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# Studies of the Hydrous Silicon-Titanium(IV) Oxide Ion Exchanger. II. Affinity for Various Cations and Thermal Stability

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The affiinity for various cations and the thermal stability were studied on hydrous silicon-titanium(IV) oxide ion exchangers with various titanium contents. An exchanger with 52 mol% Ti shows a higher affinity for an alkali metal ion having a smaller hydrated radius but similar affinity, which depends little on the pH's of solutions, for alkaline earth metal ions, except for $Ba^{2+}$. In the sorption of transition metal ions, the formation of a covalent bond is a factor in determining the selectivity of the exchanger, along with the remote coulombic interaction. The composition dependence of the affinities for $Cs^+$, $Ba^{2+}$, $Co^{2+}$, $Eu^{3+}$, and $UO_2^{2+}$ was explained in terms of the acid-base properties of the exchangers. The exchangers with 37 to 67 mol% Ti do not suffer from any drastic change in the surface area and in the crystallinity upon heating up to 540 °C, and are much more heat-resistant than the component simple hydrous metal oxides. The degree of the decrease in the exchange capacity upon heat treatment is larger in exchangers with a higher titanium content. The effect of a heat treatment on the acid-base property and the affinity for cations was also studied.

The development of thermally stable hydrous metal oxides possessing diversity in ion-exchange characteristics is very important in order to broaden the application areas of such materials. Hydrous silicon–titanium(IV) oxide ion exchangers with different titanium contents were previously prepared by mixing a titanium(IV) chloride solution and a sodium metasilicate solution at pH 7.6.[1] The acid-base property of the exchangers varied markedly with their titanium contents (hereafter, the titanium content is designated as mol% of Ti to metallic element of Ti plus Si). Hence, both the affinity for cations and the thermal stability of the materials may depend on the titanium content. Kaneko et al. showed that a silica-titania gel prepared by coprecipitation retained about 60% of the original ion-exchange capacity for $Na^+$, when it was heated at 700 °C for 2 h.[2,3] However, the dependency of the effect of a heat treatment on the composition of the materials has not yet been investigated.

The first purpose of the present investigation was to study the ion-exchange equilibrium of an exchanger with 52 mol% Ti as being representative of materials having a large ion-exchange capacity: The stoichiometry of the ion-exchange reaction, the uptake curves for alkali metal ions, and the distribution coefficients for various cations were studied. Furthermore, the dependence of ion-exchange selectivity for some cations on titanium content in the exchangers is discussed in terms of the acid-base properties of the materials, which had been clarified in a preceding paper.[1] The second purpose was to examine the effect of a heat treatment on the composition, the acid-base property and the selectivity for some cations of the hydrous silicon-titanium(IV) oxides with various titanium contents.

## Experimental

**Reagents and Apparatus.** Strontium chloride, of the highest purity grade, was obtained from Mitsuwa Kagaku Ltd. The other chemicals were of the highest purity grade supplied by Wako Pure Chemical Industries Ltd. A well-type NaI(Tl) scintillation counter (Fuji Denki, Model NDE-14001) was employed for the measurement of γ-radioactivity. The specific surface area of the samples, after being heated at 100 °C to constant weight, was determined by the BET method ($N_2$ adsorption at −196 °C) using a Yanagimoto Surface Area Measuring Apparatus, Model GSA-10. All the other apparatuses were the same as those described previously.[1]

**Ion Exchangers.** The hydrous silicon–titanium(IV) oxides were prepared by a previously described method.[1] The exchangers used in the present study were selected to cover a wide range of their acid-base properties. Their compositions and the drying temperature are shown in Table 1. As has been shown, drying temperatures up to 70 °C had little effect on the ion-exchange properties of the products.[1]

**Distribution Coefficients.** The distribution coefficients, $K_d$, were determined in the following way. One tenth gram

Table 1. Composition of the Exchangers

| Sample No. | Ti-mol% $\frac{\text{mol TiO}_2}{\text{mol (SiO}_2\text{+TiO}_2)}$ | Water content $\frac{\text{mol H}_2\text{O}}{\text{mol (SiO}_2\text{+TiO}_2)}$ |
|---|---|---|
| 1[a] | 10±1 | 1.84±0.02 |
| 2[a] | 34±1 | 2.04±0.02 |
| 3[b] | 37±1 | 1.77±0.02 |
| 4[b] | 52±1 | 1.89±0.02 |
| 5[b] | 67±1 | 1.75±0.02 |
| 6[a] | 76±1 | 2.51±0.02 |
| 7[a] | 90±1 | 2.01±0.02 |
| 8[c] | 100 | 2.31±0.02 |

a) Dried at room temperature. b) Dried at 70 °C. c) Hydrous titanium(IV) oxide, prepared by the method described previously.[1]

of each exchanger in the $H^+$ form was immersed for 4 d at 40 °C in 7 $cm^3$ of the solution with the desired pH value, which was adjusted by using a combination of 0.133 mol $dm^{-3}$ $NaNO_3$, and 0.133 mol $dm^{-3}$ $HNO_3$ or NaOH. One cubic centimeter of the solution containing metal ions to be examined was then added to the slurry to make their concentration $1\times10^{-4}$ mol $dm^{-3}$ (except carrier free $^{239}Np$ and $^{241}Am$) and the ionic strength 0.1 mol $dm^{-3}$. The metal ions were added as nitrates or chlorides. The mixture was then allowed to stand at 40 °C until the concentration of the cation in the supernatant became constant (8 to 18 d). The pH and the concentration of the cation in the supernatant were then measured. The $K_d$ values, expressed in $cm^3\ g^{-1}$, were obtained from the usual type calculation. Analyses of Cs, Ba, Mn, Co, Zn, Ce, Eu, Np, and Am, respectively, were carried out radiometrically using $^{137}Cs$, $^{133}Ba$, $^{54}Mn$, $^{60}Co$, $^{65}Zn$, $^{144}Ce$, $^{152}Eu$, $^{239}Np$, and $^{241}Am$ as tracers. The $^{239}Np$ was prepared by milking from $^{243}Am$ by the method of Sill.[4] The oxidation state of neptunium at a tracer concentration was adjusted by the method of Inoue and Tochiyama.[5] The $UO_2^{2+}$ was analyzed spectrophotometrically by using 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol as a coloring reagent.[6] The concentrations of the other cations were determined by means of atomic absorption spectrophotometry.

