Anionic Control of Autonomous Motion of Oil/Water Interface with Cationic Surfactant

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Autonomous motions of an oil/water interface can be controlled by hydrophobicity of an anion and its chemical reaction with a cationic surfactant. Hydrophobic anions generate a rhythmical motion of the contact line, and hydrophilic anions induce the Marangoni instability. A cooperative effect of them causes an outstanding motion of the interface.

Autonomous motion of a liquid interface may realize a moving chemical device responding to the surrounding matter.[1] It looks like a biological motion. For example, one can make Ca-sensitive motions of a droplet.[2] However, it is unclear in general how the environmental chemicals control the motion. Oil/water interface containing a surfactant octadecyltrimethyl-ammonium chloride ($C_{18}TAC$) and iodide anions generates various kinds of interfacial motions.[3] The role of $C_{18}TAC$ is studied well, and the adsorption onto a solid surface is a key phenomenon.[1a,4] In contrast, the role of the anions is unclear. Here, we used two kinds of anionic chemicals, phenylboronic acid (PB), and/or di-2-ethylhexylphosphoric acid (DEHPA) to investigate the effect on the interfacial motion. The hydrophobic anion DEHPA generates a periodic change in the droplet shape resulting from a periodic change of the contact angle of oil/water interface to the glass. The relatively hydrophilic anion (PB) causes a translation of a droplet mainly due to Marangoni instability in the oil/water interface. When both kinds of anions coexist, the variety of the interfacial motion significantly grows. In the iodide anion system, I^- plays the role of PB. Coexistence of I^- and I_3^- produces a similar cooperative effect.

PB and DEHPA were purchased from Wako Chemical and Aldrich, respectively. Reagent grade of nitrobenzene and $C_{18}TAC$ were provided by Wako chemical. All of the chemicals

Figure 2. Time-dependency of $\gamma\cos\theta$ after the contact of oil and water phases. Concentrations of anions are (a) 50 mM DEHPA and (b) 50 mM PB. (c) 25 mM DEHPA and 25 mM PB. The ordinate is set to be zero before pouring the oil phase, and only the relative change is meaningful.
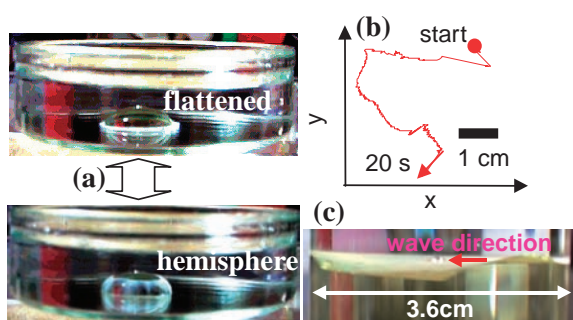

Figure 1. Examples of interfacial motion. (a) Two extreme shapes in the oscillatory change of an oil droplet. The droplet contains 100 mM DEHPA. (b) Trajectory of the droplet motion with 100 mM PB during 20 s. (c) Spontaneous wave propagation with 90 mM PB and 10 mM DEHPA.
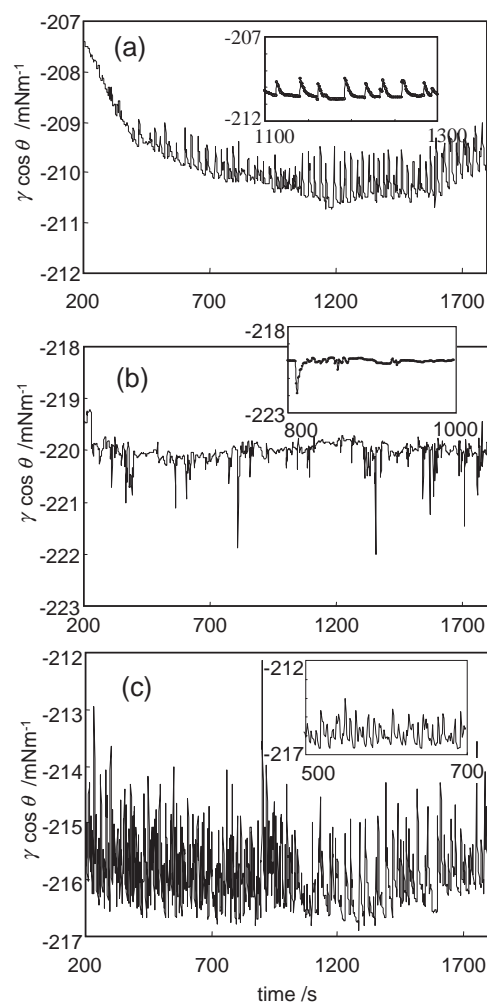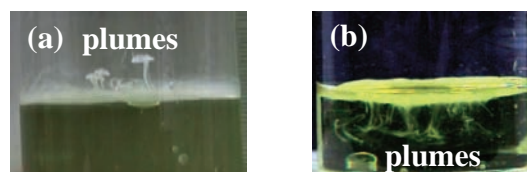

Figure 3. Plumes observed in the PB (a) and KI (b) systems. Concentration of PB and KI are 100 mM and the saturation, respectively. Organic solvents are nitrobenzene.

