

# Neutron Diffraction Study on the Local Structure around Chloride Ions in Anion Exchange Resins

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Ion exchange resins have wide application in extensive fields of fundamental sciences and industries. In order to obtain structural information on the correlation between the cation and the ion exchanging group [1], and on the hydrogen-bonded network among water molecules within the resins [2], neutron diffraction with isotopic substitution method has frequently been adopted.

In the present report, we describe the results of neutron diffraction on hydrated anion exchange resins (AER) containing  $^{35}\text{Cl}/^{37}\text{Cl}$  isotopically substituted chloride ions to investigate the environmental structure around the chloride ion which is interacting with the anion exchange group,  $(\text{CH}_3)_3\text{N}^-$ .

Anion exchange resins (Amberlite IRA402BL,  $\text{Cl}^-$  form) with different  $^{35}\text{Cl}/^{37}\text{Cl}$  ratios (equilibrated with  $\text{D}_2\text{O}$ ), I (AER- $^{35}\text{Cl}$ )0.0679( $\text{D}_2\text{O}$ )0.9321, 99.0%  $^{35}\text{Cl}$ , and II (AER-natCl)0.0679( $\text{D}_2\text{O}$ )0.9321, 75.8%  $^{35}\text{Cl}$  (natural abundance), were prepared by repeated soaking of the OH-form resins by aqueous  $\text{Na}^+\text{Cl}$  solutions. Light water molecules within the resins were exchanged to  $\text{D}_2\text{O}$  in order to obtain good statistical accuracy of the observed difference function. The resin beads were sealed in a cylindrical quartz cell (12.0 mm in inner diameter and 1.1 mm in thickness).

Neutron diffraction measurements were carried out at 298 K using the ISSP diffractometer 4G (GPTAS) installed at the JRR-3M research reactor with an incident neutron wavelength of 1.092(3) Å. Beam collimations used were  $40'-80'-80'$  in going from the reactor to the detector. Scattered neutrons were collected over the angular range of  $3 < 2\theta < 118$  deg. which corresponds to  $0.30 < Q < 9.86$  1/Å. The pre-

set time was set to 410s. The total number of observed counts was at least 1100000 counts, and regarded as high as 1800000 counts. Measurements were made in advance for an empty cell, a vanadium rod of 10 mm in diameter, and an instrumental background. After corrections for the background, absorption and multiple scattering, the observed count rates were converted to the normalized scattering cross section by use of corrected scattering intensities from the vanadium rod.

The first-order difference function [3],  $\Delta\text{Cl}(Q)$ , which involves information on the local structure around the chloride ion, was obtained from the numerical difference between scattering cross sections observed for the samples I and II. In the present experimental conditions, the observed  $\Delta\text{Cl}(Q)$  involves  $\text{Cl}^- \dots \text{D}_2\text{O}$  and  $\text{Cl}^- \dots (\text{CH}_3)_3\text{N}^-$  contributions. The distribution function,  $G_{\text{Cl}}(r)$ , (Fig. 1) derived from the Fourier transform of the observed  $\Delta\text{Cl}(Q)$  is characterized by a well resolved first peak at around  $r = 2$  Å, followed by the second peak appearing at  $3 < r < 4$  Å. These peaks should involve contributions from  $\text{Cl}^- \dots$  the nearest neighbor  $\text{D}_2\text{O}$  molecules as well as  $\text{Cl}^- \dots (\text{CH}_3)_3\text{N}^-$  interactions. The first peak may contain both contributions from  $\text{Cl}^- \dots \text{D}(\text{D}_2\text{O})$  and  $\text{Cl}^- \dots \text{H}(\text{CH}_3)$  interactions. The former contributes as a positive peak in the distribution function, while the latter should appear as a negative peak. Structural parameters for the  $\text{Cl}^- \dots \text{D}_2\text{O}$  and  $\text{Cl}^- \dots (\text{CH}_3)_3\text{N}^-$  interactions were determined by the least squares fitting analysis of the observed  $\Delta\text{Cl}(Q)$  function. It has been revealed that the chloride ion is neighboring on a  $(\text{CH}_3)_3\text{N}^-$  group of the ion exchange resin with the nearest neighbor  $\text{Cl}^- \dots \text{N}$  dis-

tance of 3.10(3) Å. The average number of D<sub>2</sub>O molecules within the first hydration shell of the chloride ion was determined to be 2.4(1) with the nearest neighbor Cl...D(D<sub>2</sub>O) distance of 2.25(2) Å.

#### References

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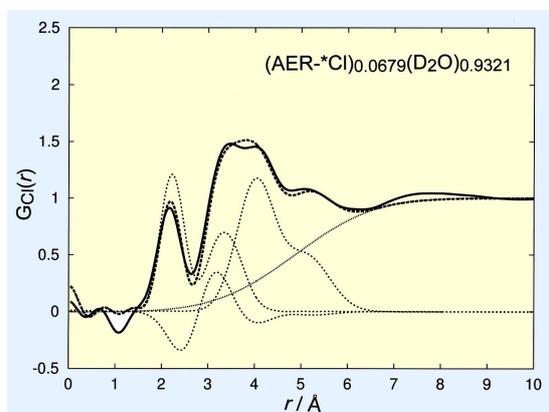


Fig. 1. Observed distribution function around the chloride ion in the anion exchange resin (solid line). The Fourier transform of the best-fit of the calculated  $\delta Cl(Q)$  function (thick broken line).