

Measurement of Complexation Rate of Palladium(II) with Pyridylazo Ligand at the Heptane-Water Interface by Centrifugal Liquid Membrane-resonance Raman Microprobe Spectroscopy

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The complexation kinetics of palladium(II) with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) at the heptane-water interface was investigated by resonance Raman spectroscopy combined with a centrifugal liquid membrane method. It was demonstrated that this method was advantageous for the kinetic studies of complex formation proceeding at the liquid-liquid interface.

The liquid-liquid interface plays an important role in the reaction kinetics of the solvent extraction, the liquid membrane separation and the interfacial synthesis.¹ Therefore, many studies on the measurement method of the interfacial reaction have been studied, so far. But, to our knowledge, Raman spectroscopy has never been used for the kinetic study at liquid-liquid interface. Application of Raman spectroscopy to interfacial reaction is expected to allow us to discuss in detail on the structure of the interfacial species. Recently, we developed a new in situ Raman spectroscopic method, a centrifugal liquid membrane-resonance Raman microprobe spectroscopy (CLM-RRMS),² in which the Raman microscopy was combined with the centrifugal liquid membrane (CLM) method³ to measure Raman spectra of the interfacial species. Some studies on resonance Raman spectroscopy of the liquid-liquid interface have been reported using the total reflection method.^{4,5} This method, however, is difficult to be used for the measurement of the reaction kinetics at the interface, when the two phases are rather thick and the reactant species are suffered from a slow diffusion or convection process. In CLM-RRMS, a thin two-phase layer is formed on the wall of a rotating optical cell by a centrifugal force. Thus, the diffusion in the bulk phases is promoted by the intrinsic molecular diffusion coefficient. Therefore, CLM-RRMS allows us to measure the change in the concentration of the adsorbates with the time resolution of a few seconds. In this study we applied the resonance centrifugal liquid membrane-resonance Raman microspectroscopy to the measurement of the complexation rates of Pd(II) with 5-Br-PADAP (HL) at the heptane-water interface and demonstrated that this method was useful for the kinetic measurement of the interfacial reaction.

The apparatus of CLM-RRMS was the same as the one reported previously² and schematic drawing of the apparatus was shown in Figure 1. Heptane (0.100 cm^3) and the Pd(II) aqueous solution (0.250 cm^3) were put into the cylindrical cell, whose inner diameter and inner length were 19 mm and 30 mm, respectively. After the high-speed rotation at about 10000 rpm, an aliquot of heptane solution of HL (0.050 cm^3) was injected into the cylindrical cell through a hole with 2 mm diameter at the flat wall in order to initiate the complexation of Pd(II). The heptane phase and the aqueous phase were $77 \mu\text{m}$ and $128 \mu\text{m}$ in thickness, respectively. The interfacial area (S_i) between two phases was 19.4 cm^2 . The excitation beam (514.5 nm) by an Ar⁺-ion laser was focused at

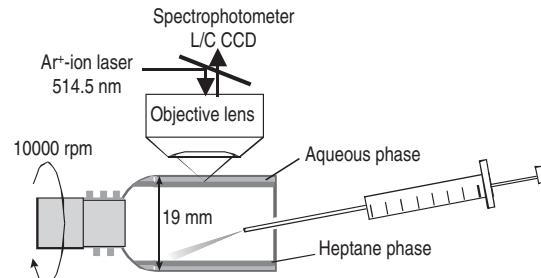


Figure 1. Schematic drawing of an observation part in a centrifugal liquid membrane-resonance Raman microprobe spectroscopy.

the heptane-water interface through the objective lens. The back scattering was collected by the same objective lens and was led to a spectrophotometer with a liquid-nitrogen-cooled CCD detector. The laser power was 40 mW and the integration time to measure a Raman spectrum was 5 s. Raman spectra were measured from 1800 to 800 cm^{-1} . The complexation rate of Pd(II) with 5-Br-PADAP at the interface was monitored by the Raman intensity at 1599 cm^{-1} , which was assigned to phenyl or pyridyl ring stretching of PdLCl. Although an intrinsic depth resolution of Raman microscopy was obtained as $4 \mu\text{m}$, an effective depth resolution of this method was estimated as ca. $70 \mu\text{m}$ from the measurement of the distribution of Raman intensity of PdLCl at the interface, resulting from the vibration of the cylindrical cell under the high-speed rotation.² The Raman intensity change was fitted to an exponential curve by the least-squares regression, and the initial complexation rate defined as $r^0 = (d[PdLCl]_i/dt)_{t=t'}$ (t' represents the HL injection time) was calculated by differentiating the exponential curve at the HL injection time. The observed frequencies were calibrated with respect to the Raman peaks of toluene and were accurate to within $\pm 2 \text{ cm}^{-1}$. All measurements were carried out in the thermostated room at $298 \pm 2 \text{ K}$. The Pd(II) concentration was changed from 8.0×10^{-5} to $4.0 \times 10^{-4} \text{ mol dm}^{-3}$. The ionic strength and pH were fixed with HCl at 0.1 mol dm^{-3} and 1.0, respectively.

