

Local structures of ions at ion-exchange resin/solution interface

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Abstract

The local structures of Cl^- and Br^- in anion-exchange resins have been studied by X-ray absorption fine structure (XAFS), and separation selectivity is discussed on the basis of results. When two different anion-exchange resins having trimethylammonium and dimethylammonium groups as anion-exchange groups are employed for ion-exchange experiments, slightly higher Br^- selectivity has been obtained with the former. XAFS has indicated that the average hydration numbers for a given anion is not affected by the structure of the ion-exchange group, but that the extent of ion-association between the anion and the ion-exchange groups depends on the type of the ion-exchange group. Shorter interaction distance (and in turn stronger ion-association) has been confirmed for the dimethylammonium-type resin, and is consistent with lower Br^- selectivity of this resin.

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1. Introduction

Ion-exchange resins have most frequently been used as stationary phases in ion chromatography [1–5]. Developing ion-exchange resins with high separation capability, high separation selectivity, and high chemical/physical durability is still required for further advancements of ion chromatographic methodology. Although trial and error has been a usual way to develop new stationary phases, understanding ion-exchange mechanisms on the molecular bases is undoubtedly an essential approach to the exploitation of novel ion-exchange resins with desired capability. However, ion-exchange systems are so complex that we should take into consideration a number of parameters, i.e. electrostatic interaction between counterions and ion-exchange groups, effects of resin matrices, solvation of counterions, etc. Applicable methods are therefore very few, and it is in general very difficult to study ion-exchange systems from molecular viewpoints.

We recently indicated that X-ray absorption fine structure (XAFS) is a useful method to probe the local structures of ions in ion-exchange resin, and thus that the extensive application of this method should reveal the selectivity origin

in ion-exchange separation [6–11]. This method provides the information not only on the types and number of scattering atoms surrounding an absorbing (targeted) atom but also the distance between the absorbing and the scattering atoms and in turn its local structure. In addition, XAFS has very high elemental selectivity, and light elements hardly influence the spectral measurements of heavier elements. Although ion-exchange systems are very complex as stated above, resin matrices and solvent molecules are usually composed of relatively light elements (hydrogen, carbon, nitrogen, and oxygen atoms are main components), and do not interfere with the XAFS measurements of most of targeted ions. In this paper, we would like to show the local structures of Cl^- and Br^- in anion-exchange resins, and discuss the relation between their local structures and separation selectivity.

2. Experimental

2.1. Resins and solvents

Br^- - and Cl^- -form anion-exchange resins were prepared from Amberlyst A-21 and A-26 (Rohm and Hass Co.), Amberlyst A-21 is a weak-base anion-exchange resin having $-\text{N}(\text{CH}_3)_2$ groups as anion-exchange sites, whereas Am-

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berlyst A-26 is a strong-base anion-exchange resin having $-\text{N}^+(\text{CH}_3)_3$ groups as anion-exchange sites. Both are macroreticular type resins. Amberlyst A-21 (R3) was treated with aqueous hydrochloric acid or hydrobromic acid to allow the complete protonation of the tertiary amino groups. Amberlyst A-26(R4), which is provided as a Cl^- -form resin, was treated with aqueous sodium bromide solutions (ca. 0.2 M) several times to allow complete replacement of counteranions. Four resin samples were thus prepared, which are hereinafter referred to R3Cl, R3Br, R4Cl, and R4Br. The resins were repeatedly rinsed with acetone, methanol, and water, powdered (particle sizes smaller than 40 μm , typically 5–20 μm), and repeatedly rinsed with the same solvents, and then dried over P_2O_5 in vacuum. The ion-exchange capacities of dried R3Cl, R3Br, R4Cl, and R4Br were 4.14 ± 0.04 , 4.26 ± 0.00 , 3.60 ± 0.01 , and 3.62 ± 0.01 mmol g^{-1} , respectively. Water was purified with a Milli-Q system.

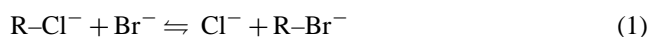
2.2. XAFS measurements

All of XAFS spectra were measured at BL-9A (at Cl K -edge) and BL-10B (at Br K -edge) of Photon Factory, High Energy Accelerator Research Organization (KEK-PF) in Tsukuba, Japan. The samples sealed in polyethylene pouches were sandwiched by plastic holders. Sample thickness (0.2–3.0 mm) was adjusted by inserting spacers between the plastic holders so that an appropriate signal jump could be obtained. All of XAFS measurements were carried out at room temperature (ca. 297 K). The spectra were analyzed according to our previous work [6].

