Bromomalonic-acid-induced transition from trigger wave to big wave in the Belousov-Zhabotinsky reaction

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The Marangoni effects on chemical waves in the ferroin-catalyzed Belousov-Zhabotinsky reaction were studied. The main purpose of the present study was to understand the mechanism of the big wave, an accelerative chemical wave involving surface-tension-driven fluid motions. Spatiotemporal variations of surface tension caused by a chemical wave were measured using the Wilhelmy method. The transition from conventional trigger waves to big waves, due to a concentration change of bromomalonic acid, was observed. The strong surface activity of the bromomalonic acid which was responsible for the transition was also observed. It led to an acceleration of the big waves through the Marangoni effect.

I. INTRODUCTION

Heat or mass transfer at free liquid surfaces gives rise to fluid motions due to local gradients of surface tension. This phenomenon, widely known as the Marangoni effect, leads to specific instabilities both in time and space, e.g., convections and waves [1]. Recently, Marangoni instabilities coupled to chemical reactions have received much attention from new schemes of transport in liquid/vapor systems [2]. In particular, chemical waves coupled to convective motions in excitable media have been noted in the last decade [3–15]. One of the typical systems is a trigger wave (TW) in the Belousov-Zhabotinsky reaction (BZR) [16]. Since the BZR is an exothermic reaction involving surface-active compounds, TW's may lead to fluid motions due to spatiotemporal inhomogeneities in physicochemical quantities such as surface tension [3–6], temperature [7,8], and density [8]. In such fluid motions, because the buoyancy effect is suppressed in thin layers, Marangoni effects play major roles.

Recently, an interesting type of TW was discovered in a ferroin-catalyzed BZR system [9–15]. This wave, named a big wave (BW) [9,10] or the hydrochemical soliton [11], propagates with a large velocity and nonzero acceleration, accompanied by large hydrodynamical motions as well as solitary surface deformation [10–15]. A remarkable characteristic of a BW is to propagate with a velocity that increases with time, which cannot be described by simple reaction-diffusion mechanisms. In addition, a BW is accompanied with surface flow, whose velocity is equal to the propagating velocity and is typically 30 times larger than that in a conventional TW [9,10]. These hydrodynamic properties can be explained by Marangoni effects, as reported previously [10–15]. However, the following problems on BW's are yet unsolved: (i) The origin of the Marangoni instability is not clear, i.e., whether it is due to mass capillarity or thermocapillarity. (ii) The control parameter for the transition from a TW to a BW has not been determined. (iii) The mechanism of acceleration is not understood sufficiently. These questions must be clarified in order to understand the mechanism of BW's. Especially for the mass capillarity, the surface tension variation with a concentration change of surface-active ferroin is not strong enough for the generation of a BW, unlike the results in previous studies [6,17]: That is, the spatial distribution profile of ferroin in a BW was almost similar to that in a TW [15], which means no concentration difference between them at the wave fronts. Other candidates therefore should be considered.

In this paper a quantitative measurement of surface tension caused by a TW will be shown. Then contributions of heat and surface-active compounds to the Marangoni effects will be discussed. In particular it will be reported that a strong surface activity of bromomalonic acid (BrMA), the concentration C of which is largely varied during the reaction, can generate a BW. It will be concluded that the transition from a TW to a BW is caused by the solutal Marangoni instability at a high concentration of BrMA.

II. EXPERIMENTAL METHOD

The experiments were carried out in a conventional setup [16] in BZR solutions of the following composition: 300-mM sulfuric acid, 320-mM sodium bromate, 20-mM malonic acid (MA), 0–80-mM BrMA, and 3.7-mM ferroin. This composition was realized by *in situ* bromination of MA [18]. The pure water (relative resistance ~ 20 MΩ m) was prepared through a unit with 0.5 μm of membrane filter and ion-exchange resin (Advantec Toyo, Aquarius GSU-901). 5.0 ml of the solution was placed in an optically flat petri dish of 95-mm diameter, giving a layer thickness of 1 mm. This medium showed a quasiexcitable state with a long period of auto-oscillation (typically 8–10 min). The circular wave was triggered by immersing a silver wire in diameter of 1–2 mm into the solution.