Firstly, it was confirmed that the Raman intensity was proportional to the interfacial concentration of PdLCl. Because PdLCl existed only at the heptane-water interface and all HL molecules reacted at the equilibrium in the present conditions,² the interfacial concentration of PdLCl ($[PdLCl]_{i,T}$) at the equilibrium was calculated as $[PdLCl]_{i,T} = [HL]_T V_o / S_i$, where $[HL]_T$ and V_o are the total HL concentration and the volume of the heptane phase, respectively. Raman intensity obtained by CLM-RRMS at 1599 cm^{-1} showed a good linearity against $[HL]_T$ in the range of 1.2×10^{-6} – $1.3 \times 10^{-5} \text{ mol dm}^{-3}$. Thus, we could get a linear correlation between the Raman intensity and the interfacial concentration of $[PdLCl]_{i,T}$ in the range of 9.2×10^{-12} – $1.0 \times 10^{-10} \text{ mol cm}^{-2}$. Significant Raman intensity of PdLCl could be measured even at the lower interfacial concentration than the ordinary saturated interfacial concentration ($10^{-10} \text{ mol cm}^{-2}$).

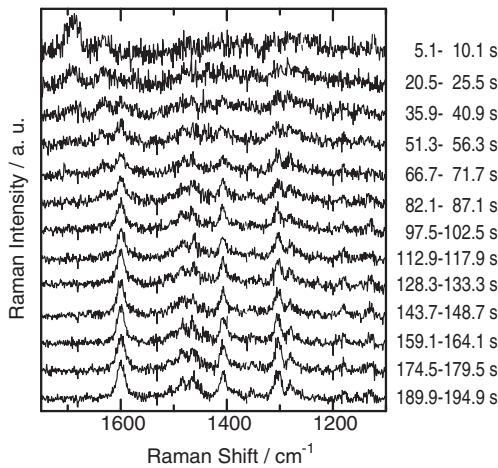


Figure 2. Change of resonance Raman spectrum with the complexation of Pd(II) with 5-Br-PADAP at the heptane-water interface. Aqueous phase: $\text{PdCl}_2 8.0 \times 10^{-5} \text{ mol dm}^{-3}$, $\text{HCl} 0.1 \text{ mol dm}^{-3}$, pH 1.0; heptane phase: 5-Br-PADAP $7.8 \times 10^{-6} \text{ mol dm}^{-3}$, $t' = 4 \text{ s}$. Final volumes of the aqueous and heptane phase were 0.250 and 0.150 cm^3 , respectively. Laser power was 40 mW and the integration time for each spectrum was 5 s .

Secondly, in order to obtain the complexation rate of PdLCl at the heptane-water interface, the resonance Raman spectral change was measured by CLM-RRMS. Figure 2 shows a typical result of the spectral change in the complexation of PdLCl. In these Raman spectra, Raman spectrum of heptane was already subtracted. Raman intensity of PdLCl increased with the increase in the interfacial concentration of PdLCl. Figure 3 shows the kinetic formation profiles of PdLCl measured by CLM-RRMS and a conventional CLM spectrophotometry. Wavelengths at 452 and 580 nm refer to the absorption maxima of HL in heptane and PdLCl at the interface, respectively. The kinetic profile of the increase in the Raman intensity of PdLCl at 1599 cm^{-1} was good agreement with that in the absorbance of PdLCl at 580 nm . As mentioned above, the initial complexation rate (r^0) of PdLCl at the heptane-water interface was obtained from the Raman intensity change. When the complexation rate is governed by the formation of 1:1 complex in the aqueous phase and at the interface at pH 1.0, the r^0 is given by the following equation:⁶

