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Transfer Mechanism of Dodecyl Sulfate with Methylene Blue across an Oil/Water Interface Studied by Single-Droplet Injection and Microabsorption Methods

Katsumi Chikama,* Takayuki Negishi,† and Kiyoharu Nakatani*,†

Analysis Research Department, Chemical Research Laboratories, Nissan Chemical Industries, Ltd.,
Funabashi 274-8507

†Department of Chemistry, University of Tsukuba, Tsukuba 305-8571

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The ion-pair extraction mechanism in a dodecyl sodium sulfate (Na^+DS^-)/Methylene Blue (MB^+Cl^-) system was kinetically investigated by single microdroplet techniques. A single tributyl phosphate microdroplet was injected into an aqueous solution and the extraction rate of MB^+ by DS^- into the single droplet was measured with time using a microabsorption method. The MB^+ concentration in the droplet at the extraction equilibrium was independent of the pH in water, while the extraction rate was highly influenced by the pH. The characteristic pH dependence of the MB^+/DS^- extraction was considered in terms of the mass transfer of MB^+, DS^- and H^+ as individual ions across the oil/water interface.

A study of mass transfer (MT) across an oil/water interface is very important for a fundamental understanding of liquid/liquid extraction and chemical reactions in oil/water and water/oil emulsion systems. MT processes across an oil/water interface are governed by diffusion in the oil and water phases, ion-pair formation, complexation, permeation and adsorption/desorption at the interface, and so forth. In particular, the chemical and physical processes at an oil/water interface play important roles in the overall MT rate. Ion-pair extraction is one of the liquid/liquid extraction techniques. As a typical ion-pair extraction, an anionic surfactant in water is extracted into an oil phase with a cationic dye, such as Methylene Blue. The surfactant concentration in water is then determined as the dye concentration in the oil or water phase using a conventional absorption method. In general, an anionic surfactant dissociates in water, dependent on the pH. Therefore, the pH dependence of the ion-pair extraction is indispensable for separating a surfactant dissolved in water. For ion-pair extraction, quantitative analytical and thermodynamic studies have already been reported.[1,2]

A kinetic analysis of ion-pair extraction across an oil/water interface is very difficult, and has been rarely reported. Ion-transfer processes have been successfully investigated by electrochemical and spectroscopic methods using polarized oil/water interface techniques.[3–9] However, because the MT of an ion pair occurs as a neutral species while constructing an oil/water interface, a kinetic analysis of ion-pair extraction will not be demonstrated by stationary oil/water systems with a mm-sized interface. Several efforts have been devoted to direct kinetic analyses of the MT of a neutral species.[10–20] Using high-speed stirring or mixing methods, the MT processes of a neutral species across an oil/water interface were investigated in a large number of microdroplets in water. The technique is based on efficient MT across the oil droplet/water interfaces for smaller droplets because the interfacial area/volume ratio of a droplet increases with decreasing droplet size. However, the transfer mechanism can not be understood in detail since various-sized oil droplets exist in the system. To analyze interfacial MT processes, such as ion-pair extraction in a microdroplet system, single-droplet measurements are absolutely necessary.

We analyzed the electrochemically induced MT of neutral redox species across an oil droplet/water interface using single microdroplet manipulation and electrochemical methods.[18–20] Although adsorption/desorption and extraction processes of the solutes could be analyzed in detail by the single microdroplet technique, the MT measurements were limited for a redox species by the technique. Recently, on the other hand, we developed a microabsorption technique combined with microcapillary manipulation and injection methods.[21,22] Therefore, the interfacial MT of a dye can be measured as the time dependence of an absorption spectrum after the injection of an oil droplet into an aqueous dye solution. In the present study, the ion-pair extraction of a dodecyl sulfate anion with Methylene Blue as a typical extraction system was demonstrated using microcapillary-manipulation/injection and microabsorption methods. The ion-pair extraction mechanism was considered based on the pH dependence of the extraction rate.

