Hydration of counterions in cation exchange resins studied by X-ray absorption fine structure†

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X-Ray absorption fine structure has revealed that K^+ is partially desolvated when transferred into the interior of cation-exchange resin, while Rb^+ and Sr^{2+} keep their first hydration structures.

Ion-exchange has found a variety of fundamental and practical applications, including separation of ions, catalytic reactions, water treatments *etc*. One of the important tasks in current ion-exchange studies is to develop materials that exhibit novel function or selectivity. The recent developments of nanotechnology have allowed us to prepare various materials with well-controlled architectures, which are expected to have different functionality from conventional materials with random structures.[1] For the innovation of ion-exchange, there is an entirely different approach, which is based on the understanding of its molecular processes such as thermodynamics, kinetics, and structures.[2] Ion-exchangers are mostly used in aqueous solutions, and, therefore, effects of water should always be taken into consideration for the understanding of chemistry taking place therein. Although the involvements of hydration in the determination of separation selectivity in ion-exchange have been recognized for many years, the structural origin of ion-exchange selectivity has not been completely elucidated. Earlier studies indicated that the adsorption of water on ion-exchange resins strongly depended on types of counterion.[3] Although various theories have been devised to interpret adsorption isotherms of water on ion-exchange resins, it is not straightforward to gain structural insights based only on such data.

The local solvation structures of counteranions in anion-exchange resins have been studied by X-ray absorption fine structure (XAFS)[4,5] and neutron diffraction.[6] Both approaches have indicated that Cl^- and Br^- are partly dehydrated and form direct ion-pairs with anion-exchange groups.[4–6] Although Tromp and Neilson[7] also implied the possibility of the invasion of the formation of a direct ion-pair between Li^+ and sulfonate groups in a cation-exchange resin by neutron diffraction, the results were not as clear as those for halide anions in anion-exchange resins. The local structures of counterions should be related to those in bulk aqueous solutions. Studies of the ion–water interactions in the gas phase have revealed that the bonding of a halide ion with a water molecule is weaker than that of an alkali cation when they have close atomic numbers.[8] This explains the above findings that a counteranion is partly dehydrated when it is transferred into an anion-exchange resin; when a hydrated anion is placed under the influence of a strong electrostatic field created by positively charged ion-exchange groups, some of the coordinating water molecules are stripped off because of the relatively weak interaction between an anion and water. If the binding of water to a cation is much stronger than that to an anion, the first coordination shell of the cation is preserved even when it is transferred into a cation-exchange resin. In the present paper, our attention is mainly focused on the local structures of countercations in a cation-exchange resin well swollen in water. The structural exploration has been done with XAFS.

After Amberlite 200CT-Na (a macroreticular-type cation-exchange resin with Na^+ as a countercation) was rinsed well with water, its countercation was replaced by K^+, Rb^+, or Sr^{2+} by repeated treatments with aqueous KCl, RbCl or $SrCl_2$. The resins were thoroughly rinsed with water and were ground into fine particles of diameters smaller than 10 μm in a mortar. The resins were dried at 130 °C over P_2O_5 and were sealed in polyethylene pouches. The dried resin samples were prepared immediately before XAFS measuments under a dried N_2 atomosphere.

Transmission XAFS measurements at the K K-edge, the Rb K-edge, and the Sr K-edge were performed at room temperature (25 °C) at the beamlines BL-7C and BL-9A of the Photon Factory of High Energy Accelerator Research Organization (KEK) in Tsukuba, Japan. Higher harmonic X-rays were removed by a Si mirror. Incident and transmitted X-ray intensities were determined with ionization chambers filled with appropriate gasses. The thickness of a sample was adjusted so that appropriate signal intensity was obtained. Scattering amplitudes and phase shifts for model systems were calculated with FEFF8.02. The curve-fittings in the *k*-space were carried out with the number of coordinating atoms, the energy shift, the distance between the absorbing and scattering atoms, and the Debye–Waller factor as parameters with the Artemis ver.0.7 program.[9,10]

