XAFS Study of Thermal Effect on Hydration Structures of Inorganic Ions in Ion-Exchange Resins

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1 Introduction

Temperature has been recognized to be a very important factor affecting the separation selectivity of ionic solutes in ion-exchange chromatography [1]. We have recently investigated the effect of temperature on the retention of alkali and alkaline-earth metal ions on a strongly acidic sulfonated ion exchanger over a wide temperature range, 40-175 °C, using superheated water, i.e., liquid water under pressure at temperatures above 100 °C, as the mobile phase and showed that the selectivity coefficient for a pair of alkali metal ions or that of alkaline-earth metal ions approaches unity as temperature increases [2]. We also demonstrated in a recent paper that temperature exerts a similar effect on anion-exchange selectivity [3]. It is presumed that the dependence of ion-exchange selectivity observed for simple inorganic ions on temperature can be attributed to the change in hydration of the ions in the solution phase and/or in the ion-exchange resin with temperature; hydration of ions can be assumed to become weaker as the temperature increases due to disruption of ion-dipole bonding by thermal motion of water molecules resulting in reduction of the difference in hydration structure between different ions. In this study, we use XAFS to investigate the hydration of some alkali and alkaline-earth metal ions and halide ions not only in solution but also in the ion-exchange resins in the temperature range from ambient temperature to 175 °C [4].

2 Experiment

A high temperature and high-pressure XAFS cell designed in our laboratory was composed of a block of stainless steel (SUS304) fitted with two opposing 5 mm diameter × 0.9 mm thick beryllium windows for transmission of X-ray beam. Aqueous solutions of 0.1 mol L^{-1} $Sr(NO_3)_2$ and KBr, 0.05 mol L^{-1} Rb_2SO_4 and 0.5 mol L^{-1} KI were delivered into the cell with a HPLC pump, whereas water slurries of Sr^{2+} and Rb^+ forms of MCI GEL CK10S (sulfonated polystyrene-divinylbenzene copolymer, particle diameter = 11 μm, Mitsubishi Chemical, Tokyo Japan) were poured directly into the cell. Then the pressure was applied at 3 MPa employing the HPLC pump and a back pressure regulator. The temperature of the cell was maintained to within ± 2 °C using a PID temperature controller.

Strontium-K edge, bromine-K edge, and rubidium-K edge XAFS spectra were collected on beam-line BL-9C or BL-12C of PF-KEK. The XAFS measurements at iodine-K edge were carried out at the beam-line AR-NW10A. The scattering amplitudes and phase shifts for the model systems were calculated with the FEFF8.20 program.

3 Results and Discussion

Figure 1 shows the k^3-weighted XAFS oscillations, $k^3\chi(k)$, acquired over temperatures for Rb^+ in aqueous solution, where k is the wavenumber of the photoelectron ejected in the absorption process. As shown in this figure, increasing the temperature from ambient to the superheated region produces a definite change in the hydration structure. Particularly, the decrease in the amplitude of the oscillations shows a decrease in the hydration number of the first water solvation shell. The similar effect of temperature on ionic hydration structure was also observed for Sr^{2+}, Br^-, and I^-. The decrease in the coordination number is consistent with a reduction in the number of ion-water bonds at elevated temperatures, which can be attributed to dehydration by thermal motion
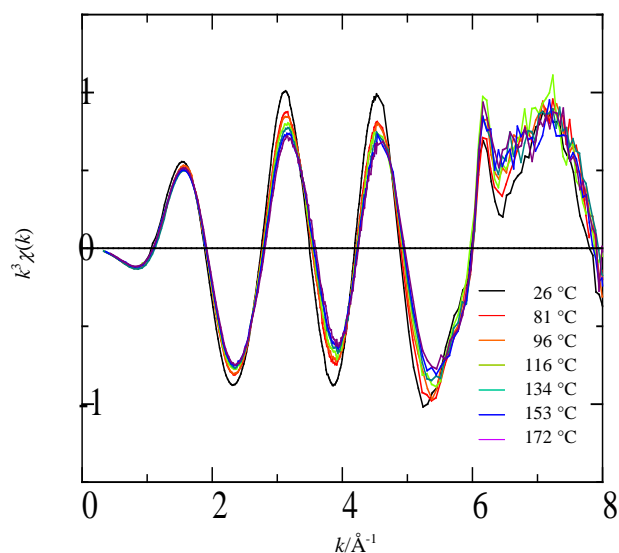

