).
[2] M. Tokita and T. Tanaka, *Science*, **253**, 1121 (1991).
[3] M. Tokita, *Jpn. J. Appl. Phys.*, **34**, 2418 (1995).
[4] Y. Hirokawa and T. Tanaka, *J. Chem. Phys.*, **81**, 6379 (1984).
[5] A. Einstein, *"Investigations on the Theory of Brownian Movement"* (Dover, New York, 1956).
[6] A. H. Muhr and J. M. V. Blanshard, *Polymer*, **23**, 1012 (1982).
[7] M. Tokita, T. Miyoshi, K. Takegoshi, and K. Hikichi, *Phys. Rev.*, **E53**, 1823 (1996).
[8] *"CRC Handbook of Chemistry and Physics"* (54th eds., CRC Press, Cleveland, Ohio, 1973~1974).