

X-ray absorption spectroscopy investigation of the local chemical interactions between Hg and self-assembled monolayers on mesoporous supports

K.M. Kemner[•], X. Feng[•], J. Liu[•], G.E. Fryxell[•], L.-Q. Wang[•],
A.Y. Kim[•], M. Gong[•], and S. Mattigod[•]

[•]Environmental Research Division, Argonne National Laboratory, Argonne, IL 60439 USA

[•]Pacific Northwest National Laboratory, Richland, WA 99352 USA

Introduction

The synthesis of mesoporous silica has greatly expanded the possibilities for the design of open-pore structures. Because of their large surface area, well defined pore size, and pore shape, these materials have great potential in environmental and industrial processes. However, many applications (e.g., adsorption, ion exchange, catalysis, and sensing) require the materials to have specific attributes such as binding sites, stereochemical configuration, charge density, and acidity [1]. Functional groups (thiol groups in this particular material's case) have been introduced to the pore surface of mesoporous silica as the terminal groups of organic monolayers. The resulting material, called functionalized monolayers on mesoporous supports (SAMMS), is a useful environmental remediation agent because it can efficiently remove mercury and other heavy metals (such as lead and silver) from contaminated aqueous and organic solutions. Mercury and heavy-metal contamination is a serious problem at waste-contaminated sites.

Methods and Materials

To elucidate the specific chemical interactions between Hg and the SAMMS material, x-ray absorption spectroscopy (XAS) measurements at the Hg LIII absorption edge were made on three Hg-laden SAMMS samples, as well as on HgS, HgO, and HgI₂ powder standards. Some of the solutions used to introduce the Hg to the SAMMS material simulated radioactive wastes in holding tank L at the U.S. Department of Energy's Savannah River Site (SRS) or nonradioactive vacuum pump oil waste from the SRS tritium facilities. Single-phase solutions of monomethyl mercury, mercury iodide, and mercury nitrate were also introduced to the SAMMS material. More details of the sample preparation have been described elsewhere [2].

The XAS experiments at the Hg LIII absorption edge were performed on beamline X18B at the National Synchrotron Light Source (NSLS) and at the Materials Research Collaborative Access Team (MR-CAT) insertion device beamline at the Advanced Photon Source (APS). Measurements of tape mounts of HgS, HgI₂, and HgO powder standards were made in the transmission mode. Measurements on the SAMMS samples were made in the fluorescence mode by utilizing the Stern-Heald configuration [3] and in the transmission mode. The absorption signal of the HgS standard was monitored simultaneously with an additional ion chamber on the down side of the experiment to ensure consistent determination of incident x-ray energies, thus allowing the investigation of the valence state of Hg in the SAMMS. For the standards and the SAMMS materials, multiple sample thicknesses were measured to investigate

the uniformity of the prepared samples. In all cases, the edge-step height scaled linearly with the sample thickness. The linearity of the detector-sample experimental setup [4] was tested when a new sample was mounted for an XAS measurement. These tests indicated less than 0.15% nonlinearity in the response between the ionization chambers with 50% attenuation of the incoming x-ray beam. Data reduction and analysis were performed in adherence to recommended procedures [5].

Results

Comparison of the Hg XANES region for the SAMMS samples and the HgS and HgO standards (valence II) indicated that Hg was in the same valence state in all samples. Figure 1a illustrates the single-scan quality of the $\chi(k) \cdot k^3$ data for the SAMMS samples investigated. Figure 1b shows the Fourier transform (1.2–11.5 Å⁻¹ with Hanning windows of 0.25 Å⁻¹) of the k^3 -weighted data in Figure 1a.

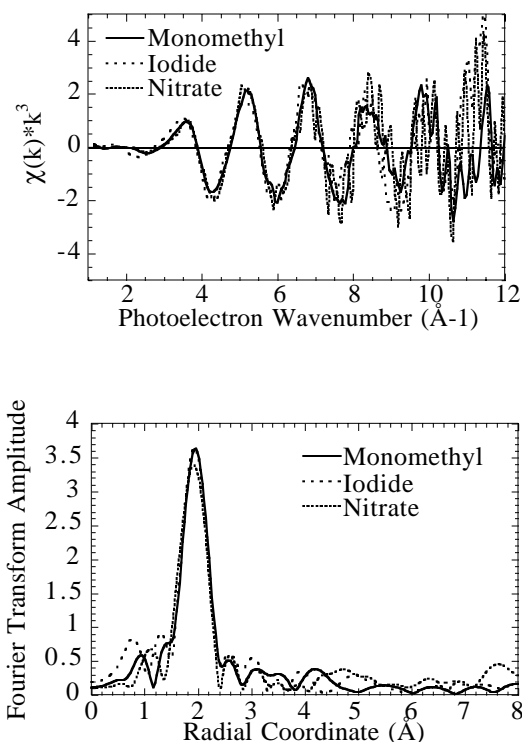


Figure 1: (a) $\chi(k) \cdot k^3$ data for dried SAMMS material after introduction to HgI₂, CH₃Hg, and HgNO₃ solutions. (b) Fourier transform of $\chi(k) \cdot k^3$ data (1.2–11.5 Å⁻¹).

