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# Frequency-Multiplying Bifurcation in the Oscillatory Belousov–Zhabotinskii Reaction Proceeding in Interacting Water Droplets of the Reverse Microemulsions of the Aerosol OT in Octane

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The ferroin-catalyzed Belousov–Zhabotinskii oscillatory reaction exhibits frequency-multiplying bifurcation including frequency doubling, tripling, and quadrupling when it proceeds in water-in-oil microemulsions of the anionic surfactant Aerosol OT. This bifurcation occurs only when the water volume fraction $\phi_w$ is large enough (>0.05) and the system is not flowed (batch conditions) or is flowing at a very low rate. Bubbling gas through the reactor prohibits bifurcation. Clusters of microemulsion droplets (possibly in the percolation structure) appearing at relatively high $\phi_w$ are suggested to behave as minioscillators, and their mutual coupling determines the mode of bifurcation. It is also suggested that bromine produced in oscillatory reactions is stored in the organic phase and governs the frequency-multiplying bifurcation by enhancing the coupling between clusters.

## Introduction

Investigation of oscillatory chemical reactions in interacting micro- and nanodroplets, such as reverse micelles,[1-5] is a new field in the study of nonlinear chemical systems. Interest in this field can be attributed to the similarity of such systems to interacting living cells, and to the possibility of discovering still unknown fundamental physical and chemical laws governing the behavior of nonlinear systems.

We expect well-known oscillatory reactions, such as the Belousov–Zhabotinskii (BZ) reaction,[6,7] to display new properties in micelles for several reasons. First, if the bulk water of the reaction mixture is dispersed into many micro- or nanodroplets, then the nonlinear properties of the system will be exhibited not only in individual droplets but also in interactions between droplets. These properties should depend on droplet characteristics such as average droplet size, average distance between droplets, extent of their aggregation, and rate of mass exchange between them. The simplest model of this type of system is referred to as "couple nonlinear oscillators".[8-11] Second, the inner fluctuations $\delta C_i$ of concentrations $C_i$ of intermediates are considerable in droplets in contrast with "ordinary" coupled oscillators.[12-14] The smaller the droplet size, the larger the fluctuations. As a result, droplets are expected to display new dynamical properties which depend on their size. When droplets are small enough, some of $\delta C_i$ can even be on the order of $C_i$ and the critical concentrations for bifurcation can be in the fluctuation region $C_i \pm \delta C_i$. The behavior of the assembly of nanodroplets under such conditions is unpredictable.

In our previous paper,[5] we showed that the manifestation of oscillations in the BZ system in water-in-oil reverse micelles (microemulsions[15]) made of the anionic surfactant Aerosol OT (AOT) depends on their size and concentration. We have shown theoretically[4,5] that the dependence may be attributed to a new

reaction route in which intermediates participating in two successive reactions are concentrated and retained in a micellar water core long enough ($\approx$1 ms) so that they have no time to escape from a given micelle in the time scale of the reactions. The appearance of the new route depends on the numbers of bromate molecules, catalyst, and other reaction intermediates per micelle. This route exists if and only if any one of these numbers is less than unity.

The BZ reaction is known[16-24] to exhibit various dynamical behaviors such as stationary, bistable, oscillatory, quasiperiodic, chaotic, etc. In addition, there are more elaborate oscillatory regimes: two different oscillatory states under the same conditions,[18] sequential oscillations with gradual changes in oscillation frequency,[23-25] and a regime with large-amplitude oscillations followed by a train of small-amplitude low-frequency oscillations in the oxidized state.[21,22]

Balasubramanian and Rodley[1] showed that incorporation of the BZ oscillator into reverse micelles of AOT under batch conditions produced a gradual decrease in the oscillation period in contrast to the case of reference oscillations in an aqueous homogenous medium, where the oscillation period increases. We report here experimental results on new properties of the BZ reverse micelle system, specifically, the spontaneous bifurcation accompanied by multiplication of the oscillation frequency. The oscillation period changes gradually or sharply (in a threshold manner) with time, depending on the size and concentration of the microemulsion droplets. The latter characteristic is new, not only for the BZ reverse micelle reaction but also for all chemical oscillatory reactions reported so far.

## Experimental Section

The following analytical-grade chemicals were used without further purification: $NaBrO_3$, malonic acid (MA) (Wako), $Fe_2SO_4 \cdot 7H_2O$, 1,10-phenanthroline, $H_2SO_4$ (Katayama), and bis-(2-ethylhexyl) sodium sulfosuccinate (AOT) (Nakarai). *n*-Octane and dodecane (Katayama) were purified by intensive

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stirring with concentrated sulfuric acid for 2—3 h. Ferroin was obtained by mixing the solutions of 1,10-phenanthroline and $Fe_2SO_4$ in a molar ratio of 3:1. Water was deionized and distilled twice.

