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# Monitoring of molecular behavior of a chemical oscillation system at a liquid/liquid interface using a time-resolved quasi-elastic laser scattering method

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## Abstract

A time-resolved quasi-elastic laser scattering (QELS) technique was applied to monitor the molecular number density at a water/nitrobenzene (W/NB) interface of a W–NB–W three phase chemical oscillation system. We successfully monitored the oscillations of interfacial molecular number density, electric potential, and turbidity simultaneously by a newly developed chemical oscillation — QELS combination system. We observed for the first time that monolayer of the surfactants covers the interface almost throughout the oscillation and that the oscillation occurs simultaneously with a catastrophic disintegration of the monolayer after the increase of molecular number density. We proposed a new model for the chemical oscillation based on the obtained molecular description. © 1998 Elsevier Science Ltd. All rights reserved.

**Keywords:** Laser scattering; Chemical oscillation; Liquid/liquid interface; CTAB

## 1. Introduction

Nonlinear phenomena have attracted much attention in chemistry since they are fundamentally important in physicochemical systems such as chemical sensors, biological membranes, and solvent extractions. Chemical oscillation systems have been studied extensively as part of the nonlinear phenomena from a variety of viewpoints, including physicochemical interests in their chaotic behavior and as chemical approaches to biological phenomena [1]. Yoshikawa and Matsubara [2] were the first to report a chemical oscillation system made up of three layers. It consisted of a nitrobenzene layer (NB) separating two aqueous layers, one of which contained a surfactant and an alcohol (W1), and the other a saccharide (W2). With this system, it is possible to observe a sustained and spontaneous oscillation of the electric potential difference between the

two aqueous layers. The oscillation has spike-shaped patterns, which resemble those observed in biomembranes such as neuron systems. It is desirable to clarify the mechanism of the oscillation at a molecular level because this would provide great insight into excitability in biological systems and facilitate the design of new oscillation systems suitable for biomimetic sensors.

A variety of studies have been carried out to elucidate the mechanism of the chemical oscillation. As mentioned above, the electrical potential oscillation has been first observed for the system: Pt electrode/W1/NB/W2/(Ag/AgCl electrode). It is natural to think that the phenomena at the electrode/liquid interfaces are not essential for the electrical oscillation because such oscillations have not been observed for electrode/liquid interfaces. Thus a number of studies have been performed to clarify the dynamic behavior of the liquid/liquid interfaces. The oscillation patterns of electric potential and pH have been examined with various chemical species in the liquid phases [3,4], and the ion transfer potential has been determined using voltam-

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metric techniques [5]. Two types of oscillation models have been proposed so far. Yoshikawa and Matsubara [2] proposed that the dominant factor for the electric potential oscillation was the behavior of surfactant cations at one of the interfaces in the system, and that changes, like spike patterns, were attributable to the disappearance of an interfacial monolayer. On the other hand, Maeda et al. [5] reported that the oscillation amplitude corresponded to the difference of the ion transfer potential, suggesting the dominant factor was molecular transfer across the interface. Although no explanation for the chemical oscillation systems has been established so far, there is no doubt that molecular behavior at the liquid/liquid interface plays an important role in the chemical oscillations. Therefore, in order to elucidate their mechanism, monitoring of the solute molecules at the interface is highly desirable.

We have reported an application of a quasi-elastic laser scattering (QELS) method to monitoring the interfacial molecular number density of lipid and surfactant systems [6–9]. The interfacial molecular number density can be monitored as a function of capillary wave frequency by using the QELS, because this frequency is a function of interfacial tension, which depends on molecular number density at the interface. Since the QELS technique does not require any mechanical probe be inserted into the interface and it does not give any chemical and mechanical disturbances, it should be one of the most suitable ways to probe the molecular behavior at the interface of the chemical oscillation *in situ*.