3. Results and discussion

3.1. Separation selectivity of R3 and R4 resins

The R3 and R4 resins have different ion-exchange groups. Barron and Fritz [3,4] studied effects of the structure of ion-exchange groups, and revealed that larger and polarizable anions were more preferably retained on the resins with bulky ion-exchange groups. Also, studies of ion-association in non-aqueous solvents indicated that tertiary ammonium ions were more likely to form ion-associates with anions than quaternary ammonium ions [12]. These previous studies imply that different separation selectivity is obtained with the R3 and R4 resins. The ion-exchange selectivity coefficients ($K_{\text{Cl}}^{\text{Br}}$) for the following reaction were determined in 0.1 M electrolyte solutions;



The $K_{\text{Cl}}^{\text{Br}}$ values for R3 and R4 were 3.28 and 3.53, indicating that the selectivity of R3 to Br^- is slightly lower than that of R4. These selectivity coefficients are consistent with the tendency reported by Barron and Fritz. Although ion-exchange experiments cannot provide the direct information

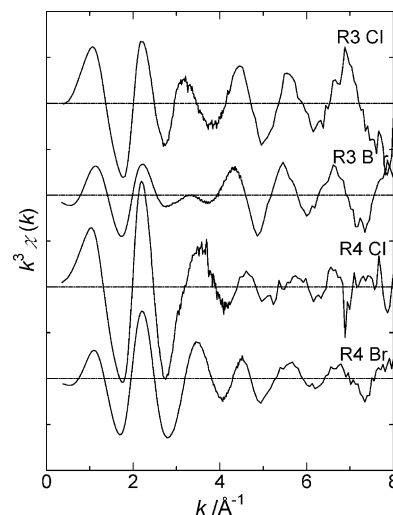


Fig. 1. χ^2 spectra for dried resins.

of the ionic interaction, the slightly lower selectivity of R3 to Br^- should be related to the larger ion-association ability of tertiary ammonium ions. The structural feature is discussed on the basis of the XAFS analyses shown in the following section.

3.2. Local structures of Cl^- and Br^- in the dried resins

The local structures of Cl^- and Br^- in the dried resins are discussed before the discussion of those in the resins soaked in water. Although the counteranions should form the tight ion-associates with the ion-exchange groups in the dried resins, the detailed structures have not been known. The resins are so hygroscopic that a special care should be paid to their treatments; the resins were dried as stated above, and then transferred into a polyethylene pouch under dried N_2 atmosphere immediately before XAFS measurements. Fig. 1 shows the χ^2 spectra for Cl^- and Br^- in the dried R3 and R4 resins. The oscillation intensity for R4 simply decreases with increasing k , suggesting that scattering groups are present in the first coordination shell of the counteranions. In contrast, the oscillation intensity for R3 first decreases with increasing k , but again increases when k exceeds 4 \AA^{-1} . The increase in the oscillation intensity at $k > 4 \text{ \AA}^{-1}$ is ascribed to the formation of a well-defined second coordination shell.

Table 1 summarizes the results of the analyses of the spectra. The results for the R4 resins are relatively simple. For both R4Cl and R4Br, the number of the scattering atoms was estimated ca. four, indicating that the counteranions are present in the tripod consisting of three methyl carbon atoms (Fig. 2a). A molecular model indicated that the distance between the halide anion and the methyl carbon atoms is slightly shorter than that between the anion and the ammonium nitrogen, but that a difference between these is too marginal to be detected by XAFS. In addition, carbon and nitrogen atoms have similar backscattering ability, and this also makes difficult to distin-

Table 1
Structural parameters for Cl^- and Br^- in the dried R3 and R4 resins

Resin	Scattering atom	N^a	r (Å) ^b	σ (Å) ^c
R3Cl	N	1.08	3.02	0.13
	C	3.12	3.58	0.19
R3Br	C (or N)	2.03	3.27	0.11
	C	2.24	3.41	0.14
R4Cl	C (or N)	4.52	3.27	0.25
R4Br	C (or N)	4.27	3.53	0.20

^a The number of scattering atoms.

^b The distance between the absorbing and scattering atoms.