Spatiotemporal developments of chemical waves were observed via a video camera system with a charge-coupled device camera (Panasonic NV-X100), and an image-capturing
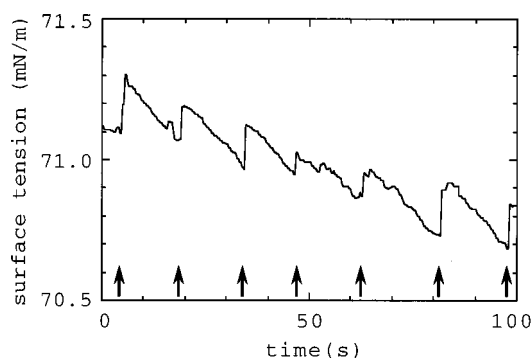
FIG. 1. Temporal variation of the surface tension caused by a chemical wave train. The arrow indicates the passage of a wave front at a measuring point.

FIG. 2. C_0 dependence of the chemical wave propagation. The transition point C_0^* is 50 mM.

board system (Scion LG-3 and NIH-Image). The surface tension of the solution was measured using the Wilhelmy method with surface tension measurement unit (Cahn DCA322). The probes were platinum wires 1 mm-in diameter and 50 mm$\times$5 mm of filter paper sheets (10.3 mm of effective contour length). The top of a sample container was covered with wet filter papers, avoiding water evaporation. Experiments were done in a clean room (class 10 000), which was kept at 18.0$\pm$1.0 °C and controlled in range from 40% to 60% of relative humidity. The hydrophobicity of substances, represented by a parameter log P of the octanol-water partition coefficient, was estimated numerically from Rekker's fragment method [19] using a software package (BIOBYTE, CLOGP for Windows). A temperature change due to heat by chemical reaction in homogeneously stirred BZR solutions was measured by use of a K-type thermocouple. Using a spectrophotometer (Jasco Ubest-50), the concentration of ferroin was determined from the absorbance at 680 nm, at which the molar extinction coefficient of ferroin was 413$\pm$7 M^{-1} cm^{-1}, while it was negligible for ferroin.

III. RESULTS AND DISCUSSION

Spatiotemporal variations of surface tension caused by chemical waves were investigated experimentally from the viewpoint of the Marangoni effects. A variation of the surface tension due to a train of TW's (target wave; wavelength $\sim$2 mm and velocity $\sim$0.1 mm/s) is shown in Fig. 1. The arrow in the figure indicates the passage of a wave front at a probe. Two characteristics of the variation, i.e., oscillation in short-period ($\sim$20 s) and long-period monotonic decreases, are noted in Fig. 1. The former, the amplitude of which is about 0.2 mN/m, is synchronized to a concentration oscillation of ferroin [17]. On the other hand, the latter may be caused by in elevation of temperature or the adsorption of other surface-active products with slow dynamics. This will be discussed below.

In the present study, BrMA has been prepared at a high concentration in order to investigate the influence of BrMA on, the dynamics of the chemical waves. Figure 2 shows the dependence of the chemical wave propagation on the BrMA concentration prepared at the beginning of measurements (denoted by C_0). The ordinate and the abscissa are of the magnitude of acceleration of the wave front and the normal-
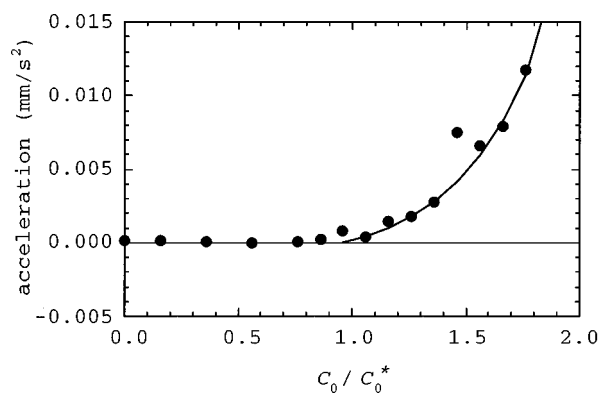
ized concentration C_0/C_0^*, respectively. The result implies that $C_0=C_0^*$ is a transition point from a TW to a BW with C_0. Here C_0^* is determined experimentally as 50 mM. In the region $C_0>C_0^*$, the acceleration has a nonzero value, and increases exponentially with C_0, while it has a zero value in $C_0<C_0^*$. For other substances in the BZR, such as bromate, bromide ion, sulfuric acid, MA and ferroin, accelerative propagation cannot be observed over the wide concentration areas in those chemicals. Therefore, it is determined that C_0 is a control parameter for BW's.

