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Studies of the Hydrous Titanium Oxide Ion Exchanger. II. The Equivalence of the Exchange Adsorption of Cations and the Dissociation Constant

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In order to elucidate the fundamental properties of hydrous titanium oxide as a cation exchanger, the authors examined the stoichiometry of cation exchange and the acid-base property of the exchanger by means of titration curves. The results may be summarized as follows: 1. The equivalent exchange between the hydrogen ion and either the sodium or strontium ion holds over a wide range of conditions, such as the pH, the ionic strength, and the particle size of the exchanger. 2. The method of conditioning for obtaining the exchanger in the pure hydrogen form has been established. 3. The water content in the exchanger depends on the ionic composition. 4. This hydrous titanium oxide is a four-functional, weakly acidic cation exchanger and has the following apparent pK values: pK_1 6.7±0.1, pK_2 10.3±0.2, pK_3 12.3±0.2, and pK_4 13.2±0.2. The corresponding apparent ion exchange capacities are 2.2±0.1, 1.2±0.2, 0.7±0.3, and 0.2±0.3 meq. Na^+/g respectively.

Hydrous titanium oxide ion exchangers were synthesized by various methods, and their composition, ion exchange capacity, stability against various chemicals, and thermal stability were investigated, in the previous paper.[1] The exchangers in the hydrogen form have the composition of $TiO_2 \cdot (2.0—2.2)H_2O$ and a larger exchange capacity (about 3 meq.Cu(II)/g) than the value (1.6 meq.Cu(II)/g) obtained by Heitner-Wirguin *et al.*[2,3] The exchanger is semitransparent, consisting of nearly amorphous particles which are hard enough to be ground into fine particles suitable for column operations. It is stable in both alkaline and dilute acid solutions($<$0.1 M).

The release of hydrogen ions by the adsorption of cations on this material strongly suggests that the mechanism of adsorption is ion exchange, but to substantiate the mechanism unambiguously it is necessary to confirm quantitatively the stoichiometric exchange of the ions concerned. This has been undertaken by using the relation that, for the stoichiometric uptake of ions, the plot of the logarithm of the distribution coefficient *vs.* the pH should be a straight line with a slope corresponding to the valency of cations exchanged.[4] However, this relation is valid only if the concentration of exchanging metal ions is very small in comparison with both the hydrogen-ion concentration and the adsorption capacity of the adsorbent; hence, it is limited to a rather narrow range of experimental conditions. Therefore, from papers hitherto published we cannot exclude the possible participation of mechanisms, such as some specific chemical reaction, surface adsorption, or coprecipitation, other than an ion-exchange reaction.

The purpose of the present investigation is to understand the fundamental properties of hydrous titanium oxide as a cation exchanger through examinations of the validity of the equivalent exchange of cations and of the titration curves, which are useful for understanding the acid-base property of the exchanger.

Experimental

Reagents and Apparatus. The strontium and cesium hydroxide solutions were prepared by passing strontium and cesium chloride solutions through a column packed with Dowex-I anion exchange resin in the OH^- form. All the other reagents were the same as have previously been described.[1]

β-Ray counting was undertaken by the use of a Kobe Kogyo Corp. G. M. counter, Model EA-11, coupled with a Kobe Kogyo scaler, Model SA-250. Except for it, all the apparatuses were the same as have previously been described.

Analytical Method. Alkali metal ions were converted to the corresponding pure chloride and indirectly determined by titrating Cl^- ions by means of Fajans' method. Sr^{2+} was determined chelatometrically.[5] OH^- and CO_3^{2-} were determined by a differential titration, using phenolphthalein and methyl orange as indicators. Cl^- was determined by means of Fajans' method, except for cases where the Cl^- ion was not intentionally added, but came from the ^{22}Na tracer solution. In the latter case, it was estimated by means of the electroneutrality relationship.

Synthesis. The synthetic method No. 7′ described in the preceding paper was used throughout this work. The outline was as follows. Into 200 ml of a 2.2 M $TiCl_4$ solution prepared by diluting liquid $TiCl_4$ with water, 800 ml of a 2.8 M NaOH solution was added at an average rate of 25—30 ml/min. Immediately after the addition, the precipitate was filtered through Toyo No. 1 filter paper under suction, removed from the funnel, dispersed into fresh water, and aged. This procedure was repeated until the pH of the filtrate approached a constant value (about 10). Finally, the precipitate was filtered and air-dried. Since the ion exchange capacity of the material thus prepared fluctuated from batch to batch (3.4—3.7 meq./g), samples of the same batch were employed throughout each series of experiments.