^c Debye–Waller coefficient.

guish them. The number of the scattering atoms (ca. four) is thus understandable if the structure illustrated in Fig. 2 is assumed. Thus, both Cl^- and Br^- are similarly located in the tripod of trimethylammonium group in the R4 resin, albeit

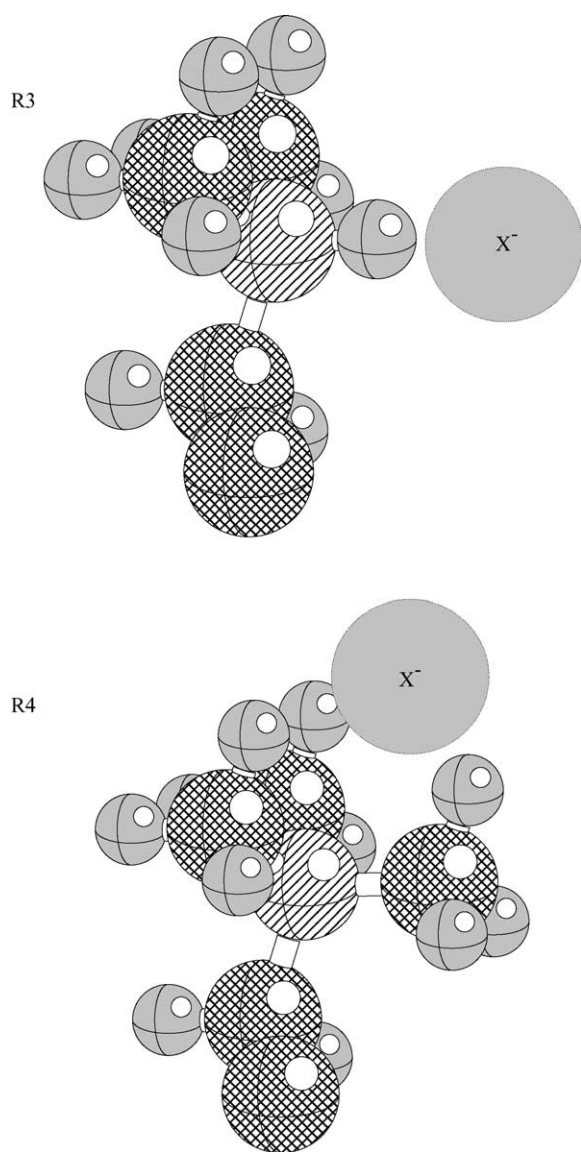


Fig. 2. Possible structures for a halide anions (X^-) in the dried R3 and R4 resins.

the shorter distance for Cl^- reasonably reflects its smaller ionic size.

In contrast, the results for the R3 resins are slightly complicated. As noted above, the spectral features clearly indicate the well-defined second coordination shell. If the halide anions directly interact with the ammonium hydrogen, the ammonium nitrogen should exist in the first coordination shell. The distances between the halide anions and the closest scattering atom are 3.02 and 3.27 Å for Cl^- and Br^- , respectively, which are shorter than that between the anions and methyl carbon atoms. The shorter distances must imply the stronger interaction between these. Fig. 2 shows a possible local structure of the halide anion in the dried R3 resin. When the halide anion is directly bound by the ammonium hydrogen, three carbon atoms (two methyl carbon and one methylene carbon atoms) comprise the second coordination shell; R3Cl is the case, because $N = \text{ca. } 1$ for the first coordination shell and $N = 3$ for the second. However, the coordination numbers for R3Br show a slightly different feature; $N = 2.03$ for the first and $N = 2.24$ for the second coordination shell. The structure capable of explaining these results has not been deduced, but should be similar to that for R3Cl. Although the different structures for the R3 and R4 resins should be related to the different ion-exchange selectivity, the discussion should be made based on the structures determined in the resins soaked in water as shown in the following section.

3.3. The local structures of Cl^- and Br^- in the resins soaked in water

Figs. 3 and 4 show the χk^3 spectra for the resins soaked in water. The spectra for hydrated Cl^- and Br^- in bulk solution as well as those for the dried resins are also depicted in the figure for comparison. Although the spectra for the resins soaked in water are strongly affected by coordinating water molecules rather than by the ion-exchange groups, clear contributions from the latter groups can be seen at $k = 2$ to 3 \AA^{-1} . We employed the following linear combination to extract these two contributions from complex spectra, because usual analysis methods were not applicable [8].

$$\chi = \alpha \chi_{\text{dry}} + \beta \chi_{\text{hyd}} \quad (2)$$

where χ , χ_{dry} , and χ_{hyd} are the χ spectra obtained for a given resin soaked in water, for the dry resin, and for the hydrated ions, respectively, and α and β are coefficients representing the contributions from χ_{dry} and χ_{hyd} , respectively. This equation assumes that the χ spectra are additive and that the coordination distances of $\text{X}-\text{O}$ (in H_2O) and $\text{X}-\text{C}$ or $-\text{N}$ (in $-\text{NHMe}_2^+$ for R3 or $-\text{NMe}_3^+$ for R4) are unchanged. This equation very well describes experimental spectra as shown as broken curves in Fig. 3 with α and β coefficients listed in Table 2. However, as indicated in our previous paper, this equation is liable to underestimate α coefficient due to the assumption that the distance between the halide anions and the ion-exchange groups is unchanged even when

