

Direct Observation of Dynamic Molecular Behavior at a Water/Nitrobenzene Interface in a Chemical Oscillation System

Tetsuya Takahashi, Hiroharu Yui, and Tsuguo Sawada*

Department of Advanced Materials Sciences, Graduate School of Frontier Sciences, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, and Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Corporation (JST), 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Received: September 10, 2001; In Final Form: December 7, 2001

Nonlinear behavior of ionic surfactant (SDS) molecules at a water/nitrobenzene (W/NB) interface in a chemical oscillation system was investigated by monitoring interfacial tension ($\Delta\gamma$) using time-resolved quasi-elastic laser scattering (QELS). Simultaneous measurement of electrical potential (ΔV) allowed extraction and discussion of the time course of $\Delta\gamma_a$ which represents the contribution of the interfacial molecular behavior to $\Delta\gamma$. No change of $\Delta\gamma_a$ was observed in the induction period which lasted about $10-10^3$ s. This indicated that no efficient adsorption of surfactants onto the W/NB interface occurred although the surfactants diffused toward the interface. After this induction period, $\Delta\gamma_a$ showed a sudden decrease with electrical potential oscillation; i.e., the molecular adsorption occurred rapidly and collectively with changes of interfacial tension and electrical potential. Chemical oscillation was brought about by this unusual adsorption behavior. It appeared that some hindrance effect toward adsorption was induced at the liquid/liquid interface, which resulted in the formation of a large concentration gradient at the sub-interfacial region and led to the collapse and sudden adsorption of SDS. After the chemical oscillation, which was a relaxation process, $\Delta\gamma_a$ increased gradually. $\Delta\gamma_a$ was fitted by combining Langmuir adsorption–desorption and Frumkin adsorption isotherms. It was concluded that the relaxation process was governed by molecular desorption and had an extraordinarily long time scale ($\sim 10^3$ s). The mechanism of these features was considered in terms of deceleration of counterion-binding because SDS molecules could not be desorbed to the NB phase without the formation of ion pairs. These unusual molecular behaviors indicated that some barrier-like effect which hindered adsorption and desorption played a key role in the nonlinear oscillation behavior induced at the liquid/liquid interface.

Introduction

Interfaces play a key role in modern science and technology^{1–5} and the unique features and phenomena induced at them have attracted the interest of researchers in many different fields. In particular, liquid/liquid interfaces have drawn much attention; not only do these interfaces have structural and dynamical nonlinear properties which are not observed in bulk liquids, but also they are integral to many biological systems.^{6–16} Chemical oscillation systems at the liquid/liquid interface have been extensively studied from the viewpoints of fundamental scientific interest in nonlinear phenomena, and of applications to new type sensors, for example, using electrical excitability in biomembranes.^{6–12}

Dupeyrat and Nakache⁶ were first to observe a chemical oscillation system using a water/oil two-phase system. Their system was expanded to a water/oil/water three-phase system, and many others have now observed sustained and spontaneous chemical oscillations^{8–14} as well as other nonlinear behavior such as rhythmic oscillation of pH and electrical potential.^{6–14} However, despite these extensive efforts, a consensus has not been reached about how these nonlinear effects are induced at the interface. A molecular level understanding is essential for elucidating this nonlinear behavior.

Here we report the direct investigation of interfacial molecular behavior during chemical oscillation with simultaneous measurements of interfacial tension and interfacial electrical potential. We have developed a quasi-elastic laser scattering (QELS) method which allows noncontact and nonperturbative measurement of dynamic interfacial tension.^{17,18} The QELS method can be easily applied to liquid surfaces and also liquid/liquid interfaces because of its simple in-situ optical setup. We have used the QELS technique to investigate dynamic interfacial molecular behavior in various processes such as a mass transfer of surfactants at a water/nitrobenzene (W/NB) interface^{19–22} and a phase transfer catalytic reaction.^{23–25}

In the present study, we examined the mechanism of nonlinear chemical oscillation from the viewpoint of dynamic molecular behavior induced at a liquid/liquid interface. The QELS method was applied to a chemical oscillation system which consisted of W/NB two phases. Interfacial tension acutely reflects surfactant adsorption–desorption behavior, lateral interfacial molecular interactions, and the electrostatic effect due to a diffusive electric double layer. To evaluate the electrostatic term contained in interfacial tension, we also measured interfacial electrical potential simultaneously with the QELS measurement. Thus, we could discuss the interfacial molecular behavior and electrostatic effect independently. Finally, we were able to directly observe the molecular behavior at the liquid/liquid interface.

