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A liquid/liquid interface excited by stimulation with water

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ABSTRACT

An immiscible interface, which was composed of $CaCl_2$ aqueous and ester phases, was excited by the addition of a small amount of water. The excitation, i.e., burst and flow at the interface, was observed above a critical concentration of $CaCl_2$ in the aqueous phase. The critical concentration and degree of excitation depended on the kind of ester. The mechanism of excitation is discussed in relation to the interfacial tension and the Marangoni effect.

1. Introduction

Excitable systems have been investigated at immiscible interfaces [1–9] not only to develop an artificial membrane but also to better understand the mechanism of excitation and signal propagation in biology, such as impulses in a nerve cell. The difference in the concentrations of inorganic ions, such as Na^+ and K^+, at the nerve membrane, i.e., nonequilibrium of the chemical potential of ionic species, plays an important role in the excitation of nerve cells. In contrast, most of the driving force of artificial excitable membranes without an external force, such as d.c. voltage, is due to the difference in interfacial tension under the presence of surface active substances [2–6].

In this study, a liquid/liquid interface was excited by a difference in the concentration of an inorganic ion. To clarify the nature of this excitation, the concentration of $CaCl_2$ in the aqueous phase at the boundary between with and without excitation was determined, and the velocity of flow along the interface was analyzed depending on the kind of ester of acetic acid. The mechanism of excitation is discussed in relation to the interfacial tension and the dissolution of pure water into the ester phase.

2. Experimental

All chemicals were analytical grade and used without further purification. Water was first distilled and then purified with a Millipore Milli-Q filtering system (pH of the obtained water: 6.3, resistance: >20 MΩ). A $CaCl_2$ aqueous solution (5 ml) was poured into a glass cell (20 mm (width) × 10 mm (depth) × 40 mm (height)) as an aqueous phase. One milliliter of ester of acetic acid (methyl acetate, ethyl acetate, *n*-propyl acetate, *n*-butyl acetate, *n*-pentyl acetate, or *n*-hexyl acetate) as an organic phase was gently put on the aqueous phase. The needle of a microsyringe containing pure water was inserted askew into the aqueous phase under the organic phase, with the tip of the needle located at the center of the aqueous phase (minimum distance between tip and interface: 4 mm). Five microliters of pure water was injected from the syringe for each experiment. All of the experiments were performed at room temperature. Movement of the ester/aqueous interface was monitored with a digital video camera (SONY DCR-DVD508, minimum time-resolution: 1/30 s), and then analyzed by an image-processing system (Image J, NIH, USA). The interfacial tension was measured with a surface tensiometer (CBVP-A3, Kyowa Interface Science Co., Ltd., Saitama, Japan) with the platinum blade (diameter: 0.5 mm, length: 20 mm) impaled into the interface. Plastic beads (DIAION, HP20S, relative density: 1.01, Mitsubishi Chemical Co., Ltd., Japan) were distributed on the interface to visualize the flow around the interface.

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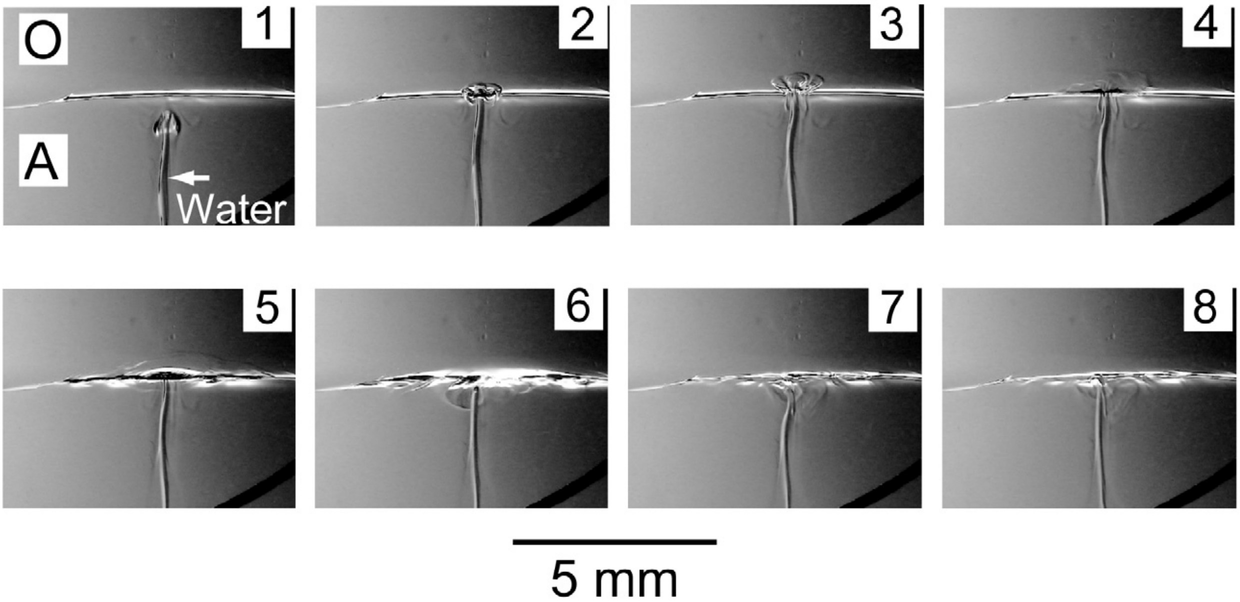
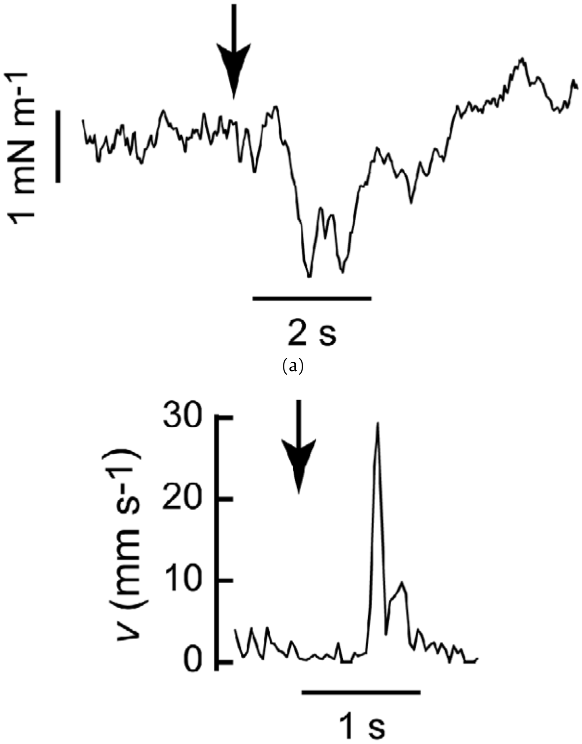


