10B/2002G234

Extraction and structural properties of rhodium-tin complexes in solution

Hirokazu NARITA*[1], Mikiya TANAKA[1], Tsuyoshi YAITA[2], Yoshihiro OKAMOTO[2]
[1] Research Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan
[2] Department of Materials Science, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan

Introduction

The addition of $SnCl_2$ to Rh in HCl solution markedly accelerates the Rh extraction from the aqueous to organic phases[1]. Rh(III) complexes in HCl solutions are reduced to Rh(I) by the oxidation of Sn(II) to Sn(IV). However, detailed extraction properties in this system have not been obtained yet. This work investigated the extraction mechanism of Rh and Sn using *N*,*N*-dioctyl hexanamide (DOHA) by XAFS measurements.

Experimental

Aqueous sample solutions were prepared by adding $SnCl_2$ to Rh in 1 M HCl solutions ([Sn(II)]/[Rh]=0 or 12; [Rh]=0.1M). The DOHA complex was prepared by solvent extraction from the [Sn(II)]/[Rh]=12 – 1 M HCl solution. All of XAFS spectra were measured in transmission mode at the BL-10B station in the KEK-PF. The experimental data were analyzed by WinXAS Ver. 2.3 [2] and fit using theoretical phase and amplitudes calculated from the program FEFF 8 [3]. The $[RhCl_5(H_2O)]^{2-}$ anion [4] and $[Rh(SnCl_3)_4(SnCl_4)]^{5-}$ anion [5] were used for the FEFF calculations as model compounds. The amplitude reduction factor, S_0^2, was held fixed at 0.9 in all the fits. 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 EXAFS spectra and the corresponding Fourier transforms of (a) Rh in 1 M HCl solution (in the absence of Sn(II)), (b) [Sn(II)]/[Rh]=12 – 1 M HCl solution, and (c) the DOHA complex. In the Fourier transform for the Rh in 1 M HCl solution, a broad peak appears, which corresponds to the Rh-O/-Cl correlations. The curve fits indicate the presence of 1.4(9) water molecules at 2.06(2) Å and 4.6(8) Cl^- ions at 2.33(1) Å. In the presence of Sn(II) (spectrum (b)), another peak appears at the larger *R* and the peak for the Rh-O/-Cl correlations disappears, suggesting that the inner coordination sphere of the Rh in the [Sn(II)]/[Rh]=12 – 1 M HCl solution consists of Sn. The coordination number of the Rh-Sn correlation is 5.3(6). Since the XANES results showed that the Rh in this solution is monovalent, the $[Rh(SnCl_3)_5]^{4-}$ complex should be the dominant species. The EXAFS data and the corresponding FTs for the DOHA complex are very similar to those for the [Sn(II)]/[Rh]=12 – 1 M HCl solution, and thus the curve fitting results are almost the same (4.7(8) Sn at 2.56(1) Å). These structural parameters indicate that the aqueous phase complex anion is extracted into the organic phase without any structural changes. Consequently, the extraction mechanism with excess Sn(II) could be determined to be an ion-pair formation with the protonated DOHA.

$$[Rh(SnCl_3)_5]^{4-} + 4[H{\cdot}DOHA]^+ \leftrightarrow [Rh(SnCl_3)_5(H{\cdot}DOHA)_4] \qquad (1)$$

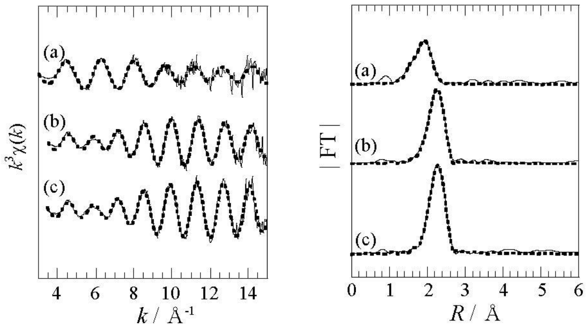

Fig 1. Rh K-edge EXAFS spectra (left) and the corresponding FTs (right) of (a) Rh in 1 M HCl solution, (b) [Sn(II)]/[Rh]=12 – 1 M HCl solution and (c) the DOHA complex. The phase shifts are not corrected. Experimental data (solid line), theoretical fit (dashed line).

Table 1: Structural parameters

		CN	*r*/Å	σ^2(x10^{-3})/ Å^2	ΔE_0/eV	R^a
(a)	Rh-O	1.4(9)	2.06(2)	0.21(10)	3.3(5)	2.8
	Rh-Cl	4.6(8)	2.33(1)	2.4(5)		
(b)	Rh-Sn	5.3(6)	2.54(1)	4.1(7)	2.3(5)	4.2
(c)	Rh-Sn	4.7(8)	2.56(1)	2.8(9)	6.4(9)	8.9

[a] residual: $R=\Sigma\,|k^3\chi\,(k)obs-k^3\chi\,(k)calc|/\Sigma|k^3\chi\,(k)obs|$

References

[1] E. Benguerel et al., "Solvent Extraction in the Process Industries", Vol.1, Elsevier Applied Science, Amsterdam (2000).
[2] T. Ressler, J. Synch. Rad., **5**, 118 (1998).
[3] A. L. Ankudinov et al., Phys. Rev. B **58**, 7565 (1998).
[4] P. G. Bugli et al., Acta Cryst. B**37**, 1394 (1981).
[5] T. Kimura et al., J. Solid State Chem., **34**, 369 (1980).

* hirokazu-narita@aist.go.jp