Investigation of the $\chi(k) \cdot k^3$ data in Figure 1a or the Fourier transform of the $\chi(k) \cdot k^3$ data in Figure 1b indicates that the average local chemical environment surrounding the Hg in each of the SAMMS samples studied is very similar

For the Fourier-filtered data range (1.1–2.5 Å⁻¹, uncorrected for electron phase shift), and for the fitting range (2.8–11.5 Å⁻¹) used here, the maximum number of fit parameters that may vary at one time is more than seven [6]. A two-shell fit to the data (one Hg-S shell and one Hg-O shell), with the coordination numbers, radial distances, and x-ray absorption fine structure (XAFS) Debye-Waller factors allowed to vary during the fit, resulted in a six-variable fit. Therefore, a two-shell approach may be used to fit the data. The most realistic, best fit to the experimental data was identified by monitoring the χ^2 value for all realistic fitting scenarios. Realistic fitting scenarios were restricted to positive values for coordination number, radial distances, and XAFS Debye-Waller factors.

The results of the best two-shell fits to the data for SAMMS material loaded with monomethyl Hg or HgNO₃ indicate Hg-O coordination numbers of 0–0.06. The results of the best two-shell fit to the data for SAMMS material loaded with HgI₂ indicate a Hg-O coordination number of 0.4. If the Hg in the SAMMS material had bonded to a single S atom and a bridging O atom, the average coordination number for Hg in the samples would have been one S and one O.

To illustrate the statistical significance of the Hg-O correlation for a two-shell fit to the data, a two-shell fit with two separate Hg-S shells was attempted. This comparison removed any dependence of the normalized minimum χ^2 value on the number of floating variables used during a fit. For this scenario, the best fits to the data for all SAMMS material samples resulted with one coordination shell of 1.8–2.2 Hg-S correlations and a radial distance of 2.39–2.41 Å plus another coordination shell of 0–0.2 Hg-S correlations and a radial distance of 2.1 Å. More importantly, however, the normalized χ^2 parameter for these fits, relative to the normalized χ^2 parameter for the Hg-S and Hg-O two-shell fit attempt, decreased by 0.1. Stated more simply, the presence of an additional coordination shell of less than 0.2 Hg-S correlations resulted in a better fit to the Fourier-filtered data than the presence of any Hg-O correlations. Thus, the use of any Hg-O correlations to fit the Hg LIII absorption edge XAS data did not result in a statistically significant increase in the goodness of the fit.

The best single-shell fits to the Fourier-filtered first-shell peak, for all Hg-loaded SAMMS materials investigated, resulted in 1.85–2.2 Hg-S correlations at a distance of 2.39–2.41 Å, and XAFS Debye-Waller factors of 0.0067–0.0091 Å². These values represent the differences in the best-fit results among the three SAMMS material samples measured. The variance due to correlations of the fitting variables (i.e., an increase of +1 in the χ^2 parameter) for all samples was less than 0.4 for coordination number, 0.01 Å for radial distance, and 0.0018 Å² for XAFS Debye-Waller factor.

Discussion

Had the counter ion in solution with the Hg somehow remained in contact with the Hg after it had reacted with the SAMMS material, the local chemical environment of the Hg would have changed noticeably because the backscattering amplitudes of CH₃, I, and NO₃ ions are very different. Because this result is not seen with qualitative inspection of the Fourier transforms of the different SAMMS samples, this result indicates that the presence of these counter ions in solution has very little effect on the final binding configuration of the Hg to the SAMMS surface.

To balance the charge between the Hg(II) and the thiol group of the SAMMS surface, the Hg probably binds to the SAMMS in one of two ways. The Hg atom can bind to two S atoms at the surface of the SAMMS, or the Hg atom can bind to a single S atom at the SAMMS surface and be linked to an adjacent Hg atom by a common oxygen atom. These two possibilities were investigated in an attempt to fit the SAMMS data with the Hg-S and Hg-O standards.

Our XAS results indicate that the majority of the Hg in the SAMMS materials studied did not have the local chemical environment of one S and a bridging O atom. Further, these results indicate that the majority of the Hg in the all the SAMMS material investigated was bonded to two S atoms.

Acknowledgments

Use of the APS was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38. Research carried out (in part) at the NSLS, Brookhaven National Laboratory, which is supported by the U.S. department of Energy, division of Materials Sciences and Division of Chemical Sciences. Additional funding for research provided by the Department of Energy Environmental Management and Science Program (EMSP).

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