1696 *Bull. Chem. Soc. Jpn. Vol. 79, No. 11, 1696–1703 (2006)*

Chemically Driven Tension Fluctuation and Motion of Interface with Divalent Cation and Di(2-ethylhexyl)phosphoric Acid

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Fluctuation in the interfacial tension in an oil/water interface composed of di(2-ethylhexyl)phosphoric acid (DEHPA) and divalent cations (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) were investigated. Only a combination of Ca^{2+} and DEHPA caused noticeable tension fluctuation and spontaneous interfacial flow. Light-scattering experiments and the extraction of cations with DEHPA indicated that both a high reactivity between cation and DEHPA, of which only Ca^{2+} had a high reactivity, and strong attractive interactions between $M(DEHP)_2$ molecules were required for fluctuation. These may induce a collective desorption of $Ca(DEHP)_2$. This was supported by the observation of alternating pH-change with *m*-Cresol Purple. An N-shape dependency of interfacial pressure on the DEHPA concentration was observed only for Ca-containing interface. Due to this dependency, there was a DEHPA concentration range in the interfacial pressure vs the concentration curve, which satisfies two different conditions. First, the dependency of the interfacial pressure on the concentration is negative, and second, there are other two concentrations with the same interfacial pressure value. The DEHPA concentration range involving tension fluctuation almost agreed with the concentration range, which is discussed. The interface may be a chemical generator predicted by Vedove and Sanfeld.

Spontaneous motion of liquids or their interface is one of the simplest systems that can turn chemical energy directly into work. Such liquid motions are driven by the nonlinear dynamics of interfacial properties, such as oscillation of interfacial tensions. Complete understanding of the physical chemistry of nonlinear dynamics may help in the design of chemical systems to obtain work from substances in the environment, which can be utilized for power sources in micro or nano spaces. In particular, the control of nonlinear dynamics by surrounding chemicals is one of the most interesting topics in this field, because it seems to mimic biological functions with a simple system that can be addressed by chemists and chemical engineers. Therefore, nonlinear dynamics with chemical reactions are fascinating from a fundamental point of view.

Interfacial turbulence and tension oscillation or fluctuation in a surfactant-adsorbed oil/water interface have been explained using the Marangoni instability, which is purely a hydrodynamic phenomenon. Since Sterling and Scriven[3] proposed a dimensionless number, called the Marangoni number, many papers have been published on this subject.[4–6] It is widely accepted that the thermal Marangoni effect can be understood simply in terms of hydrodynamics. An infinitesimal fluctuation in the local interfacial tension, which is produced by convective noise etc., develops with hydrodynamic instability. On the other hand, such a well-accepted understanding is not obtained for the interfacial turbulence and tension oscillation or fluctuation with chemical reactions at the interface. Sherwood and Wei studied interfacial turbulence with chemical reaction.[7] Brian and Smith[8] applied Pearson's theory[9] for thermal Marangoni instability to a mass-transfer situation, and their theory can be extended to interface involving chemical reactions.[10–12] In this context, chemical reactions only give a chemical species, the reaction product, at the interface, which changes the local interfacial tension. Then, the evolution of fluctuation in interfacial tension can be described by a combination of hydrodynamic effect and chemical kinetics. However, only the instability that induces macroscopically observable tension oscillation or fluctuation is still a hydrodynamic effect, and chemical or thermodynamic instability does not play an essential part in the nonlinear or oscillatory kinetics.

Since the 1980's, the possibility of another underlying instability has been considered. Although none of them mention common kinetics, chemical or thermodynamic instability is commonly used to explain the nonlinear phenomenon. Dupeyrat and Nakache[13,14] discovered a unique interface composed of cationic surfactant, water, and nitrobenzene, which provides a macroscopic wave at the interface. They studied the interfacial tension and interfacial potential, and they pointed out that, after the adsorption of surfactant, the interface must become surfactant-free again for the next adsorption. They mentioned that the renewal of interface is necessary. Nakache et al. applied this idea to a different interface composed of bis(2-ethylhexyl)hydrogenphosphate (i.e., di(2-ethylhexyl)phosphoric acid), water, and oil.[15] The renewal of the interface is made by interfacial chemical reaction and allows surfactants to be adsorbed onto the interface. Then, the dynamic interfacial tension changes in an oscillatory manner. They do not mention the role of chemical or thermodynamic instability explicitly. However, the renewal of the interface would be impossible without chemical and/or ad/desorption kinetics, because renewal is achieved without the help of convective mass-transfer due to the Marangoni effect. Yoshikawa and

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Published on the web November 9, 2006; doi:10.1246/bcsj.79.1696

Matsubara began mentioning the importance of chemical or thermodynamic instability in the 1980s.[16] Yoshikawa et al. proposed a model to calculate oscillatory changes in the interfacial properties based on the N-shaped instability of the Π–A isotherm,[17] where Π and A denote the interfacial pressure and area, respectively. In actual experiments, the instability is observed as a hysteresis loop of the dynamic Π–A isotherm,[18] which was described in terms of surface elasticity by Lucassen and van den Tempel.[19]

