Introduction

The electrostatic interaction between oppositely charged ions is an important driving force of various chemical processes, such as ion association, ion-pair extraction, ion exchange, and ion transport. Combining such an interaction with some other functions of recognizing specific ions provides much higher affinities in modern supramolecular chemistry. On the other hand, simple multiplicity also enhances the strength of this interaction. Cationic polyelectrolytes stoichiometrically associate with anionic polyelectrolytes in water and occasionally form precipitates called polyion complexes. This is the basis of colloidal titration of polyelectrolytes.1 The clumping phenomena generally observed between anion-exchange resins (AXRs) and cation-exchange resins (CXRs) in mixed bed operation are attributed to the electrostatic interaction between the charged groups on the surfaces of these resins.

Furthermore, a wide variety of findings and applications have been reported between AXRs and anionic polyelectrolytes or between CXRs and cationic polyelectrolytes. Oligomers derived from ion-exchange resins, humic acid and cells irreversibly adsorb on the surface of oppositely charged resins to degrade the performance (called clogging). Intentional modifications of ion-exchange resins with small amounts (up to a few mol%) of oppositely charged polyelectrolytes were, on the other hand, proposed rather for both anti-clumping and anti-clogging.2,3 Such modified resins have been reported to have higher selectivity to monovalent ions than divalent ions.4–6 Modifications of CXRs with excess cationic polyelectrolytes provided the function as AXRs for ion chromatography (surface agglomeration).7,8 Inhibition of protein refolding by self-aggregation was suppressed by ion-exchange resins having the opposite charges9 as well as by those having the same charges.10 While practical applications have been widely developed as mentioned above, they are occasionally contradictory to one another. Fundamental knowledge on the interactions between ion exchange resins and oppositely charged polyelectrolytes is limited.

In a previous paper, we have analyzed the interactions of anionic polyelectrolytes with the anion exchange liquid membrane consisting of poly(vinyl chloride), tridodecylmethylammonium salts, and o-nitrophenyloctylether.11 It has been found that a portion of polyacrylate (PA) penetrates into the membrane phase by coextraction with proton, which avoids possible contact between bulky ammonium ions on formation of multiple ion pairs in ion exchange. In this paper, we have studied the interactions of AXRs with PAs in detail.

Experimental

Reagents and chemicals

Two gel-type strongly basic anion-exchange resins of different cross-linking degrees (CL) but of comparable exchange capacities (EC) were used for the Br-forms, which were stored and manipulated in a glove box kept at 25°C and relative humidity of 50%; Dowex 1, EC of 3.00 meq g⁻¹, CL of 2%, 100 – 200 mesh (abbreviated as I-3×2) and EC of 2.96 meq g⁻¹, CL of 8%, 100 – 200 mesh (I-3×8). Polyacrylates of different mean molecular weights, PA(4.5 kDa, Na-form, Rohm & Haas), PA(25 kDa, 250 kDa, H-form, Wako Pure Chemicals) were dissolved in water or in an NaOH solution to give 10⁻¹ eq L⁻¹ solutions at pH 8.3; the equivalent amount of functional group divided by the volume...
was used as the concentration unit of PAs. Solutions of PA(25 kDa) and PA(250 kDa) were dialyzed with cellulose tubes (the molecular weight cut-off of 12 – 14 kDa) to remove PA of the smaller molecular weights; CO₂ was absorbed into the PA solutions during this operation under the present experimental conditions. All the PA solutions were conductometrically titrated using standard poly(diallyldimethylammonium chloride) solution (Wako Pure Chemicals) to determine the precise concentration.

Procedure

Ion-exchange resins of 1 mg (total equivalent amount of the functional group, TAAXR of 3 μmol) were shaken with 25 mL of 10⁻³ to 10⁻² eq L⁻¹ PA solutions (total amount, TAAP from 0.25 to 80 μeq) at 130 strokes min⁻¹ for 48 h, unless otherwise stated. PA solutions showed characteristic pH changes upon dilution as shown in Fig. S1 (Supporting Information). Although chemical equilibrium is generally analyzed under the controlled conditions such as the buffered pH and the constant ionic strength, addition of a buffer or a supporting electrolyte to the present reaction system would induce ion exchange with anions included in the buffer or in the supporting electrolyte and would make the reaction system complicated and far from practical conditions. Thus, simply diluted solutions of PA were reacted with the resin, and pH was measured before and after equilibration.

