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Convective instability and electric potential oscillation in a water–oil–water system

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Abstract

A convective instability is observed in an aqueous solution of surfactant which attaches to a nitrobenzene layer. Small convective rolls at first occur on the wall of the cell and their scales grow to the cell size. The rolls consist of flows rising along the wall and descending at the center of the cell. The convective roll structure begins to oscillate with growth and changes to a transient turbulence. After the transient turbulence the flow structure goes back to the initial convective roll. This cycle's period is about 2 to 10 minutes and continues for about 1 hour. Simultaneous measurements of the electrical potential and the light intensity of shadowgraph reveals that the burst of the potential oscillation previously reported occurs when the transition to turbulence takes place. The convective flow is supposed to facilitate accumulation of surfactant on the interface.

Keywords: Water–oil interface; Potential oscillation; Convective instability; Marangoni instability

1. Introduction

Oscillatory behavior at the interface between two immiscible fluids has been studied from both a hydrodynamic and an electrochemical point of view; the observed phenomena are concerned with the direct conversion of chemical energy into mechanical energy. The oscillatory behavior is two-fold; one is the oscillatory deformation of the interface accompanied by fluid motion and the other is the oscillation of the electric potential difference across the interface.

The deformation of the interface is supposed to be driven by a spatial gradient of the interfacial tension, which is caused by fluctuations of temperature and/or chemical concentrations on the interface. This is known as the so-called Marangoni effect and some experimental and many theoretical studies have been reported. Kai et al. [1,2] experimentally observed various types of the interfacial deformations—rotating solitary wave, periodic and non-periodic oscillation, multiple wave trains and intermittent behaviour—using an aqueous solution of surfactant (trimethylstearylammonium chloride) and nitrobenzene containing iodide. The linear stability of systems subject to the Marangoni effect has been dis-

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cussed in many theoretical approaches [3,4] since the first study by Sternling and Scriven [5]. Moreover, a mechanism of the morphology of interfacial deformation was also theoretically studied [6]. In those theoretical studies, it was assumed that secondary flows in the form of convective rolls occur near the interface and take up an important role in the interfacial deformation. The flow near the interface, however, has not clearly been observed except in a few reports [7].

On the other hand, the oscillation of electric potential across the interface has extensively been studied by Yoshikawa and co-workers [8,9]. They composed a water–oil–water system in a U-shaped tube with an aqueous mixture of surfactant and alcohol in one arm, nitrobenzene containing 2,2′-bipyridine on the bottom and an aqueous solution of NaCl in another arm. They measured the difference of electric potential between the two aqueous phases. They observed a periodic burst type of oscillations of the electric potential and of the interfacial tension in agreement with each other. The period and the amplitude of the oscillatory burst of potential were of the order of 10 minutes and 10 mV, respectively. Suzuki et al. reported the occurrence of a short period potential oscillation which was superposed on the above long period potential oscillation [10]. Furthermore, Yoshikawa et al. reported that the wave form and the frequency of the potential oscillation depended on the kind of the components (surfactant, alcohol and other chemical additives) and their concentrations [8]. An extension of the duration of the potential oscillation was tried by Sha et al. [11]. They obtained a stable potential oscillation that continued for 120 hours by using a thin membrane micropore pipette having a very small interface ($\sim 2\ \mu\text{m}\ \phi$) instead of a U-shaped tube and reported the period was proportional to the interfacial area. Moreover, they found by means of simultaneous electric measurements and microscopic observation that the potential change was synchronous with an expansion and a shrinkage of the lipid aggregate on the interface and a burst of droplets generated from it in succession [12].

It was supposed the oscillation was caused by an iteration of the following physical processes. At first, surfactant and alcohol molecules in an aqueous phase move toward the interface and gradually accumulate near the interface. When each concentration of surfactant and alcohol attains a critical value, both are abruptly transferred to the oil phase and form inverted micelles in a cooperative manner. The resultant abrupt decrease of surfactant at the interface generates the burst of potential. The mechanism of successive accumulation of surfactant and alcohol molecules near the interface has not yet been fully accounted for. The hydrodynamic motion based on the Marangoni effect seems to take up an important role in the transfer of those substances. Thus we have attempted in this study to observe flows near the water–oil interface by a flow visualization method. Moreover, we have carried out simultaneously observations of the hydrodynamic motion near the interface and measurements of the potential difference across the interface. As a result, a convective flow was found to occur near the interface which leads to a transient turbulence accompanied with the electric potential burst.