Sanfeld and co-workers[1,2,20] first highlighted the importance of the surface elasticity for the stability of liquid interfaces. They carried out a thorough mathematical treatment of the linear stability analysis of interfacial dynamics, focusing on the effects of chemical and ad/desorption kinetics on interfacial stability. Following Sanfeld et al., a negative value for the surface elasticity is a necessary condition for the instability, and chemical and/or ad/desorption kinetics are possible origins of fluid motion in the interface. In this context, Marangoni instability itself, is necessary for interfacial motion; however, it is regarded as a kind of side-effect of tension oscillations or fluctuations, which are induced by a chemical generator with oscillatory dynamics.[1,2] The N-shape dependency of Π on the area introduced by Yoshikawa et al.[17] includes a negative value of surface elasticity. Thus, we can consider that Yoshikawa et al. calculated an interfacial rhythm on the basis of nonlinear dynamics with negative surface elasticity. Sawada et al.[21,22] measured dynamic interfacial tension of the interface discovered by Nakache and co-workers[13,14] with a non-contact optical technique. They concluded that surfactant molecules are collectively adsorbed onto the oil/water interface when a certain threshold condition is satisfied.[22] This suggests that chemical and/or ad/desorption kinetics play an essential role in the interfacial motion.

Authors have studied the tension fluctuation and spontaneous motion of the oil/water interface composed of di(2-ethylhexyl)phosphoric acid (DEHPA) and calcium chloride, and pointed out that interfacial flow is generated by chemical reaction and ad/desorption of DEHPA and Ca^{2+}.[23,24] We estimated the kinetic energy of interfacial flow based on Brownian dynamics and compared the kinetic energy with the amplitudes of tension fluctuation. Following these results, we suggested that the essential instability is not hydrodynamic, but thermodynamic. However, further investigations are necessary to elucidate the above point. In this work, we investigated the dynamics of oil/water interfaces composed of DEHPA and $M(OH)_2$, where M denotes a divalent cation, such as Mg^{2+}, Ca^{2+}, Sr^{2+}, or Ba^{2+}. A neutralization reaction occurs between DEHPA and $M(OH)_2$. This is advantageous to study the relationship between the chemical reaction and the interfacial dynamics, because the chemical equilibrium can be controlled by the pH of the aqueous phase. Moreover, changing the cation does not strongly alter the hydrodynamic properties of the solutions, such as viscosity and density (buoyancy). The former is important because viscosity is the only parameter in the Marangoni number that dampens the interfacial motion. Buoyancy is also important, since there are cases where interfacial turbulence or convective rolls with the neutralization reaction are generated by the lateral gradient of the buoyancy force, i.e., the Rayleigh–Benard instability.[25] The heat of neutralization reaction is almost independent of the cation species, and hence a lateral gradient of the buoyancy force scarcery depends on the cation species. If the interfacial dynamics strongly depends on cation species, it may be attributed to the chemical nature of the cations and reactive product, $M(DEHP)_2$. We obtained such a strong dependency of interfacial dynamics, and only calcium caused clear tension fluctuation and interfacial motion. Intermolecular interactions between $M(DEHP)_2$ molecules were evaluated by using light scattering, and the interfacial composition of surfactants was estimated based on the equilibrium interfacial tension. The extraction equilibrium of cations was also examined. As a result, we concluded that there are two key parameters for the onset of instability. One is the attractive interaction between $M(DEHP)_2$ molecules, which would be responsible for novel ad/desorption behavior of surfactants. This interaction may generate a negative surface elasticity. Another is the interaction between M^{2+} and HDEHP, where HDEHP is the nondissociated form of DEHPA. This interaction is required to form $M(DEHP)_2$, especially under acidic conditions where tension fluctuation is observed. Only a combination of calcium and DEHPA satisfies the above two conditions simultaneously. The interface may be one of the chemical generators predicted by Vedove and Sanfeld,[1,2] though they did not mention the possibility in their paper of dealing with interfacial dynamics composed of DEHPA and cobalt.[26] The tension fluctuation occurs at every point in the interface, and the timing or phase of the fluctuations was not synchronized over the whole interface. This generates inhomogeneous interfacial tension, which results in spontaneous interfacial flow due to the Marangoni effect.

Experimental

Materials. DEHPA (>98%) was provided by Tokyo Kasei and used without further purifications. Reagent grade of heptane, magnesium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, magnesium chloride, calcium chloride, strontium chloride, barium chloride, sodium chloride, and sodium hydroxide were purchased from Kanto chemical and used without further purification. *m*-Cresol Purple was purchased from Acros and used as received. Fully deionized water (ORGANO PRO 150) was used.