**Stoichiometry of Ion-Exchange Reaction.** One and two grams of the exchanger, respectively, in the $H^+$ form(Sample No.4) were immersed in 100 and 200 $cm^3$ of 0.1 mol $dm^{-3}$ NaOH, 0.05 mol $dm^{-3}$ $SrCl_2$ or $BaCl_2$ solution for 8 d at 20 °C in a nitrogen atomosphere, with intermittent shaking. The pH of the solutions of the alkaline earth metal ions was adjusted to 7.2 by adding each hydroxide and 2-morpholinoethanesulfonic acid. This was followed by chemical analysis; the stoichiometry of cation exchange was evaluated from the difference between the initial and final concentrations of the respective ions present in the solutions. Sodium ions were converted to the equivalent amount of sodium chloride by evaporating the solution with HCl and indirectly determined by titrating the $Cl^-$. The $Cl^-$ were determined by Fajans' method after the solution had been neutralized. The $Sr^{2+}$ and $Ba^{2+}$ were assayed by compleximetric titration: The Zn–EDTA displacement method, using eriochrome black T as an indicator. In the experiments for $Na^+$, the $OH^-$ and $CO_3^{2-}$ were determined by differential titration. In the case of alkaline earth metal ions, the amount of hydrogen ions released was estimated from the volume of a standard NaOH solution needed to bring the pH of the equilibrium solution back to the initial value of 7.2.

**Heat Treatment.** About 5 g of the exchanger in the $H^+$ form was heated in air to a constant weight at a constant temperature, which was controlled within an accuracy of 1% by using an automatic temperature controller (Chino Workers Ltd., Model 175). After being cooled over $P_2O_5$, the sample was weighed and then immersed in water overnight. The sample separated from water was allowed to stand to a constant weight in a desiccator containing a saturated $NH_4Cl$ solution (humidification). The water-recovery of the heat-treated samples was calculated from the difference in water contents between samples cooled over $P_2O_5$ immediately after the heat treatment and subjected to the humidification.

The other experimental procedures were the same as those described previously.[1]

## Results and Discussion

**(I) Ion-Exchange Properties of the Exchanger with 52 mol% Ti. (a) Stoichiometry of Ion-Exchange Reaction.** Table 2 shows the results concerning the stoichiometry of the exchange reaction between the hydrogen ions on the exchanger (Sample No. 4 in Table 1) and the alkali metal or the alkaline earth metal ions in the solutions. The ratios of the equivalent of the hydrogen ions released to that of the metal ions sorbed were unity within the limits of experimental error, though slightly smaller than unity for $Sr^{2+}$. These results indicate that the sorption of ions is caused primarily by a stoichiometric ion-exchange reaction, with certain reservation in the possible participation of a reaction other than the ion exchange.

**(b)Acid-Base Properties.** In order to study the acid-base property of the exchanger, the uptake curves for $Na^+$ and $Cl^-$ were measured as a function of pH, as shown in Fig. 1. This figure reveals that this material is a cation exchanger, since no $Cl^-$ was taken up at all. The exchange capacities for $Na^+$ increased with pH over wide range (pH>3.5), so that the exchanger is considered to have many kinds of weakly dissociable ion-exchange sites. The uptake curves for $Li^+$ and $K^+$ showed a pH dependency similar to that for $Na^+$, though the ion-exchange capacities for those ions differed with each other: $K^+>Na^+>Li^+$ at pH<10, and the reverse order at pH>10. This result suggests the dependence of the relative affinity for alkali metal ions on the pH of the solutions.

**(c) Selectivity for Cations.** The $K_d$ values for $Eu^{3+}$ in various concentrations are plotted against pH in Fig. 2. The linear relation held between log $K_d$ and pH; the slopes of the straight lines increased with a decrease in the concentration, approaching 3 when it became extremely dilute ($1\times10^{-7}$). This may be

Table 2. Verification of the Stoichiometry of Cation Exchange

| System | (I)<br>$H^+$ released | (II)<br>Metal ions taken up | Stoichiometry |
|---|---|---|---|
| | meq $g^{-1}$ | meq $g^{-1}$ | (I)/(II) |
| $Na^+/H^+$ | 3.37±0.09 | 3.39±0.04 | 0.99±0.03 |
| $Sr^{2+}/H^+$ | 0.96±0.01 | 1.00±0.02 | 0.96±0.02 |
| $Ba^{2+}/H^+$ | 0.82±0.01 | 0.80±0.02 | 0.98±0.03 |

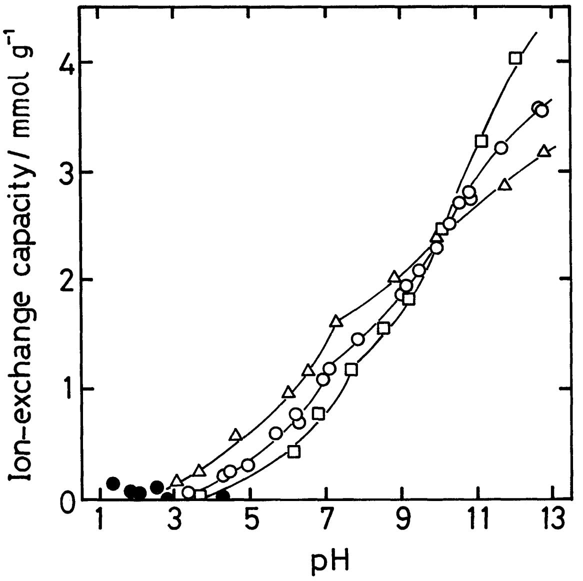

Fig. 1. Uptake curves for alkali metals and chloride ions. Conditions; exchanger: 0.15 g of sample No. 4, solution: 15 $cm^3$, ionic strength: 0.1 mol $dm^{-3}$, contact time: 7 d at room temperature. Ions; □: $Li^+$, ○: $Na^+$, △: $K^+$, ●: $Cl^-$.

