

Effect of Intercalated Alkylammonium on Cation Exchange Properties of $H_2Ti_3O_7$

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Cation exchange was studied on alkylammonium intercalated $H_2Ti_3O_7$ in comparison with $H_2Ti_3O_7$ itself. Alkylammonium exchanged for proton in advance made it possible for alkali and alkaline earth metal ions to be taken up into $H_2Ti_3O_7$ in chloride solution. Only alkylammonium was exchanged with hydrated alkali and alkaline earth metal ions. In hydroxide solution, proton was exchanged with alkali metal ions as well as alkylammonium ion. Dependence on pH and preference on ion exchange were affected by the previous uptake of alkylammonium into $H_2Ti_3O_7$. © 1987 Academic Press, Inc.

Introduction

There is a series of alkali titanates having the general formula $A_2Ti_nO_{2n+1}$, where A is an alkali metal and $1 \leq n \leq 8$. Formation of their fibrous crystals has been investigated (1, 2). Hexatitanate fiber is getting to be important as a substitute for asbestos. Some of the titanates, $2 \leq n \leq 4$, have a layered structure and large cation exchange capacities (3-5). They have possible applications as cation exchangers that are stable to high radiation field and high temperature.

Sodium trititanate ($Na_2Ti_3O_7$) has a layered structure and its interlayer cation is exchangeable (4). Its fibrous crystal was recently grown (6). The cation exchange

properties have been studied on $Na_2Ti_3O_7$ and its alkali extracted product, $H_2Ti_3O_7$ (7-9). Pronounced pH dependence and a sharp preference for lithium among alkali metal ions due to the difference in reaction rates were observed on cation exchange reactions of $H_2Ti_3O_7$ (8). The trititanate formed n -alkylammonium complexes by ion exchange reaction (10). The alkylammonium complexes have expanded interlayer distances. An expansion of interlayer distance and its successive diffusion of interlayer ions are important for ion exchange reaction in layered compounds. The prior expansion with alkylammonium absorption may make the following ion exchange reaction easy. The alkylammonium complexes have possibilities to take in the cations which could not be

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exchanged by $\text{H}_2\text{Ti}_3\text{O}_7$ and also to enhance the exchange reaction rate.

Interlayer dodecylammonium in muscovite was exchanged for Al^{3+} and Si^{4+} in xylene (11). Intercalated *n*-butylammonium in α -zirconium phosphate (ZrP) has been exchanged for Cu^{2+} , Ni^{2+} , and $\text{Cu}(\text{NH}_3)_4^{2+}$, which cannot be directly intercalated into ZrP (12). The effect of intercalated organic ions on the reaction rate, pH dependence, and ion preference on exchange had not yet been reported in these investigations. There have been no reports of cation exchange on an organic complex of layered titanate.

This paper deals with cation exchange reactions with alkali and alkaline earth metal ions of *n*-alkylammonium complexes of $\text{H}_2\text{Ti}_3\text{O}_7$. The effect of interlayer alkylammonium on the ion exchange property will be discussed. The exchange with alkali metal ions was first studied on $\text{H}_2\text{Ti}_3\text{O}_7$ -methylammonium and *n*-propylammonium complexes in aqueous solutions of ACl and AOH , where *A* is Li, Na, or K. Then pH dependences of the reactions were studied on $\text{H}_2\text{Ti}_3\text{O}_7$ and its alkylammonium complexes. Effect of the interlayer alkylammonium was also examined on exchange preference. Finally, the exchange with alkaline earth metal ions was investigated in their chloride aqueous solutions.