The QELS has been mainly used to measure liquid/gas interfaces and has been scarcely applied to liquid/liquid interfaces. Furthermore, most of the previous studies using the QELS have been performed on static systems [10,11]. In order to apply the QELS to the monitoring of the molecular behavior at chemically oscillating liquid/liquid interfaces, time required for data acquisition has to be shortened, unlike when observing static systems. Owing to our developments in the optical equipment and the electronic signal processing, we are able to obtain a QELS spectrum with a 1 s data acquisition time. In this paper, we present the results of coincident measurements of the QELS, the electric potential, and the turbidity in the water–nitrobenzene–water (W–NB–W) chemical oscillation system. Since the behavior of the surfactants has been reported to play an important role in the oscillation [12], we focus on the molecular behavior at the W1/NB interface and propose a model for molecular behavior at the interface based on the experimental results.

## 2. Experimental

The newly developed QELS system for coincident measurements is shown in Fig. 1. Since experimental details of the QELS equipment were described in our previous reports [6–9], only a brief outline follows here. A beam from a He–Ne laser passes through a liquid/liquid interface, at which the beam is quasi-elastically scattered by the interfacial capillary waves. The scattered light is accompanied by a Doppler shift, and the frequency shift is the same as the capillary wave frequency. The frequency shift is measured using an optical heterodyne technique. The incident beam is divided in front of the cell using a diffraction grating, and one of the diffracted beams is mixed with the scattered light to generate an optical beat. The optical beat is detected by a photodiode and the beat frequency is recorded by a digital spectrum analyzer to obtain a power spectrum. The peak position of the power spectrum is the same as the beat frequency, i.e. the capillary wave frequency.

In order to achieve coincident measurements of the QELS and electric potential, the QELS equipment was optimized regarding several points. The measurements were performed in the transmission configuration,

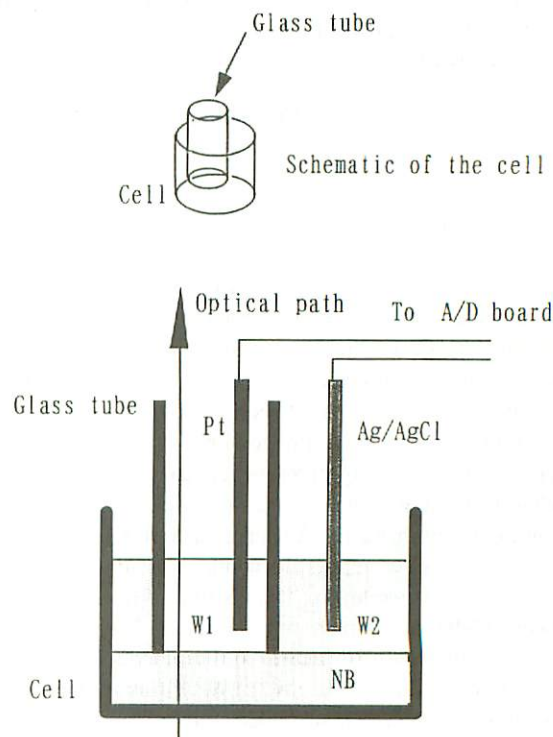


Fig. 1. Schematic illustration of the setup for the chemical oscillation system including the optical path of the QELS experiment.



making the system more stable to low frequency vibrations. The scattering angle was fixed at 9.5 mrad, for which the power spectrum of the signal had sufficient intensity and separation from the low frequency noises due to the external vibrations. In order to suppress the external mechanical vibrations, the optics and chemical oscillation cell were mounted on a suspended optical platform.

The chemical oscillation cell was a beaker-shaped cell with a glass tube inside, which was supported with a clamp on a stand (Fig. 1). First a nitrobenzene solution (NB) of picric acid was poured into the cell. The bottom of the tube was set at the NB level. Next, an aqueous solution (W2) of glucose was poured into the cell, along the outside of the tube and an aqueous solution (W1) of cetyltrimethylammonium bromide (CTAB) and 1-butanol was poured into the glass tube. In this way, the two aqueous phases were successfully separated by the NB phase, forming the W1–NB–W2 three-phase system. After the formation of the phases, Ag/AgCl electrode and Pt electrode were immersed in W2 and W1, respectively. The inner tube was adjusted to minimize the distance between the end of the tube and the W1(W2)/NB interfaces.