2. Materials and methods

2.1 Experimental system

The shadowgraph system used for the flow visualization is shown in Fig. 1. The pattern of the flow was observed by casting a beam of light on the sample in the cell. Owing to a gradient in the refractive index depending on the concentration of chemicals—not on a temperature gradient —the light passing through the sample is deflected by a small angle and causes a shadowgraph image. The shadowgraph patterns was rear-projected either on a paper screen which was used for taking photographs or on a photodiode for recording the temporal change of light intensity at one point in the shadowgraph pattern corresponding to the flow structure. The photodiode was placed at about 3 mm above the interface image, because the change of the shadowgraph pattern occurred mainly near the interface. The amplified voltage of the photodiode output

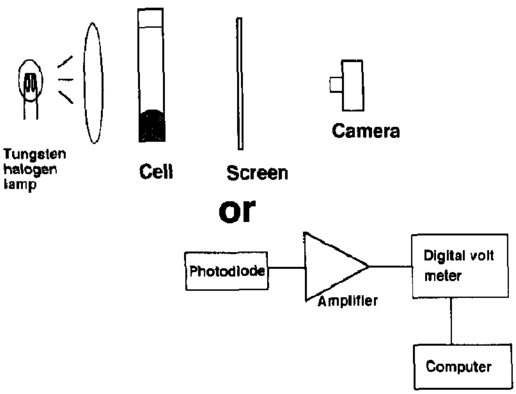

Fig. 1. Experimental system for flow visualization. The screen and camera are used for taking pictures. The photodiode is used for recording the temporal changes of the light intensity at one point in the convective layer.

was measured with a digital voltmeter and the time series of its data was stored in a computer.

Figure 2 shows the experimental system for simultaneous measurements of both the light intensity and the potential difference; the light intensity was measured with the above mentioned system and the potential difference picked up through salt bridges with Ag/AgCl electrodes was amplified and stored in a computer. This setup is the same as that used in our previous report [10].

2.2 Cells and sample

Two types of Pyrex cells were used; one was of a standard type ($10 \times 10 \times 45$ mm^3) and the other was a U-shaped cell.

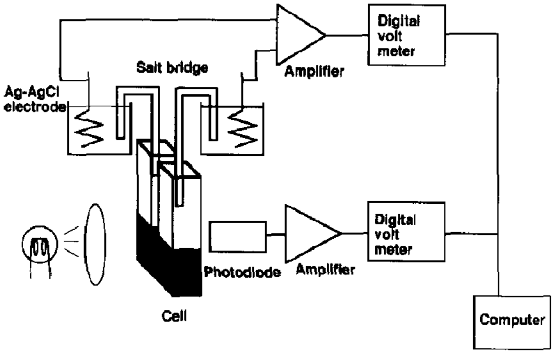

Fig. 2. Experimental system for simultaneous measurement of the light intensity and the potential.

The standard cell was mainly used for flow visualization. In this case, nitrobenzene (1 ml) was placed in the bottom of the cell, and an aqueous mixture (3 ml) of sodium oleate (0.4 mM) and 1-propanol (20%) was poured on the nitrobenzene layer.

The U-shaped cell was used for simultaneous measurements of the point light intensity and the potential difference between the two aqueous phases. In this cell, a water–oil–water interface system was composed as follows; nitrobenzene (3 ml) was placed in the bottom of the cell, and an aqueous solution of surfactant (sodium oleate; 0.4 mM) and 1-propanol (20%) was put in one arm of the U-shaped cell and an aqueous solution of NaCl (0.5 M) was put in the other.

The concentration of sodium oleate and 1-propanol in the surfactant solution were set in the range where the periodic burst of potential appeared [10].

3. Results

3.1 Flow patterns

A time series of the shadowgraph patterns of the sample in the standard cell is shown in Fig. 3. The two vertical black lines in Fig. 3 are the shadows of the cell walls. The curved dark zone is the interface between the aqueous phase and the oil phase. The interface has a convex meniscus, so that the incident beam on the interface is scattered and the meniscus part is dark. The bright part under the dark meniscus zone is the oil phase and the whole part above the meniscus is the aqueous phase. A pair of bright and dark lines in the middle of the aqueous phase is considered to be due to a steep gradient of the concentration of aggregation products of surfactant and nitrobenzene. A small amount of nitrobenzene is considered to diffuse into the surfactant phase as the interface reaction proceeds. Results of a spectrochemical analysis in the ultraviolet region also revealed that the concentration of nitrobenzene in the layer between the dark meniscus and the pair of bright and dark lines was higher than that in the aqueous phase above

