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Development of Micelle-Mediated Sr(II) Fluorescent Analysis System

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Abstract : Fluorescent probes are useful for the selective detection of trace amount of ions and biomolecular imaging in living cells. Various kinds of metal ion-selective fluorescent compounds have been developed, and some compounds have been applied as effective metal ion-selective fluorescent probes. However, because competition between the ligand and water molecules for the metal ion constitutes a major contribution to the stability of a complex in aqueous solution, it is difficult to develop a highly sensitive, selective, and stable fluorescent probe in aqueous solution. The micelles, these are formed in the surfactant aqueous solution, provides a unique hydrophobic nano-environment for stabilizing metal-organic complexes in aqueous solution. Therefore, we focused on the unique properties of micelles to develop a new fluorescence analysis system. We have been developed a fluorescence analysis system for Sr(II) by using a Sr(II) fluorescent sensor, N-(2-hydroxy-3-(1H-benzimidazol-2-yl)-phenyl)-1-aza-18-crown-6-ether (BIC), and studied its complexation behavior with Sr(II) in micellar solution. We revealed that the stability constant of Sr(II)-BIC complex was 10 times higher than that in aqueous solution. In addition, its detection limit value was also improved up to 300 times by this system. However, the mechanisms of these phenomena have remained obscure. In this study, we investigated the structure of Sr(II)-BIC complex in aqueous micellar solution by combining use the extended X-ray absorption fine structure (EXAFS) and neutron reflectivity (NR) method to understand the unique properties of the fluorescence analysis system from the view point of structural chemistry. EXAFS and NR experiments were performed on BL-27B at KEK-PF and on BL17 SHARAKU at J-PARC MLF, respectively. The obtained EXAFS spectra and their fitting results indicated that Sr(II) and BIC formed a Sr(18-crown-6-ether)-like complex in aqueous micellar solution. The EXAFS results also indicated that the hydrophilic head group of surfactant molecule was directly coordinated with Sr(II). In addition, the NR results also indicated that Sr(II)-BIC complex would interact with the surface of micelle molecules. Therefore, we concluded that Sr(II), BIC, and surfactant molecule formed a ternary complexes in aqueous micellar solution, and at least, it is clear that the improvement of the stability constant in micellar solution is attributed to the result of the formation of Sr(BIC)(surfactant) complex.

Keywords : micell, fluorescent probe, neutron reflectivity, EXAFS
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