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Aspects of the Belousov−Zhabotinsky Reaction in Polymer Gels

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The Belousov−Zhabotinsky (BZ) reaction in a gel system was studied as a function of initial concentration of substrates (malonic acid, sodium bromate, and nitric acid), through which the understanding of the reaction mechanism has been attempted. We prepared gels composed of cross-linked *N*-isopropylacrylamide networks to which ruthenium catalyst was covalently bonded. To compare the period and waveform of the BZ oscillations in the solution with those in the gel, an image processing method was developed and applied to the gel system. We monitored the oscillating change in the mole fraction of oxidized ruthenium catalyst. The period dependence on the initial substrate concentrations showed that there is a marked difference between the solution and gel systems. In particular, malonic acid and $NaBrO_3$ affect the period over their low concentration ranges. A marked effect of malonic acid concentration appeared in the waveform in the gel but not in the solution. By analyzing these results with the Field−Körös−Noyes (FKN) mechanism, diffusion limitation of substrate and product was found to play an important role in the oxidizing and reducing rates of the ruthenium catalyst within the gel system.

Introduction

The Belousov−Zhabotinsky (BZ) reaction,[1] an oscillating reaction accompanying a rhythmical change in the redox potential, is a subject of both chemical and biological interest. The understanding of the BZ reaction in terms of the Field−Körös−Noyes (FKN) mechanism[2−4] allows us to divide the overall reaction into three main processes: consumption of Br^- ions (process A), autocatalytic formation of $HBrO_2$ (process B), and formation of Br^- ions (process C). The elementary reactions which constitute each process have been elucidated by many researchers.[5,6]

The BZ reaction in a thin layer of unstirred solutions, as well as in matrix-supported solutions, enables us the observation of concentric or spatial pattern formations due to propagating chemical waves.[7] Use of gels as a supporting matrix has provided several advantages in the understanding of the BZ mechanism.[8] Through the video recording, the velocity of the BZ waves was determined and discussed in relation to the kinetics of the autocatalytic reaction step (process B). It is generally found that the results obtained from the gel system may be compared with a theoretical prediction without special care for effects of hydrodynamic convection.

We have attempted to induce the BZ reaction within the gel that undergoes a volume phase transition in response to changes in the surrounding conditions such as solvent composition and temperature.[9−13] For this purpose, we prepared gels composed of cross-linked *N*-isopropylacrylamide (NIPAAm) networks to which ruthenium tris(2,2′-bipyridine) ($Ru(bpy)_3$), a catalyst for the BZ reaction, was covalently bound. The gel swelled at the oxidized state of $Ru(bpy)_3$ and deswelled at the reduced state

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of $Ru(bpy)_3$; the swelling−deswelling change took place periodically in a special case. The swelling−deswelling cycle of a miniature gel piece was found to be synchronized with the chemical oscillation. In the case of a rectangular thin membrane, however, the mechanical oscillation was observed only at a limited area of one end at the major axis.[9,10] In this case, we may neglect the change in the gel volume during the BZ reaction. This phenomenon was explained by a theoretical model simulation.[12,13]

A possible observation of the redox oscillations within the gel phase allows us to directly compare with those in a stirred solution. We recorded a color change on the inside of a thin gel membrane due to the periodically occurring oxidation and reduction of the $Ru(bpy)_3$ moieties and converted the recorded color change into a change of time-dependent 8-bit gray scale at a fixed position on the gel. These procedures are similar to Müller et al.[14] and Nagy-Ungvarai et al.[15] who have transformed the measured gray scale distribution in unstirred solution systems into the corresponding concentrations of oxidized catalyst according to the Lambert−Beer law. Then, oscillating redox changes within the gel can be given in a complete wave based on the molar fraction of the oxidized species against time. The present study intended to see the aspect of BZ oscillations in the gel system through comparison with bulk oscillations.

