EXAFS of Cadmium Phosphate Solutions

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Introduction

The main factors influencing the mobility of metal ions in the environment are adsorption to minerals surfaces 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 phosphate solutions at different metal concentrations and different metal:phosphate 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 orthophosphate (99% assay) from Alfa-Aesar was used and dissolution was made possible by adding phosphoric acid, which also overloaded the solution with phosphate groups increasing the probability of its binding to the cadmium cation. The solution *cdpo15* was prepared following Caminiti et al.[2] to test the EXAFS results against those obtained by x-ray scattering. A 1 mol/l $CdClO_4$ aqueous solution was also prepared to compare the first hydration sphere of the phosphate solutions to that of a known cadmium octahedral hydration.[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 μx=1. The incident- and transmitted-beam ion chambers were filled with nitrogen and argon gas, respectively. Three to 4 scans were taken and averaged for each sample. No hydrolysis bubble formation was observed during the measurements, which were performed at the MR-CAT 10-ID beamline at the APS.

Table 1. Composition of the studied solutions in mol/l.

Sample	Description		$Cd_3(PO4)_2$	H_2PO_4
$CdClO_4$	$CdClO_4$	1.0mol/l	-	-
cdpo15	$Cd:PO_4$=1:5	1.0mol/l	0.3333	4.3333
cdpo100	$Cd:PO_4$=1:100	0.1mol/l	0.0333	9.9333

Results

The raw data were reduced following standard data analysis techniques.[4] The k^3-weighted Fourier transforms uncorrected for phase shift are shown on Fig. 1. k^3 weight was chosen to emphasize the contribution of the heavier P atom. Qualitatively, we see a very slight reduction in amplitude in the region first shell and a developing peak at 2.9 Å with phosphate overloading. Other than that, the spectra follow quite closely that of the perchlorate solution.

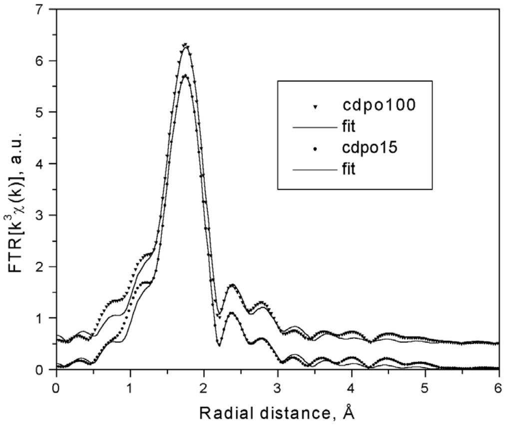

FIG. 1. FTR[$k^3\chi(k)$] of the experimental data for the phosphate and perchlorate solutions.

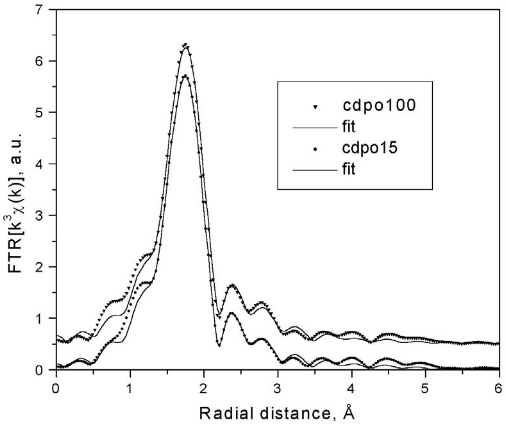

FIG. 2. Multiple-data-set fits for the cadmium phosphate cdpo 15 and cdpo 100 solutions. Data (symbols), fit (line).

Discussion

The system was modeled using the published crystallographic structure of β’-tricadmium phosphate.[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 and Cd-P paths were found to be the main contribution and were included in the fit. The $CdClO_4$ solution was used to calibrate the $S0^2$ parameter. To constrain some fitting parameters we assumed that the distances of the shells did not vary from sample to sample and that the disorder of an attached phosphate group is the same, only the coordination numbers are changed. Thus, multiple-data-set and multiple k-weighting fits were done with a model consisting of an O and P shell. All distances were varied and equal for all samples, as well as the Debye-Waller factor of the P shell. The number of P in sample *cdpo15* were set to that found in reference 2. to resolve the high correlation between the number and Debye-Waller factor parameters for such a weak signal. The results are shown in Table 2, and the fits are shown on Fig. 2. From Table 2 we see that the binding of a phosphate

Table 2. Results from the fit. The perchlorate sample was fit independently. The other two samples are fit simultaneously. The O and P shells are varied independently for each sample, except for the distances and P Debye Waller factors, which are varied, but constrained equal for all samples. The number of P atoms in cdpo15 *is constrained to 0.95 after Caminiti et al.*[2]

Sample	**N_O**	**$\sigma_O^2[10^{-3}$ Å$^2]$**	**R_O[Å]**	**N_p**	**$\sigma_p^2[10^{-3}$ Å$^2]$**	**R_p[Å]**
$CdClO_4$	6.0±0.3	8.5±0.6	2.26±0.00	0.0	-	-
cdpo15	6.0±0.2	9.3±0.5	2.26±0.00	0.95	11.1±3.1	3.43±0.02
cdpo100	6.0±0.2	9.6±0.6	2.26±0.00	1.5±0.3	11.1±3.1	3.43±0.02

group to a hydrated cadmium ion preserves the number of nearest-neighbor oxygens, but increases slightly the disorder relative to the perchlorate solution. We are also able to see an increase in the number of P around cadmium, both qualitatively and quantitatively, indicating binding of the phosphate group to the cation. In summary, we have found a clear “signature” of a phosphoryl ligand binding a cadmium atom in the EXAFS spectrum. We have developed and tested an EXAFS model for quantifying that interaction, which we intend to use in determining the mechanism of Cd binding to the biomass.

Acknowledgments

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