

Local Structure of Bromide Ion Bound on Ion-Exchange Resin

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Introduction

Chromatography is one of popular techniques in the fields of separation and analytical sciences. Various phenomena occurring in a chromatographic column and separation mechanisms were analyzed by empirical models such as a phase separation model. Phase separation model is useful to the clarification of weak phase-phase(mobile-stationary) interactions. In ion-exchange chromatography, interactions of counter ions with a solvent and an ion-exchange site are governed by electrostatic forces which are capable of affecting a long-range field, so this simple phase separation model is inapplicable to ion-exchange chromatography. We have studied the solvated structures of Br⁻ in anion-exchange resins swollen by water and some organic solvents with EXAFS.

Experimental

Resins. Ion-exchange resins with bromide ions as counter-ions were produced from Amberlyst (Rohm and Hass Co.). Amberlyst A-26 have chloride ions as counter-ion on -N⁺(CH₃)₃ group and chloride ions on the resins were replaced by bromide ions.

Solvents. Solvents soaked the resins were water, methanol (MeOH), acetonitrile (AN), acetone, dimethyl sulfoxide (DMSO), and *N,N*-dimethylformamide (DMF). All of them are Wako special-grade. They were dried and distilled before experimental use.

All XAFS spectra were recorded at BL-10B of Photon Factory, High Energy Accelerator Research Organization in Tsukuba.

Results and Discussion

Figure 1 shows EXAFS $\chi(k)k^3$ spectra for the resins in various solvents. The oscillations for resins at Br K-edge were quickly reduced due to the long distance between bromide ion and the neighboring scattering atoms, hydrogen atoms of methyl groups of resin or solvents. The $\chi(k)k^3$ spectra for resins in aprotic solvents also resemble each others. All spectra have the same structure for $k = 0 - 2.5 \text{ \AA}^{-1}$.

The results by curve-fitting for EXAFS spectra using FEFF calculation are shown in Table 1. FEFF calculations were carried out using the models of Br-O (3.2 Å) and Br-C (3.5 Å). The former was used for analyzing the spectra for the resins in protic solvents and the latter was used for analyzing the spectra for resin in aprotic solvents. The results suggest that some of bromide ions leave the ion-exchange site and are hydrated

in the bulk solution. Whereas, bromide ions in aprotic solvents does not strongly interact with solvent molecules and remain on the resin site.

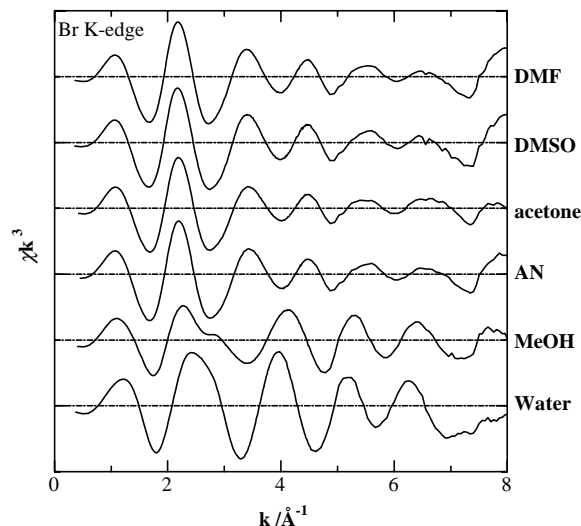


Fig. 1. EXAFS $\chi(k)k^3$ spectra for resin in various solvents.

TABLE 1. EXAFS parameters by Curve-fitting

Solvents	$r / \text{\AA}$	N^a	$\sigma / \text{\AA}^{-1}$
water	3.22	3.44	0.121
MeOH	3.02	1.74	0.101
AN	3.50	4.45	0.174
acetone	3.55	3.79	0.185
DMSO	3.61	4.57	0.169
DMF	3.64	4.10	0.169
Br ⁻ in water	3.20	6.0	0.144

References

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