X-ray Absorption Fine Structure of Halide Ions in Anion-Exchange Resins

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(Manuscript submitted February 14, 2003; accepted March 25, 2003)

Although the structures of ions in ion-exchange resins are of fundamental importance, very few studies have been reported because of the lack of efficient approaches. X-ray absorption fine structure is one of the most efficient tools for studying structural aspects involved in ion-exchange processes because it is highly selective to an element of interest and is applicable to any materials and phases. The structures of Cl\(^-\) and Br\(^-\) an anion-exchange resin are discussed by this approach; the structures both in dry resins and in resins soaked in solvents are compared to reveal the effects of ion-exchange groups and solvents.

1 Introduction

Ion-exchange is in general regarded as a matured technique, because a number of useful materials are commercially available and have been employed in various applications. However, some important aspects have not been well elucidated, which include e.g. molecular mechanisms governing separation selectivity and the local structures of molecules involved in the ion-exchange processes, because of the lack of an efficient approach. Although some investigations have been carried out to understand these molecular features, unambiguous conclusions have not been drawn. In inorganic ion-exchangers, the structures of counterions and roles of surrounding molecules (solvents and matrices) have been relatively well studied [1]; the rigid and crystalline structures of these materials have allowed the advancements in fundamental researches. In contrast, the molecular features have not been well understood in polymer-based ion-exchangers despite its significant part played in the history of ion-exchangers. Ion-exchange experiments are usually done in electrolyte solutions, where solvent molecules interact not only with counterions but also with the ion-exchange groups and resin matrices. Thus, a means, which allows us to selectively probe a target molecule in this complex system without interferences from coexistent materials, makes a significant contribution to the understanding of ion-exchange processes on molecular bases.

The authors believe that X-ray absorption fine structure (XAFS) is a one of the best approaches for this purpose because of its high elemental selectivity. Although recent developments in laser chemistry have permitted to study various species in various environments, samples should be optically transparent. This often restricts the design of experiments. Since both solvent molecules and matrices of polymer-based ion-exchangers
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principally comprises carbon, oxygen, and hydrogen atoms, these are X-ray transparent (though, in most cases, UV-visible opaque) when heavier atoms (most of atoms studied by this approach are the cases) are studied. Thus, we can approach a target atom without interferences from matrices and solvents even when the target is embedded in the matrices. In the previous paper, we discussed the structure of Br\textsuperscript{-} in anion-exchange resins soaked in various solvents, including water, methanol, and aprotic solvents, and found some interesting features.\[2\] However, studying a single type of ion cannot lead to the elucidation of separation selectivity in ion-exchange. In the present paper, results for Cl\textsuperscript{-} are compared with those obtained for Br\textsuperscript{-} in the same systems to discuss a molecular origin in the separation selectivity in ion-exchange.

2 Experimental

2.1 XAFS measurements

All XAFS measurements were performed at BL-9A and BL-10B of Photon Factory, High Energy Accelerator Research Organization in Tsukuba, Japan. It was rather difficult to measure XAFS spectra at Cl-K edge because of the relatively low energy (2.82 keV), but has become feasible using the focused intense X-ray beam at BL-9A. The measurements were done with a usual transmission mode.

2.2 Anion-exchange resin

Polystyrene-based anion-exchange resin Amberlyst 26 was used as a sample. This resin is a strong base anion-exchanger having \(-N(Me)\textsubscript{3}\textsuperscript{+}Cl\textsuperscript{+}\) as an anion-exchange group, and is hereinafter named R4. The resin was rinsed in a Soxhlet’s extractor with acetone and methanol. After being rinsed with water very well, resins were powdered, and then dried over P\textsubscript{2}O\textsubscript{5} in vacuo. The resin soaked in an appropriate solvent (or dried resin) was sealed in a polyethylene pouch, and provided for XAFS measurements by sandwiching it between plastic holders. The thickness of the resin samples was adjusted so that appropriate signal intensity was obtained; the typical thickness was 2 mm for the Br\textsuperscript{-}-form resin and 0.1-0.2 mm for the Cl\textsuperscript{-}-form resin.

3 Results and Discussion

3.1 Selectivity of the resin in several solvents

The R4 resin is a usual quaternary ammonium ion type anion-exchange resin, and shows high selectivity toward Br\textsuperscript{-} over Cl\textsuperscript{-} in water. The ion-exchange selectivity coefficient determined by equilibrating R4Br in 0.1 M (M = mol dm\textsuperscript{-3}) NaCl aqueous solution was 3.53. This value decreased to 0.68 in methanol (MeOH) and 0.33 in N,N-dimethylformamide (DMF); thus, in these solvent, R4 is selective to Cl\textsuperscript{-}. This reversed selectivity was found by chromatographic experiments as well.\[3\] The ion-exchange selectivity can be intuitively related to the solvation of these anions. The solvation Gibbs free energy is reported as \(-347\) kJ mol\textsuperscript{-1} in water, \(-334\) kJ mol\textsuperscript{-1} in MeOH, and \(-301\) kJ mol\textsuperscript{-1} in DMF for Cl\textsuperscript{-}, and \(-321\) kJ mol\textsuperscript{-1} in water, \(-310\) kJ mol\textsuperscript{-1} in MeOH, and \(-291\) kJ mol\textsuperscript{-1} in DMF for Br\textsuperscript{-}.\[4\] Chloride has smaller crystalline ionic radius, and thus undergoes stronger electrostatic attraction by the ion-exchange groups than bromide in the absence of solvents. In aprotic solvent such as DMF, the solvation toward anions is particularly weak, and the direct interaction (ion-association) between oppositely charged ions, which should reflect crystalline radii, determines ion-exchange selectivity. This explanation appears sound; however, does this inference give reasonable interpretation to the selectivity in

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protic solvents as well?

