

Effect of tin concentration on the inner coordination structure of rhodium complexes in HCl solution

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Introduction

The addition of stannous chloride to Rh^{3+} in HCl solution drastically improves Rh extraction [1]. In order to develop this method for use with industrial-scale solutions, a speciation of Rh under different conditions in terms of selecting appropriate extractants or resins is important, since the separability of Rh depends strongly upon the structure of the Rh complex ions. In this study, structural changes of Rh solution complexes as a function of Sn concentration were investigated with the XAFS method.

Experimental

Sample solutions were prepared by adding SnCl_2 to Rh in 3 M HCl solutions ($[\text{Rh}] = 0.1 \text{ M}$). 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+} solutions; its coordination number is known to be six. This value was found to be 0.89 for the Rh^{3+} and held constant using it during the fits of the Rh 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

In the Rh–Sn complexes in 3 M HCl solution, the dominant species at $[\text{Sn}]/[\text{Rh}] = 0$, $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ (Rh–O: $CN = 0.7(3)$, $r = 2.06(3) \text{ \AA}$, $\sigma^2 = 0.0004 \text{ \AA}^2$; Rh–Cl: $CN = 5.3(3)$, $r = 2.321(8) \text{ \AA}$, $\sigma^2 = 0.0034 \text{ \AA}^2$; $\Delta E_0 = 5.4$), becomes the Rh–Sn complexes, $[\text{RhCl}_x(\text{H}_2\text{O})_y(\text{SnCl}_3)_{6-x-y}]^{3-}$ ($1 \leq x \leq 5$, $0 \leq y \leq 1$), with an increase in the $[\text{Sn}]/[\text{Rh}]$ value, and then the $[\text{Rh}(\text{SnCl}_3)_5]^{4+}$ complex (Rh–Sn: $CN = 5.1(9)$, $r = 2.510(7) \text{ \AA}$, $\sigma^2 = 0.0032 \text{ \AA}^2$, $\Delta E_0 = 7.4$) is exclusively formed at $[\text{Sn}]/[\text{Rh}] = 12.4$.

The distribution of the $[\text{RhCl}_x(\text{SnCl}_3)_{6-x}]$ ($0 \leq x \leq 5$) and $[\text{Rh}(\text{SnCl}_3)_5]^{4+}$ complexes in 3 M HCl as a function of the $[\text{Sn}]/[\text{Rh}]$ value was given only in the ^{119}Sn NMR study [4]. Therefore, the number of Sn in the inner coordination sphere of Rh in the paper was compared with that obtained in this study. Figure 1 shows the plots of the CN of Sn and total CN (Sn + O + Cl) in the inner coordination sphere of the Rh versus the $[\text{Sn}]/[\text{Rh}]$ value.

The CN of Sn is almost the same for the two methods at $[\text{Sn}]/[\text{Rh}] \leq 4$, while a slight difference arises above that point. The NMR study indicates that the $[\text{Rh}(\text{SnCl}_3)_5]^{4+}$ complex is the exclusive product at $[\text{Sn}]/[\text{Rh}] = 5$. On the other hand, the presence of Rh–Cl coordination at $4.5 \leq [\text{Sn}]/[\text{Rh}] \leq 6.4$ is obvious from the curve-fitting results of the Rh K-edge EXAFS. Since the metal concentration in the present study was 100 times greater than that generating the NMR data, despite the same hydrochloric acid concentration (3 M), some discrepancy between the two sets of results is not surprising.

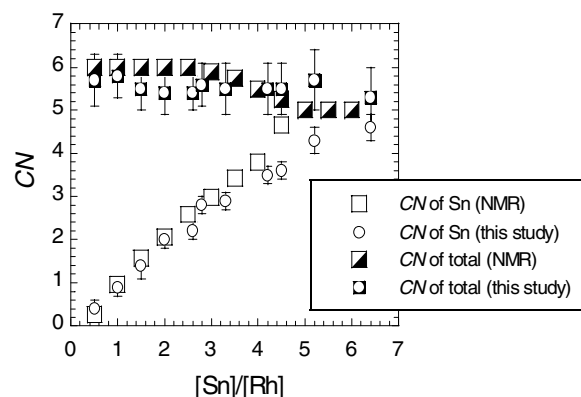


Fig. 1. Relationship of the CN of Sn and the total CN (Sn + O + Cl) in the inner coordination sphere of the Rh to the $[\text{Sn}]/[\text{Rh}]$ value. NMR data from ref 4.

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References

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