Structural Evaluation of the Aggregate of Palladium(II)–Pyridylazophenol Complex at the Heptane-Water Interface by the Centrifugal Liquid Membrane Method

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The formation and aggregation of the Pd(II) complex with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (HL) at the heptane-water interface was investigated by UV-vis absorption and resonance Raman spectrometry using the centrifugal liquid membrane (CLM) method. The interfacial aggregate had an absorption maximum wavelength at 488 nm, showing a hypsochromic shift from the absorption maximum wavelength at 580 nm of the complex monomer (PdLCl). The critical aggregation concentration of PdLCl was determined to be $2.6 \times 10^{-10}$ mol cm$^{-2}$. The observed UV-vis absorption and resonance Raman spectra implied that the ligand in the interfacial aggregate was mainly in the state of azo form, because the spectra were very similar to those of the PdLCl complex obtained in a low-polarity solvent such as toluene.

1. Introduction

The liquid-liquid interface has received a great deal of attention in various fields of separation chemistry, biochemistry and electrochemistry [1-3], because the liquid-liquid interface has specific characteristics, such as amphiphilic and two-dimensional media, low capacity, orientational confinement for the adsorbates and so on. The formation of aggregates is one of the most specific reactions at the liquid-liquid interface. In particular, the aggregate formation of metal complexes at the interface is a very interesting subject in solvent extraction kinetics and separation of metal ions [4]. Compared with the studies on the aggregation in the bulk phase, studies at the liquid-liquid interface, however, have not been carried out extensively, because it is difficult to measure the liquid-liquid interface directly. In order to deepen the understanding of interfacial aggregation, further studies on interfacial aggregation are required.

The centrifugal liquid membrane (CLM) method which has been developed by Nagatani and Watarai is the most versatile technique for research of the interfacial reaction [5]. In this method, the ultra-thin two-phase liquid membranes are produced in a rotating optical cell. This method enables us to measure absorption spectra of adsorbates effectively at the liquid-liquid interface [6-8].

Figure 1. Structure of PdLCl.
which can be combined with other spectroscopic methods such as fluorometry [9], resonance Raman spectrometry [10-13], and circular dichroism spectropolarimetry [14,15]. Several studies on the interfacial aggregate formation of metal complexes have been carried out using CLM [16-21]. For example, Yulizar and coworkers reported detail studies on the interfacial aggregation of complexes of Ni(II) [17] and Fe(II, III) [18] with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP or HL).

5-Br-PADAP was introduced by Gusev and Shchurova [22] and was used as a sensitive reagent in the determination of trace metal ions. 5-Br-PADAP forms stable and colored complexes with various metal ions as a trident ligand. It forms a 1:1 square-planar complex with palladium(II) leaving one site for the coordination of another ligand. The Pd(II)–5-Br-PADAP–chloro (PdLCl, Figure 1) complex has high interfacial adsorptivity and high molar absorptivity (4.33 x 10^4 dm^3 mol^-1 cm^-1 at 564 nm in toluene [23]). The PdLCl ligand exists as a mixture of imine and azo resonance forms and the ratio of the imine to the azo form depends on the polarity of the solvent [24]. In previous work, we showed that the PdLCl complex adsorbed at the liquid-liquid interface mainly existed in the imine form under the strong influence of the aqueous phase [11].

In this paper, we report the interfacial aggregation of PdLCl in the heptane-water system. The structure of the PdLCl interfacial aggregate is evaluated using the CLM method combined with UV-vis spectrometry and resonance Raman microprobe spectrometry.

2. Experimental

2.1 Reagents

5-Br-PADAP (Tokyo Chemical Industry) was used as purchased and dissolved in heptane. For the purification of heptane, heptane (G.R., Katayama Chemical) was stirred with concentrated sulfuric acid for one day (repeated three times), washed successively with distilled water and 5% sodium hydroxide aqueous solution, dehydrated by calcium chloride dehydrate overnight, and fractionally distilled. A stock solution of palladium(II) was prepared by dissolving palladium(II) chloride (99.99%, Wako Pure Chemicals) in 0.1 M chloride acid. Water was distilled and deionized with a Milli-Q system (Milli-Q SP.TOC., Millipore). All other chemicals were of analytical reagent grade, and were used without further purification. Crystals of PdLCl were prepared by the solvent evaporation method from the toluene solution as reported previously [25]. A given amount of PdLCl crystal and about 200 mg KBr were added into a mortar and ground together. The resulting powder was pressed to make a KBr pellet containing PdLCl, whose diameter and thickness were 10 and 2 mm, respectively.