Experimental Section

Preparation of Poly(NIPAAm-*co*-Ru(bpy)$_3$) Gels. Copolymer gels consisting of NIPAAm chains with covalently bound $Ru(bpy)_3$ residues were prepared according to our previous methods.[9] NIPAAm (Eastman Kodak Co., Rochester, NY) was purified by recrystallization from its toluene solution with *n*-hexane. Ruthenium(4-vinyl-4′-methyl-2,2′-bipyridine)bis(2,2′-bipyridine)bis(hexafluorophosphate) ($Ru(bpy)_3$) was synthesized according to Ghosh and Spiro.[16] Both monomers (NIPAAm, 0.156 g; $Ru(bpy)_3$, 8.2 mg) were dissolved in 1 mL of O_2-free methanol and then mixed with 2.8 mg of *N*,*N*′-methylenebisacrylamide (cross-linker; Kanto Chemical Co., Tokyo, Japan) and 6.6 mg of 2,2′-azobisisobutyronitrile (initiator; Wako Pure Chemical Industries Co., Osaka, Japan). This monomer solution was quickly injected into a space (0.5 mm) between two Mylar sheets which had been backed by a glass plate and separated by a Teflon spacer. The gelation was carried out at 60 °C for 18 h. To remove unreacted monomers, the gel membrane obtained was immersed in pure methanol for a day without stirring; this procedure was allowed to continue for a week with fresh methanol. Finally, the purified membrane was carefully hydrated through dipping it in a graded series of water−methanol mixtures, for 1 day each in 25, 50, 75, and 100% (v/v) of water. The immobilization yield of $Ru(bpy)_3$ within the gel was 5% (of the total monomer used in the polymerization), as estimated from the amount of the complexes extracted with methanol.

Measurements of Oscillation Profiles in Gels. The gel membrane was cut into rectangles (side lengths, about 1 × 20 mm); the section was then immersed into 8 mL of an aqueous solution containing malonic acid (MA), sodium bromate, and nitric acid maintained at 20 °C. In general, sulfuric acid is used as an acidic medium in the BZ reaction. In a series of our studies for the gel system, however, nitric acid has been used because the swelling difference between Ru(II) and Ru(III) states is more remarkable (see ref 9). Therefore, we used nitric acid also in this experiment. In the condition that the total length of the gel changes only a little, the propagation of chemical waves in the gel was observed under a microscope (Leica, model M420) equipped with a black-white CCD camera (SONY, model SSC-M370) and a video recorder (Panasonic, model AG-6760). When a miniature gel piece whose size is smaller than the chemical wavelength is used, periodic changes in gel volume become significant. In this case, it has become apparent that the swelling−deswelling oscillations affect the profiles of chemical oscillations within the gel (we will report this feedback effect from mechanical to chemical oscillation in the next paper). To minimize the mechanical effect and discuss the BZ profiles based on only diffusion effect, here we used the rectangular gel strip under the condition that the total gel length changes little. We used monochromatic light passed through a blue filter (Kenko B-390) on the halogen light source. Color changes due to the periodic oxidation and reduction of the $Ru(bpy)_3$ moieties within the gel were measured by means of transmitted light. The time-dependent change in transmittance was then converted to gray scale changes. The video images were transferred through a digital time base corrector (FOR.A, model FA-310) to a computer (NEC, model PC-9801RA) equipped with an image acquisition board (MICRO-TECHNICA, MT98-MN). The redox reaction was thus recorded as 8-bit gray scale changes.

A one-pixel line along the length of recorded gel image was stored at regular time intervals (3 s). The stored pixel line images were sequentially lined up as a function of time by the computer. This image processing procedure constructs a spatio-temporal diagram. From the diagram obtained, the time-dependent change in the oxidized fraction of $Ru(bpy)_3$ at a fixed position of the gel was expressed as 8-bit gray scale changes by using the image processing software (NIH image 1.61). To determine a base on the scale for completely oxidized $Ru(bpy)_3$, the measurement was carried out in an aqueous mixture of $Ce(SO_4)_2$ (0.001 M) and HNO_3 (0.3 M), while pure water was used for the reduced complex. These procedures allow us to give the BZ reaction in the gel as an oscillation of the mole fraction of the oxidized complex.

Measurement of Oscillation Profiles in Bulk Solution. The oscillation of redox potential in the stirred aqueous BZ solution containing of MA, $NaBrO_3$, HNO_3, and $Ru(bpy)_3Cl_2$ (0.33m M) was studied by the usual potentiometric method with a Pt electrode under air. The recorded redox potential was then converted into the concentration of the oxidized complex.

Results and Discussion

Characteristics of the BZ reaction in the gel system would have some resemblance to that of gel-immobilized enzyme reactions. For the latter, the effects of immobilization have been classified as follows: (i) conformational and steric effects; (ii) partitioning effects; (iii) microenvironmental effects; and (iv) diffusional or mass-transfer effects (e.g., see ref 17). All effects other than conformational changes and steric hindrances alter the rate of immobilized enzyme reaction by causing differences between the bulk and matrix phases in the concentrations of substrates, products, and effectors. Thus, a kinetic study of the reactions in the bulk and the immobilized system as a function of initial substrate concentrations would be a classic and reliable approach for seeing this aspect of the gel-supported BZ reaction.

