January, 1985] © 1985 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 58, 97—102(1985) 97

Synthetic Inorganic Ion-exchange Materials. XXXVII. Ion-exchange Behaviors of Alkylammonium Ions on Hydrous Titanium Dioxide

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(Received June 11, 1984)

Ion-exchange behavior of alkali hydroxide and alkylamines having different sizes and forms on hydrous titanium dioxide ion exchanger (HTDO) were studied. The uptakes of all the cations by HTDO indicated the ion-exchange stoichiometry at a pH range studied. The pH titration curves vary, depending on the cation species and the strength of the bases used: amorphous HTDO(Am-HTDO) behaves as a bifunctional acid towards strong bases and as a monofunctional acid towards weak bases. Am-HTDO shows an affinity series in the increasing order: large ions($(C_2H_5)_3NH^+$, $(CH_3)_4N^+$, and $(n\text{-}C_4H_9)_4N^+$)<ions in medium size ($CH_3NH_3^+$, $n\text{-}C_3H_7NH_3^+$, $n\text{-}C_4H_9NH_3^+$ *etc.*)<small ions(Na^+, K^+, and NH_4^+). The large ions suffer from a strong steric effect, because of the limited space of the ion-exchange site available. The results correlate with the pore size distribution: the pore radius ranged from 4 to 7 Å in Am-HTDO degassed at 40 °C by a rotary pump. The maximum volume occupied by the alkylammonium ions exchanged (0.2—0.3 cm^3/g), calculated by assuming cations to be unhydrated, is in good agreement with the value determined by N_2 gas adsorption (0.16 cm^3/g). An anatase-type HTDO showed a larger steric effect for uptake of the alkylammonium ions than that by the Am-HTDO, due to a decrease in the ion-exchange cavity.

Recently, ion-exchange selectivities on synthetic inorganic ion exchange materials have been studied.[1—4] Hydrous oxides and hydroxides of multivalent metals are reported to behave as selective ion exchangers towards a few metal ions. Hydrous titanium(IV) oxide showed selectivity for uranium(VI) in sea water.[5—7] Hydrous tin(IV) antimonate exhibited a unique selectivity sequence of $Na^+<K^+<Rb^+<Cs^+ \ll Li^+$ in an increasing order.[8] Hydrous manganese(IV) oxide in cryptomelane-type showed an unusual selectivity sequence towards alkali metal ions: $Li^+<Na^+<Cs^+ \ll K^+, Rb^+$. This exchanger shows a high selectilvity for the ions having the effective ionic radius[9] of 1.4 Å.[10,11] Crystalline antimonic(V) acid cation exchanger shows an excellent selectivity towards metal ions having an effective ionic radius of about 1 Å.[3] Cations larger than 6 Å in diameter cannot enter the cavity of crystalline antimonic acid.[12] Adsorption of Alkyl Orange dyes on silica gel indicated that a correlation exists with the molecular size of the dye.[13] It has been known that clinoptilolite cannot exchange alkylammonium ions larger than 6 Å.[14] These behaviors are well known as the ion-sieve action. No ion-sieve effect was observed on γ-zirconium phosphate ion exchanger, because of expansion along the c-axis by exchanging the large organic ions.[15] A steric effect can be expected for large spherical cations and long cations exchanged by HTDO, if it has a rigid framework and a small ion-exchange cavity.

The present paper describes the ion-exchange behaviors of univalent cations having different van der Waals dimensions on HTDO.

Experimental

Ion-exchange Material. Am-HTDO was prepared by hydrolysis of $TiCl_4$ solution with NaOH solution.[16] Am-HTDO in H^+ form was obtained by removing Na^+ ions by percolation of 0.1 M HCl (1 M=1 mol dm^{-3}) solution into a column of Am-HTDO containing Na^+ ions (1 cmϕ×10 cm).

X-Ray and Thermal Analyses. X-Ray analysis with the powder method was carried out using Ni-filtered Cu-*Kα* radiation with a JEOL diffractometer, Model JDX-7E. Thermogravimetry(TG) and differential thermal analysis (DTA) were undertaken with a Rigaku Denki thermoflex type thermal analyzer, Model 8001, at a heating rate of 10 °C min^{-1}.