2.2 UV-vis absorption spectral measurement

The principle of the CLM method has been described elsewhere [5]. The apparatus used for the CLM method was the same as reported previously [7]. Heptane (0.050 cm^3) and an aqueous solution (0.250 cm^3) of 1.0 x 10^-3 mol dm^-3 Pd(II) were introduced into a cylindrical cell, whose inner diameter and length were 1.9 and 3.0 cm, respectively. The cylindrical cell was placed horizontally in a diode array spectrophotometer (Hewlett-Packard HP8452A). After high-speed rotation at 10000 rpm by the high-speed motor (Nakanishi Inc., NK-260), an aliquot of the heptane solution of HL (0.200 cm^3) was injected into the cylindrical cell through a 2-mm diameter hole at the flat wall in order to initiate the complexation of Pd(II). All of the absorption spectra of the bulk phases and the interface were measured in the wavelength range of...
300 – 750 nm. The heptane phase and the aqueous phase were 129 μm and 128 μm in thickness, respectively. The interfacial area (S) between the two phases was 19.4 cm². The ionic strength and pH were fixed at 0.1 mol dm⁻³ and 1.0, respectively, with hydrochloric acid. The concentration of HL was varied in the ranges of 2.5 × 10⁻⁶ – 1.0 × 10⁻⁴ mol dm⁻³. The absorption spectrum of the KBr pellet containing the PdLCl crystal was measured with a UV-vis spectrophotometer (V-570, Jasco).

2.3 Resonance Raman spectral measurement

The resonance Raman spectra of the complex and the PdLCl aggregate at the heptane-water interface were measured by CLM-resonance Raman microprobe spectroscopy (CLM-RRMS). The apparatus and the CLM-RRMS measurement have been described in detail in the previous report [10]. An Ar⁺-ion laser excitation beam (514.5 nm) was focused at the heptane-water interface through the objective lens (Mitutoyo, 45×, NA 0.55). The back scattering was collected by the same objective lens and passed to a spectrophotometer (Jobin Yvon, HR-320) with a liquid-nitrogen-cooled CCD detector (Roper Scientific, LN/CCD-1100-PB/UVAR/1). The laser power and the exposure time to acquire Raman scattering in the time-resolved measurements were set at 120 mW and 5 s, respectively. The resonance Raman spectra of the interfacial complex or PdLCl aggregate at equilibrium were measured at a laser power of 40 mW and an exposure time of 50 s. Raman spectra were measured from 1800 to 800 cm⁻¹. The observed frequencies were calibrated with respect to the Raman peaks of toluene and were accurate to within ±2 cm⁻¹. Resonance Raman spectrum of the KBr pellet containing PdLCl was also measured. The KBr pellet was measured on a glass plate. The excitation wavelength, laser power and the exposure time were 514.5 nm, 40 mW and 10 s, respectively.

3. Results and Discussion

3.1 UV-vis absorption spectra

Figure 2 shows the typical absorption spectral change associated with the complexation of PdLCl at the heptane-water interface produced by the CLM method. The formation of the interfacial PdLCl complex and the aggregation proceeded in the following way. First, the absorbance around 556 nm was increased and the absorbance around 452 nm was decreased by the complexation of Pd(II) with HL (Figure 2a). Then,
the absorbance around 556 nm was decreased and a new absorption band of the aggregate appeared at 488 nm (Figure 2b). Finally, a further increase in the absorbance of the aggregate was observed (Figure 2c). Similar spectral changes were observed always under the conditions where the PdLCl aggregate was formed. Figure 3 shows the absorption spectra of PdLCl observed by the CLM method at various HL concentrations at equilibrium. In a previous paper [7], we reported that PdLCl is not extracted into heptane and exists only at the heptane-water interface. If PdLCl exists completely as a monomer at the interface, the apparent interfacial concentration of PdLCl ([PdLCl]) at equilibrium is defined as [PdLCl] = [HL]T/V_o/S_i, where [HL]T and V_o are the initial HL concentration in heptane and the volume of the heptane phase, respectively. The absorption spectra changed in three steps as the [PdLCl] increases. First, at lower apparent interfacial concentrations, the absorption spectrum having a maximum around 580 nm was observed, which was assigned to the PdLCl monomer formed at the heptane-water interface. Secondly, the absorption at 556 nm increased with an increase in the apparent interfacial concentration. This spectral change may be caused by the dimerization of PdLCl. In a previous study [25], we found that PdLCl formed a dimer by a π-stacking interaction in the crystal from an X-ray structural analysis. Finally, the absorption spectrum having a maximum at 488 nm were observed at higher apparent interfacial concentrations. This spectrum was assigned to the interfacial aggregate of PdLCl. The absorption maximum wavelength of the aggregate was blue-shifted about 92 nm with respect to that of the PdLCl monomer complex. This may be attributed to the PdLCl-PdLCl interaction and suggests the formation of H-aggregates at the heptane-water interface. Although the molar absorptivity at 488 nm (about 3 × 10^4 dm^3 mol^-1 cm^-1) of the PdLCl aggregate was smaller than that at 580 nm (4.22 × 10^4 dm^3 mol^-1 cm^-1 [7]) of the PdLCl monomer at the heptane-water interface, it was a relatively large value. This suggested that the charged quinone structure was retained in the PdLCl aggregate. In a previous study [17], it was reported that the absorption maximum wavelength of a NiL2 aggregate at the heptane-water interface was red-shifted compared with that of the NiL2 complex and the molar absorptivity of the former was larger than that of the latter. These results for the NiL2 aggregate were completely opposite to those for the PdLCl aggregate obtained in the present study. In order to determine the critical interfacial concentration required to generate the PdLCl aggregate, the dependency of the absorbance at 488 nm on the apparent interfacial PdLCl concentration was investigated.