In the present case in which oscillating redox changes take place, however, one should encounter a principal difficulty about how to estimate the oxidizing and reducing rates. To overcome this difficulty, we attempt to examine the period and waveform of oscillations in the solution and the gel system as a function

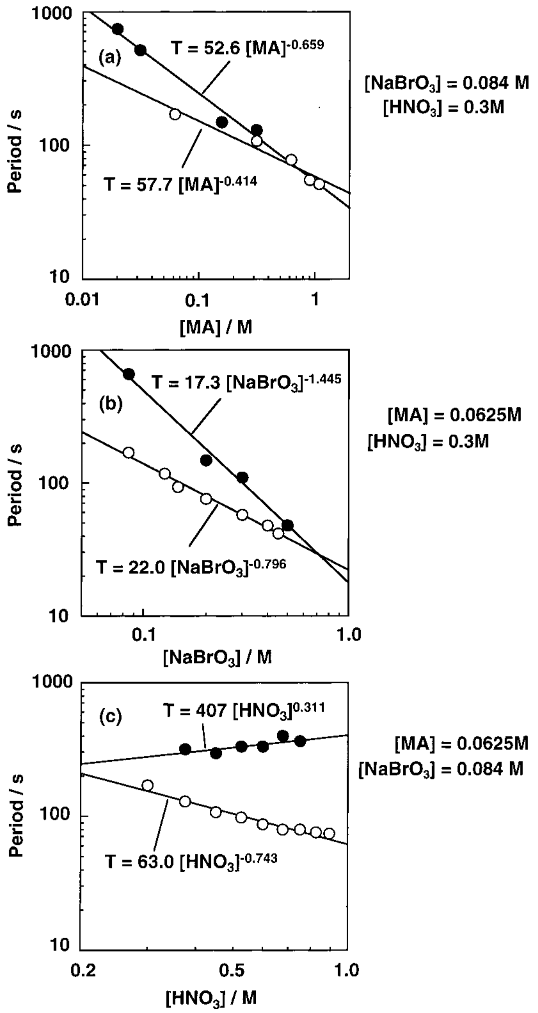

Figure 1. Plots of period against the initial concentration of a substrate under fixed initial concentration of the others for the solution (○) and the gel (●) system.

of initial substrate concentrations. In particular, we expected that a detailed analysis of the waveform would provide useful information about diffusional or mass-transfer effects of substrates and/or products on the oxidation and reduction of the ruthenium complex bound to the polymer networks in the gel.

Period Dependence on Initial Substrate Concentrations. The period of the BZ waves in solution systems varies depending on the initial concentration of the substrates.[18] The period should be an indicator for the overall reaction, through the measurements of which we first tried to look at differences between the bulk and gel systems. Figure 1 shows logarithmic plots of the period (*T* in s) vs initial molar concentration of one substrate under fixed concentrations of the other substrates. A good linear relation was obtained not only for the bulk solution but also for the gel; thus, we may express *T* as $a[\text{substrate}]^b$ where *a* and *b* are empirical constants and brackets denote initial molar concentration. Since our measurements of oscillations were completed while a few percent of the initial quantity of the substrates were consumed, [substrate] at a certain measuring time may be approximated to its initial concentration.

As shown in Figure 2, each result in Figure 1 for the solution or the gel system can also be expressed by a linear line; therefore, we may obtain the following empirical relations: For the solution system,

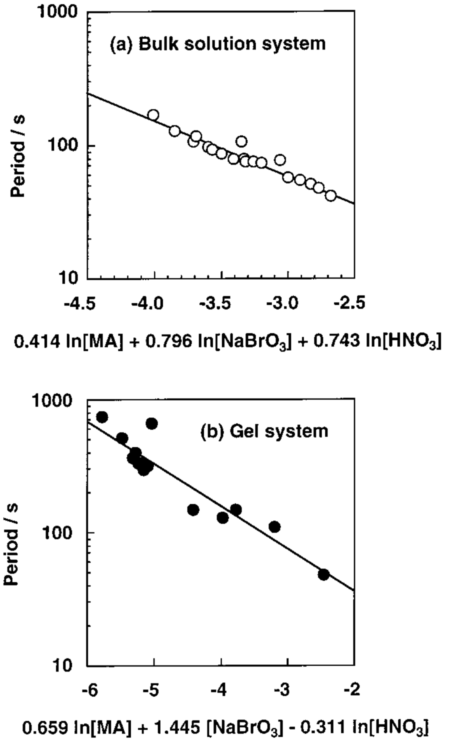

Figure 2. Period as a function of the initial concentrations of malonic acid, sodium bromate, and nitric acid for the solution (a) and the gel (b).