Pore Size Distribution. The nitrogen gas adsorption isotherm of Am-HTDO was determined at 77 K by using N_2 gas adsorption equipment (Calro Erba, Co., Model Sorptomatic 1800). Prior to the measurement, degassing with a rotary pump was carried out until about 0.5 g of Am-HTDO in 50—100 mesh size became constant at 40 °C. A cross section of 16.2 Å^2 for N_2 molecule was employed.

pH Titration Curves. A 0.125 g portion of Am-HTDO in H^+ form was added into 12.5 cm^3 of (MCl+HCl) or (MCl+MOH) mixed solution of the ionic strength 0.1 at 30±0.5 °C in a thermostated bath, where M=Na, NH_4, and alkylammonium. It was shaken intermittently and allowed to stand until the concentration of M^+ ions became constant within the experimental error. Thereafter, pH values and the concentration of M^+ and Cl^- in the supernatant solution were determined. The pH measurement was carried out using a Toa Dempa pH meter, Model HM-5A. The concentrations of M^+ and Cl^- ions in the solution were determined by an "ion-exchange and titration" method: After neutralizing a 10 cm^3 aliquot with a standardized 0.1 M HNO_3 or 0.05 M NaOH solutions, the solution was percolated through Dowex 50W-X8 ion-exchanger column in H^+ form (1.0 cmϕ×10 cm) and then washed with water. The effluent was collected and titrated with standardized 0.05 M NaOH solution. The amount of M^+ ions in the solution was determined by sub-

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tracting the amount of NaOH used for neutralization from the amount of the titrant. Cl^- ions in the equilibrated solution were determined by titrating with 0.03 M $AgNO_3$ solution using fluorescein as indicator after neutralization. Thus, the uptakes of M^+ and Cl^- ions by the Am-HTDO were calculated from the difference relative to the initial concentration.

Chemicals. $(n\text{-}C_4H_9)_4NOH$ was supplied as a 10% aqueous solution by Tokyo Kasei Ind. and other chemicals were supplied by Wako Pure Chemical Ind., Ltd. All chemicals were of analytical grade and used without further purification. Alkylammonium chloride solutions were prepared by neutralizing with dilute HCl solution.

Results and Discussion

Am-HTDO as an Ion-exchange Material. The Am-HTDO was characterized by X-ray diffraction and thermal studies. The X-ray powder pattern showed almost no distinct peak, indicating the product to be nearly amorphous. The crystallite sizes were estimated to be smaller than 20 Å in diameter. DTA curve showed an endothermic peak based on dehydration up to 200 °C and a sharp exothermic peak due to the transformation from nearly amorphous to the anatase modification at 400 °C. These features are in good agreement with those reported in our previous paper.[17] The composition of Am-HTDO obtained from the weight loss was $TiO_2 \cdot 1.84H_2O$ by assuming that the ignition product is TiO_2. The same composition was obtained in Am-HTDO kept in air at RT for 8 months, but it showed a weak anatase-type diffraction pattern, yielding a crystallite of about 30 Å.

Pore Size Distribution. The adsorption-desorption isotherm of N_2 gas on Am-HTDO was measured; this gives important informations about the pore structures of the solid. It shows the Langmuir-type[18] (Fig. 1). There was almost complete reversibility through the entire pressure range studied. A straight line was obtained on the BET plot,[19] giving S_{BET}= 345 m²/g and C_{BET}=194. As long as the constant C_{BET} is lower than 200, a surface area, S_t, obtained by V_l-t plot based on the "MP method" by Brunauer, Mikhail and Bodor[20] shows good agreement with S_{BET}. In the present sample, S_t was 356 m²/g, showing a discrepancy of 3.2%. This is a reasonable agreement, which permits use of V_l-t plot.

The pore volume distribution curve of Am-HTDO is shown in Fig. 2. The degassed Am-HTDO consists largely of micropores of 4—7 Å in hydraulic radius. The total pore volume was 0.16 cm³/g. A sample degassed with a rotary pump until a constant weight was achieved showed a composition of $TiO_2 \cdot 1.2H_2O$. Hence, the skeleton of the Am-HTDO is still covered with hydrated and interstitial water. If the water could be removed more extensively without destruction of the ion-exchange sites or crystallization, a wider dis-

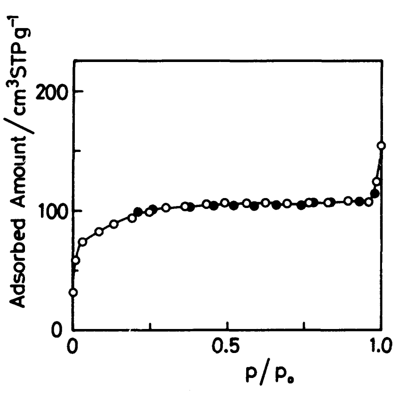


Fig. 1. Adsorption-desorption isotherm of N_2 on Am-HTDO at 77 K.