* Author to whom correspondence should be addressed. Tel: +81-3-5841-7236. Fax: +81-3-5841-6037. E-mail: ksawada@mail.ecc.u-tokyo.ac.jp.

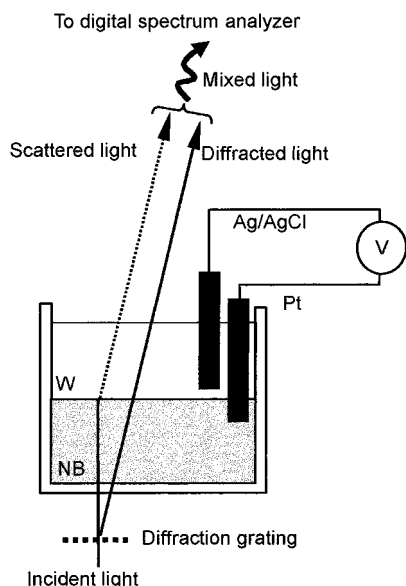


Figure 1. Schematic diagram of the liquid/liquid chemical oscillation system, including the optical path for the QELS measurement: W, water phase; NB, nitrobenzene phase; V, potentiometer.

Experimental Section

The principle of the QELS method has already been described elsewhere.^{26,27} A brief outline is as follows. A capillary wave scatters the incident laser beam, which is normal to the interface, quasi-elastically with a Doppler shift (Figure 1). The scattered beam is optically mixed with a local beam produced by a diffraction grating to generate an optical beat in the mixed light. The optical beat frequency has the same frequency as the Doppler shift, i.e., the capillary wave frequency. The capillary wave frequency f is approximately related to the interfacial tension γ by Lamb's equation which follows hydrodynamics theory,²⁸

$$f = \frac{1}{2\pi} \left(\frac{\gamma}{\rho_w + \rho_o} \right)^{1/2} k^{3/2} \quad (1)$$

where ρ_w and ρ_o are densities of the water and oil (in this study; NB) phases, respectively, and k is the wavenumber of the capillary wave. Interfacial tension γ is calculated using Lamb's equation and measured f .

According to Davies equation, which describes the interfacial excess energy, the interfacial tension, $\Delta\gamma$, can be separated into contributions of interfacial adsorption molecules, $\Delta\gamma_a$, and the diffusive electric double layer, $\Delta\gamma_d$. Extraction of $\Delta\gamma_a$ from $\Delta\gamma$ allows us to discuss the interfacial molecular behavior directly. Separation of $\Delta\gamma$ into $\Delta\gamma_a$ and $\Delta\gamma_d$ is carried out by means of the following theory. $\Delta\gamma$ is expressed by the following form:^{29,30}

$$\Delta\gamma = \Delta\gamma_a + \Delta\gamma_d \quad (2)$$

where

$$\Delta\gamma_a = RT\Gamma_\infty \ln \left(1 - \frac{\Gamma}{\Gamma_\infty} \right) + \beta\Gamma^2 \quad (3)$$

is the equation which takes account of the activity of adsorption molecules and lateral molecular interactions at the interface (Frumkin's adsorption isotherm), and Γ and Γ_∞ are instantaneous and saturation interfacial concentrations of surfactant, respectively. β is a parameter denoting the interaction between

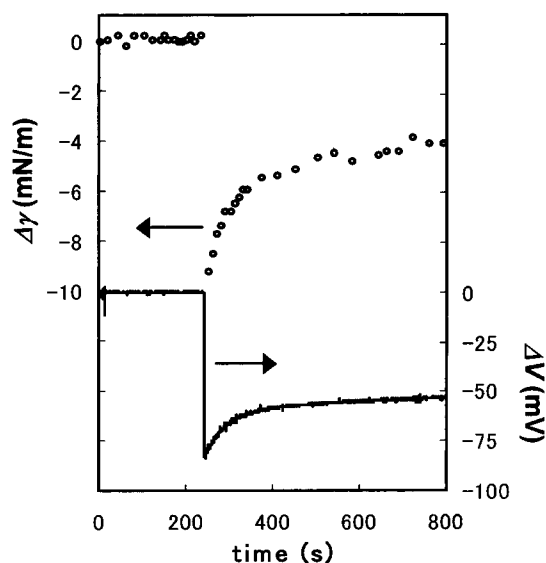


Figure 2. Time courses of the interfacial tension $\Delta\gamma$ (open circles) and the electrical potential ΔV (solid line): NB phase, 10 mL; W phase, 0.1 M NaCl 20 mL; 50 μ L of 10 mM SDS solution was injected at time zero.