$$T_s = 2.97\ [MA]^{-0.414}[NaBrO_3]^{-0.796}[HNO_3]^{-0.743} \qquad (1)$$

and for the gel system,

$$T_g = 2.66\ [MA]^{-0.659}[NaBrO_3]^{-1.445}[HNO_3]^{0.311} \qquad (2)$$

From the results in Figures 1 and 2, we can clearly say that there is a difference in the BZ oscillations between the bulkand gel systems. Several marked features showing this are as follows: (i) Concentration dependence becomes stronger in the gel system than in the solution system. (ii) At [MA] and $[NaBrO_3] > 0.3$ M, however, there is little difference between the solution and gel systems. (iii) HNO_3 has an opposite effect on the period of oscillations in the solution and the gel system. (iv) However, the magnitude of this effect in the gel system is smaller than that in the solution system (in other words, in the gel, *T* little depends on $[HNO_3]$). These results could be understood by considering the usual immobilization effect; i.e., difficulties in the diffusion or mass transfer of the substrate (from the bulk to the gel) as well as the product (from the gel to the bulk) due to immobilization of the ruthenium catalyst. For example, the observed effect of MA at low [MA] levels would be explained by assuming that the rate of reduction of the Ru(III) becomes slow because of a limited diffusion of MA from the bulk phase. In contrast, H^+ ions are consumed during both the formation of $HBrO_2$ and the oxidation of the Ru(II) but produced in the reduction of Ru(III) with MA (see the elementary reactions in the FKN mechanism; Table 3.1 in ref 4). Thus, little influence of $[HNO_3]$ due to the transfer of H^+ ions from the bulk to the gel phase would be observed. Solely on the basis of the period dependence on initial substrate concentrations, however, it is rather difficult to discuss in full the immobilization effect on the oxidation and reduction rates of the ruthenium complex.

Regions of Initial MA and $NaBrO_3$ Concentrations for Stable Oscillations. Prior to the analyses of the waveforms

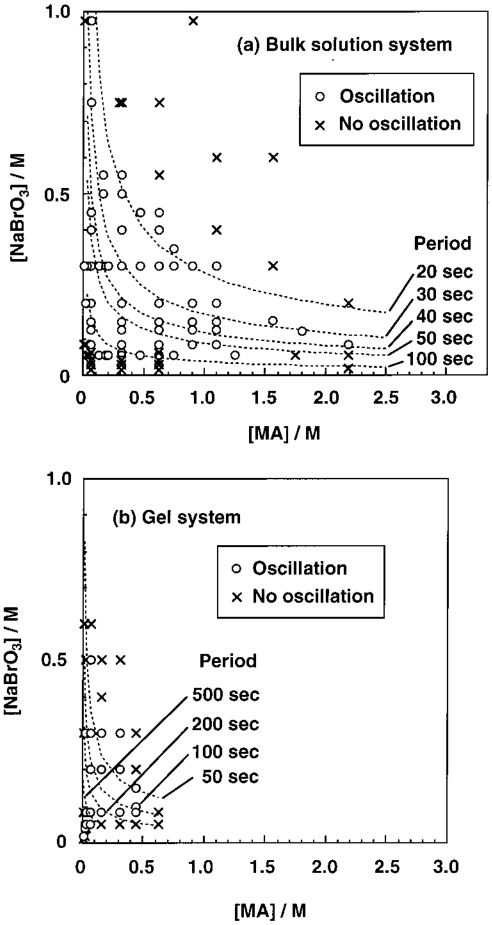

Figure 3. Phase diagrams of stable oscillating region given by the initial concentrations of malonic acid and sodium bromate under a fixed concentration (0.3 M) of nitric acid.

based on oscillating concentration changes of the oxidized (or reduced) ruthenium complex, we studied the substrate concentration ranges at which a stable and periodic oscillation takes place. Figure 3 shows typical examples of [MA] vs [NaBrO$_3$] plots at a fixed [HNO$_3$] (0.3 M). There are the upper and lower limits of [MA] and [NaBrO$_3$] bringing about stable BZ oscillations. At [HNO$_3$] = 0.3 M, the region between both limits is narrower for the gel than for the solution.