Fig. 1 and 2 show the XAFS spectra for K^+, Rb^+, and Sr^{2+}, respectively. In each figure, three spectra are compared, which were obtained with the dried resin, the water-swollen resin, and the ion dissolved in water. The XAFS parameters determined by curve-fitting are also summarized in Table 1. The range of curve-fitting was severely restricted for Rb^+ by the multielectron excitation at k = *ca.* 6.1 $Å^{-1}$, and thus the parameters are less reliable for this ion. The coordination numbers for K^+ and Rb^+ in water are reported to be 4–6, depending on the methods employed, and that for Sr^{2+} is 6.[9] The present analyses indicate $N = 4$ for K^+, $N = 3.5$ for Rb^+, and $N = 6.2$ for Sr^{2+}. The coordination distances are also consistent with the reported values.[11]

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† Electronic supplementary information (ESI) available: The results of the curve-fitting to the XAFS χ spectra shown in Fig. 1 and a fitting to an equation, $\chi = \alpha_1\chi_1 + \alpha_2\chi_2$, for K^+ in the hydrated resin. See DOI: 10.1039/b810997d

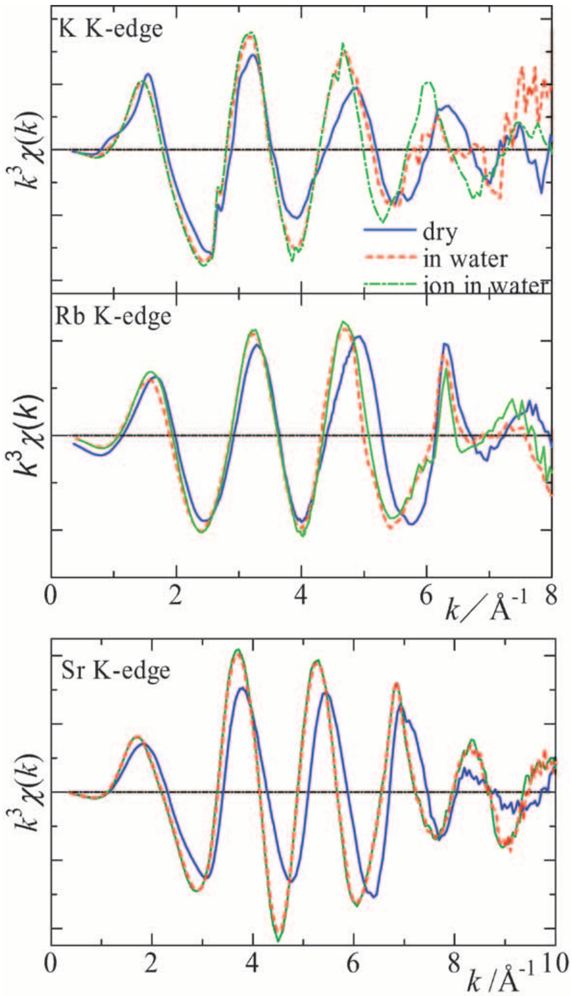

Fig. 1 Comparison of XAFS χ spectra obtained for K^+, Rb^+, and Sr^{2+} in water and those for the ions in dried and hydrated resins.

