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Chemical waves in self-oscillating gels

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The behaviors of a poly(*N*-isopropyl acrylamide) (PNIPA) gel coupled with the Belousov-Zhabotinsky (BZ) reaction has been investigated as a function of temperature and catalyst concentration. In this type of gel, the chemical oscillation in the BZ reaction induces periodic and autonomous swelling-shrinking volume changes of the gel, and conversely a volume change of the PNIPA gel affects the propagation of the chemical wave. Our attention was focused on the effects of mechanical changes on the chemical wave by utilizing the thermally driven volume phase transition of the gel. Both the velocity and the frequency of the chemical wave increased with increasing temperature, and abruptly decreased at the volume transition temperature of the gel, T_c. The diffusion of $HBrO_2$, which is essential for wave propagation, was hindered with increasing temperature. The diffusion of $HBrO_2$ through the gel network in the low temperature region was explained in the same way as a simple diffusion of inactive molecules through a restricted environment.

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I. INTRODUCTION

Polymer gels are well known to exhibit an extremely large volume change in response to a change in external conditions such as temperature and solvent composition [1–8]. Very recently, Yoshida and co-workers reported a gel exhibiting a spontaneous swelling-shrinking oscillation without any external stimuli [9,10]. Such self-oscillating gels were realized by combining mechanical properties of gels with the Belousov-Zhabotinsky (BZ) reaction, which is known as a typical chemical oscillatory reaction exhibiting spatiotemporal patterns [11,12]. The self-oscillation of the volume may make it possible to apply hydrogels as functional materials including self-walking actuators, pacemakers, and drug delivery systems synchronized with cell cycles. The use of gels in the BZ reaction system has been so far confined to eliminating hydrodynamic convection disturbing chemical patterns [13] and localizing the BZ reaction in a restricted region [14,15]. It is essential for such purposes that the interaction between the gel structure and the reaction-diffusion system is negligibly small. Gel systems have brought about a considerable development in the study of chemical waves. In particular, localized reaction systems offered the possibility of studying behaviors of chemical waves different from those of conventional chemical waves [16–19]. In these gel systems, gels are no more than the media supporting the reaction, and their structures do not change through the BZ reaction. In self-oscillating gels, in contrast, the polymer network itself takes part in the BZ reaction, because the catalyst is covalently bonded to the polymer chain. As a result, the reaction medium can change in time and space. This means that the chemical reaction induces changes in the gel structure, and induced structural changes should conversely affect the propagation of the chemical wave. Thus this self-oscillating gel system is interesting not only for functional materials but also as a different type of oscillatory chemical reaction system.

In this work, we investigate the behavior of chemical waves in a self-oscillating hydrogel in which the catalyst is covalently bonded to poly(*N*-isopropyl acrylamide) (PNIPA). Our attention is particularly focused on effects of the volume phase transition of the gel on the propagation of chemical waves. Thermally sensitive PNIPA gels have been extensively used as the most suitable candidate for studies of volume phase transitions and critical phenomena [20,21]. The PNIPA gel is in a swollen phase at lower temperatures and in a shrunken phase at higher temperatures. Both the velocity and the frequency of the chemical wave are measured as a function of temperature and catalyst concentration. The diffusion coefficient of the autocatalytic species is calculated from these data, and its temperature dependence is interpreted in terms of changes in the gel structure.

II. EXPERIMENT

We synthesized ruthenium (4-vinyl-4′-methyl-2,2′-bipyridine)bis(2,2′-2′-bipyridine)bis(hexafluorophosphate) $[Ru(vmbpy)(bpy)_2(PF_6)_2]$ as a polymerizable catalyst according to the procedure of Ghosh and Spiro [22], in order to covalently bond the catalyst ruthenium (II) tris-(2,2′-bipyridine) $[Ru(bpy)_3]$ to the polymer chain. The NIPA gels with $Ru(bpy)_3$ were prepared by a free radical copolymerization in 1 ml of methanol at 60 °C; the methanol has been previously purged with nitrogen gas. The reagents used were as follows: NIPA monomer (0.156 g), $Ru(vmbpy)(bpy)_2(PF_6)_2$ (8.2 mg), *N*,*N*′-methylenebis(acrylamide) (2.8 mg) as a cross-linker, and *N*,*N*′-azobis(isobutyronitrile) (6.56 mg) as an initiator. A capillary with an inner diameter of 525 μm was used to make a uniform cylindrical shape. The cylindrical gels after gelation were washed with methanol to remove unreacted compounds, with the methanol being gradually replaced by water, and then stored in pure water. The synthesized gel

