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Effect of Microgravity on the Spatial Oscillation Behavior of Belousov−Zhabotinsky Reactions Catalyzed by Ferroin

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The propagation behavior of chemical waves in the Belousov−Zhabotinsky reaction was examined experimentally for the first time under microgravity conditions. This study was motivated by the work of Kondepudi and Prigogine (1981), who pointed out theoretically that a diffusion reaction system with nonlinear and nonequilibrium characteristics may receive a great amplification of the subtle effect of gravity on elementary reactions. In the present study, the free-fall facility at the Japan Microgravity Center in Hokkaido (JAMIC) was utilized to maintain a quality of 10^{-5} g for about 10 s. To prevent convection due to surface tension, a thin planar vessel closed to air was used in both normal and microgravity runs. Concentric patterns induced spontaneously in the vessel fixed in the vertical position were elongated downward and shortened upward under normal gravity. Under microgravity, however, propagation speed was almost the same in traveling directions. To discuss the effect of convection, propagating speed in gel matrix was also observed in similar experiments under microgravity conditions, but no apparent influence was revealed.

Introduction

The driving force of mass transfer in chemical reactions is the concentration gradient, and the important feature that carries the substance is convection. Convection[1] occurs due to two factors: one is the buoyancy in the gravitational field known as Rayleigh−Benard instability, and the other is nonuniformity in the heterogeneous boundary tension, the Marangoni instability, which has no relation to the gravity. The Belousov−Zhabotinsky (BZ) reactions have been studied in terms of the latter convection where the reaction solution was mostly open to air at a free surface, as in a Petri dish.[2−6]

In the theoretical approach of a reaction−diffusion system far from equilibrium, Kondepudi and Prigogine[7] introduced a term for the gravitational effect to the differential equation of the system and pointed out the great amplification of the subtle effect of gravity. The present experimental study was initially motivated by their theoretical work, and we focused our attention on the gravitational effect on spatial patterns of the BZ reactions.[8]

In this study, the free-fall facility at JAMIC (Japan Microgravity Center at Kami-Sunagawa, Hokkaido) was used to achieve a microgravity environment. The microgravity level[9] of 10^{-5} g is maintained for 9.8 s of high quality. By using a closed reaction vessel, the convection factor of boundary tension was excluded. A planar reaction vessel 1.0 mm in depth was used in a vertical position, and the influence of gravity on the propagation direction and the velocity of chemical waves was examined. Similar experiments were carried out on the earth by tilting the vessel from horizontal to vertical. Aqueous solutions were used in most experiments for measurement of convective effects, and the results were compared with those obtained in gel matrix.

Experimental Section

Reagents. All the reagents were of guaranteed grade and used without further purification. The chemical oscillation systems were composed of sodium bromate, sulfuric acid, malonic acid, and ferroin. Each initial concentration for on-the-earth experiments was 0.288 M, 0.240 M, 0.0972 M, and 0.962 mM, and for free-fall experiments 0.620 M, 0.169 M, 0.196 M, and 0.493 mM in aqueous solutions and 0.70 M, 0.25 M, 0.70 M, and 3.36 mM in the gel matrix of water glass (6.42−7.04%) .[10] Deionized water supplied by JAMIC was used without further purification.

Apparatus and Procedure. The handmade experimental system[11] was assembled in a steel frame of 870 mm (width) × 425 mm (length) × 443 mm (height). The reaction vessel was composed of an acryl spacer (1.0 mm thick) with an inlet and an outlet of solution and sandwiched between two glass plates of 5.0 mm (thickness) × 128.0 mm (width) × 128.0 mm (height). It was fixed vertically and illuminated from behind by a 3 W fluorescent lamp. Wave motion was monitored throughout using an 8 mm video camera. Image data were collected by a monochrome CCD camera (XC-77, Sony) with an 8 mm video deck (Hi8, CCD-TR1000, Sony). The area of the visual field in a typical run was from 21 mm × 20 mm to 15 mm × 14 mm. The image data were printed out using videocopy processor (SCT-P70, Mitsubishi Electric Co.) directly or after image processing on STM-STS2 (Unisoku Co.).[12]

The same vessel was used for experiments under normal gravity. The tilt angle, *x*, of the reaction vessel was changed from horizontal to vertical as 0 (horizontal), 30, 45, 60, and 90° (vertical). After a time interval enough to neglect the transient hydrodynamic effect in inflow of solution,[13] image data of chemical patterns were acquired to a computer every 20 s via a digital camera (Fotoman Plus, Logitech Inc.) driven by software (Aldus Digital Darkroom, Silicon Beach Software, Inc.).