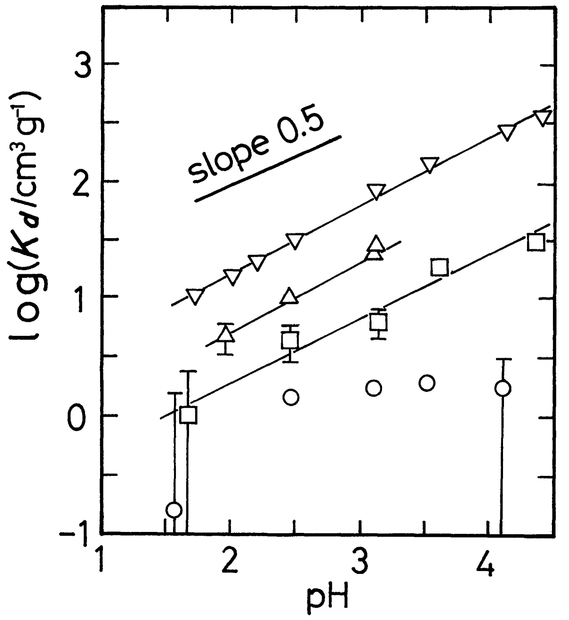

Fig. 3. Log $K_\mathrm{d}$ for alkali metal ions as a function of pH. Ionic strength: 0.1 mol $dm^{-3}$ ($HNO_3$–$NaNO_3$–$NaOH$). Exchanger: No. 4. Cations; ○: $Li^+$, □: $K^+$, △: $Rb^+$, ▽: $Cs^+$.

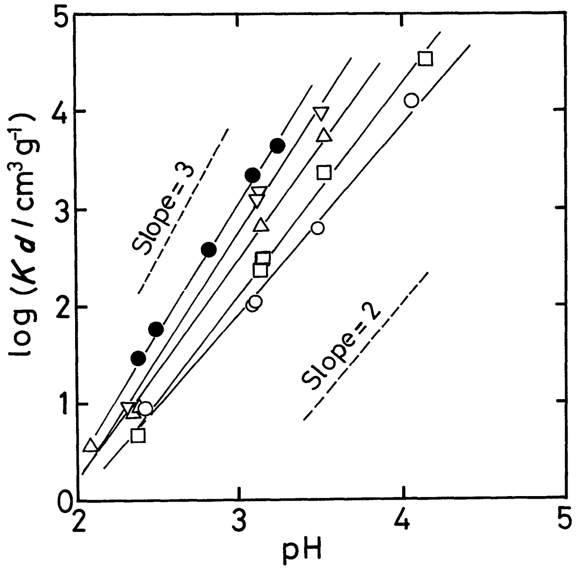

Fig. 2. Effect of the concentration of $Eu^{3+}$ on $K_\mathrm{d}$. Exchanger: No. 4. Initial concentration of $Eu^{3+}$/mol $dm^{-3}$; ○: $1\times10^{-4}$, □: $1\times10^{-5}$, △: $1\times10^{-6}$, ▽: $1\times10^{-7}$, ●: $6\times10^{-10}$.

ascribed to the limited amount of cation-exchange sites in the pH range studied (Fig. 1). Hence, it is preferable to use a concentration lower than $10^{-7}$ mol $dm^{-3}$ for strictly comparing the selectivity of the exchanger between various cations. The lack of sensitivity of the analytical methods, for some cations, however, makes this very difficult. Thus, the $K_\mathrm{d}$ values for the cations were compared at the lowest possible and constant initial concentration of the cations in solution, that is, $1\times10^{-4}$ mol $dm^{-3}$.

Figure 3 shows the pH dependency of the $K_\mathrm{d}$ values for alkali metal ions. A nonlinear relation between $\log K_\mathrm{d}$ for $Li^+$ and pH is due to the much smaller affinity of the exchanger for $Li^+$ than for $Na^+$ used as a back-ground salt. The slope of the straight lines (0.5) for other alkali metal ions was half the charge of the cations. This observation can be understood by applying the model proposed by the present authors for treatment of the stoichiometry of the metal-ion sorption on hydrous metal oxides;[#] the metal ions in question (counter cations) in the exchanger phase exist mostly as free ions and the charge balance in this phase is achieved by the sodium ions of the supporting electrolyte (back-ground cations). Figure 3 also shows that the selectivity for alkali metal ions decreases in the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$, as expected from Fig. 1; that is, the selectivity increases with decreasing hydrated ionic radius.

Figure 4 indicates that the $K_\mathrm{d}$ values depend little on the pH of the solutions for alkaline earth metal ions, except for $Ba^{2+}$. This observation suggests that such a small amount of alkaline earth metal ions lighter than $Ba^{2+}$ may be sorbed by a reaction other than the ion exchange, a possibility pointed out in the stoichiometry of the uptake of $Sr^{2+}$ (Table 2). For $Ba^{2+}$, a lin-

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[#] The model assumes that hydrous metal oxides are weakly acidic cation exchangers having a discrete exchanger phase between the matrix and the surrounding solution, where the charge balance and the mass action law hold. The counter cations distribute between this phase and bulk aqueous phase.[7)]

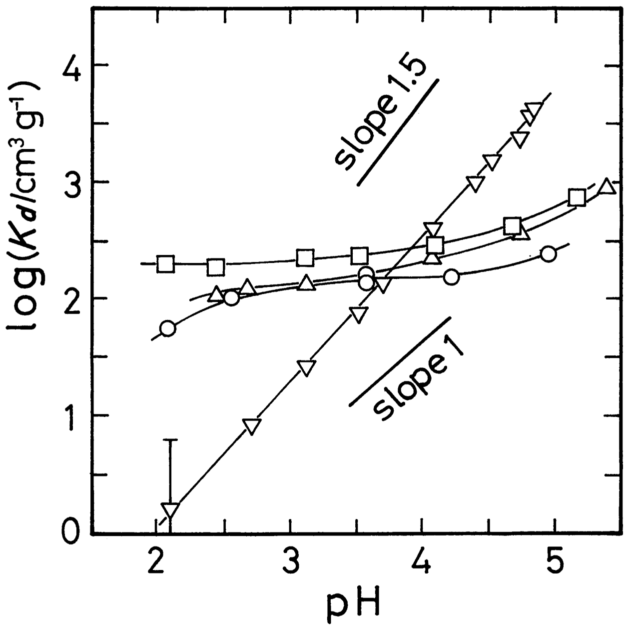

Fig. 4. Log $K_d$ for alkaline earth metal ions as a function of pH. Ionic strength: 0.1 mol dm$^{-3}$ ($HNO_3$–$NaNO_3$–$NaOH$). Exchanger: No. 4. Cations; ○: $Mg^{2+}$, □: $Ca^{2+}$, △: $Sr^{2+}$, ▽: $Ba^{2+}$.