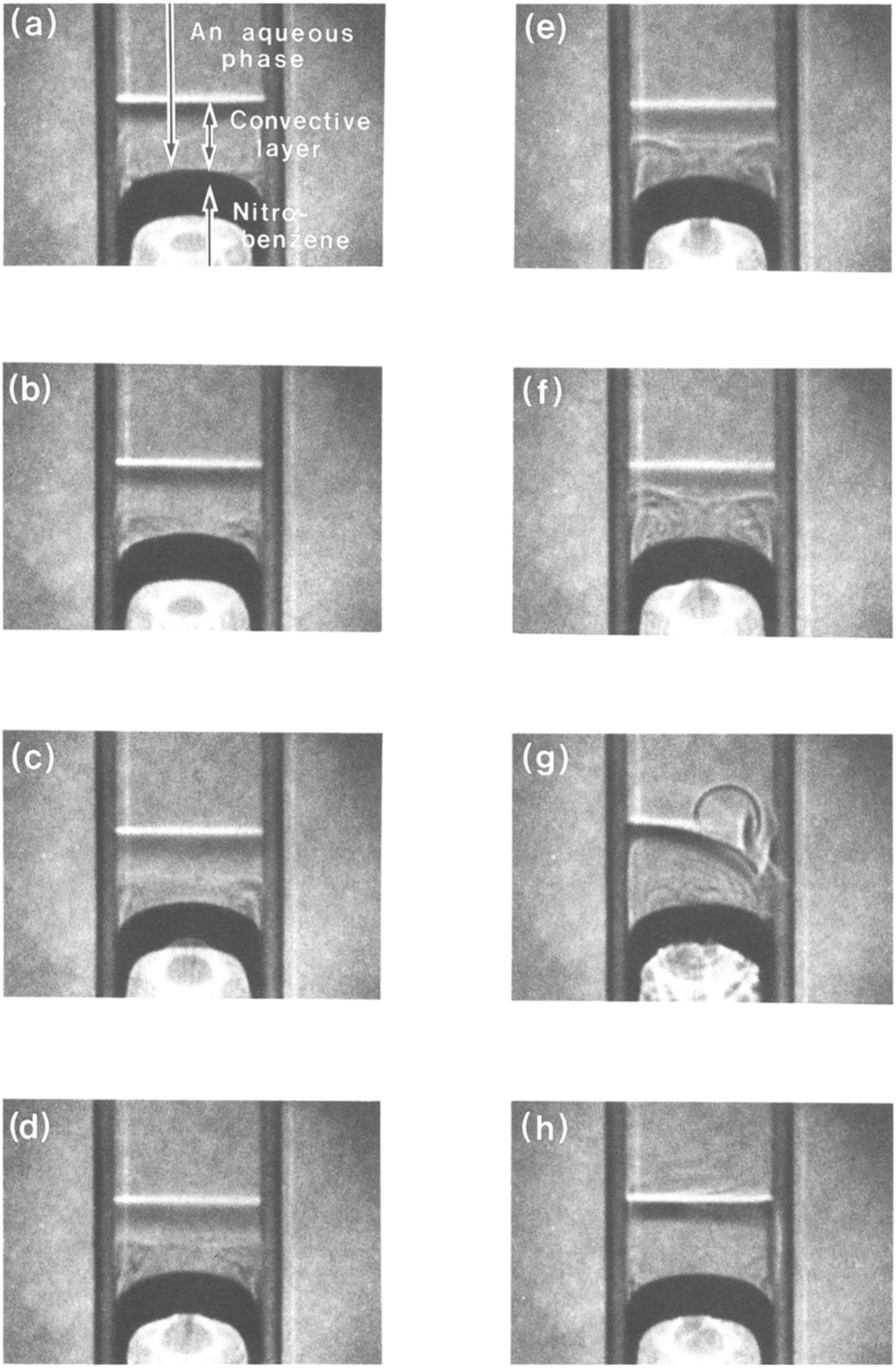

Fig. 3. Shadowgraph patterns. Each picture was taken at an interval of 30 s. The two vertical black lines are shadows of the cell walls. The curved dark zone is the interface forming a meniscus between an aqueous phase and an oil phase. The part under the dark meniscus zone corresponds to the oil phase and the whole part above the meniscus corresponds to the aqueous phase. A pair of bright and dark lines in the middle of the aqueous phase is considered to be due to a steep gradient of the concentration of aggregation products of surfactant and nitrobenzene.