adsorption molecules, R is the gas constant, and T is absolute temperature. Frumkin's equation allows us to discuss dynamic interfacial tension.^{31–33}

$$\Delta\gamma_d = -\frac{8RTc_c}{\kappa} \left[\cosh \left(\frac{F\Delta V}{RT} \right) - 1 \right] \quad (4)$$

Here c_c is the bulk concentration of counterions (Na^+), ΔV is the measured electrical potential across the W/NB interface, κ is the Debye parameter, and F is the Faraday constant. $\Delta\gamma$ can be experimentally measured using the QELS method, and $\Delta\gamma_d$ can be calculated from experimental values simultaneously measured by an electrochemical technique. We extract $\Delta\gamma_a$ by subtracting $\Delta\gamma_d$ from $\Delta\gamma$; $\Delta\gamma_a$ is then used to discuss independently the molecular behavior at an interface.

The QELS measurement apparatus (Figure 1) has been reported previously.^{17–25} The optical beat was detected by a photodiode and the beat frequency spectrum was measured with a digital Fast Fourier Transform (FFT) analyzer (Sony Tektronix Co., model 3056). The standard deviation of beat frequency data for the W/NB interface was calculated as 0.1 kHz. The accuracy of interfacial tension was estimated as ± 0.2 mN/m from eq 1. An Ag/AgCl electrode and a Pt electrode were immersed in W and NB phases, respectively. The electrical potential of the NB phase against the W phase ΔV was measured with a potentiometer. The liquid/liquid interface was prepared by gently pouring NaCl (Wako; special grade) aqueous phase onto NB (Kanto Chemical; special grade; 99.5% purity) in a quartz glass cell. All experiments were performed at room temperature. Sodium dodecyl sulfate (SDS) (Kanto Chemical Co., Inc; first grade) solution was injected with a microsyringe inserted below the air/W interface (a point far from the W/NB interface). Ultrapure water (from Millipore Milli-Q system) was used for all aqueous sample preparations. All chemicals, except as noted above, were reagent grade and used without further purification.

Results and Discussion

Figure 2 shows typical chemical oscillation of interfacial tension and electrical potential caused by SDS injection using the microsyringe. Both the interfacial tension and electrical potential prior to the SDS injection were regarded as zero. Time

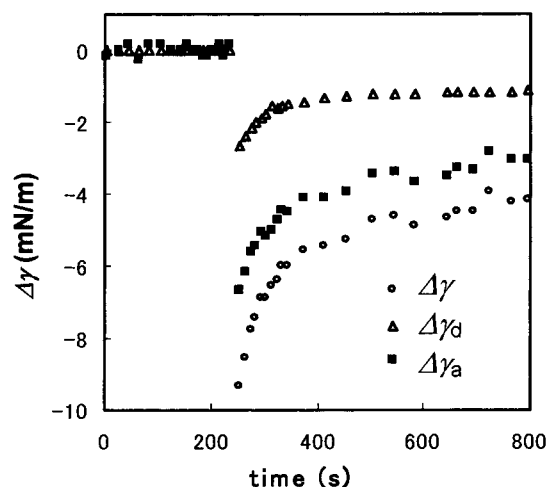


Figure 3. Separation of $\Delta\gamma$ (open circles) from Figure 2 into $\Delta\gamma_a$ (shaded squares) and $\Delta\gamma_d$ (open triangles).

zero indicated the SDS injection point. The interfacial tension values were acquired at intervals of 10 s; then the data were averaged. Obviously, the interfacial tension and electrical potential changed simultaneously. The characteristics of chemical oscillation were as follows: during the initial $10\text{--}10^3$ s, the interfacial tension and the electrical potential did not show any change (the induction period), then they changed suddenly (the oscillation), before slowly recovering toward their initial values (relaxation process). When the oscillation occurred, we observed that the interface flipped. In the QELS measurement, unfortunately, the scattered beams from the interface fluctuated strongly when the liquid/liquid interface flipped, and data collection was impossible for 20–30 s after oscillation took place.

