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Studies of the Hydrous Tin(IV) Oxide Ion-exchanger. II. Some Properties as a Cation-exchanger

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In order to elucidate the fundamental properties of hydrous tin(IV) oxide as a cation-exchanger, the stoichiometry of cation exchange and its acid-base property were studied by means of the uptake curves for alkali-metal ions. The results are summarized as follows: 1) The equivalent exchange between the hydrogen ion and either alkali-metal or alkaline-earth-metal ions holds, irrespective of the ionic strength of the solution and the extent of exchange. 2) The water content in the exchanger depends on the ionic composition. 3) This material is an amphoteric ion-exchanger, with at least two kinds of weakly dissociable ion-exchange sites, and the conditional dissociation constant depends on the ionic composition of the exchanger. The stability to various reagents was also examined.

Several studies have been carried out on the ion-exchange property of hydrous tin(IV) oxide,[1-8] but different compositions and ion-exchange properties have been reported by different investigators. This may be due to the irreproducibility of the synthesis; hence, a detailed examination of the synthetic procedure is indispensable to undertaking any further study of this material. With this point in mind, the relation between the yield of hydrous tin(IV) oxide and the conditions of precipitation for various synthetic systems, and the ion-exchange properties relevant to the synthesis were investigated in a previous paper.[9] There is little choice between the $Na_2[Sn(OH)_6]$–H_2SO_4 and $SnCl_4$–NH_3 aq systems with respect to yield or physical and ion-exchange properties, but the former system is inferior to the latter in its very lengthy washing. The exchanger is semitransparent and consists of nearly amorphous particles which are hard to be ground into particles suitable for column operation, and can be converted to the pure hydrogen form by conditioning with 0.1 mol dm^{-3} HCl. The exchanger of the H^+ form prepared from the $SnCl_4$–NH_3 aq system has a composition of $SnO_2\cdot 2.18H_2O$ and an ion-exchange capacity of 1.18 mmol Na^+ g^{-1} (at pH 11.3). This is stable for longer than 15 months after preparation when it is stored over a saturated NH_4Cl solution.

Of the many properties which have not been investigated in detail, the acid-base property and the mechanism of adsorption are very important in understanding the material as an ion-exchanger. This induced us to examine the validity of the equivalence of cation-exchange reactions on the exchanger prepared from the recommended $SnCl_4$–NH_3 aq system and the uptake curves for various alkali-metal ions, which are useful for understanding the acid-base property of the exchanger.

Experimental

Reagents and Apparatus. The hydroxide solutions of the alkali-metal and alkaline-earth-metal ions except those of the lithium and sodium ions were prepared by passing corresponding chloride solutions through a column packed with Dowex 1-x8 anion-exchange resin in the OH^- form. All the other chemicals used were of the highest-purity grade obtained from Wako Pure Chemical Industries, Ltd. All the apparatuses were the same as described previously.[9]

Preparation of the Ion-exchanger. The synthetic system No.5 described in the preceeding paper was chosen for the preparation of the ion-exchanger.[9] Into 0.5 dm^3 of a 1 mol dm^{-3} $SnCl_4$ solution prepared by diluting liquid $SnCl_4$ with water, 1.5 dm^3 of 2% NH_3 aq was added, drop by drop, at an average rate of 20—30 cm^3 min^{-1}. The precipitate thus formed was separated from the mother liquor by a combination of decantation and filtration through Toyo No.1 filter paper under suction, uniformly dispersed into distilled water, and filtered again after being completely sedimentated. This procedure was repeated until no chloride ion was detected in the filtrate. Then the precipitate was filtered and sufficiently air-dried at room temperature. The resulting product was then immersed in distilled water to break it down into fine particles. The grains were dried again at room temperature. Particles larger than desired, if any, were ground in a porcelain mortar and sieved to obtain the required particle sizes. The exchanger of a desired particle size (100—200 mesh) was converted to the H^+ form by treating it with a 0.1 mol dm^{-3} HCl solution by the procedure described previously.[9] Finally, the exchanger was air-dried and stored in a desiccator containing a saturated NH_4Cl solution(relative humidity: 79% at 25 °C).

Conversion to Na^+ Form. The exchanger in the H^+ form was immersed in an alkaline solution, prepared by the combination of 0.1 mol dm^{-3} NaCl and 0.1 mol dm^{-3} NaOH(ionic strength=0.10, pH=11.0). Then the slurry was poured into a glass column, through which the same solution was subsequently passed until the pH of the effluent approached that of the influent. The column was then washed with distilled water, followed by acetone. Then the exchanger was taken out of the column, air-dried for 30 min, and stored in a desiccator containing saturated NH_4Cl and 5 mol dm^{-3} NaOH solutions.

