Research Group for Bioactinides Chemistry

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The research objectives of the group are to elucidate a chemical states change of actinides and lanthanides including nano-particles formation in the biological reaction environments. In the year of 2012, characterization of uranium and iodine in saline groundwater by SEC-UV-ICP-MS and adsorption of lanthnides ions on liposome have been studied.

Characterization of uranium and iodine in saline groundwater by SEC-UV-ICP-MS

We have elucidated that nano-particles of rare earth elements were developed on the cell surface of microorganisms [1,2]. The size and characteristics of nano-particles in the solution should be revealed. As a technique for investigating the size and characteristics of nano-particles in solutions, size exclusion chromatography (SEC) coupled on-line to ultravioletevisible (UV-Vis) detection and multi-element-specific detection methods such as inductively coupled plasma mass spectrometry (ICP-MS) has been used recently [3]. The advantage of this technique is that elements attached to or presented within the nano-particles are monitored through a simple procedure. In SEC-UV-Vis-ICP-MS analysis, nano-particles are separated through an SEC column on the basis of their size and consequent rate of elution; the separated colloids are then detected with a UV-Vis detector, and the elements associated with the nano-particles are detected by ICP-MS. In principle, all nano-particles are eluted with mobile phases from an SEC column. In practice, most packing materials (stationary phase) have a negative charge on the surface, and thus cations and cationic paricles adsorb on the packing materials while anions and anionic colloids are repelled. The anions and anionic nano-particles are also separated through an SEC column and appear on an SEC chromatograph. Using SEC-UV-Vis-ICP-MS analysis, we have investigated the chemical species of uranium and iodine in the saline groundwater collected near Horonobe, Japan, where an underground research laboratory (URL) has been under construction in sedimentary rock for research and development of technologies for the geological disposal of high level radioactive waste (HLW) [4]. Uranium is a representative actinide.

The saline groundwater was collected at a depth of about 500 m in Horonobe, Japan, where is rich in saline (Na 4900 ppm, Cl 7600 ppm), iodine (42 ppm), and methane gas. We analyzed the colloids and ions of this groundwater mainly by employing a SEC-UV-Vis-ICP-MS technique and focused on the speciation of uranium and iodine, both of which are of particular importance for radioactive waste disposal. For this purpose, the groundwater sample was introduced to SEC columns after being passed through a 0.45 mm filter but without further pretreatment, such as isolation of colloids.

The chromatographic profiles obtained with two different SEC columns were compared. We revealed that uranium present in the groundwater at several tens of ppt was associated with low molecular weight silica species with a neutral charge. The silica species were virtually free of metal elements such as Na, K, Mg, Ca, and Al. This study also found that almost all of the iodine in the groundwater was iodide (I^-). The groundwater contained an unidentified organic colloid that was not a carrier for the radioactive waste-relevant elements Se, Sr, I, Cs, Th, and U.

Adsorption of lanthnides ions on liposome

The surface of microorganisms, i.e. the biomembrane, is composed mainly of phospholipids and membrane proteins. The phospholipids have a phosphate group as shown in Fig. 1. Here we used a simplified model system, liposome to investigate the understanding the adsorption behavior of lanthanide ions on a phospholipid membrane without any biological activity.

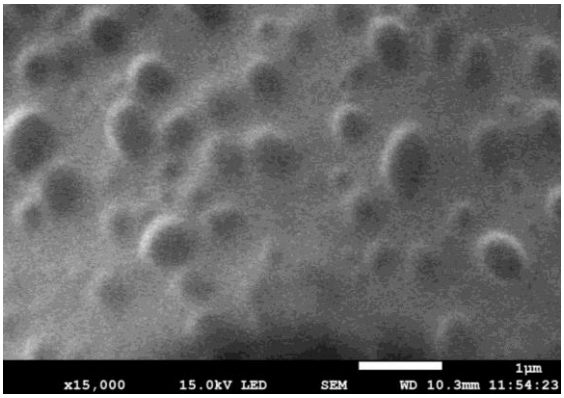

Fig. 1 SEM image of the liposome in ionic liquid. The oval balls in the image are the liposome.

The adsorption behavior of lanthanide ions (except for Pm) on liposomes composed of phosphatidylcholine and cholesterol was examined to understand the interaction between lanthanide ions and the phosphoryl moiety of phospholipids [5]. The adsorption amount of lanthanide ions enhanced with an ascent in pH in the weakly acidic condition. Selective adsorption with the local maximum at the Eu^{3+} ion and local minimum at the Er^{3+} ion was observed, similar to the selective adsorption of the bacterial cell surface, but different from that of synthetic Ln resin, which is composed of di(2-ethylhexyl)orthophosphoric acid. These results indicate that the adsorption of lanthanide on the phospholipid is not derived by simple adsorption on orthophosphate functional groups, but by the composition and molecular structure of the phospholipid. Our results strongly suggest that liposomes can be used as a simple biomembrane model without any biological activity for the study of adsorption of lanthanide ions.

References

[1] M. Jiang, *et al*., Chem. Geol., **277**, 61(2010).
[2] M. Jiang, *et al*., Geochim. Cosmochim. Act., 93, 30(2012).
[3] B. B. M. Sadi, *et al*., J. Enviorn. Monit., 4, 1010(2002).
[4] N. Kozai, *et al*., Water Res., 47, 1570 (2013).
[5] S. Yamasaki, et al., Chem. Lett., in press.