

EXAFS Investigation of Adsorption and Separation Phenomena of Metal Ions in Organic Resin - Specific Coordination Properties in Micropores

Organic resin extractants, such as ion-exchange resins, are simple but powerful materials for separating, removing, and purifying chemical substances. Hence, they are widely employed not only in basic and applied research but also in various industrial fields. The practical application of organic resin extractants utilizes a unique property of the solid-liquid interface formed between the resin surface and the solution phase. That is, the chemical environment formed at the resin-solution interface is significantly different from that in bulk solution. For instance, the hydration of ions is weakened and, consequently, other complexation is enhanced in organic resins. This special effect in organic resins has been recognized for a long time; nevertheless, it has still not been sufficiently substantiated by experimental evidence because of the experimental difficulty in investigating such a limited minimal field in the resin. Accordingly, the chemical phenomena occurring inside organic resins remain conjectural, and they are still open to debate for the most part. To investigate the chemical phenomena in resins, extended X-ray absorption fine structure (EXAFS) spectroscopy is a very powerful tool. This technique is highly element-selective and can qualitatively distinguish different chemical species such as bulk species in the solution phase and adsorbed species formed at the resin-solution interface. In this study, we employ EXAFS spectroscopy to investigate the adsorption and separation phenomena of lanthanides (Ln(III)) by a tertiary pyridine resin [1]. The tertiary pyridine resin (Fig. 1) is an effective extractant for the separation of trivalent actinides (An(III)) and Ln(III) and, interestingly, its adsorption and separation behavior depends on the counter anions in the solute [2].

The tertiary pyridine resin used in this study was synthesized by the copolymerization of 4-vinylpyridine and *m/p*-divinylbenzene. The cross-linking and porosity of the resin were reduced as much as possible (i.e., 10 wt% cross-linking with 20 vol%

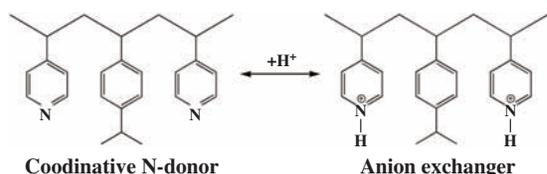


Fig. 1. Structure of tertiary pyridine resin and its protonation reaction.

porosity) to increase the number of pyridine functional groups and to decrease the volume of solution in the resin. The synthesized resin was washed, dried, and equilibrated with HCl/MeOH or HNO₃/MeOH solution containing Ln(III). After achieving the adsorption equilibrium, the resin was filtered to remove excess solution and placed in a polystyrene cuvette or polyethylene bag for the EXAFS measurement.

The *K*-edge X-ray absorption spectra of Ln(III) were collected at the high-energy undulator beamline BL11XU using a Si(311) monochromator. The *L*_{III}-edge X-ray absorption spectra of Ln(III) always suffer from the multielectron excitation effect (MEE), which causes another oscillation in their EXAFS spectra [3], which deteriorates the accuracy of data analysis. However, there is no disturbance due to MEE in the *K*-edge region. Therefore, we can obtain more reliable results by measuring the *K*-edge spectra. All the measurements were performed in transmission mode at ambient temperature.

Figure 2 shows the Fourier transforms (FTs, = radial structural functions) of the *K*-edge EXAFS spectra for La(III) in different chemical environments containing chloride ions (Cl⁻). The results of curve fitting reveal that La(III) ions are hydrated by 9-10

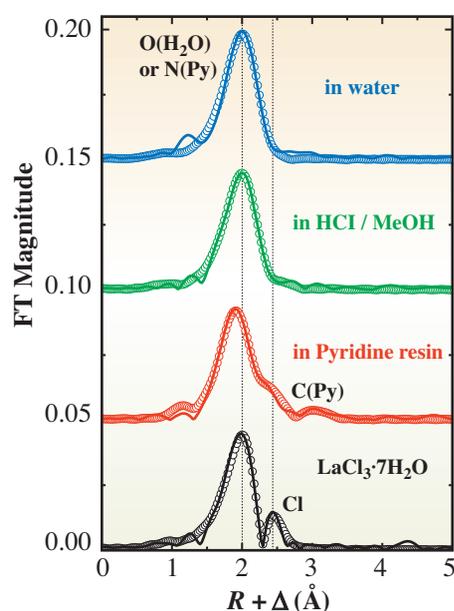


Fig. 2. Fourier transforms of La *K*-edge EXAFS spectra for La(III) in water, in HCl/MeOH mixed solution, adsorbed in the tertiary pyridine resin from HCl/MeOH solution, and in hydrated LaCl₃ crystal: solid lines; experimental data, circles; theoretical fit. Solvent composition of HCl/MeOH mixture: 6.0 M HCl (solute)/50 vol% MeOH in solvent.