Reverse micelles containing the BZ system were prepared from aqueous soluiton I (AS(I)), containing $H_2SO_4$ (0.6 M) and MA (0.5 M) and aqueous solution II (AS(II)), containing ferroin (4.48 mM) and $BrO_3^-$ (0.2 M). These solutions were prepared separately for several reasons. Ferroin cannot be mixed with $H_2SO_4$ because the former is rapidly bleached by dissolved air in acidic media. Mixing of $H_2SO_4$ with $BrO_3^-$ should be avoided because preparation of micelles of a relatively large size is prevented when they are mixed together at high concentrations. For the same reason, the bromate concentration was reduced by a factor of 6 from the one used previously.[4,5] We also increased [MA] by a factor of 4 from that used in the previous work[5] to shorten the period of oscillations. The concentrations of $H_2SO_4$, MA, and $BrO_3^-$ employed here are very close to those used earlier.[1,2] Throughout this paper, the concentration of species X based on the whole volume ($V_0$) is denoted by [X] while that based on $V_w$ is denoted by $[X]_w$. Initial concentrations are denoted by $[X]_0$ or $[X]_{0w}$.

Two stock microemulsions of reverse micelles were prepared. Stock microemulsion I was prepared by adding 10 mL of AS(I) to 15—60 mL of the 1 M solution of AOT in octane. Similarly, stock microemulsion II was prepared by adding AS(II) to an octane solution of AOT in the same volume ratio as in the case of microemulsion I. Each microemulsion was then shaken and stirred with a Teflon-coated stirrer bar until clear. The resulting transparent microemulsions of reverse micelles were diluted with pure octane until a desired volume fraction of water $\phi_w$ was achieved. The quantity $\phi_w$ is the volume fraction of water defined by $\phi_w = V_w/V_0$, where $V_w$ is the volume of the aqueous phase added to the volume $V_{oil}$ of AOT solution in octane and $V_0$ is the total volume of the system ($V_0 = V_{oil} + V_w$). By diluting the stock microemulsion of reverse micelles in this way, one can obtain the desired concentration of micelles $C_m$ with a radius of micellar water core $R_w$. Micellar size depends primarily on the water/surfactant molar ratio $\omega = [H_2O]/[AOT]$, as $R_w \approx 0.175\omega$ nm.[26,27] Reverse micelles thus prepared were found to be stable for at least one day, and they gave the same oscillatory behavior as those used immediately after preparation. In some cases, we used dodecane in place of octane.

The BZ reaction was run in a thermostated Teflon reactor of cylindrical shape with flat silica windows and a Teflon plug. Stock microemulsions I and II, appropriately diluted with octane, were supplied to the reactor separately by two glass syringes with the same flow rate ($k_0/2$ each, so that the total flow rate is $k_0$) through Teflon tubing connected to the bottom of the reactor. The syringes were driven by a Micro Feeder (Furue, Model JP-V). The optical path length of the reactor was 3 cm. All the experiments were performed at $20 \pm 0.1$ °C. In a typical experiment, the reactor of volume $V_0$ (=20 mL) was quickly filled with microemulsions I and II at a maximum rate of 6 mL/min until the mixture of microemulsions started to pour out through a thin Teflon tube connected to the cell plug. Then the rate of reagent feeding was reduced to zero or to $k_0 = 0.013$ mL/min, which corresponds to a residence time of $\tau = V_0/k_0 = 26$ h. Stirring at 500—700 rpm with a Teflon-coated magnetic stirrer bar, 1.2 cm long and 4 mm in diameter, was continued throughout the experiment. In some experiments, nitrogen gas or air was bubbled into the reactor using a peristaltic pump (3.3 mL/min) after being passed through a cylinder containing octane to prevent evaporation of octane from the microemulsion.

The reaction was followed by monitoring the ferriin (Fe-(phen)$_3^{3+}$) absorbance at 610 nm on a home-made spectrophotometric setup. The accuracy of absorption measurements was 0.001 OD. The optical range was 3.5 units. A 30 W halogen—tungsten lamp was used as a light source. Light was passed through the cell after passing through a heat filter and an appropriate interference filter.

## Results

Figure 1a shows a typical time course of oscillations in the ferriin absorbance at 610 nm. Oscillations start at $t = 0$, corresponding to the reduction of the flow rate to $k_0 = 0.013$ mL/min. A clear frequency doubling is observed after four low-frequency oscillations. Figure 1b shows that frequency doubling does not occur under the same experimental conditions as in Figure 1a when air is bubbled through the reactor. Bubbling oxygen-free nitrogen has the same effect as air. More likely, some volatile species, which is important to the appearance of the bifurcation, is removed by the gas bubbling. The most probable candidate is $Br_2$ produced during the reaction.