○: adsorption, ●: desorption.

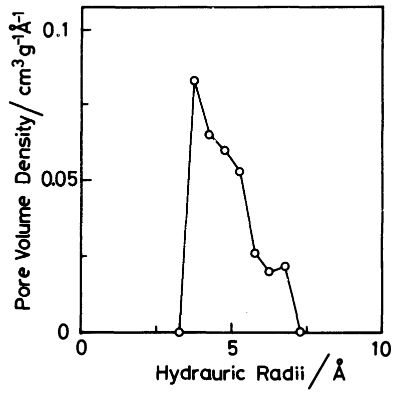


Fig. 2. Pore volume distribution curve of Am-HTDO.

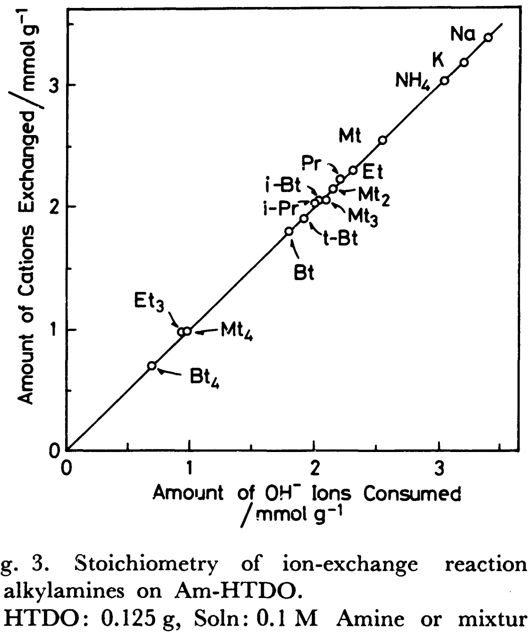
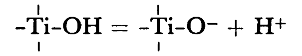


Fig. 3. Stoichiometry of ion-exchange reaction of alkylamines on Am-HTDO.

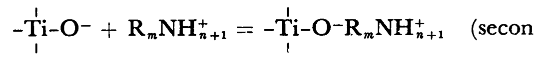
HTDO: 0.125 g, Soln: 0.1 M Amine or mixture of amine and the chloride, Total vol: 12.5 cm³, Temp: 30 °C. Marks: Mt=$CH_3NH_3^+$, Et=$C_2H_5NH_3^+$, Pr=$C_3H_7NH_3^+$, Bt=$C_4H_9NH_3^+$, Mt_2=$(CH_3)_2NH_2^+$, Mt_3=$(CH_3)_3NH^+$, Mt_4=$(CH_3)_4N^+$, Et_2=$(C_2H_5)_2NH_2^+$, Et_3=$(C_2H_5)_3NH^+$, Bt_4=$(n\text{-}C_4H_9)_4N^+$.

tribution of pores accessible to nitrogen molecules would be obtained. However, degassing at elevated temperatures destroys the exchange sites.

Ion-exchange Stoichiometry for Various Alkylammonium Ions. The uptake of cations with different dimensions was studied in alkaline media(Fig. 3). The amount of hydroxide ions consumed was in good agreement with the amount of cation exchanged. This indicates the stoichiometry of the exchange reaction for all the cations used. Accordingly, almost all protons in Am-HTDO behave as a Brönsted acid. The uptake occurs through two possible schemes: One includes an exchange process with a replaceable proton,