Ion-exchange Stoichiometry. The test samples employed were subjected to three kinds of chemical pretreatments by means of the column method to be described below. The columns used for treating 10 g and 5 g portions of the exchanger were 1.0 cmϕ× 15 cm and 0.7 cmϕ× 15 cm respectively. About a 500 ml portion of the conditioning solution per 10 g of the exchanger was passed through at a flow rate of 0.7—1 ml/min.

Sample A: No pretreatment.

Sample B: Sample A was treated with a 0.1 M HCl solution.

Sample C: About 5 g of Sample A was immersed in 100 ml of a 1 M NaOH solution for 2 days and then treated with the 0.1 M HCl solution.

Sample D: Sample B was treated with a 0.1 M NaOH solution and next with the 0.1 M HCl solution.

Following each single treatment, the exchanger was washed until the effluent was neutral. The particle sizes of the material employed were 65—100, 100—200, and 200—350 meshes.

A half-gram portion of each sample was immersed in 50 ml of a suitable solution (NaOH spiked with ^{22}Na, NaOH–NaCl with ^{22}Na, or $Sr(OH)_2$ with ^{89}Sr) in a tightly stoppered vessel for longer than two days at room temperature, with intermittent shaking. This was followed by chemical analysis and by the measurement of the radioactivity of the solution in a suitable aliquot.

Titration Curve. In 50 ml of a MOH or MOH–MCl solution (M=Na, K, Cs) of a suitable concentration (ionic strength: 0.10 or 1.0 M), 0.5 g of the sample was immersed for 2—3 days at room temperature, followed by the pH measurement and by the chemical analysis of the solution. When the ionic strength was 0.10 M, the amount of ion taken up by the exchanger was evaluated from the difference between the initial and the final concentrations of the ions present in the solution. In the case of the ionic strength of 1.0 M, the amount of uptake was estimated either from the decreased amount of the OH^- ion in the solution or from the weight increase in the exchanger. For the latter, the solid phase was weighed after it had been separated from the solution; it was then washed with acetone, air-dried, and humidiated over a desiccator containing a saturated NH_4Cl solution. This method is warranted by the results, to be described later.

Results and Discussion

Weight Change in the Exchanger with the Change in the Ionic Composition. The change in weight of the exchanger with that of the ionic composition was measured by directly weighing the exchanger before and after a suitable treatment which produced a desired ionic composition. The ionic composition was obtained from the difference in the alkali-metal-ion concentrations of the solution before and after treating the exchanger. The weight increment obtained by direct weighing is plotted in Fig. 1 against that calculated from the change in the ionic composition by assuming that only the difference in the weight of the ions exchanged affects the weight of the exchanger. If this assumption is valid, a straight line with a unit slope passing through the point of origin should be obtained (broken line in Fig. 1). For the sodium ion this relation hold except for the large amount of uptake and can be used for the determination of sodium ion in the exchanger, as has been decribed earlier. In the cases of potassium and cesium ions, the curves deviate appreciably from the broken line. This deviation can naturally be considered to be mainly due to the change in the water content in a hydrous oxide such as this. On the basis of this consideration, we can estimate the change in the water content of the exchanger from the data in Fig. 1.

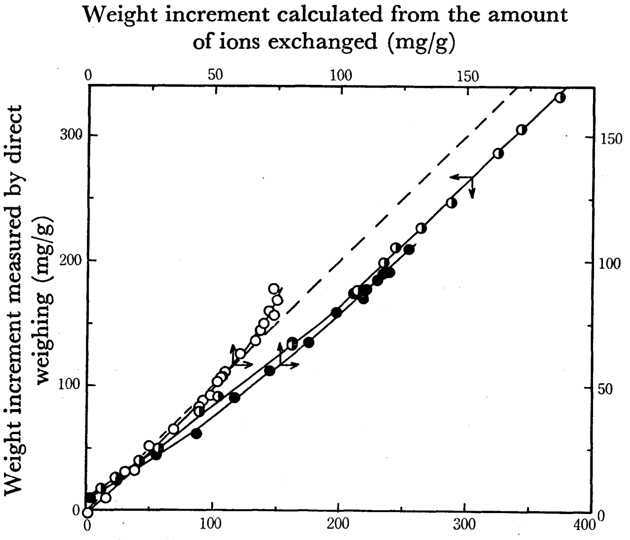

Fig. 1. Weight increase of the exchanger by ion exchange.
○: Na^+ 0.10M; ●: K^+ 0.10M; ◑: Cs^+ 0.10M.

