Volume of Space within Cation-Exchange Resins Determined by Penetration of Inorganic Salt Solutions

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Abstract

Penetration of salt solutions into cation exchange resins was used to measure the volume of a space within the resin phase (the inner space), which was usable for ion exchange in principle but not fully in practice. The average volume of the inner space per functional group was significantly dependent on the type and the concentration of the salt (250 - 450 Å³) for the resin having the cross-linking degree of 8 %, while being less dependent on the type and the concentration of the salt (160 - 240 Å³) for the resin having the cross-linking degree of 12 %. The salt concentration ratio of the solution filling the inner space to the outer solution decreased with a decrease in concentration of the outer salt solution, due to the osmotic pressure and decreased with an increase in cross-linking degree, due to the less volume and the higher independency of the inner space.

Keywords: Cation-exchange resin, inner volume, osmotic pressure, penetration of solution.
Introduction

Ion exchange resins (IXRs) are widely used for sample pretreatment prior to analysis as well as for manufacture of chemical substances and for environmental preservation. The fundamental features of the conventional IXRs based on polystyrene-divinylbenzene (PS-DVB) copolymer once settled have been spotlighted by modern instrumental analyses and by deeper consideration, as summarized in a recent review. One of the topics is the sizes of quantitatively exchangeable ions. It has been recognized that the saturated exchange capacity of tetraalkylammonium (TAA⁺) ion on a cation exchange resin (CXR, -R⁻,M⁺) decreases with an increase in the alkyl (R) group of TAA⁺ (R, abbreviation, volume: methyl, TMA⁺, 140 Å³; ethyl, TEA⁺, 250 Å³; propyl, TPA⁺, 360 Å³) and with an increase in cross-linking (CL) degree (CL degree, saturated % exchange for TMA⁺ and TEA⁺: 2, 100, 100; 5, 90, 87; 10, 69, 63; 15, 63, 48). The phenomena was discussed first in relation to the size or the size distribution of micropores estimated by calculation or experimentally. Later, the importance of rigidity, was also pointed out; the rigidity suppresses swelling and deformation of the resin to accommodate large ions. Recently, we proved that TPA⁺ was not quantitatively exchanged on a CXR having a common exchange capacity of around 4 mmol g⁻¹ but was quantitatively exchanged on a CXR having a low exchange capacity of around 1 mmol g⁻¹ at a fixed CL degree of 2 %. Based on these results and the additivity of the molar volumes about the constituents of the CXRs, we have indicated another factor that large ions like TPA⁺ collide with each other at adjacent sites such as to interfere with complete exchange on the CXR having the common exchange capacity. The ion whose volume exceeds the mean volume of the space per functional group inevitably may not be quantitatively exchanged.

In this context, the volume of a space within the resin phase (hereinafter, referred to as the inner space, Scheme 1), which is usable for ion-exchange in principle but not fully in
practice, may be estimated from the adsorption isotherms of water to IXRs. The adsorption isotherms indicate that the hydration number is independent of the CL degree at the relative humidity up to around 50% but decreases with an increase in CL degree at the relative humidity of 100% (CL degree,%, hydration number 1, 50.9; 2, 32.6; 4, 19.3; 8, 9.9; 12, 8.4).

The roughly estimated volumes of the inner space by neglecting the volume of a cation and the electrostriction are respectively 1500, 1000, 600, 300, and 240 Å$^3$ per functional group. It is understood that swelling due to the osmotic pressure and to the hydrating tendency of the counter cation is balanced with cross-linking at these volumes. These volumes are, however, determined only in pure water, and no data are available on the volumes in practical salt solutions. More scientifically rigorous treatment of the data is also necessary.

It has been well known that IXRs retain more than the equivalent amounts of counter ions in concentrated salt solutions at a few mol L$^{-1}$. Since an excess counter ion exists with a co-ion in the form of a salt, the phenomena is named as non-exchange or super-equivalent sorption of a salt. Soldatov et al. determined the chemical amounts of a salt and water penetrating in the resin phase of an anion exchange resin (AXR) at the CL degree of 8% and analyzed these data with regard to specific interactions such as formation of -R$^+$,Na$^+$,(Cl$^-$)$_2$.

