Diverse Secondary Interactions between Ions Exchanged into the Resin Phase and Their Analytical Applications

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The research activities by the author’s group to elucidate the chemical states of ions within the ion exchange resin phase are summarized. The resin with the higher exchange capacity has the smaller space available for ion exchange, and the higher cross linking degree interferes more with swelling of the resin. As a result, diverse secondary interactions between exchanged ions are observed on the resins of high exchange capacities and high cross linking degrees: the van der Waals contact results in incomplete exchange or enhanced dehydration of ions, hydrogen bond formation between acidic anions, and coadsorption of anions with metal ions. Contribution of the simple ion exchange mechanism to the reactions of iminodiacetate-type chelating resins with metal ions in the acidic media is quantitatively discussed. The resulting complexes were successfully applied to preconcentration and separation of anions.

Keywords Ion exchange resin, hydration state, coadsorption, hydrogen bond, preconcentration, separation

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chelating resins with metal ions, which inspired the idea of volume available for ion exchange,\textsuperscript{25-29} and the analytical applications of the metal complexes with a chelating gel as the composite material for preconcentration and separation of anions are also briefly reviewed.\textsuperscript{30-35}

\section*{2 Background Information}

\textbf{2-1 Resins}

The properties of the resins used are summarized in Table 1.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Resin & \textit{EC} & Void & \textit{r}_{\text{void}} & Remark & Ion & \textit{r} \\
\hline
 & mmol g\textsuperscript{-1} & \AA\textsuperscript{3} & \AA & & & \AA \\
\hline
\textbf{Cation-exchange resin} & & & & & & \\
CG-4.6×4 & 4.55 & Not available & 4.0 & Amberlyst 252 & Li\textsuperscript{+} & 3.4 \\
CG-4×2 & 3.95 & 320 & 4.0 & Dowex 50W & Na\textsuperscript{+} & 3.8 \\
CG-4×4 & 4.00 & 290 & 4.1 & Dowex 50W & K\textsuperscript{+} & 4.2 \\
CG-4×8 & 4.07 & 260 & 4.2 & Dowex 50W & Rb\textsuperscript{+} & 4.3 \\
CG-3.7×8 & 3.65 & 290 & 4.1 & Amberlite IR120B & Cs\textsuperscript{+} & 4.5 \\
CG-1×2 & 1.29 & 1500 & 7.1 & Prepared & H\textsuperscript{2}PO\textsubscript{4}\textsuperscript{-} & 5.3 \\
CG-1×5 & 0.96 & Not available & 7.1 & Prepared & Not available & \\
CP-4×12 & 3.91 & 280 & 4.0 & Amberlite 252 & Not available & \\
\textbf{Chelating resin} & & & & & & \\
IP-2 & 2.10 & Not available & 4.0 & Amberlite IRC-718 & Prepared & \\
IG-0.03 & 0.03 & Not available & 4.0 & Toyopearl 650M & Prepared & \\
\textbf{Anion-exchange resin} & & & & & & \\
AG-3.5×2 & 3.45 & 410 & 4.6 & Dowex I & F\textsuperscript{-} & 4.1 \\
AG-3.5×4 & 3.48 & 410 & 4.6 & Dowex I & Cl\textsuperscript{-} & 4.6 \\
AG-3.5×8 & 3.46 & 410 & 4.6 & Dowex I & Br\textsuperscript{-} & 4.8 \\
AG-1.5×1 & 1.45 & 1350 & 6.9 & Prepared & H\textsubscript{3}PO\textsubscript{4}\textsuperscript{-} & 5.3 \\
AG-0.9×2 & 0.87 & 2500 & 8.4 & Prepared & & \\
\hline
\end{tabular}
\caption{Properties of resins and ions}
\end{table}

\textsuperscript{a} Radius of hydrated ion. \textsuperscript{b} Radius of naked ion.
The first letter of the abbreviated name indicates whether it is a cationic (C), chelating (I), or anionic (A) resin, the second letter specifies whether it is a gel (G) or porous (P), the first digit shows the approximate exchange capacity (EC), and the second digit the cross-linking degree (CL), if available. The cation exchange resins (CXRs) of low EC were synthesized by polymerization, while the anion exchange resins (AXRs) of low EC were derived from the Merrifield resin.