The regions for all of the substrates including HNO$_3$ leading to stable oscillations are summarized as follows. For the solution, 0.05 M < [MA] < 2 M; 0.05 M < [NaBrO$_3$] < 1 M; 0.2 M < [HNO$_3$] < 1 M. For the gel, 0.02 M < [MA] < 0.5 M; 0.02 M < [NaBrO$_3$] < 0.5 M; 0.3 M < [HNO$_3$] < 0.8 M.

A shift of the upper limit to a low concentration range, the trend of which is observed in the gel system for all the substrates, is the prime cause of narrowing the region in which stable oscillations take place. Another trend of the gel system is that at all of the concentrations bringing about the oscillation, the period becomes longer as compared with the solution system. In general, the oscillation period in reaction−diffusion systems becomes shorter than that in bulk oscillations (see Figure 2b in ref 19) under the same concentration of substrates. From these results, it is suggested that an effect other than organization of traveling waves acts on local oscillations in our gel system. These would be again interpreted in terms of a limited diffusion or mass-transfer of the substrates. Even when the concentrations of two substrates (e.g., MA and HNO$_3$) are sufficiently high within the gel phase, a limited diffusion from the bulk phase of another substrate (BrO$_3^-$) fails to generate the BZ oscillations.

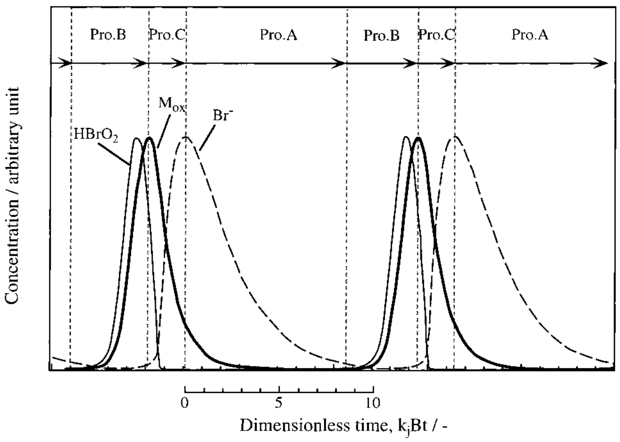

Figure 4. Time profiles of HBrO$_2$, Br$^-$, and M$_{ox}$ concentrations caluculated from the Tyson version of the Oregonator model[20] with A = 0.084, B = 0.0625, H = 0.3, $\epsilon = 0.248$, $q = 0.0008$, $\epsilon' = 0.0033$ and $f = 1$. Here, A = [BrO$_3^-$]; B = [MA]; H = [H$^+$]; $q = 2k_3k_4/(k_2k_5)$; $\epsilon = k_j\mathrm{B}/(k_5\mathrm{HA})$; $\epsilon' = 2k_4k_j\mathrm{B}/(k_2k_5\mathrm{H}^2\mathrm{A})$. Terms k_1−k_5 are the rate constant for each elementary reaction defined by the FKN scheme,[4] k_j is the rate constant of the overall reaction in process C, and f is the stoichiometric factor in process C.

Under conditions near such a set of the substrate concentrations, we observed quasisinusoidal, low amplitude oscillations which suggest the approach of a bifurcation to either an oxidized or reduced steady state.

Effects of Initial Substrate Concentrations on Waveform. Before comparing the waveforms in the solution and the gel system, we will provide the outline of mathematical treatments of the FKN scheme.[2−4] According to this scheme, the overall reaction may be divided into the following three main processes:

$$\mathrm{A{:}\ \ BrO_3^- + 2Br^- + 3H^+ \rightarrow 3HOBr}$$

$$\mathrm{B{:}\ \ BrO_3^- + HBrO_2 + 2M_{red} + 3H^+ \rightarrow 2HBrO_2 + 2M_{ox} + H_2O}$$

$$\mathrm{C{:}\ \ 2M_{ox} + MA + BrMA \rightarrow} f\mathrm{Br^- + 2M_{red} + other\ products}$$

To mathematically express the FKN scheme, the Oregonator model[3] has widely been employed. Figure 4 shows schematic illustration of evolution of HBrO$_2^-$, Br$^-$, and M$_{ox}$ concentrations numerically simulated from the Tyson version[20] of the Oregonator model.