Analytical Methods. The Cl^- ions were determined by the Fajans method after the solution had been neutralized. The alkali-metal ions were converted to the corresponding pure chlorides and indirectly determined by titrating the Cl^- ions. The Sr^{2+} and Ba^{2+} ions were assayed by a compleximetric titration: the Zn–EDTA displacement method, using eriochrome black T as an indicator. The OH^- and $CO_3{}^{2-}$ ions were determined by differential titration. The water content in the exchanger was calculated from the weight loss when it was heated in air at 850 °C to a constant weight.

Chemical Stability. In 30 cm^3 of a suitable solution, 0.25 g of the exchanger in the H^+ form was immersed for 4 d at room temperature. The tin dissolved in the supernatant solution was determined spectrophotometrically.[10]

Ion-exchange Stoichiometry. The exchanger in the H^+ form was immersed in an alkaline solution of metal ions, of suitable concentrations(ionic strength=0.0024—0.022), in a nitrogen atmosphere for longer than 2 d at room temperature, with intermittent shaking. This was followed by chemical analysis, and the ratio of the amount of metal ions taken up in the exchanger to that of the hydrogen ions released from the exchanger was evaluated from the difference between the initial and final concentrations of the respective ions present in the solution.

The other experimental procedures were the same as those previously described.[9)]

Results and Discussion

Chemical Stability. To examine the chemical stability of the exchanger, the amount of tin dissolved in various reagents was measured. The results, shown in Table 1, indicate that, in neutral or alkaline solutions, the exchanger was unstable to NaOH and K_2CO_3, whereas it was fairly stable to NaCl, Na_2CO_3, and aqueous NH_3. In acid solutions, it was very stable to HNO_3 and H_2SO_4, but dissolved appreciably into HCl, $HClO_4$, and $H_2C_2O_4$, even at concentrations as low as 1 equivalent dm^{-3}. These results show that this exchanger is easily attacked by the acids having a strong tendency to complex tin(IV) and the bases which form soluble hexahydroxostannates. As it is known that α-stannic acid dissolves easily in K_2CO_3 and that β-stannic acid is stable to HNO_3 and H_2SO_4, the charscteristics of this exchanger are intermediate between those of α- and β-stannic acids. Because β-stannic acid is the dehydration product of α-stannic acid, this exchanger is considered to be more dehydrated and more condensed than α-stannic acid.

Table 1. Chemical stability[a)]

Reagent	Solution Concentration	Amount of Sn dissolved
	mol dm^{-3}	wt%
NaOH	0.10	10
	0.94	19
NH_3 aq	0.10	0.14
	1.1	0.95
K_2CO_3	0.050	14
Na_2CO_3	0.050	<0.05[b)]
NaCl	0.10	<0.05[b)]
HNO_3	1.1	<0.05[b)]
	2.8	0.38
H_2SO_4	0.61	<0.05[b)]
	1.6	0.36
HCl	0.10	<0.05[b)]
	0.54	0.43
	1.2	1.7
	2.9	100
$HClO_4$	0.98	0.20
	3.1	100
Oxalic acid	0.50	7.0
Tartaric acid	0.50	<0.05[b)]
Citric acid	0.50	1.4

a) Exchanger; 100—200 mesh, H^+ form. Conditions; exchanger: 0.25 g, solution: 30 cm^3, contact time: 4 d at room temperature. b) Limit of detection.

Dependence of Exchange Capacity on Particle Size. The ion-exchange capacity for the Na^+ ion was measured as a function of the particle size, as is shown in Table 2. This table shows that the capacity was independent of the particle size. Hence, it can be concluded that the exchange sites are distributed uniformly in the particle.