The volumes available for ions in the resins were estimated as follows: the volume of one functional group associated with a certain ion could be calculated from the exchange capacity and the density of the dried resin, while the volume of the same functional group without ion could be estimated based on the additivity of molar volumes. The difference between these volumes, called void, allows for the space for ions. On the assumption that the entire volume is effectively used, the maximum radius of the spherical species occupying this space in the dry state, \( r_{\text{void}} \), is estimated as shown in Table 1; all these numbers indicate the radius based on only the additivity without considering the effect of cross-linking. The radius decreases to 60% with an increase in capacity by 4 times. Some attempts to experimentally determine the space available for ion exchange are now in progress in our laboratory.

2.2 Ions

The properties of the ions used are also summarized in Table 1. The radius of each of the hydrated alkali metal ions and anions in water was simply estimated by the sum of the ionic radius and twice the van der Waals radius of oxygen (2.8 Å) to a precision of 0.1 Å. The radius of quaternary ammonium ion (QA) was calculated from the partial molar volume at infinite dilution. As a rough image, the radii of hydrated alkali metal ions and naked QAs cover a comparable range of 3.2 – 4.5 Å, while the radii of hydrated anions are appreciably larger than those of cations.

3 Incomplete Exchange by Bulky Ammonium Ions Due to van der Waals Contact

The exchange equilibria of K⁺ on CXRs (CG-1×2, 4×2, 4×8) by QAs (TMA⁺, tetramethyl-; TEA⁺, tetraethyl-; TPA⁺, tetrapropyl-ammonium ion) were studied (Fig. 1). Quantitative exchange was observed for all QA on CG-1×2 but only for TMA⁺ on CG-4×2 and on CG-4×8. The maximum exchange reached 98% for TEA⁺ and 92% for TPA⁺ on CG-4×2, and 82% for TEA⁺ and 60% for TPA⁺ on CG-4×8. Although such phenomena found as early as the 1950s were attributed to the size-exclusion effect, the mean diameters of micropores in CXRs suspended in water (343 Å at divinylbenzene content of 1%; 151 Å at 2%; 58 Å at 4%; 30 Å at 8%; 15 Å at 16%) was much larger than twice the ionic radius of QAs (Table 1). A comparison of the ionic radii of these ions with the radius of the void of each resin indicates that the possible van der Waals contact between bulky QAs at high loading into the resin phase rather interferes with the quantitative exchange (Scheme 1(a)).

4 Enhanced Dehydration of Strongly Hydrated Ions Due to van der Waals Contact

The hydration number \( n_{\text{M}} \) was determined for alkali metal ions (M⁺) quantitatively exchanged on the same three CXRs at the relative humidity of 50% and is plotted against the radius of the hydrated ion \( r_{\text{hyd}} \) in Fig. 2. At this humidity, only strongly bound water molecules remained. The \( n_{\text{M}} \) values of weakly hydrating ions like K⁺, Rb⁺, and Cs⁺ were around 2 on all resins. In contrast, the \( n_{\text{M}} \) values of strongly...
hydrating ions decreased with increases in EC and CL: 3.8 on CG-1\times2, 3.6 on CG-4\times2, and 3.0 on CG-4\times8 for Li\(^+\); and 3.6 on CG-1\times2, 2.8 on CG-4\times2, and 2.5 on CG-4\times8 for Na\(^+\). These ions keep their hydration numbers in water and may form separated ion-pairs on the resins of low EC and of low CL, while the possible van der Waals contact between hydrated ions at high loading enhances dehydration on the resins of high EC and high CL (Scheme 1(b)).

The hydration numbers \(n_X\) of singly charged anions \(X^-\) quantitatively exchanged on five AXRs (AG-3.5\times8, \times4, \times2, AG-1.5\times1, AG-0.9\times2) at the relative humidity of 50\% are shown as the function of EC and CL in Fig. 3.\(^2\) Similarly, the \(n_X\) values of weakly hydrating anions were independent of the resin \((\text{e.g., around } 0.9 \text{ for } \text{ClO}_4^-)\), while those of F\(^-\) decreased from 6.6 to 5.6, those of Cl\(^-\) from 3.4 to 2.4, and those of Br\(^-\) from 2.5 to 1.7 with increases in EC and CL. This also indicates that the possible van der Waals contact between hydrated anions at high loading enhances dehydration.