Next, we separated $\Delta\gamma$ into $\Delta\gamma_a$ and $\Delta\gamma_d$ as shown in Figure 3. In some oscillation models, it has been proposed that surfactants (DS ions and/or SDS molecules) are adsorbed gradually at the interface in the induction period.^{8–12} In addition it has also been proposed that when the interfacial adsorption concentration of surfactants reaches a critical value, the electrical potential oscillation takes place. However, there are opposite interpretations for the cause of electrical potential oscillation, i.e., the destruction^{8–10} or formation^{11,12} of a critical interfacial layer of adsorbed surfactant molecules. In each case, if the gradual molecular adsorption occurs as proposed, we would expect to observe a gradual decrease of $\Delta\gamma_a$. However, in Figure 3, contrary to expectations from the former models, no remarkable change of $\Delta\gamma_a$ was observed in the induction period within the detection limit (8×10^{-12} mol/cm²) of our apparatus.³⁴ This indicates that no efficient adsorption of surfactants onto the W/NB interface occurred although the ions diffused toward the interface (Figure 4a). After the induction period, however, $\Delta\gamma_a$ showed a sudden and drastic decrease and the electrical potential changed rapidly. The decrease of $\Delta\gamma_a$ was due to the molecular adsorption onto the interface. Therefore, this result means that rapid and collective adsorption of SDS molecules and/or DS ions (Figure 4b) brought about the chemical oscillation (Figure 4c). Such a catastrophic adsorption of surfactant has not been taken into account in previously proposed models.

We noted that surfactant adsorption was hindered in the induction period. While molecular adsorption was prevented at the sub-interface region, surfactants were accumulating at the sub-interface region and the concentration gradient of surfactants grew larger. When concentration at the sub-interface region

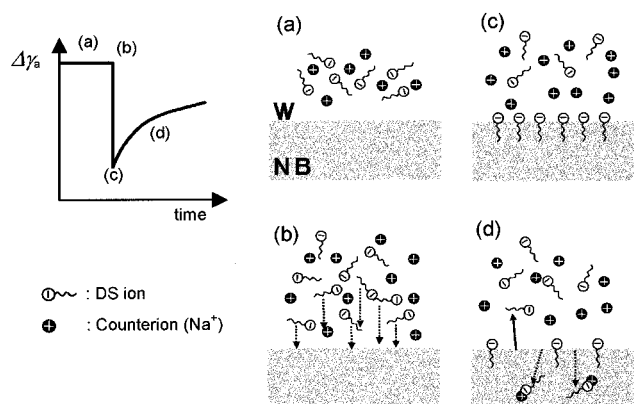


Figure 4. Schematic representation of interfacial molecular behavior bringing about the chemical oscillation.

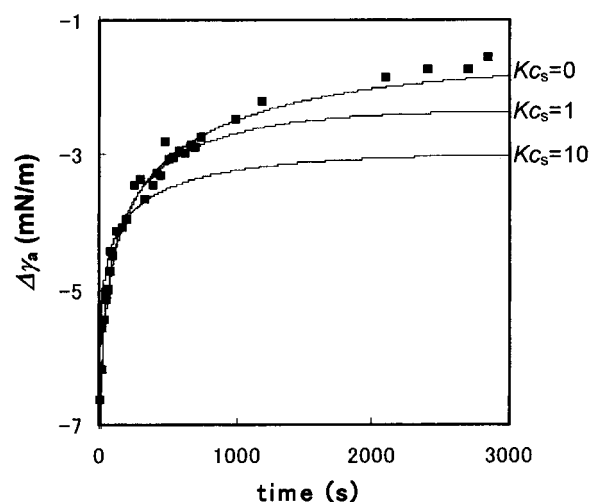


Figure 5. Relaxation process of the $\Delta\gamma_a$ from Figure 3. The solid line represents the best fit by eqs 6 and 7.

reached a threshold, the large concentration gradient collapsed and drastic adsorption took place.