Stoichiometry and Reversibility of Exchange Reaction. Table 3 presents the results concerning the stoichiometry of the exchange reaction between hydrogen ions on the exchanger and alkali-metal or alkaline-earth-metal ions in the solution. When the concentration of carbonate ions in a solution was decreased during contact, the amount of hydrogen ions released was determined from the difference in the sum of the carbonate and hydroxide ions before and after the equilibrium. As is shown in the last column of Table 3, the equivalent ratio of hydrogen ions released to metal ions absorbed became unity within the limits of experimental error. Therefore, the equivalent ion exchange holds irrespective of the ionic strength of the solutions, the extent of the exchange, and the kind of metal ion. From the stoichiometry of ion exchange and the dependence of the exchange capacity on the particle size, this material acts as an ideal cation-

Table 2. Dependence of cation-exchange capacity on particle size[a)]

Mesh size	Cation-exchange capacity for Na^+			
	A[b)]		B[c)]	
	pH	(mmol g^{-1})	pH	(mmol g^{-1})
16—28	7.52	0.61±0.02	11.39	1.22±0.02
28—42	7.49	0.61±0.02	11.38	1.24±0.02
42—70	7.49	0.61±0.02	11.36	1.22±0.03
70—100	7.48	0.60±0.02	11.35	1.22±0.02
100—200	7.52	0.63±0.02	11.40	1.19±0.02
200—350	7.53	0.62±0.03	11.38	1.21±0.02

a) Conditions; exchanger: 0.25 g, solution: 30 cm^3, at room temperature. b) A: 28.4 cm^3; 0.10 mol dm^{-3} NaCl+1.6 cm^3; 10.10 mol dm^{-3}; NaOH. c) B: 26.0 cm^3; 0.10 mol dm^{-3}; NaCl+4.0 cm^3; 0.10 mol dm^{-3}; NaOH.

Table 3. The verification of the equivalence of the exchange

System	Ionic strength	Duration of immersion	(I) Metal ions uptaken	(II) H^+ released	Stoichiometry (I)/(II)
	mol dm^{-3}	d	mequiv. g^{-1}	mequiv. g^{-1}	
Li^+/H^+	0.022	4	1.46±0.02	1.49±0.04	0.98±0.04
	($OH^-/Cl^-=1.0$)[a)]	4	1.47±0.02	1.51±0.04	0.97±0.04
Na^+/H^+	0.020	4	1.14±0.02	1.12±0.04	1.02±0.05
	($OH^-/Cl^-=0.86$)[a)]	4	1.13±0.02	1.11±0.04	1.02±0.05
Sr^{2+}/H^+	0.0024	2	0.90±0.03	0.87±0.03	1.03±0.06
		4	1.22±0.03	1.17±0.02	1.04±0.05
Ba^{2+}/H^+	0.0024	3	1.06±0.05	1.06±0.03	1.00±0.07

a) : Molar ratio.

exchanger, possessing exchange sites distributed uniformly in the particle.

Figure 1 shows the forward and backward uptake curves for sodium ions. Since these curves agree with each other, the exchange reaction can be said to proceed reversibly, and it seems that no structural change would occur upon ion-exchange.

Change in Water Content of the Exchanger. The change in the water content of the exchanger with the amount of alkali-metal ions uptaken is shown in Table 4, where the amount of water and of metal ions uptaken is normalized to the value per mole of tin in the exchanger. If we compare this value with the water content in the H^+-form exchanger, 2.16±0.01 mol H_2O (mol Sn)$^{-1}$, it is clear from Table 4 that the decrease in the water content is brought about by the uptake of alkali-metal ions. As part of water is removed from the exchanger by the release of H^+ ions from the OH group by ion-exchange, the water content, as estimated from the weight loss, should be corrected by adding half the amount of metal ions uptaken if the water content in the H^+ form is compared with that in the metal form. The corrected values are shown in the last column of Table 4, which shows that the water content decreased at first to a minimum and then increased gradually with the amount of alkali-metal ions in the exchanger. Furthermore, the water content is greater for larger hydrated cations, suggesting that these cations are uptaken as hydrated ions. As will be reported in a following paper, the order of selectivity for alkali-metal ions $Li^+ \gg Na^+ > K^+ > Rb^+ \approx Cs^+$, leads to the assumption that alkali-metal ions are present in the anhydrous state. This contradicts the foregoing suggestion. These results can be understood by considering that, at the early stage of exchange, the interstitial water is excluded by ingoing anhydrous cations, which have a larger volume than the proton. When the amount of cations uptaken exceeds a certain limit, the exchanger swells to relax the distortion produced in the structure of the matrix, so it can accommodate a larger ammount of water.