Methods. The dynamic interfacial tension was measured using the Wilhelmy technique as reported elsewhere.[24] A glass container with 52 mm diameter was used. It is already confirmed that the geometry of the container (liquid phases) does not affect the dynamic interfacial tension.[23,24] The dynamic interfacial tension was taken every 0.5 seconds. Interfacial tension under equilibrium was measured using the drop-weight method. The same volumes of organic and aqueous phases were violently stirred for 20 min, and both phases were separated. A syringe with stainless steel needle was connected to a syringe pump that pushes out an aqueous solution with a constant flux of $5.8 \times 10^{-3}\,\mathrm{cm^3\,s^{-1}}$. A growing pendant drop of aqueous solution was made at the tip of the needle, which was immersed in the equilibrated organic phase, and the time required for the detachment of the droplet was measured. Several experiments were performed under the same conditions, and the mean time was determined. The interfacial tension was calculated according to the method of Harkins and Brown.[27] A local fluctuation of pH near the oil/water interface with *m*-Cresol

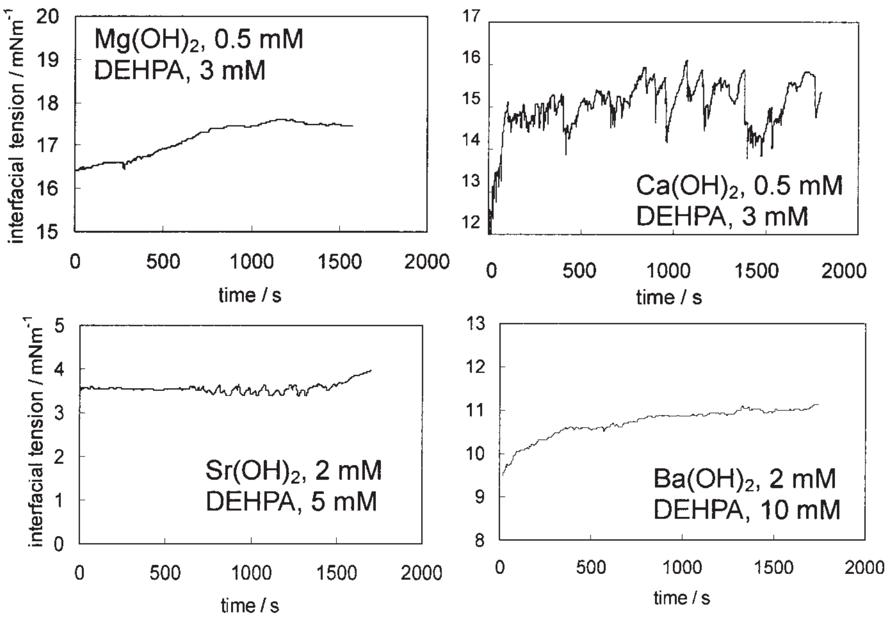

Fig. 1. Dynamic interfacial tension is shown for four kinds of cations. Concentrations of electrolyte and surfactant are shown. Temperature is 25 °C.

Purple was observed. While maintaining the concentration of *m*-Cresol Purple at $1\,g\,L^{-1}$, tension fluctuations in the oil/water interface containing Ca^{2+} were observed.

The extraction of cations with DEHPA was performed. Both aqueous and organic phases were strongly stirred for two hours. The volumes of both phases were equal to each other at $20\,cm^3$. After complete phase separation, the concentration of the cation in the aqueous phase was measured using atomic absorption spectrometry and inductively coupled argon plasma emission spectroscopy.

Static light scattering was used to evaluate the intermolecular interactions between $M(DEHP)_2$, where $M(DEHP)_2$ was a reaction product of cation M and DEHPA. DEHPA was dissolved in heptane, and 5 M sodium chloride was dissolved in water. Both solutions were poured into a glass vial, and sodium hydroxide of the same mole amount as DEHPA was added to it. After mixing the solutions, only the organic phase was taken. Due to the high concentration of NaCl, almost all of the DEHPA remained in the organic phase.[28] The organic phase was stirred with an aqueous solution of metal chloride ($MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$) for twenty minutes. The concentration of the aqueous phase was 2 M for $MgCl_2$, $CaCl_2$, and $SrCl_2$. It was 1.3 M for $BaCl_2$, due to the solubility. After complete phase separation, only the organic phase was taken and stirred again with an aqueous phase involving the same metal chloride. The volume ratio of organic:aqueous phases in this experiment was 1:5. This procedure was repeated five times. The pH of the aqueous phase was kept almost neutral throughout the procedure, and the pH of the final solution was about 7. All of the cations were easily extracted into the organic phase with DEHPA at neutral pH. Due to the concentration of metal chlorides, almost all of DEHPA was converted to $M(DEHP)_2$ in the organic phase. Essentially, the same technique was employed in a previous paper.[29] The organic phase is completely transparent, and thus, the light-scattering intensity of the organic phase was measured as a function of the $M(DEHP)_2$ concentration. The scattering angle was 90 degrees. We evaluated the second virial coefficient from the scattering intensity.

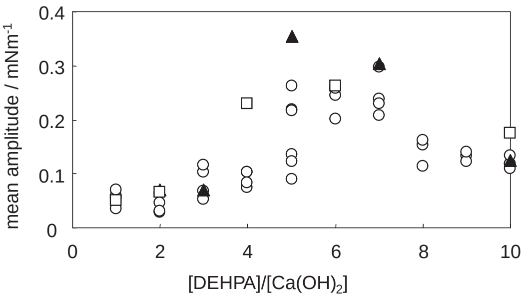

Fig. 2. Mean amplitude is shown against the molar ratio. Concentrations of $Ca(OH)_2$ are 1 mM (○), 0.1 mM (▲), and 0.5 mM (□). Temperature is 25 °C. Tension oscillation appears random, and thus precise determination of the mean amplitude is difficult. We performed the experiments many times for $Ca(OH)_2 = 1\,mM$, and the mean amplitudes are shown.

