Resonance Raman Spectroscopic Detection of Pyridylazo Complex Formed at Liquid–Liquid Interface in Centrifugal Liquid Membrane System

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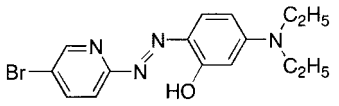
A new method of resonance Raman microprobe spectroscopy combined with a centrifugal liquid membrane (CLM) method was constructed and successfully applied to the detection of the complex of palladium(II) with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) formed at the heptane/water interface. The depth profiles of resonance Raman intensities of Pd(II)–5-Br-PADAP complex along the axis perpendicular to the interface confirmed that the complex existed only at the liquid–liquid interface.

Liquid–liquid interface is expected to be an effective reaction or synthetic field, because the concentration of adsorbate at the interface is used to become higher than those in bulk phases. Recently, several spectroscopic methods to measure interfacial species directly have been reported.[1] But, there are few reports[2,3] in which vibrational spectroscopy such as Raman spectroscopy has been applied to the measurement of the liquid–liquid interface, though the vibrational spectroscopy is highly informative for the discussion of structural properties of a sample.

In the present study, a new Raman spectroscopic method was proposed for the detection of the interfacial complex formed between Pd(II) and 5-Br-PADAP[4] in the heptane/water system; the Raman microscopy was combined with the centrifugal liquid membrane (CLM) method,[5] that could make a stable and thin two-phase liquid membrane and could reduce the undesirable Raman scattering from bulk phases.



5-Br-PADAP

5-Br-PADAP, 2-(5-bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulfopropylamino)phenol (5-Br-PAPS) disodium salt (Dojindo Laboratories), malachite green (MG) oxalate (G.R., Wako Pure Chemicals) and palladium(II) chloride (99.99%, Wako Pure Chemicals) were used as purchased. Stock solutions of $PdCl_2$ and 5-Br-PADAP were prepared by dissolving them in 0.1 mol dm^{-3} hydrochloric acid and heptane, respectively, and those of 5-Br-PAPS and MG were prepared with pure water. MG and 5-Br-PAPS were used as the indicators to measure the positions of an inner surface of the cylindrical cell and the bulk aqueous phase, respectively. Heptane (G.R., Katayama Chemical) was purified with same means in the literature.[6] Water was purified by a Millipore Milli-Q SP.TOC.

Figure 1 shows the apparatus of Raman microscopy combined with CLM cell. The heptane solution and the aqueous solution were put into the cylindrical cell, whose height and outer diameter were 3.3 and 2.1 cm, respectively. The cylindrical cell was placed horizontally under the objective lens (Mitutoyo, 45×, NA 0.55) and rotated at about 10,000 rpm by the high-speed motor (Nakanishi Inc., NK-260) fixed on a XYZ-stage. The heptane phase was spread as an inner liquid membrane and the aqueous phase as an outer liquid membrane by a centrifugal force under the rotating condition. The apparatus of Raman microscopy that contained an Ar^+-ion laser (Spectra-Physics, Stabilite 2017), a liquid-nitrogen-cooled/CCD detector (Roper Scientific, LN/CCD-1100-PB/UVAR/1) and a spectrophotometer (Jobin Yvon, HR-320) was constructed by Photon Design (Japan). The laser beam of 514.5 nm wavelength was focused into the sample through the objective lens. The scattering light was collected by the same objective lens. The focal point was moved along the Z-axis, which was perpendicular to the interface, in the range from 530 and 925 μm by controlling the height of XYZ-stage. The position of Z = 0 was defined at an outer surface of the cylindrical cell. The laser power was kept at 40 mW. To improve the S/N ratio and to reduce the photo-breaching of reagents, the exposure time was chosen as short as 15 s. The concentrations of 5-Br-PADAP, $PdCl_2$ and 5-Br-PAPS were 1.7×10^{-5}, 3.3×10^{-4} and 1.0×10^{-4} mol dm^{-3}, respectively. Ionic strength was adjusted to 0.1 mol dm^{-3} with HCl or $NaClO_4$. The volumes of the heptane phase and the aqueous phase were fixed at 0.300 cm^3. Moreover, the measurement was carried out with a cylindrical cell in which MG adsorbed at the inner surface in order to determine its position. The MG adsorbed cell was prepared in the following ways; the MG aqueous solution of 1.1×10^{-2} mol dm^{-3} was introduced into the cylindrical cell, and after a few minutes, it was taken out, and then the cell was dried in an oven. All measurements were carried out in the thermostated room at 298 ± 2 K. Absorption spectrum of Pd(II)–5-Br-PADAP complex was also measured by CLM method with V-570 UV/VIS/NIR spectrophotometer (Jasco).