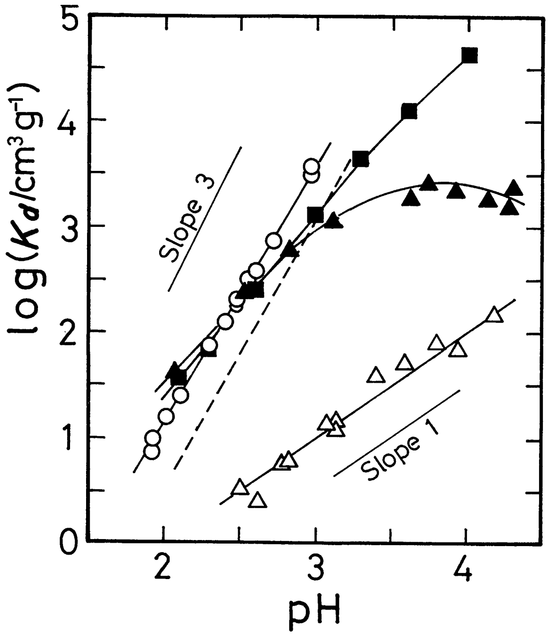

Fig. 6. Log $K_d$ for actinoid ions as a function of pH. Ionic strength: 0.1 mol dm$^{-3}$ ($HNO_3$-$NaNO_3$-$NaOH$). Exchanger: No. 4. Concentration of cations; ■: $UO_2^{2+}$ 1×10$^{-4}$ mol dm$^{-3}$, ▲: $NpO_2^{2+}$ trace in 4×10$^{-4}$ mol dm$^{-3}$ $KMnO_4$, △: $NpO_2^{+}$ trace, ○: $Am^{3+}$ trace, -----: $Eu^{3+}$ trace.

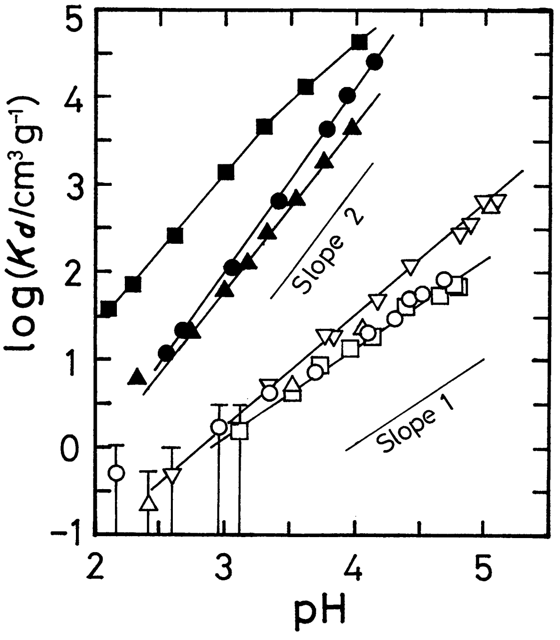

Fig. 5. Log $K_d$ for transition metal ions as a function of pH. Ionic strength: 0.1 mol dm$^{-3}$ ($HNO_3$-$NaNO_3$-$NaOH$). Exchanger: No. 4. Cations; ■: $UO_2^{2+}$, ○: $Mn^{2+}$, □: $Ni^{2+}$, △: $Co^{2+}$, ▽: $Zn^{2+}$, ●: $Eu^{3+}$, ▲: $Ce^{3+}$.

ear relation with a slope of about unity held between log $K_d$ and pH.

Figure 5 shows the pH dependency of the $K_d$ values for bi- and tervalent transition metal ions. The linear relations between log $K_d$ and pH were observed for all ions; the slopes of the straight lines increased with the charges of the ions. The order of selectivity for transition metal ions was $UO_2^{2+}$>>$Eu^{3+}$=$Ce^{3+}$>>$Zn^{2+}$>$Ni^{2+}$=$Mn^{2+}$=$Co^{2+}$. The results in Figs. 4 and 5 indicate that the affinity appears to increase with ionic potential of hydrated cations, since their ionic radii are, on the whole, larger for bivalent transition metal ions than for alkaline earth metal ions. This order and the selectivity series for alkali metal ions conform to the ion-hydration theory, which claims that the strength of the electrostatic interaction between hydrated cations and fixed anionic sites determines the selectivity of the strongly acidic resin.[8]

Figure 6 shows the results for some actinoid ions. For neptunium and americium, a tracer concentration was used, whereas the concentration of uranium was 1×10$^{-4}$ mol dm$^{-3}$. If we are to compare the affinity for these ions on the same concentration basis, $UO_2^{2+}$ may have an affinity higher than that of $NpO_2^{2+}$ and $Am^{3+}$ since the $K_d$ strongly depends on the concentration of the ions to be sorbed (Fig. 2). The deviation from linearity above pH 2.5 for $NpO_2^{2+}$ is attributable to its hydrolysis. $Am^{3+}$ had appreciably higher affinity than $Eu^{3+}$, in spite of their similar ionic radii; ionic radii with coordination number 6 are 0.112 nm for $Am^{3+}$ and 0.109 nm for $Eu^{3+}$.[9] In addition, $UO_2^{2+}$ and $NpO_2^{2+}$ had $K_d$ values higher than those expected from their charges; the affinity for these ions was greater than, or similar to that for tervalent cations. These findings cannot be explained only in terms of the electrostatic interaction between the hydrated cations and the anionic sites in the exchanger. It may therefore be considered that, in the ion-exchange reactions for transition metal ions, the formation of covalent bonds between the anionic sites and metal ions plays an important role for determining the selectivity of the exchanger together with the remote coulombic interaction. A similar consideration was applied for simple hydrous metal oxide ion exchangers, as had been described in previous papers.[10–12]

**(II) Relation between the Selectivity for Cations and the Composition of the Exchangers.** As described previously, the acid-base property of the exchangers depends strongly on their titanium content.[1] Hence, the selectivity for cations is expected to vary with the composition of the exchangers. The $K_d$ values for Cs$^+$, Ba$^{2+}$, Co$^{2+}$, Eu$^{3+}$, and UO$_2^{2+}$ were measured on exchangers with 10, 34, 76, and 90 mol% Ti and hydrous titanium(IV) oxide.