The supernatant was used to determine the equivalent amounts of PA penetrating into the resin (INPA) and of Br⁻ eluting from the resin (OUTBr), while the resin was subjected to IR spectroscopy. INPA was determined by colloidal titration of PA in the supernatant before and after the reaction. PA of the higher molecular weight (25, 250 kDa) slowly adsorbed to the glassware, so that its concentration was reduced. Adsorption in a blank without the resin was corrected for PA(25 kDa), while quantitative evaluation for PA(250 kDa) was discarded. OUTBr was determined by potentiometry with a Br⁻ ion selective electrode. The interference by PA in batchwise measurement was taken into account, using a series of calibration curves in the presence of varying concentrations of PAs (Fig. S2, Supporting Information). In continuous monitoring, the ion selective electrode was covered with the same cellulose tube as in dialysis to avoid the exposure of the electrode surface to PAs (Supporting Information). In continuous monitoring, the ion selective electrode was covered with the same cellulose tube as in dialysis to avoid the exposure of the electrode surface to PAs (Supporting Information).

The difference IR spectra of the bulk resin ground were measured by KBr disk method with the Br⁻-form resin as a reference material (Jasco, 460Plus). The IR spectra of the resin surface (depth of around 2 μm) were measured by attenuated total reflectance (ATR) method using a diamond prism (Jasco, ATR PRO450-S). The distribution of chemical elements on the resin surface was measured by an electron probe micro analyzer (EPMA, CXA-733, Jeol). The depth of around several 10s of nm was analyzed with an acceleration voltage of 5 kV.

Results and Discussion

Preliminary studies

Time courses of INPA/TAAXR and OUTBr/TAAXR were monitored in the reactions of I-3×8 with 10⁻¹ eq L⁻¹ PA(4.5, 25, 250 kDa) solutions; the equivalent amount of PA was around 10 times larger than that of the functional group in the resin under such conditions. In the case of PA(4.5 kDa), INPA/TAAXR and OUTBr/TAAXR synchronously increased up to around 70% over a period of 5 h (Fig. 1a). This indicates simple ion exchange of Br⁻ by PA. In the case of PA(25 kDa), OUTBr/TAAXR increased up to 50 or 60% within 5 h and then slightly decreased, while INPA/TAAXR slowly increased up to a comparable level over a period of 30 h (Fig. 1b). According to INPA/TAAXR, the ion exchange by PA(25 kDa) was much slower than that by PA(4.5 kDa). In the case of PA(250 kDa), OUTBr similarly increased over 5 h, while INPA after 48 h remained as low as 10% (not shown). Such asymmetric behaviors observed between INPA/TAAXR and OUTBr/TAAXR indicate some reaction other than simple ion exchange of Br⁻ by PA.

Reactions of resins with PAs

Based on these findings, three PAs at varying concentrations were reacted with two resins. INPA/TAAXR and OUTBr/TAAXR after 48 h with regard to several representative reaction systems are plotted against the initial or total concentration of PA in Fig. 2; the broken lines indicate curves expected for the quantitative reaction on the resin phase. Figure 2b is limited to the data of up to log(CBr/eq L⁻¹) = −3.5, due to the precision of INPA/TAAXR calculated from the difference in free PA concentration before and after the exchange reaction. The difference IR spectra of the resins reacted with PA at the concentration of 10⁻³ eq L⁻¹ are given in Fig. S3 (Supporting Information), and several of them are shown in Figs. 3a - 3c.