Experimental

Tributyl phosphate (TBP; Tokyo Kasei Kogyo Co., Ltd., GR grade) was purified by vacuum distillation after successively washing with an aqueous sodium hydroxide solution and water. Water was deionized after distillation (Milli-RX 12α, Millipore Inc.). Methylene Blue (MB^+Cl^-; Tokyo Kasei Kogyo Co., Ltd., GR grade), dodecyl sodium sulfate (Na^+DS^-; Tokyo Kasei Kogyo Co., Ltd., GR grade), hydrochloric acid (Tokyo Kasei Kogyo Co.,

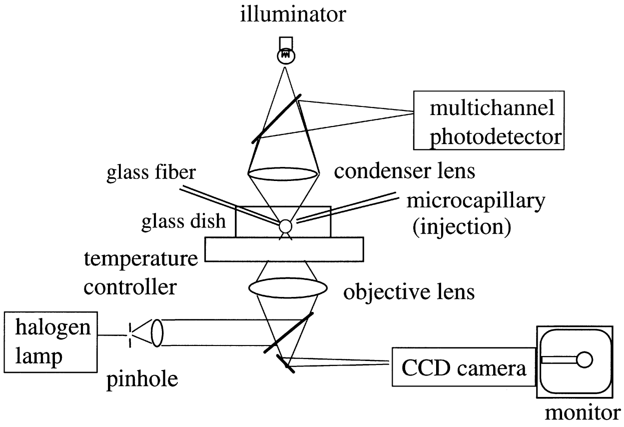

Fig. 1. Block diagram of microcapillary-manipulation/injection and microabsorption methods.

Ltd., ER grade) and sodium chloride (Wako Pure Chemical Industries, Ltd., GR grade) were used without further purification. TBP-saturated water containing MB^+Cl^- (1×10^{-5} M, 1 M = 1 mol/dm^3) and Na^+DS^- (5×10^{-5} M) and water-saturated TBP were used as the water and oil phases, respectively. The pH and ionic strength of the water phase were adjusted by hydrochloric acid and sodium chloride.

The extraction of MB^+ from water into a single TBP droplet was measured using microcapillary-manipulation/injection and microabsorption methods (Fig. 1). A water phase (2.5 cm^3) was poured into a glass dish on a stage of an optical microscope (IX-70, Olympus Co.). A single TBP droplet (radius; r_d = 30–60 μm) was injected into the water phase through a microcapillary with a tip diameter of ~20 μm using a microcapillary manipulation/injection system (MN-151, MMW-200/IM-16, Narishige Co., Ltd.), and was contacted on a glass fiber (~20 μm in diameter). The microabsorption technique for single microparticles has been reported elsewhere.[21,22] Briefly, a probe beam from a halogen lamp (PHL-150, Mejiro Precision Co.) was introduced into the microscope through an objective lens (× 60) and focused onto a single droplet (spot size; 2–3 μm). The transmitted light intensity that passed through the droplet center was collected by a condenser lens and detected by a multichannel photodetector (PMA11, C7473-36, Hamamatsu Photonics Co.). The incident light intensity near the droplet was used as a reference to record the absorption spectrum. All measurements were performed at 295 K using a temperature controller (MD-10RF-O, Kitazato Supply Co., Ltd.).

The distribution of DS^- between TBP and the water phases was determined as the amount of sulfur in the TBP. Aqueous Na^+DS^- (5×10^{-5} M, 50 cm^3) and TBP (3 cm^3) solutions were vigorously stirred. After the emulsion was separated into two phases, 0.1 g of TBP was put into a quartz cell and burned at 1223 K (QF-02, Mitsubishi Chemical Co.). The generated gas was collected in an alkaline buffer solution (2×10^{-3} M Na_2CO_3/2×10^{-3} M $NaHCO_3$) and the sulfate ions dissolved in the alkaline solution were measured by ion chromatography (DX-500, Dionex Co.).