Since the slopes of the straight lines between log $K_d$ and pH unchanged with varing titanium content, the stoichiometric relation in the sorption is independent of the composition of the materials. In order to clarify the relation between the affinity for cations and the composition of the exchangers, the $K_d$ values at pH 4 were plotted against titanium content (Fig. 7). The $K_d$ values for Cs$^+$ and Ba$^{2+}$ increased with titanium content up to 52 mol%, and decreased with its further increase. On the other hand, the $K_d$ values for transition metal ions increased with titanium content, with a small trough at Ti-90 mol%.

The ion-exchange capacity can be used as a measure of the degree of dissociation of the OH groups in the exchangers. As was made clear from a preceding paper,[1] the degree of dissociation shows a plateau between exchangers with 10 to 76 mol% Ti, with a maximum at 52 mol% Ti, and is smaller for 90 mol% Ti than for the simple hydrous titanium(IV) oxide. These findings are consistent with the view that the dependence of the $K_d$ values for Cs$^+$ and Ba$^{2+}$ on the composition of the exchangers is determined by the electrostatic interaction between the ions and the dissociated sites in the exchanger. The dependence of the $K_d$ values for transition metal ions cannot be understood by a purely coulombic interaction with the anionic sites, but may be due to the formation of a covalent bond. The hydrous titanium(IV) oxide possessing exchange sites of low acidity showed the highest affinity for transition metal ions among the exchangers of various composition. The fact that the $K_d$ values for all kinds of cations were smaller for the exchanger with 90 mol% Ti than for the simple hydrous titanium(IV) oxide is attributable to the lower exchange capacity of the former than the latter.

**(III)Effect of Heat Treatment. (1)Water Content and Physical Property.** Figure 8 shows the relation between the heat-treatment temperatures and the water content of the exchangers immediately after the heat treatment, or subjected to humidification. Irrespective of the titanium content, the amount of water contained in the exchangers immediately after a heat treatment at 240 °C was reduced to less than 10% of the original value; it then gradually decreased with temperature. On the other hand, the water content of

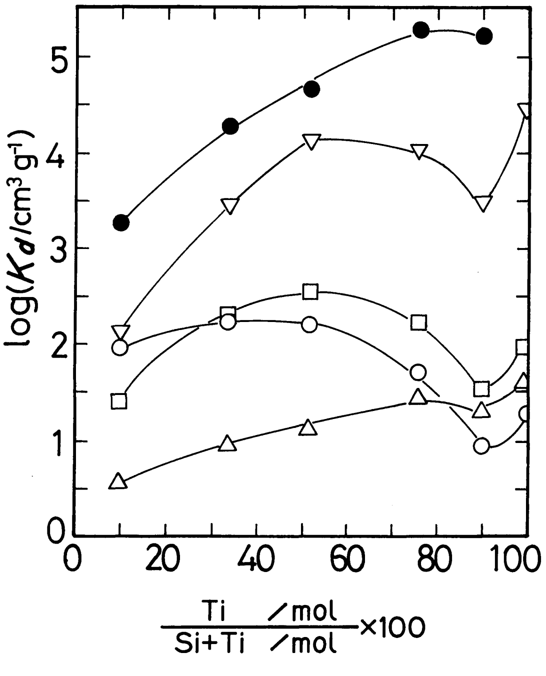

Fig. 7. Dependence of $K_d$ for some cations on the composition of the exchangers. Ionic strength: 0.1 mol dm$^{-3}$ (HNO$_3$-NaNO$_3$-NaOH). pH: 4. Cations; ○: Cs$^+$, □: Ba$^{2+}$, △: Co$^{2+}$, ▽: Eu$^{3+}$, ●: UO$_2^{2+}$.

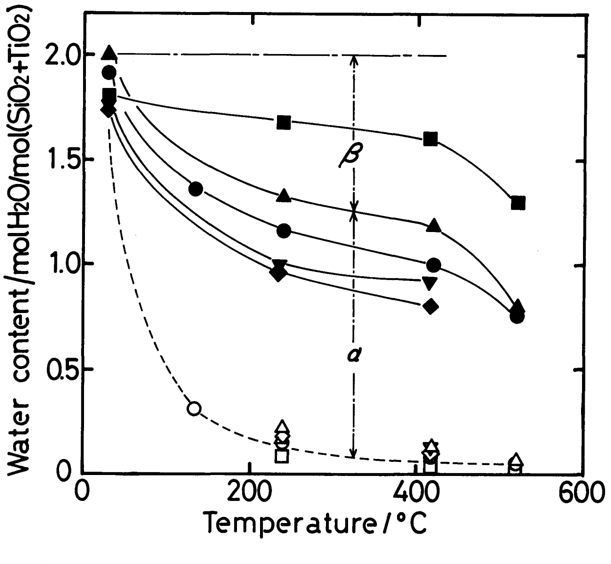

Fig. 8. Effect of heat treatment on the water content of the exchangers. Exchangers; □: No. 1, ▽: No. 3, ○: No. 4, ◇: No. 5, △: No. 7, Open marks: Immediately after heat treatment. Filled marks: Immersed in water, dried over saturated NH$_4$Cl solution. (α): Water recovered by humidification. (β): Water released irreversibly.

exchangers subjected to humidification varied with the titanium content. For an exchanger with 10 mol% Ti heated up to 420 °C, about 1.6 moles of water per 1 mole of the metallic elements were recovered, indicating that over 90% of the water lost by the heat treatment was recovered by humidification. When exchangers with 37 mol% or more Ti were heated at 240 °C, 0.7 to 0.8 mole of water per 1 mole of metallic elements was released irreversibly; the irreversible loss of water then gradually increased with temperature; even at such high temperature as 540 °C, the exchangers preserved matrices which could accomodate 0.7 to 1.3 mole of water per 1 mole of the metallic elements.

Figure 9 shows the effect of a heat treatment on the specific surface area. For an exchanger with 10 mol% Ti, only a little decrease was observed in the surface area, indicating that the distribution of pore diameter in the sample did not change upon heat treatment up to 540 °C. The surface areas of exchangers with 52 and 90 mol% Ti gradually decreased with the temperature; the decrease was larger in the exchanger with 52 mol% Ti. This means that the micropores were destroyed by a heat treatment more markedly in the former. The exchangers with some titanium content maintained large surface areas of 130 to 340 $m^2 g^{-1}$, even when they were heated at 540 °C.