Let us compare the waveform from the theoretical model simulation with our experimental results. Figure 5 shows typical oscillating profiles obtained in the bulk system. The results are arranged in such a way that the concentration of either MA or BrO$_3^-$ is varied over a wide range at a fixed concentration of the other two, the value of which are sufficiently high to generate stable oscillations (see Figure 3). A decrease in the substrate concentration causes an increase in the period without a large broadening of the peak width, even when not only [MA] but also [BrO$_3^-$] was varied. This clearly indicates that neither process B (oxidation) nor process C (reduction) is a rate-limiting step in the overall BZ reaction, at least under our experimental conditions (compare Figure 5 with Figure 4). In other words, process A, corresponding to the consumption of bromide ions, becomes a dominant factor in increasing the period. This is

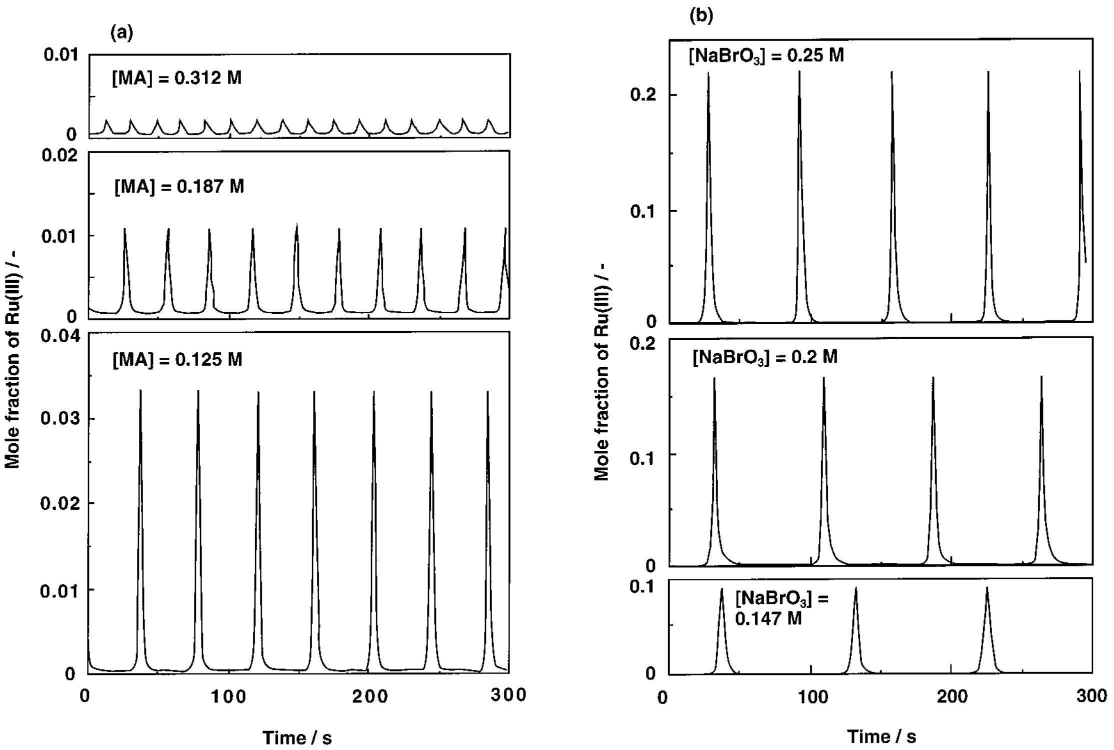

Figure 5. Oscillating profiles of redox changes given by mole fraction of oxidized catalyst in bulk solutions containing different initial concentrations of MA (a) and $NaBrO_3$ (b). [MA] was varied at [$NaBrO_3$] = 0.3 M, [HNO_3] = 0.3 M, while [$NaBrO_3$] was done at [MA] = 0.0625 M, [HNO_3] = 0.3 M.