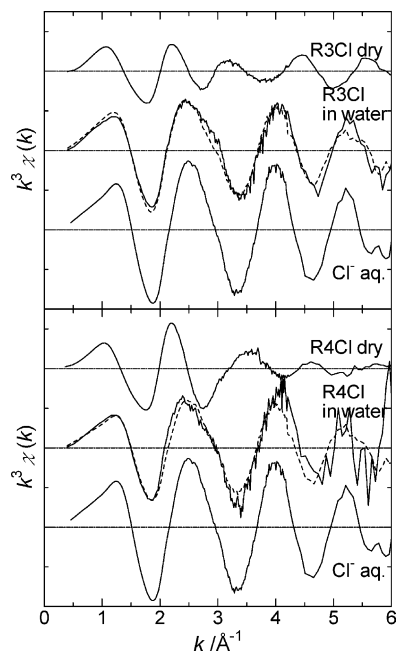


Fig. 3. χk^3 spectra for the R3Cl and R4Cl resins. Solid curves represent experimental spectra. Broken curve shows the result of the calculation based on Eq. (2).

water molecules coordinate the former [8]. When the halide anions are hydrated, the interaction between them and the ion-exchange groups becomes weak; this weak interaction should result in the thermal fluctuation and in the weak oscillation intensities over higher k range. Thus, α coefficient

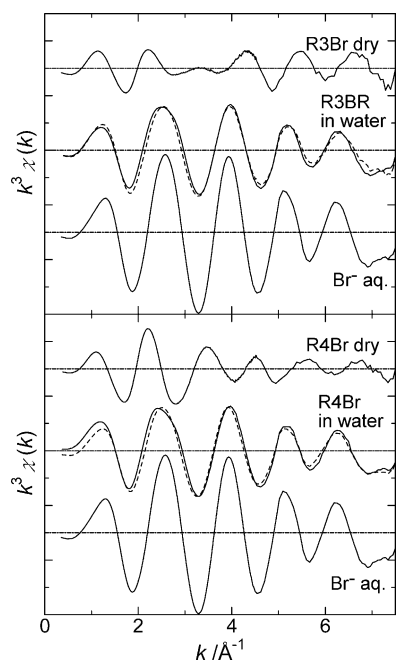


Fig. 4. χk^3 spectra for the R3Br and R4Br resins. Solid curves represent experimental spectra. Broken curve shows the result of the calculation based on Eq. (2).

Table 2

α and β coefficients (in Eq. (2)) determined for the halide anions in the R3 and R4 resins soaked in water

	R3Cl	R3Br	R4Cl	R4Br
α	0.34 (0.24)	0.50 (0.37)	0.07 (0.15)	0.25 (0.21)
β	0.72 (0.07)	0.56 (0.08)	0.70 (0.07)	0.59 (0.08)
$6\beta^a$	4.3	3.3	4.2	3.5

^a Average hydration number of an anion in a resin.

is underestimated by the curve-fitting based on Eq. (2), but can be a good measure for evaluating the dissociation of the counteranions from the ion-exchange groups and discussing the strength of the ion-association between these. The α coefficients obtained for the R3 resins are obviously larger than the corresponding values for the R4 resins, implying the strong binding of the halide anions by the ion-exchange groups even when the resins are soaked in water. Stronger binding of the counteranions by the $-\text{NHMe}_2^+$ group than the $-\text{NMe}_3^+$ group is consistent with the shorter distance between the counteranions and the nearest scattering atom (Table 1).

Another important parameter governing separation selectivity is the extent of the hydration of a counteranion in the resin. Table 2 indicates that β coefficients are more reliable than α coefficients. Since it has been reported that six is the most probable hydration number of Cl^- and Br^- in bulk solutions [13–15], 6β should be equal to their average hydration number in the resins. Interestingly, the average hydration number in the resins is dependent on the nature of the anions, but independent of the type of the resins. When ions are transferred from bulk solution to the interior of the resin, partial dehydration occurs; this process is thermodynamically unfavorable. This disadvantageous free energy change is recovered by the electrostatic interaction between the ions and ion-exchange groups. The average hydration numbers of Cl^- and Br^- in the resins are not affected by the structures of the ion-exchange groups as far as the present resins are concerned, indicating that the same dehydration energy is required for the transfer of a given anion into the resin. As discussed above, the ion-exchange selectivity coefficients for these anions are different for the R3 and R4 resins. This difference should thus come from the electrostatic interaction between the anions and ion-exchange groups. Although we cannot quantitatively evaluate electrostatic stabilization, the shorter interaction distances for the R3 resin should be responsible for this selectivity modification. This feature must be instructive for designing ion-exchange resins showing selectivity different from existing ones.

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