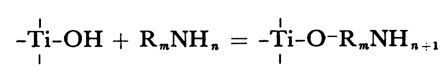


$$-\underset{|}{\overset{|}{\mathrm{Ti}}}\mathrm{-OH} = -\underset{|}{\overset{|}{\mathrm{Ti}}}\mathrm{-O^-} + \mathrm{H^+} \qquad \text{(first step)}$$



$$-\underset{|}{\overset{|}{\mathrm{Ti}}}\mathrm{-O^-} + \mathrm{R}_m\mathrm{NH}^+_{n+1} = -\underset{|}{\overset{|}{\mathrm{Ti}}}\mathrm{-O^-R}_m\mathrm{NH}^+_{n+1} \qquad \text{(second step)}$$

and the other occurs through hydrogen bonding,



$$-\underset{|}{\overset{|}{\mathrm{Ti}}}\mathrm{-OH} + \mathrm{R}_m\mathrm{NH}_n = -\underset{|}{\overset{|}{\mathrm{Ti}}}\mathrm{-O^-R}_m\mathrm{NH}_{n+1}$$

where m and n are integer, and R denotes alkyl groups. However, the titration method cannot distinguish between the dissociation step and the adsorption step, because of the difficulty of the measurement of the H^+ ion concentration in the solid phase.

pH Titration Curve. It has been known that the Am-HTDO ion exchanger has an amphoteric character in aqueous solutions. The ion-exchange capacity towards Na^+ and Cl^- ions depends upon the pH of the solution used. The pH titration of the Am-HTDO ion exchanger was carried out in a pH range from 2 to 12, by using bases with different strengths, and geometrical forms and sizes in order to investigate the details of the change in the exchange capacity with pH values. A distinct break point can be found on each titration curve with strong bases at pH 7.5—8 irrespective of the geometrical dimensions of the cations (Fig. 4), while no break point is observed on the titration curves with weak bases over a wide range of pH studied (Fig. 5). Therefore the Am-HTDO acts as an apparent bifunctional acid towards strong bases and as an apparent monofunctional acid towards weak bases.

In the titration of a soluble weak acid with a strong base, generally the pH discontinuity at the end point is more obscure with decreasing strength of the base. Moreover, a steric effect also occurs in the case of the titration of inorganic ion-exchange materials having a rigid three-dimensional structure, as described below. The titration curves in Figs. 4 and 5 suggest these effects.

The uptakes for these cations were determined (Figs. 6 and 7). These results correspond well to each pH

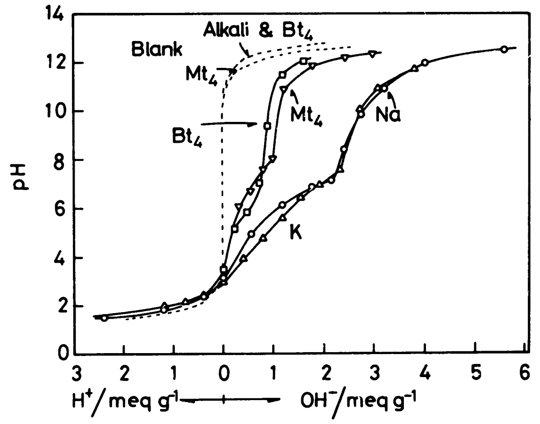


Fig. 4. pH Titration curves of Am-HTDO with strong bases having different size parameters.
Am-HTDO: 0.125 g, Soln: 0.1 M (MCl+HCl or MOH) mixed soln. (M=Bt_4, Mt_4, Na, and K). Notations are the same as in Fig. 3. Total vol.: 12.5 cm^3, Temp: 30±0.5 °C.

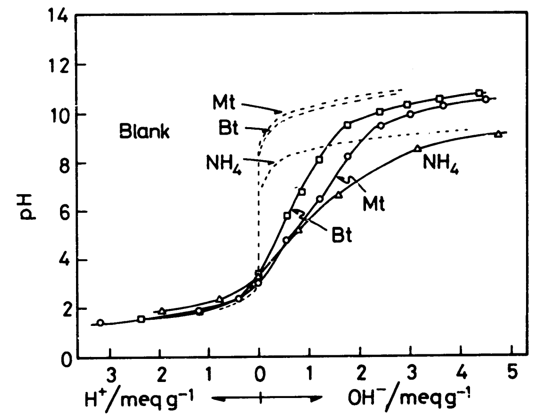


Fig. 5. pH Titration curves of Am-HTDO with weak bases having different size parameters.
The experimental conditions are the same as in Fig. 4.

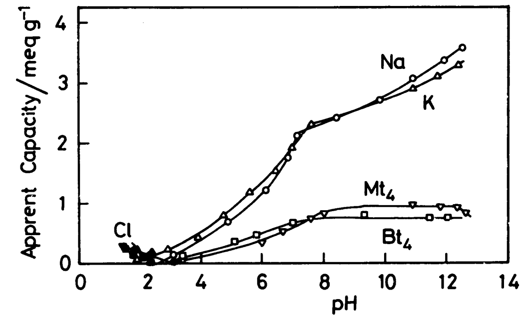


Fig. 6. Apparent capacities of spherical ions with different size parameters as a function of pH. Conditions are the same as in Fig. 4. Open marks are for cations and closed marks are for coexisting Cl^- ions.