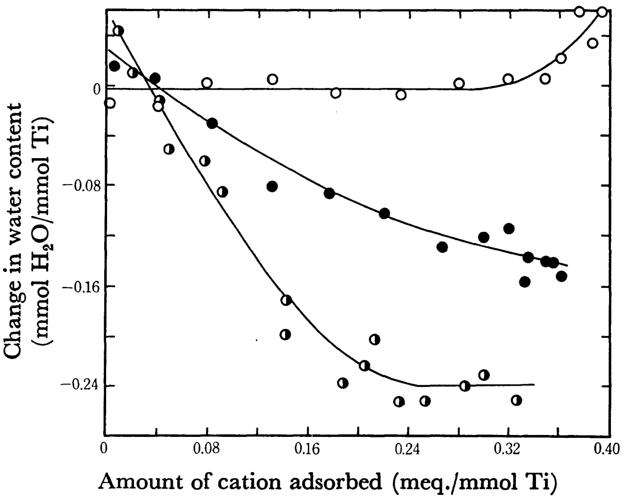

Fig. 2. Change in water content of the exchanger by cation exchange. Marks are the same as used in Fig. 1.

Figure 2 shows the change in the water content of the exchanger in mmol H_2O/mmol Ti against the amount of alkali metal ions taken up in meq./mmol Ti. The horizontal line observed in the case of the sodium ion leads to the conclusion that the exchange between sodium and hydrogen ions causes no change in the water content. The slight deviation from the line in the range of large amounts of sodium-ion uptake is probably due to the reaction with carbon dioxide in the atmosphere during the course of air-drying and humidiating. This explanation is supported by the observations to be described in the next section. Since the same phenomena should also be observed in potassium and cesium exchanges, the curves in Fig. 2 do not show the change in water content quantitatively, especially in the range of higher alkali contents, but the effect is not very large. Therefore, it is evident from Fig. 2 that the ion with the larger ionic radius—that is, with the weaker hydration power, can expel a larger amount of water in the exchanger.

Stoichiometry of the Exchange Reactions. Table 1 represents the experimental results concerning the stoichiometry of the exchange reaction on Samples A

Table 1. The verification of equivalent exchange on the hydrous titanium oxide

Sample and mesh size		Run	Added (meq./g)			
			Na^+	OH^-	CO_3^{2-}	Cl^-
A 65–100	c)	1	10.20±0.00	9.97±0.00	0.15±0.02	0.08±0.02
		2	10.28±0.00	10.05±0.00	0.15±0.02	0.08±0.02
		3	0	0	0	0
	d)	1	10.20±0.00	9.97±0.00	0.15±0.02	0.08±0.02
		2	10.28±0.00	10.05±0.00	0.15±0.02	0.08±0.02
		3	0	0	0	0
B 65–100		1	9.60±0.02	9.43±0.02	0.16±0.01	0.01±0.05
		2	9.54±0.02	9.37±0.02	0.16±0.01	0.01±0.05
		3	0	0	0	0

Sample and mesh size		Run	Remaining (meq./g)				
			Na^+		OH^-	CO_3^{2-}	Cl^-
			1a)	2b)			
A 65–100	c)	1	7.21±0.15	9.28±0.03	8.79±0.03	0.42±0.01	0.07±0.07
		2	7.42±0.15	9.36±0.03	8.90±0.01	0.39±0.01	0.07±0.05
		3	—	0.23±0.01	−0.02±0.01	0.22±0.01	—
	d)	1	—	9.01±0.06	8.79±0.03	0.15±0.02	0.07±0.11
		2	—	9.12±0.06	8.90±0.01	0.15±0.02	0.07±0.09
		3	—	0	0	0	0
B 65–100		1	7.18±0.18	7.30±0.04	7.10±0.01	0.14±0.02	0.06±0.07
		2	7.07±0.18	7.25±0.01	7.01±0.01	0.14±0.00	0.10±0.02
		3	—	0.00±0.00	0.00±0.00	0.00±0.00	—