5 Enhanced Dehydration and Intermolecular Hydrogen Bond Formation of H\(_2\)PO\(_4^-\) on AXRs

The ion-exchange equilibria of Br\(^-\) on AG-0.9\times2 and AG-3.5\times8 by phosphate were analyzed by taking into consideration the contribution of 1:1 and 1:2 species.\(^2\) The selectivity coefficients of 1:1 species \(K_{11}\) were constant on AG-0.9\times2 but increased at a % exchange higher than 70 on AG-3.5\times8 by about unity in logarithmic scale (Fig. 4). This indicates the cooperation between H\(_2\)PO\(_4^-\). The hydration number of H\(_2\)PO\(_4^-\) on AG-0.9\times2 of the largest void was as large as 6.1. The number, however, decreased with increases in EC and CL and was as low as 2.4 on AG-3.5\times8 as shown in Fig. 3.\(^2\) The infrared spectra of the H\(_2\)PO\(_4^-\)-form resins indicate the intermolecular hydrogen bonds only at high loading into AG-3.5\times8. Thus, high loading
of H₃PO₄⁻ into the resin of high EC and high CL induces formation of the intermolecular hydrogen bonds accompanied by dehydration so as to avoid the possible van der Waals contact between hydrated ions (Table 1, Scheme 1(c)). Upon heating, facile intermolecular dehydration giving diphosphate was observed only on this resin.

6 Hydration States of Multivalent Cations and Their Coadsorption with Anions

The hydration numbers of multivalent ions on CP-4×12 were determined and are shown as the function of the radius of hydrated ions in Fig. 5.21 The n_M values of monovalent ions were substantially equal to those on CG-4×8 (Fig. 2) and were independent of the resin type whether gel or porous. The n_M values of divalent ions decreased from 8 to 6, and those of trivalent metal ions from 12 to 8 with an increase in r_hyd. Because the spaces available for these ions are formally twice or three times larger than those for monovalent ions and because the hydration of these ions is much stronger than that of monovalent ions, the divalent and trivalent metal ions are fully hydrated or occasionally hold even a part of the second hydration shell in the resin phase and form separated ion pairs with two or three exchange groups (Scheme 1(d)).

When the increasing amounts of certain anions (P(V), P(III), P(I), Se(IV), OH⁻) were present in the exchange of trivalent metal ions (M³⁺: Fe³⁺, Al³⁺, Ga³⁺, In³⁺, Sc³⁺) into CP-4×12 or CG-4.6×4 under the conditions of metal ions in excess against exchange groups, an increase in adsorption of metal ions accompanied by adsorption of these anions was observed as shown in Fig. 6(a). This indicates coadsorption of anions in spite of the same electric charge with the functional group. Coadsorption of hydroxide was observed even on the resin of the lower EC, CG-1×5, but phosphate simply interfered with the exchange as a masking reagent (Fig. 6(b)). The Mössbauer spectra of the Fe³⁺-OH⁻-type resins indicated the presence of two species on CP-4×12 or CG-4.6×4, but one of these species prevailed on CG-1×5. The common species was assigned to [(−S)₂Fe-OH⁻] (−S⁻: cation exchange group), while the species found only on the resin of high EC to [(−S)₂Fe-O-Fe(S⁻)₂] (Scheme 1(e, f)). The coadsorption in the presence of P(V) was attributed to [(−S)₂Fe-(HPO₄⁻)-Fe(S⁻)₂]. These two species can exist only on the CXRs of high EC, which guarantees the close placement of metal ions to be bridged by anions like O²⁻ or HPO₄²⁻.

7 Reaction of IDA Resin and Gel with Excess M(II), M(III), and M(IV)

The effect of pH on the reaction of iminodiacetate-type chelating resin (IP-2, -LH₂) with trivalent metal ions (M³⁺) under the conditions of metal ions in excess against the functional group is given in Fig. 7.25 Trivalent iron as well as Al³⁺, Ga³⁺, and In³⁺ formed only the 2:1 species according to Eq. (1) as shown in Fig. 7(a).

\[
M^{3+} + 2(-LH_2) \rightleftharpoons [(−L)(−LH)M] + 3 H^+ \quad (1)
\]

In contrast, Sc³⁺, Y³⁺, and La³⁺ formed not only the 2:1 species but the 3:1 species given by Eq. (2) at the lower pH as shown in
As a result, these metal ions are adsorbed in the pH range, which is lower by 1.5 than that expected provided only \([(-L)(-LH)M]\) is formed.