Results and Discussion

Dynamic Interfacial Tension. Examples of dynamic interfacial tension with oscillatory change, in which calcium chloride was employed as the electrolyte, were reported in a previous paper.[24] Essentially the same results were obtained when calcium hydroxide was used instead of calcium chloride and when other organic solvents, such as toluene and hexane, were used. The amplitude of the fluctuation was calculated as the difference between neighboring local extremes of the time course in interfacial tensions, as shown in Fig. 1. The mean amplitude is shown in Fig. 2. The abscissa is the molar ratio of DEHPA to $Ca(OH)_2$. The mean amplitude increases with an increasing molar ratio and reaches a maximum near a ratio of 4–6, above which the amplitude begins to decrease. We measured the dynamic interfacial tension with other metal hydroxides. Molar ratios from 0.5 to 10 were studied. Examples of the results are shown in Fig. 1. The mean amplitude

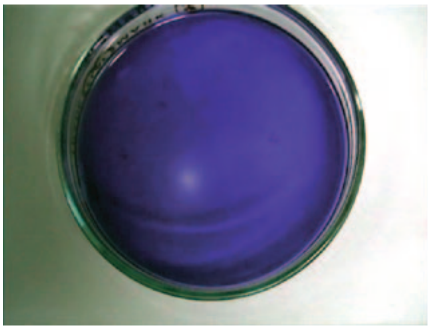

Fig. 3. Color change of aqueous phase with *m*-Cresol Purple. The elapsed time after contact between the organic and aqueous phases is 3.5 s. The most distinct colorless portion exhibits the pH being almost neutral. Purple portion corresponds to pH ≈ 11. The colorless portion appears randomly anywhere in the interface and fades out gradually. Concentrations of $Ca(OH)_2$ and DEHPA are 1 and 5 mM, respectively.

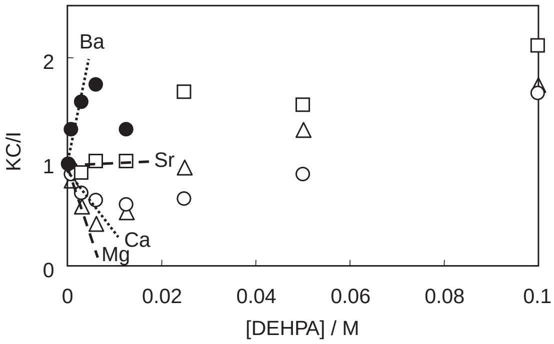

Fig. 4. Dependency of osmotic compressibility on surfactant concentration. Solid lines are drawn so as to correlate each symbol near the intercept with zero concentration. Cation species are shown in the figure. Mg (△), Ca (○), Sr (□), and Ba (●). Temperature is 25 °C.

shown in Fig. 2 is rather small because the fluctuation is comprised of a large number of small amplitudes and a small number of large amplitudes. However, it is clearly shown in Fig. 1 that the behavior of the Ca-containing system is quite different from those of other kinds of cations. Weak tension fluctuation was observed only for the $Sr(OH)_2$ system, but no tension fluctuation was obtained for $Mg(OH)_2$ and $Ba(OH)_2$ systems. As shown in Fig. 2, the dependency of the mean amplitude on the molar ratio is almost independent of the concentration of $Ca(OH)_2$. This indicates that the tension fluctuation is controlled by a single parameter, i.e., the molar ratio.

Figure 3 shows a snap shot of the oil/water system with *m*-Cresol Purple and $Ca(OH)_2$ (see attached movie file). The depths of both phases are 1.5 mm each, and hence, we can see the color of the aqueous phase near the interface. It is purple when the pH is near 10 and weak yellow (almost colorless) for 5–8 of pHs. The pH of the initial aqueous phase is about 11, and thus, the color is purple. When the aqueous phase makes contact with the organic phase containing DEHPA, DEHPA molecules are adsorbed into the interface. Usually, then, the pH near the interface gradually decreases. However, Figure 3 shows quite different characteristics. After pouring the organic phase onto the purple-colored aqueous phase, a weak yellow (almost colorless) portion suddenly appears. Then, the colorless portion expands due to the Marangoni effect and fades out. The colorless portion is acidic or neutral, which indicates that a large number of DEHPA molecules are adsorbed to the interface. This colorless portion appears randomly and successively after the contact of both phases. The alternate change in the color suggests that the adsorbed density of DEHPA or its reaction product, $Ca(DEHP)_2$, changes alternately within the interface. This corresponds to the renewal of the interface, indicated by Nakache et al.[15] When other metal hydroxides were used, the pulse-like change of the color was not observed. Consequently, a collective desorption followed by a collective adsorption of DEHPA is considered to occur in the Ca-containing interface alone. The viscosity and density of the organic and aqueous solutions are almost unchanged by the metal species. This suggests that the reason for the difference is attributed to a chemical or molecular nature, rather than a hydrodynamic one.

