



Effects of halide ions on the acceptor phase in spontaneous chemical oscillations in donor/membrane/acceptor systems

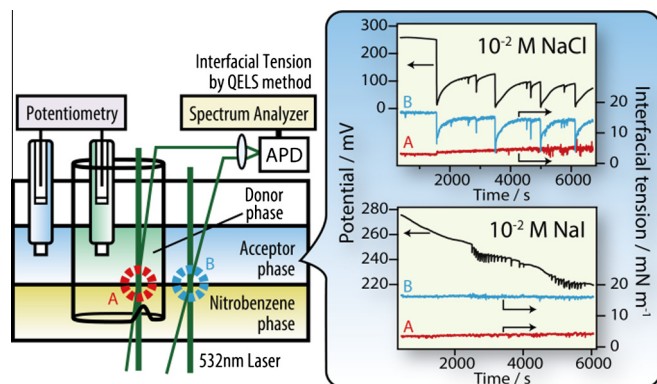


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GRAPHICAL ABSTRACT



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ABSTRACT

The effects of halide ions on the acceptor phase in the chemical oscillation in donor/membrane/acceptor systems were examined. The transfer of cetyltrimethylammonium (CTA⁺) ions from the donor phase and their adsorption and desorption at the membrane/acceptor interface led to spontaneous, nonlinear oscillations of the electric potential. Chloride ions stabilized the adsorption of CTA⁺ ions and gave rise to a large-amplitude, long-interval, and a long relaxation-time constant. On the contrary, iodide ions, which are more hydrophobic than chloride ions, demonstrated opposite results. This mechanism was proposed based on the simultaneous time-resolved measurements of the interfacial tensions at both the donor/membrane and membrane/acceptor interfaces and observation of the convective flow due to Marangoni instability.

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1. Introduction

Spontaneous, nonlinear oscillations of electric potential across an interface have been observed in several immiscible-liquid systems; the phenomenon likely results from the transport process

of surfactant molecules. These systems are far from equilibrium, and the oscillation mechanism is related to various factors that not only include the properties of the surfactant molecules and the types of solutes but also their geometric configurations. Multiple experimental and numerical approaches have been adopted, but researchers have not yet determined a conclusive mechanism behind these oscillations [1]. The most acceptable mechanism is based on Marangoni instability, which induces a convective flow

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at the interface due to the gradient of the interfacial tension between the two immiscible-liquid layers such as water and oil. The non-uniform interfacial-tension distribution is caused by fluctuations of the temperature or the molecule content adsorbed at the interface, and it is very difficult to anticipate the onset of such an oscillation. When the surfactant solution is introduced in the vicinity of the oil/water interface using a capillary tip in the aqueous phase, the inhomogeneous interfacial tension and the tangential convective flow along the interface can be observed [2]. Furthermore, a continuous supply of the surfactant solution leads to the complete synchronization of the electric potential and the interfacial tension. Therefore, it can be inferred that the oscillation pattern of the electric potential strongly depends on the interfacial activity and partition ratio of the surfactant. These properties of the surfactants are influenced by the solutes in each phase. The types of electrolytes and their concentrations in the aqueous phase change the interfacial activity of surfactants, and researchers have analyzed the oscillation-pattern dependences [2–5]. Small amounts of supporting electrolytes, such as tetrabutylammonium ions and halide ions, in the oil phase have also been related to the relaxation of the electric potential [6]. Kovalchuk et al. focused on molecular behaviors and discussed chemical oscillation influenced by the changes in the ionic strength and pH in terms of the adsorption and desorption of surfactants in the oil/water system [7,8]. Shioi et al. studied the oscillatory instability generated by chemical reactions of Ca^{2+} and Fe^{3+} cations with bis(2-ethylhexyl) phosphate in a biphasic system [9]. They discussed the chemical-species dependences by way of the oscillatory motions of droplets formed in the liquid and the behavior of solid-liquid interfaces when a voltage was applied to glass/oil-water systems [10,11].