Sample and mesh size		Run	(i) meq./Na^+ adsorbed/g		(ii) meq./H^+ released/g	(ii)/(i)	
			1a)	2b)		1a)	2b)
A 65–100	c)	1	2.99±0.15	0.92±0.03	1.18±0.03	0.40±0.03	1.28±0.07
		2	2.86±0.15	0.92±0.03	1.15±0.01	0.40±0.03	1.25±0.05
		3	—	—	—	—	—
	d)	1	—	1.19±0.06	1.18±0.03	—	0.99±0.08
		2	—	1.16±0.06	1.15±0.01	—	0.99±0.06
		3	—	—	—	—	—
B 65–100		1	2.42±0.20	2.30±0.06	2.33±0.03	0.97±0.10	1.01±0.04
		2	2.47±0.20	2.29±0.03	2.36±0.03	0.96±0.09	1.03±0.03
		3	—	—	—	—	—

a) γ-Counting. b) Titration. c) Experimental values. d) Corrected values.

and B For Sample A, the ratio of hydrogen ions released to the sodium ions adsorbed was 1.26 (an average of the data on the last column of the table) if we determine the sodium-ion concentration by Fajans' method. This value is somewhat greater than unity, which would be obtained if the ion-exchange stoichiometry holds. The blank Run No. 3 shows that, even in distilled water, some sodium carbonate is released. Assuming that the sodium carbonate comes entirely from the sample, and that the sodium carbonate in the sample completely dissolves in the solution, we may conclude that Sample A contains 0.23 meq. sodium ion/g as a carbonate. This value is also in good agreement with the increase in the carbonate-ion concentration in the sodium hydroxide solution during equilibration with the exchanger. Therefore, the sodium ions originating from the sodium carbonate in the sample can be estimated from the increment in the carbonate ions in solution. When such an amount of sodium ions is subtracted from that in the equilibrium solution, it is revealed that the equivalent exchange holds in each run, as is indicated by the corrected values in the same table.

On the other hand, an average of the ratios of the hydrogen ions released to the sodium ions adsorbed was 0.40, if we calculated the amount of sodium ions adsorbed simply from the difference between the initial and the final activities of the sodium-22 present in solution, assuming a constant specific activity throughout the experiment. This value contradicts the one mentioned above. This discrepancy can be understood by considering that Sample A is not in the pure hydrogen form, but partly in the sodium form.

Assuming that the sodium ion in the exchanger is present as sodium carbonate and fixed ions which are distributed uniformly, and that the specific activity of sodium-22 becomes constant throughout the system after the equilibrium is reached, we obtain the following equations from the conservations of the sodium ion and radioactivity:

$$\bar{w}_i(m_i-Me/2000) + e + w_iV_i = \bar{w}_f m_f + w_f V_f \qquad (1)$$

$$a_iV_i = a_fV_f + S\bar{w}_f m_f \qquad (2)$$

$$S = a_iV_i/[\bar{w}_i(m_i-Me/2000)+e+w_iV_i] \qquad (3)$$

where w represents the concentration of sodium ions in the liquid phase in meq.$\mathrm{Na^+}$/ml; $\bar{w}$, the concentration of sodium ions fixed in the exchange site in meq.$\mathrm{Na^+}$/g; V, the volume of the liquid phase in ml; m, the weight of the exchanger in g; a, the activity concentration in the solution in cpm/ml; e, the amount of sodium carbonate in the sample in meq.; M, the molecular weight of the sodium carbonate, and S, the specific activity of sodium-22 in cpm/meq.$\mathrm{Na^+}$ after the equilibrium was reached. Furthermore, the i and f suffixes refer to the initial and the final states respectively.

TABLE 2. THE COMPARISON BETWEEN CALCULATED AND EXPERIMENTAL VALUES OF $\bar{w}_i$

Sample	Run	m_i (g)	$\bar{w}_i^{\mathrm{calcd}}$ meq./g	$\bar{w}_i^{\mathrm{calcd}}$ based on $\mathrm{H^+}$ form	$\bar{w}_i^{\mathrm{exp}}$ meq./g
A	1	0.5017	2.71±0.32	2.90±0.35	2.32
	2	0.4979	2.48±0.32	2.64±0.34	
B	1	0.4983	0.15±0.32	0.15±0.32	0.08
	2	0.5016	0.11±0.42	0.11±0.42	