Light Scattering and Extraction Equilibrium. Collective adsorption and/or desorption probably reflects a strong attractive interaction between surfactant molecules. Figure 4 shows the ratio C/I against the concentration of $M(DEHP)_2$ in the organic phase, where I and C represent the light scattering intensity and the concentration, respectively. The value of C/I is scaled so that the extrapolation of $C \to 0$ approaches unity. Then, one obtains

$$\mathrm{K}C/I = (1/RT)(\partial\pi/\partial C) = 1 + \mathrm{B}C + \ldots \tag{1}$$

Here, π stands for the osmotic pressure. R and T are the gas constant and temperature, respectively. K is a constant. B represents the second virial coefficient, which is related to intermolecular interaction potential ϕ between $M(DEHP)_2$. However, it is noted that metal salts of DEHPA often form rod-like reverse micelles in oil.[28,29] Then, the second virial coefficient is not equal to the integral of $[\exp(-\phi/k_\mathrm{B}T) - 1]$, where k_B represents the Boltzmann constant. In this case, the negative value of the second virial coefficient indicates the formation of large or long reverse micelles. However, taking into account that the formation of large aggregates is a result of a strong attractive interaction between surfactants, the negative value of the second virial coefficient indicates the presence of an attractive interaction between $M(DEHP)_2$ molecules. The results shown in Fig. 4 indicates that there is a strong attractive interaction between $Mg(DEHP)_2$ molecules and between $Ca(DEHP)_2$ molecules in the organic phase. Formation of long rod-like aggregates for the $Ca(DEHP)_2$ system has been reported.[29] Collective desorption of $Ca(DEHP)_2$ and $Mg(DEHP)_2$ is very likely, but tension fluctuation is not observed for the Mg-containing interface.

The interaction between DEHPA and the cation may play a decisive role, because DEHPA is a well-known chemical for the extraction of metal ions.[26,30] The following reaction scheme can be considered to occur at or near the oil/water interface.

$$\begin{aligned}&(\mathrm{HDEHP}) \rightleftharpoons \mathrm{H}^+ + \mathrm{DEHP}^-\\&\mathrm{M}^{2+} + 2\mathrm{DEHP}^- \rightleftharpoons (\mathrm{M(DEHP)_2})\\&\mathrm{H}^+ + \mathrm{OH}^- \rightleftharpoons \mathrm{H_2O}\end{aligned} \tag{2}$$

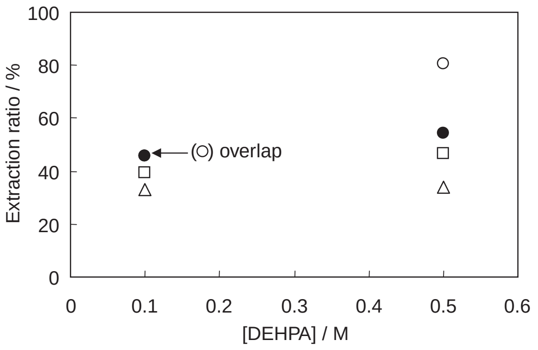

Fig. 5. Extraction ratio of divalent cations by DEHPA. 10 mM solutions of metal chloride were used. Keys are the same as used in Fig. 4. Temperature is 25 °C.

Here, HEDHP and $DEHP^-$ are the nondissociated and proton-free forms of DEHPA, respectively. The parentheses mean that the species is dissolved in the organic phase. The extraction of cations by DEHPA has been fully investigated. However, each study determines the extraction equilibrium and kinetics from the viewpoint of a unit operation. In this work, experiments were performed in association with the tension fluctuation, and thus, the experiments are new carried out.

Figure 5 shows the extraction ratio E, defined by $1 - [M^{2+}]/[M^{2+}]_0$, where $[M^{2+}]$ and $[M^{2+}]_0$ denote cation concentrations under equilibrium and under the initial state, respectively. The extraction ratio was insensitive to the cation species when metal hydroxides were used. For the metal chloride system, however, the cation species strongly influenced the extraction ratio. The difference between the hydroxides and the chlorides is attributed to the difference in pH values. When the aqueous phase is more acidic, the dependency of the extraction ratio on the cation species is stronger. This is shown in Fig. 5, where metal chloride is used. The result shows that the extraction ratio of magnesium is much lower than that of calcium. The degree of dissociation of HDEHP is large when the aqueous phase is basic. See Eq. 2. Then, electrostatic interaction between $DEHP^-$ and M^{2+} takes a major part in the interaction to form $M(DEHP)_2$, which is oil-soluble, and thus, the dependency of the extraction ratio on the cation species is very weak at higher pH. However, the extent of HDEHP dissociation is smaller when the aqueous phase is acidic. In this case, a direct interaction between HDEHP and M^{2+} must take part in the interaction to form $M(DEHP)_2$. The low extraction ratio for magnesium in acidic conditions suggests that the direct interaction is the weakest for magnesium. It can be concluded that the weak interaction between Mg^{2+} and HDEHP is responsible for the no tension fluctuation of the Mg-containing interface. Thus, calcium must have two important properties: a strong attractive interaction between $Ca(DEHP)_2$ molecules and a strong direct interaction between Ca^{2+} and HDEHP.