In an exchanger with 52 mol% Ti, the X-ray diffraction pattern showed an amorphous structure which did not change, even when it was heated at 540 °C. A broad peak observed in an exchanger with 10 mol% Ti shifted to the position of hydrous silicon oxide when the exchanger was heated at 540 °C. An exchanger with 90 mol% Ti showed the peaks characteristic of anatase, which were intensified with the heat treatment.

These results suggest that a heat treatment does not largely change the structure of the exchangers, nor destroy the space which can accomodate water molecules.

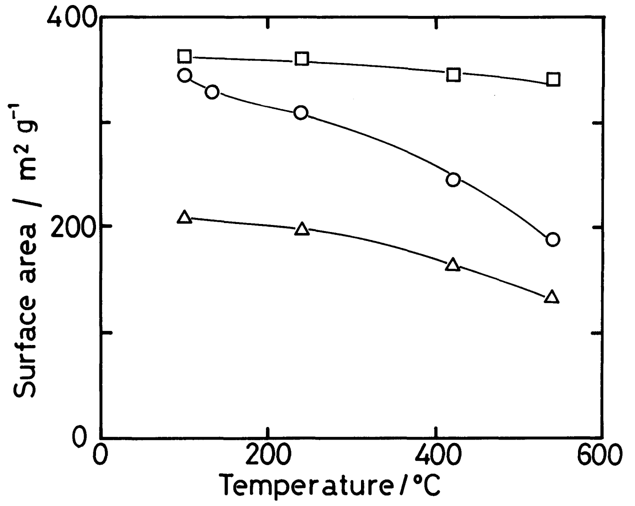

Fig. 9. Effect of heat treatment on the surface area of the exchangers. Exchangers; □: No. 1, ○: No. 4, △: No. 7.

The DTA and the TGA curves were measured on the heat-treated and humidified exchangers. In the DTA curves, one large endothermic peak with shoulders appeared in the range below 250 °C due to a loss of water. The large endothermic peak at 80 °C is considered to correspond mainly to the release of water recoverable by humidifying, that is, a certain kind of zeolitic water. The shoulders observed at the high- and the low-temperature sides, respectively, of the peak are attributable to the bound water liberated by the condensation of the hydroxyl groups and to the adherent water in the exchanger matrices.[7,9]

In order to further examine the decrease in the water content of the heat-treated and humidified exchangers, the difference in the amount of water molecules released at various temperatures between the materials with and without heat treatment was estimated from the TGA curves (Fig 10). When the exchangers with 52 and 67 mol% Ti were thermally treated, the amount of water released did not change up to 100 °C; it then significantly decreased with temperature up to 250 °C, showing a decrease in water content upon heat treatment. The water bound strongly to the exchanger matrix is, therefore, released irreversibly when the exchangers are heat-treated at temperatures higher than 240 °C. When exchangers with 10 and 90 mol% Ti were heat-treated, the amount of water released increased up to 100 °C and decreased with temperature from 100 to 250 °C. In an exchanger with 10 mol% Ti,

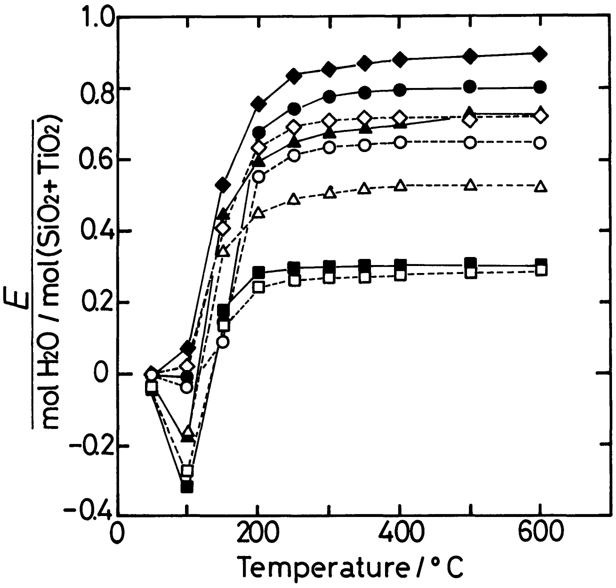

Fig. 10. Difference ($E$) in the amount of water released at various temperatures between the samples with and without heat treatment. Exchangers; □: No. 1, ○: No. 4, ◇: No. 5, △: No. 7. Open marks: Samples heat-treated at 240°C. Filled marks: Samples heat-treated at 420°C.

the increase of the water of low binding energy is similar to, or cancels out, the decrease of the water of high binding energy. This is why the exchanger with 10 mol% Ti lost only a small amount of water by heat treatment, when it was subjected to the humidification.

From the above observations, the effect of a heat treatment on the composition of composite exchangers can be summarized as follows. When the exchangers are heat-treated at temperatures up to 420 °C, a disordered network structure, originally formed during precipitation, is stabilized by an irreversible release of some part of the bound water. The matrices of the exchangers with 37 to 67 mol% Ti, thus formed, can accomodate an approximately constant amount of water which can be recovered by humidification. However, regarding exchangers with 10 and 90 mol% Ti, the recovery of such zeolitic water increases with the heat treatment. With the stabilization of the network structures, the water molecules formed by the condensation of the OH groups together with the water molecules bound to them are released irreversibly.

**(2)Acid-Base Property.** In order to examine the effect of a heat treatment on the acid-base property of the exchangers, the uptake curves for Na$^+$ were measured for the exchangers with 52 mol% Ti (Fig. 11). It should be noted that the ion-exchange capacities of the samples are normalized to the number of moles of Na$^+$ taken up per 1 mol of the metallic elements constituting the samples. The pH's, at which the inflection point was observed (pH 7) and the sorption of Na$^+$ commenced, did not shift by heat treatment. This indicates that the acidity of the exchange sites is not significantly affected by a heat treatment. The ion-exchange capacity in the pH range lower than the inflection point decreased with the temperature for the heat treatment, while, in a pH range higher than that point, the curves were parallel with each other. This observation indicates the destruction of the exchange sites by heat treatment mainly occurs in more acidic sites. For example, when the exchanger was heated at 540 °C, it retained about 35 and 70% of the original ion-exchange capacities at pH 7 and 12, respectively.