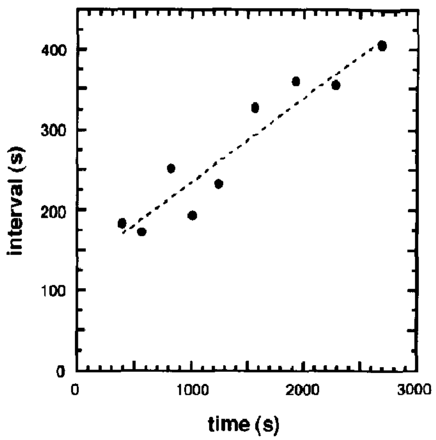

Fig. 4. Temporal variation of the period of the flow structure change, which is determined by occurrence of transient turbulence. The interval of transient turbulence increases with time.

the bright line. This layer was found to increase in thickness as time proceeds and a convective flow was observed in it. Thus we call this layer a convective layer.

The pictures in Fig. 3 which were taken at 30-s intervals, show one cycle of the periodic instability. Firstly, no structure was seen in the convective layer and the bright line on the upper boundary of the convective layer was clear (Fig. 3a). Secondly, small convection rolls occurred on the wall near the interface (Fig. 3b) and grew to distinct convective rolls (Fig. 3c–f). The structure of the rolls was torus-like; the flow rose along the walls and descended at the center of the cell. In the mature roll state (Fig. 3f), a pulsation of the strong down-flow occurred as if it was attracted by the oil phase and the roll size strongly fluctuated. Finally the torus structure broke down and evolved into transient turbulence, in which it was observed that some aqueous solution flew into the oil phase through the interface (Fig. 3g). After the transient turbulence, the flow returned to its initial quiet state (Fig. 3h). The above cycle took about 3.5 min. The flow structure change is repeated and its period is gradually increasing as shown in Fig. 4.

3.2 Light intensity

Fig. 5 shows a temporal variation of the light intensity measured with the photodiode. The light intensity depends on the distribution of the refractive index in the sample.

For example, a sequence of the light intensity from 1000 to 1250s in Fig. 5 exhibits one cycle of the flow pattern change. At the initial stage of the cycle, a convective roll flow is formed and the distribution of the refractive index is spatially ordered, so that the bright part appears at an edge of roll. The rise in the light intensity reflects this ordering process. Fluctuations generated in the latter half of the cycle represents the fact that the size of the roll pulsated and its edge swayed in the beam. In this range, the velocity of the roll flow increased considerably, so that the fluctuation seems to be a precursor of the turbulence. The transient turbulence at the end of the cycle brought about an abrupt decrease of the light intensity due to a scattering of the incident light. Each cycle of the light intensity change in Fig. 5 corresponds to a visualized flow structure change shown in Fig. 3.

3.3 Light intensity and potential difference

Figure 6 shows temporal variations of both the light intensity and the potential difference in the U-shaped cell.

The profile of the light intensity in the U-shaped cell is similar to that in the standard cell; the light intensity globally rises, fluctuations are

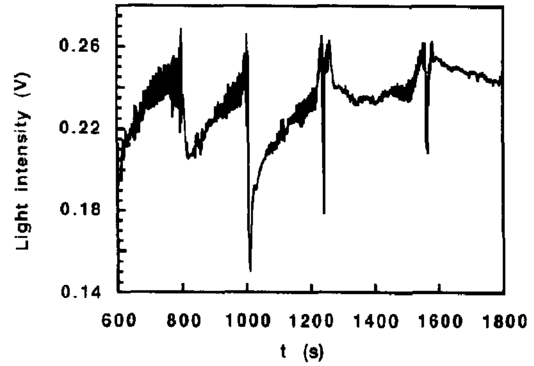

Fig. 5. Temporal variation of the light intensity. The abscissa t expresses the time after composing the water–oil system. Each cycle consists of a rise of light intensity, an oscillation and an abrupt decrease, which correspond to a growth of convective rolls, its pulsative motion and a transition to the transient turbulence, respectively.