Fig. 1 Plot of $k^3\chi(k)$ for rubidium ion as a function of wavevector for a series of temperatures from 26 to 172 °C. Sample solution: 0.05 mol L^{-1} Rb_2SO_4. [Reproduced from Fig. 1 in reference 4 by permission of The Royal Society of Chemistry]
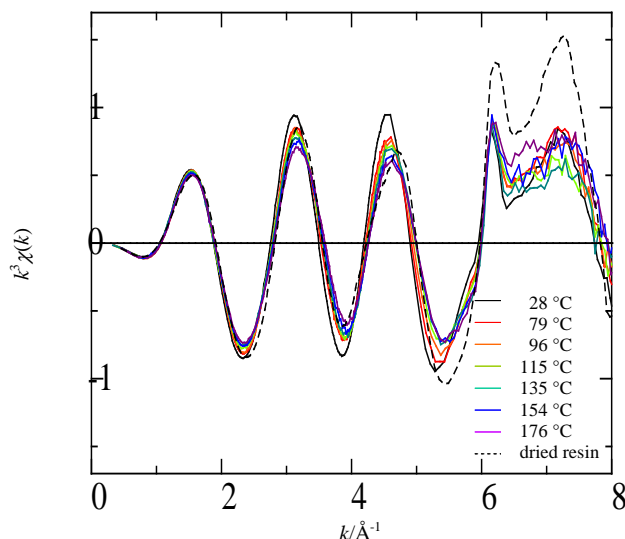
Fig. 2 Plot of $k^3\chi(k)$ for rubidium ion in the hydrated and dried cation-exchange resins as a function of wavevector for a series of temperatures from 28 to 176 °C. [Reproduced from Fig. 7 in reference 4 by permission of The Royal Society of Chemistry]

of water molecules around the ions or the change in coordination structure.

Figure 2 shows the XAFS spectra obtained for Rb^+ present as the counterion of fixed sulfonate groups in the water-swollen cation-exchange resin as well as in the dried resin. In the resin soaked in water, the fixed sulfonate groups and counterions are hydrated. The spectral transitions observed for Rb^+ and Sr^{2+} in the hydrated resin are similar to those for the ions in aqueous solution, suggesting that these cations have nearly the same structures of their first hydration shells in the interior of the cation-exchange resin as those in aqueous solution. These results suggest that the hydration structures of Rb^+ and Sr^{2+} in the cation-exchange resin soaked in water can be assumed as approximately identical to those in aqueous solution even at elevated temperatures and thermal dehydration occurs not only in solution but also in the interior of the resin.

If the counterions form contact ion-pairs with the sulfonate groups, the direct coordinating atom is the same as that of water, *i.e.*, oxygen. Consequently XAFS parameters do not provide clear information on the local structure of the countercations in the hydrated resin. However, there are slight phase shifts in oscillation in high k region for Rb^+ in the cation-exchange resin at elevated temperatures as shown in Fig. 2, which suggests a superposition of the spectra due to different coordination structures. The qualitative differences between water-swollen and dry conditions are seen in these figures; the phase of the oscillation for Rb^+ in the cation-exchange resin shifts to higher k value when the resin is dried.

The estimated hydration numbers for the dry resin samples are 3.0 and 5.2 for Rb^+ and Sr^{2+}, respectively. If

a cation is bound to one sulfonate group, the coordination number can be assumed to be four from the consideration of the contribution of sulfur atom to the oscillation amplitude [5]. Although the hydration number is slightly smaller than 4, Rb^+ can be considered to form 1:1 direct contact ion pair with sulfonate groups in the dried resin. On the other hand, Sr^{2+} may partly bind to two sulfonate groups.

The slight variation in oscillation of the XAFS spectra with temperature observed for the water-swollen cation-exchange resin samples imply that small amounts of Rb^+ and Sr^{2+} may directly bind to the sulfonate groups in the resin at elevated temperatures. Since the ion-exchange capacity of the cation-exchange resin is 2.3 meq mL^{-1}, the concentrations of these ions in the resin can be assumed to be more than 2 and 1 mol L^{-1} for Rb^+ and Sr^{2+}, respectively. In these concentrated solutions, the possibility of contact ion-pair formation could not be ruled out at elevated temperatures. The change in the coordination number of Rb^+ and Sr^{2+} with an increase in temperature for the resin samples was smaller than that observed for the corresponding aqueous solution samples. This can be ascribed to strong binding of Rb^+ and Sr^{2+} to sulfonate ions in the resin phase by Coulomb force. The observed phase shifts in the XAFS spectra are too small to accurately evaluate the contribution from the contact ion-pairs. It is thus presumed that most of the ions may bind to the fixed ions with bridging water molecules under the conditions examined in this study. However, the results shown above suggest that the structure of the hydrated ion-exchange resin approximates to that of the dried one as temperature increases. The dehydration reaction of the ion-exchange resin may be schematically expressed as follows:

$$-SO_3^-\cdots H_2O\cdots A^{n+} \rightleftharpoons -SO_3^-\cdots A^{n+} + H_2O$$
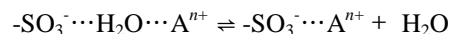
The separation selectivity for a pair of alkali metal ions, alkaline-earth metal ions, and halide ions in ion-exchange processes decreases with increasing temperature as we have already demonstrated [2, 3]. This equilibrium will shift right if the temperature is increased. At elevated temperatures, electrostatic charge screening no longer effectively occurs, which may lead to smaller ion-exchange separation selectivity for different ions having an identical charge.

References
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