If the interaction between a solvated counterion and ion-exchange group occurs (similar to solvent-shared ion-pair formation), the radius of a solvated ion should be reflected in ion-exchange selectivity. If counterions keeping their hydration structures interact with the ion-exchange groups, the columbic interaction for Cl\(^-\) may be weaker than that for Br\(^-\); following this explanation, MeOH must be intermediate. However, it is obvious that thermodynamic data based on the evaluation of the distribution of ions, ion-exchange selectivity etc give no direct evidence on the interaction between counterions and ion-exchange groups. These aspects are discussed in the following section on the basis of results of XAFS measurements, which are capable of revealing the structural features.

3.2 XAFS of counterions in the anion-exchange resin

Fig.1 compares the \(\chi(k)k^3\) spectra of Cl\(^-\) and Br\(^-\) dissolved in water and MeOH together with those for the resin samples, i.e. dry, soaked in water, MeOH, and DMF. The spectra for Cl\(^-\) are noisy due to the low X-ray energy as well as to the inhomogeneous sample thickness and particle sizes. However, the similarity of the spectrum for dried resin and that for the resin soaked in DMF clearly implies that the local structures of Cl\(^-\) in these two samples is identical. The same is true for the Br\(^-\)-form resin. This indicates that counterions are strongly bound by the ion-exchange groups in an aprotic solvent and the preferable selectivity toward small ions emerges. These spectra in k space were analyzed by curve-fitting with the model calculated with FEFF ver.8.20 (see ref.2 for detailed data analysis). The distance was determined as 0.349 nm (\(\sigma=0.0141\), \(\sigma\), Debye-Waller coefficient) for Cl\(^-\)-C and 0.364 nm (\(\sigma=0.0212\)) for Br\(^-\)-C in DMF, when methyl carbons in the ion-exchange group are assumed to be scattering atoms. The nitrogen atom in the methyl group is also located at a similar distance from the halide ion, and thus contributes to the XAFS oscillation. Since these two different contributions cannot rigorously be separated, the
distances reported above are average of X-C and X-N (X, halide). The numbers of scatter atoms are also estimated as 4.48 and 4.10, suggesting that these anions are entrapped in the tripod composed of three methyl groups of the ion-exchange site (total four atoms, three carbon atoms and a nitrogen atom, can be scattering atoms).

In comparison with the results obtained in DMF, the analyses of the spectra in water and MeOH are very complicated. It is obvious that the spectra obtained in these protic solvents have different oscillation structures from those for the dried resin or the resin soaked in DMF, implying that the counterions strongly interact with solvent molecules. A very important feature is that the spectrum obtained in water or MeOH has two peaks at $k=20-30$ nm$^{-1}$ as shown in Fig. 1. The peak at $k=ca$ 22 nm$^{-1}$ is the same as seen in the spectra of the dried resin and the resin soaked in DMF, while that at $k=ca$ 28 nm$^{-1}$ is the same as obtained for the solvated ions (the spectra for solvated ions are also given in Fig.1). In the previous paper,[2] we studied the local structures of Br$^-$ in ion-exchange resins soaked in these solvents in detail, and concluded that this strange spectrum results from the superimposition of two spectra with different oscillation structures, i.e. the spectra of the dried resin and solvated Br$^-$. Although detailed analyses for the spectra of the Cl$^-$-form resin were not possible due to high noise levels, basic trends seen for Cl$^-$ are the same as those seen for Br$^-$, suggesting that two different structures coexist in both cases. The previous calculation indicated that at most ca 30-40 % bromide ions are dissociated by solvation with water or MeOH, and residual parts are still bound by the ion-exchange groups. Although the same calculation could not be applied to the Cl$^-$-form resin, it must be reasonable to conclude that a similar degree of Cl$^-$ is dissociated from the ion-exchange groups by solvation. However, an important conclusion is that a major part of Cl$^-$ or Br$^-$ is still directly bound by the ion-exchange site, and a solvent-shared ion-pair, which is inferred from the thermodynamic data, is minor even though it is present. Although the detailed mechanisms governing separation selectivity have not been elucidated, it should be noted that the structure of Cl$^-$ in the resin is not very different from that of Br$^-$. The structural studies with resins equilibrated at different partial water-vapor pressures are in progress in our laboratory to elucidate the roles of a solvent in determining separation selectivity, and will be reported in the near future.

The authors acknowledge the financial supports by the Salt Science Foundation. This work was performed under the approval of Photon Factory Advisory Committee (Proposal Nos. 98G311 and 2001G114).

References

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