Penetration of Hydrophilic Anions into Strongly Acidic Cation-exchange Resin Aided by Bridging Complexation

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Several anions were found to penetrate into a strongly acidic cation-exchange resin by the aid of complexation with Fe^{3+} ion to give dimeric species, such as $[(\text{–S})_2Fe(A)Fe(S\text{–})_2]$ (–S: benzenesulfonate bound to polymer network; A^{2-}: $HPO_4{}^{2-}$, $HPO_3{}^{2-}$), and species having a composition of (–S):Fe:A = 2:1:1 (A^-: OH^-, $H_2PO_2{}^-$).

We have recently proposed a new method to identify the species adsorbed to ion-exchange resins and gel phases. This utilizes the adsorption isotherms measured under the conditions of excess metal ions against the functional groups, in contrast to the conventional method. Application of this method to adsorption of trivalent metal ions (M^{3+}) to an iminodiacetate-type ($\text{–}LH_2$) chelating resin clearly indicated the presence of an additional species $[(\text{–}LH)_3M^{III}]$ for some metal ions, as well as a common species $[(\text{–}L)(\text{–}LH)M^{III}]$.[1] These species were later confirmed both by X-ray diffraction and hydration studies.[2,3] In a systematic application of this methodology, we have eventually found that hydrophilic anions do penetrate into a strongly acidic cation-exchange resin by the aid of complexation, in spite of the Donnan exclusion effects. The stoichiometric study has demonstrated that the occurrence of coadsorption depends on the number of hydrolysable protons of the conjugate acid used and on the coordinating and bridging abilities of the resulting anion.

The effect of pH on the adsorption of Fe^{3+} to the strongly acidic cation-exchange resin (Amberlite 252, Na-form of benzenesulfonate abbreviated as (–S)Na, exchange capacity (*EC*) of 3.83 mmol g^{-1}) in small excess metal ion against benzenesulfonate group is shown in Figure 1a.[4] With an increase in pH, the adsorption increased to 33%, and to 50% of *EC*, but then decreased due to precipitation of hydroxide. The first plateau is expected in trivalent metal ions, $[(\text{–S})_3M^{III}]$, while the second plateau in divalent metal ions, $[(\text{–S})_2M^{II}]$. Thus, singly hydrolyzed iron, $Fe(OH)^{2+}$, is adsorbed or OH^- is coadsorbed with Fe^{3+}.

When varying amounts of acids or salts were added to this reaction system at a fixed pH of 1.1, no changes were found for HNO_3, HCl, SCN^-, and CH_3COOH, while a simple decrease was found for HF at $>10^{-3}$ mol dm^{-3} , due to the enhanced complexation in an aqueous phase. In contrast, the adsorption increased to 50% of *EC* at the maximum and then decreased in the cases of H_3PO_4 (Figure 1b), H_3PO_3, and H_3PO_2 (Figure 1c). In accordance with the increase in adsorption of Fe^{3+}, the coadsorption of the anion increased to 25% of *EC* for H_3PO_4 and H_3PO_3, while to 50% for H_3PO_2 at the maximum. The differential FT-IR spectrum between the resin in the form of $[(\text{–S})_3Fe]$ and that obtained in the presence of H_3PO_4 showed peaks characteristic of $HPO_4{}^{2-}$ rather than $H_2PO_4{}^-$ (see Supporting Information).[5]

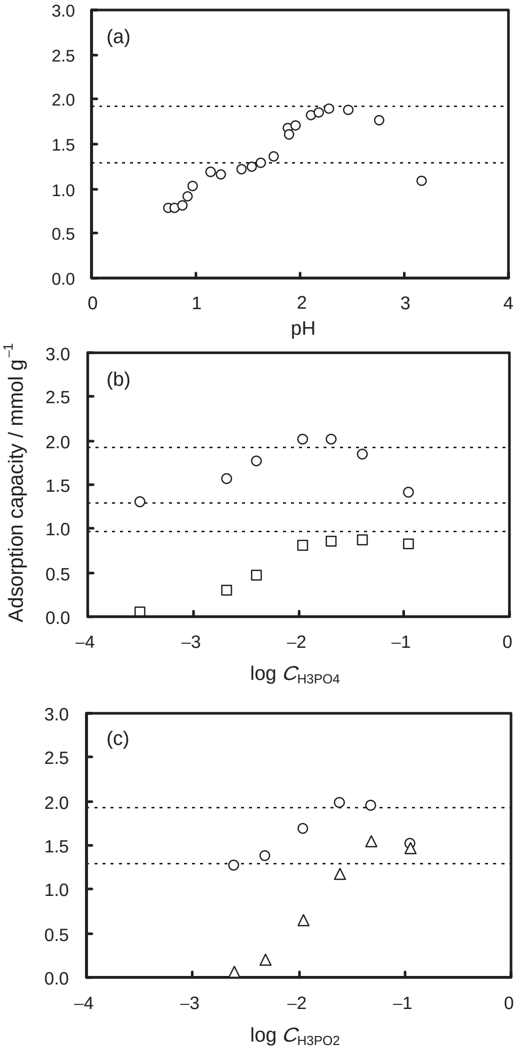

Figure 1. Effects of pH (a) and concentrations of phosphoric acid (b) and phosphinic acid (c) on the adsorption capacities of Fe^{3+} (○) and phosphorus (□, △). Horizontal lines correspond to 50%, 33%, and, if present, 25% of functional group.