Focusing on Marangoni effects, several experiments have been carried out in order to clarify the origin of the transition between two chemical waves (TW's and BW's). Figure 3(a) shows the surface activities of MA and BrMA. Here BrMA has been prepared *in situ* in the BZR without the catalyst. The data points have been obtained from values at steady states ($\sim$10 min). The two results are well fitted to the exponential curves. These results imply that both MA and
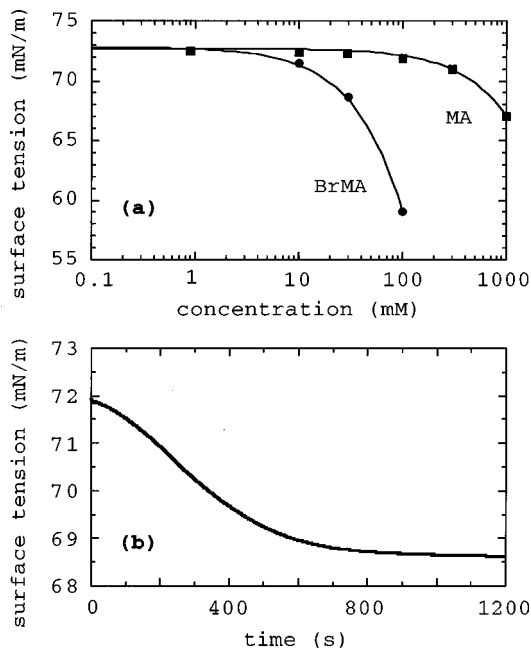

FIG. 3. (a) Surface activity of MA and BrMA. BrMA was prepared *in situ* in the BZR without ferroin. (b) Temporal change of the surface tension due to the adsorption process of BrMA.
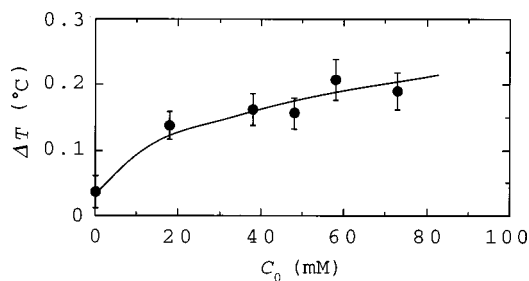
FIG. 4. Dependence of ΔT on C_0 in the stirred BZR. ΔT increases monotonically with C_0.

FIG. 5. C_0 dependence of ΔC_F in the BZR. ΔC_F is almost constant at $C_0 > 30$ mM.

BrMA are surface active, and the latter is more active than MA. Figure 3(b) shows the relaxation characteristic of surface tension due to adsorption process of BrMA at an air/water interface, of which the relaxation time is 280 s. Figure 4 shows a temperature elevation ΔT during a cycle of the reaction under the calmly stirred condition, which is typically 0.1–0.2 °C. Such a temperature elevation may be regarded like that at the front of the chemical wave. As shown in Fig. 4, ΔT increases monotonically with an increase of C_0. Figure 5 shows the amplitude ΔC_F of the oscillation of ferroin concentration for varing C_0 in the stirred system. ΔC_F is almost constant with 0.5 mM when C_0 is larger than 30 mM.

