

Measurement of the Aggregates of Anionic Porphyrin with Cationic Surfactants at the Supercritical Carbon Dioxide/Water Interface by Total Internal Reflection Spectroscopy

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A total internal reflection (TIR) spectrometric device was developed for direct measurement of adsorbates at the supercritical carbon dioxide (SC-CO₂)/water interface. The aggregation of diprotonated 5,10,15,20-tetraphenyl-21H,23H-porphinetetrasulfonic acid (H₄tpps²⁻) with cationic surfactants, cetyltrimethylammonium ion (CTA⁺), at the SC-CO₂/water interface was studied using this device. Dependence of the TIR absorption spectra on CTA⁺ concentration and CO₂ pressure were investigated, and the interfacial CTA⁺ concentration was found to cause changes in the interfacial H₄tpps²⁻ species present. Increasing the CO₂ pressure changed the interfacial species from the H₄tpps²⁻ monomer to the H₄tpps²⁻ J-aggregate because the interfacial CTA⁺ concentration increased as the pressure increased.

1. Introduction

Supercritical fluid extraction (SFE) of organic compounds and metal complexes from aqueous media has become a feasible separation method alternative to solvent extraction [1,2]. Among the supercritical fluids used in SFE, supercritical carbon dioxide fluid (SC-CO₂) has been widely used as the extraction medium, since it is non-toxic, cheap, environmentally acceptable and has a relatively mild critical point. Many studies on supercritical carbon dioxide (SC-CO₂) extraction of analytes from liquid matrix have been reported in recent years [3,4]. Clarification of chemical reactions at the SC-CO₂/water interface is important to understand the SC-CO₂ extraction mechanism and kinetics. However, studies on the SC-CO₂/water interface have been performed only by the interfacial tension determination [5,6]. Therefore, the development of spectroscopy analysis of the SC-CO₂/water interface is demanded, because the spectroscopy analysis allows us to obtain the much information about chemical species at the SC-CO₂/water interface. In this study, we developed the total internal reflection (TIR) spectroscopic system for measurement of the reaction at SC-CO₂/water interface and investigated the aggregation of water-soluble porphyrin with cationic surfactants at the SC-CO₂/water interface.

2. Experimental

2.1 Reagents

Cetyltrimethylammonium chloride (CTAC) was purchased from Tokyo Kasei (Japan). 5,10,15,20-Tetraphenyl-21H,23H-porphinetetrasulfonic acid disulfuric acid tetrahydrate (H₆tpps•2H₂SO₄•4H₂O) was purchased from Dojindo (Japan). Each stock solution was prepared in

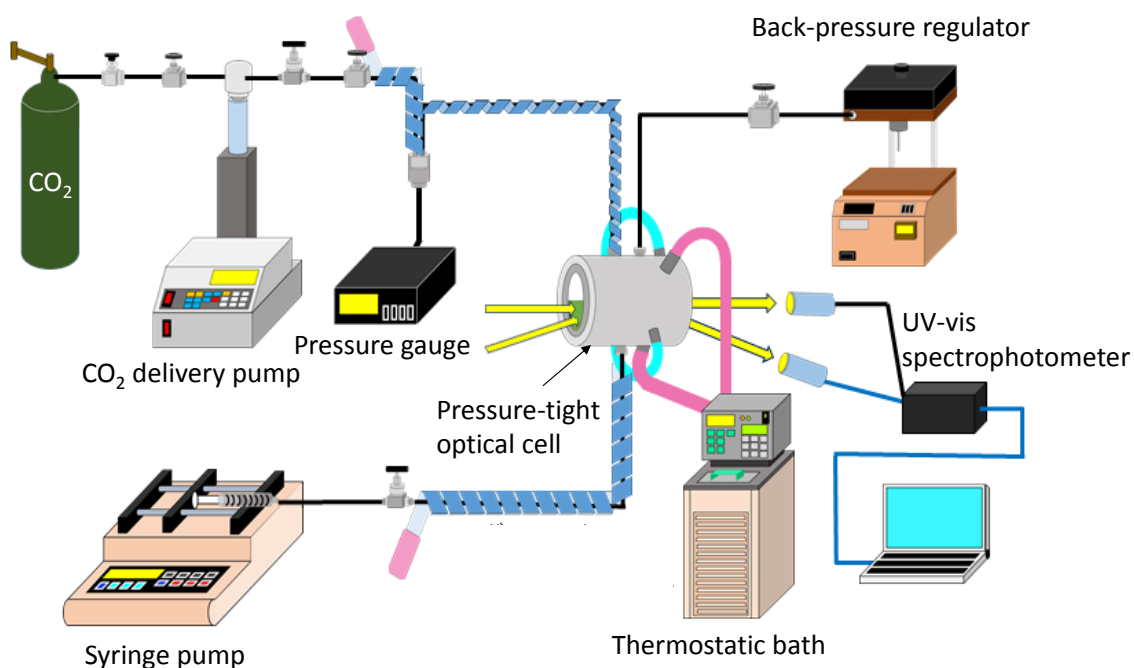


Figure 1. Schematic of the apparatus used to measure TIR spectra from the supercritical CO₂/water interface.

pure water. Liquid CO₂ (99.99%) was purchased from Taiyo Nissan Co. Ltd. Water was double distilled and purified further using a Milli-Q system (Millipore). All other chemicals were of analytical reagent grade and were used without further purification.