Table 1. Amounts of alkylammonium ions having different dimensions exchanged by Am-HTDO

Cations	Dimension of Cations in Å a)				Amounts exchanged	pH
	pK_a d)	x-direction (length)	y-direction (width)	z-direction (height)	mmol/g	
NH_4^+	9.25	2.86	2.86	2.86	3.05	9.50
$CH_3NH_3^+$	10.65	4.9_1	4.0_0	4.0_0	2.55	11.0
$C_2H_5NH_3^+$	10.80	5.9_0	4.8_8	4.0_0	2.31	12.1
$(CH_3)_2NH_2^+$	10.73	6.4_2	4.2_8	4.0_0	2.25	12.3
n-$C_3H_7NH_3^+$	10.70	7.2_6	4.8_8	4.0_0	2.21	12.1
i-$C_3H_7NH_3^+$	—	6.5_2	5.5_6	4.7_7	2.03	12.1
$(CH_3)_3NH^+$	9.8 e)	6.4_2	6.1_0	4.1_7	2.06	11.6
n-$C_4H_9NH_3^+$	10.77	8.4_2	4.8_8	4.0_0	1.80	11.0
i-$C_4H_9NH_3^+$ b)	—	7.5_1	5.5_6	4.7_7	2.05	12.0
$(C_2H_5)_2NH_2^+$ b)	10.9 e)	7.5_9	6.0_5	4.0_0	2.25	12.3
t-$C_4H_9NH_3^+$	10.83	6.5_2	6.1_8	5.6_8	1.92	12.1
$(CH_3)_4N^+$	—	6.4_2	6.1_0	6.2_2	0.95	12.0
$(C_2H_5)_3NH^+$	10.8 e)	7.5_9	7.2_7	4.1_7	0.98	12.2
$(n$-$C_4H_9)_4N^+$ b)	—	9.9_3	9.6_1	9.7_3	0.75	12.0
Na^+ c)	—	2.04	2.04	2.04	3.40	12.0
K^+ c)	—	2.76	2.76	2.76	3.20	12.0

a) Ref. 14. b) Estimated according to Ref. 14. c) Ref. 9. d) Ref. 27. e) Ref. 28.

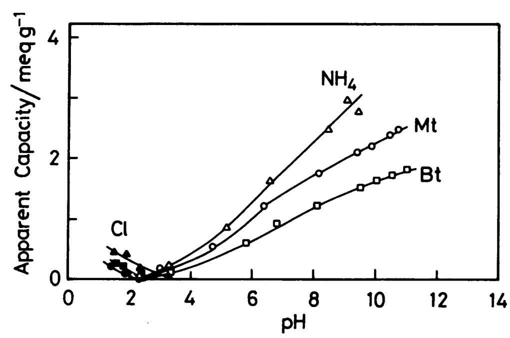


Fig. 7. Apparent capacities of NH_4^+ and nonspherical alkylammonium ions having different size parameters as a function of pH. Conditions are the same as in Fig. 5. Open marks are for cations and closed marks are for coexisting Cl^- ions.

titration curve in Figs. 4 and 5, indicating that the ion-exchange reaction is predominant over the whole range of pH studied. The apparent capacities for Na^+, K^+, $(CH_3)_4N^+$, and $(n$-$C_4H_9)_4N^+$ ions increase monotonically up to pH 7.5—8. At higher pH, the uptakes for Na^+ and K^+ ions having a small size show further increase, but those for large $(CH_3)_4N^+$ and $(n$-$C_4H_9)_4N^+$ ions constant up to pH 12. These suggest that smaller cations (Na^+, K^+) among strong bases can easily approach the ion-exchange sites present in micro-pores, while larger cations ($(n$-$C_4H_9)_4N^+$, $(CH_3)_4N^+$) are difficult of access to the micro-pores. At lower pH than 2, anion uptakes are predominant and a small uptake of Cl^- ions can be observed.

On the contrary, the apparent capacity for NH_4^+, $CH_3NH_3^+$, and n-$C_4H_9NH_3^+$ ions monotonically increases up to pH 10—11. With increasing dimensions, the apparent capacity decreased, when it was compared at pH>4.