If we dilute the initial microemulsions of reverse micelles with pure octane by a factor of 2, so that the volume fraction of the aqueous phase $\phi_w$ decreases from 0.11 to 0.055, no frequency doubling is observed even without bubbling through the reactor (Figure 1c). The same effect is observed for more extensive dilution, $\phi_w = 0.03, 0.02$, and 0.01. Maintaining the experimental conditions of Figure 1c, we may cause bifurcation either by replacing octane with dodecane or by lowering the rate of reagent feeding from $k_0 = 0.013$ mL/min down to 0 (the batch condition). In the former case, a sharp frequency-doubling bifurcation occurs, while, in the latter case, a frequency-tripling bifurcation appears after six low-frequency oscillations, as shown in Figure 2a. Figure 2a also shows what happens when the nitrogen bubbling is applied during the course of high-frequency oscillations. A few minutes after bubbling starts, the system turns into a state with the more reduced form of the catalyst, while the oscillation frequency is reduced to $1/2$ and reaches the value which might be achieved if bubbling was started at the beginning.

In some cases, instead of doubling and tripling, the quadrupling of oscillation frequency is observed. Figure 2b shows such an example for the same experimental conditions as in Figure 1a except for $\omega = 9.8$ instead of $\omega = 18$. The dependencies of oscillation periods on time for the experiments shown in Figures 1 and 2 are summarized in Figures 3 and 4. Figure 4 also presents the oscillation period versus time for the reference oscillations in water (curve w). $N_2$ bubbling has no visible effect on the reference BZ reaction. It is noteworthy that all the above experiments are reproducible; i.e., repetitions of the experiments show frequency multiplication after the same number of oscillations.

Curve 1 in Figure 3 (data from Figure 1a) shows that the period shortens abruptly from 9.6 to 4.8 min and then decreases rather smoothly to 4.5 min. For curve 2 in Figure 3 (data from Figure 2a), the oscillation period shortens from 9.9—10.1 min through a single intermediate point of 8.6 to 3.4—3.3 min; i.e., the oscillation frequency triples. After this bifurcation, the period decreases to 2.2 min smoothly. Upon switching on $N_2$ bubbling, the oscillation period jumps to 4 min, whereas it might have been 2 min without bubbling; i.e., bubbling reduces the oscillation frequency by a factor of 2. For curve 3 of Figure 3 (data from Figure 2b), the period shortens abruptly from 8 min through an intermediate point of 4 min to 2.3—2.2 min and then decreases smoothly to 1.4 min. In this case, the oscillation frequency quadruples, or doubling occurs twice. For the
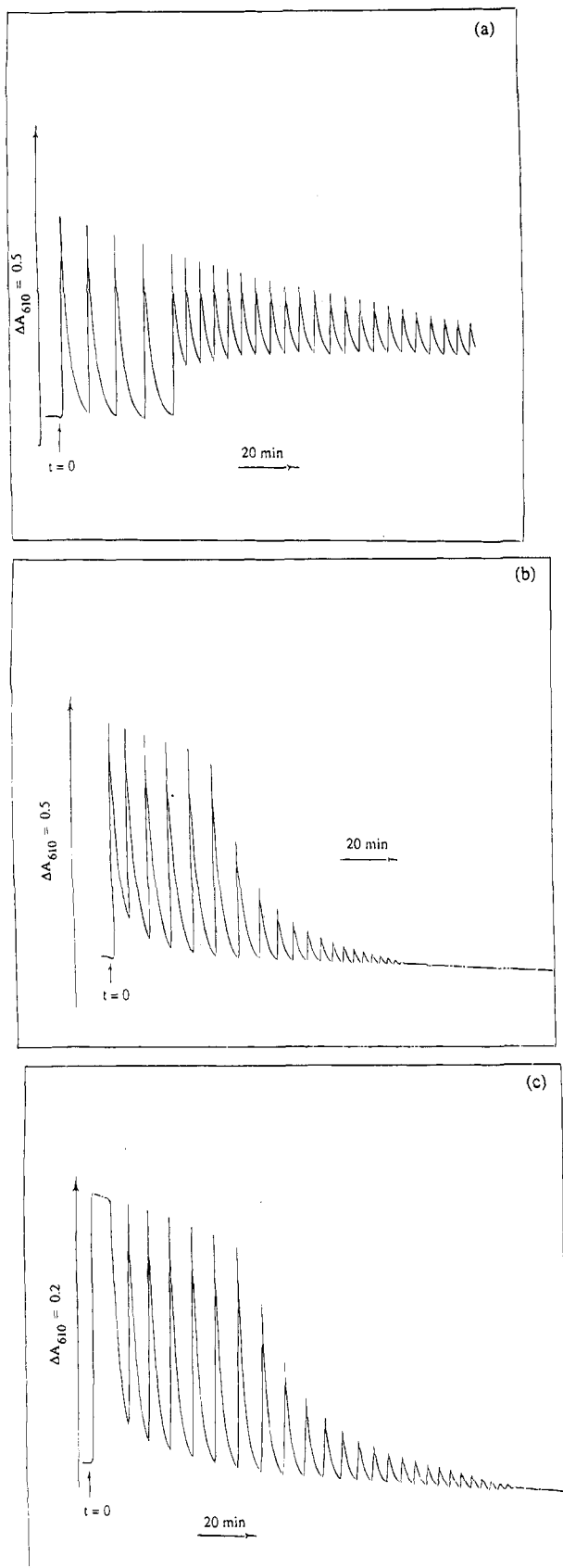
**Figure 1.** Kinetics of the ferroin-catalyzed BZ reaction in AOT reverse micelles in octane. (a) $\omega = 18$, $k_0 = 0.013$ mL/min, $\phi_w = 0.11$, and the stirring rate is 720 rpm. The initial concentration of reagents in the aqueous phase is $[H_2SO_4]_{ow} = 0.3$ M, $[BrO_3^-]_{ow} = 0.1$ M, $[MA]_{ow} = 0.25$ M, $[ferroin]_{ow} = 2.24$ mM. No bubbling. (b) The experimental conditions are the same as those in part a, except for the air bubbling through the reactor at 3.3 mL/min. (c) The experimental conditions are the same as those in part a, except for $\phi_w = 0.055$.