Fig. 1. Snapshots of excitation at an organic (*n*-butyl acetate phase, indicated as **O**)/water (2 M $CaCl_2$ aqueous phase, indicated as **A**) interface after the addition of water (side view). The snapshots were taken at intervals of 0.2 s (**1**–**3**, **5**–**8**) and 1/30 s (**3**–**5**).

3. Results

Fig. 1 shows snapshots of the movement of the interface with the addition of water. Within 1 s after the injection of water, the front of the water flow reached the interface (**1**, **2** in Fig. 1). The front of water passed through the interface (**2**) and a raised interface increased in size (**3**). The raised interface rapidly collapsed (**4**), and rapid flow outward from the raised interface was generated along the interface (**4**–**6**). The disturbed interface blew over with time (**7**, **8**). Here, we defined this series of phenomena (**1**–**8**) as "excitation." In contrast, we considered the phenomena "no excitation" when slow outward flow was observed but not collapse. After the injection of water, while the up-flow of water was maintained for a few seconds, one excitation was observed for each 5-µl injection. A second excitation was sometimes observed when 10 µl was injected.

Fig. 2 shows the time-variation of (a) the interfacial tension and (b) the velocity of flow (v) along the interface. In this experiment, a platinum blade (diameter: 0.5 mm) in the place of the Wilhelmy plate was placed in contact with the location at $L = 5$ mm, where L was the minimum distance between the location of the platinum blade and that of the collision between water and interface along the long axis of cell. The amplitude of the change in the interfacial tension decreased with the increase in L, but the influence of convective flow on the platinum blade was significantly large within $L = 5$ mm. v was measured at the interface 5 mm from the collision between the up-flow of water and the interface, and the direction of outward-flow from the center of the interface in the cell was defined as positive. v was measured by tracking the beads which were floated on the ester/aqueous interface. To reduce the influence of the existence of the plastic beads on the phenomenon, 10–15 beads were dropped on the interface and we confirmed that the phenomenon was not changed with the addition of the beads. When the raised interface collapsed, the interfacial tension decreased by 2 $\mathrm{mN\,m^{-1}}$, i.e., the change from 17 to 15 $\mathrm{mN\,m^{-1}}$. The interfacial tension then gradually increased up to the initial value during restoration of the interface to the initial state. After the raised interface collapsed, flow along the interface was rapidly generated for ca. 0.2 s. The relative density between pure water and 2 M $CaCl_2$ was 1.17 at 295 K.



(a)

(b)

Fig. 2. Time-variation of (a) interfacial tension and (b) the velocity of flow along the interface (v). The experimental conditions were the same as those in Fig. 1. Water was injected to the aqueous phase at the time indicated by the downward arrow.

Fig. 3 shows the concentration of $CaCl_2$ at the boundary between with and without excitation (C_b) and the mean velocity of flow along the interface (v_m) depending on (a) the number of carbon atoms (n) in the ester of acetic acid ($CH_3COOC_nH_{2n+1}$) and (b) the difference in interfacial tension between ester/water and ester/2 M $CaCl_2$ aqueous phase $\Delta\gamma$. Here, C_b was measured by microscopic observation. v_m was obtained as the mean value of v for 0.2 s after the interface between the 2 M $CaCl_2$ aqueous and ester phases was excited, and the reproducibility was examined at least