Our interpretation is consistent with some other experimental and theoretical reports. The observed nonlinear adsorption behavior can be reduced to the Marangoni effect, in which enormous chemical energy originating in the gradient is converted into mechanical energy.^{35–38} Thus, we expected that some mechanical effect should be induced in chemical oscillation. It was reported that convection in the bulk accompanied chemical oscillation.^{11,12} Moreover, for theoretical support, the magnitude of the adsorption rate has been estimated and the adsorption rate of ionic surfactants was very fast ($1\text{--}10^{-3}$ s).^{29,30} These results strongly indicate that the hindrance of adsorption, caused at the liquid/liquid interface, is essential for the nonlinear molecular behavior. The cause of such a barrier-like effect at a liquid/liquid interface is considered latter in this report.

Then we focused on the time course of the relaxation process. Figure 5 shows the relaxation of $\Delta\gamma_a$ from Figure 2. We considered dynamic interfacial molecular behavior in the relaxation process by fitting the theoretical equation to the experimental $\Delta\gamma_a$ data. Shioi et al.³¹ have already demonstrated the validity of Langmuir adsorption–desorption kinetics, so we used it here,

$$\frac{d\theta}{d\tau} = -\theta + Kc_s(1 - \theta) \quad (5)$$

where θ is the dimensionless interfacial concentration, τ is time

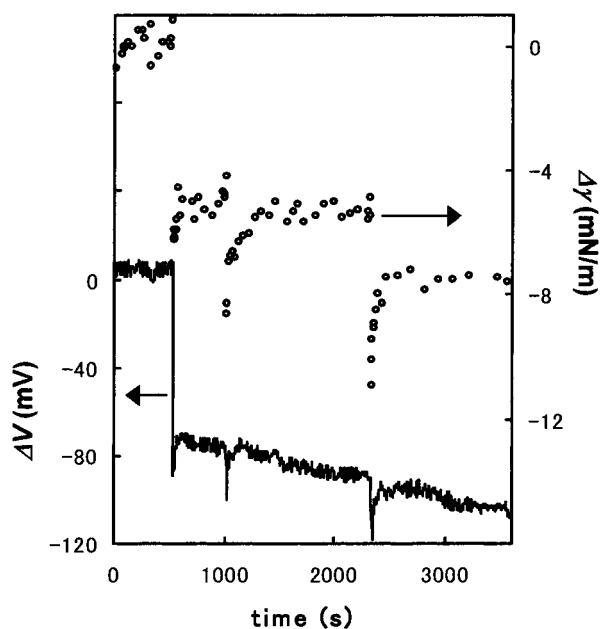


Figure 6. Successive chemical oscillation brought about by continuous SDS injection using a perista pump: NB phase, 20 mL; W phase, 6 mL; injected SDS concentration, 5 mM; SDS flow rate, about 8.5 $\mu\text{L}/\text{min}$.

scaled by the desorption rate constant, K is an equilibrium constant, and c_s is bulk concentration of surfactant. Assuming that $\theta = 1$ at $\tau = 0$, we obtained

$$\theta(t) = \frac{1}{1 + Kc_s} [\exp\{-(1 + Kc_s)\tau\} + Kc_s] = \frac{1}{1 + Kc_s} \left[\exp\left\{-(1 + Kc_s)\frac{t}{\alpha}\right\} + Kc_s \right] \quad (6)$$

where α denotes the desorption rate constant. Since Frumkin's equation allows us to discuss dynamic interfacial tension,^{31–33} the time course of $\Delta\gamma_a$ was expressed as follows from eq 3:

$$\Delta\gamma_a(t) = RT\Gamma_0 \ln(1 - \theta(t)) + a\theta(t)^2 + \Delta\gamma_a^e \quad (7)$$

where Γ_0 is an amount of surfactant adsorption at the chemical oscillation, $a = \beta\Gamma_0^2$ and $\Delta\gamma_a^e$ is the equilibrium $\Delta\gamma_a$ measured experimentally. Combining eqs 6 and 7, we fit the relaxation data of $\Delta\gamma_a$ as shown in Figure 5. To fit them, we had to postulate the value of Kc_s , which represents the contribution of molecular adsorption in eq 6. In Figure 6, Kc_s was varied from 0 to 10. The smaller the Kc_s value was, the better the data were fit. The postulation of $Kc_s = 0$ gave the best fitting. This means the contribution from molecular adsorption can be neglected in the relaxation process. Molecular desorption from the interface is recognized as the dominant behavior (Figure 4d). The hindrance of molecular adsorption is due to the absence of a concentration gradient sufficient for molecular adsorption after the oscillation, similar to that of the induction period, because the SDS concentration at the sub-interface was very low due to collective adsorption.