reference oscillations in water (Figure 4), the period grows smoothly from 2.4 to 4.6 min, before oscillations cease.

Figures 5 and 6 show variation in the oscillation amplitude and in $[ferriin]_{min}$, the minimum concentration of ferriin in a single oscillation period, with time. Figure 5 compares the results shown in Figure 1a and b, which differ in the bubbling condition. Figure 6 compares the results shown in Figures 1c and 2a, which differ in the rate of reagent feeding. Comparing these results with those of Figure 3, we can see that a spontaneous change in the oscillation frequency is accompanied by sharp changes in oscillation amplitudes and in the oxidation state of the catalyst. It is to be noted that the catalyst tends to turn into a completely reduced form as $t \rightarrow \infty$ when bifurcation doesn't occur, while it approaches a partly oxidized state when a sharp change in the oscillation frequency takes place.

## Discussion

Of all the observations reported above, the most interesting is the fact that in several cases the oscillation frequency of the BZ reaction in reverse micelles changes abruptly by an integer factor in the course of oscillations. It is most likely that a combination of physical and chemical factors characterizing the system governs such a bifurcation. The physical factors are the flow conditions, the droplet size, the mode of interdroplet interactions, and the extent of droplet aggregation, while the chemical factor is the variation in reagent concentrations during the course of reactions. Although the nature of microemulsions and their dynamical behavior are not known well enough to discuss the mechanism of the observed phenomenon in detail, it is clear that the physical factors would remain unchanged during a single experiment and thus cannot be a direct cause of the frequency-multiplying bifurcation. They are, however, important in providing an adequate condition for the bifurcation to occur. On the other hand, the chemical composition changes as the overall reaction proceeds (note that the present experiments are performed under batch or very low flow rate conditions, where the stationary conditions as in the CSTR experiments do not hold). Therefore, accumulation or depletion of some chemical species may initiate the bifurcation in the course of the reaction. In the discussion below we shall examine chemical and physical factors which, in combination, may lead to the observed phenomena.

As for the chemical factor, the aforementioned experiments suggest that an increase in the bromine concentration is the most probable cause of the frequency-multiplying bifurcation. This is justified by the experiments on air and nitrogen bubbling through the reactor. In all cases, bubbling leads either to the damping of the existing high-frequency oscillations or to their prohibition. The same conclusion is drawn from the experiments under increased $k_0$ or decreased $\phi_w$, where no frequency-doubling bifurcation is observed. Both factors should result in the decrease of the bromine concentration in the system; a higher $k_0$ increases the rate of removal of $Br_2$ which is produced in the course of the reactions, while the system with lower $\phi_w$ contains a lower amount of aqueous phase, resulting in a slower overall production of $Br_2$.