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[PNIPA-co-Ru$(bpy)_3$] with a transparent orange color was cut into lengths of 5 mm, and then immersed in the BZ reaction solution of $[NaBrO_3]=0.084M$, $[CH_2(COOH)_2]=0.625M$, and $[HNO_3]=0.3M$. The temperature of the solution was controlled within ±0.1 °C. The color change between orange and green due to the redox reaction did not take place in the solution, but was confined within the gel. The features of the propagation of the chemical wave and the resulting oscillation of the gel were monitored through a charge-coupled device camera attached to a microscope and recorded on a videotape recorder. One end of the gel was fixed at the vessel, while the other end was left free. From the recorded video images, one pixel line images along the length of the gel were sampled every 1 s. The recorded images were transformed to spatiotemporal patterns through computer processing.

All measurements were carried out after the size of the gel reached an equilibrium value each time the temperature was changed. Such an experimental procedure takes a long time to cover the temperature range investigated here. Since our experiments were performed in a closed reactor, the BZ reaction solution evolved irreversibly toward thermodynamic equilibrium and ultimately the chemical oscillation ceased after a long elapsed time. Hence, the BZ reaction solutions, including gels, were renewed before any degradation in the BZ reaction occurred.

III. RESULTS AND DISCUSSION

When the gels reached equilibrium at a given temperature, oxidizing waves were successively initiated at the fixed edge of the gel and propagated toward the free edge. When the gel had not yet reached thermal equilibrium, on the other hand, oxidizing waves were initiated at the free edge, and moved into the gel. Figure 1 shows the spatiotemporal evolution of chemical waves and the volume oscillation of the gel. Here light and dark gray regions correspond to oxidized and reduced states of Ru$(bpy)_3$, respectively. Figure 1(a) shows the case of the gel in thermal equilibrium at 20 °C. The edge of the gel oscillates with an amplitude of 20 μm. The gel starts to contract when oxidizing waves coming from the fixed edge arrive at the free edge. Figure 1(b) shows the case of the gel in the shrinking process driven by increasing the temperature to 24 °C. The edge oscillates with an amplitude of 40 μm. Contrary to the case of the gel at thermal equilibrium, the gel starts to swell when oxidizing waves start to enter the free edge. Thus the oscillation of the gel is synchronized with the propagation of the chemical wave, but the phase difference between them depends on the state of the gel. This can be explained as follows. In the oxidized state, the gel swells due to an increase in hydration of polymer chains induced by an increase in the charge from Ru$(bpy)_3^{2+}$ to Ru$(bpy)_3^{3+}$ [9,10]. Therefore, the gel starts to shrink when oxidizing waves leave the free edge, and starts to swell when oxidizing waves enter the free edge.

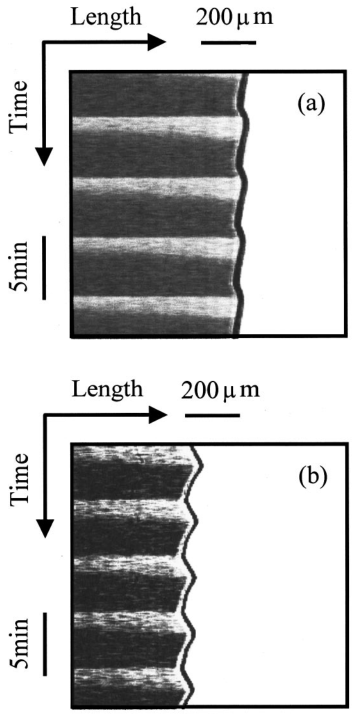

FIG. 1. Spatiotemporal pattern of chemical waves and the volume oscillation at the free edge of an *N*-isopropylacrylamide-Ru$(bpy)_3$ copolymer gel (a) in thermal equilibrium at 20 °C and (b) in the shrinking process at 24 °C. Light and dark gray regions correspond to oxidized and reduced states of Ru$(bpy)_3$, respectively.

