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A Novel Interfacial Engine between Two Immiscible Liquids

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A novel wave form of interfacial engine (a set of self-organized waves between two immiscible liquids) was observed by use of an aqueous solution of mixed surfactants (HTAB and dioctylsulfosuccinate).

Synchronized wave-like movement can sometimes be observed at the interface between two immiscible liquids.[1-6] It occurs spontaneously and continues for more than several minutes. It has been observed in a system composed of an aqueous phase containing one kind of ionic surfactant (hexadecyltrimethylammonium bromide (HTAB)[1-5] or sodium dodecylsulfate[6]), and an organic phase containing ionizable species with the charge opposite to that of the surfactant ($KI+I_2$[1-5] or bipyridine[6]) in a cylindrical glass container. Because this phenomenon can be regarded as a kind of energy transduction from electrochemical potential energy of solutes to the mechanical energy of waves,[1,2] a set of the interfacial waves can be called "interfacial engine".

Interfacial engines have been observed with high reproducibility only when the system is composed of HTAB and $KI+I_2$. Because of lack of comparable experimental systems, the mechanism of this exciting phenomenon has not clearly been understood yet. We found the second experimental system in which we could observe reproducibly the behavior of interfacial engine. Furthermore, the wave form of the interfacial engine in this novel system was different from that of previous one.

The experimental conditions were as follows: An aqueous phase was a mixed solution of HTAB (Merck Co.) and dioctylsulfosuccinate sodium salt (DOSS, Aldrich Chemical Co.). The concentration of HTAB was less than 10 mM (mM = mol m^{-3}). The DOSS concentration was less than that of HTAB. An organic phase was a nitrobenzene solution (guaranteed grade) containing 1.5 mM of picric acid. Glass vials of 37 mm internal diameter (i.d.) and test tubes of 14.4 mm i.d. were purchased from Iwaki Glass Co. and were used without any treatment. The volumes of the aqueous and the organic phases were equal: 20 mL for the use of the vials and 2 mL for the test tubes. The wave motion at the interface was recorded through a video camera (National NV-M21). All the experiments were carried out at 25 °C.

Vigorous turbulence occurred at the interface soon after the aqueous solution was in contact with the organic solution in the vial (Fig. 1). Various modes of wave motions were observed within the first 60 s: generation of waves (wave source), collision of waves followed by degeneration (wave sink) or penetration of waves (solitary waves). Three or four waves synchronized finally to form an interfacial engine, propagating in the same direction with the same velocity of 10.4 cm s^{-1} (Fig. 2). While the movement proceeded, gradual deposition of white viscous precipitates was observed on the interface.

Excitability of the interface is greatly dependent on the composition of the surfactants. The number of waves per second passing through an arbitrary point of glass ware, or simply the frequency of interfacial engine, is a good measure of excitability. The frequency of interfacial engine became maxi-

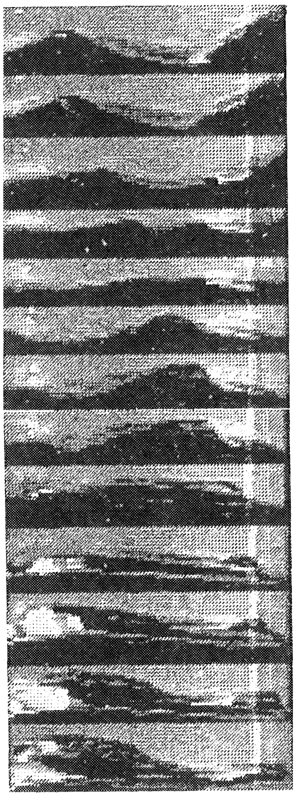

Fig. 1.

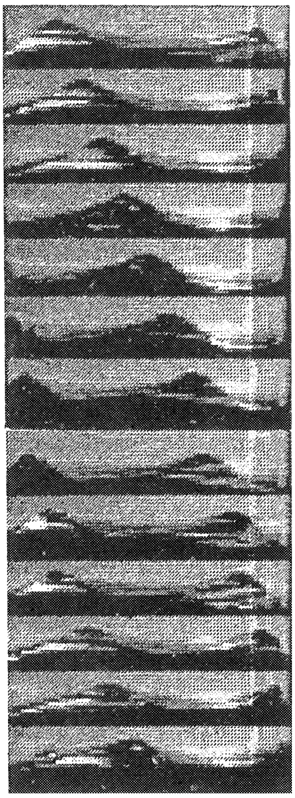

Fig. 2.

Fig. 1. Interfacial turbulence observed at 10 s after the aqueous phase (the upper light phase, containing 10 mM HTAB and 5 mM DOSS) and the organic phase (the lower dark phase, 1.5 mM picric acid in nitrobenzene) was in contact in a glass vial (i.d.= 37 mm). The time interval is 1/30 s.

Fig. 2. Time course of the interfacial engine at 60 s after contact.

mum when the concentration ratio of HTAB to DOSS was about 2 (Fig. 3). At around this concentration ratio the aqueous solution became turbid and viscous, suggesting the formation of great aggregates of ion complexes or mixed micelles. When the ratio of the surfactants was close to 1, white precipitate appeared in the solution and the solution was no longer homogeneous. No waves were observed when the ratio was lower than 1.