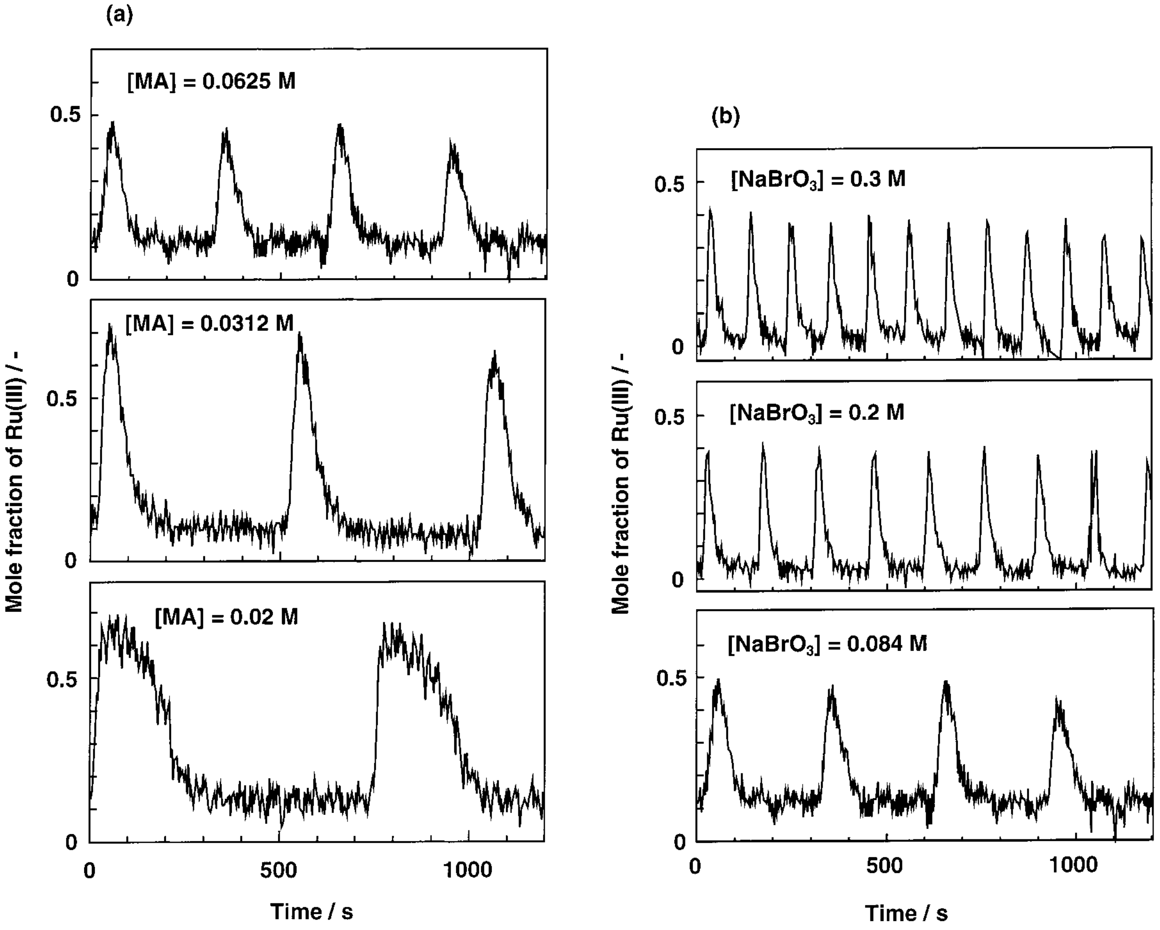

Figure 6. Oscillating profiles of redox changes given by mole fraction of oxidized catalyst in gels containing different initial concentrations of MA (a) and $NaBrO_3$ (b). [MA] was varied at [$NaBrO_3$] = 0.084 M, [HNO_3] = 0.3 M, while [$NaBrO_3$] was done at [MA] = 0.0625 M, [HNO_3] = 0.3 M.

identical with the results by Krinsky et al.[21] Thus, a decrease in the overall reaction rate in process A allows for the ruthenium complex to hold on in the reduced state for a long time. This agrees with the fact that T_s in eq 2 is more sensitive to $[BrO_3^-]$ than [MA].

As can be seen from Figure 6, the effect of the substrate concentrations on the waveform in the gel system is markedly different from that in the solution system. A decrease in [MA] causes a slow reduction of the Ru(III) in process C due to a lowering of mass-transfer rate of MA molecules. This is the reason for a gentle fall in the mole fraction of the oxidized species after the attainment to a maximal value (see Figure 6a). With respect to the effect of $NaBrO_3$, Figure 6b indicates that the runup to a maximal oxidation is little affected by $[BrO_3^-]$. By comparing this with Figure 4, we may say that the oxidation in process B is considerably fast even at a relative low $[BrO_3^-]$. Therefore, the effect of reduced mass-transfer rate of BrO_3^- due to the immobilization becomes rather stronger in process A than in process B. This is not surprising because Br^- ions as the product in process C should be accumulated in the gel phase because of a limitation of their diffusion to the bulk phase. This could require a large quantity of BrO_3^- ions in the gel system rather than in the bulk system to consume Br^- ions in process A. As a result, a decrease in [MA] and an increase in $[Br^-]$ within the gel phase play important roles in the matrix-supported BZ oscillation under a low bulk concentration of MA and $NaBrO_3$. The former effect appears in process C, while the latter appears in process A. Other than the diffusion effect, we cannot neglect the possibility that the local mechanical changes of the gel (see ref 13) affect the chemical oscillation profiles in our gel system. In addition, there is a possibility that the chemical reaction between the amide group of the gel and hypobromous acid, a process generating bromide, take places.[22] The produced bromide can slow the wave propagation. These problems are currently under investigation.