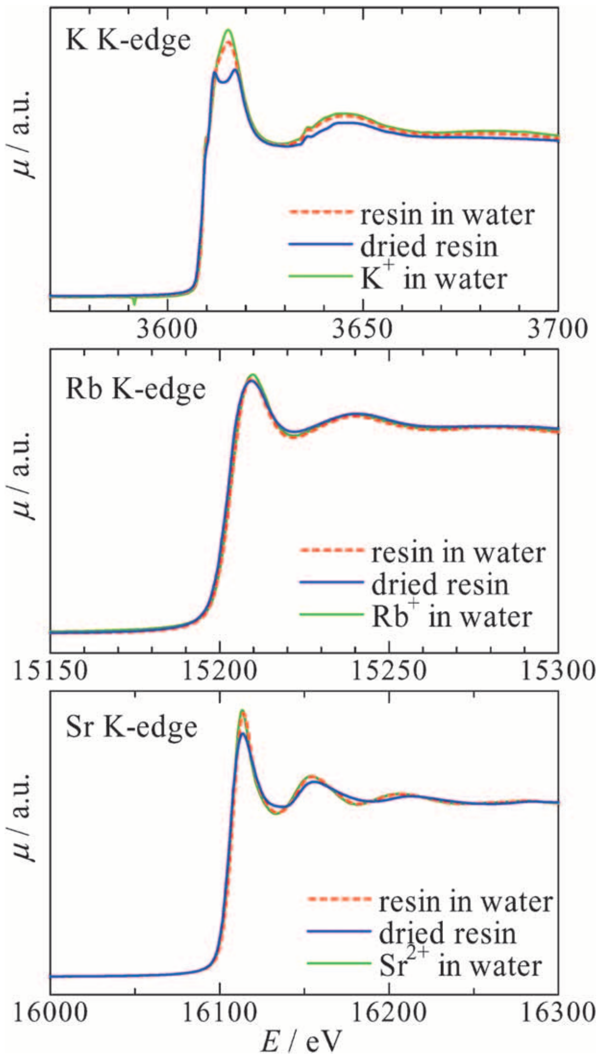

Fig. 2 XANES spectra obtained at the K, Rb, and Sr K-edges.

In the dried resins, countercations should form direct ion-pairs with the sulfonate groups ($–SO_3^-$). If a cation is entrapped at the center of a tripod of three oxygen atoms in a sulfonate group, a sulfur atom is located slightly further apart from the cation than the oxygen atoms. A two-shell model was not applicable to the present cases because of limited k ranges available for data analyses. Therefore, the contribution from the sulfur atom was estimated by the FEFF calculation on the model system of $–S{\equiv}O_3–K^+$, where the distance between K^+ and O was kept at 2.750 Å and that between K^+ and S was 2.867 Å. The model calculation has indicated that the $K \rightarrow S \rightarrow K$ and $K \rightarrow O \rightarrow K$ paths similarly contribute to the oscillation amplitude; the former is only 7.5% higher than the latter. Since a sulfur atom has higher back-scattering ability than an oxygen atom but is located slightly farther away, these two effects are cancelled out and result in similar effects of these different paths. Thus, the presence of a sulfur atom should be just equivalent to the addition of one more oxygen atom near the metal ion, because a difference in the distance between K–O and K–S cannot be resolved. This situation is similarly applicable to other cations studied in this work.

The coordination numbers for dried resins were $N = 3.1$ for K^+, $N = 3.7$ for Rb^+, and $N = 3.7$ for Sr^{2+}. If a cation is entrapped by one $–SO_3^-$ group, N should be four from the above consideration. Although the N values are slightly smaller than 4, we can say that most of the countercations form 1 : 1 ion pairs with the $–SO_3^-$ groups. Since the alkali metal cations are monovalent, this conclusion must be reasonable. Sr^{2+} is divalent, and, thus, an intuitive stoichiometric consideration suggests that two sulfonate groups are detected

Table 1 XAFS parameters determined from the spectra in Fig. 1

K K-edge (Fitting; $k = 2.0–7.0$ Å^{-1})			
	K^+ in water	**Resin in water**	**Dried resin**
r/Å	2.76 (0.07)	2.76 (0.52)	2.75 (0.21)
N	4.04 (0.77)	4.55 (5.82)	3.13 (1.60)
σ/Å	0.16 (0.07)	0.17 (0.19)	0.16 (0.12)
Rb K-edge (Fitting; $k = 1.8–5.0$ Å^{-1})			
	Rb^+ in water	**Resin in water**	**Dried resin**
r/Å	2.78 (0.06)	2.81 (0.19)	2.73 (0.15)
N	3.58 (1.68)	3.21 (4.66)	3.67 (4.40)
σ/Å	0.15 (0.11)	0.14 (0.21)	0.17 (0.17)
Sr K-edge (Fitting; $k = 2.0–10.0$ Å^{-1})			
	Sr^{2+} in water	**Resin in water**	**Dried resin**
r/Å	2.54 (0.02)	2.54 (0.02)	2.47 (0.02)
N	6.22 (1.06)	5.96 (0.99)	3.67 (0.81)
σ/Å	0.10 (0.05)	0.10 (0.05)	0.08 (0.06)

