The Role of Coexisting Ions in a Chemical Oscillation Induced by Ionic Surfactant Molecules at a Water/Nitrobenzene Interface

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Chemical oscillation induced by ionic surfactant molecules at a water (W)/nitrobenzene (NB) interface is investigated by simultaneous monitoring of electrochemical potential and interfacial tension. The presence of hydrophilic ions in the organic (NB) phase is found to drastically accelerate the relaxation process of electrical potential, indicating that ion exchange critically affects the desorption of ionic surfactant molecules from the interface and the deformation of an electrical double layer at the interface. In addition, two-step relaxation of the electrical potential is found, that provides information on the origin of the electrical potential generated in chemical oscillations. The mechanism for the nonlinear oscillatory behavior of the ionic surfactant molecules at the W/NB interface is considered in terms of the remarkable difference in diffusion speed in the aqueous bulk phase and across the W/NB interface due to the contribution of the water molecules that hydrate the surfactant molecules.

Introduction

The kinetics of oil/surfactant/water systems has attracted much attention for more than three decades in terms of chemical nonlinear phenomena such as autocatalytic kinetics,[1] phase-transfer catalytic reactions,[2] kinetic bistability,[3] and so on. In particular, nonlinear phenomena accompanied by periodic changes of electrochemical potential have been the subject of many research activities since Dupeyrat and Nakache[4] reported on periodic macroscopic movements and generation of electrochemical potential at an oil/water interface in 1978. These authors found such nonlinear behavior at a water/nitrobenzene interface with positively charged cationic surfactants such as hexadecyltrimethylammonium chloride (CTAC) or hexadecyltrimethylammonium bromide (CTAB). They explained the nonlinear behavior on the basis of formation of ion pairs between the positively charged cationic surfactants in the aqueous phase and negatively charged picrate anions derived from 2,4,6-trinitrophenol (picric acid) dissolved in the oil phase. The ion pairs formed at the water/nitrobenzene interface were assumed to be removed from the interface by a phase transfer process, and oscillatory behavior was explained in terms of the Marangoni effect.

Later, Yoshikawa and Matsubara[5] further investigated the above system and proposed a mechanism for the periodic behavior that involved the formation of inverted micelles which suddenly moved to the oil phase after the concentration of adsorbed surfactants reached a critical value. They extended the experiment to a water/oil/water three-phase system in a U-shaped glass tube that gave spontaneous and stable oscillatory

behavior over a long period.[6] In the three-phase system, the presence of alcohol molecules in the aqueous phase was essential to observe periodic behavior and the alcohol concentration in the aqueous phase critically affected the oscillatory behavior. Since then, various characteristics of nonlinear behavior have been investigated and several mechanisms for the nonlinear behavior have been proposed by research groups including ours;[7–15] however, the mechanism at a molecular level has not been clarified yet and no consensus has been achieved. The difficulty in the explanation seems to come from the complexity and diversity of the systems.

Recently, we revisited one of the simplest systems, the water/nitrobenzene−sodium dodecyl sulfate (SDS) two-phase system, where the presence of alcohol molecules is not required.[16] The simultaneous measurement of interfacial tension by a time-resolved quasi elastic laser scattering (QELS) technique revealed unexpected behavior, i.e., surfactants were not adsorbed in an induction period and sudden and corrective adsorption to the interface took place, accompanied by electric potential generation.[16] In contrast, the relaxation of the electric potential was extremely slow (c.a. 1000 s) and its time scale was not explained in terms of ordinary desorption or inverted micelle formation.

In the present paper, we investigated the mechanism of the relaxation process in terms of coexisting ions in the oil phase. We found that the presence of hydrophilic ions in the oil phase drastically accelerates the relaxation of the electrical potential. The simultaneous measurement of the interfacial tension revealed that the desorption of the surfactants is also accelerated, indicating ion exchange between the ionic surfactants and the hydrophilic ions drastically affects the relaxation of chemical oscillation. The mechanism of the nonlinear behavior in the two-phase system without alcohol molecules was considered in terms of hindrance of the adsorption and desorption by the presence of the water molecules that hydrate the surfactant molecules.