Conclusions

Aspects of the Belousov−Zhabotinsky reaction in polymer gels were studied as a function of the initial concentrations of the substrates (malonic acid, sodium bromate, and nitric acid) using an image processing method. We expressed oscillating redox changes in the gel as a change in mole fraction of the oxidized catalyst, and therefore compared the period and waveform of oscillations in the gel with those in the solution. The results obtained are summarized as follows: (i) There is a marked difference in the period dependence on initial substrate concentrations between the solution and the gel. (ii) A decrease in the initial concentration of $NaBrO_3$ has a strong effect on the period; that is, an increase in the period both in the gel and the solution system. (iii) The substrate concentration little affects the waveform in the solution, while the waveform in the gel was changed with the initial concentrations of substrates, in particular with a decrease in the concentration of malonic acid. (iv) Analyses of the observed changes in the waveform with the Oregonator model strongly suggested that a limitation of the diffusion of the substrates from the bulk to the gel phase, as well as of the products from the gel to the bulk phase, plays an important role in the oxidizing and reducing rates of the ruthenium catalyst.

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References and Notes

(1) Zaikin, A. N.; Zhabotinsky, A. M. *Nature* **1970**, *225*, 535−537.

(2) Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649−8664.

(3) Field, R. J.; Noyes, R. M. *J. Chem. Phys.* **1974**, *60*, 1877−1844.

(4) Field, R. J.; Burger M. *Oscillations and Traveling Waves in Chemical Systems*; John Wiley & Sons: New York, 1985.

(5) Györgyi, L.; Turanyi, T.; Field, R. J. *J. Phys. Chem.* **1990**, *94*, 7162−7170.

(6) Turanyi, T.; Györgyi, L.; Field, R. J. *J. Phys. Chem.* **1993**, *97*, 1931−1941.

(7) Reusser, E. J.; Field, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 1063−1071.

(8) Yamaguchi, T.; Kuhnert, L.; Nagy-Ungvarai, Zs.; Müller, S. C.; Hess, B. *J. Phys. Chem.* **1991**, *95*, 5831−5837, and earlier references therein.

(9) Yoshida, R.; Takahashi, T.; Yamaguchi, T.; Ichijo, H. *J. Am. Chem. Soc.* **1996**, *118*, 5134−5135.

(10) Yoshida, R.; Takahashi, T.; Yamaguchi, T.; Ichijo, H. *Adv. Mater.* **1997**, *9*, 175−178.

(11) Yoshida, R.; Yamaguchi, T. *Biorelated Polymers and Gels: Controlled Release and Applications in Biomedical Engineering*; Okano, T., Ed.; Academic Press: Boston, 1998; Chapter 3.

(12) Yoshida, R.; Takahashi, T.; Yamaguchi, T.; Ichijo, H.; Kokufuta, E. *ACH−Models in Chemistry* **1998**, *135*, 409−416.

(13) Yoshida, R.; Kokufuta, E.; Yamaguchi, T. *CHAOS* **1999**, *9*, 260−266.

(14) Müller, S. C.; Plesser, T.; Hess, B. *Physica D* **1987**, *24*, 71−86.

(15) Nagy-Ungvarai, Zs.; Tyson, J. J.; Müller, S. C.; Watson, L. T.; Hess, B. *J. Phys. Chem.* **1990**, *94*, 8677−8682.

(16) Ghosh, P. K.; Spiro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 5543−5549.

(17) For example: Kokufuta, E. *Prog. Polym. Sci.* **1992**, *17*, 647−697.

(18) Smoes, M.-L. *J. Phys. Chem.* **1979**, *71*, 4669−4679.

(19) Aliev, R. R.; Biktashev, V. N. *J. Phys. Chem.* **1994**, *98*, 9676−9681.

(20) Tyson, J. J. *Ann. N. Y. Acad. Sci.* **1979**, *316*, 279−295.

(21) Krinsky, V. I.; Agladge, K. I. *Phyisca D* **1983**, *8*, 50−56.

(22) Lazar, A.; Försterling, H.-D.; Farkas, H.; Simon, P.; Volford, A.; Noszticzius, Z. *CHAOS* **1997**, *7*, 731−737.