Acid-Base Properties. In order to study the acid-base property of the exchanger, the uptake curves for sodium and chloride ions were measured as a function of the pH, as is shown in Fig. 2. This figure reveals that this material is an amphoteric ion-exchanger

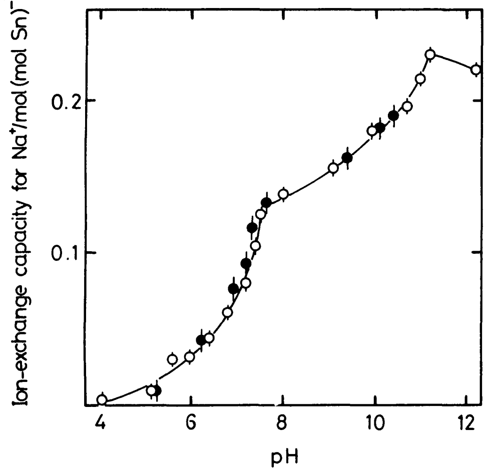

Fig. 1. Reversibility of exchange reaction between Na^+ and Cl^- ions.
○: Forward reaction, ●: Reverse reaction. Conditions; exchanger: 0.25 g, solution: 20 cm^3, temperature: R.T..

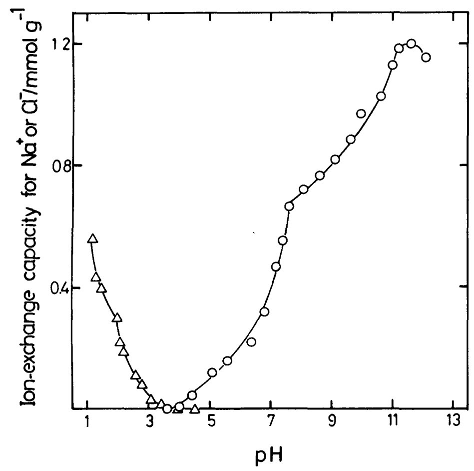

Fig. 2. Uptake curves for Na^+ and Cl^- ions.
Ions; ○: Na^+, △: Cl^-. Conditions; exchanger: 0.25 g, solution: 30 cm^3, ionic strength: 0.10, temperature: R.T..

Table 4. Change in water content of the exchanger by cation exchange

System	Amount of M^+ uptaken	Weight loss[1]		M^+ content	Water content	
	$\frac{\text{mmol } M^+}{\text{g } M^+ \text{ form}}$	wt%	$\frac{\text{mmol } H_2O}{\text{g } M^+ \text{ form}}$	$\frac{\text{mol } M^+}{\text{mol Sn}}$	$\frac{\text{mol } H_2O(I)}{\text{mol Sn}}$	$\frac{\text{mol } H_2O(II)^{a)}}{\text{mol Sn}}$
$\frac{Li^+}{H^+}$	0.19±0.02	19.9±0.2	11.0±0.1	0.036±0.003	2.08±0.03	2.10±0.03
	0.83±0.02	18.9±0.2	10.5±0.1	0.156±0.003	1.98±0.03	2.06±0.03
	1.42±0.02	18.5±0.2	10.3±0.1	0.271±0.003	1.95±0.03	2.09±0.03
	1.74±0.02	18.5±0.2	10.4±0.1	0.332±0.004	1.96±0.03	2.13±0.03
$\frac{Na^+}{H^+}$	0.16±0.02	19.2±0.2	10.7±0.1	0.030±0.002	2.00±0.03	2.02±0.03
	0.32±0.02	17.8±0.2	9.9±0.1	0.060±0.002	1.85±0.03	1.88±0.03
	0.54±0.02	17.4±0.2	9.7±0.1	0.101±0.003	1.80±0.03	1.85±0.03
	0.81±0.02	17.2±0.2	9.5±0.1	0.152±0.004	1.79±0.03	1.87±0.03
	1.22±0.02	16.8±0.2	9.3±0.1	0.231±0.004	1.77±0.03	1.91±0.03
$\frac{Cs^+}{H^+}$	0.19±0.02	18.7±0.2	10.4±0.1	0.036±0.004	1.99±0.03	2.01±0.03
	0.28±0.02	18.0±0.2	10.0±0.1	0.054±0.004	1.93±0.03	1.96±0.03

1) : Calcinated at 850°C. a) : Water content(II)=Water content(I)+1/2 (M^+ content). Exchanger: H^+ form, 100—200 mesh, $SnO_2\cdot(2.16\pm0.01)H_2O$.

possessing a larger ion-exchage capacity for cations than for anions and having an isoelectric point close to pH 4. The inflection points at pH 7.6 and pH 2.0 for cation and anion exchanges respectively suggest that the exchanger has at least two kinds of dissociable ion-exchange sites.