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Experimental Section

The principle and apparatus of the time-resolved QELS technique have been reported previously,[16,17] thus only a brief outline is necessary here. When a laser beam is passed through the water/nitrobenzene (W/NB) interface, some part of the incident light is scattered by the capillary wave at the interface. The frequency of the scattered light is shifted to the extent of the frequency of the capillary wave. The scattered light is optically mixed with a local oscillator which has the same frequency as the light source. The mixed light has a beat component and this optical beat signal is detected by a photodiode and the beat frequency spectrum is measured with a digital Fast Fourier Transform (FFT) analyzer (Sony Tektronix Co., model 3056). The beat frequency (i.e. the frequency of the capillary wave) is related to the interfacial tension according to Lamb's equation:

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

where ρ_w and ρ_o are densities of water phase and oil phase, respectively. k is the wavenumber of the capillary wave, and γ is the interfacial tension which is calculated from the equation by using the measured f. The standard deviation of beat frequency data for the W/NB interface is calculated as 0.1 kHz. The accuracy of interfacial tension is estimated as ±0.2 mN/m. Ag/AgCl electrodes equipped with salt bridges containing a concentrated aqueous solution of KCl are immersed in W and NB phases, respectively. The electrical potential of the W phase against the NB phase ΔV is measured with a potentiometer. The W/NB interface is prepared by gently pouring 0.1M LiCl (Wako; special grade) aqueous solution onto NB phase (Kanto Chemical; special grade; 99.5% purity) containing 0.01 M tetra-*n*-butylammonium tetraphenylborate (TBATPB) in a quartz glass cell. Here, LiCl and TBATPB are supporting electrolytes. TBATPB is obtained by mixing tetra-*n*-butylammonium bromide (Kanto Chemical; Cica Regent) and sodium tetraphenylborate (Kanto Chemical; Cica Regent) in water and recrystallizing the precipitate of tetra-*n*-butylammonium tetraphenylborate in the solution. Sodium dodecyl sulfate (SDS) (Kanto Chemical Co., Inc; first grade) solution (10 mM) is injected with a syringe pump (LMS model 210) into the water phase (a point far from the W/NB interface) at 3μL/min. Ultrapure water (from Millipore Milli-Q system) is used for all aqueous sample preparations. All experiments are performed at room temperature (298 K).

Results and Discussion

Figure 1 shows the simultaneous observation of the time course of the electric potential across the interface and the interfacial tension at a chemical oscillation induced at the W/NB interface by successive introduction of SDS into the water phase. Our latest published research had shown that the decrease of the interfacial tension comes from the adsorption of DS$^-$ ions and the abrupt generation of electric potential occurs simultaneously with the sudden and corrective adsorption of the SDS onto the interface.[16] Compared to this former work, we were able to measure a more stable oscillation due to improvement of the electrodes. Under the experimental conditions mentioned above, the absolute value of the electric potential at the peaks was almost constant at about 200 mV. In contrast, the baseline of the electric potential gradually increased. Corresponding to the increase of the electric potential, we also observed a gradual
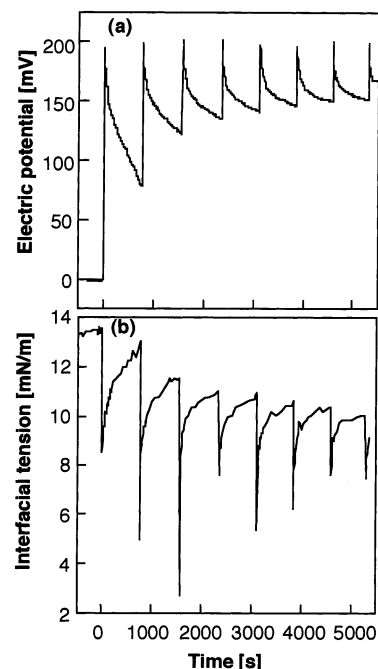