Results and Discussion

The relation between propagation directions and the speed of chemical waves was examined quantitatively under normal

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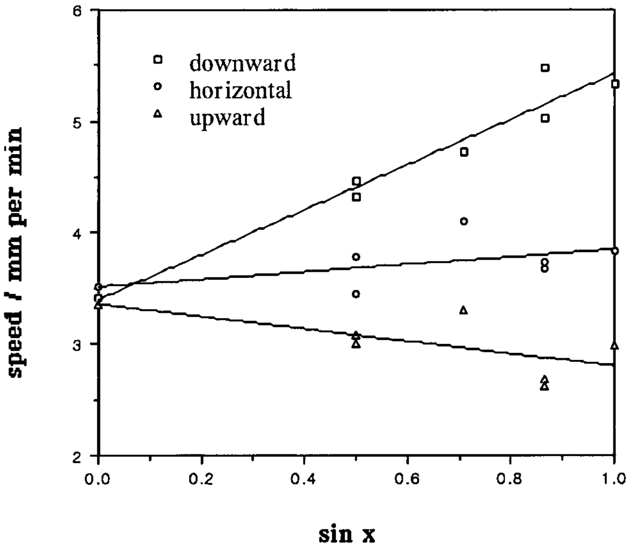

Figure 1. Effect of gravity components on the propagation speed of chemical waves.

gravity conditions. In the present study, the vessel was closed to air without dead space. Therefore, neither convection due to the evaporation-cooling effect at the surface of the reaction solution[4] nor the influence of oxygen on oscillations[14] was involved. The movement of wave fronts in three directions, downward, horizontal, and upward, was measured as the difference relative to a fixed point on the monitor. The perpendicular distribution of chemical waves indicated by Miike[15] was not taken into consideration. The propagation speed, which was obtained from the propagation distance and time, was plotted against the gravity component, sin x, as shown in Figure 1. Each traveling direction was clearly distinguished. The slopes of fitted lines against sin x were 2.02, 0.33, and −0.56 mm/min for downward, horizontal, and upward directions, respectively, with an error range in standard deviation (SD) of 2.0%. Since each propagation speed observed at sin x = 0 was almost the same as 3.42, 3.51 and 3.36 mm/min with an SD of 1.8% for respective directions, they were considered to be equal (mean = 3.43 mm/min) within error ranges.

The propagation speed of chemical waves observed in Figure 1 was distinctly forwarded to the direction of gravity and vice versa. There were some factors that accelerated the wave propagation in relation to gravity. Even in the famous Liesegang rings formed within a gel in a test tube, details in the location of microcrystal bands are influenced by gravity.[16−19] The mechanism must be different in the BZ reaction where considerable heat evolution synchronized with potentiometric oscillations of bromide was observed in the system catalyzed by cerium(IV) salts under compulsory stirring of batch and flow runs[20,21] and catalyzed by ferroin.[22] The thermally convective instability[6] in the very local area is very important. Pojman and Epstein[23] discussed the relation of concentration, thermal gradient, partial molar volume, and density gradient. It is reasonable to consider that the density gradient caused by the thermal effect induced the propagation flux to result in a convection cell so that the speed was biased to gravity.

Plots of the propagation distance of patterns against time before free fall[1] (indicated with a minus sign), as shown in Figure 2a, were essentially the same as those in Figure 1. The slopes were 17.4 (0.966), 12.5 (0.960), and 8.64 (0.931) mm/min for downward, horizontal, and upward directions, respectively, the normalized error in parentheses being the correlation coefficient of linearity. Under a gravity-free condition, propagation distance against time was not influenced by traveling directions owing to the disappearance of convection. The plots were within a narrow range as shown in Figure 2b, the slopes of the fitted lines being 11.7(0.920), 11.5(0.903), and 8.58(0.867) mm/min for the downward, horizontal, and upward directions, respectively. Each initial concentration of starting materials was selected so that chemical oscillations may continue as long as possible, because of inevitable time lag (typically about 40 min) before the free fall. However, the ambiguity corresponding to aging of the reaction solution was estimated with an SD of 1.52% or better and was not serious for measurements.

The temperature distribution was observed at six points near the reaction vessel. The temperature changed gradually from 24 to 26 °C for about 80 min of necessary operations, such as free falling and recovery, due to the heat released from the CCD camera and the fluorescent lamp. However, it was considered that the temperature in the vessel was almost constant during the short time of free fall. For this reason, the strict temperature control was omitted in the setup. The effect of Rayleigh−Benard convection in the reaction vessel was also considered