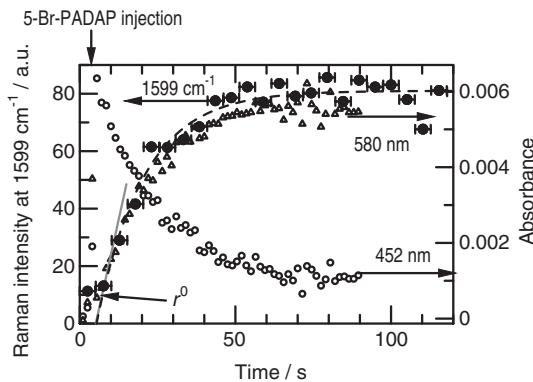


Figure 3. Complexation kinetic profiles of PdLCl at the interface; (●) Raman intensity at 1599 cm^{-1} measured by CLM-RRMS, (○) the absorbance at 452 nm measured by CLM spectrophotometry, (△) the absorbance at 580 nm measured by CLM spectrophotometry. $[\text{Pd(II)}]_T = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{HL}]_T = 7.8 \times 10^{-6} \text{ mol dm}^{-3}$, $[\text{Cl}^-] = 0.1 \text{ mol dm}^{-3}$, pH 1.0.

$$r^0 = [\text{Pd(II)}]_T \{ (k_{a,\text{HL}}[\text{HL}] + k_{a,\text{H}_2\text{L}^+}[\text{H}_2\text{L}^+])V_a/S_i + (k_{i,\text{HL}}[\text{HL}]_i + k_{i,\text{H}_2\text{L}^+}[\text{H}_2\text{L}^+]_i) \} \quad (1)$$

where the subscript a and i refer to the aqueous phase and the interface, respectively, H_2L^+ to a protonated HL, V_a to the volume of the aqueous phase and $k_{a,\text{HL}}$, $k_{a,\text{H}_2\text{L}^+}$, $k_{i,\text{HL}}$ and $k_{i,\text{H}_2\text{L}^+}$ are the rate constants for the reaction of Pd(II) with HL and H_2L^+ in the aqueous phase and at the interface. Figure 4 shows the plots of the value of r^0 against the concentration of Pd(II) for both measurements of Raman intensity change by CLM-RRMS and the absorbance change by CLM spectrophotometry.⁶ Both values for r^0 were in good coincidence, showing a linear correlation with the Pd(II) concentration as expected from Eq. 1. The dashed line shown in Figure 4 is the one calculated from Eq. 1 using the values of $k_{a,\text{HL}} = k_{a,\text{H}_2\text{L}^+} = 5.7 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_{i,\text{HL}} = 53 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and $k_{i,\text{H}_2\text{L}^+} = 5.1 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.⁶

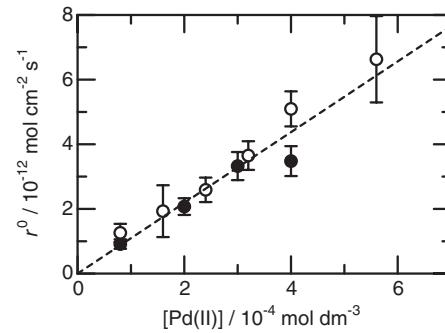


Figure 4. Dependency of the initial complexation rate (r^0) on the aqueous phase concentration of Pd(II); (○) the absorbance change measured by CLM spectrophotometry and (●) the Raman intensity change measured by CLM-RRMS: $[\text{HL}]_T = 7.8 \times 10^{-6} \text{ mol dm}^{-3}$, $[\text{Cl}^-] = 0.1 \text{ mol dm}^{-3}$, pH 1.0. The broken line is the one calculated by using the rate constants estimated in ref. 6.

It was demonstrated in this study that CLM-RRMS was useful for the kinetic measurement of the interfacial complexation. To our knowledge, this is the first report on the measurement of the reaction kinetics proceeding at the liquid-liquid interface with a time resolution of several seconds by the resonance Raman spectroscopy. This method is also applicable to the studies of other interfacial reactions such as an aggregate formation and an electron transfer reaction. A complementary use of CLM-resonance Raman spectrometry and CLM-UV-vis absorption spectrometry will provide a powerful approach for the study of the interfacial kinetic mechanisms.

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