Figure 1. (a) The time course of electric potential. Time 0 indicates the onset of the first oscillation. (b) The simultaneous measurement of the time course of interfacial tension. The value at the onset of each oscillation fluctuated due to the macroscopic wavelike interfacial movements and the subsequent fluctuation of the scattered light. A few tens of seconds after the onset of oscillation, we could measure the interfacial tension correctly again.

decrease of the interfacial tension. Unfortunately, the value of the interfacial tension fluctuated at the time the electrochemical potential was generated and it was not correctly measured due to the flip (sudden straining) motion of the W/NB interface. The gradual increase of the baseline of electric potential and corresponding decrease of interfacial tension indicated that some of the surfactant DS$^-$ ions at the interface remained in the proceeding oscillation phenomenon and accumulation of the DS$^-$ ions at the interface took place. Of interest to us was that though the baseline of the electric potential gradually increased and the interfacial tension decreased correspondingly, the value of the generated electrical potential and periodic time of oscillation remained almost constant. Namely, though the surface coverage of the DS$^-$ ions gradually changed, the periods of the oscillation did not change. In our experimental setup, the inflow speed of the surfactant was always constant. Thus, these features indicated that the conditions for the onset of the oscillation were determined primarily, not by the surface coverage of the surfactant molecules, but by their concentration in the aqueous sub-phase. Under our experimental conditions, the period of the oscillation was about 750 s. This time scale was extremely long in terms of normal molecular desorption (milliseconds) and micelle formation (several tens of seconds at most). This result indicated that some hindrance effect toward the desorption of DS$^-$ ions to the oil phase was at work in our oscillation system, where no external electric fields were applied and no additional molecules that could assist the ion pair formation were present.

Next we investigated the change of relaxation time in the presence of hydrophilic anions in the oil phase that had the same electronic charge as the surfactant molecules. If these anions are present at the interfacial region, we can expect that an ion exchange between them and the charged surfactant molecules would occur and this would accelerate the desorption of the surfactant molecules. Then we measured the chemical oscillation
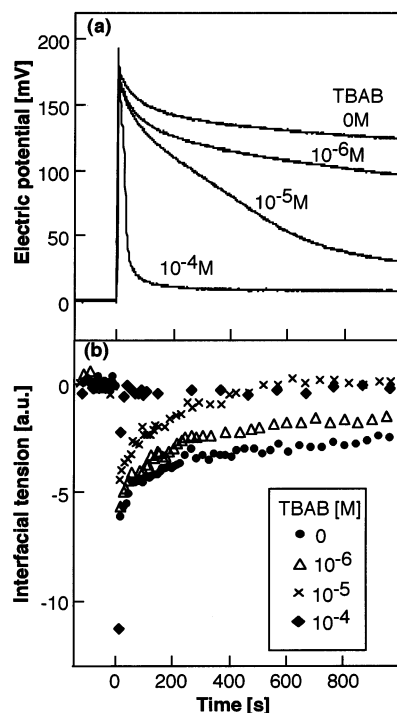
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Figure 2. (a) Time courses of electric potential while varying the concentration of TBAB (●) Free, (△) 10^{-6} M, (×) 10^{-5} M, and (◆) 10^{-4} M. (b) Simultaneous measurements of the time courses of interfacial tension.

Figure 3. The time course of the electric potential at the Br^- concentration 3×10^{-5} M under the condition that only the first oscillation was induced.

Figure 4. Simultaneous measurements of (a) electric potential and (b) interfacial tension at the Br^- concentration 3×10^{-5} M under the condition that only the first oscillation was induced.