Now let us consider the origin of the Marangoni effects inducing the transition. For further discussion, we define $\Delta \gamma_T$ and $\Delta \gamma_C$ as surface tension changes due to ΔT and a change of C, respectively. Based on the above results, it can be suggested that the transition may occur through the following three factors: (i) the surface activity of BrMA, (ii) the heat generation due to the production process of BrMA, and (iii) the surface activity due to ferroin concentration change induced by the reaction of BrMA.

To begin with the surface activity of BrMA, the hydrophobic parameters $\log P$ of BrMA and MA have been obtained numerically as -0.106 and -0.759, respectively [20]. These calculated results show that BrMA is more hydrophobic than MA, which is consistent with the results in Fig. 3(a). Accordingly, the change of C due to the BZR can induce a large variation of the surface tension of the solution. Since an increase of C during a cycle of the reaction (denoted by ΔC) is almost the same as that of the catalyst concentration during the reaction, $\Delta \gamma_C$ at the wave front can be estimated to be 0.52 mN/m at $C_0 = C_0^*$. In addition, Fig. 4 shows that ΔT increases monotonically with an increase of C_0. Here ΔT increases in proportion to ΔC [21]. Therefore, it can be said that ΔC increases with an increase of C_0. Since BrMA is surface active, the increase of ΔC due to C_0 leads to an increase of $\Delta \gamma_C$.

Next let us discuss the temperature dependence of the surface tension. The temperature elevation ΔT due to one cycle of the reaction is 0.20 °C at most, as shown in Fig. 4. Then $\Delta \gamma_T$ is the order of 10^{-2} mN/m in pure water at 20 °C, which cannot account for the surface tension variation obtained in Fig. 1. $\Delta \gamma_T$ is about 0.026 mN/m at $C_0 = C_0^*$ ($\Delta T = 0.16$ °C), which is 20 times smaller than $\Delta \gamma_C$. Therefore the temperature elevation is not responsible for the present Marangoni convection inducing the transition. The
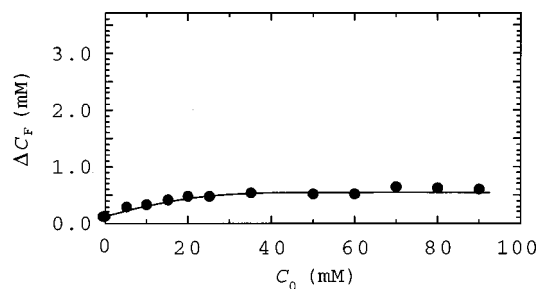
result reported by Böckmann et al. [5] supports our argument well. Now we shall mention the concentration change of ferroin. As shown in Fig. 5, ΔC_F is constant in the region $C_0 > C_0^*$, i.e., it does not depend on C_0. Thus the acceleration in Fig. 2 does not depend on the concentration of ferroin. That is, the surface activity of ferroin does not contribute to the transition. On the basis of these arguments, it can be concluded that the transition originates from the surface activity of BrMA, and therefore the increase of $\Delta \gamma_C$ leads to an increase of acceleration.

Finally, we would like to mention the surface adsorption process of BrMA reducing the surface tension. The process has a finite relaxation time in the unstirred system, as shown in Fig. 3(b), which is longer than the period of the oscillation of the BZR. On the other hand, the adsorption of ferroin occurs very quickly, as shown in Fig. 1 [17]. Therefore, it can be said that the time scale of the surface tension variation due to the adsorption of ferroin does not compete with that of BrMA at the wave front. The former is much faster than the latter. Accordingly, the latter becomes more effective at the tail of the wave. Thus there are two characteristic time scales in adsorption processes of surface active substances in the BZR, which induces a local inhomogeneity of the two chemicals to enhance the local surface tension difference. Then they lead to strong Marangoni convections.