Similar behaviors were observed for divalent metal ions (M\(^{2+}\)). Common metal ions formed only the 1:1 species given by Eq. (3), while Ca\(^{2+}\) formed not only the 1:1 species but the 2:1 species in the acidic media as given by Eq. (4).

\[
M^{2+} + (-LH_2) \rightleftharpoons [(-L)M] + 2 H^+ \quad (3)
\]

\[
M^{2+} + 2(-LH_2) \rightleftharpoons [(-LH)_2M] + 2 H^+ \quad (4)
\]

The hydration number of 3.3 for \([(-L)Ca]\) indicates that Ca\(^{2+}\) is coordinated by terdentate IDA, while that of 5.9 for \([(-LH)_2Ca]\) indicates that Ca\(^{2+}\) simply forms ion pairs with keeping the hydration sphere.

The reaction of IP-2 with Zr\(^{4+}\) shows formation of the 2:1 species as given by Eq. (5), while that of IG-0.03 shows formation of the 1:1 species as given by Eq. (6).

\[
Zr^{4+} + 2(-LH_2) \rightleftharpoons [(-L)_2Zr] + 4 H^+ \quad (5)
\]

\[
Zr^{4+} + (-LH_3) \rightleftharpoons [(-L)Zr(OH)_2] + 4 H^+ \quad (6)
\]

The different behaviors are attributed to the distance between IDA groups, although the difference in polymer matrix (porous polystyrene resin in contrast to polyvinyl gel) may also be a contributing factor. The reactions of IDA resins having the lower EC with divalent and trivalent metal ions are now under investigation.

8 Preconcentration and Chromatography of Anions on Chemically Immobilized Zr(IV)

Figure 8 shows that the 1:1 complex of Zr(IV) with IG-0.03 has high affinities for several anions (A\(^-\): F\(^-\), H\(_2\)PO\(_4\)\(^-\), H\(_2\)AsO\(_4\)\(^-\), HSeO\(_3\)\(^-\)) in the acidic media by the ligand substitution reactions given by Eqs. (7) - (9), as in the case of Zr(IV)-aminopolycarboxylate complexes in aqueous solutions.

\[
[(-L)Zr(OH)_2] + H^+ + H_{n-1}A^- \rightleftharpoons [(-L)Zr(OH)(H_{n-1}A)] \quad (7)
\]

\[
[(-L)Zr(OH)(H_{n-1}A)] + H^+ + H_{n-1}A^- \rightleftharpoons [(-L)Zr(H_{n-1}A)_2] \quad \text{(only for F\(^-\))} \quad (8)
\]

\[
[(-L)Zr(OH)_2] + K^+ + H_{n-1}A^- \rightleftharpoons [(-L)Zr(OH)(H_{n-1}A)] - K^+ \quad \text{(only for F\(^-\))} \quad (9)
\]

At high pH, on the other hand, the complex showed negligible affinities for anions, due to the acid dissociation reaction given by Eq. (10).

\[
[(-L)Zr(OH)_2] + K^+ + OH^- \rightleftharpoons [(-L)Zr(OH)_3] - K^+ \quad (10)
\]

Thus, these anions could be adsorbed in the acidic media and reversibly desorbed simply by an increase in pH; e.g. Fig. 9 for phosphate. The % adsorption of these anions decreased with a decrease in anion concentration, e.g., F\(^-\) recovery was 98% at 10\(^{-4}\), 81% at 10\(^{-5}\), 42% at 10\(^{-6}\) mol L\(^{-1}\). Utilization of the flow system, however, showed satisfactory recovery even at lower concentrations. Fluoride in high purity NaCl (24 ng g\(^{-1}\) as NaF in 99.99% NaCl) and phosphate at sub-ng mL\(^{-1}\) in environmental water were successfully determined in the flow system containing this composite material for separation and preconcentration.

The same type of gel was also applied to the ligand exchange chromatography of organic anions such as benzoate derivatives in immobilized Zr(IV) affinity chromatography. Furthermore, the Zr(IV) complex with tetraphenylporphine was successfully used as a carrier or a mobile anion exchanger in the PVC membrane for potentiometry of citrate.

9 Conclusions

Diverse interactions between ions exchanged into the common ion exchange resins of higher exchange capacities are indicated by comparing their performance with those of lower exchange capacities. Solid phases of further low exchange capacities eliminate such interactions and emphasize the interaction with the polymer matrix in ion chromatography to give high selectivities. It is hoped the findings in this review, such as facile condensation of dihydrogen phosphate or coadsorption of...
anions with cations, will promote new applications of common ion-exchange resins.

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