Results and Discussion

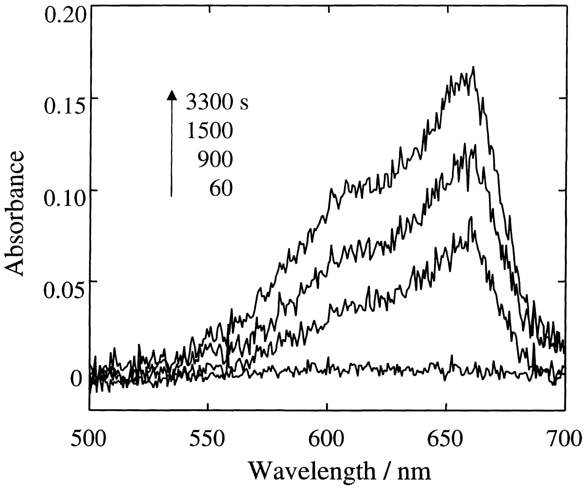

Fig. 2. Time dependence of the absorption spectrum of MB^+ in a single TBP droplet after injection of the droplet into an aqueous MB^+ and DS^- solution (r_d =39 μm, pH = 2).

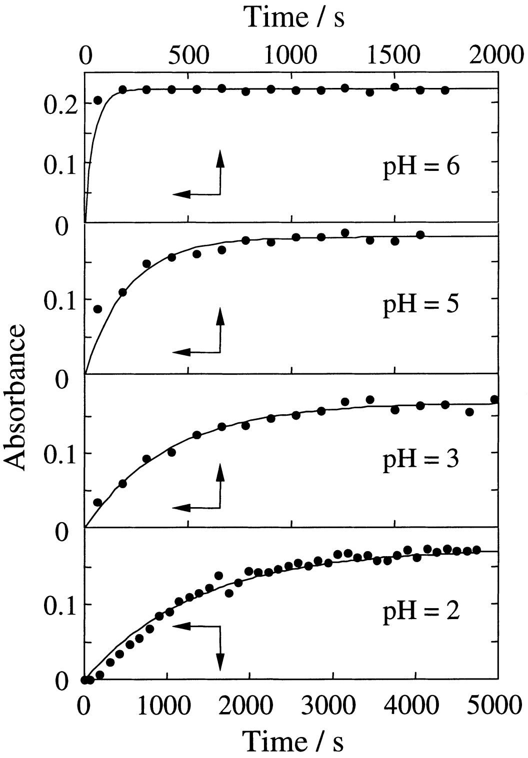

Fig. 3. pH dependence of the extraction rate of MB^+ in the presence of DS^- from water into single TBP droplets (r_d ~ 40 μm). The solid curves represent the calculation by Eq. 2.

Single-Droplet Measurements of Ion-Pair Extraction. The absorption spectra of a single TBP droplet (r_d = 39 μm) after the injection of a single droplet into an aqueous solution are shown in Fig. 2. The shape of the absorption spectrum was the same as that of a dilute TBP solution of MB^+DS^-, and did not change during the extraction processes. The absorbance of MB^+ increased with increasing extraction time (t). Since MB^+ was not extracted into a TBP droplet without Na^+DS^-, the extraction of MB^+ proceeded with DS^- as an ion pair.

Fig. 3 shows the t dependence of the absorbance at 660 nm of MB^+ ($A(t)$) extracted into single droplets with r_d ~ 40 μm at various pH in the water phase. The extraction rate significantly depended on the pH. As the pH decreased, the time required for the extraction equilibrium drastically increased. Because the saturated absorbance had analogous values at pH = 2–6, the MB^+ concentration in TBP ($[MB^+(TBP)]_{eq}$) at the extraction equilibrium was independent of the pH in the water phase. In the present system, the numbers of MB^+ and DS^- molecules extracted into the droplet were much smaller than those in the water phase because of the small volume ratio of the single droplet (3×10^{-7} cm^3) to the water phase (2.5 cm^3). Therefore, the MB^+ ($[MB^+(w)]_{eq}$) and DS^- ($[DS^-(w)]_{eq}$) concentrations in the water phase at the extraction equilibrium can be assumed to be equal to those before the extraction of the solutes. The partitioning ratio of MB^+, P_{MB} (= $[MB^+(TBP)]_{eq}/[MB^+(w)]_{eq}$), was determined to be ~40 in single-droplet measurements. The liquid/liquid extraction of an anionic surfactant with MB^+ as an ion pair is frequently used as a quantitative analytical method for surfactants in water at various pH values.[1,2] It is noteworthy that the pH in the water phase significantly influences the extraction rate of MB^+ with DS^-.