The ion-exchange reaction and its equilibrium constant can be written:

$$\overline{\mathrm{H}} + \mathrm{Na} = \overline{\mathrm{Na}} + \mathrm{H},$$

and:

$$K = K' \cdot \frac{\bar{f}_{\mathrm{Na}}}{\bar{f}_{\mathrm{H}}} = \frac{[\overline{\mathrm{Na}}]\bar{f}_{\mathrm{Na}}a_{\mathrm{H}}}{[\overline{\mathrm{H}}]\bar{f}_{\mathrm{H}}a_{\mathrm{Na}}},$$

where a superscript bar indicates the exchanger phase; [ ], the concentration; a, the activity of ions in the solutions; $\bar{f}$, the activity coefficient of ions in the exchanger, and K' ($\equiv[\overline{\mathrm{Na}}]\cdot a_{\mathrm{H}}/[\overline{\mathrm{H}}]\cdot a_{\mathrm{Na}}$), the conditional selectivity coefficient. By introducing the total specific ion-exchange capacity, $[\bar{S}]=[\overline{\mathrm{Na}}]+[\overline{\mathrm{H}}]$, we get:

$$\frac{1}{[\overline{\mathrm{Na}}]} = \frac{1}{[\bar{\mathrm{S}}]} + \frac{a_{\mathrm{H}}}{K[\bar{S}]}\cdot\frac{\bar{f}_{\mathrm{Na}}}{\bar{f}_{\mathrm{H}}}\cdot\frac{1}{a_{\mathrm{Na}}} = \frac{1}{[\bar{\mathrm{S}}]} + \frac{a_{\mathrm{H}}}{K'[\bar{\mathrm{S}}]}\cdot\frac{1}{a_{\mathrm{Na}}}.$$

If K' is assumed to be constant, the $1/[\overline{\mathrm{Na}}]$ *vs.* $1/a_{\mathrm{Na}}$ plot will show a linear relation, because $[\bar{\mathrm{S}}]$ and a_{H} are constant in the present experiment. Table 5 shows the ion-exchange capacities of the exchanger for sodium ions, measured at a constant pH (11.00±0.03) as a function of the sodium-ion concentration in the solution. The plot of $1/[\overline{\mathrm{Na}}]$ *vs.* $1/a_{\mathrm{Na}}$, however, was not linear, as is shown in Fig. 3. In the calculation of a_{Na} for making this plot, the values of γ_{Na} given by Kielland[11] were used except in the case of the ionic strength, 0.5, where γ_{Na} was estimated by means of this relationship: $\gamma_{\mathrm{Na}}=\gamma_{\pm\mathrm{NaCl}}/\gamma_{\pm\mathrm{KCl}}$. The non-linearity does not support the assumption that K' is constant, even in the pH region, where the same kind of acidic site takes part in the exchange reaction. Hence, either the $\bar{f}_{\mathrm{Na}}/\bar{f}_{\mathrm{H}}$ ratio or K changes as the exchange reaction proceeds. The change in the $\bar{f}_{\mathrm{Na}}/\bar{f}_{\mathrm{H}}$ ratio may be brought about by the variation in the electric field in the exchanger, which would be strongly affected by the ratio of dissociated to undissociated OH groups. The dissociation of an OH group may affect the electric distribution of other OH groups. This will result in a successive change in the dissociation constant with the change in the ionic composition of the exchanger, even in the same kind of exchange site. We can not decide which is more important, the ratio of the activity coefficients in the exchanger or the dissociation constant of the exchange site, as a reason for the non-constancy of K'. In any event, this material is an amphoteric ion-exchanger possessing at least two kinds of weakly dissociable ion-exchange sites. Furthermore, for the same functional group, the degree of dissociation depends on its ionic composition.

TABLE 5. EFFECT OF $\mathrm{Na^+}$ CONCENTRATION ON THE ION-EXCHANGE CAPACITY

Concentration of $\mathrm{Na^+}$ $\frac{[\mathrm{Na^+}]}{\mathrm{mol\,dm^{-3}}}$	Activity of $\mathrm{Na^+}$ $\gamma^{*}_{\mathrm{Na}}[\mathrm{Na^+}]$	Ion-exchange capacity[a)] $\frac{[\overline{\mathrm{Na}}]}{\mathrm{mmol\,g^{-1}}}$
1.0×10^{-2}	9.3×10^{-3}	0.974±0.006
5.0×10^{-2}	4.3×10^{-2}	1.094±0.006
1.0×10^{-2}	8.2×10^{-2}	1.160±0.006
5.0×10^{-1}	3.6×10^{-1}	1.29 ±0.01

a) : Column exchange capacity at pH 11.0. *: Activity coefficient of $\mathrm{Na^+}$ ion; J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