The appearance of high-frequency oscillations can hardly be accounted for by the production of new organic substrates or by the depletion of the initial reagents, because high-frequency oscillations can easily be brought back to low-frequency ones by bubbling gas through the reactor (see Figure 2a and curve 2 of Figure 3). This can never occur if the frequency-multiplying bifurcation is due to a new substrate or to the depletion of the reactants. In typical cases of sequential oscillations reported so far,[23-25] high-frequency oscillations are observed at the

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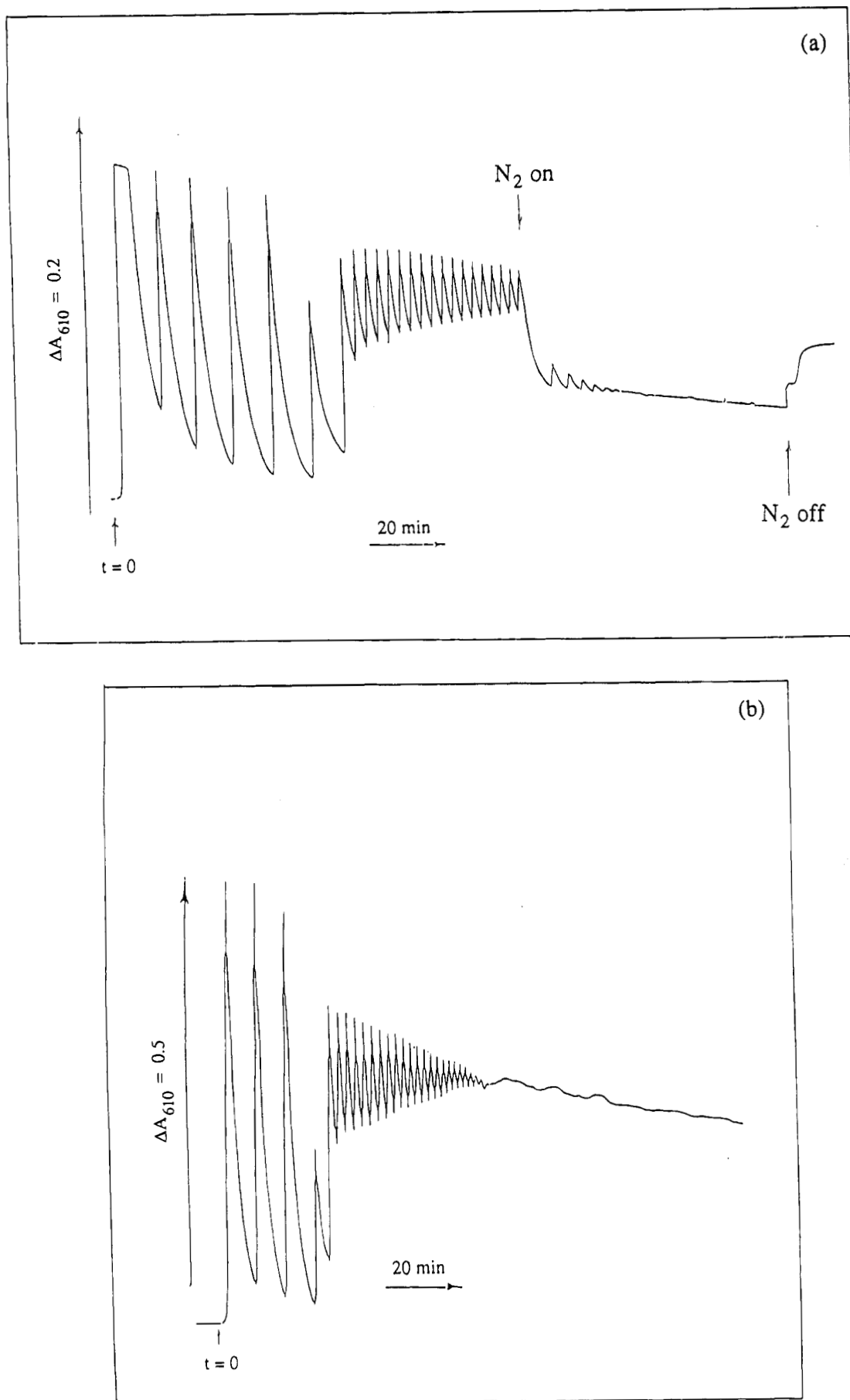*J. Phys. Chem., Vol. 99, No. 18, 1995* **6947**