2.2 Apparatus

Figure 1 is a schematic of the TIR spectroscopic system developed in this study. The system has a CO₂ delivery pump (SCF-Get; Jasco), a syringe pump (KD210; Muromachi), a pressure tight optical cell (Jasco), a UV-vis spectrophotometer (USB3000; Ocean Optics), an arc lamp light source (APEX SOURCE ARC 150W XE OF; Newport), and a back-pressure regulator (880-80; Jasco). The pressure-tight optical cell is cylindrical and made of stainless steel with a 10 cm³ inner volume, 15 mm path length, a pair of quartz windows (22 mm diameter, 15 mm thick), and a water jacket to control the temperature. Optical fibers and a focus lens are used to irradiate the sample and collect the reflected light. A polarization prism is placed between the pressure-tight optical cell and optical fiber on the irradiation side. Temperature of the pressure-tight optical cell is monitored using a digital temperature indicator (Fenwal), and pressure inside the cell is monitored using a digital pressure gauge (Toyo Sokki).

2.3 Measurement of total internal reflection spectra at the SC-CO₂-water interface

An aqueous solution (5.7 mL) containing H₂tpps⁴⁻ and CTA⁺ was added to the pressure-tight optical cell using a syringe pump. CO₂ was then introduced into the cell using a CO₂ delivery pump, and the cell pressure was controlled using a back-pressure regulator. Temperature inside the cell was maintained at 318 K using a water jacket and a thermostat-controlled water circulator. The system was left to equilibrate for 7 h, light was irradiated obliquely to the interface from the aqueous medium side,

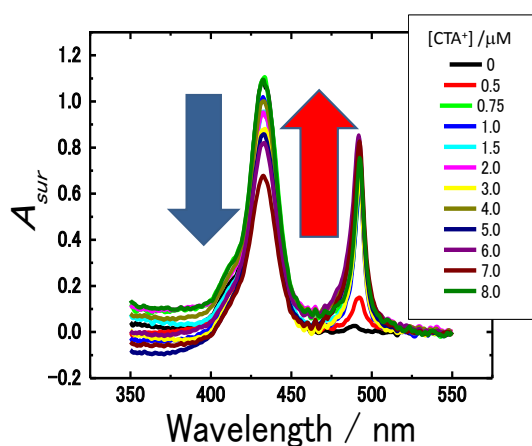


Figure 2. s-Polarized TIR spectra of H_4tpps^{2-} at the various CTA^+ concentrations. $[H_2tpps^{4-}] = 2.0 \mu M$; pressure = 10 MPa; temperature = 318 K.

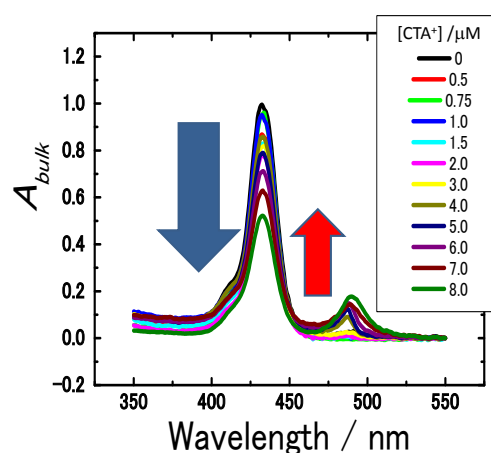


Figure 3. Absorption spectra of H_4tpps^{2-} in the aqueous phase at the various CTA^+ concentrations. $[H_2tpps^{4-}] = 2.0 \mu M$; pressure = 10 MPa; temperature = 318 K.

and the TIR spectrum was measured. The refractive index of water (1.34) are larger than those of CO_2 and $SC-CO_2$ (1.02–1.12, respectively [7]). The incidence angle was fixed at 68° . The TIR absorbance, A_{TIR} , was defined as $\log(R_0/R)$, where R_0 and R are the reflectivities in the absence and presence of the absorbate, respectively. The absorption spectrum of the aqueous phase was measured simultaneously. H_2tpps^{4-} concentration was maintained at $2.0 \mu M$, and CTAC concentration was varied from 0 to $9 \mu M$. Pressure was varied from 1 to 10 MPa, and CO_2 pressure and temperature were maintained within 0.2 MPa and $0.1^\circ C$, respectively, of the desired value.