Since the water content of the exchanger does not change in the exchange between sodium and hydrogen ions, as is shown in Fig. 1, $V_i = V_f = V$. Combining Eqs. (1)—(3), we obtain:

$$\bar{w}_i = 2000[(a_iw_f/a_f-w_i)V-e]/(2000m_i-Me) \qquad (4)$$

We can calculate $\bar{w}_i$ by substituting the data in Table 1 into Eq. (4). Table 2 shows the results, together with the values determined directly by chemical analysis. The average of these results, 2.60±0.32 meq.$\mathrm{Na^+}$/g of Sample A, agrees with the analytical value, 2.32 meq.$\mathrm{Na^+}$/g of Sample A, within the limits of experimental error. Accordingly, the isotopic-exchange equilibrium is reached in the exchanger. Furthermore, the average of $\bar{w}_i^{\mathrm{calcd}}$ in terms of meq./g of the hydrogen form is 2.77±0.35, as is indicated in the next to the last column of the same table. It is nearly equal to the apparent capacity, 2.6 meq./g (Fig. 4), at pH 10.4, which corresponds to that of the filtrate in the final stage of synthesis. The amount of sodium ions adsorbed by Sample A is 1.18±0.06 meq./g, which corresponds to 1.23±0.06 meq./g of the hydrogen form. This value plus $\bar{w}_i^{\mathrm{calcd}}$ is 4.00±0.41 meq./g, which agrees, within the limits of experimental error, with the ion-exchange capacity obtained with the 0.10 M sodium hydroxide solution. From these results, one can conclude that about 75% of the exchange sites are occupied by sodium ion in the stage of synthesis and that some sodium carbonate is also present. The sodium carbonate may be admixed in the stage of aging and/or during storage, when the sodium ions in the exchanger are expelled to form carbonate by means of the action of atmospheric carbon dioxide.

In Sample B, the ratio of hydrogen ions released to sodium ions adsorbed is 1.02±0.04, as is shown in the last column of Table 1. Therefore, the equivalent exchange is also valid for this sample. The one obtained by the radiometric method is also nearly unity, but it seems a little lower. The results of the blank Run No. 3 show that this sample does not contain carbonate. The sodium content, calculated from the data in Table 1 by means of Eq. (4), is 0.13±0.37 meq./g (Table 2), which agrees with the analytical value, 0.08 meq./g, within the limits of experimental error. The conclusion can be derived directly from these results that the treatment with the 0.1 M hydrochloric acid solution can remove carbonate and most of the sodium ions.

The amount of sodium ions adsorbed plus the $\bar{w}_i^{\mathrm{calcd}}$ value obtained by the radiometric method, 2.43±0.42 meq./g of the hydrogen form, is smaller than the value on Samples C and D, about 3.5 meq./g. The reason for this discrepancy is not clear, but the treatment with 0.1 M hydrochloric acid solution alone is not sufficient to activate all the exchange sites and so is incomplete.

The results on Samples C and D were obtained by means of the radiometric method. Table 3 shows the equivalent exchange between sodium and hydrogen ions

TABLE 3. THE VERIFICATION OF EQUIVALENT EXCHANGE ON THE HYDROUS TITANIUM OXIDE

Sample and mesh size	Ionic strength (M)	Run	(i) meq. $\mathrm{Na^+}$ adsorbed/g	(ii) meq./$\mathrm{H^+}$ released/g	(ii)/(i)
C 65—100	0.10	1	3.42±0.17	3.43±0.01	1.00±0.05
		2	3.35±0.17	3.36±0.02	1.00±0.06
		3	3.42±0.17	3.38±0.03	0.99±0.06
D 65—100	0.10	1	3.69±0.19	3.62±0.04	0.97±0.05
		2	3.51±0.20	3.69±0.04	1.05±0.07
D 100—200	0.10 ($\mathrm{OH^-/Cl^-}$=0.20)[a]	1	1.71±0.18	1.70±0.01	1.01±0.12
		2	1.67±0.18	1.71±0.01	1.04±0.11
		3	1.70±0.18	1.70±0.01	1.01±0.12
D 200—350	0.10	1	3.73±0.15	3.85±0.02	1.03±0.05
		2	3.82±0.15	3.86±0.02	1.01±0.05
D 200—350	0.028 ($\mathrm{OH^-/Cl^-}$=1.6)[a]	1	1.70±0.04	1.68±0.01	1.00±0.03
		2	1.70±0.05	1.69±0.01	1.00±0.04
		3	1.72±0.03	1.69±0.01	0.98±0.03

a) Molar ratio.