**Figure 2.** Kinetics of the ferroin-catalyzed BZ reaction in AOT reverse micelles in octane. (a) Experimental conditions are the same as those in Figure 1c, except for $k_0 = 0$. Nitrogen bubbling was started at "N$_2$ on" and terminated at "N$_2$ off". (b) The experimental conditions are the same as those in Figure 1a, except for $\omega = 9.8$.
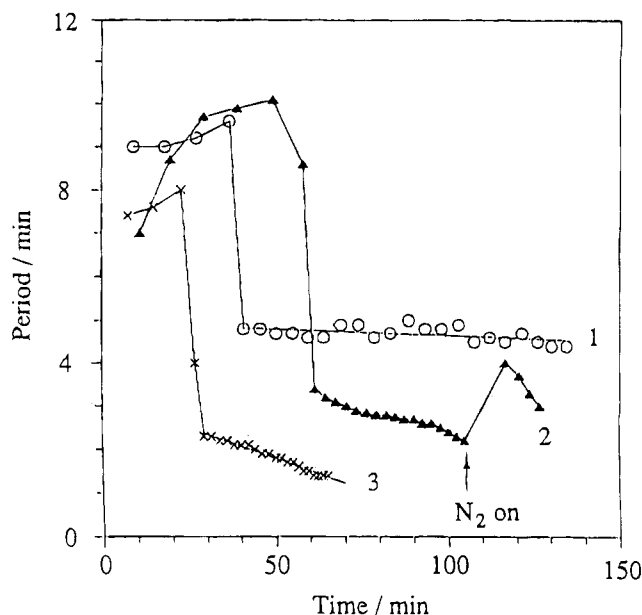
**Figure 3.** Oscillation period versus time. Curves 1, 2, and 3 correspond to the amplitude versus time curves in Figures 1a, 2a, and 2b, respectively.
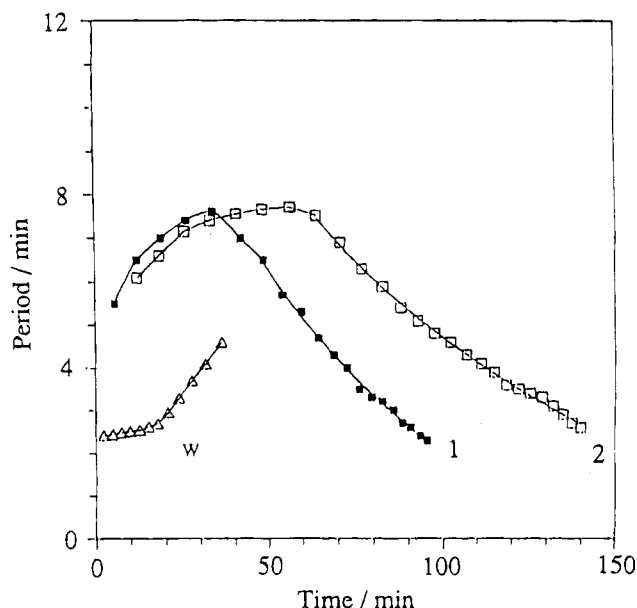


**Figure 5.** Oscillation amplitude (△, ▲) and minimum concentration of ferriin (□, ■) versus time for the curves shown in Figure 1a (□, △) and Figure 1b (■, ▲) with different bubbling conditions. An amplitude of 100% corresponds to the total concentration of the catalyst.



**Figure 4.** Oscillation period versus time. Curves 1 and 2 correspond to the amplitude versus time curves in Figures 1b and 1c, respectively. Curve w is for the reference aqueous BZ oscillations.



**Figure 6.** Oscillation amplitude (△, ▲) and minimum concentration of ferriin (□, ■) versus time for the curves shown in Figure 1c (■, ▲) and Figure 2a (□, △) with different feeding rates. An amplitude of 100% corresponds to the total concentration of the catalyst.

beginning, which is quite natural, since the coexistence of high-frequency and low-frequency oscillations terminates with the progress of the former. In our case, however, the picture is quite the opposite; low-frequency oscillations are followed by high-frequency ones. The possibility of degradation of the AOT molecules by the BZ solution, such as the bromination of acid-catalyzed hydrolysis of AOT, has also been excluded, since the ^{1}H-NMR and mass spectra give no indication of chemical change of AOT after the BZ oscillations in reverse micelles.[2]