3. Results and Discussion

3.1 Aggregation behavior of H_4tpps^{2-} with CTA^+ at the $SC-CO_2$ /water interface

Figures 2 and 3 show s-polarized TIR and the aqueous phase's absorption spectra, respectively, at the various CTA^+ concentrations measured using the apparatus developed in this study. Two bands at 434 nm and 492 nm in Figures 2 and 3 were assigned to the H_4tpps^{2-} monomer in the aqueous phase and the H_4tpps^{2-} J-aggregate at the $SC-CO_2$ /water interface. The TIR absorbance at 434 nm decreased and that at 492 nm increased with an increase in the CTA^+ concentration as shown in Figure 2. A similar spectral change in the aqueous phase was observed in Figure 3. However, the absorbance at 492 nm in Figure 3 was much smaller than that in Figure 2. This result indicated that the H_4tpps^{2-} J-aggregate was mainly formed at the $SC-CO_2$ /water interface. The TIR absorption spectrum of the H_4tpps^{2-} J-aggregate at the $SC-CO_2$ /water interface could be obtained by the deduction of the absorption spectrum in the aqueous phase. Figure 4 shows the plots of the TIR absorbance at 492 nm of the H_4tpps^{2-} J-aggregate at the $SC-CO_2$ /water interface after the deduction of the absorbance in the aqueous phase against the concentration of CTA^+ . The TIR absorbance at 492 nm became constant near $1 \mu M$ of CTA^+ . This result indicated that the interfacial concentration of H_4tpps^{2-} J-aggregate was saturated about $1 \mu M$ of CTA^+ .

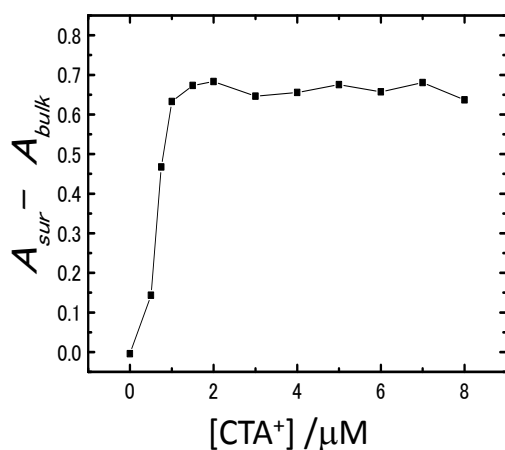


Figure 4. Dependency of the TIR absorbance of the interfacial H_4tpps^{2-} J-aggregate on the CTA^+ concentration. $[H_2tpps^{4-}] = 2.0 \mu M$; pressure = 10 MPa; temperature = 318 K.

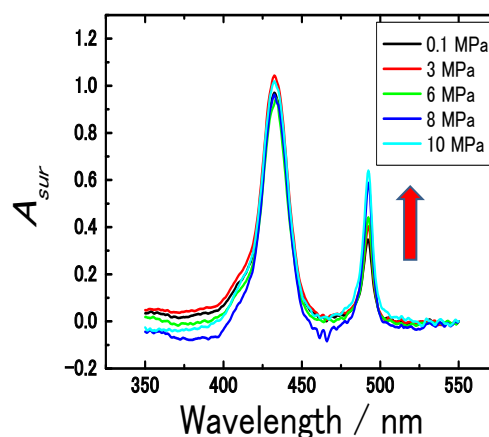


Figure 5. s-Polarized TIR spectra of H_4tpps^{2-} at the various pressures. $[H_2tpps^{4-}] = 2.0 \mu M$; $[CTA^+] = 1 \mu M$; temperature = 318 K.

Pressure-dependent TIR absorption spectra were measured at a constant CTA^+ concentration (1 μM) to determine the effect the CO_2 pressure on H_4tpps^{2-} aggregation at the SC- CO_2 -water interface. Figure 5 shows the s-polarized TIR spectra at the various CO_2 pressures. The TIR absorbance at 492 nm increased with an increase in the CO_2 pressure. As the pressure increases, the adsorptivity of CTA^+ at the SC- CO_2 /water interface may become higher [8]. That is, the interfacial concentration of CTA^+ at high pressure is higher than that at low pressure. This may cause the higher interfacial concentration of H_4tpps^{2-} and the formation of H_4tpps^{2-} J-aggregate with CTA^+ . The result obtained implies that it is possible to change the interfacial chemical species by changing the pressure in the SC- CO_2 /water system.

4. Conclusion

In this study, we developed a TIR spectrometric device for direct measurement of the adsorbate at the SC- CO_2 /water interface. The aggregation of H_4tpps^{2-} with CTA^+ at the SC- CO_2 /water interface was studied using this device. The TIR spectra of the H_4tpps^{2-} J-aggregate formed at the SC- CO_2 /water interface could be observed. The method developed in this study allows us to obtain much information on the chemical species at the SC- CO_2 /water interface. Therefore, this may promote further development on the investigation in the supercritical CO_2 extraction.

Acknowledgement

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