A replaceable proton responsible for the ion-exchange reaction on various hydrous oxides and composite oxides has been determined by the butylamine titration method.[21,22] Johnson used butylamine as the titrating base for the reasons that it does not disturb the coloration at the end point using Hammet indicators and is not volatile. Many other authors have employed this base to determine the surface acid-sites.[23,24] The present results show that all the ion-exchange sites of Am-HTDO cannot be determined by the technique using this amine because of the steric hindrance. An alkali hydroxide or NH_3 aq. should be employed for the determination of the total protons responsible for the ion-exchange reaction of hydrous oxides of multivalent metals. However, an objection to the use of KOH can be found in the literature:[25] A silicate bond, $-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-$, is broken by the uptake of K^+ ions and the simultaneous consumption of OH^- ions on silica gel and the structure is rearranged. An uptake of Na^+ ions on hydrous tin(IV) oxide obeys a reversible ion-exchange reaction.[26] Hence, the breaking reaction of an $-\overset{|}{\underset{|}{Sn}}-O-\overset{|}{\underset{|}{Sn}}-$ bond will not be probable. Whether such a reaction including a break of $-\overset{|}{\underset{|}{Ti}}-O-\overset{|}{\underset{|}{Ti}}-$ occurs or not cannot be decided by the forward pH titration technique only.

Exchanged amounts of the alkylammonium ions having different van der Waals dimensions are compared in Table 1. Small spherical cations (NH_4^+, Na^+, and K^+) of diameter<3 Å and ellipsoidally-shaped cations (n-$C_4H_9NH_3^+$ ions, *etc.*) can be exchanged to a greater extent. However, large ions>6 Å in dimension cannot fully replace a proton in the ion-exchange sites. Pore sizes of Am-HTDO vary over a range of 4—7 Å in radius (Fig. 2). These large organic ions are known to behave as a breaker of water structure in inorganic ion exchangers and exclude water molecules within the exchangers.[12] Water molecules in the Am-HTDO will be excluded more effectively than the degassing with a rotary pump when these large cations approach the ion-exchange sites. Thus, these alkylammonium ions can be exchanged.

The cross-section and volume of unhydrated cations were calculated, assuming the cations to be spheres (Na^+, NH_4^+) or prisms of elliptical cross-section (Table 2). The amounts of cations exchanged were plotted against the cross-section and the volume of the alkylammonium ion (Fig. 8 top and bottom, respectively). Uptakes of alkylammonium ions showed weak dependence on the cross-section, except n-$C_4H_9NH_3^+$, $(C_2H_5)_3NH^+$, and $(CH_3)_4N^+$ ions. These latter ions are very long or else very large spheres. The geometrical hindrance dose not permit these cations to be exchanged completely.

The uptakes decrease approximately linearly with increasing volumes of the unhydrated cations. The extent of the decrease is large for long (n-$C_4H_9NH_3^+$), wide ($(C_2H_5)_3NH^+$) or large spherical cations ($(CH_3)_4N^+$, $(n$-$C_4H_9)_4N^+$). It is due to the steric effect by these cations.

The maximum volume available for the ingoing ions can be estimated to be 0.2—0.3 cm³/g. This value is comparable with that determined by N_2 adsorption (0.16 cm³/g). It may be due to the effect of exclusion of water molecules by large cations exchanged that the former value is slightly large.

It has been known that an Am-HTDO in H^+ form is crystallized to an anatase-type while it is kept in the atmosphere at room temperature for a long period.[29]

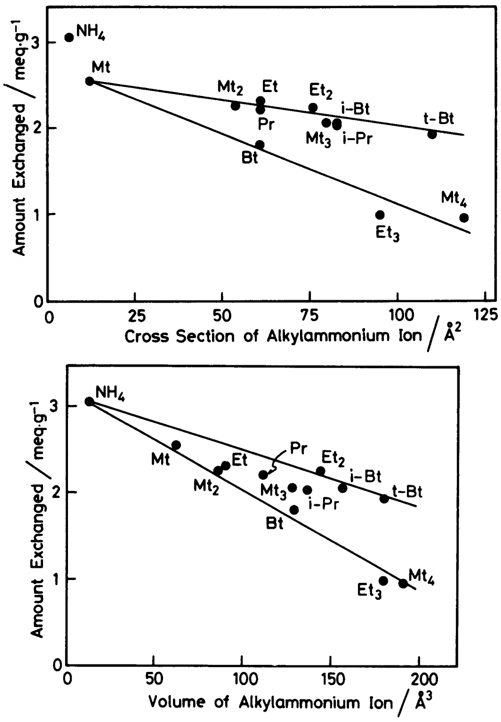


Fig. 8. Effect of the cross-section (top) and the volume (bottom) of unhydrated alkylammonium ions on the amount exchanged by Am-HTDO in H^+ form. Marks are the same as in Fig. 3.