As shown in Fig. 1, the chemical oscillation induces a periodical volume change in the gel. Conversely, mechanical changes in the gel probably induce changes in the diffusion and the local concentrations of reactants at the same time, and consequently affect the propagation of the chemical wave. At the present stage, however, the magnitude of such a feedback effect cannot be evaluated. Instead, we investigated effects of mechanical changes on the chemical wave by externally changing the gel structure. This was accomplished by utilizing the thermally driven volume phase transition inherent in PNIPA homopolymer gels. The volume phase transition of a PNIPA homopolymer gel in pure water takes place around 34 °C. Figure 2 shows the temperature dependence of the diameter of the cylindrical gel when the temperature was raised from 18 up to 33 °C. Here the diameter d is normalized with respect to that when the gel was formed

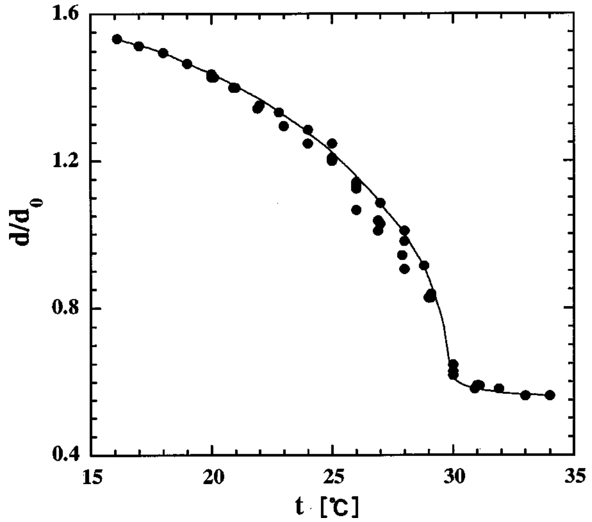

FIG. 2. Diameter of a PNIPA-co-Ru$(bpy)_3$ gel as a function of temperature. The line is merely a guide to the eye.

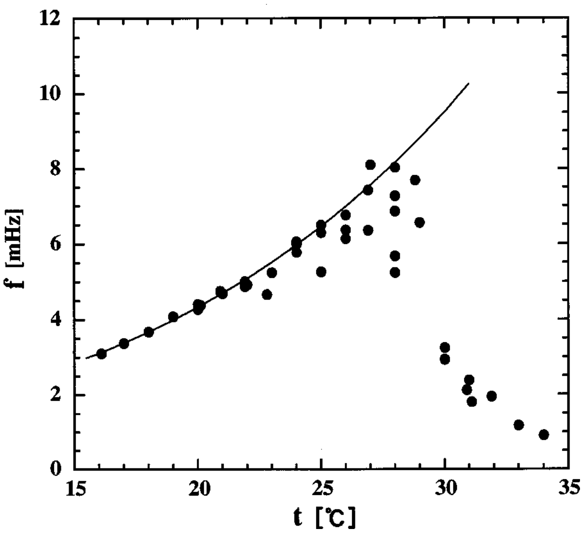

FIG. 3. Frequency of the chemical wave in the PNIPA-co-Ru(bpy)$_3$ gel as a function of temperature. The line represents an Arrhenius plot with the activation energy of 58.0 kJ/mol in the Ru(bpy)$_3$ system.

(d_0). The change of d is slightly discontinuous at about 29 °C. We regarded this temperature as the volume transition temperature T_c. Volume oscillation as shown in Fig. 1 was always observed below T_c. However, since its amplitude was always very small compared with d, its contribution to d was neglected.

Figure 3 shows the temperature dependence of the frequency of the chemical oscillation. With increasing temperature, the frequency increases below T_c, and then abruptly decreases near T_c, which synchronizes with an abrupt decrease in d. It has been reported that the rate constant of the autocatalytic reaction in aqueous solution has a temperature dependence described by an Arrhenius relationship [23],

$$k_s \sim \exp(-E_a/RT), \tag{1}$$

where R is the gas constant, T is the absolute temperature, and E_a is an activation energy of 58.0 kJ/mol in the Ru(bpy)$_3$ system [24]. The solid line in Fig. 3 represents an Arrhenius plot with an activation energy of 58.0 kJ/mol. It should be noted that the frequency below T_c apparently has the same temperature dependence as k_s. This is an interesting result, since the frequency of the chemical wave is not necessarily determined only by the rate constant of the autocatalytic reaction [25]. Above T_c, in contrast, the frequency steeply decreases in spite of enhancement of the reaction by a temperature increase. This may be related to changes in reactant concentration in the gel induced by shrinkage, since concentrations of reactants in the gel are no longer homogeneous, unlike below T_c.