in the presence of a small amount of tetra-*n*-butylammonium bromide (TBAB) that dissociates to the water-insoluble cation TBA^+ and hydrophilic anion Br^- in the oil phase. TBA^+ was already present as a supporting electrolyte at 0.01 M, thus we could discuss the effect of the presence of the Br^- ions on the relaxation process. The results are shown in Figure 2. The relaxation time was drastically accelerated when Br^- was added in the oil phase. This result suggested that the ion exchange between DS^- and Br^- critically affected the relaxation dynamics. In addition, it could be considered that the main origin of the electric potential was derived from the electrical double layer formed by DS^- and the counterions Na^+ at the interface. In general, the relaxation process has been considered in terms of the ion pair formation at the interface. Our results demonstrated that the ion exchange could drastically accelerate the relaxation process in a chemical oscillation induced by the charged surfactants. In addition, under an appropriate condition, we could observe two steps in the relaxation of electric potential. Figures 3 and 4 show simultaneous measurements of the time courses of electric potential and interfacial tension when the concentration of TBAB was 3×10^{-5} M. The decrease of electric potential was reaccelerated at around 250 s, where the interfacial tension recovered to the baseline. The recovery of the interfacial tension indicated that there were few surfactant molecules at the interface. Thus, some other factor must also contribute to generation of electrical potential with a long lifetime besides the electrical double layer that was composed of the ionic surfactants (DS^- ions) and the counterions (Na^+) in the water phase. We considered that some of the DS^- ions formed ion pairs with Na^+ in the water phase, while others formed ion pairs with TBA^+ in the oil phase. In the latter case, the remaining counter Na^+ ions in the water phase and supporting electrolyte TPB^- in the oil phase could also form an electric double layer and contribute to the generation of electrical potential. After the formation and desorption of the ion pairs of DS^- and TBA^+ from the interface, the relaxation of the electric double layer
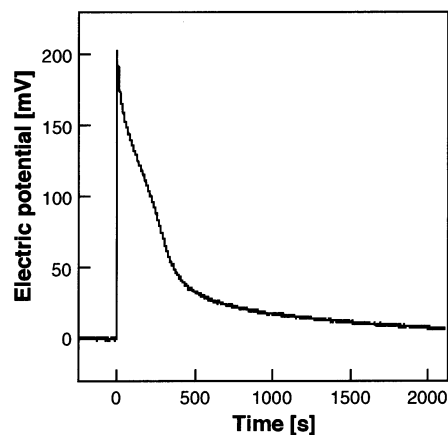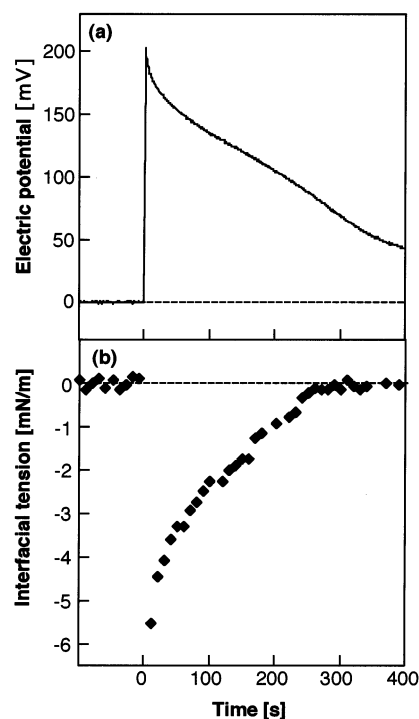
between Na^+ and TPB^- across the W/NB interface was considered to be accelerated and this led to the slow decay of the electrical potential. Since Na^+ and TPB^- favored the water phase and the oil phase, respectively, we considered that this relaxation occurred on a long time scale.

From these observed results, we considered molecular behavior at the onset of the oscillation and the subsequent relaxation process to be as follows. To induce abrupt and corrective adsorption of the surfactants, their diffusion should be very slow at the interface compared to that in the water phase. Namely, accumulation of the surfactants at the sub-interfacial region in the water phase should take place. When a steep gradient of the concentration of surfactant molecules is formed at the interfacial region and the concentration gradient reaches some critical value, chemomechanical transduction is induced, which is part of the Marangoni effect. However, it seems curious to us that the surfactant molecules are not adsorbed on the interface immediately. Why is such an accumulation of the