Table 4. The verification of equivalent exchange on the hydrous titanium oxide

Sample and mesh size	Ionic strength (M)	Run	(i) meq. Sr^{2+} adsorbed/g 1[a)]	2[b)]	(ii) meq. H^+ released/g	(ii)/(i) 1[a)]	2[b)]
D 65—100	0.068	1	3.77±0.01	3.79±0.01	3.74±0.04	0.99±0.02	0.99±0.02
		2	3.77±0.01	3.79±0.00	3.73±0.07	0.99±0.02	0.98±0.02
		3	3.79±0.01	3.80±0.00	3.76±0.06	0.99±0.02	0.99±0.02

a) γ-Counting. b) Titration.

which takes place in these samples. This relationship holds exactly, irrespective of the particle size, the ionic strength, and the kind of anion.

Table 4 shows that the same is also true when the strontium ion is used as the exchanging cation. Since the carbonate-ion concentration decreased in this run, the amount of hydrogen ions released was estimated from the difference in the sum of carbonate and hydroxide ions before and after the equilibration.

As the results presented above show, the pure-hydrogen-form exchanger can be obtained by treating the air-dried gel first with the 0.1 M hydrochloric acid solution and next with the 0.1 M sodium hydroxide solution, followed by the 0.1 M hydrochloric acid solution. It acts as an ideal cation exchanger, and an equivalent exchange of cations occurs on the exchange sites uniformly distributed in it.

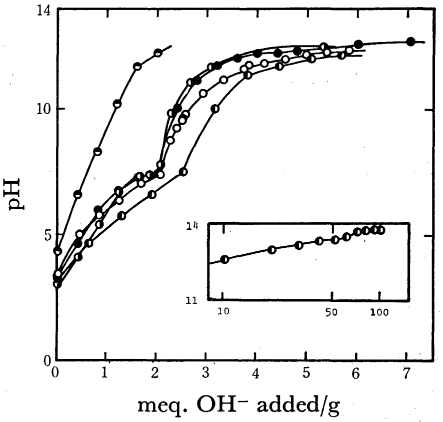

Fig. 3. Titration curves of the exchanger for various alkali metal ions. ◐: Na^+ 1.0M; ◓: K^+ (Ref. 6) 0.1M; ○: Na^+ 0.10M; ●: K^+ 0.10M; ◑: Cs^+ 0.10M.

Acid-base Properties. In order to study the acid-base property of the exchanger, titration curves were constructed by various alkali metal hydroxides, as is shown in Fig. 3. The features are not different from each other except in minor details. The curves obtained with a solution with an ionic strength of 0.10 M present a steep pH jump at pH 7.4. The curve for the potassium ion possesses a small flat portion at pH 12.2, whereas those for the other ions do not.

The titration curve with the sodium hydroxide-sodium chloride mixed solution with an ionic strength of 1.0M also shows a steep pH jump at pH 7.4 and another, less pronounced one at pH 13.5. From these observations, this exchanger can be inferred to possess four kinds of exchange sites.

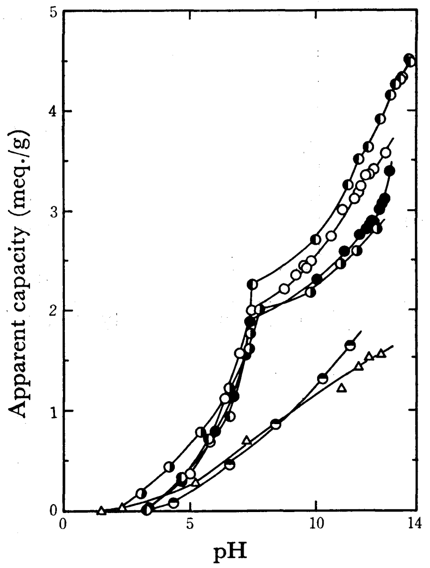

Fig. 4. Apparent capacity of the exchanger as a function of pH. △: Na^+ (Ref. 7); other marks are the same as those in Fig. 3.

The apparent exchange capacity is plotted as a function of the pH in Fig. 4. The curves are consistent with the titration curves, but show some features more clearly. Irrespective of the ionic strength and the kind of ion employed, the first inflecting point appears at pH 7.4, where the first pH jump is observed in the titration curves. While the point indicating the beginning of the participation of the third exchange site is not distinctly observed in the titration curves, it appears more clearly in the cases of the potassium and sodium ions for $\mu=0.10$ at pH 12.2 and 12.0 and in the case of the sodium ion for $\mu=1.0$ at pH 11.7 in Fig. 4. In the latter case, an additional jump in pH is observed at pH 13.5, where a corresponding discontinuity is also observed in Fig. 4.