Duration time of the interfacial engine was prolonged drastically from 1-2 min to 10-20 min when the concentration ratio of the surfactants reached to 2 (Fig. 4). The value of duration time was greatly dependent on the size of the system; for example the wave-like motion continued for more than 30 min by use of the vials instead of the test tubes. This size-effect is quite reasonable because the value of duration time

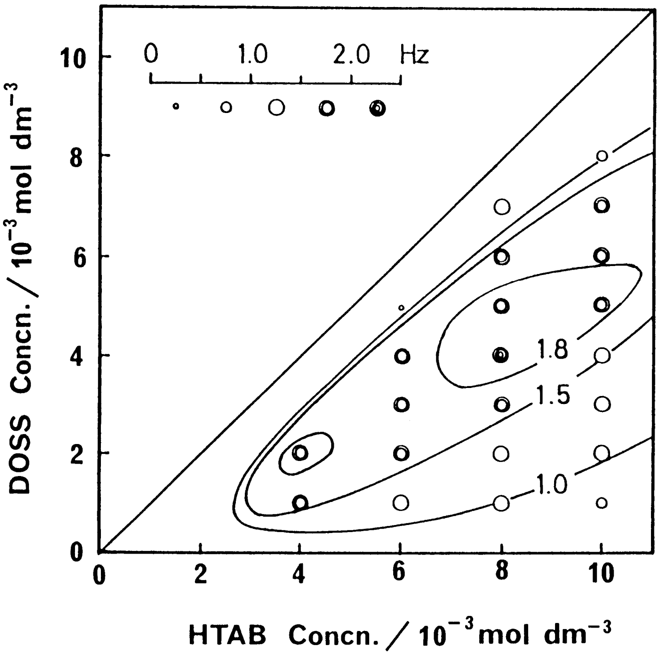

Fig. 3. The frequency profile of the interfacial engine on the HTAB-DOSS concentration plane. Average of five runs by use of test tubes (i.d.=14.4 mm). The ridge of the frequency value appeared where [HTAB]/[DOSS]=2.

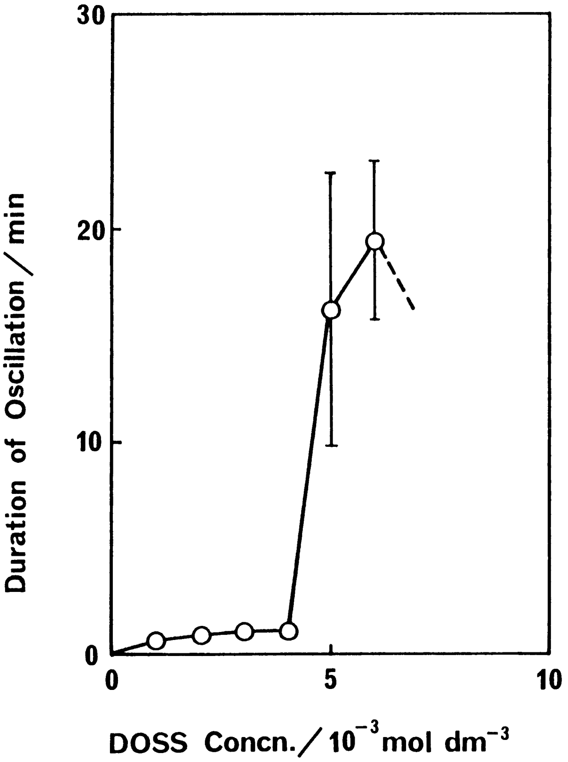

Fig. 4. The duration time of interfacial movement as a function of DOSS concentration in water. The concentrations of picric acid in nitrobenzene and of HTAB in water were 1.5 mM and 10 mM, respectively. The mean values of five runs by use of test tubes are plotted. The error bars for [DOSS]<5 mM are smaller than the open circles.

is also a good measure of the displacement from an equilibrium state.

The wave form gives us an important information on the phenomena just occurring at the exciting interface. The wave form can be approximated by two exponential functions corresponding to the advancing and the receding parts of the waves.[7) The ratio of time constants appearing in the exponentials was about 2 in the present system (the advancing motion was twice faster than the receding, see Fig. 2), whereas this ratio is about 0.5 in the previously reported HTAB-KI-I_2 systems.[1,2,7) In other words, the advancing parts of the present waves are much steeper than those of previous ones. When DOSS was absent, however, the waves which could be observed only occasionally had the time-constant ratio of about 0.5, either. It is obvious that coexistence of anionic surfactant DOSS with cationic HTAB brought about this difference in the form of interfacial waves. As the interfacial waves were not observed by use of hydrophobic containers (trimethylsilanized glass containers or teflon beakers), the interfacial engine seems to be caused by the wetting transition of the contact line defined by the interface and the wall of a container. On the basis of this assumption, we can give explanation to the difference in the wave forms; the coexisting DOSS increases the adsorption rate of HTAB at the interface and the glass wall, and hence, wettability of the organic phase to the wall increases more rapidly, resulting in the formation of much steeper advancing parts of the interfacial waves.

Although the detail of the mechanism is still an open question, an understanding of interfacial engines will be accelerated from now on through comparison of different wave forms in different experimental systems.

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