SYNCHRONIZATION AND CHAOS IN THE DISCRETE CHEMICAL OSCILLATION SYSTEM

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Coupled chemical oscillator systems have been studied to provide insights in understanding important features of biological phenomena such as heart contraction and collective oscillations in intracellular calcium concentration. In particular, coupling in the Belousov-Zabotinskii (BZ) reaction system has been extensively studied, using two or three continuous stirred tank reactors (CSTR's) [1-5]. Unfortunately, in the case of a CSTR, a extension to the system with many oscillators is not so easy. In this work, we investigate the properties of the coupling in the discrete BZ reaction system consisting of cation exchange beads loaded with ferroin. Our attention is particularly focused on the coupling between two beads in no contact with each other.

The cation exchange beads of about 500 μm in diameter were loaded with ferroin of a specified concentration. Then those beads were suspended in the BZ solution placed in a Petri dish, where the temperature of BZ solution was maintained at 23.0±0.05℃. The redox reaction confined to the surface of the beads was monitored through a CCD camera attached to a microscope and recorded on a video tape recorder. The change in color was detected as the change in light intensity through an image processor, where the intensity was obtained by averaging the gray level of the fixed small area on the bead surface, as shown in Fig.1. Thus we regarded the cation exchange bead as a chemical oscillator.

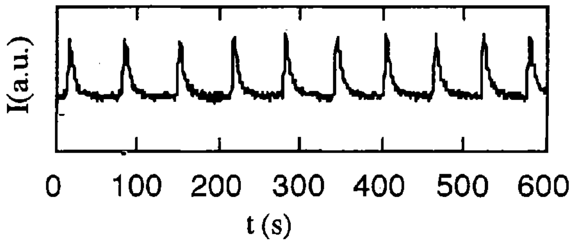

Fig.1. Light intensity averaged over the fixed area on a single bead as a function of time, where peaks correspond to the oxidized state.

The coupling is accomplished by a mass diffusion, so that a time delay is inherent in this coupling. Here the coupling strength can be controlled by varying the distance d between two beads: the larger d, the smaller the coupling strength. Here the distance d refers to the spacing between beads, so that d=0 means that beads are in contact with each other. In contrast to usual coupled oscillators such as CSTRs, the coupled frequency was found to be higher than that of the faster oscillator. Here the oscillator acting as a pacemaker was spontaneously determined depending on the phase of each oscillator at the beginning of coupling. These results suggest that the synchronization is not attributed to a simple entrainment of the slower oscillator by the faster one. Two oscillators may fall into a new type of coupled state which is probably self-

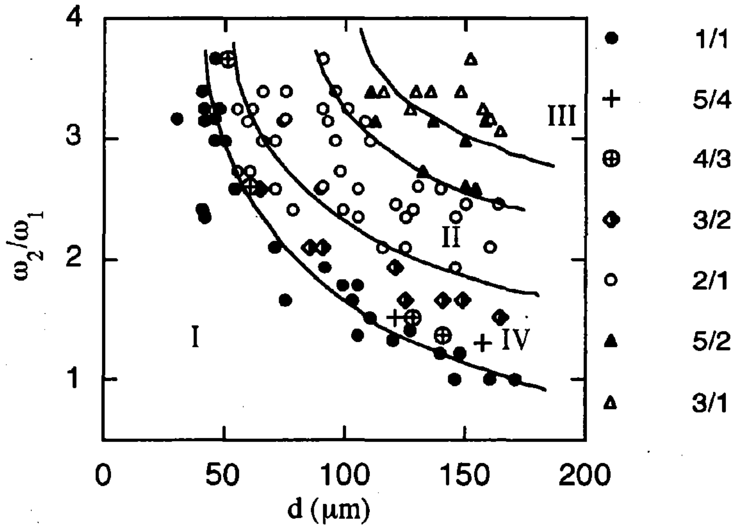

Fig.2. Phase diagram of the coupling state. The ordinate axis denotes the natural frequency ratio of faster oscillator to slower one, ω_2/ω_1, and the abscissa axis denotes the distance between two oscillators, corresponding to the coupling strength. Symbols denote the representative frequency ratios in the coupled state.

organized with some interactions through excitable media.

The features of coupled states were investigated as a function of d and ω_2/ω_1, where ω_1 and ω_2 are the natural frequencies of slower and faster oscillators, respectively. It was found that there are three coupling regimes depending on d: a tight coupling regime, a weak coupling regime and a uncoupled regime. In the tight coupling regime (d <120 μm), two oscillators cause synchronization with the fixed phase difference, that is, an entrainment of 1:1. In the region of d >200 μm, each oscillator independently oscillates with its own natural frequency, corresponding to the uncoupled regime. At an intermediate distance, the entrainment occasionally occurs and consequently the frequency ratio takes intermediate values between those in tight coupling and uncoupled regimes, corresponding to the weak coupling regime. The coupling in this regime occasionally occurred, and its state was metastable. Various coupling states were found in the weak coupling regime, depending on both natural frequencies of two oscillators and d, as shown in Fig.2. The region I corresponds to the tight coupling regime. The boundary curve separating the region I from another region is seen to rise rapidly with decreasing d. There may exist the critical distance d_c, below which the entrainment of 1:1 necessarily occurs, no matter how large the natural frequency ratio. In regions II and III, the frequency ratio takes n+1/1 with n being an integer. These regions including the region I are dominant in the whole diagram, and those coupling states are quite stable.

In region IV which is located in the boundary between stably coupled regions I and II, various entrainments were observed depending sensitively on d. The coupled frequency ratio takes n+1/n with n being an integer of not less than 2. Furthermore, the regular coexistence of two frequency ratios n+1/n and n+2/n+1, for example, 2/1 and 3/2, was also observed. In the stable coupling state, the pacemaker is usually fixed on either of two oscillators. In the coexistence state of two modes, in contrast, the alternative replacement of the pacemaker occurred. This indicates that such a coupling state is metastable. Such an alternative replacement may come from a compensation effect for the weakly frustrated oscillators as observed in the coupled system using CSTR's. On increasing ω_2/ω_1, the boundary region between regions I and II becomes narrow, as seen in Fig.2 In this region we observed the irregular behaviors in both interval and height of peak, as shown in Fig.3 (a). The corresponding power spectrum is shown in Fig.3(b). Sharp peaks and associated harmonics entirely disappear, while those clearly appear in the power spectrum of the periodic oscillation, shown in Fig.1. This irregular behavior is probably chaotic, which may correspond to one predicted by Tomita and Kai [6].

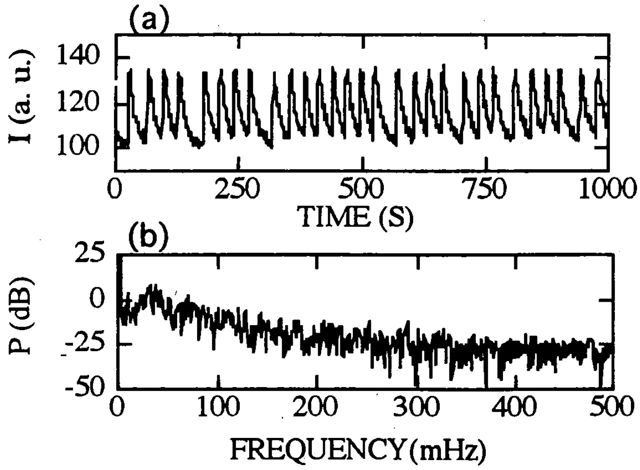

Fig.3.Time series (a) and power spectrum (b) in the boundary region between regions I and II in Fig.2.

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