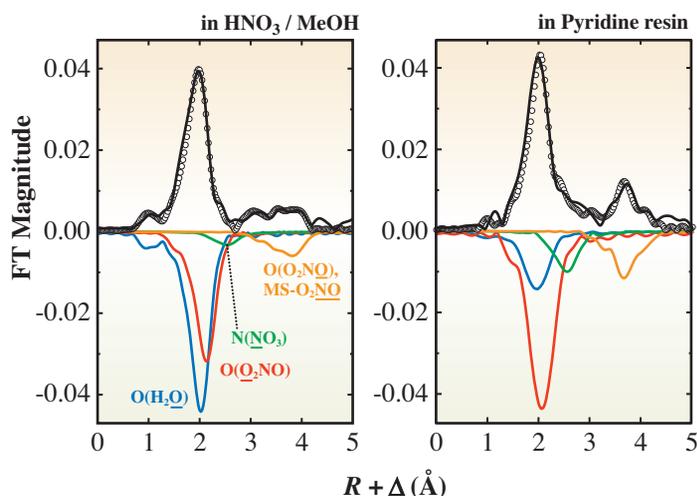


Fig. 3. Fourier transforms of Nd *K*-edge EXAFS spectra for Nd(III) in HNO₃/MeOH mixed solution and adsorbed in the tertiary pyridine resin from HNO₃/MeOH solution: solid lines; experimental data, circles; theoretical fit. Solvent composition of HNO₃/MeOH mixture: 6.8 M HNO₃ (solute) / 50 vol% MeOH in solvent.

water molecules in water and HCl / MeOH solution, while the hydration becomes weaker and, consequently, the Cl⁻ complexation is enhanced in the resin phase. Also, the FT for the resin sample shows an additional distinguishable peak at around $R + \Delta = 3.0 \text{ \AA}$, which corresponds to the single scattering of C atoms of directly coordinating pyridine groups. This suggests that the pyridine groups in the resin directly

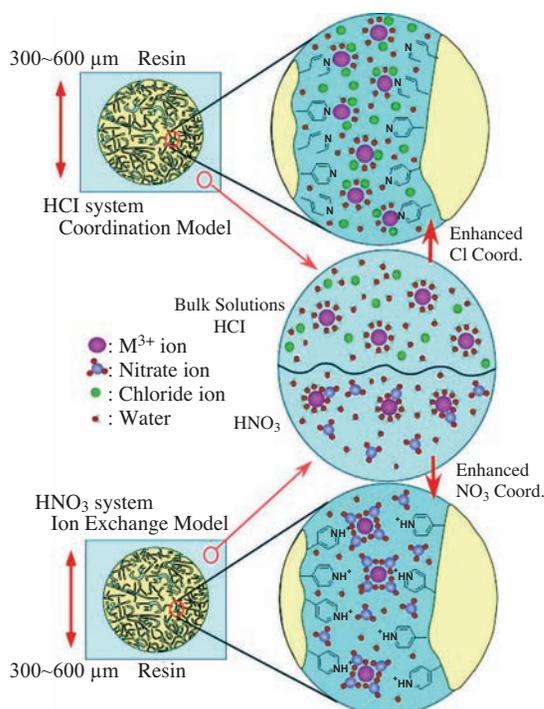


Fig. 4. Proposed adsorption mechanism of An(III)/Ln(III) ions by the tertiary pyridine resin.

coordinate to Ln(III) ions in the chloride solution system. In the HSAB theory by Pearson *et al.* [4], pyridine is classified as a soft donor ligand. In fact, soft donor ligands bind An(III) more strongly than Ln(III) and exhibit high selectivity for An(III) over Ln(III). Therefore, the observed An(III)/Ln(III) intergroup separation by the pyridine resin in chloride solutions [2] is considered to originate from the direct interaction of pyridine groups with An(III) and Ln(III) ions in the resin phase.

On the other hand, Fig. 3 shows the FTs of the *K*-edge EXAFS spectra for Nd(III) in HNO₃ / MeOH mixed solution and that adsorbed in the pyridine resin. The results of curve fitting indicate that Nd(III) ions are coordinated by two nitrate ions (NO₃⁻) with a bidentate mode in the solution phase, forming a cationic nitrate complex of [Nd(NO₃)₂(H₂O)_{*m*}]⁺, whereas the nitrate complexation is further enhanced in the resin phase, resulting in the formation of an

anionic nitrate complex, [Nd(NO₃)₄(H₂O)_{*n*}]⁻. The actual adsorption and separation behavior of An(III)/Ln(III) by the pyridine resin in nitrate solutions differs from that in the previous chloride solution system [2] but it is analogous to the behavior of that by anion exchange resins [1]. In fact, as illustrated in Fig. 1, the tertiary pyridine resin can also function as an anion exchanger by protonating pyridine groups. Considering these facts, we can conclude that the adsorption and separation of An(III)/Ln(III) in the nitrate solution system is caused by an “anion exchange” interaction, in which the protonated pyridine groups interact with the negatively charged metal-nitrate complexes. The proposed adsorption mechanism of An(III)/Ln(III) ions by the tertiary pyridine resin is illustrated in Fig. 4.

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