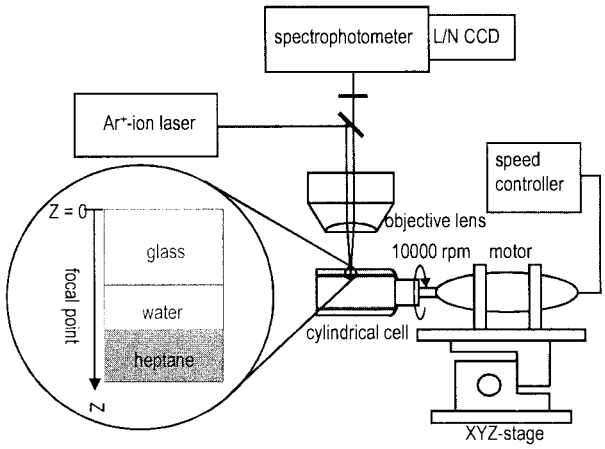


Figure 1. Schematic drawing of the apparatus for CLM-Raman microprobe spectroscopy.

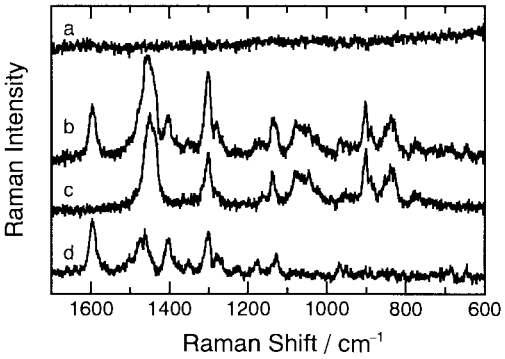


Figure 2. Raman spectra measured at the various focal points by CLM-Raman microprobe spectroscopy. Aqueous phase: $PdCl_2$ 3.3×10^{-4} mol dm^{-3}, HCl 0.1 mol dm^{-3}, pH 1.0; heptane phase: 5-Br-PADAP 1.7×10^{-5} mol dm^{-3}. The volumes of both phases were 0.300 cm^3. Z-position of the focal point: (a) 660 μm (the aqueous phase), (b) 740 μm (the interface), (c) 820 μm (the heptane phase). (d) the difference spectrum between the spectra in the presence of Pd(II)–5-Br-PADAP complex and the absence of the complex at Z = 740 μm.

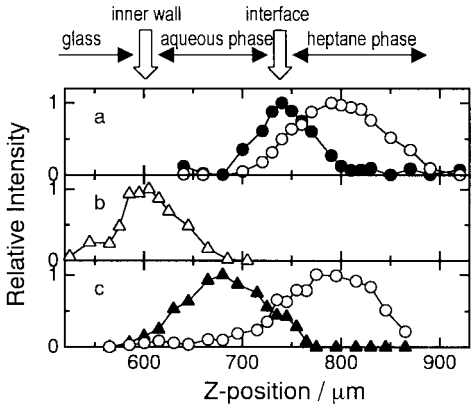


Figure 3. Depth profiles of the relative Raman intensities along the Z-axis under the various systems. ●: Pd(II)–5-Br-PADAP complex (1597 cm^{-1}), ○: heptane (902 cm^{-1}), △: MG (1617 cm^{-1}), ▲: 5-Br-PAPS (1623 cm^{-1}). (a) Experimental conditions were same in Figure 2. (b) MG was adsorbed at the inner surface of the cylindrical cell, and no solution. (c) 5-Br-PAPS 1.0×10^{-4} mol dm^{-3}, $NaClO_4$ 0.1 mol dm^{-3}, pH 6.8, in the aqueous phase. Each volume of the aqueous phase and the heptane phase was 0.300 cm^3.