Figure 3. Absorption spectra of PdLCl at the heptane-water interface observed by the CLM method

Figure 4. Dependency of the absorbance at 488 nm observed by the CLM method on the apparent interfacial PdLCl concentration.
As shown in Figure 4, the absorbance at 488 nm drastically increased at a higher apparent interfacial concentration of $2.6 \times 10^{-10}$ mol cm$^{-2}$. Therefore, the critical aggregation concentration of PdLCl was estimated as $2.6 \times 10^{-10}$ mol cm$^{-2}$, which is close to that of NiL$_2$ ($2.4 \times 10^{-10}$ mol cm$^{-2}$) [17].

Figure 5 shows the normalized absorption spectra of the solid PdLCl for the KBr pellet, the aggregate and the monomer formed at the heptane-water interface. The absorption spectrum of the metal–5-Br-PADAP complex depends on the solvent, since the ratio of the azo and imine resonance structures of the ligand is changed by the dielectric constant of the solvent [24]. In the previous work, it was found that the PdLCl complex at the liquid-liquid interface mainly exists in the imine form under the strong influence of the aqueous phase [11]. The absorption spectrum of the aggregate was different from those of the crystal and the monomer at the heptane-water interface. The absorption spectrum of the aggregate is similar to that of the toluene solution. Each spectrum has a shoulder peak around 655 nm, which is characteristic for PdLCl in a low-polarity solvent. PdLCl favors the azo form in a low-polarity solvent. Therefore, it is concluded that PdLCl in the aggregate exists in the azo form.

### 3.2 Resonance Raman spectra

Figure 6 shows the change of the resonance Raman spectrum due to the complexation and the aggregation of PdLCl at the heptane-water interface. In these Raman spectra, the background Raman spectrum of heptane was already removed. The resonance Raman spectra of the PdLCl complex increased up to 56 s, and then the shape of Raman spectra obviously changed due to the aggregation of PdLCl. There were several differences between the resonance Raman spectra of the complex and the aggregate, such as lower shifts in some peak positions and the changes in the relative intensity of some peaks. However, the spectral pattern was basically the same. This result implied that there was no large structural change of PdLCl with the aggregation, supporting the formation of H-aggregation at the heptane-water interface.

Figure 7 shows the resonance Raman spectra of PdLCl in various circumstances. The Raman spectra of
the solvents were already removed in Figure 7. The resonance Raman spectrum of the aggregate implied that the aggregate was mainly formed with an azo form complex, because the Raman spectrum of the aggregate was more similar to the spectra of the PdLCl complex obtained from a low-polarity solvent (toluene) than a high-polarity solvent (ethanol). The bands at 1476, 1461, 1300, and 1285 cm⁻¹ of the aggregate were assigned to \( \nu(C=C) \) of the pyridine ring in the azo form, \( \nu(CNNC) \) in imine form, \( \nu(CNNC) \) in azo form and \( \nu(CNNC) \) in imine form, respectively, by comparison with the band assignments reported for pyridylazophenol complexes [26-29]. In the previous study, we found that the ratios of resonance Raman intensities at the peaks of around 1476 and 1461 cm⁻¹ (\( I_{1476}/I_{1461} \)) and 1300 and 1285 cm⁻¹ (\( I_{1300}/I_{1285} \)) depended on the dielectric constant of the solvent [11]. The values of \( I_{1476}/I_{1461} \) and \( I_{1300}/I_{1285} \) in the resonance Raman spectrum of the interfacial PdLCl aggregate were 1.28 and 3.31, respectively. These values were close to those obtained in low-polarity solvents such as toluene and chloroform [11]. This suggested that PdLCl in the aggregate at the heptane-water interface was little affected by the influence of the aqueous phase, whereas the PdLCl complex adsorbed at the heptane-water interface was. The band position at 1595 cm⁻¹, which was assigned to the benzene and pyridine rings stretching [26-29] in the crystal, was shifted to 1590 cm⁻¹ in the aggregate. This was attributed to the extensive \( \pi \)-stacking in the H-aggregate of the aromatic rings of the PdLCl molecules in the aggregate, which was more than that in the crystal where dimer formation dominated. This was supported by the result that the UV-vis absorption spectrum for the aggregate was shifted to lower wavelength than that for the crystal.

4. Conclusion

The structure of the PdLCl aggregate at the heptane-water interface was evaluated using the CLM method combined with UV-vis absorption spectrometry and resonance Raman microprobe spectrometry. The absorption maximum wavelength of the aggregate was blue-shifted from 580 nm (PdLCl monomer complex) to 488 nm, suggesting the formation of an H-aggregate at the heptane-water interface. The critical aggregation concentration of PdLCl was determined to be \( 2.6 \times 10^{-10} \) mol cm⁻². The UV-vis absorption and the resonance Raman spectra of the aggregate implied that the aggregate contained the complex mainly in the azo form.

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