Determination of the Ion-Pair Extraction Rate. The extraction processes are expected to be governed by the diffusion of the solutes in the water and TBP phases and the MT at the droplet/water interface. In the single microdroplet/water system, the diffusion time (t_{dif}) from the droplet/water interface to the droplet interior was determined to be 1.6 s, using $r_d = (2D_o t_{dif})^{1/2}$ (D_o; diffusion coefficient of the solute in TBP, 5×10^{-6} cm^2/s as a typical value). Furthermore, the MT rate from the bulk water phase to the droplet surface is fast due to spherical diffusion of the solute, and is estimated to be 1.3×10^{-3} cm/s using $k_{dif} = D_w/r_d$, where k_{dif} and D_w are the diffusion-limited MT rate constant from water to the droplet surface and the diffusion coefficient of the solute in water (~5×10^{-6} cm^2/s), respectively.[19] The time scale in the absorption spectrum measurements of the single microdroplets is much longer than the MT rates in both phases. Therefore, $A(t)$ is expected to be ascribed to the MT at the droplet/water interface. In actual ion-pair extraction, the extraction processes of MB^+ with DS^- consist of ion transfers of MB^+ and DS^- across the droplet/water interface, the ion-pair formation in the both phases, the adsorption of DS^- at the droplet/water interface, and so forth. As a first approximation, we analyzed the observed extraction rate as the overall MT of MB^+ at the droplet/water interface. The time dependence of the MB^+ concentration in the microdroplet ($[MB^+(TBP)]$) is given by

$$d[MB^+(TBP)]/dt = (A/V)(k_1[MB^+(w)]_s - k_{-1}[MB^+(TBP)]), \quad (1)$$

where k_1 and k_{-1} are the apparent interfacial MT rate constants from water into the droplet and from the droplet into water, respectively. A and V are the surface area ($4\pi r_d^2$) and the volume ($(4/3)\,\pi r_d^3$) of the droplet, respectively. The MB^+ concentration in the vicinity of the droplet surface in water ($[MB^+(w)]_s$) is assumed to be equal to $[MB^+(w)]_{eq}$ due to the efficient MT from water to the droplet, as discussed above. Using $P_{MB} = [MB^+(TBP)]_{eq}/[MB^+(w)]_{eq} = k_1/k_{-1}$, we obtain

$$[MB^+(TBP)] = [MB^+(TBP)]_{eq}[1 - \exp\{-(3k_1/r_d P_{MB})t\}]. \quad (2)$$

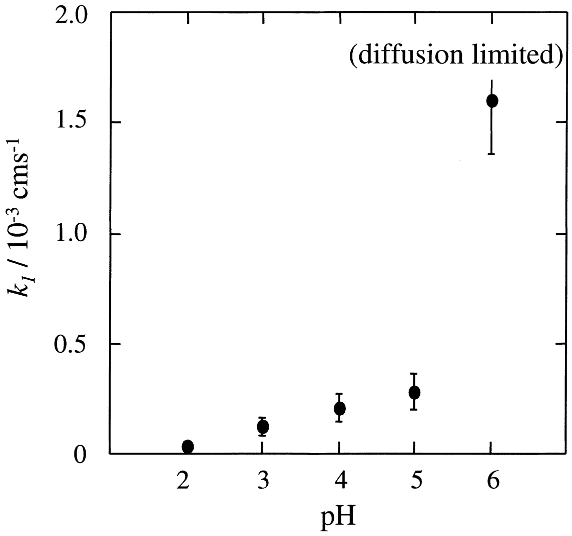

Fig. 4. The MT rate constant of MB^+ in the presence of DS^- (k_1) from water into single TBP droplets (r_d ~ 40 μm) at various pH in water.

