

## A novel strategy for improving selectivity in ion-exchange separation through studying the hydration of counter ions

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Ion-exchange has been utilized in various application as a versatile and effective means for material separation. Although it is in general regarded as a mature technique, molecular mechanisms of ion-exchange processes have been little known. The most essential and basic questions to be answered are how separation selectivity in ion-exchange emerges and whether counterions are dissociated from the ion-exchange groups or not. A number of thermodynamic data compiled in this area have implied the significant involvements of ion solvation in the determination of ion-exchange selectivity, but have not given clear answers to the above questions. This situation mainly results from the lack of efficient approaches to the molecular mechanisms of ion-exchange phenomena. We recently showed that X-ray absorption fine structure (XAFS) can be an effective approach to elucidate the structures of counterions in ion-exchange resins. XAFS has very high atomic selectivity, and thus allows us to probe the local structures of counterions without the interference from resin matrices and solvents. In the present research, the local structures of Cl<sup>-</sup> and Br<sup>-</sup> in anion-exchange resins equilibrated with varied partial vapor pressures of water are studied, which provide a clue to solve the questions noted above, on the basis of XAFS, adsorption isotherms of water on the resin, and calorimetric measurements.

The detailed analyses of XAFS spectra have indicated that the counterions are bound by the ion-exchange sites even when sufficient water molecules are available for their hydration. Correcting the effects of the ion-exchange sites on the spectra has allowed us to extract the contribution from water molecules coordinating counterions. The coordination number increases with increasing number of water molecules available, but becomes constant; the average coordination numbers finally reached are 3.5-4 for both counteranions. In order to explain the results of XAFS and water adsorption isotherms, a molecular hydration model has been derived, which has successfully provided the hydration equilibrium constants in the ion-exchange resin. According to the model, counteranions bound by the ion-exchange groups are hydrated without their dissociation from the sites until the hydration number becomes three. However, when more water molecules are available for hydration, the counteranions are fully hydrated (the coordination number is six), and dissociated from the sites. In the resins studied in the present research, ca 30% of counterions are dissociated from the sites when the resins are completely swollen in water. The partial dehydration of counterions in the resins possibly determines the ion-exchange selectivity, and thus the separation can be modified by controlling the hydration state of counterions in the resin.