Based on the fundamental features of IXRs mentioned above, however, this phenomenon is rather interpretable as penetration of a salt solution in the resin, due to osmotic pressure. In this paper, we determined the chemical amounts of a salt and water penetrating in the CXRs at the CL degrees of 8 and 12% because of a known drastic change in the properties of IXRs at the CL degree of around 10% (swelling tendency, exchange kinetics or the rate of diffusion of the exchangeable ions) and estimated the volumes of the inner spaces in practical salt solutions by using the obtained data.
Experimental

Resins

Two commercially available CXRs (Amberlite 120B and Amberlite 124), each being comprised of PS-DVB copolymer as a network and sodium sulfonate group as a pendant (CXR×8, CXR×12; the digit denotes the CL degree), were examined. The CXRs in the Na-form were shaken with each MCl (M: Li, Na, K) solution at 1.0 mol L\(^{-1}\) at 25 °C for one day. After filtration and sufficient washing with water, each M-form of the two resins was dried and stored in a glove box that was maintained at 25 °C and at a relative humidity of 50 ± 2 %.

A portion of each Na-form resin was weighed and shaken with 25-mL of a 1.61mmol L\(^{-1}\) copper solution. After equilibration, the copper concentration in the supernatant was determined by atomic absorption spectrometry, and the exchange capacity was calculated as the reduction in the copper concentration (Table S-1, Supporting Information). Another portion of Na-form or a portion of other M-forms was weighed and subjected to determination of the water content by Karl-Fischer coulometry in conjunction with water vaporization (Mitsubishi Chemical, CA-100 and VA-100). The accumulated water content was determined as a function of temperature in a stepwise temperature increase mode. Examples are shown in Fig. S-1 (Supporting Information). Although the higher temperature was required for the more hydrophilic ion like Li\(^+\), heating at 275 °C was sufficient.

Procedure

First, as a special case of a relative humidity of 100 %, two differently treated M-forms of both the resins were subjected to water determination for the purpose of checking the experimental validity. The first was obtained by exposure to water for one day and by rapid (2 s) filtration, which was sufficient to remove water remaining on the resin surface (judged by the
relation between the water content and the filtration time), with a glass filter. The second was obtained by storage in a sealed tube containing saturated water vapor for one week. The water contents of these two differently treated resins agreed with each other within an experimental error of a few % (Table 1).

Then, each M-form resin (20 - 30 mg) was shaken with a series of alkali halide solutions, each containing the relevant cation and chloride \( (C_{M\text{Cl}}/\text{mol L}^{-1} = 0.2 - 4.5, 20 \text{ mL}) \). After rapid filtration, a portion of the resin was precisely weighed and was subjected to determination of the water content. Another portion was also precisely weighed and was equilibrated with water (20 mL), such as to elute the salt penetrating in the resin. The chloride concentration was determined by ion chromatography (eluent: 8 mmol L\(^{-1}\) \( p \)-hydroxybenzoic acid and 2.8 mmol L\(^{-1}\) Bis-Tris, flow rate: 1.0 mL min\(^{-1}\); column temperature: 40°C). The supernatant of the second elution contained only a negligible amount of chloride. Furthermore, the sodium concentration in the supernatant after exposure to an NaCl solution, which was determined by atomic absorption spectrometry, agreed with the chloride concentration within an experimental error. Thus, in other cases, the resin was shaken only once with water, and only the chloride content was determined.

**Results and Discussion**

**Overview**

It is assumed that each of the CXRs consists of an organic portion including a polymer network and a charged functional group (hypothetical molecular weight per functional group of \( MW_R \)), a counter cation \( M^+ \) (molecular weight of \( MW_M \)), water molecules directly interacting with the counter ion (hydration number of \( n_M \)), and a hypothetical space per functional group which may be filled with a gas or a solution (Scheme 1). When the space is
filled with an aqueous solution, water within the resin is conveniently differentiated into two: the water (given in deep blue) directly interacting with an ion-exchanged cation described above and the water (given in blue) in the filling solution including water hydrated to the cation and anion as components of the salt. The fundamental features of the ion-pairs between sulfonate group and relatively small ions, such as Li\(^+\), Na\(^+\), and K\(^+\), are assumed to be kept in aqueous solutions. The volume of the organic portion is specific for each resin and is practically constant irrespective of the type of a counter cation or the composition of a solution which is in contact with the resin, while the volume of a naked metal ion (\(V_M\)), the volume of water hydrated to the exchanged metal ion (\(V_{W,\text{exch}}\)) and the volume of the filling solution (\(V_{\text{soln}}\)) may vary according to the conditions. The sum of these three volumes is defined as a volume of the inner space per functional group (\(V_{\text{in}}/\AA^3\)), which is estimated as described below.