surfactants induced at the oil/water interface where there are no molecules occupying the adsorption sites at the interface and hindering the adsorption of DS⁻ ions transiently? As another factor hindering the adsorption, we can consider the presence of the water molecules that hydrate charged surfactants. The water molecules are stabilized by the electrostatic interaction between the charged headgroups. When the charged surfactants adsorb onto the oil/water interface and desorb to the oil phase, the surrounding water molecules should be desolvated. In addition, there may also be water molecules in a more tightly hydrogen-bonded network around the hydrophobic alkyl chain. They may also be at the oil/water interface due to the hydrophobic hydration. To adsorb to the oil/water interface, water molecules should also be desolvated and removed. This desolvation process requires excess free energy and considerable time for the charged surfactants to diffuse and adsorb to the interface. If the introduction speed of the surfactants to the interfacial region is considerably larger than the speed of adsorption to the interface, the accumulation of the surfactants at the sub-interfacial region in water phase takes place (Figure 5a). If the concentration of the DS⁻ ion exceeds the critical micelle concentration, the DS⁻ ions form micelles. The formation of the micelles contributes to hindrance of the adsorption of DS⁻ ions because the hydrophobic part of the surfactants is concealed inside the micelles. Thus, the accumulation of the surfactants proceeds further. When the concentration of the surfactants (and micelles) reaches some critical value, chemical energy is transformed to mechanical energy as a result of the instability caused by the drastic difference in the concentration. This abrupt energy conversion is considered to perturb the interface mechanically and to trigger the abrupt and corrective adsorption of the accumulated charged surfactants at the water phase to the W/NB interface. The abrupt adsorption of the charged surfactants (DS⁻ ions) leads to the formation of the electric double layer with the counterions (Na⁺) at the interface that leads to the abrupt generation of electric potential (Figure 5b).

Next we considered the mechanism of the relaxation of the electric potential. The water molecules around the charged headgroups of adsorbed surfactants should be desolvated when the surfactants desorb to the oil phase. In addition, the charged surfactants have to form ion pairs with counterions in order to exist stably in the oil phase. However, there are also water molecules that hydrate around the original counterions in the aqueous phase. Thus, these water molecules also have to be desolvated when the charged surfactants and counterions form ion pairs (Figure 5c). Thus, we considered that this process requires considerable time to proceed (Figure 5d). However, if there are hydrophilic ions which have the same charge as the adsorbed surfactant molecules at the interfacial region, we can consider the desorption of charged surfactant molecules proceeds quickly by an ion exchange mechanism (Figure 5e). This is because formation of the ion pair between the charged surfactant and its counterion is not required in this case. If the ion exchange proceeds, the relaxation of the electric potential due to the deformation of the electric double layer should also take place (Figure 5f).

To examine the ion exchange mechanism for the acceleration in the relaxation process of the chemical oscillation, we varied the kind of hydrophilic anions (Cl⁻, Br⁻, and I⁻) in the oil phase and investigated the dependence of the desorption rate of DS⁻ ions on the standard free energy of transfer of those anions. Since the ion exchange should occur at the oil/water interface, we expected that the more the standard free energy of transfer
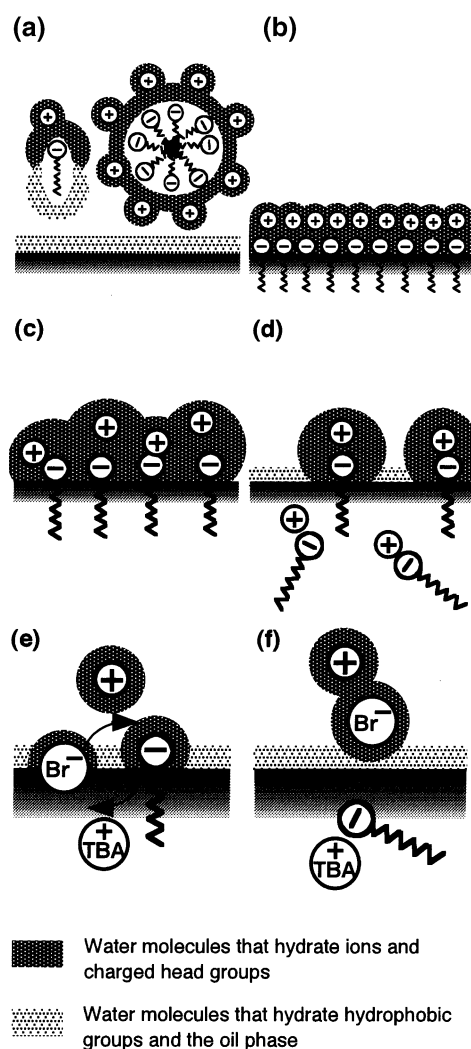