Equilibrium Interfacial Tension. In a previous paper, the authors reported equilibrium interfacial tension between $CaCl_2$-containing aqueous and DEHPA-containing organic phases.[23] There was a DEHPA concentration range where the interfacial tension increases with an increase in the DEHPA concentration. This concentration range approximately agrees with that where the tension fluctuation is observed under the non-equilibrium state. Thus, the increase in interfacial tension is closely related to the tension fluctuation. However, the relationship was not discussed in detail. In the present study, the pH of the aqueous phase decreases with an increase in DEHPA concentration, which controls the chemical equilibrium shown in Eq. 2.

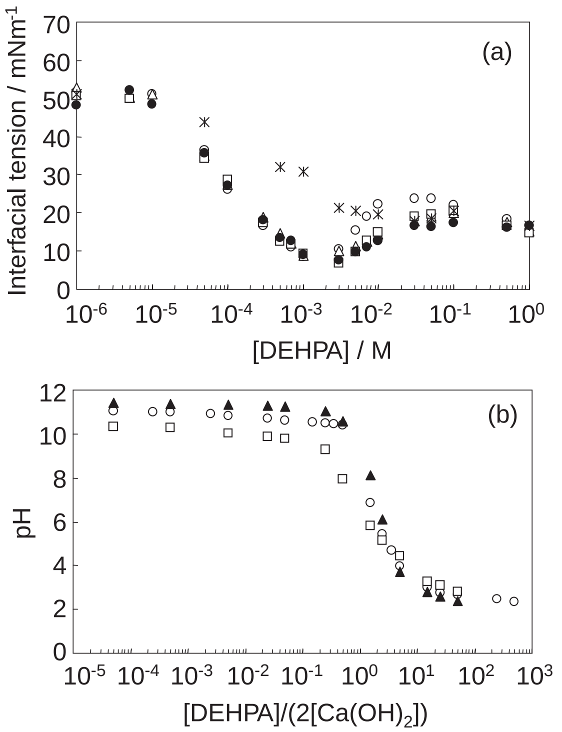

Fig. 6. Equilibrium interfacial tension is shown against DEHPA concentrations. Keys are the same as used in Fig. 4. Data with * are for the system with NaOH. Concentration of metal hydroxide is 1 mM for divalent cations and 2 mM for NaOH. (b) Variation of pH with respect to the molar ratio. Concentrations of $Ca(OH)_2$ are 1 mM (○), 2 mM (▲), and 0.5 mM (□). Temperature is 25 °C.

Figure 6a shows the equilibrium interfacial tension versus the concentration of DEHPA. Data are shown for five different aqueous phases: 2 mM-NaOH, 1 mM-$M(OH)_2$ where M denotes Mg, Ca, Sr, or Ba. Though the solubility of $Mg(OH)_2$ in water is less than 1 mM, it can be dissolved in the aqueous phase that is in contact with DEHPA-containing organic phase. When the DEHPA concentration increases above 2 mM, i.e., the neutralization point, the interfacial tension begins to increase in the $M(OH)_2$ system. One of the reasons for this increase is attributed to the change in pH of the aqueous phase. Figure 6b shows the pH versus the molar ratio [DEHPA]/(2[$Ca(OH)_2$]). The interfacial tension begins to increase at the inflection point of the curve correlating pH and the molar ratio. When the aqueous phase is acidic, the degree of dissociation of HDEHP to $DEHP^-$ and H^+ is low. Since the head group of HDEHP is not ionized, the interfacial tension at lower pH becomes larger. However, taking into account that the interfacial tensions with $M(OH)_2$ differ from that with NaOH, the pH is not the only reason for the increase.

The interfacial pressure, $\Pi = \gamma_{O/W} - \gamma$, is shown in Fig. 7,

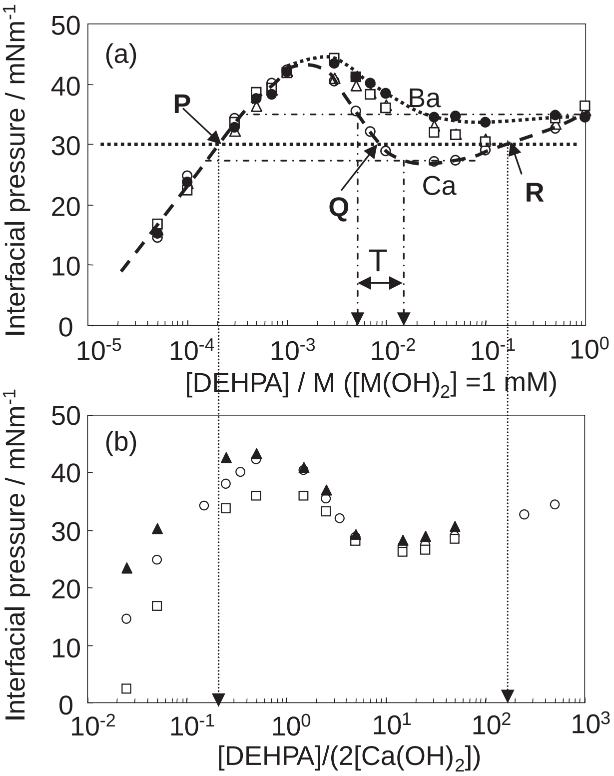

Fig. 7. Π versus DEHPA concentration (a) and the molar ratio (b). Keys are the same as Figs. 4 for (a) and 2 for (b). Dotted line in (a) represents $\Pi = 30\,\text{mN m}^{-1}$. It crosses over the dashed curve at three different points, P, Q, and R. Horizontal line with three different crossing points cannot be drawn for the dotted curve of the Ba system. DEHPA concentration range denoted as T is for a negative dependency of the pressure curve and with a horizontal line crossing over the pressure curve at three different points. Temperature is 25 °C.

