# EXAFS of Cadmium Acetate Aqueous Solutions

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## Introduction

Two of the main factors influencing the mobility of metal ions in the environment are adsorption to minerals and adsorption to the biomass. In an effort to study the latter we are using EXAFS to investigate the mechanism of adsorption of cadmium to the cell walls of the bacteria *B.Subtilis*. These cells are known to have predominantly acetate- and phosphate-like binding sites, and previous titration studies have indicated different binding at different pH.[1] To be able to separate, identify, and quantify the two sites we need a good understanding of their isolated contributions in the EXAFS spectrum. This has prompted us to study a series of cadmium acetate solutions at different metal concentrations and different metal:acetate ratios.

## Methods and Materials

The samples were prepared by mixing the appropriate amount of reagents and diluting them with DDI water to a known volume. The identification names and compositions in mol/l are listed in Table 1. Cadmium acetate dihydrate (99.999%) from Alfa-Aesar was used and overloading was achieved with ammonium acetate. Solutions cdac14 and cdac24 were prepared after Caminiti et. al.[2] to test our EXAFS results against theirs obtained by x-ray scattering and NMR. The last column shows the expected average number of bound acetates using the stability constants given in the same reference.[2] A 1 mol/l CdClO4 aqueous solution was prepared because of its known octahedral hydration sphere.[3] All samples were loaded into slotted Plexiglas holders covered with thin Kapton film and measured in transmission. Their thickness was chosen to achieve an edge step close to $\mu x=1$. The incident- and transmitted-beam ion chambers were filled with nitrogen and argon gas, respectively. Three to 4 scans from each sample were taken and averaged. No hydrolysis bubble formation was observed during the measurements, which were performed at the MR-CAT beamline 10-ID at the APS.

## Results

The raw data were reduced following standard data analysis techniques.[4] The $k^2$-weighted Fourier transforms uncorrected for phase shift are shown on Fig. 1. Qualitatively, we see a change in amplitude in the region 1.3-2.4 Å as the Cd:acetate ratio and the Cd concentration changes, and a feature at 3.5-4.2 Å. Other than that, the spectra seem to follow that of the perchlorate solution.

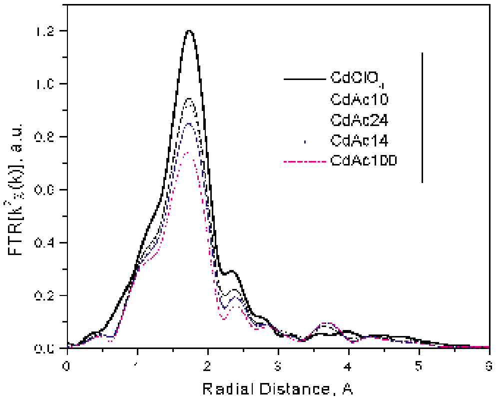

*FIG. 1. FTR[$k^2\chi$] of the experimental data for the acetate and perchlorate solutions.*

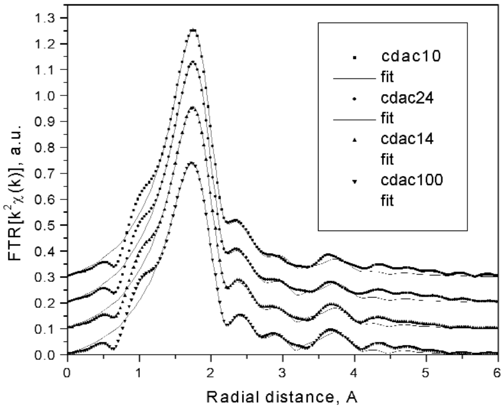

*FIG. 2. Multiple-data-set fits for the cadmium acetate solutions. Data(symbols), fit(line).*