Figure 5. Model for the chemical oscillation induced for the water/nitrobenzene−ionic surfactants (SDS) two-phase system. (a) Accumulation of the surfactant molecules at the sub-interfacial region in aqueous phase. Not only monomers but also micelles are expected to exist at the higher concentration. (b) Sudden and corrective adsorption of the ionic surfactants is induced by the chemomechanical transfer (a kind of Marangoni effect). The electric double layer between the adsorbed ionic surfactants and their counterions (Na⁺) is abruptly formed and this phenomenon can be considered to be the main cause for the generation of the electric potential. (c), (d) Desorption of ionic surfactant molecules without hydrophilic ions (Br⁻) in the oil phase. (c) Formation of ion pairs with counterions in the aqueous phase at the W/NB interface. (d) Desorption of the (surfactant−counterion) ion pairs from the interface to the NB phase. The relaxation of electric potential proceeds by the deformation of the electric double layer due to the desorption of the ion pairs. (e), (f) Desorption of the ionic surfactants (DS⁻) from the interface in the presence of hydrophilic ions (Br⁻) at the interfacial region. It should be noted that the interface should have some region where both nitrobenzene and water molecules are mingled at the molecular level, though they are macroscopically immiscible. (e) The ion exchange between (DS⁻) and Br⁻ takes place quickly at the interfacial region. By the ion exchange, desorption of the DS⁻ ions is accelerated by Br⁻ transferred from the interface to the aqueous phase. (f) Desorbed DS⁻ ion forms an ion pair with TBA⁺ in the oil phase, which was originally the counterion of Br⁻. Depending on the concentration of Br⁻, some of the DS⁻ ions remain at the interface and desorb by the above-mentioned (c) and (d) processes.

of the anions from the interface to the water phase decreases, the more efficiently the ion exchange occurs between the hydrophilic anions and DS⁻ ions, resulting in the acceleration of the desorption of the DS⁻ ions from the interface. When the
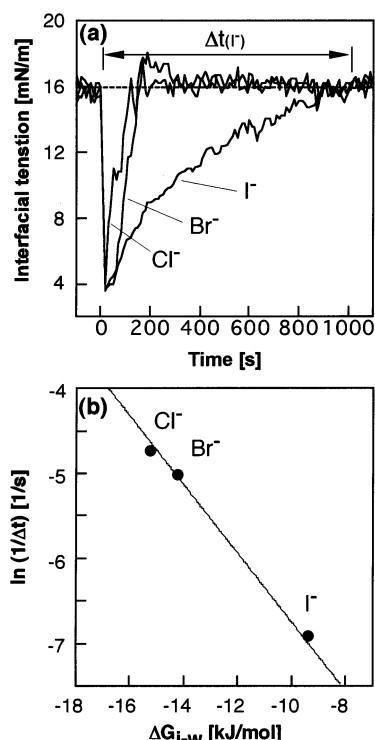
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Figure 6. (a) Time courses of the interfacial tension when hydrophilic anions (Cl^-, Br^-, and I^-) were in the oil phase. The concentration of these anions was 1.0×10^{-4} M. (b) Dependence of the desorption rates ($\ln(1/\Delta t)$) on the standard free energy of ion transfer from the water/nitrobenzene interface to the water phase ($\Delta G_{i-w} = \Delta G_{o-w}/2$). The solid straight line with slope $-1/RT$ (R: gas constant, T: temperature 298 K) was obtained by the least-squares fitting method.