where γ and $\gamma_{\mathrm{O/W}}$ represent the interfacial tensions with and without surfactant, respectively. Π increases with an increase in DEHPA concentration below 1 mM, where Π is independent of the cation species. However, Π decreases beyond 1 mM. In this region, Π of the Ca^{2+}-containing interface is lower than that with other cations. These low values of Π are independent of $Ca(OH)_2$ concentrations and controlled by the molar ratio $[DEHPA]/(2[Ca(OH)_2])$, as shown in Fig. 7b. This implies that the Π is governed, not by the ionic strength of the bulk phase, but by the molar ratio of HDEHP, $DEHP^-$, and $Ca(DEHP)_2$ in the interface. Electrostatic screening due to cations is not the major reason for the reduction in Π, because the screening effect is mostly independent of the cation species, but is dependent on $Ca(OH)_2$ concentrations. However, experimental results show that Π depends not on the concentration, but on the cation species.

The low Π for calcium indicates that the attractive interaction between adsorbed molecules is strong for Ca^{2+}-containing interface compared to the other cations in the range of $1 < [DEHPA]/(2[Ca(OH)_2]) < 100$. The attractive interaction reduces Π. This is consistent with the result of the light-scattering experiment shown in Fig. 4.

Kurumada et al.[29] showed that $Ca(DEHP)_2$ molecules form

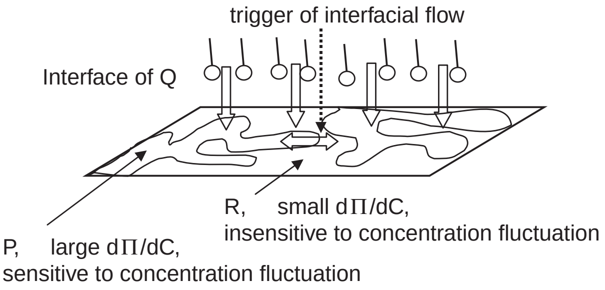

Fig. 8. Schematic representation of interface corresponding to point Q. Adsorption and desorption of DEHPA continue under nonequilibrium, which causes inhomogeneous growth of interfacial pressures.

rod-like reverse micelles with large aggregation number in organic phase. We can consider that a certain aggregation of $Ca(DEHP)_2$ molecules in the interface is responsible for the collective desorption of the aggregates, which leads to the formation of rod-like reverse micelles. For the Mg^{2+}-containing interface, however, the results of both Π and light scattering appear inconsistent. The adsorption density of $Mg(DEHP)_2$ at the interface may be very low due to the weak reactivity between Mg^{2+} and HDEHP.

There is a N-shaped dependency of Π on the DEHPA concentration in the Ca-containing system. If $\Pi = 30\,\text{mN m}^{-1}$, for example, a horizontal line crosses over the pressure curve at three points, P, Q, and R. As shown in Fig. 2, outstanding tension fluctuation is observed when the molar ratio is in the range $4 < [DEHPA]/[Ca(OH)_2] < 8$. The range of the DEHPA concentration, which is $5 < [DEHPA]/[Ca(OH)_2] < 15$, where a horizontal line can be drawn that crosses the pressure–concentration curve at three different points, is shown by T in Fig. 7a. Taking into account the experimental accuracy, both ranges agree closely with each other. For P and R, Π increases with the increase in the DEHPA concentration. This is quite usual. For point P, $DEHP^-$ and $Ca(DEHP)_2$ are the major species at the interface since the aqueous phase is basic. At point R, HDEHP and $Ca(DEHP)_2$ are dominant at the interface because the aqueous phase is acidic. At point Q, however, Π decreases with increasing DEHPA concentration. The interface at point Q contains comparable amounts of $DEHP^-$, $Ca(DEHP)_2$, and HDEHP. At point Q, HDEHP replaces $DEHP^-$ with an increase in DEHPA concentration, and $Ca(DEHP)_2$ molecules are always present. In this state, $DEHP^-$ and $Ca(DEHP)_2$ may form microdomains with the adsorption density being equal to that of point P. At the same time, HDEHP and the rest of $Ca(DEHP)_2$ molecules may gather in another microdomain with an adsorption density being equal to that of point R. The physical image is shown schematically in Fig. 8. It is well known that such a microphase separation is observed at the liquid surface.[31,32] The interface begins to form two kinds of microdomains, P and R, under nonequilibrium. When DEHPA molecules come to the interface, Π of both microdomains fluctuate. The dependency of Π on the fluctuation of the DEHPA concentration in the adjacent bulk phase is highly sensitive at point P, but it is insensitive at point R. This can be accepted because the derivative of Π with respect to the DEHPA concentration is much larger at point P than that at point R. Thus, the flux of DEHPA molecules generates lateral gradient in Π. If the lateral gradient exceeds a certain threshold, it can be a trigger for the evolution of an interfacial flow. Figures 6b and 7b show that the pH values of aqueous phases adjacent to interfaces P and R are about 10 and 2, respectively. Thus, this type of spontaneous flow must accompany the variation in pH, which agrees with the result shown in Fig. 3.