On the basis of these considerations, we may assume that $Br_2$ dissolution in the organic phase is a key factor controlling frequency-multiplying bifurcation. The organic phase serves as a reservoir of $Br_2$ which regulates $[Br_2]_w$ by supplying $Br_2$ back to the aqueous phase when $[Br_2]_w$ decreases in the course of the reaction. $Br_2$ in the aqueous pseudophase controls the bromide ion concentration through the following reactions:
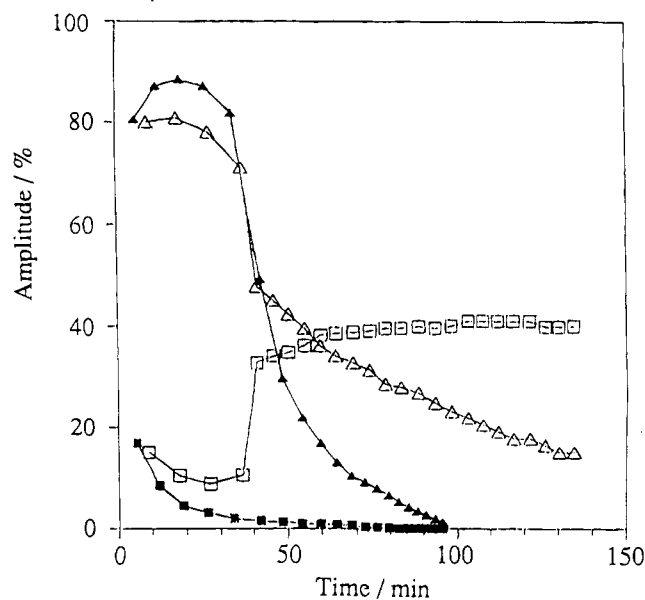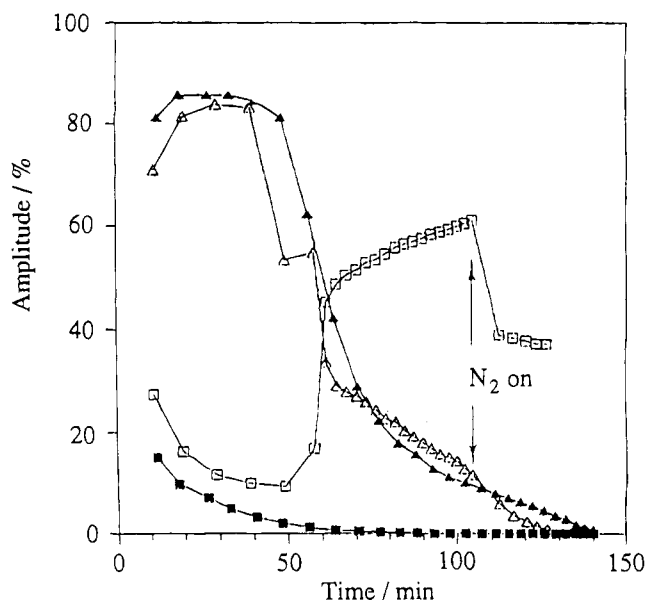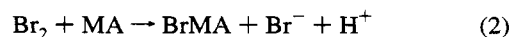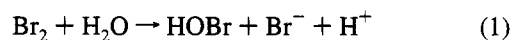
$$Br_2 + H_2O \rightarrow HOBr + Br^- + H^+ \qquad (1)$$

$$Br_2 + MA \rightarrow BrMA + Br^- + H^+ \qquad (2)$$

where BrMA is bromomalonic acid. The bromide ion plays a key role in controlling oscillations in the Field–Koros–Noyes (FKN) mechanism.[28] However, this control mechanism itself does not explain why the frequency is multiplied by an integer factor of 2, 3, or 4 or why the highest oscillation frequency corresponds to that in the reference aqueous solution. On the other hand, the type of bifurcation reported here is commonly observed in physical[29] and chemical[30] systems of coupled oscillators. By analogy we assume that coupling between aggregates (clusters) of nanodroplets is important in the present case. The role of bromine in the organic phase is to enhance the

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communication between clusters (minioscillators), resulting in a synchronization of oscillation phases over the whole system.

Let us now examine the possibility of the existence of such clusters. The concentration of micelles $C_m$ can be determined from the following relation:[4,5]

$$C_m V_m N_A = \phi_w \qquad (3)$$

where $V_m = (4\pi/3)R_w^3$ is the volume of the micellar water core, $R_w \approx 0.175\omega$ nm, and $N_A$ is Avogadro's number. Taking $\phi_w = 0.11$, we get $C_m = 1.4$ mM for $\omega = 18$ and $C_m = 8.7$ mM for $\omega = 9.8$. For $[\text{ferroin}]_{ow} = 2$ mM, the overall concentration is $[\text{ferroin}]_0 = [\text{ferroin}]_{ow} \times \phi_w = 0.22$ mM. Thus, one molecule of ferroin is contained in every 6 droplets of microemulsion for $\omega = 18$ and in every 40 droplets for $\omega = 9.8$. This means that a majority of droplets contain no catalyst. A cluster consisting of a large number of droplets would be required to accommodate all the reacting intermediate molecules.