near the ion. However, interestingly, the XAFS spectra indicate that only one sulfonate group is present in the close vicinity of Sr^{2+}. The sulfonate groups should be located at appropriate positions for two sulfonate groups to bind Sr^{2+} simultaneously. The movement of the sulfonate groups to the appropriate positions to bind multivalent cations may severely be restricted in the macro-reticular resins. However, the entire charges in a resin particle should basically be balanced by the stoichiometric ratio of the $-SO_3^-$ groups and Sr^{2+}.

When the resins are soaked in water, both the $-SO_3^-$ groups and counterions are hydrated. Since the M–O ($-SO_3^-$) distance is almost the same as M–O (H_2O) distance, XAFS parameters do not provide clear information on the local structure of the countercations in the hydrated resin. The comparison of the spectral features gives us qualitative but important implications. The spectrum for hydrated Rb^+ perfectly agrees with that for Rb^+ in the hydrated resin. Similarly, the spectrum for hydrated Sr^{2+} also completely overlaps with that for Sr^{2+} in the hydrated resin. It is thus strongly suggested that these cations are completely hydrated even in the interior of the cation-exchange resin; the water-shortage circumstance in the resin does not cause the dehydration of these cations. This is apparently supported by the XANES spectra shown in Fig. 2; no clear difference is seen in the spectra for the hydrated ions and hydrated resins. It should be noted that the above discussion holds only for the first coordination shell, because XAFS cannot probe the long-distance structures in a solution phase. The conductivity measurements of ion-exchange membrane have suggested that these ions are basically entrapped by the electrostatic field of fixed charges because the conductivity of a multivalent ion is much lower than the corresponding value measured in bulk water.[12] Thus, the hydrated countercations probably sit on the sulfonate groups, as schematically illustrated in Fig. 3.

In contrast, the spectrum for K^+ in the hydrated cation-exchange resin has the spectral features both for hydrated K^+ and for K^+ in the dried resin. The χ spectrum obtained for K^+ in the swollen resin (Fig. 2) completely overlaps that for the hydrated ion in the range of $k < 4.5$ Å^{-1}, but has features for K^+ in the dried resin for $k > 4.5$ Å^{-1}, suggesting that two major scattering paths that cannot be resolved by usual curve-fitting are involved. Similarly, the XANES spectrum for hydrated resin shows an intermediate feature of those of dried resin and hydrated K^+. It is known that the XANES spectra of K^+ largely depend on the local structure of K^+.[13] We have indicated that the following linear combination is useful to separate the contributions from two different paths, and allowed the discussion of the hydration of bromide ions in an anion-exchange resin[5] and micelles.[14]

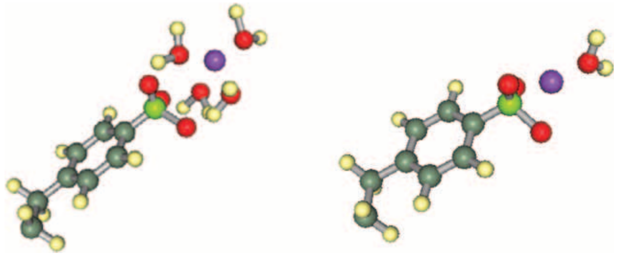

Fig. 3 Local structures of countercations. Rb^+ adopts the left configuration, whereas K^+ adopts the two different structures depicted here. It is not clear whether K^+ directly bound by the sulfonate group is completely dehydrated or a few water molecules still hydrate it.