were used without further purification. PB and/or DEHPA were dissolved in nitrobenzene. Aqueous phase containing 1.15-mM $C_{18}TAC$ was used in this system. Self-movement of the oil droplet and the spontaneous wave occurring in a cylindrical glass vial with 3.6-cm diameter were observed. We measured a time course of $\gamma \cos \theta$ of the oil/water interface at a glass surface. Here, γ and θ represent the interfacial tension and the contact angle, respectively. Wilhelmy technique was applied and the experimental procedure is essentially the same as reported elsewhere.[5] As another experiment, we examined a mass transfer of iodide anions in the oil/water system. The sample preparation is essentially the same as reported previously[4] but tri(*n*-butyl) phosphate (TBP) was used instead of nitrobenzene, since nitrobenzene has an adsorption of the UV light which overlaps the adsorption due to iodide anions. After contacting the organic and the aqueous phases, the adsorption spectrum of the organic phase is taken.

A nitrobenzene droplet (100 µL) containing PB exhibits a translation on a glass in $C_{18}TAC$-containing aqueous phase, while the droplet including DEHPA shows an oscillatory change in the droplet shape without a translation (Figure 1). When PB and DEHPA are mixed, the oil droplet moves violently with the translation and the shape changes.

The motion of the oil droplet is closely related to the autonomous motion of oil/water interface along the glass surface. This autonomous motion may be observed as a spontaneous wave along a vertical glass wall. When a flat interface with DEHPA-containing oil is formed in a cylindrical glass vial, a certain restricted portion of the contact line constituted of the oil/water interface and the cylindrical sidewall goes up and down rhythmically. Amplitude of the motion is very small, and we measured the autonomous motion as the change of $\gamma \cos \theta$ along the Wilhelmy plate made of a glass. The result is shown in Figure 2a. The upward spikes are recorded almost periodically. Each spike corresponded to the occurrence of the above motion at a point along the Wilhelmy plate. On the contrary, PB-containing organic phase does not produce such a movement of the contact line. Instead, a number of plumes grow at the oil/water interface as shown in Figure 3a. This plume is observed when $C_{18}TAC$ and PB coexist and hence is induced by the Marangoni instability due to the chemical reaction. We were able to see a longitudinal interfacial wave propagating radially, which is born at the plume point. This effect is shown as a change in $\gamma \cos \theta$ shown in Figure 2b. When PB and DEHPA are mixed, the motion of the contact line becomes more outstanding as shown in Figure 1c. The corresponding $\gamma \cos \theta$ is shown in Figure 2c. A cooperative effect of PB and DEHPA plays a key role in the outstanding motion, which also causes a violent motion of the oil droplet.

The distribution coefficients D of PB and DEHPA between an organic and an aqueous phases are examined.[6] Both of the D values are high under an acidic condition. They steeply fall around the neutral pH to reach a low value. However, the D value of PB is lower than that of DEHPA in the whole pH. In acidic conditions, the difference is more than an order of magnitude. It may be assumed that the hydrophobicity (hydrophilicity) controls the interfacial dynamics. We examined the assumption for the iodide anion system. When we used KI-saturated TBP containing I_2, various kinds of motion of the contact line were observed along a glass surface (See Figure A in Supporting In-

formation).[7] This is essentially the same as interfacial motions for iodine-containing nitrobenzene.[3] Then, I_3^- and I^- play the roles for the hydrophobic and hydrophilic anions, respectively (See Figure B in Supporting Information).[7] The I^- in the organic phase rapidly moves to the aqueous phase, while almost all of I_3^- remains in the organic phase. This characteristic is not affected by the concentrations of $C_{18}TAC$. When the hydrophilic anion I^- is dissolved in nitrobenzene with higher $C_{18}TAC$ concentration (15 mM), the plumes due to the Marangoni instability appear (Figure 3b). No plume appears without I^-, and hence the chemical reaction of $C_{18}TA^+$ and I^- is necessary for the plumes. However, the outstanding motion of the contact line is observed only when I^- and I_3^- (I_2) coexist. Thus, we may conclude for both the systems that the hydrophilic species can cause the Marangoni instability with $C_{18}TAC$, and that the coexistence with hydrophobic species results in the outstanding motion of the contact line along the glass surface. For the iodide anion system, the molar ratio between I^- and I_3^- is controlled by the chemical equilibrium. In this point, the PB/DEHPA system is useful for the study of the anionic control of the interfacial dynamics.

Cationic head group of $C_{18}TA^+$ is adsorbed onto the glass surface as a bilayer.[1a] The bilayer may be converted to a monolayer since the outer monolayer is chemically desorbed by the hydrophobic species (DEHPA or I_3^-) with the movement of the contact line. As a result, the surface is wetted by the organic phase which corresponds to the upward spike in Figure 2a. When the Marangoni instability coexists, the movement of the contact line is significantly affected by the convection. The two kinds of anions produce a cooperation of the contact line motion and the Marangoni convection. Elucidation of the mode selection of autonomous motions of an oil/water system is interesting for the study of chemosensitive motions of surfactant adsorbed interface. The present result gives a fundamental information for the physicochemical understanding of the mode selection.

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7 Supporting Information is available electronically on the Journal Web site; http://www.csj.jp/journals/chem.-lett/index.html.