The following parameter values for the model were obtained for $Kc_s = 0$: $\Gamma_0 = 4.13 \times 10^{-11} \text{ mol}/\text{cm}^2$, $\alpha = 1.7 \times 10^3 \text{ s}$, and $a = 0$ (attributable to Langmuir's equation). A simple equation assuming desorption control fit the relaxation data very well ($r^2 = 0.987$); therefore, it was reasonable to assume that molecular desorption was carried out in the relaxation process.

A particularly interesting point is that the time scale of molecular desorption α was exceptionally long. In some

systems,^{31,32} surfactants are desorbed in the form of reversed micelles, and the slow dynamics of relaxation is associated with the formation of reversed micelles. This time scale is, however, at most about 50 s. In the chemical oscillation system observed here, the time scale of desorption was 2 orders of magnitude slower than that. In the present system, SDS concentration at the sub-interface was much lower than the critical micelle concentration (cmc), so that the surfactants were desorbed from the interface after forming ion pairs. This formation of ion-pairs is considered to be the rate-determining step. Thus, the exceptionally slow relaxation of $\Delta\gamma_a$ indicates that hindrance of the counterion-binding process took place at the liquid/liquid interface.

Next we considered the cause of these unusual phenomena, i.e., hindrance of molecular adsorption in the induction period and the extraordinarily slow relaxation. These molecular behaviors suggest the existence of some kind of interfacial barrier effect at liquid/liquid interface. As for the cause for this effect, the contribution of specific solvent structure and/or molecular interactions which are characteristic at liquid/liquid interfaces can be considered. From the viewpoint of a specific structure, hydrophobic hydration of water molecules in the interfacial region adjacent to the hydrophobic phase might contribute to such unusual behavior. Results obtained by SFG techniques have demonstrated a structure and ordering of hydration water at liquid/liquid interfaces.^{1,39–43} For example, weak hydrogen bonding and a strong orientation effect on hydration water were observed at neat $\text{CCl}_4/\text{H}_2\text{O}$ and hydrocarbon/ H_2O interfaces.³⁹ It was also found that the hydrogen-bonding network of hydration water was well ordered, like ice, on a $\text{CCl}_4/\text{water}$ interface with adsorbed charged surfactants.^{1,40–43} In addition, hydrophobic hydration has been known to also occur at surfactant molecules, that is, hydrophobic groups of surfactants were considered to be surrounded by a more extended hydrogen-bonding network.⁴⁴ In each case, the water molecules in the hydration region strongly interacted with the hydrophobic molecules to the extent that the normal hydrogen-bonding network structures were rearranged. In these hydration areas, many physical properties will drastically change on a nanometer scale. We are now investigating the relationships between nonlinear molecular behavior and specific interactions and structures induced by hydrophobic hydration at liquid/liquid interfaces.

After the oscillation, molecular adsorption was not observed again as in the induction period. If the hindrance effect of molecular adsorption reappears and accumulation of the surfactants at the sub-interfacial region occurs again, the continuous injection of SDS should lead the surfactants concentration to the threshold again and this leads to the onset of next chemical oscillation. Figure 6 shows the chemical oscillation caused by continuous SDS injection using a perista pump. This result supports our conclusion that the hindrance of adsorption is renewed after the oscillation and is repeated in a series of successive chemical oscillations. On the other hand, the successive oscillation in Figure 6 is similar to the well-known self-electrical potential and interfacial tension oscillation. Self-oscillation systems are interesting because of their rhythmic repetitious behavior.^{7–14} Therefore, we considered that the hindrance effect which was repetitively induced at the liquid/liquid interface is essential for self-oscillation. Further investigation from the viewpoint of liquid/liquid interfacial molecular behavior of nonlinear oscillation is invaluable to elucidate the rhythmic mechanism observed in a variety of self-oscillation systems.