ion exchange occurs at the interface, the decrease of the standard free energy of the anions is the change of free energy of transfer from the interface to the water phase (ΔG_{i-w}). However, it is considered that although water and nitrobenzene are immiscible, the interface between them should have some region where the water molecules and nitrobenzene molecules are mingled at the molecular level. Thus, we roughly estimated the average of the free energy of the anion at the interface (G_i) as the mean value of the free energy of the anion in the water phase (G_w) and that in the oil phase (G_o), namely, $G_i = (G_w + G_o)/2$. Then ΔG_{i-w} value was $G_w - G_i = (G_w - G_o)/2 = \Delta G_{o-w}/2$, where ΔG_{o-w} is the standard free energy of transfer from the oil phase to the water phase. The ΔG_{i-w} ($= \Delta G_{o-w}/2$) values of Cl^-, Br^-, and I^- at the water/nitrobenzene interface were -15.3, -14.3, and -9.4 kJ/mol, respectively, as calculated from the ΔG_{o-w} values obtained by electrochemical measurements.[18] Figure 6a shows the time courses of the interfacial tension when the hydrophilic anions were added into the oil phase. The concentrations of these ions were set at 1.0×10^{-4} M. Here, the desorption rate was determined by $1/\Delta t$, where Δt is the period for the interfacial tension to become the initial value again after the oscillation. Δt values of each ion (Cl^-, Br^-, and I^-) were 110, 150, and 1000 s, respectively. Figure 6b shows the dependence of the desorption rate of the DS^- ions on ΔG_{i-w} of Cl^-, Br^-, and I^- from nitrobenzene to water. We can consider that the desorption rate is proportional to the exponential of $-\Delta G_{i-w}/RT$ (R: gas constant, T: temperature). We plotted the dependence of the log value of the desorption rate ($\ln(1/\Delta t)$) on the standard free energy of transfer from the interface to water phase (ΔG_{i-w}). The solid straight line with the slope $-1/RT$ (R: gas constant, T: 298K) was obtained by the least-squares fitting method. The line fit the experimental results quite well. This result strongly

supported the ion exchange model and we could consider that the ΔG_{i-w} value of the coexisting ions in the oil phase strongly affected the desorption rate, namely, the relaxation process in the chemical oscillation induced by the adsorption of charged surfactants.

Conclusion

Nonlinear oscillation behavior of ionic surfactant molecules (SDS) induced at a water/nitrobenzene interface was investigated by monitoring interfacial tension and electrical potential simultaneously. We focused on the contribution of the coexisting ions in the oil phase to the relaxation process of the chemical oscillation, which affects the nature of successive oscillations, e.g., the oscillation period, duration of the oscillation, and so on. We found that the coexistence of hydrophilic anions in the oil phase accelerated the relaxation process. We considered the mechanism in terms of ion exchange between the hydrophilic anions and adsorbed ionic surfactants at the interface. To examine the ion-exchange model, the dependence of the relaxation rate on the standard free energy of transfer of the anions from the interface to the water phase was investigated and a strong relation between them was observed. It was also found that the relaxation of electrical potential consisted of two decay components, indicating that not only the electrical double layer between the adsorbed DS^- and counter Na^+ ions in the aqueous phase, but also the Na^+ ions in the aqueous phase and TPB^- ions in the oil phase contributed to the generation of electrical potential. Simultaneous measurements of interfacial tension suggested that the electrical double layer consisting of the latter pair lasted longer than the layer formed by the former pair. Ion transfer across the interface between two immiscible liquids and structure at liquid/liquid interfaces is a fundamental and important process.[19−22] Recently, transfer of relatively large ions across the water/nitrobenzene interface has been studied experimentally and theoretically.[23,24] However, little information on the ion transfer of large ionic surfactants across the liquid/liquid interface and the related structural change of this interface is available at the molecular level. Further spectroscopic measurements and theoretical investigations on ion transfer of these oil/surfactants/water systems are expected to provide detailed information on complex molecular behavior in these nonlinear electrochemical systems at the molecular level.

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