Figure 4 shows the temperature dependence of the velocity of the chemical wave. With increasing temperature, the wave velocity v_g gradually increases below T_c, and then steeply decreases near T_c, which is similar in shape to Fig. 3. In this temperature range, the wave velocity v_s in aqueous solution has been reported to show a temperature dependence of Arrhenius type with an activation energy of 37.6 kJ/mol [24]. A gradual increase in v_g below T_c cannot be described by such an Arrhenius relationship. In fact, the ratio of v_g to v_s was 0.56 at 20 °C, and this ratio became smaller with increasing temperature. Thus the behavior of v_g is entirely different from that of v_s.

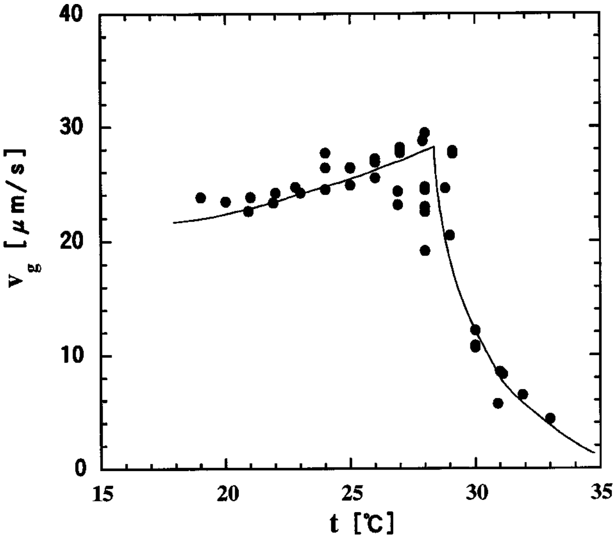

FIG. 4. Velocity of the chemical wave in the PNIPA-co-Ru(bpy)$_3$ gel as a function of temperature. The line is merely a guide to the eye.

It is necessary to represent the wave velocity in terms of the diffusion and concentration in order to understand the observed reduction of the wave velocity in the gel. It is well established that the wave velocity in aqueous solution is determined by the initial concentrations of sulfuric acid and sodium bromate, in addition to the diffusion and the reaction step of the autocatalytic species HBrO$_2$. To a good approximation, the form of the dependence of v_s on these quantities is given by [26,27]

$$v_s = (k_s D_s)^{1/2}([\mathrm{H}^+][\mathrm{BrO_3}^-])^{1/2}, \tag{2}$$

where D_s is the diffusion coefficient of HBrO$_2$. In order to represent the wave velocity in the gel, on the other hand, the following factors must be taken into account: the difference between reactant concentrations inside and outside the gel, the restricted diffusion of HBrO$_2$ and other species through the polymer network, and the modified rate constant of the autocatalytic reaction. Based on Eq. (2), the form of v_g can then be written as

$$v_g = (k_g D_g)^{1/2}(K_{\mathrm{H}^+} K_{\mathrm{BrO_3}^-}[\mathrm{H}^+][\mathrm{BrO_3}^-])^{1/2}, \tag{3}$$

where k_g is the rate constant of the autocatalytic reaction in the gel, D_g the diffusion coefficient of HBrO$_2$ in the gel, and K_{H^+} and $K_{\mathrm{BrO_3}^-}$ the partition coefficients of sulfuric acid and sodium bromate, respectively. Since the rate constants k_g and k_s are quantities related to the autocatalytic reaction itself, they are considered to take the same values irrespective of differences in reaction medium and reactant concentration. Thus the ratio of the diffusion coefficient of HBrO$_2$ in the gel to that in the solution is given by