Conclusion

We investigated the mechanism of a chemical oscillation system from the viewpoint of dynamic interfacial molecular behavior. Simultaneous measurements of interfacial tension ($\Delta\gamma$) by QELS and interfacial electrical potential (ΔV) were carried out so that we could extract and discuss directly the time course of the contribution of the interfacial energy change due to the adsorption and desorption ($\Delta\gamma_a$). No change of $\Delta\gamma_a$ was seen in the induction period and a new, exceptionally slow relaxation was observed. A unique solvent structure due to hydrophobic hydration and/or molecular interaction at the liquid/liquid interface was suggested to be the cause for some barrier-like effect which induced the unusual adsorption and desorption behavior of surfactant molecules at the liquid/liquid interface. However, the mechanism of the barrier-like effect is not yet clear. Further investigation of the dynamic molecular behavior, focusing on specific intermolecular interactions and solvent structure at the liquid/liquid interface will provide molecular-level understanding of this barrier-like effect.

Acknowledgment. We are grateful to Dr. K. Arai and Prof. F. Kusu (Analytical Chemistry Laboratory of Tokyo University of Pharmacy and Life Science) for helpful discussions and suggestions. The present research was supported by the Grant-in-Aids for Scientific Research (B) (No. 12450336) by the Ministry of Education, Science, Sports, and Culture, Japan.