Although the selectivity of carboxylate with a short alkyl chain is lower than that of Br⁻, both INPA/TAAXR and OUTBr/TAAXR in Fig. 2a indicate quantitative exchange of Br⁻ on I-3×2 by PA(4.5 kDa). Multiplicity in electrostatic interaction
enhanced the exchanging ability of carboxylate group. The difference IR spectrum of the bulk resin showed absorption around 1570 cm

−1 characteristic of carboxylate (Fig. 3a). These results suggest ion exchange of Br– by PA (path 1 in Scheme 1).

The reactivity of PA(25 kDa), in contrast, was much lower than that of PA(4.5 kDa) and some difference between INBr/TAAXR and OUTBr/TAAXR was observed (Fig. 2b). The IR spectra of the bulk resin showed another peak at 1670 cm

−1 assigned to \( \text{CO}_3^{2–} \) (Fig. 3b), as well as the higher absorption by carboxylate. CO2 was involved under the present experimental conditions and was exchanged as \( \text{CO}_3^{2–} \) along with a concomitant decrease in pH during the slow exchange by PA(25 kDa). The asymmetric behaviors observed in the reaction of I-3×8 with PA(25 kDa) shown in Fig. 1b suggest temporary exchange by \( \text{CO}_3^{2–} \), part of which is subsequently exchanged by PA(25 kDa). A slight decrease in OUTBr also indicates the exchange of \( \text{CO}_3^{2–} \) by Br– in this reaction system; the exchange by PA decreases pH and reduces the fraction of \( \text{CO}_3^{2–} \) in an aqueous phase.

In the reaction of I-3×2 with PA(250 kDa), the IR spectra of the bulk resin showed absorption of only \( \text{CO}_3^{2–} \) (thin line in Fig. 3c). The IR spectrum of the resin surface measured by ATR method, on the other hand, showed absorption by carboxylate as a shoulder, as well as high absorption of \( \text{CO}_3^{2–} \), which was slightly shifted to a lower wavenumber (thick line in Fig. 3c). These suggest surface adsorption of PA(250 kDa). Neither subsequent penetration of nor further ion exchange by PA(250 kDa) was observed.

In order to confirm the generality in exchange by or adsorption of polyelectrolytes on the surface, the reaction of poly(styrenesulfonate) (PSS, Fluro Chem.) with I-3×8 was also examined. OUTBr/TAAXR became constant at about 10% after 1 h as in the case of PA(250 kDa), and penetration of PSS after 5 h was comparable to this value (not shown). The reaction was fast and symmetric due to a lack of basicity, but % exchange was low. The difference IR spectrum of the bulk resin did not show any absorption, while the IR spectrum of the resin surface clearly showed absorption characteristic of PSS (Fig. S4, Supporting Information). Furthermore, quantitative EPMA analysis indicates a decrease in atomic abundance of Br from 5.55 ± 0.03% to 3.39 and an increase in abundance of sulfur from 0.01 to 2.52% (Fig. S5, Supporting Information). In contrast to the bulk resin, around 40% of Br– was replaced by PSS on the surface of the resin. These results show that PSS exchanges Br– on the resin surface but does not penetrate into the resin. The lower % exchange by PA(250 kDa) is also attributed to the same reason.

In the reaction of I-3×8 with PA(4.5 kDa) was necessary to completely exchange Br– (Fig. 2c). The IR spectra indicate simple ion exchange by PA (Fig. S3, Supporting Information). The high cross-linking of 8% interfered with penetration of and interaction with PA(4.5 kDa).

According to the IR spectra of bulk resins (Fig. S3, Supporting Information), unique ion exchanges by PA and by \( \text{CO}_3^{2–} \) were individually observed in the reactions with PA(4.5 kDa) and with PA(250 kDa), while both these exchanges were observed in the reaction with PA(25 kDa).