\[
V_{\text{in}} = V_M + V_{W,\text{exch}} + V_{\text{soln}} \tag{1}
\]

**Volume of hydrated water**

Each M-form of the two resins was equilibrated at a relative humidity of 50 % and at 25 °C. Only the strongly hydrating water molecules remained in the resin, as expected from the adsorption isotherms of water to IXRs.\(^9\) An exchange capacity (EC\(_M\)/mmol g\(^{-1}\)) and a water content (\(W_M\)) are expressed by eqs. 2 and 3, and the values of MW\(_R\) and \(n_M\) may be determined from these values obtained for each M-form of the two resins.

\[
\text{EC}_M = \frac{1000}{(\text{MW}_R + \text{MW}_M + 18 \times n_M)} \tag{2}
\]

\[
W_M = \frac{(18 \times n_M)}{\text{(MW}_R + \text{MW}_M + 18 \times n_M)} \tag{3}
\]

The previous works on both the CXRs and the anion exchange resins showed the consistency of
For the respective resins irrespective of their ionic forms and demonstrated the soundness of this approach.\textsuperscript{8,15} In this work, the values of EC\textsubscript{M} and W\textsubscript{M} were determined with regard to the Na-form (M = Na) as described in Experimental section to evaluate MW\textsubscript{R} and n\textsubscript{Na} for both the resins, and n\textsubscript{M} of the other forms (M = Li, K) were calculated only from W\textsubscript{M} with use of MW\textsubscript{R} obtained with regard to the Na-form.

\begin{equation}
 n\textsubscript{M} = W\textsubscript{M} \times \frac{(MW\textsubscript{R} + MW\textsubscript{M})}{(18 \times (1 - W\textsubscript{M}))} \tag{4}
\end{equation}

The n\textsubscript{M} values of the respective alkali metal ions on CXR\times8 are similar to but are slightly smaller than those on CXR\times12 (Table 1). The humidity of 50 % may induce more shrinking, due to the lower CL degree of CXR\times8, such as to enhance dehydration of the metal ion, compared with that for CXR\times12. Thus, the $V_{\text{W,exch}}$ expressed in terms of Å\textsuperscript{3} was calculated by eq. 5, on the assumption that electrostriction of water is negligible within the precision of the present experiments.

\begin{equation}
 V_{\text{W,exch}} = n\textsubscript{M} \times 30 \tag{5}
\end{equation}

The $V_{\text{M}}$ values were calculated by using their ionic radii.\textsuperscript{16}

\textit{Volume of inner space and inner/outer concentration ratio}

Each M-form of the two resins was equilibrated with a corresponding MCl solution at varying concentrations. A portion of the resin was subjected to determination of a mass fraction of water (MF\textsubscript{W, total}, the sum of the two types of waters), while another portion being subjected to determination of a mass fraction of the salt (MF\textsubscript{S}). Since the consumption of water or a salt by penetration of the solution was negligibly small, the salt concentration after
equilibration ($C_{\text{out}}$) was equal to the initial concentration within an error of 0.001 mol L$^{-1}$.

$$C_{\text{out}} = C_{\text{MCl}}$$  \hspace{1cm} (6)

The mass fraction of the organic portion and the naked counter ion, $M_{\text{FRM}}$, is given by:

$$M_{\text{FRM}} = 1 - M_{\text{F}} - M_{\text{W,total}}$$  \hspace{1cm} (7)

The mass fraction of water directly interacting with the ion-exchanged cation, $M_{\text{F},\text{exch}}$, is given by:

$$M_{\text{F},\text{exch}} = 18 \times n_{\text{M}} \times M_{\text{FRM}}/(M_{\text{W,R}} + M_{\text{W,M}}).$$  \hspace{1cm} (8)