$$\frac{D_g}{D_s} = \frac{C {v_g}^2}{{v_s}^2}, \tag{4}$$

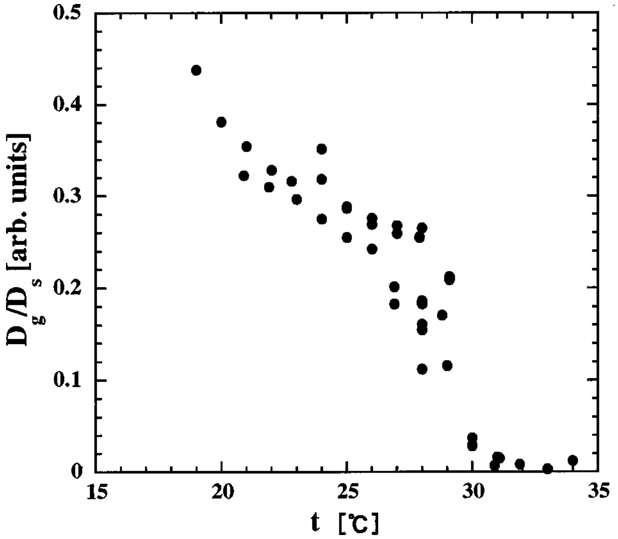

FIG. 5. Ratio of the diffusion coefficient of $HBrO_2$ in the PNIPA-co-Ru(bpy)$_3$ gel to that in solution as a function of temperature.

where C is a constant and it is assumed that both K_{H^+} and $K_{BrO_3^-}$ remain unchanged over the whole temperature range studied. The temperature dependence of D_g/D_s is shown in Fig. 5, where an Arrhenius temperature dependence for v_s is assumed. The data show some scatter, especially around T_c. In spite of that, the ratio decreases with increasing temperature except around T_c. As will be discussed later, the apparent hump around T_c may be associated with dynamic density fluctuations of the gel network.

If the messenger species ($HBrO_2$) interacts negligibly with the polymer chain of the gel, D_g is determined only by the mesh size of the polymer network. According to a calculation based on hydrodynamic theory, the diffusion coefficient of inactive molecules D is described by

$$\frac{D}{D_s}=\exp\left(-\frac{R_h}{\xi}\right), \tag{5}$$

where R_h is the hydrodynamic radius of a Brownian sphere and ξ the correlation length of the polymer network [28,29]. This formula has been supported by the measurement of diffusion coefficients of probe molecules in poly(acrylamide) gels [30]. We assume that Eq. (5) is applicable to the present case.

The polymer network of the gel fluctuates in time and space. The cooperative diffusion coefficient characterizing such fluctuations is very small compared with the diffusion coefficient of small compact molecules such as $HBrO_2$. Therefore, the polymer network may be regarded as a porous medium with an average pore size ξ for the diffusion of small molecules [31]. Shrinkage of the gel with temperature results in a relative increase in the gel concentration. An increase in the gel concentration decreases the correlation length of the polymer network [31]. Thus we can say that the average mesh size decreases with shrinkage of the gel. In other words, the average mesh size is an increasing function of gel size. Now we assume that the average mesh size is proportional to the diameter of the gel, namely, $\xi \propto d$. This assumption seems reasonable in the low temperature region where the polymer network is moderately homogeneous. In the high temperature region, in contrast, density fluctuations of the gel network become pronounced. Consequently, the gel network becomes heterogeneous; some portions of the gel swell and the other portions shrink [32]. In the shrunken state, therefore, the average mesh size might not quantitatively have a linear relationship to d. However, as a first approximation this assumption might be allowable. Figure 6 shows a semilogarithmic plot of D_g/D_s against d_0/d. The D_g/D_s ratio is fitted to a straight line in the low temperature region, but it deviates from a straight line around T_c and in the shrunken state, as shown in Fig. 6. This indicates that interaction between the gel structure and the diffusion-reaction system is no longer negligible expect in the low temperature region.