**Reaction of resins with PAs in the presence of acid**

The resin of I-3×2 having the highest affinity was reacted with PAs in the presence of 10−2.5 mol L−1 HClO4. The difference IR spectra of the resin reacted with PA(4.5 kDa) did not show absorption due to \( \text{CO}_3^{2–} \) but showed absorption of polyacrylate as well as other characteristic absorption bands at 1730 and 1100 cm−1, which are respectively assigned to polyacrylic acid and \( \text{CIO}_4^{–} \) (Fig. 3d). This indicates that part of PA penetrates as an acid into the resin phase (path 2 in Scheme 1).
of protonated species was also observed in ion exchange of PA on the anion exchange membrane and of mono- and di-carboxylates on AXRs.\textsuperscript{11–14}

**Interconversion between three species**

The interconversion of three species identified above or the reversibility of the reactions shown in Scheme 1 was examined using PA(4.5 kDa) and I-3\textsuperscript{以前}. The IR spectrum of the product on the reaction of (\textsuperscript{1}R,\textsuperscript{pa}–) with 10\textsuperscript{–2} mol L\textsuperscript{–1} NaClO\textsubscript{4} (Fig. 3e) indicates absorption by perchlorate and no absorption by PA; the return path of 1 (1) was quantitatively achieved. This agrees with the recent finding that the PAs in the "snake-cage resin" was partly eluted.\textsuperscript{15,16} The ion exchange of (\textsuperscript{1}R,\textsuperscript{pa}–) was, however, incomplete by a lower concentration of 10\textsuperscript{–2} mol L\textsuperscript{–1} NaClO\textsubscript{4} or by a 10\textsuperscript{–1} mol L\textsuperscript{–1} NaBr of the lower selectivity.

The concentration of HClO\textsubscript{4} was critical in order to make free poly(acrylic acid) penetrate into the resin phase (path 2), and 10\textsuperscript{–2.5} mol L\textsuperscript{–1} partly formed free poly(acrylic acid) as described in the previous section. The excessively high concentration, e.g., 10\textsuperscript{–2.2} mol L\textsuperscript{–1}, on the other hand, rather exclusively formed (\textsuperscript{1}R,\textsuperscript{ClO}\textsubscript{4}–). The path 2 was achieved by the stoichiometric amount of NaOH in the presence of 10\textsuperscript{–1} mol L\textsuperscript{–1} NaClO\textsubscript{4}.

The reaction of (\textsuperscript{1}R,\textsuperscript{pa}–) with 10\textsuperscript{–2} mol L\textsuperscript{–1} HClO\textsubscript{4} only partly formed but the reaction with 10\textsuperscript{–1} mol L\textsuperscript{–1} HClO\textsubscript{4} quantitatively formed free poly(acrylic acid) in the resin phase (Fig. 3f, path 3). Isosbestic points were observed in the reaction of (\textsuperscript{1}R,\textsuperscript{pa}–) with 10\textsuperscript{–1.5} – 10\textsuperscript{–2} mol L\textsuperscript{–1} HBr solutions (Fig. 3g). This indicates the conversion without elution of PA. The path 3 was simply achieved by NaOH.

**Conclusions**

The interactions of PAs with AXRs were studied by reaction stoichiometry and spectroscopy. PA(4.5 kDa) quantitatively replaced Br\textsuperscript{–} in the AXR of the low cross-linking degree to give (\textsuperscript{1}R,\textsuperscript{pa}–). In contrast, PA(250 kDa) exchanged Br\textsuperscript{–} only on the surface of AXRs but did not penetrate into the resins. CO\textsubscript{2} was involved in the system to induce exchange with CO\textsubscript{3}\textsuperscript{2–}. Using the slightly acidic condition caused substantially no exchange by CO\textsubscript{3}\textsuperscript{2–} but induced coextraction with proton to form free acid of Hpa in the resin phase. PA(4.5 kDa) penetrating into the resin phase as (\textsuperscript{1}R,\textsuperscript{pa}–) or free Hpa was reversibly eluted under the appropriate conditions.

**Acknowledgements**

We thank JASCO support for the IR measurement of the resin surface by ATR method. This work was supported by JSPS KAKENHI Grant Numbers JP23550093 and JP26410148.
Supporting Information

Additional figures showing pH of PA solutions, effects of PA on potentiometry of bromide, and bulk and surface IR and EPMA of resins. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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