The mass fraction of water in the filling solution, $M_{\text{F},\text{soln}}$, is given by:

$$M_{\text{F},\text{soln}} = M_{\text{F},\text{total}} - M_{\text{F},\text{exch}}$$  \hspace{1cm} (9)

The mass fraction of the salt in the filling solution is given by $M_{\text{F}}/(M_{\text{F}} + M_{\text{F},\text{soln}})$. Separately, the relationship between the mass fraction and the density ($d_{\text{MCl}}$) in the binary system consisting of a salt and water was determined; $d_{\text{MCl}}$ was expressed as a function of the mass fraction (Fig. S-2, Supporting Information). By using this relationship, the density of the filling solution corresponding to each $M_{\text{F}}/(M_{\text{F}} + M_{\text{F},\text{soln}})$ measured was determined.

The volume (mL) of the filling solution per unit mass of the resin is given by:

$$(M_{\text{F}} + M_{\text{F},\text{soln}})/d_{\text{MCl}}$$  \hspace{1cm} (10)
and the volume ($\text{Å}^3$) of the filling solution per functional group is given by:

$$V_{\text{soln}} = \frac{(M_F S + M_{W,\text{soln}})/d_{MCl} \times (M_{WR} + M_{WM})/M_{RM} \times (10^8)^3/(N_A)}{(M_F S + M_{W,\text{soln}})/d_{MCl}}$$ (11)

where $N_A$ is Avogadro number. In contrast, the concentration of the filling solution, $C_{in}$ is given by:

$$C_{in} = \frac{M_F S/(M_{WM} + M_{Cl})}{((M_F S + M_{W,\text{soln}})/d_{MCl}) \times 10^3}$$ (12)

**Effects of cross-linking**

The representative data are summarized in Table S-2 (Supporting Information). The $M_{W,\text{total}}$ gradually decreased but the $M_F S$ increased almost linearly with an increase in $C_{out}$, as previously reported with regard to AXRs.$^{12,13}$ The $V_{in}$ and $C_{in}/C_{out}$ as the functions of $C_{out}$ for the two resins are respectively shown in Figs. 1(a,b) and 1(c,d). In water (at $C_{out} = 0$), appreciable amounts of water (11 - 15 molecules/functional group) penetrate the resin CXR×8 to give the $V_{in}$ value in a range of 330 - 450 $\text{Å}^3$, due to the osmotic pressure and to the hydrating properties of $M^+$; the order in the extent of expansion ($\text{Li}^+ > \text{Na}^+ > \text{K}^+$) agrees with the order of the hydrophilicity of alkali metal ions. At a low salt concentration, the $C_{in}/C_{out}$ value is appreciably less than unity, which indicates preferential penetration of water against a salt. The $V_{in}$ value decreases but the $C_{in}/C_{out}$ value increases with an increase in $C_{out}$. At a high salt concentration, an isotonic state ($C_{in}/C_{out} = 1$) is achieved as expected, where the $V_{in}$ value becomes substantially constant (250 $\text{Å}^3$), which is an inherent volume of this CXR without the effect of the osmotic pressure.

In contrast, less water (7 - 8 molecules/functional group) penetrate the resin CXR×12
in water to give the $V_{in}$ value in a range of 200 - 240 Å$^3$, which is smaller than that in the case of CXR×8, because of the higher CL degree, in spite of the high osmotic pressure. There is a small difference in the $V_{in}$ value according to the type of the cation. At a low salt concentration, the $C_{in}/C_{out}$ value is much lower (around half) than that of CXR×8. The $V_{in}$ value only slightly decreases down to 160 Å$^3$, but the $C_{in}/C_{out}$ value increases with an increase in $C_{out}$. Even at a high salt concentration, however, the $C_{in}/C_{out}$ value reaches only 0.5.