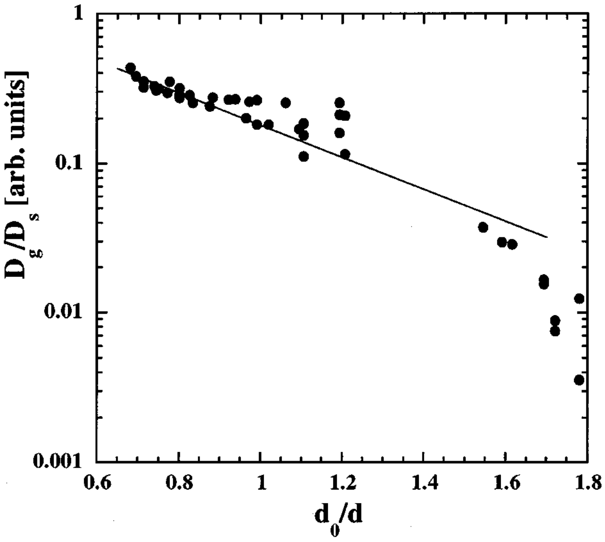

FIG. 6. Dependence of the D_g/D_s ratio on the reciprocal of the gel diameter, where d_0 is the diameter when the gel was formed, and D_g and D_s are diffusion coefficients of $HBrO_2$ in the gel and in aqueous solution, respectively. The line is merely a guide to the eye.

An important feature of the present gel is that the polymer network itself takes part in the reaction, because the catalyst is covalently bonded to the polymer chain. Hence, shrinkage of the gel would result in a relative increase of catalyst concentration; the catalyst concentration is expressed as

$$c=c_0(d_0/d)^3, \tag{6}$$

where c_0 is the initial concentration of immobilized catalyst. In this experiment c_0 is 9 mM. In the analyses described above, such effects of catalyst concentration on the chemical wave have not been considered explicitly. Figure 7 shows the dependence of the frequency of the reaction on the Ru(bpy)$_3$ concentration. We see that the frequency decreases with increase in catalyst concentration. In the most shrunken state of our experiment, the value of $(d_0/d)^3$, i.e., c/c_0, goes up to 5.7. In such a high concentration region, the effects of the catalyst concentration on the frequency will not be negligible. This may be partly responsible for the steep decrease in frequency above T_c shown in Fig. 3.

Figure 8 shows the dependence of the wave velocity on the catalyst concentration. According to earlier studies, the

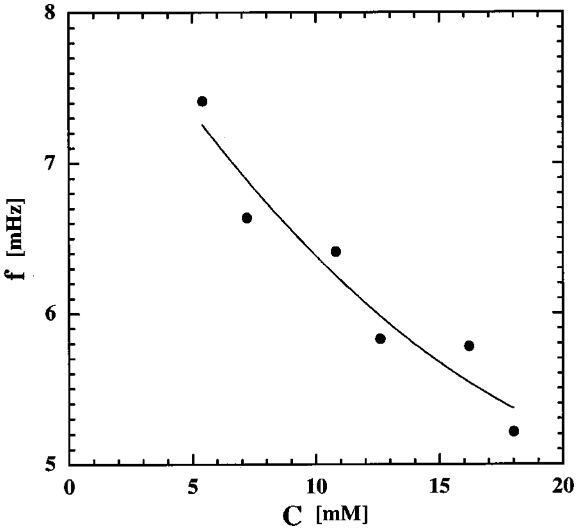

FIG. 7. Frequency of the chemical wave in the PNIPA-co-Ru(bpy)$_3$ gel as a function of Ru(bpy)$_3$ concentration. The line is merely a guide to the eye.

wave velocity v_s in aqueous solution is essentially independent of the concentration of the catalyst [24]. In the present gel, in contrast, the wave velocity v_g decreases with increase in the catalyst concentration. Such a decrease has also been observed in other porous media [18]. On the assumption that v_s is constant, it follows from Eq. (4) that the D_g/D_s ratio shows the same concentration dependence as does v_g^2. Thus the D_g/D_s ratio should decrease with increase in the catalyst concentration, as seen from Fig. 8. This decrease is probably because a large amount of the bulky Ru(bpy)$_3$ molecules behave as obstacles for the diffusion of $HBrO_2$. Since the catalyst concentration in the gel is greatly increased with shrinkage of the gel, as mentioned above, the diffusion coefficient will diminish at high temperature. This explains the smaller values of the D_g/D_s ratio, deviating from the straight line, in the shrunken state in Fig. 5.