The water content of each resin dried at a relative humidity of 40% and at 298 K was determined by Karl Fischer coulometry, and the average number of water molecules bound to Fe^{3+} was calculated. The number of 3.2 ± 0.2 is reasonable for the hexa-coordinate trivalent iron with three monodentate benzenesulfonates, $[(\text{–S})_3Fe]$. In contrast, the resins adsorbing anions were markedly dehydrated: 0.39 ± 0.05 for the resin adsorbing OH^- and 1.06 ± 0.04 for the resin adsorbing $HPO_4{}^{2-}$. Taking into consideration the hydration number, 2.7, of $H_2PO_4^-$ in the tetraalkylammonium-type anion-exchange resin, not only Fe^{3+} but phosphate is extensively dehydrated.

Based on all these findings, the adsorbed species in the presence of phosphoric acid ($pK_a = 2.2, 7.2, 12.0$) was identified as $[(–S)_2Fe(HPO_4)Fe(S–)_2]$. Another possibility of an ion pair, such as $[(–S)_2Fe]^+$, $[(–S)_2Fe(HPO_4)]^-$, is excluded by the enhanced dehydration. Although the aqueous phase consisted of 90% H_3PO_4 and 10% $H_2PO_4^-$, the adsorbed species involved HPO_4^{2-}. This further deprotonation was promoted by the interaction with two Fe^{3+} centers to give a bridging structure and by the charge compatibility. On the assumption of uniform dispersion of Fe^{3+} in the resin, the mutual distance would be 9.4 Å. On the other hand, the Fe–Fe distance in dimers bridged by carboxylates is around 3.4 Å. Taking possible changes in conformation of the benzenesulfonates in the resin phase into account, the bridging of Fe^{3+} centers by HPO_4^{2-} is plausible. The coordination sphere around Fe^{3+} is occupied by two sulfonates, half hydrogen phosphate, and one water molecule and expected to be appreciably coordination-unsaturated with monodentate sulfonates. The similar phenomenon was observed in phosphonic acid ($pK_a = 1.4, 6.5$). A minor species of HPO_3^{2-} was adsorbed from the aqueous phases consisting of 33% H_3PO_3 and 67% $H_2PO_3^-$.

In the case of phosphinic acid ($pK_a = 1.2$), on the other hand, one $H_2PO_2^-$ was taken by one Fe^{3+} under the conditions of 45% H_3PO_2 and 55% $H_2PO_2^-$; the composition of the adsorbed species is the same as that coadsorbing OH^-. Since the hydration number of the resin coadsorbing OH^- is about half and is smaller than that of $[(–S)_2Fe(HPO_4)Fe(S–)_2]$ by 0.65, some sort of bridging is expected but the exact composition is not given at this stage.[6]

The anions showing the (–S):Fe:A = 2:1:1 coadsorption have larger stability constants of Fe^{3+} complexes ($\log K_{ML} = 11.0$ for OH^-, 4.0 for $H_2PO_2^-$), while those showing no coadsorption have lower stability constants (−0.2 for NO_3^-, 0.6 for Cl^-, 2.1 for SCN^-, 3.4 for CH_3COO^-). The anions showing the adsorption of (–S):Fe:A = 4:2:1 do not always have high stability constants (4.9 for $H_2PO_3^-$, 3.5 for $H_2PO_4^-$) but possess another hydrolysable proton. The anion with a high stability constant (5.2 for F^-) does not always show coadsorption. These findings indicate that not only the high affinities to metal ions but also the number of hydrolysable protons and the bridging ability are decisive for the occurrence and the mechanism of coadsorption.

The adsorption of anions to metal ions immobilized in the resin or the gel phase is well known for those with chelating functional groups. Especially when a positive charge of a metal ion is in excess against that of a chelating group, an anion is adsorbed by ion-pair formation, such as $[(–L)In(ClO_4)]$, or by complexation, such as $[(–L)Zr(OH)_2]$.[1,7] This type of composite material has been used widely as adsorbents[8] or as stationary phases of ligand-exchange chromatography[9] and immobilized metal affinity chromatography.[10] It has been pointed out that the balance between affinities of metal ions to chelating groups and to sample anions is important for effective performances. In this work, we have first demonstrated that such adsorption of anions do occur on metal ions immobilized only by weak electrostatic interactions with stepwise nature,[11] and that the bridging abilities of anions enhance the coadsorption.[12] A systematic survey about the combination of metal ions and anions is now under investigation in our laboratory.

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References and Notes

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4 The resin was dried to a constant weight in a glove box at a relative humidity of 40% and at 298 K. Portions of the dried resin were weighed and were equilibrated respectively with a series of solutions containing a fixed concentration of Fe^{3+} and varying concentrations of conjugate acids of relevant anions (Na salt for SCN^-). The concentration of Fe^{3+} in supernatant was determined by chelatometric titration and was subtracted from the total concentration. The differential chemical amount divided by the mass of the resin gave the adsorption capacity of Fe^{3+}. The resin adsorbing Fe^{3+} and an oxoanion of phosphorus was repeatedly washed with nitric acid solutions at pH 1.1. The collected solutions were subjected to determination of phosphorus by the molybdenum blue method. The chemical amount divided by the mass of the resin gave the adsorption capacity of phosphate. These were used for calculation of the stoichiometric ratio in the resin phase.
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