The data storage system of the QELS was activated according to demand by triggering with a personal computer, which monitors the electric potential of the chemical oscillation system via an analogue/digital (A/D) converter board connected to the electrodes in the chemical oscillation cell.

Concentrations of the substances in the liquid phases were 5 mM CTAB plus 0.5 M 1-butanol for W1, 0.1 M glucose for W2, and 5 mM picric acid for NB. All the chemicals were purchased and reagent grade. Since purchased picric acid is sold wet for safety, it was dried in a desiccator before dissolving into nitrobenzene. The other substances were used without further purification.

As it has been reported that molecular transfer from W1 to NB plays an important role in the oscillation [2–4], the QELS and electric potential measurements were carried out on the W1–NB side. Turbidity measurements were also performed simultaneously by monitoring the intensity of the transmitted He–Ne laser light across the W1 and NB phases during the chemical oscillation.

### 3. Results and discussion

The time-courses of the capillary wave frequency and the electric potential during the chemical oscillation processes are shown in Fig. 2. The capillary wave frequency and the electric potential were measured simultaneously using trigger signals from the personal computer. The electric potential was moni-

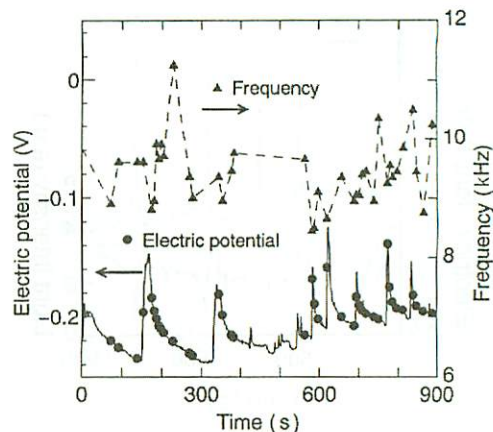


Fig. 2. Time-courses of the electric potential between the two aqueous phases and capillary wave frequency.

tored continuously as shown by the solid line in the figure. The circles on the solid line indicate the trigger points of the QELS measurement. The obtained capillary wave frequencies are depicted as triangles, and the dotted line is for an eye-guide. Spike-shaped oscillations are typically observed in the electric potential. There is a marked tendency that the peaks of the electric potential almost correspond to the minimum point of the capillary wave frequency, indicating that the interfacial tension changes simultaneously with the electric potential. It should be noted that the electric potential reflects the change of the whole interfacial area, whereas the QELS method monitors only a part of the interface which is equal to the beam diameter (0.68 mm in this case). The slight discrepancy between the changes in the potential and frequency is probably due to the difference of the observed areas of respective parameters.

It is obvious that the electric potential oscillation corresponds with the oscillation of the interfacial molecular number of CTAB. Since the capillary wave frequency is proportional to the square root of the interfacial tension which reflects the molecular number density of surfactants, the minimum points of the capillary wave frequency correspond to the maximum points of molecular number density of CTAB. In order to estimate the interfacial molecular number density, we used our previous results on the relation between capillary wave frequency and the molecular coverage with dipalmitoylphosphatidylcholine (DPPC) at the W/NB interface [6]. We have monitored phase transitions of DPPC in four states: gaseous state, liquid expanded state, liquid condensed state, and oversaturated (stacking state). In the liquid condensed and the oversaturated states, the observed capillary wave frequency was less than ca. 10 kHz. Based on the assumption that DPPC and CTAB occupy approximately the same area



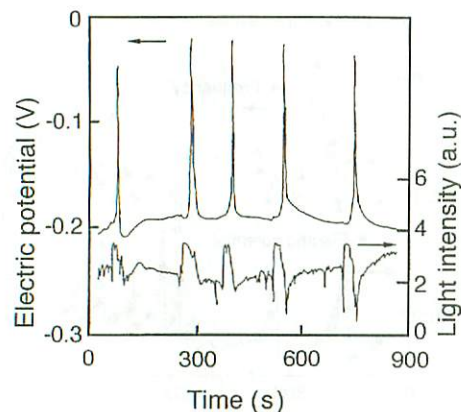


Fig. 3. Time-courses of the electric potential between the two aqueous phases and the intensity of the transmitted laser beam.

per mole, the interfacial molecular number density of the CTAB in the present study is as large as that of the DPPC in the liquid condensed and the oversaturated states. It is noteworthy that such a large number of molecules, forming a monolayer, are always present at the interface, even during the spike-shaped oscillation.