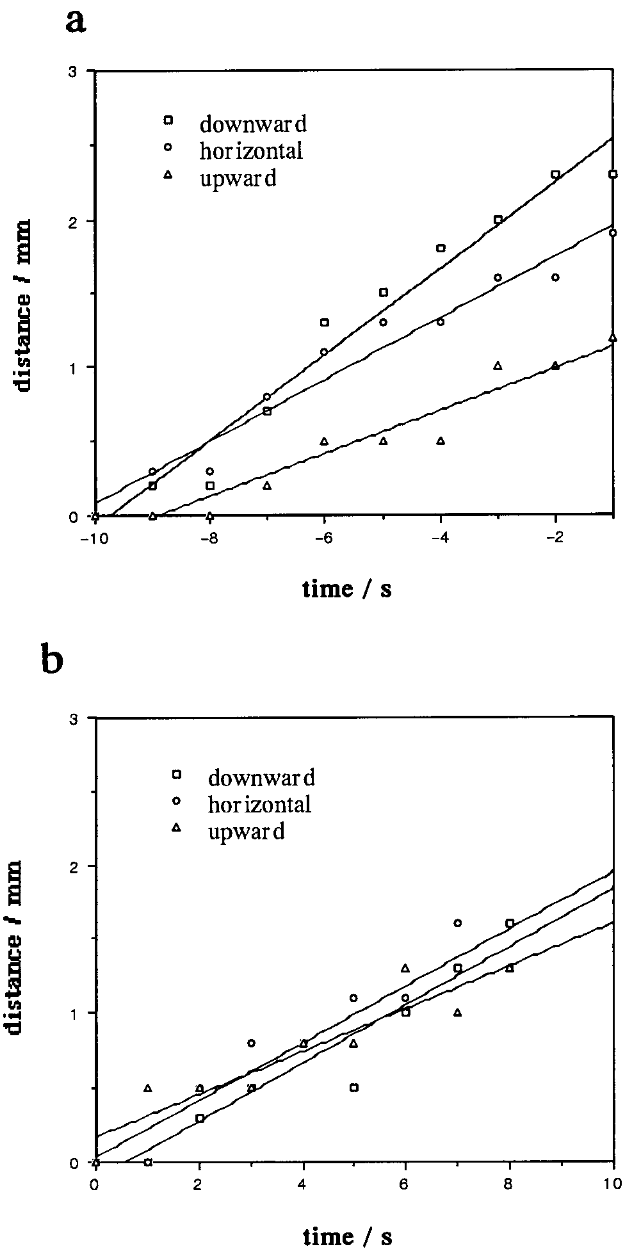

Figure 2. Effect of gravity on chemical waves (a) before free fall or under the effect of earth's gravity and (b) during free fall or under microgravity. Plots of the propagation distance against time in (a) and (b) were obtained from the same run.

to be negligible, on the basis of the ambient temperature on both sides of the vessel.

Under the gravity-free condition, thermally induced convection should also disappear. The effect of gravity on the speed of chemical waves is discussed for experiments carried out with a tube in vertical and some tilted positions in relation to the wave front and the profile,[24−33] and particularly theoretical considerations are discussed in refs 23, 34, and 35. The reaction vessel used in the present study was not a tube, but a clear wave front was not observed in several waves. The ambiguity made precision lower. The reason for the ambiguity may be explained in terms of antisymmetric fluid flow. Detailed discussion will be given separately with our microgravitational results for the tube.

The only sure way to eliminate convection is to run the BZ reaction in a gel medium.[23,36] Therefore, in the present study, convection-free experiments, in which gas release was also prevented, of trigger waves were also carried out under conditions as similar as possible. Unfortunately, the descending wave was not observed, but propagation speed was obtained for 12 waves traveling in a direction opposite and perpendicular to gravity. For six ascending waves measured at almost the center of the reaction vessel, the mean speed before free fall in the range from −10 to −1 s was 2.42 mm/min with an SD of 2.23% and 2.47 mm/min with an SD of 1.94% during a free fall of 9.8 s. The ratio of speeds during free fall and before free fall calculated for each wave had a mean of 1.03 with an SD of 2.91%. On the other hand, for six waves in the horizontal direction, propagation speeds of before free fall and during free fall were all 3.01 mm/min with an SD of 11.55% and 10.36%, respectively. The fluctuation in these cases was much larger than that of ascending waves, but the ratio of speeds was 1.00 with an SD of 4.00%. The slow speed, short time in microgravity, and small propagation distance made the results of experiments more ambiguous. However, in the present study, the propagation speed in gel did not depend upon the gravity conditions.

The BZ reaction is essentially a redox reaction of oxy compounds, and electron transfer is indispensable. The traveling mechanism of chemical waves has been discussed by many researchers.[37] The velocity of mass transfer in the spatial BZ reactions may be expressed as a function of reaction, diffusion, and convection.[38] There was a significant difference between the arithmetic mean of slopes in Figure 2b and the slope of horizontal direction in Figure 2a, such as 10.6 and 12.5 mm/min. The reason for the discrepancy over the experimental error may be the effect of mass transfer through three kinds of convection: hydrodynamic flow of the physical Rayleigh-Benard type, chemically driven convection,[39] and thermal effect produced by chemical reactions.[40] The first one can be negligible in the present experiments. The second type of convection in a reaction−diffusion system,[41] with a free surface and a cover to suppress evaporation, may play an important role in the mass transfer effect as well as diffusion. However, the situation is not the same in the reaction vessel used in this study. The third thermal convection produced by chemical reactions should give rise to anisotropic movements[42] of the chemical wave. In addition, the autocatalytic process in the BZ reaction may amplify this kind of anisotropy.

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