

## Structural study of Ni complexes in the solvent extraction system

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### Introduction

The recently growing demand for electroless nickel plating has increased the need for the recovery of nickel. We are now studying the nickel(II) extraction properties using LIX84I (2-hydroxy-5-nonylacetophenone oxime) and D2EHPA (bis(2-ethylhexyl) phosphoric acid) [1]. However, the structures of their extracted complexes are still obscure. In this study, we have investigated the coordination structures of nickel(II) complexes with LIX84I and D2EHPA by the XAFS method.

### Experimental

The Ni-LIX84I (Ni-L) and Ni-D2EHPA (Ni-D) solution complexes were prepared by solvent extraction: LIX84I or D2EHPA in *n*-dodecane – NiSO<sub>4</sub> solution adjusted to the appropriate pH value using NaOH solution. The Ni-phthalocyanine (Ni-Pc) and Ni aqueous solution (Ni-Aq) and samples were prepared by pressing the Ni-Pc solid (Aldrich) and by dissolving NiCl<sub>2</sub> into water, respectively. All of the XAFS spectra were measured in transmission mode at the BL-7C station in the KEK-PF. The experimental data were analyzed by WinXAS Ver. 3.0 [2] and fit using theoretical phase and amplitudes calculated from the program FEFF 8 [3].

### Results and Discussion

Figure 1 shows the Ni K-edge XANES spectra of the Ni-L, Ni-D, Ni-Aq and Ni-Pc samples. The spectrum of the Ni-D complex is significantly different from that of the Ni-L one but similar to that of Ni-Aq. Since the Ni(II) aqueous solution has six-coordinated Ni ions [4], the Ni(II) ion in the Ni-D complex would be octahedral. The Ni-L complex shows almost the same spectrum as the Ni-Pc complex. In the Ni-Pc complex, the Ni(II) ion is

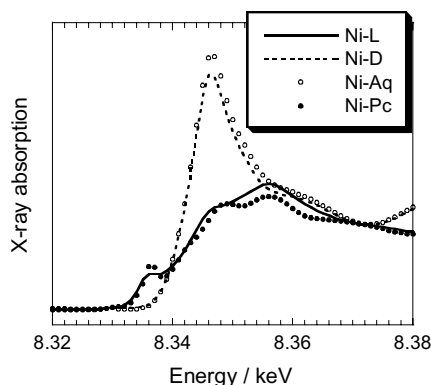


Fig. 1 Ni K-edge XANES spectra.

coordinated with nitrogen atoms in a square planar geometry [5]. Additionally, these XANES spectra have a distinct peak at ~8335 eV, which is attributed to the  $1s \rightarrow 4p_z$  transition. This peak is characteristic of a square planar metal complex [6]. Therefore, the Ni(II) ion in the Ni-L complex would be square planar.

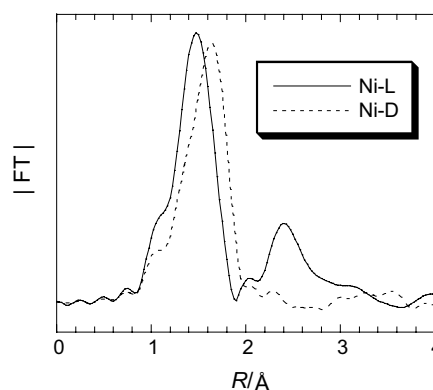


Fig. 2 Fourier transforms of Ni K-edge EXAFS spectra. The phase shifts are not corrected.

The Fourier transforms of the Ni K-edge EXAFS spectra are shown in Fig. 2. The first peak in the spectrum of the Ni-L corresponds to the Ni-O/N(oxime) correlations. In the spectrum of the Ni-D, the first peak appears at a larger *R*. This peak corresponds to the Ni-O(phosphoric acid or water) correlations. The results of the curve fits for the first peak indicate the presence of 4.1(6) O/N atoms at 1.85(1) Å for the Ni-L and 5.6(9) O atoms at 2.04(1) Å for the Ni-D. Their coordination number is consistent with the XANES data; square planar for the Ni-L and octahedral for the Ni-D. The difference in the bond distance between the Ni-L and Ni-D (0.19 Å) is similar to that of the ionic radius between the four and six coordination of Ni(II) (0.14 Å) [7].

### References

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