$$\chi = \alpha_1\chi_1 + \alpha_2\chi_2$$

where α_1 and α_2 are coefficients representing the contributions from χ_1 and χ_2. In the present particular case, χ_1 and χ_2 can be represented by the spectra for the dried resin and the hydrated potassium ion, respectively. The curve-fitting based on the above equation explains the spectrum well, with $\alpha_1 = 0.40$ ($\sigma = 0.22$) and $\alpha_2 = 0.63$ ($\sigma = 0.17$), albeit ambiguities coming from relatively large standard deviations are included in the α_1 and α_2 values. This result implies that some of the potassium ions are directly bound to the sulfonate groups in the resin, while a larger part is completely hydrated. A usual consideration will lead to the idea that poorly hydrated ions should be more easily dehydrated than well hydrated counterparts under the strong influence of an electrostatic field or water-shortage conditions. However, the present study has indicated that less hydrated Rb^+ keeps its hydration shell, whereas more hydrated K^+ is partly dehydrated. Such results are not predictable from the hydration energies of alkali cations in bulk water or from the previous studies on counter-anions in anion-exchange resins.

Notes and references

1 N. Lang and A. Tuel, *Chem. Mater.*, 2004, **16**, 1961; G. L. Price, *Catal. Prep.*, 2007, 283; T. Ikegami, J. Ichimaru, W. Kajiwara, N. Nagasawa, K. Hosoya and N. Tanaka, *Anal. Sci.*, 2007, **23**, 109.

2 Y. Kanzaki, *J. Ion Exch.*, 2007, **18**, 48; D. W. Crick and S. D. Alexandratos, *Magn. Reson. Chem.*, 1994, **32**, S40; M. Ohuchi, P. Meadows, H. Horiuchi, Y. Sakai and K. Furihata, *Polym. J.*, 2000, **32**, 760; A. Marton and Y. Miyazaki, *Prog. Colloid Polym. Sci.*, 2001, **117**, 153; V. Crupi, F. Longo, D. Majolino and V. Venuti, *J. Chem. Phys.*, 2005, **123**, 154702.

3 D. Nandan and A. R. Gupta, *J. Phys. Chem.*, 1975, **79**, 180; D. Nandan and A. R. Gupta, *J. Phys. Chem.*, 1977, **81**, 1977; D. Nandan, B. Venkataramani and A. R. Gupta, *Langmuir*, 1993, **9**, 1786; R. S. D. Toteja, B. L. Jangida, M. Sundaresan and B. Venkataramani, *Langmuir*, 1997, **13**, 2980.

4 M. Harada and T. Okada, *J. Chromatogr., A*, 2005, **1085**, 3; M. Harada, T. Okada and I. Watanabe, *J. Phys. Chem. B*, 2003, **107**, 2275.

5 T. Okada and M. Harada, *Anal. Chem.*, 2004, **76**, 4564.

6 K. Yamanaka, Y. Kameda, Y. Amo and T. Usuki, *J. Phys. Chem. B*, 2007, **111**, 11337.

7 R. H. Tromp and G. W. Neilson, *J. Phys. Chem.*, 1996, **100**, 7380.

8 Y. Marcus, *Ion Solvation*, John Wiley and Sons, Chichester, 1985.

9 D. C. Koningsberger and R. Prins, in *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*, Wiley, New York, 1988; B. K. Teo, in *EXAFS: Basic Principles and Data Analysis*, Springer Verlag, Berlin, 1986.

10 B. Ravel and M. Newville, *Phys. Scr., T*, 2005, **T115**, 1007.

11 H. Ohtaki and T. Radnai, *Chem. Rev.*, 1993, **93**, 1157.

12 V. P. Greben, *Russ. J. Electrochem.*, 1997, **33**, 366; A. Yoneda and T. Azumi, *Bull. Soc. Sea Water Sci. Jpn.*, 1975, **29**, 18.

13 X. Q. Yang, H. S. Lee, J. McBeen, Z. S. Xu, T. A. Skotheim, Y. Okamoo and F. Lu, *J. Chem. Phys.*, 1994, **101**, 3230; G. Cibin, A. Mottana, A. Marcelli and M. F. Brigatte, *Mineral. Petrol.*, 2005, **85**, 67.

14 M. Harada, H. Satou and T. Okada, *J. Phys. Chem. B*, 2007, **111**, 12136; T. Aoki, M. Harada and T. Okada, *Langmuir*, 2007, **23**, 8820.