## Discussion

The system was modeled using the known crystallographic structure of cadmium acetate dihydrate.[5] FEFF6[6] was used to generate theoretical EXAFS calculations which were refined to fit the experimental spectra using the FEFFIT program.[7] Single scattering Cd-O, Cd-C, collinear multiple scattering Cd-C-C, and triangular Cd-C-O paths were found to be significant and were included in the fit. The $CdClO_4$ solution was used to calibrate the $S0^2$ parameter. Since the only parameters expected to vary from sample to sample were the coordination numbers and, possibly, the disorder, a multiple data set fit was attempted to constrain some variables. The model consisted of an O shell, C shell, and the multiple scattering paths Cd-C-C and Cd-C-O. All distances were varied simultaneously for all samples, as well as the Debye-Waller factors of the multiple scattering paths. All other parameters were varied independently. The results are shown in Table 2, and the fits are shown on Fig. 2. The reduction in amplitude in the first peak is due to both a reduction in the average number of first-shell oxygen atoms, as well as destructive interference between the C and O atom EXAFS frequencies. The feature at 3.5-4.2 Å is reproduced quite well with contributions from the multiple scattering Cd-C-C path. Our results and trends for the numbers of acetate bound to Cd compare well to the calculated ones (Table 1) indicating that this model should enable a description of the binding site of the Cd in the biomass samples. The other structural parameters determined in this study are close to those found by other methods.[2] In summary, we have developed, calibrated, and tested an EXAFS model for a carboxyl anion binding a cadmium

*Table 1. Composition of the studied solutions in mol/l. The last column is the calculated number of bound acetates based on the measured stability constants in (2).*

| Sample | Description | Cd | $CH_3COO^-$ | $NH_4^+$ | $H_2O$ | $N_{Ac}$ |
|---|---|---|---|---|---|---|
| cdac10 | Cd:$CH_3$COO =1:10 0.5mol/l | 0.05 | 0.50 | 0.40 | 53.737 | 1.35 |
| cdac24 | Cd:$CH_3$COO =1:2 2.0mol/l | 2.00 | 4.00 | 0.00 | 43.563 | 1.70 |
| cdac14 | Cd:$CH_3$COO =1:4 1.0mol/l | 1.00 | 4.00 | 2.00 | 46.045 | 2.60 |
| cdac100 | Cd:$CH_3$COO =1:100 0.5mol/l | 0.05 | 5.00 | 4.90 | 37.415 | 2.90 |

*Table 2. Results from the fit. The O and C shells are varied independently for each sample, except for the distances which are varied but equal for all. The multiple scattering parameters are varied and equal for all samples except for the numbers, which are tied to the C shell coordination number.*

| Sample | $N_O$ | $\sigma_O^2[10^{-3}\,\text{Å}^2]$ | $R_O[\text{Å}]$ | $N_C$ | $\sigma_C^2[10^{-3}\,\text{Å}^2]$ | $R_C[\text{Å}]$ | $\sigma_{OC}^2[10^{-3}\,\text{Å}^2]$ | $\sigma_{CC}^2[10^{-3}\,\text{Å}^2]$ |
|---|---|---|---|---|---|---|---|---|
| cdac10 | 5.7±0.3 | 10.3±0.5 | 2.28±0.00 | 1.5±0.5 | 12.7±2.0 | 2.78±0.02 | 13.9±1.9 | 9.5±2.1 |
| cdac24 | 5.5±0.2 | 10.3±0.6 | 2.28±0.00 | 1.7±0.5 | 12.7±2.0 | 2.78±0.02 | 13.9±1.9 | 9.5±2.1 |
| cdac14 | 5.3±0.2 | 10.5±0.4 | 2.28±0.00 | 2.2±0.4 | 12.7±2.0 | 2.78±0.02 | 13.9±1.9 | 9.5±2.1 |
| cdac100 | 4.8±0.2 | 10.8±0.5 | 2.28±0.00 | 2.5±0.4 | 12.7±2.0 | 2.78±0.02 | 13.9±1.9 | 9.5±2.1 |

cation at different metal concentrations and cation:anion ratios, which we intend to use to determine the mechanism of Cd binding to the biomass.

## Acknowledgments

This work was supported in part by NSF Grant EAR99-05704 and DOE National and Accelerated Bioremediation (NABIR) Project. MR-CAT is supported by the U. S. Department of Energy under Contract DE-FG02-94-ER45525 and the member institutions. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, under Contract No. W-31-102-ENG-38.

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