Spontaneous flow of the present system is repeated randomly in the interface, and the single flow is pulse-like. If the essential instability is caused by a hydrodynamic effect, convective rolls often appear.[4–6] This often gives some regulated pattern in the tension oscillation or fluctuation and in the interfacial flow, e.g., Rayleigh–Benard or Benard–Marangoni patterns in shallow liquid or ordered plumes in oil/water interface with the neutralization reaction.[25] However, the present discussion leads to pulse-like behavior in the interfacial flow. This agrees well with the present experimental results.

A mathematical model[33] was proposed that indicates that the surfactant-adsorbed interface with thermodynamic instability exhibits oscillatory change in the adsorbed density when an appropriate ad/desorption rate equation is assumed. This can be regarded as a crude model for an oil/water interface composed of Ca^{2+} and DEHPA.

Microphase separation will result in a collective desorption of surfactants. $Ca(DEHP)_2$ molecules can form rod-like reverse micelles in the organic phase.[29] This may support the assumption of microphase separation. However, the formation of molecular assemblies does not always lead to oscillatory or nonlinear dynamics at an interface. Although sodium bis(2-ethylhexyl)hydrogenphosphate (NaDEHP) is a typical surfactant forming reverse micelles,[28] an NaDEHP-adsorbed interface does not exhibit tension fluctuation. It would be difficult to explain the nonlinear dynamics only on the basis of formation of the molecular assemblies and their related kinetics. It is also difficult to understand the nonlinear dynamics in terms of the diffusion rates, because they are almost independent of the cation species.

The N-shape dependency of Π may result in the formation of a hysteresis loop in the dynamic Π–A (area) isotherm, which was suggested by Makino and Yoshikawa.[18] It would be interesting to measure the dynamic behavior for the present system, although a rather complicated interpretation would be inevitable due to the presence of ad/desorption.

Conclusion

Fluctuation in interfacial tension and spontaneous interfacial flow were investigated for oil/water interfaces containing divalent cations (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) and DEHPA. Only the Ca^{2+}-containing interface exhibited a clear tension fluctuation, which is accompanied by a periodic change in the local pH of the aqueous phase near the interface. We investigated the molecular interaction between $M(DEHP)_2$ molecules by using light scattering and extracted M^{2+} with DEHPA. Here, M denotes the cation species. The attractive interaction between $M(DEHP)_2$ molecules was strong for Ca^{2+} and Mg^{2+} systems. An extraction experiment showed that the reactivity between DEHPA and Mg^{2+} was weak, especially in acidic conditions. Thus, it was concluded that strong attractive interactions and strong reactivity over a wide range of pHs are required for tension fluctuation and spontaneous interfacial flow. From measurement of Π, strong attractive interaction due to the presence of $Ca(DEHP)_2$ operated at the surfactant-coated oil/water interface. This attractive interaction reduced Π of the Ca^{2+}-containing interface, which gave an N-shaped curve in the relationship between Π and DEHPA concentration. Tension fluctuation was evident in the DEHPA concentration range where three different interfacial compositions can have the same Π. In the unstable region, microphase separation of the surfactant-adsorbed interface is possible. One domain mainly included HDEHP and $Ca(DEHP)_2$, and the other was composed of $DEHP^-$ and $Ca(DEHP)_2$. The derivative of Π with respect to the DEHPA concentration is quite different between both domains. This meant that the sensitivity of Π with respect to the fluctuation of DEHPA concentration was also different between both domains. In a nonequilibrium state, DEHPA molecules came to the interface to be adsorbed. Due to the different sensitivities, inhomogeneity in Π spontaneously grew at the interface. This was a trigger of the following evolution of macroscopic interfacial flow due to the Marangoni effect. This mechanism predicted oscillatory change in the pH near the oil/water interface, which agreed with the experimental observation with *m*-Cresol Purple. Until now, there have been two possibilities suggested for the tension fluctuation and spontaneous interfacial flow. One was a purely hydrodynamic phenomenon, Marangoni instability. Another was that a certain nonlinearity included in the chemical reaction and/or ad/desorption kinetics was associated with the onset of instability. Viscosity and density, which were key parameters in hydrodynamics, were not strongly affected by the change in cation species from Ca^{2+} to other divalent cations. Therefore, we considered that the physicochemical properties at the molecular level govern the onset of instability. Attractive interaction due to the presence of $Ca(DEHP)_2$ and the high reactivity between HDEHP and Ca^{2+} over a wide range of pHs affected the physicochemical properties.

We gratefully acknowledge the financial support from a Grant-in-Aid for Scientific Research (C) (No. 15560649), Ministry of Education, Culture, Sports, Science and Technology, Japan.

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