Another interesting fact may well be noted here. The exchange rate shown in Fig. 5 indicates that the exchange of sodium ions occurs step by step. The amount of sodium ions taken up at the end of each step is nearly the same as the value observed at the inflection point of Fig. 4. This fact not only shows that the rate of exchange is faster in the more acidic site, but also strengthens the observation about the position of the inflection point mentioned above. It can be concluded from these facts that this exchanger possesses four kinds of exchange sites. This conclusion is quite different from the findings by other workers.[6,7] The hydrous titanium oxide prepared by them shows an apparent exchange capacity of about 1.6 meq./g at

Table 5. pK values and apparent capacities of the exchanger for alkali metal ions

Ion	Ionic strength (M)		Steps				Total ion exchange capacity
			1	2	3	4	
Na^+	0.10	pK	5.20±0.04	9.00±0.15	—	—	3.4±0.1
		C[a]	2.01±0.07	1.33±0.19	—	—	
	1.0	pK	6.7 ±0.1	10.3±0.2	12.3±0.2	13.2±0.2	4.5±0.2
		C[a]	2.2 ±0.1	1.2 ±0.2	0.7±0.3	0.2 ±0.3	
K^+	0.10	pK	5.42±0.03	9.27±0.03	—	—	3.4±0.1
		C[a]	1.90±0.02	0.99±0.04	—	—	
	1.0		—	—	—	—	4.5±0.1
Cs^+	0.10	pK	5.05±0.03	—	—	—	2.8±0.1
		C[a]	2.00±0.03	—	—	—	
	0.50		—	—	—	—	3.4±0.2
Cs^+ (Ref. 4)	2.5×10^{-3}	pK	5.7	6.7	8.5	—	(0.299)
		C[b]	0.100	0.090	(0.109)	—	
	5.0×10^{-3}	pK	5.7	6.8	8.4	—	(0.292)
		C[b]	0.100	0.096	0.096	—	
	1.2×10^{-2}	pK	5.7	7.0	8.7	—	(0.298)
		C[b]	0.100	0.098	0.100	—	

a) Ion exchange capacity in meq./g. b) Ion exchange capacity in g-eq./molTiO_2.

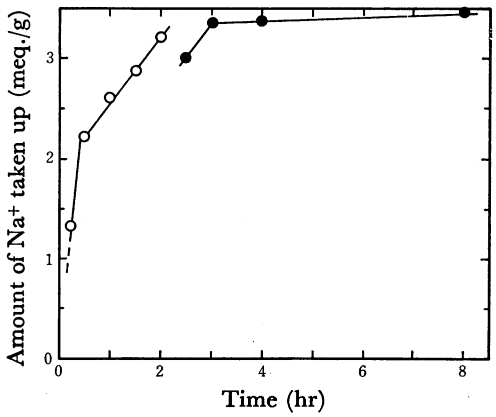

Fig. 5. Ion exchange rate of Na^+ ion. Conditions: 50 ml of 0.106 M NaOH/0.50 g of H^+ form exchanger 65—100 mesh. Temperature, ○: 22 °C, ●: 19—22 °C.

pH 12, and up to this pH the inflection point is not observed. This difference is probably attributable to the difference in their synthetic method from the present authors'.

The apparent pK values can be calculated by applying the following equation[8] to the titration curve (Fig. 3) and to the dependency of the apparent capacity on the pH (Fig. 4):

$$pK_i = pH_i + \log (M^+)_i - \log (\bar{X})_i/2$$

where $(M^+)_i$ and pH_i are the alkali-metal-ion concentration and the pH at the half-conversion point of the i-th exchange site respectively. The results are presented in Table 5, together with the results reported by Schiewer.[4] It can be concluded from the table that all the functional groups in the exchanger are weakly acidic. Since the experimental conditions used by Schiewer are appreciably different from ours, we cannot compare the results strictly, but, interestingly enough, the pK_1 value of this exchanger is almost the same as that of Schiewer, 5.7. However, the pK_2 and pK_3 values are completely different from those of Schiewer. This discrepancy may arise from the difference in structure; that is, Schiewer employed a hydrous titanium oxide suspension as an exchanger, whereas the present authors used an exchanger possessing a hard, three-dimensional network.

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