To examine the dependence of the titanium content on this effect, the ratios of the ion-exchange capacities of the samples, with and without a heat treatment

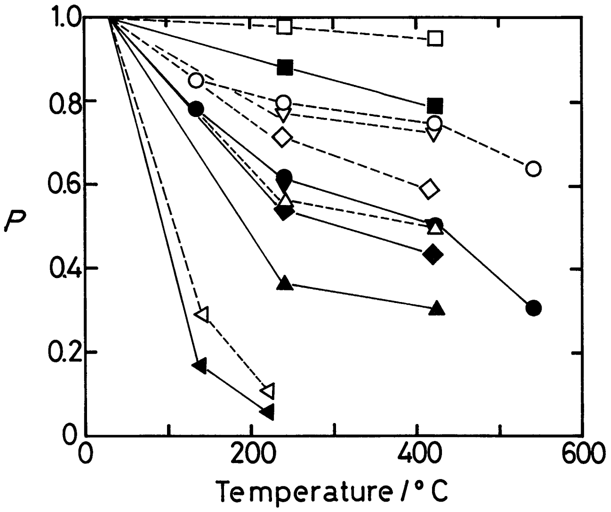

Fig. 12. The fraction of ion-exchange capacity remained after heat treatment (*P*) vs. the heating temperature. Exchangers; □: No. 1 (at pH 8 or 11), ▽: No. 3, ○: No. 4, ◇: No. 5, △: No. 7, ◁: No. 8. (filled marks: pH 7, open marks: pH 12).

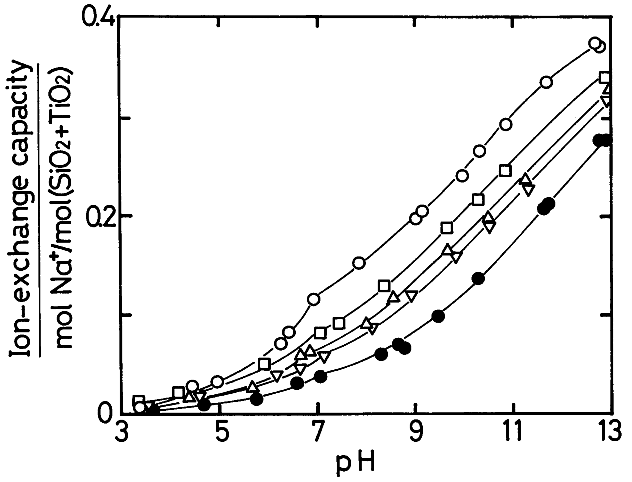

Fig. 11. Effect of heat treatment on the uptake curves for Na$^+$. Solution: 15 cm$^3$ of 0.1 mol dm$^{-3}$ NaCl–NaOH. Exchanger: 0.15 g of the exchanger with 52 mol% Ti, heat-treated at various temperatures. Temperature of treatment: ○: R.T., □: 135 °C, △: 240 °C, ▽: 420 °C, ●: 540 °C.

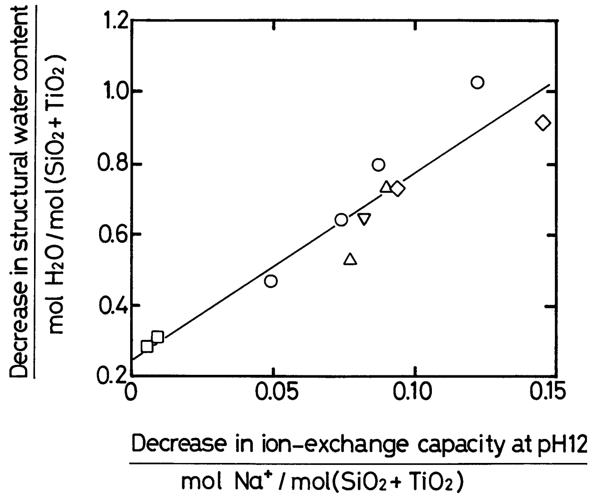

Fig. 13. Correlation between the decreases in the ion-exchange capacity at pH 12 and the structural water content. Exchangers; □: No. 1 (pH 11), ▽: No. 3, ○: No. 4, ◇: No. 5, △: No. 7.

(hereafter called the residual capacity fraction($P$)) were calculated at pH 7 and 12 from the uptake curves. An exception, however, had been made in the case of the exchanger with 10 mol% Ti. In this case, $P$ was obtained at pH 8 and 11, since the inflection point in the curve was at pH 8, and the dissolution of a part of the exchanger limited the maximum applicable pH at 11. As is shown in Fig. 12, the $P$ values decreased with increasing titanium content. In the exchanger with 10 mol% Ti, when heated at 420 °C, the capacity at pH 8 was reduced to about 83% of the original value, while the $P$ at pH 11 was as high as 0.94. This is due to the destruction of the more acidic exchange sites, because the original sample possesses a 2.6-times larger ion-exchange capacity at pH 11 than at pH 8. The $P$'s were smaller for the exchangers with 37 and 52 mol% Ti than for those with 10 mol% Ti. In spite of this fact, the exchange capacities of the exchangers with 37 and