TABLE 2. TOTAL AREA AND PORE VOLUME OCCUPIED BY ALKYLAMMONIUM IONS EXCHANGED BY Am-HTDO

Cations	Volume/Å³	Cross-Section/Å²	Total Area	Pore Volume
	of Unhydrated Cations		m²/g	cm³/g
NH_4^+	12.5	6.3	38	0.023
$CH_3NH_3^+$	62	12	72	0.095
$C_2H_5NH_3^+$	90	61	367	0.125
$(CH_3)_2NH_2^+$	86	54	325	0.116
n-$C_3H_7NH_3^+$	111	61	367	0.147
i-$C_3H_7NH_3^+$	136	83	499	0.166
$(CH_3)_3NH^+$	128	80	481	0.158
n-$C_4H_9NH_3^+$	129	61	367	0.139
i-$C_4H_9NH_3^+$	156	83	499	0.192
$(C_2H_5)_2NH_2^+$	144	76	457	0.195
t-$C_4H_9NH_3^+$	180	110	662	0.208
$(CH_3)_4N^+$	191	119	716	0.109
$(C_2H_5)_3NH^+$	180	95	571	0.106
$(n$-$C_4H_9)_4N^+$	729	293	1763	0.329
Na^+	4.4	3.2	19	0.009
K^+	11.0	6.0	36	0.021

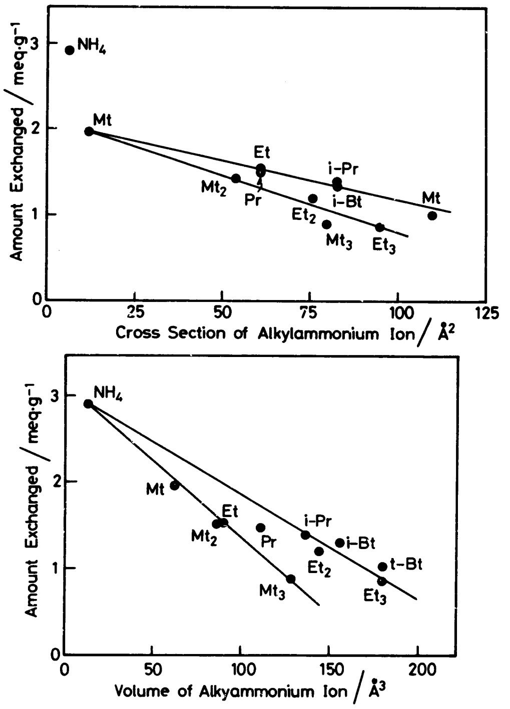


Fig. 9. Effect of the cross-section (top) and the volume (bottom) of unhydrated alkylammonium ions on the amount exchanged by An-HTDO in H^+ form. Marks are the same as in Fig. 3.

The Am-HTDO in H^+ form changed to An-HTDO having a crystallite size of about 30 Å after keeping it in the atmosphere for 8 months at room temperature. The An-HTDO showed about the same values as the Am-HTDO for the uptakes of NH_4^+ and $(C_2H_5)_3NH^+$ ions, while it showed a substantially decreased uptake for other alkylammonium ions (Fig. 9, top). This may be due to a decrease in the size of the cavity to accommodate the ingoing cations of medium size (5—7 Å). It suggests that the crystallization to the anatase-type causes shrinking of the Am-HTDO structure, followed by a decrease in the volume of the cavity necessary for the access to the ion-exchange sites. Consequently, the amounts exchanged more rapidly decreased with increasing volume of alkylammonium ions than Am-HTDO (Fig. 9, bottom). Thus, An-HTDO showed a larger steric effect than Am-HTDO.

The present authors are grateful to Mr. Kenta Ooi at the Government Industrial Research Institute, Shikoku, for the measurement of the pore size distribution.

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