Rh and Sn K-edge XAFS analysis of Rh-Sn-Cl complexes in hydrochloric acid solutions

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Introduction

The Rh-Sn-Cl complex in HCl solutions has attracted interest in metal separation studies, since the addition of $SnCl_2$ to Rh in HCl solutions markedly accelerates the Rh extraction from the aqueous to organic phases [1]. However, detailed structural parameters of the Rh-Sn-Cl complex in solution have been limited. This work investigated the coordination structure of the Rh-Sn-Cl complexes in HCl solutions based on Rh and Sn K-edge XAFS measurements.

Experimental

Sample solutions were prepared by adding $SnCl_2$ to Rh in 3 M HCl solutions ([Rh]=0.1M). All of the XAFS spectra were measured in transmission mode at the NW-10A station in the PF-AR. The experimental data were analyzed by WinXAS Ver. 2.3 [2] and fit using theoretical phase and amplitudes calculated from the program FEFF 8.2 [3]. The amplitude reduction factor, S_0^2 was refined by the curve fits to the Rh^{3+} and Sn^{4+} solutions; their coordination number is known to be six. These values were found to be 0.89 for the Rh^{3+} and 1.0 for the Sn^{4+} and held constant using them during the fits of the Rh and Sn K-edge XAFS, respectively. The coordination number, CN, the bond distance, r, Debye-Waller factor, σ^2, and the shift in threshold energy, ΔE_0, were allowed to vary in the fit.

Results and Discussion

Figure 1 shows the raw k^3-weighted Rh and Sn K-edge EXAFS spectra and the corresponding Fourier transforms (FT) of the Rh-Sn-Cl complex in 3 M HCl solutions ([Sn]/[Rh] = 1.0, 2.8). In the FT of the Rh K-edge EXAFS (1, 2), two significant peaks appeared at ~1.9 Å and ~2.3 Å. The peak at ~1.9 Å corresponds to the Rh-Cl correlation. This peak shrinks with an increase in the [Sn]/[Rh] value (1.0→2.8), while the peak at ~2.3 Å, related to the Rh-Sn correlation, increases. This means that the Cl⁻ in the inner sphere of Rh is replaced by the Sn. The obtained CN values (2.7(3) Cl⁻ and 2.7(5) Sn) at [Sn]/[Rh] = 2.8 are in good agreement with the ¹¹⁹Sn NMR result [4], which showed that the $[RhCl_3(SnCl_3)_3]^{3-}$ is dominant at [Sn]/[Rh] ≈ 3. The curve fits to the Sn K-edge EXAFS spectrum indicate the presence of 1.1(3) Rh at 2.465(14) Å and 3.2(5) Cl⁻ at 2.332(4) Å. This verifies that the Sn predominantly exists as the $[RhCl_{6-x}(SnCl_3)_x]^{3-}$ species ($x \le 3$) at [Sn]/[Rh] ≤ 3 [4]. The bond distance of the Sn-Rh correlation (2.465(14) Å) is very similar to that

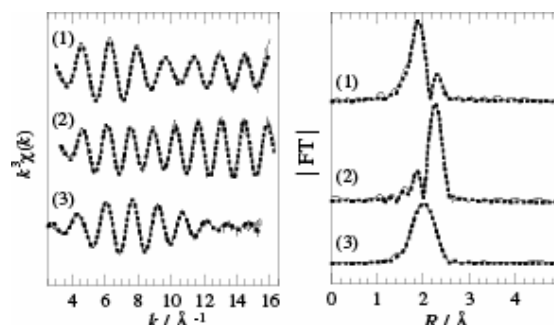obtained from the Rh k-edge EXAFS (2.453(13) Å), indicating that the fitting quality is high.

Fig 1. Rh and Sn K-edge EXAFS spectra (left) and the corresponding FTs (right) of the Rh-Sn complex in 3 M HCl solutions. (1) (Rh K-edge) [Sn]/[Rh] = 1.0, (2) (Rh K-edge) [Sn]/[Rh] = 2.8, (3) (Sn K-edge) [Sn]/[Rh] = 1.0. The phase shifts are not corrected. Experimental data (solid line), theoretical fit (dashed line).

Table 1: Structural parameters

		CN	r / Å	$\sigma \times 10^{-3}$ /Å^2	ΔE_0 / eV	R^a
(1)	Rh-Cl	4.3(3)	2.321(7)	2.9^b	3.6(3)	10
	Rh-Sn	1.1(3)	2.465(14)	3.9(14)		
(2)	Rh-Cl	2.7(3)	2.369(15)	2.9^b	4.9(8)	7.9
	Rh-Sn	2.7(5)	2.492(4)	2.9(3)		
(3)	Sn-Cl	3.2(5)	2.332(4)	3.3(9)	12(1)	4.9
	Sn-Rh	1.1(3)	2.453(13)	3.0^b		

Estimated errors in parentheses; ^{a} residual: R = $\Sigma|k^3\chi(k)$obs-$k^3\chi(k)$calc$|/\Sigma|k^3\chi(k)$obs$|\times 100(\%)$; ^{b} fixed parameter.

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