References and Notes

- (1) Miranda, P. B.; Shen, Y. R. *J. Phys. Chem. B* **1999**, *103*, 3292.
- (2) Benjamin, I. *Chem. Rev.* **1996**, *96*, 1449.
- (3) Chang, T. M.; Dang, L. X. *J. Chem. Phys.* **1996**, *104*, 6772.
- (4) Naujok, R. R.; Paul, H. J.; Corn, R. M. *J. Phys. Chem.* **1996**, *100*, 10497.
- (5) Eisenthal, K. B. *Acc. Chem. Res.* **1993**, *26*, 636.
- (6) Dupeyrat, M.; Nakache, E. *Bioelectrochem. Bioenerg.* **1978**, *5*, 134.
- (7) Larter, R. *Chem. Rev.* **1990**, *90*, 355.
- (8) Yoshikawa, K.; Matsubara, Y. *J. Am. Chem. Soc.* **1984**, *106*, 4423.
- (9) Yoshikawa, K.; Matsubara, Y. *J. Am. Chem. Soc.* **1983**, *105*, 5967.
- (10) Yoshikawa, K.; Shoji, M.; Nakata, S.; Maeda, S. *Langmuir* **1988**, *4*, 759.
- (11) Arai, K.; Fukuyama, S.; Kusu, F.; Takamura, K. *Electrochim. Acta* **1995**, *18*, 2913.
- (12) Arai, K. *Bunseki Kagaku* **1996**, *45*, 41.
- (13) Kihara, S.; Suzuki, M.; Maeda, K.; Ogura, K.; Umetani, S.; Matsui, M. *Anal. Chem.* **1986**, *58*, 2954.
- (14) Maeda, K.; Kihara, S.; Suzuki, M.; Matsui, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1995**, *295*, 183.
- (15) Sato, M.; Aoyagi, R. *Electrochim. Acta* **1995**, *40*, 2921.
- (16) Shioi, A.; Sugiura, Y.; Nagaoka, R. *Langmuir* **2000**, *16*, 8383.
- (17) Takahashi, S.; Harata, A.; Kitamori, T.; Sawada, T. *Anal. Sci.* **1991**, *7*, 645 Supplement.
- (18) Takahashi, S.; Harata, A.; Kitamori, T.; Sawada, T. *Bunseki Kagaku* **1991**, *40*, 761.
- (19) Takahashi, S.; Tsuyumoto, I.; Kitamori, T.; Sawada, T. *Electrochim. Acta* **1998**, *44*, 165.
- (20) Zhang, Z.; Tsuyumoto, I.; Takahashi, S.; Kitamori, T.; Sawada, T. *J. Phys. Chem. A* **1997**, *101*, 4163.
- (21) Zhang, Z.; Tsuyumoto, I.; Takahashi, S.; Kitamori, T.; Sawada, T. *J. Phys. Chem. B* **1998**, *102*, 10284.
- (22) Tsuyumoto, I.; Noguchi, N.; Kitamori, T.; Sawada, T. *J. Phys. Chem. B* **1998**, *102*, 2684.
- (23) Uchiyama, Y.; Tsuyumoto, I.; Kitamori, T.; Sawada, T. *J. Phys. Chem. B* **1999**, *103*, 4663.
- (24) Uchiyama, Y.; Tsuyumoto, I.; Fujinami, M.; Sawada, T. *J. Phys. Chem. B* **2000**, *104*, 4699.
- (25) Uchiyama, Y.; Tsuyumoto, I.; Kitamori, T.; Sawada, T. *Langmuir* **2000**, *16*, 6597.
- (26) Löfgren, H.; Neuman, R. D.; Scriven, L. E.; Davis, H. J. *J. Colloid Interface Sci.* **1984**, *98*, 175.
- (27) Hård, S.; Neuman, R. D. *J. Colloid Interface Sci.* **1987**, *115*, 73.
- (28) Lamb, H. *Hydrodynamics*, 6th ed.; Cambridge University Press: London, 1932.
- (29) Vlahovska, P. M.; Danov, K. D.; Mehreteab, A.; Bronze, G. *J. Colloid Interface Sci.* **1997**, *192*, 194.
- (30) Danov, K. D.; Vlahovska, P. M.; Kralchavsky, P. A.; Bronze, G.; Mehreteab, A. *Colloid Surfaces* **1999**, *156*, 389.
- (31) Shioi, A.; Nagaoka, R.; Sugiura, Y. *J. Chem. Eng. Jpn.* **2000**, *33*, 679.
- (32) Dukhin, S. S.; Kretzschmar, G.; Miller, R. *Dynamics of Adsorption at Liquid Interfaces, Theory, Experiments, Application*; Elsevier: Amsterdam, 1995.
- (33) Kralchavsky, P. A.; Danov, K. D.; Broze, G.; Mehreteab, A. *Langmuir* **1999**, *15*, 2351.
- (34) We estimated the detection limit of interfacial concentration Γ from the standard deviation for the QELS technique. In the induction period, $\Delta\gamma_d$ is regarded as zero, then $\Delta\gamma$ is attributed to only $\Delta\gamma_a$, i.e., $\Delta\gamma = \Delta\gamma_a$. Although both terms in eq 3 seem to contribute to the deviation, β included in the second term can be approximately regarded as zero in the case of oil/water interfaces.³⁰ The appropriateness of this assumption is also confirmed by our curve fitting in the relaxation process. Thus, only the first term in eq 3 is considered to be responsible for the deviation. On this assumption, Γ is described as a function of $\Delta\gamma$; $\Gamma = \Gamma_\infty\{1 - \exp(\Delta\gamma/\Gamma_\infty RT)\}$. The standard deviation of $\Delta\gamma$ is calculated as 0.2 mN/m, and Γ_∞ of SDS at liquid/liquid interface with 0.1 M NaCl is estimated as about 4×10^{-10} mol/cm² (Bonfillon, A., et al. *J. Colloid Interface Sci.* **1994**, *168*, 497). Thus, the detection limit of Γ under our experimental conditions is estimated as 8×10^{-12} mol/cm².
- (35) Chu, X. L.; Velarde, M. G. *Physicochem. Hydrodynamics* **1988**, *10*, 727.
- (36) Kovalchuk, V. I.; Kamusewitz, H.; Vollhardt, D.; Kovalchuk, N. *M. Phys. Rev. E* **1999**, *60*, 2029.
- (37) Kovalchuk, N. M.; Kovalchuk, V. I.; Vollhardt, D. *Phys. Rev. E* **2001**, *63*, 1604.
- (38) Kovalchuk, N. M.; Vollhardt, D. *J. Phys. Chem. B* **2000**, *104*, 7987.
- (39) Scatena, L. F.; Brown, M. G.; Richmond, G. L. *Science* **2001**, *292*, 908.
- (40) Gragson, D. E.; McCarty, B. M.; Richmond, G. L. *J. Am. Chem. Soc.* **1997**, *119*, 6144.
- (41) Gragson, D. E.; Richmond, G. L. *J. Phys. Chem. B* **1998**, *102*, 569.
- (42) Gragson, D. E.; Richmond, G. L. *J. Chem. Phys.* **1997**, *107*, 9687.
- (43) Du, Q.; Freysz, E.; Shen, Y. R. *Science* **1994**, *264*, 826.
- (44) Stangret, J.; Gampe, T. *J. Phys. Chem. B* **1999**, *103*, 3778.