From the result of batch experiments, we confirmed that Pd(II)–5-Br-PADAP complex was not extracted into the heptane phase. Therefore, we thought that the spectrum obtained by CLM method was ascribable to the interfacial complex.[6] The absorption spectrum of Pd(II)–5-Br-PADAP complex has a broad peak at 580 nm and the absorbance at 514.5 nm was enough for the resonance Raman spectroscopy. Figure 2a, 2b and 2c show Raman spectra observed using 0.300 cm^3 as the volumes of both phases at the three different focal points of Z = 660, 740 and 820 μm, which corresponded to the bulk aqueous phase, the interface and in the bulk heptane phase, respectively. Raman spectrum from the heptane phase (Z = 820 μm) was mainly that of heptane itself. Figure 2d shows the interfacial Raman spectrum (Z = 740 μm) which was obtained by subtracting the spectrum in the absence of the complex from that in the presence of the complex. This spectrum was due to Pd(II)–5-Br-PADAP complex formed at the heptane/water interface. The bands at 1597, 1473, 1403 and 1303 cm^{-1} were assigned to the benzene ring, pyridine ring, N=N, C–O stretchings, respectively.[7]

The relative Raman intensities of Pd(II)–5-Br-PADAP complex (1597 cm^{-1}) and heptane (902 cm^{-1}) were profiled along the Z-axis (Figure 3a). Moreover, the relative Raman intensities of MG (1617 cm^{-1}) that was adsorbed at the inner surface of the cylindrical cell and 5-Br-PAPS (1623 cm^{-1}) dissolved in the aqueous phase, which have the absorbance at 514.5 nm, were profiled for comparison (Figure 3b and 3c). The maximum in the Raman intensity of MG appeared at Z = 600 μm where was the position of the inner wall of the cell. On the other hand, the Raman intensity of 5-Br-PAPS, which existed in the aqueous phase, was distributed in the range of 600 – 740 μm with a broad maximum around 680 μm. The profile for Pd(II)–5-Br-PADAP complex was clearly different from both of MG and 5-Br-PAPS, having a maximum at Z = 740 μm (interface). The plots of the relative Raman intensities of MG and of Pd(II)–5-Br-PADAP complex in Figure 3 were fitted to Gaussian curve and the average values of Z-position were obtained as 605 ± 30 and 743 ± 26 μm, respectively. These values indicated the position of the inner surface and the heptane/water interface in each system. The relatively large deviations seemed to result from the vibration of the cylindrical cell under the high-speed rotation, because the depth resolution of Raman microscopy was obtained as 4 μm from the measurement of the dependency of the Raman intensity of silicon on the distance from the silicon surface to the focal point (data not shown). The average values gave the thickness of the aqueous phase under the CLM condition as 138 μm. This value was close to 154 μm, which value was calculated from the volume of the aqueous phase. These results confirmed that Pd(II)–5-Br-PADAP complex existed only at the heptane/water interface in the CLM system.

It was demonstrated in the present study that CLM-resonance Raman microprobe spectroscopy was very useful for the measurement of the interfacial species as well as the bulk species for the first time. This method allowed us to obtain the spatial distribution of the chemical species around the liquid–liquid interface. Moreover, in the present method, photo-breaching of the ligand and complex was reduced by the rotation of the cell; the decrease of resonance Raman intensity was less than 10% after the irradiation of 240 s. This method can be applied to the studies of various interfacial reaction systems such as complexation kinetics and redox reaction.

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