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Structure of metal ion-crown ether complexes on Au surface investigated by SEIRA and electrochemical measurements

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Host molecules such as crown ethers (CEs) hold alkali metal ions selectively. In this study, thiol derivatives of CEs are adsorbed on Au surface through Au-S chemical bonds (Figure 1), and IR spectra of $M^+ \cdot CE$ ($M = Li, Na, K, Rb,$ and Cs) complexes are measured by surface enhanced infrared absorption (SEIRA) spectroscopy. We discuss the structure of the complexes on the surface on the basis of the IR spectra. Moreover, the density of CEs on Au surface is determined by cyclic voltammetry.

Observed voltammogram shows the reduction desorption peak of thiol derivatives of 18-crown-6 (18C6) on Au surface. The surface coverage can be determined from the integral value of the desorption peak. The density of 18C6 molecules on Au surface is 1.4×10^{-12} mol/cm², which corresponds to an intermolecular distance of ~10 nm.

Figure 2 displays the SEIRA difference spectra of the $M^+ \cdot CE$ ($M = Na, Rb$) complexes on Au surface. The band at ~1100 cm⁻¹ corresponds to C-O stretching vibrations, and this band shape indicates that the frequency of C-O stretching shifts to low frequency due to the formation of the $M^+ \cdot CE$ complexes. Observed spectra show that the absorbance intensity of the Na⁺ complex is larger than that of the bare one, giving a positive peak at ~1100 cm⁻¹. In contrast, the Rb⁺ complex shows a negative peak, indicating that the absorption of the Rb⁺ complex is weaker than that of the bare one. This difference is caused by the orientation of the CE complexes on Au surface. In SEIRA spectroscopy, the IR absorption of vibrations whose dipole derivative is perpendicular to Au surface is enhanced more than the parallel one. Dipole derivatives of the C-O stretching vibrations are almost parallel to the crown cavity. Hence, the C-O stretching vibrations of the Rb⁺·15C5 complex are parallel to Au surface. In contrast, the Na⁺·15C5 complex is located perpendicularly. To confirm this assignment, we measured by IR spectra of bulk solutions, and the spectra show a similar sigmoidal feature for both of Na⁺ and Rb⁺. This result supports the explanation described above.

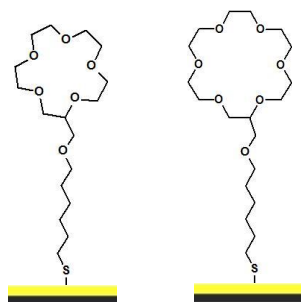


Figure 1. Thiol derivatives of CEs on Au

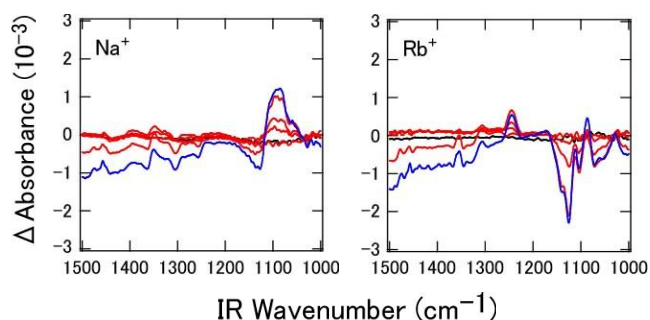


Figure 2. SEIRA difference spectra