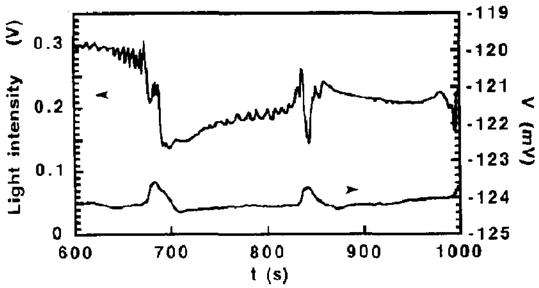

Fig. 6. Temporal variations of the light intensity and the potential difference. The left ordinate is the light intensity and the right ordinate is the potential difference. The sharp descend of the light intensity coincides with the burst of the electric potential.

observed in the latter half of the period and an abrupt decrease occurs at the end of the period. The electric potential difference between the two aqueous phases has peaks when the light intensity sharply decreases. No change in the potential difference occurs before the potential peak appears, though the light intensity vibrates during the period from 750 to 830 s, which corresponds to the oscillatory fluctuation of the roll size. The light intensity reflects only a local structure of the flow passed through by the beam, but the electric potential is a macroscopic quantity which is averaged over a wide space range. The burst of the potential difference, therefore, occurred only at a drastic change such as a transition from the convective flow to turbulence.

4. Discussion

The occurrence of the cyclic changes in the convective flow structure was found in the water–oil interface system composed of the aqueous solution of surfactant and nitrobenzene. It was found that the peak of the long period potential oscillation previously reported coincided with the time of the periodic transitions to the turbulence in the convective layer.

The convective flow is supposed to be generated by the Marangoni effect which is driven by the following process. An adsorption and a microscopic aggregation of surfactant and alcohol molecules on the interface generates the fluctuation of the interfacial tension, which causes a macroscopic convective flow. In our system shown in Fig. 3, the convective flow transfers surfactant and alcohol molecules from the bulk to the interface and gives rise to an enhancement of their concentrations in the central part of the interface. The concentration enhancement promotes the convective flow, hence the process forms a positive feedback route. When the concentrations of surfactant and alcohol at the interface exceed some threshold, the molecules rapidly aggregate by plunging into the oil phase; this is accompanied by a burst in electric potential and induces a transient turbulence in the convective layer. After the rapid aggregation has exhausted the free molecules at the interface, the convective flow due to the Marangoni effect ceases for a while. Thus the process is composed of an accumulation stage and a rapid exhaustion stage; the present result manifests that the accumulation process is strongly coupled with the convective flow in a synergetic way.

In the present study, the short period oscillation reported in the previous paper [10] has not been observed and the duration of the periodic bursts of potential (the long period oscillation) was very short compared with that in the previous report. This is supposed to be due to the difference in the system size; amounts of the surfactant solution and nitrobenzene were $\frac{1}{3}$ and $\frac{1}{5}-\frac{3}{5}$ of those in the previous study, respectively, but the area of the interface was smaller only by 10%. Thus, the chemical substances exhausted rapidly and the short period oscillation whose life time was much shorter than that of the long period oscillation is considered to have remained unobserved. The duration, therefore, decreased and the burst interval was not stable.

Our results suggest that flow subject to the Marangoni effect plays an important role in the accumulation of surfactant molecules at the interface, and therefore in the occurrence of the electric potential oscillation. As such, the phenomenon can be considered to be the result of a strong coupling effect of a diffusion–reaction process and hydrodynamic instability.

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References

1 S. Kai, E. Oonishi and M. Imasaki, J. Phys. Soc. Jpn. 54 (1985) 1274.
2 S. Kai, S.C. Muller, T. Mori and M. Miki, Physica D 50 (1991) 412.
3 W. Dalle Vedove and A. Sanfeld, J. Colloid Interface Sci. 84 (1981) 318.
4 M. Sakata and T. Funada, J. Phys. Soc. Jpn. 50 (1981) 696.
5 C.V. Sternling and L.E. Scriven, AIChE J. 5 (1959) 514.
6 R. Takaki and K. Sannomiya, Forma 4 (1989) 35.
7 H. Linde, P. Schwartz and H. Wilke, in: Dynamics and instability of fluid interface, ed. T.S. Sørenzen, Lecture notes in physics, vol. 105 (Springer-Verlag, Berlin, 1979) p. 75.
8 K. Yoshikawa, M. Shoji, S. Nakata, S. Maeda and H. Kawakami, Langmuir 4 (1988) 759.
9 K. Yoshikawa, S. Maeda and H. Kawakami, Ferroelectrics 86 (1988) 281.
10 H. Suzuki, Y. Tsuchiya and T. Kawakubo, Biophys. Chem. 40 (1991) 149.
11 S. Sha, T. Nakamoto, T. Moriizumi, Jpn. J. Appl. Phys. 30 (1991) L1435.
12 S. Sha, T. Nakamoto, T. Moriizumi, Jpn. J. Appl. Phys. 30 (1991) L1774.