IV. CONCLUSION

In the present study, a spatiotemporal variation of surface tension due to a chemical wave in the BZR has been measured by the Wilhelmy method. It is clarified that the variation is caused by a concentration change of BrMA as well as ferroin. The transition from a TW to a BW is induced by the surface activity of BrMA. The critical concentration of BrMA at the transition point is 50 mM. Then the acceleration increases monotonically with an increase of the concentration. It is worth mentioning the existence of two different time scales in surface-active substances which play an important role to induce the BW. However, the mechanism of acceleration of the BW is not yet clear. Further study is required from hydrodynamical points of view.

[1] J.R.A. Pearson, J. Fluid Mech. **4**, 489 (1958); L.E. Scriven and C.V. Sterling, Nature (London) **187**, 186 (1960).

[2] L.M. Pismen, J. Colloid Interface Sci. **102**, 237 (1984); T. Funada and M. Sakata, J. Phys. Soc. Jpn. **57**, 476 (1988); L.M. Pismen, Phys. Rev. Lett. **78**, 382 (1997).

[3] S.C. Müller, T. Plesser, and B. Hess, Ber. Bunsenges. Phys. Chem. **89**, 654 (1985).

[4] H. Miike, S.C. Müller, and B. Hess, Phys. Rev. Lett. **61**, 2109 (1988); T. Sakurai, E. Yokoyama, and H. Miike, Phys. Rev. E **56**, 2367 (1997).

[5] M. Böckmann, B. Hess, and S.C. Müller, Phys. Rev. E **53**, 5498 (1996).

[6] K. Matthiessen, H. Wilke, and S.C. Müller, Phys. Rev. E **53**, 6056 (1996).

[7] K.I. Agladze, V.I. Krinsky, and A.M. Pertsov, Nature (London) **308**, 834 (1984).

[8] J.A. Pojman and I.R. Epstein, J. Phys. Chem. **94**, 4966 (1990).

[9] H. Miike, H. Yamamoto, M. Momota, and H. Hashimoto, in *Pattern Formation in Complex Dissipative Systems*, edited by S. Kai (World Scientific, Singapore, 1992), p. 191.

[10] H. Miike, H. Yamamoto, S. Kai, and S.C. Müller, Phys. Rev. E **48**, 1627 (1993).

[11] S. Kai and H. Miike, Physica A **204**, 346 (1994).

[12] S. Kai, T. Ariyoshi, S. Inanaga, and H. Miike, Physica D **84**, 269 (1995).

[13] O. Inomoto, T. Ariyoshi, S. Inanaga, and S. Kai, J. Phys. Soc. Jpn. **64**, 3602 (1995).

[14] O. Inomoto, T. Ariyoshi, S. Inanaga, and S. Kai, Int. J. Bifurcation Chaos Appl. Sci. Eng. **7**, 989 (1997).

[15] O. Inomoto, A. Sakaguchi, and S. Kai, in *Complexity and Diversity*, edited by R. Nakamura (Springer-Verlag, Tokyo, 1997), p. 135.

[16] *Oscillations and Traveling Waves in Chemical Systems*, edited by R. J. Field and M. Burger (Wiley, New York, 1985).

[17] K. Yoshikawa, T. Kusumi, M. Ukitsu, and S. Nakata, Chem. Phys. Lett. **211**, 211 (1993); T. Kusumi, K. Yoshikawa, and S. Nakata, in *Far-From-Equilibrium Dynamics of Chemical Systems*, edited by J. Gorecki, A.S. Cukrowski, A.L. Kawczynski, and B. Nowakowski (World Scientific, Singapore, 1994), p. 87.

[18] H.-D. Försterling, L. Stuk, A. Barr, and W.D. McCormick, J. Phys. Chem. **97**, 2623 (1993).

[19] R.F. Rekker, *The Hydrophobic Fragmental Constant* (Elsevier, Amsterdam, 1977); A.J. Leo, Chem. Rev. **93**, 1281 (1993).

[20] Y. Sudo (private communication).

[21] E. Kőrös, M. Orbán, and Zs. Nagy, Acta Chim. Acad. Sci. Hung. **100**, 449 (1979).