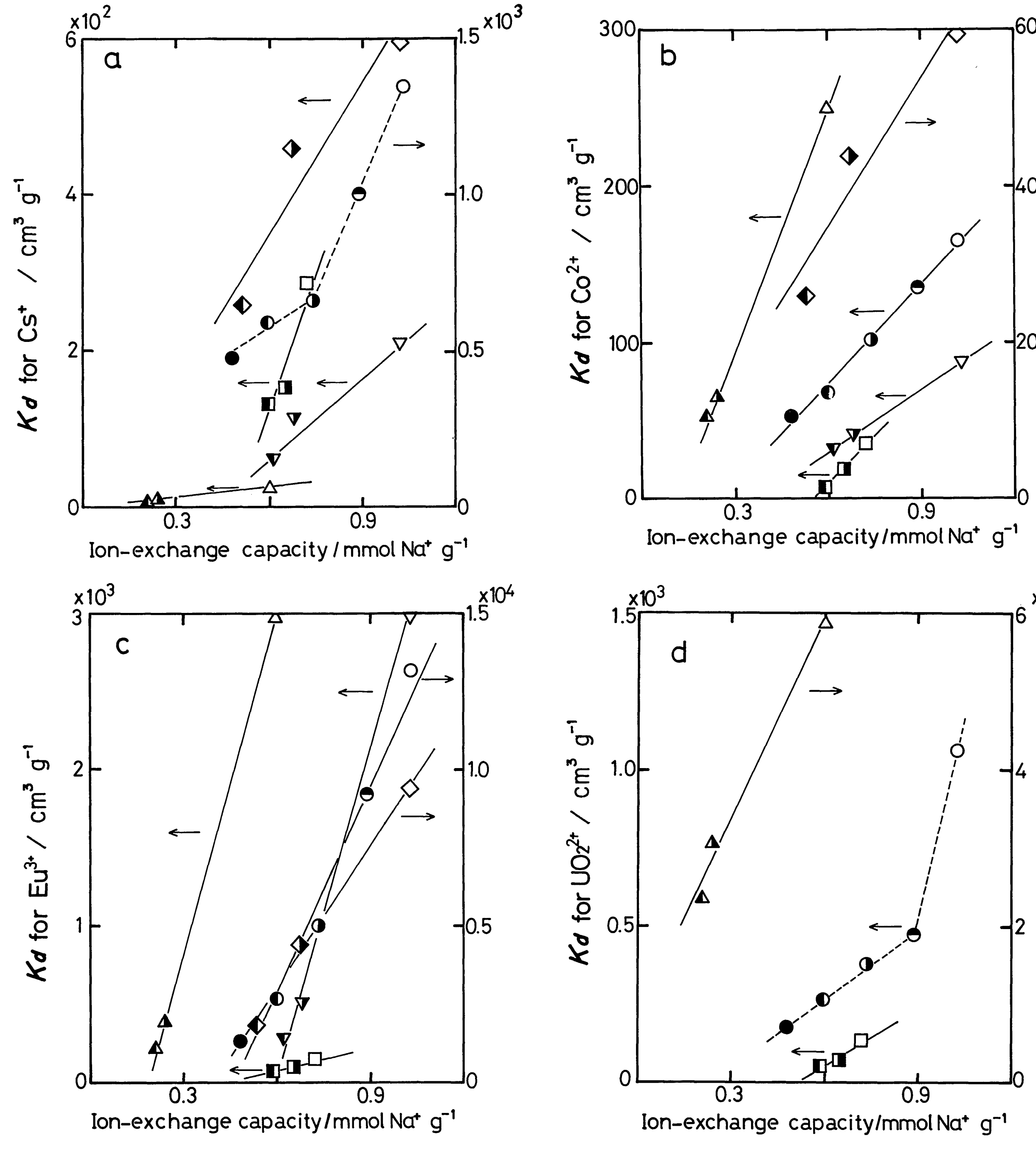

Fig. 14. Relation between the $K_d$ values for some cations and ion-exchange capacity for $Na^+$ at the inflection points of the exchangers with or without heat treatment. a: $Cs^+$, b: $Co^{2+}$, c: $Eu^{3+}$, d: $UO_2{}^{2+}$. Exchangers; □: No. 1, ▽: No. 3, ○: No. 4, ◇: No. 5, △: No. 7. Temperature of treatment; □▽○◇△: R.T.; ◒: 135 °C; ◨▼◑◆▲: 240 °C; ◧▼◐◆▲: 420 °C; ●: 540 °C.

52 mol% Ti heated at 420 °C are larger, by 0.025 at pH 7 and by 0.10 at pH 12, than those of the exchanger with 10 mol% Ti heated at the same temperature. This is due to the very large original exchange capacity of the former. The exchanger with 67 mol% Ti, having an acid-base property similar to those with 37 and 52 mol% Ti, showed a $P$ that was somewhat smaller than the latter. The exchanger with 90 mol% Ti, having the smallest ion-exchange capacity at room temperature, showed the smallest $P$ among all the exchangers examined.

From these observations, the exchangers with 37 to 52 mol% Ti are considered most suitable for use at elevated temperatures. As the $P$ of the hydrous titanium(IV) oxide were smaller than 0.11 at 220 °C, it is apparent to give an excellent thermall stability to the hydrous titanium(IV) oxide by complexing with hydrous silicon oxide.

When the amount of the structural water loss upon heating and the decrease in the ion-exchange capacities at pH 12 are compared (Fig. 13), there exists a strong correlation between them (the correlation coefficient 0.95). We can, therefore, conclude that the irreversible loss of structural water causes a decrease in the ion-exchange capacity.

**(3)Distribution Coefficient.** The distribution coefficients, $K_d$, for $Cs^+$, $Co^{2+}$, $Eu^{3+}$, and $UO_2^{2+}$ for the heat-treated exchangers with various titanium contents were determined at various pH's and their concentrations. A heat treatment did not alter the dependence of the $K_d$ values on the pH, nor on the concentrations although the absolute values of $K_d$ for these ions decreased with increasing heating temperature. These observations suggest that the stoichiometric relation governing the exchange reaction does not change with heat treatment.

Figures 14a to 14d show a correlation between the ion-exchange capacities of the more acidic sites, and the $K_d$ values for $Cs^+$ and $Co^{2+}$ at pH 5, for $Eu^{3+}$ at pH 4, and for $UO_2^{2+}$ at pH 3. There is a strong correlation between them in a given exchanger (correlation coefficients $>0.92$), except $Cs^+$ and $UO_2^{2+}$ in the exchanger with 52 mol% Ti; ion-exchange capacities at the pH adopted for measuring the $K_d$ values governs the affinity for the cations. In addition, the $K_d$ values depend on the ion-exchange capacity more strongly (larger slope) in exchangers with a higher affinity for a cation than in those with lower affinity. The $K_d$ values for $Cs^+$ and $UO_2^{2+}$ on the exchanger with 52 mol% Ti did not change linearly with the exchange capacities. Though the reason for this rather anomalous phenomenon is not clear, it may be that changes in some properties other than the ion-exchange capacity brought about by a heat treatment, affect the affinity for $Cs^+$ and $UO_2^{2+}$.

The effect of a heat treatment on the ion-exchange properties of the hydrous silicon–titanium(IV) oxides can be summarized as follows. When the exchangers were heated, structural water (OH groups and the water molecules bound to them) is released irreversively, causing a decrease in the ion-exchange capacity of the stronger acidic sites. The amount of decrease in the ion-exchange capacity upon heating increases with the titanium content in the exchangers, resulting in a lowering of the affinity for various cations. In an exchanger with a given Ti content, the effect of a decrease in the ion-exchange capacity upon heating on the affinity for cations is more prominent for cations with higher- than with lower-$K_d$ values.

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