In a 3 mol L$^{-1}$ NaCl solution, for example, the molar ratio of [(-R,Na$^+$) : (NaCl) : (water dissolving NaCl in the inner space)] was [1 : 0.3 : 6.9] for CXR×8 and was [1 : 0.075 : 3.1] for CXR×12. While penetration of both NaCl and water is more suppressed in CXR×12 than in CXR×8, penetration of NaCl is more disturbed than that of water. In the case of CXR×8, the $V_{in}$ value is large and the inner space is less independent to be connected and form a larger space, where appreciable amounts of hydrated Na$^+$ and Cl$^-$ (volumes of hydrated ions by using the sum of the distance between Na$^+$ or Cl$^-$ and water oxygen and the van der Waals radii of oxygen as a radius: $^{17}$ 310 Å$^3$ for Na$^+$; 410 Å$^3$ for Cl$^-$) may be accommodated. In the case of CXR×12, on the other hand, the $V_{in}$ value is smaller than that of CXR×8 and the inner space is more independent from each other, such that a space large enough to accommodate the hydrated Na$^+$ and Cl$^-$ may be less abundant than in the case of CXR×8. This may be one reason for the well-known drastic change in the properties of IXRs described in Introduction at the CL degree of around 10%.

**Conclusions**

Penetration of salt solutions into cation exchange resins was used to measure the volume of the inner space, which was usable for ion exchange in principle but not fully in practice. The average volume of the space per functional group was 250 - 450 Å$^3$ for CXR×8, which
significantly varied with the type and the concentration of the salt, and was 160 - 240 Å$^3$ for CXR×12, which was less dependent on the type and the concentration of the salt. These volumes are comparable to but are slightly larger than the volume of the quantitatively exchangeable largest tetraalkylammonium cation.$^{2-4,8}$ The $C_{\text{in}}/C_{\text{out}}$ value, which was low at the low $C_{\text{out}}$ due to the osmotic pressure, increased with an increase in $C_{\text{out}}$ to reach an isotonic state for CXR×8 but not for CXR×12. The $C_{\text{in}}/C_{\text{out}}$ value, on the other hand, decreased with an increase in CL degree, due to the less volume and the higher independency of the inner space.

Acknowledgements

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Supporting Information

Additional tables (determination of exchange capacities, parameters related to penetration of salt solutions) and Additional figures (mass fraction of water as the function of temperature, relation between the density and the mass fraction of each salt solution). This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

References


Scheme 1  Image of CXR at relative humidity of 50 % (upper) and in contact with aqueous solution containing salt, MCI (lower).  The dotted line indicates the boundary of CXR and the colored area on the left side of this line corresponds to the inner space.  MW\_X: molecular weight of X; MF: mass fraction of X (R: resin; M: alkali metal ion; W: water; S: salt solution); n\_M: hydration number of M\textsuperscript{+}; C\textsubscript{in} and C\textsubscript{out}: salt concentrations in inner and outer solutions, respectively.  See text for MF\_W,Y (Y: total, exch, soln).
Table 1. Properties of cation-exchange resins

<table>
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<tr>
<th>Resin Form</th>
<th>EC$_{Na}$ mmol g$^{-1}$</th>
<th>$w_{Na}$ %</th>
<th>MW$_{CR}$ g mol$^{-1}$</th>
<th>$n_{M}$</th>
<th>Water content, %$^a$</th>
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</thead>
<tbody>
<tr>
<td>CXR×8 Li</td>
<td>19.4</td>
<td>3.65</td>
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<td>2.1</td>
<td>44.7</td>
<td>40.5</td>
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<td>3.1</td>
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<td>39.8</td>
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</tr>
<tr>
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<td>14.4</td>
<td>2.1</td>
<td>3.1</td>
<td>32.2</td>
<td>34.0</td>
</tr>
</tbody>
</table>

a. Corresponding to MF$_{W_{total}}$ in contact with salt solutions.
b: After immersion in water and filtration;
c: After storage in a sealed tube saturated with water vapor.
Figure Captions

Fig. 1  Changes in $V_{\text{in}}$ (a,b) and $C_{\text{in}}/C_{\text{out}}$ (c,d) as the function of $C_{\text{out}}$ for CXR×8 (a,c) and CXR×12 (b,d). Salt: (○) LiCl, (△) NaCl, (□) KCl.
Fig. 1  Changes in $V_{in}$ (a,b) and $C_{in}/C_{out}$ (c,d) as the function of $C_{out}$ for CXR×8 (a,c) and CXR×12 (b,d). Salt: (○) LiCl, (▲) NaCl, (□) KCl.
Graphical Index

Cross-linking degree at 8%

Cross-linking degree at 12%