The $A(t)$ curves were analyzed based on Eq. 2, as shown in Fig. 3. Figure 4 summarizes the k_1 values for various pH values. k_1 increased with increasing pH. Since it took 1 min for a single microdroplet injection and beam focusing onto the droplet, we may not quantitatively discuss the extraction rate at pH = 6. Nonetheless, the k_1 value at pH = 6 is close to the diffusion-limited MT rate constant discussed above (1.3×10^{-3} cm/s). Furthermore, k_1 was independent of r_d (4.5×10^{-5} cm/s at r_d = 26 μm, 4.1×10^{-5} cm/s at r_d = 40 μm, for pH = 2). These results indicate that the ion-pair extraction rate can be successfully analyzed based on the present model. The extraction rate is limited by the interfacial MT at the droplet/water boundary, which is highly dependent on the pH.

Transfer Mechanism of DS^- with MB^+. At pH < 1, MB^+ has been reported to be associated with a hydrogen ion (MBH^{2+}) in water, and MBH^{2+} can be spectroscopically identified by its characteristic absorption bands.[23] However, the absorption bands of MBH^{2+} were not observed in both the water (pH = 2–6) and TBP phases. Thus, the present ion-pair extraction is not influenced by the reaction. The interfacial tension was measured by a pendant drop method in the TBP/water system. The interfacial tension was 7–8 mN m^{-1} in both the absence and presence of MB^+ in the water phase at pH = 2 and 6 (without DS^-), respectively, indicating that MB^+ does not adsorb on the TBP/water interface. On the other hand, although the interfacial tension was ~5 mN m^{-1} in the presence of DS^-, this value was independent of the pH. Therefore, the characteristic pH dependence of the ion-pair extraction rate is not ascribed to the adsorption of the solutes on the TBP/water interface.

Although MB^+ was not extracted into the droplet without DS^-, DS^- may be extracted with a hydrogen ion as an ion pair in the absence of MB^+. To confirm the extraction of DS^- with H^+, a partitioning ratio of DS^-, P_{DS} (= $[DS^-(TBP)]_{eq}/[DS^-(w)]_{eq}$, $[DS^-(TBP)]_{eq}$; DS^- concentration in TBP), was determined by an ordinary extraction experiment in the TBP/water system without MB^+ using ion chromatography. Figure 5

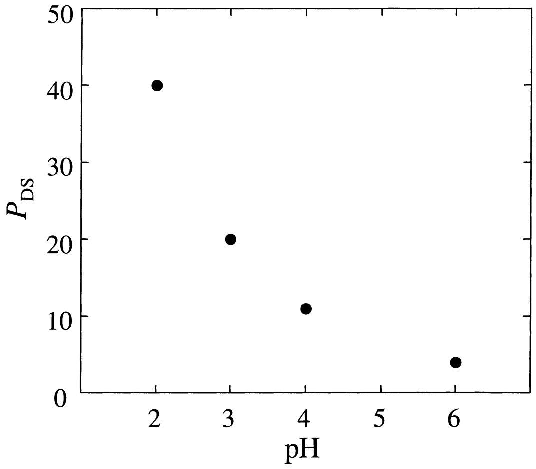

Fig. 5. The partitioning ratio of DS^- in the absence of MB^+ (P_{DS}) at various pH in water.

shows P_{DS} at various pH values. P_{DS} increased with decreasing pH in the water phase, indicating that DS^- is extracted into the TBP phase with H^+ in the absence of MB^+. It is noteworthy that P_{DS} without MB^+ at pH = 2 is almost the same as with P_{MB} at pH = 2 (~40).