Using eq 3, the average distance $L_{cc}$ between the centers of two adjacent droplets of the microemulsion can be estimated as

$$L_{cc} = (C_m N_A)^{-1/3}$$
$$= (V_m/\phi_w)^{1/3} = (V_d/\phi_d)^{1/3} \qquad (4)$$

where $V_d$ is the volume of a droplet including the AOT shell and $\phi_d$ is the corresponding volume fraction. The relationship between $\phi_d$ and $\phi_w$ is[31]

$$\phi_d/\phi_w = 1 + M_A d_w/(M_w d_A \omega) \qquad (5)$$

where $M_w$ and $M_A$ are the molecular weights of water and AOT, respectively, and $d_w$ and $d_A$ are their bulk densities, respectively. It follows from eq 5 that

$$R_d = (\phi_d/\phi_w)^{1/3} R_w \qquad (6)$$

where $R_d$ is the droplet radius including the AOT shell. Using $M_A = 444.5$, $d_A = 1.14$ g/mL,[32] $M_w = 18$, and $d_w = 1.00$ g/mL in eqs 4–6, $L_{cc}$ for $\phi_w = 0.11$ is estimated as $L_{cc} \approx 1.29(2R_d)$ for $\omega = 18$ and $L_{cc} \approx 1.14(2R_d)$ for $\omega = 9.8$. Thus, the emulsion droplets are located rather close to each other. The average distance between them exceeds only slightly the sum of the radii of adjacent droplets, being 1.34 times larger for $\omega = 18$ and 1.18 times larger for $\omega = 9.8$. As a consequence, the droplets can easily form clusters or dynamical aggregates. Under such a condition, it is known that the percolation structure, or even a bicontinuous structure of water and oil, may appear.[33,34] The effect of percolation is known to manifest itself as a sharp increase in specific conductivity at 25 °C and $\phi_d > 0.17$,[34] which, according to eq 5, corresponds to $\phi_w > 0.077$ for $\omega = 18$ or $\phi_w > 0.053$ for $\omega = 9.8$ in our experiments. The existence of percolation structures at relatively high values of $\phi_w$ may be consistent with the fact that the frequency-multiplying bifurcation can occur only for sufficiently high values of $\phi_w$ ($\phi_w > 0.05$).

Unlike single droplets of the microemulsion, large clusters loaded with the BZ system may be regarded as individual oscillators. Communication, mass exchange, and phase synchronization between these clusters may be performed by single droplets acting as shuttles or by molecules like $Br_2$, which is soluble both in water and oil. The extent of communication by single droplets may not vary drastically in a single run of experiments. On the other hand, $Br_2$ is piled up in the organic phase as the overall reaction proceeds. An increase in $[Br_2]_{oil}$

may affect the mode of coupling between clusters and lead to the frequency-multiplying bifurcation at some critical value of $[Br_2]_{oil}$.

Assume that clusters of droplets have their own oscillation period $T$ which corresponds to the period for the reference bulk BZ oscillation. When many clusters interact with each other, oscillations with periods $T$, $2T$, $3T$, and so on may be produced depending on the coupling strength between them. A similar phenomenon has been observed for two coupled oscillators with different frequencies.[30] The stronger the coupling, the shorter the oscillation period observed. This is the very case observed in our experiment; i.e., the oscillation period decreases with time as $[Br_2]_{oil}$ increases. For $t \to \infty$, the period approaches its intrinsic value $T$ as whole clusters synchronize completely (Figure 3, curves 2 and 3). On the other hand, curve 1 approaches $2T$ rather than $T$. This is presumably because the experimental conditions, $k_0 = 0.013$ mL/min and $\omega = 18$, for curve 1 are insufficient for a complete synchronization. The flow rate for curve 2 is $k_0 = 0$, where more $Br_2$ is piled up in the organic phase than in the case of curve 1 to realize a complete synchronization. Curve 3 is for $\omega = 9.8$ instead of $\omega = 18$ in the case of curve 1. If the microemulsion droplets form clusters, the ratio of the mean distance between the centers of adjacent clusters to the average diameter of a cluster is the same as $L_{cc}/(2R_d)$ given above for the emulsion droplets; the ratio is 1.14 for $\omega = 9.8$ and 1.29 for $\omega = 18$, independent of the number of droplets in a cluster. Therefore, more extensive interaction between clusters is expected for $\omega = 9.8$ (curve 3).

The existence of clusters is also substantiated by the appearance of the frequency-doubling bifurcation for the replacement of octane by dodecane under the same experimental conditions as in Figure 1c, where no frequency-multiplying bifurcation is oberved. It is known that an increase in the solvent chain length causes an enlargement of clusters and an increase in the rate of intermicellar exchange of reactants.[35,36] The initial coupling strength for the dodecane system would be higher than that for the octane system but still insufficient to exhibit a complete synchronization. The coupling is increased with increasing $[Br_2]_{oil}$ to cause the frequency doubling.

In this paper, we have presented a new finding of the frequency-multiplying bifurcation for the BZ reaction in reverse micelles. We have suggested a role of $Br_2$ in controlling the coupling strength between clusters made of a relatively large number of droplets in the reverse micelles. Further studies are needed to substantiate the model proposed here, to demonstrate experimentally the existence of clusters in the microemulsion of reverse micelles loaded with the BZ system and to establish how $Br_2$ controls the coupling strength between clusters.

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