In the analyses presented so far, we have assumed that the partition coefficients of proton and bromate in Eq. (3) remain unchanged when the gel shrinks. This assumption seems reasonable in the swollen state. However, it is probable that this assumption becomes invalid at high temperature; shrinkage of the gel with temperature hinders the diffusion of these reactants through the network, and consequently their concentrations are no longer homogeneous. In the shrunken state, the concentration distribution of these reactants may be established along the direction perpendicular to the gel surface. This is also responsible for the deviation of the D_g/D_s ratio from the straight line shown in Fig. 5.

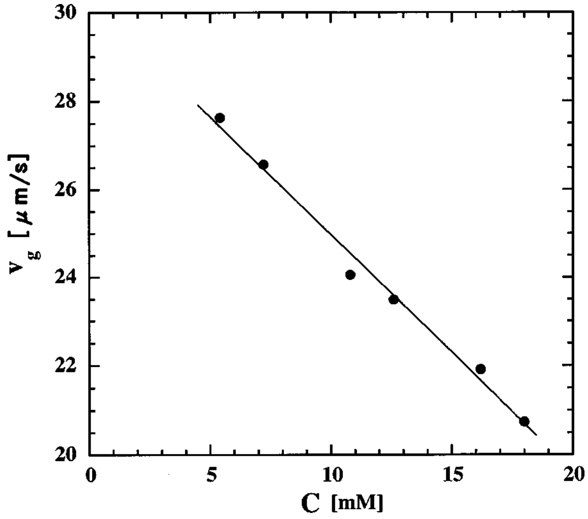

FIG. 8. Velocity of the chemical wave in the PNIPA-co-Ru(bpy)$_3$ gel as a function of Ru(bpy)$_3$ concentration. The line is merely a guide to the eye.

In the case of the PNIPA gel, it is well known that the correlation length of dynamic density fluctuations of the polymer network diverges at the volume transition point [33,34]. Density fluctuations of the polymer network create swollen and shrunken regions in the gel even if the total volume of the gel remains unchanged. Thus the effective pore size of the network is determined by the correlation length of such fluctuations. In other words, the assumption that the average pore size is proportional to the gel diameter becomes invalid near the transition point. The increase in the correlation length increases the pore size of the network, and consequently induces an increase in diffusion coefficients. The apparent hump around T_c seen in Fig. 5 may be related to such fluctuations. Unfortunately, data vary widely around T_c. In this region, it took a long time for the gel to attain a steady state, which is probably due to critical slowing down. Since long-time use of the batch reactor caused a degradation of the BZ reaction, we were often forced to renew samples when the temperature was changed. There was some difference in the characteristics of the samples used, which is probably caused by the sample preparation. This may be responsible for the scattering of data. At the present stage, we cannot conclude whether the hump observed around T_c is due to an enhancement of dynamic density fluctuations or not.

IV. CONCLUSION

We have investigated the behavior of a chemical wave in a gel exhibiting spontaneous and periodic volume oscillation. The difference between the phases of the mechanical oscillation and the chemical one has been found to change depending on whether the gels reach equilibrium at a given temperature or not. We have found that both the velocity and the frequency of the chemical wave change in response to a volume change of the gel. Such changes have been qualitatively analyzed using a simple theory of diffusion. At low temperature, the gel structure does not affect the diffusion-reaction system. Hence, the change in the wave velocity can be explained in terms of the restricted diffusion of $HBrO_2$ through the gel network. At high temperature, the change of the wave velocity cannot be explained by simple diffusion theory. This is probably because inhomogeneities in reactant concentrations and the increase in the amount of bulky catalyst hinder the diffusion and the rate of reaction. It would be of interest to see if an anomalous increase of density fluctuations around T_c affects the behavior of chemical waves. For this purpose, it is essential always to maintain the BZ reaction system at a definite state far from equilibrium. This would become feasible by establishing a net flux of reagent through the system as in a continuously fed unstirred reactor

[35]. Then the whole temperature range studied can be covered with only one sample. Work along this line is in progress. The present paper has not been concerned with the feedback effect of the mechanical oscillation on the chemical one. Such an effect is an interesting problem characteristic of the present system and will be the subject of on-going investigations.

Observation of phenomena such as those described in this study is possible only in a gel system in which the catalyst is covalently bonded to the polymer chain. Immobilization of the catalyst in the gel can also be achieved by adsorption. In that case, however, the catalyst easily escapes from the gel during several periods of the redox reaction. Therefore, such a gel system is not suitable for the long-time observation required for this study.

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