Moreover, we found a great change in the interfacial turbidity during the oscillations. The time-courses of transmitted laser intensity through the W1–NB phases and the simultaneously measured electric potential are presented in Fig. 3. Intensity of the transmitted light is a maximum at the beginning of the spike-shaped oscillation of electric potential, and it drops to a minimum around the end of the oscillation of electric potential. Since the CTAB micelles are the only light-scattering substance in the W1–NB phases, the change in turbidity is due to the change in the aggregation states of CTAB molecules. The maximum point in the transmitted light intensity is the point at which the concentration of the CTAB micelles becomes the lowest. This indicates that the micelles in the W1 phase collapse to form monolayer at the interfacial regions just before the beginning of the pulse-shaped oscillation of the electric potential.

The above results cannot be explained by a simple conventional assumption that the electric potential oscillation is due to the change of the density of the electrical double layer formed by the CTAB monolayer at the W1/NB interface [2]. Thus, we propose a new model based upon our experimental results. The dominant factor for the oscillation is mass transfer across the W1/NB interface, and the change in the electric potential is due to the transfer of charged species. Although presently we cannot conclude directly which species transfer across the interface during the chemical oscillation, CTA cations composing micelles are

reasonable candidates, as deduced from the averaged capillary wave frequency during the whole period of the oscillation and the results of turbidity measurements. The oscillation of the electrical potential which occurs simultaneously with the changes of both the turbidity and the capillary wave frequency is considered to be due to the transfer of CTA cation from the interfacial region to the W1 phase and the NB phase as micelles. Therefore, the decrease in the turbidity which occurs before the electrical oscillation is due to the adsorption of CTA cations onto the interface from the micelles in the W1 phase. In a word, the oscillation can be explained by the formation and rupture of interfacial monolayer.

In Fig. 4 we schematically illustrate the oscillation based on our model. It consists of three stages: (1) The surfactant molecules form both micelles and a monolayer at the interfacial region. (2) A catastrophic collapse of micelles occurs around the interface and the molecules are adsorbed as a monolayer onto the interface. (3) A rupture of monolayer occurs when attaining a critical value of molecular number density. Some molecules at the interface are transferred to the NB phase, forming molecular aggregates such as reversed micelles. The interfacial molecular number density returns to that in stage (1) and molecular transfer across the interface pauses. At present we think our results suggest that the chemical oscillation is generated by the fluctuation between the transfer rate from the W1 phase to the interface and that from the interface to the NB phase.

In summary, we applied the QELS method to monitoring molecular number density at the W/NB interface of a chemical oscillation system. We observed an interfacial molecular transfer which occurs simultaneously with the generation of spike-shaped peaks in the electric potential and we proposed a model based on the obtained molecular description of the chemical oscillation. We believe that the time-resolved QELS

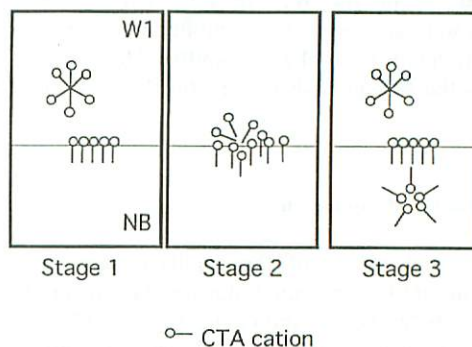


Fig. 4. Schematic illustration of the oscillation based upon our present model.

method will be a powerful tool for monitoring the dynamics at liquid/liquid interfaces.

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