According to an ion-pair extraction model in polar organic solvent/water systems, such as the nitrobenzene/water and 1,2-dichloroethane/water systems, a cation or anion individually transfers from water to oil, depending on the transfer free energy, and the electroneutrality is held in both phases.[24,25] Based on the extraction model, the ion-pair extraction of $CH_3(CH_2)_nSO_3^-$ (n = 5–8), similar to the structure of DS^-, and a tetrabutylammonium cation has been reported to be thermodynamically analyzed in the 1,2-dichloroethane/water system.[25] On the other hand, the ion-pair extraction rate of tetrabutylammonium picrate from water to nitrobenzene has been reported to be fast using the kinetic and thermodynamic data of the individual ions.[24] In the present system, the dielectric constant of TBP is relatively high (~8).[26] When the electric conductivity of the TBP phase was measured using 10 cm^3 of water and 10 cm^3 of TBP, the electric conductivity at $[MB^+(w)] = 1 \times 10^{-5}$ M and $[DS^-(w)] = 5 \times 10^{-5}$ M (0.52 μS cm^{-1} at pH = 2, 0.42 μS cm^{-1} at pH = 6) was higher than that in the absence of MB^+ and DS^- (0.03 μS cm^{-1} at pH = 6, 0.26 μS cm^{-1} at pH = 2). The electric conductivity at $[DS^-(w)] = 5 \times 10^{-5}$ M and pH = 2 in the absence of MB^+ was 0.41 μS cm^{-1}, suggesting that DS^- with H^+ is extracted into TBP. Therefore, the ion-pair extraction in the present system will proceed by MT of the individual ions.

Based on these results, the mechanism of ion-pair extraction in the MB^+/DS^- system is discussed. At low pH, DS^- is extracted with H^+ and/or MB^+ into the droplet during the initial stage of the distribution, since the H^+ concentration in water is much higher than $[MB^+(w)]$ (1×10^{-5} M). Because MB^+ is a hydrophobic compound compared with H^+, H^+ is slowly exchanged with MB^+ across the droplet/water interface over prolonged time. Therefore, the overall extraction time of MB^+ is extremely long at low pH values. At higher pH, on the other hand, DS^- is directly extracted with MB^+ to maintain electroneutrality in the droplet because of the low H^+ concentration. Thus, MB^+ is rapidly distributed into TBP with DS^-. When ionic strength effects at pH = 3 and 6 in the water phase were observed using sodium chloride, the extraction rate was independent of the ionic strength. As separate single microdroplet measurements, when rhodamine 6G was used as a cationic dye for the ion-pair extraction of DS^-, the extraction time required for the distribution equilibrium was extremely long (~3000 s) at pH = 2 and r_d = 30 μm. For the ion-pair extraction of MB^+ with a hexafluorophosphate anion, on the other hand, the time for the extraction equilibrium of MB^+ was shorter than 60 s at r_d = ~40 μm, independent of the pH. Therefore, we consider that the characteristic behavior of ion-pair extraction in the MB^+/DS^- system can be ascribed to the H^+ extraction with DS^- across the droplet/water interface.

Conclusion

The mechanism of the ion-pair extraction of DS^- with MB^+ as a typical extraction system was analyzed using the microcapillary-manipulation/injection and microabsorption methods. As a quantitative analytical method at the extraction equilibrium, DS^- is generally extracted into an organic phase with MB^+ at low pH in water. In this study, although the MB^+ concentration at the extraction equilibrium was independent of the pH, the extraction rate significantly decreased with decreasing pH. A kinetic analysis revealed that the extraction process is governed by the MB^+, H^+ and DS^- transfers across the oil/water interface, and the exchange of H^+ (distributed in the oil phase) with MB^+ (in water) at the interface. It is concluded that the single microdroplet measurements are sufficient to analyze the microscopic mechanism of various chemical processes across the oil/water interface.

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