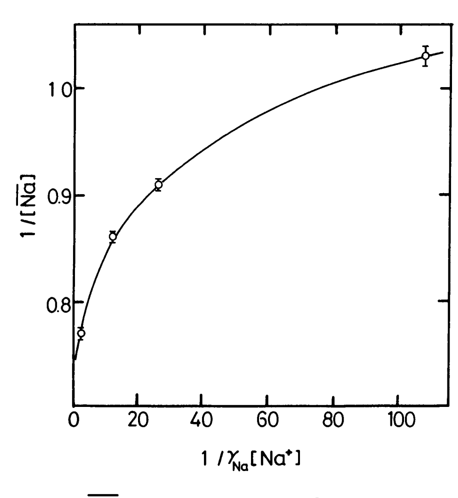

Fig. 3. $1/[\overline{\mathrm{Na}}]$ *vs.* $1/\gamma_{\mathrm{Na}}[\mathrm{Na^+}]$ plot.
$[\overline{\mathrm{Na}}]$: Column exchange capacity for $\mathrm{Na^+}$ ion at pH 11.0 ($\mathrm{mmol\,g^{-1}}$). $\gamma_{\mathrm{Na}}[\mathrm{Na^+}]$: Activity of $\mathrm{Na^+}$ ion in the equilibrium solution.

In order to compare the ion-exchange behavior for the $\mathrm{Na^+}$ ion with that for other cations, uptake curves were obtained for other alkali-metal ions, as is shown in Fig. 4. The curve of the $\mathrm{Li^+}$ ions was similar to that of the $\mathrm{Na^+}$ ions, but the specific ion-exchange capacity was greater for $\mathrm{Li^+}$ than for $\mathrm{Na^+}$, by 0.2 and 0.3 $\mathrm{mmol\,g^{-1}}$ respectively, at the first and second stages. Because the hydrous tin(IV) oxide possesses a micropore structure and because its mean pore radius is as small as 0.5 nm, as was reported by Selim and Zeidan,[12] the difference between the ion-exchange capacity of

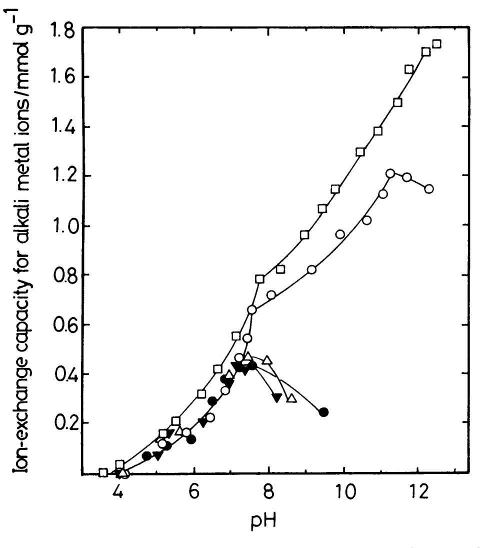

Fig. 4. Uptake curves for various alkali metal ions.
Ions; □: $\mathrm{Li^+}$, ○: $\mathrm{Na^+}$, ▼: $\mathrm{K^+}$, ●: $\mathrm{Rb^+}$, ○: $\mathrm{Cs^+}$.
Conditions; exchanger: 0.25 g, solution: 30 $\mathrm{cm^3}$, contact time: 4 d at room temperature.

these two ions may be attributable to an ion-sieving effect of this material. On the other hand, the uptake curves for the K^+, Rb^+, and Cs^+ ions agreed with that for the Na^+ ion in the lower pH region until the ion-exchange capacity reached around 0.45 mmol g^{-1}, whereupon it began to decrease steeply. This phenomenon can be ascribed to the dissolution of a part of the exchanger, which was verified by analyzing the amount of tin dissolved in the supernatant solution; the exchanger began to dissolve into the solution of K^+, Rb^+, and Cs^+ ions at a pH of around 7, in spite of the fact that no dissolution was observed in the solution of Na^+ and Li^+ ions. The unstability of the exchanger in alkaline solutions of heavy alkali-metal ions reflects the characteristics of α-stannic acid, which has a high solubility in K_2CO_3 and KOH. For α-stannic acid prepared by a similar method, the ion-exchange capacity for the K^+ ion was reported by Abe and Ito and by Sautereau *et al.* to be 0.54 and 0.75 mequiv. g^{-1} respectively at pH 10.[3,8] The reason for this contradiction may be the difference in the duration of immersion when the specific ion-exchange capacity was measured.

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