Yoshikawa et al. extended the chemical oscillation to three-phase systems in which two aqueous phases are separated by an immiscible-oil membrane [12–14]. The aqueous phase containing a surfactant is called the donor phase, and the other, containing some type of solute, is called the acceptor phase. As a practical application, a sensing system for taste substances that were introduced to the acceptor phase was developed. Using this three-phase system, the features of the electric-potential oscillation, i.e., the amplitude and frequency, between the two aqueous phases, were found to be strongly dependent on the chemical species in the aqueous phase. Researchers determined that the electrolytes in the acceptor phase affected the diffusion rate close to the water/oil interface. Arai et al. reported that the structure of the surfactant monolayer adsorbed at the interface between the acceptor and oil phases (hereafter abbreviated as the acceptor interface, and similarly the interface between the donor and oil phase is abbreviated as the donor interface) was changed via the electrostatic interaction with chemical species in the acceptor phase [15,16]. Kovalchuk and Vollhardt performed a numerical simulation in an oil/water/oil system and compared it with the experimental results [17]. They concluded that the chemical oscillation was caused by Marangoni instability at the acceptor interface and was similar to oscillations produced in a two-phase system using surfactants introduced from a point source [18]. On the other hand, the simultaneous measurement of the electric potential and the interfacial tension showed that the oscillation was fully synchronized with the surfactant adsorption and desorption at the donor interface [19]. As described above, there were some controversial results on the behavior of the surfactant molecules in the three-phase system.

We have achieved simultaneous measurements of the electric potential between two aqueous phases and the interfacial tension of both the donor and acceptor interfaces via the quasi-elastic laser scattering (QELS) method [20]. In our study, a three-phase oscillatory system was set up by separating two aqueous phases by

inserting a hollow, cylindrical tube with a V-shaped deformation into the oil phase, which had a role in forming a preferential diffusion path to the acceptor interface for CTA^+ ions in the oil phase, according to the method outlined in previous reports [16,21,22]. Ionic surfactant (cetyltrimethylammonium bromide, CTAB) with 0.1 mol/L 1-butanol was dissolved in the aqueous donor phase and poured into the cylindrical tube, and then the aqueous acceptor phase, containing 0.1 mol/L NaCl solution, was also added outside of the cylindrical tube. The oil phase was composed of tetrabutylammonium tetraphenylborate (TBATPB) in nitrobenzene.

According to our results, the oscillatory profiles of the electric potential were completely synchronized with those of the interfacial tension of the acceptor interface, whereas the interfacial tension of the donor interface was slightly increased. Therefore, we concluded that the electric-potential changes in the three-phase system were derived from the adsorption and desorption processes of the surfactant at the acceptor interface. When the potential dropped, a synchronized change of the interfacial tension was observed, and a convective flow, and jostling and shaving at the acceptor interface were induced by the Marangoni instability due to the inhomogeneous interfacial tension distribution.

Our proposed model was as follows. Cetyltrimethylammonium (CTA^+) ions diffused from the donor phase to the outside of the cylindrical tube via the V-shaped deformation in the oil phase and adsorbed at the acceptor interface locally, leading to a local decrease of the interfacial tension. The instability due to such local adsorption of the surfactant was enhanced inhomogeneous interfacial tension, and as a result, the convective flow from the tube to the vessel wall was induced. Therefore, a large quantity of CTA^+ ions were fed and adsorbed simultaneously at the acceptor phase, and so, abrupt drops in both the interfacial tension and the electric potential were observed. Afterward, the adsorbed CTA^+ ions were desorbed from the acceptor interface, and the interfacial tension and the electric potential returned gradually. Because such a series of adsorption and desorption of surfactant repeated periodically, an electric potential was oscillated. The addition of short chain alcohols, such as 1-butanol, to the donor phase increased the dissolution of CTA^+ ions in the oil phase [23]. Therefore, we determined that adsorption and desorption behaviors of CTA^+ ions at the acceptor interface were critical in the chemical oscillation of a three-phase system. According to the proposed model, we expected that the oscillatory phenomenon could be controlled by way of the chemical species in the acceptor phase affecting the adsorption behavior of the surfactant. However, to the best of our knowledge, there have been no systematic studies on the dependence of oscillation on the chemical species in the acceptor phase so as to control the interfacial activity and solubility of the surfactant molecules.

In the present work, we focused on the adsorption stability of the surfactant owing to the co-existence of halide ions (Cl^- , Br^- , and I^-), which function as the counter ions for the CTA^+ ions as well as a stabilizer for adsorption at the oil/water interface. Due to the hydrophobicity of iodide ions [24–26], CTA^+ ions were expected to form ion pairs with them, leading to desorption from the interface and dissolution in the oil phase, whereas chloride ions stabilized the adsorption of the CTA^+ ions via electrostatic interaction, resulting in the promotion of adsorption [25,27]. Furthermore, the non-linear response was likely related to the Marangoni instability, so the convective flow was estimated to confirm its relevance. The effects of halide ions in the acceptor phase on the three-phase oscillatory system were analyzed by observing the convective flow and the interface movement as well as by measuring the electric potential and the interfacial tensions of the donor and acceptor interfaces simultaneously.

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