

Coordination property of the Ni–Phenolic Oxime–Organophosphoric acid complexes in solution

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Introduction

The rate of Ni(II) extraction with LIX84I (2-hydroxy-5-nonylacetonophenone oxime) is significantly accelerated by adding a small amount of D2EHPA (bis(2-ethylhexyl) phosphoric acid) [1]; however, the detailed role of D2EHPA remains unclear. In this study, we investigated the structure of the extracted complexes in the Ni–LIX84I–D2EHPA extraction system, and the effect of the D2EHPA addition on the extraction rate and the coordination geometry of Ni(II) by XAFS measurements.

Experimental

The Ni–LIX84I–D2EHPA solution complexes were prepared by solvent extraction: LIX84I and/or D2EHPA in *n*-dodecane–NiSO₄ solution adjusted to the appropriate pH value using NaOH solution. All of the XAFS spectra were measured in transmission mode at the BL-7C and 10B 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

The variation in the Ni(II) coordination structure with the addition of D2EHPA to LIX84I was investigated by changing the molar ratio of [D2EHPA]/[LIX84I] (0 (Ni-L), 0.1, 0.2, 0.5, 1, [LIX84I] = 0 (Ni-D); [D2EHPA]+[LIX84I] = 0.6 M; [Ni]_{org} = 0.1 M) in the organic phase during the extraction. Figures 1A and 1B show the Ni K-edge XANES and the FTs of the *k*³-weighted EXAFS spectra of the Ni–LIX84I–D2EHPA system, respectively. In Fig. 1A, the peak corresponding to 1s→4p_z transition (~8339 eV) decreases with an increase in the D2EHPA concentration, while the peak around 8349 eV increases. This means that the Ni(II)

coordination changes from square-planar to octahedral [4]. In Fig. 1B, with the increasing D2EHPA concentration, the peak around 1.5 Å relating to the Ni–O/N correlation in the square-planar Ni–L complex (*N*: 4.1(6), *r*: 1.85(2) Å) shrinks, and the intensity of a new peak at ~1.7 Å increases. The peak position (~1.7 Å) is similar to that of the first shell in the Ni–D complex (*N*: 5.6(9), *r*: 2.04(2) Å). Therefore, this new peak can be assigned to the correlation in the inner coordination sphere of an octahedral complex. This is consistent with the XANES result.

In the 0.5 M LIX84I system, the Ni(II) extraction is very slow. In contrast, the addition of D2EHPA (0.5 M LIX84I–0.05 M D2EHPA system) accelerates the extraction; the shaking time to obtain the nearly 100% extraction is reduced from 80 min to 40 min. However, the XAFS spectra are virtually the same between two samples; thus, the extracted complexes consist mainly of the Ni–L complex. Taking into account the large difference in the extraction rates between two systems and the predominance of the Ni–L complex in the extracted complexes, the acceleration effect would not result from the formation of the complexes that can be rapidly extracted. Therefore, D2EHPA can play the role of a phase transfer catalyst in the Ni(II)–LIX84I system.

References

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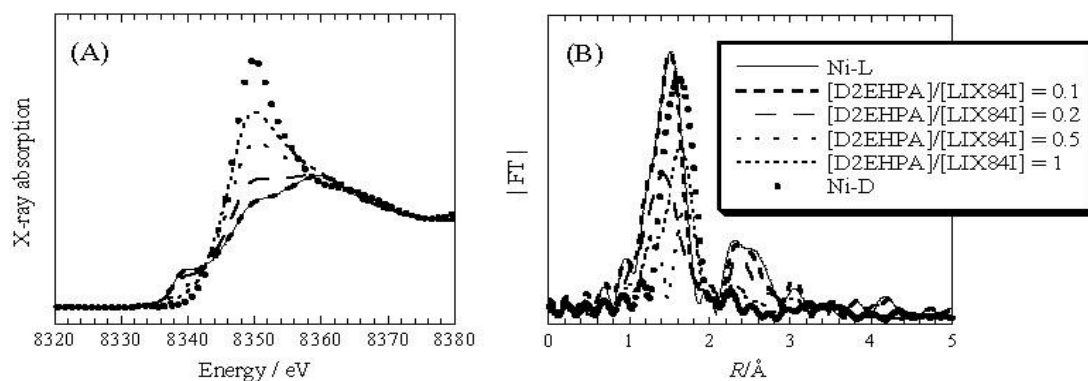


Fig. 1 (A) Ni K-edge XANES spectra and (B) the FTs of the *k*³-weighted EXAFS spectra of the Ni-L, Ni-D and Ni–LIX84I–D2EHPA solution ([D2EHPA]/[LIX84I] = 0.1–1). The phase shifts are not corrected.