Experimental

$\text{Na}_2\text{Ti}_3\text{O}_7$ was prepared by heating a mixture of Na_2CO_3 and TiO_2 in a molar ratio of 1:3 at 800°C for 20 hr and for another 20 hr after grinding. $\text{H}_2\text{Ti}_3\text{O}_7$ was obtained by removing Na^+ of $\text{Na}_2\text{Ti}_3\text{O}_7$ (ca. 50 g) in 1 dm^3 of 0.5 M HCl at 30°C for 3 days. The acid solution was renewed every day in order to remove alkali completely from the compounds. The products were washed with distilled water and dried in vacuum at 30°C . $\text{H}_2\text{Ti}_3\text{O}_7$ (ca. 10 g), whose average

particle size was $1.3 \mu\text{m}$ by SEM observation, was sealed in glass tubes with a 40% aqueous solution of methylamine (ca. 20 cm^3) and a 50% solution of *n*-propylamine. Durations of reaction were 30 days at 60°C . The glass tubes were shaken well during the reaction to keep it homogeneous. The amine solution was renewed every 10 days. The reactions could be assumed to attain equilibrium in 30 days under these conditions (10). Excess amounts of amine were removed when the reactions were completed. The products were washed with acetone and dried in air. Chemical formulae of the alkylammonium products were $(\text{CH}_3\text{NH}_3)_x\text{H}_{2-x}(\text{Ti}_3\text{O}_7)$ and $(n\text{-C}_3\text{H}_7\text{NH}_3)_y\text{H}_{2-y}(\text{Ti}_3\text{O}_7)$, where $0.7 \leq x \leq 0.8$ and $0.5 \leq y \leq 0.8$. Their average particle size was $1.2 \mu\text{m}$.

Cation exchange reactions with alkali metal ions were studied on methylammonium and *n*-propylammonium complexes. The samples (ca. 500 mg) were equilibrated with 40 cm^3 of aqueous solution of LiCl , NaCl , KCl , LiOH , NaOH , and KOH for 3 days at 60°C . The solutions were prepared from boiled CO_2 free water and their alkali concentrations were 0.1 M . The bottles were filled with nitrogen gas and sealed. The bottles were shaken well during the reaction. The products were washed with distilled water and dried in vacuum at 30°C . The interlayer distances were estimated by X-ray powder diffractometry using silicon as an internal standard (Rigaku-Denki diffractometer using $\text{CuK}\alpha$ radiation). The products were dissolved in a mixed solution containing 15 times of $(\text{NH}_4)_2\text{SO}_4$ and 55 times of H_2SO_4 in weight at about 230°C . Amounts of alkali were determined by the method of standard addition of atomic absorption (Jarrel-Ash AA-1). The amount of titanium was determined by colorimetry using 4,4'-methylene-diantipyrine (Jasco UVDEC-2). Dehydration processes and water contents of the products (ca. 10 mg) were estimated

by TG-DTA (Rigaku-Denki Thermoflex). C, H, and N contents of the alkylammonium complexes and the exchanged products were determined by conventional chemical analysis (Yanaco CHN-Corder MT-2).

Dependence on pH of the exchange reactions was studied on $\text{H}_2\text{Ti}_3\text{O}_7$ and its alkylammonium complexes. The samples (ca. 500 mg) were equilibrated by soaking in 40 cm^3 of aqueous mixed solution of LiCl and LiOH having various ratios in polyethylene bottles for 3 days at 60°C. Then the cation preferences were studied on methylammonium and *n*-propylammonium complexes (ca. 500 mg) in 160 cm^3 of 0.1 *M* total alkali concentration containing equal amounts of LiCl, NaCl, KCl, and CsCl for 3 days at 60°C. They were also investigated in mixed hydroxide solution.

Cation exchange with alkaline earth metal ions was also studied on $\text{H}_2\text{Ti}_3\text{O}_7$ and its alkylammonium complexes. The samples (ca. 500 mg) were equilibrated with 40 cm^3 of aqueous solution of 0.1 *M* MgCl_2 , CaCl_2 , and SrCl_2 . The amounts of alkaline earth metals in the products were determined by atomic absorption.

Results and Discussion

1. Cation Exchange with Alkali Metal Ions

Lithium uptake into $\text{H}_2\text{Ti}_3\text{O}_7$ was sluggish in 0.1 *M* LiOH and was not possible in 0.1 *M* LiCl solution. Exchange rates of lithium uptake were studied on $(\text{CH}_3\text{NH}_3)_{0.78}\text{H}_{1.22}(\text{Ti}_3\text{O}_7)$ and $(n\text{-C}_3\text{H}_7\text{NH}_3)_{0.81}\text{H}_{1.19}(\text{Ti}_3\text{O}_7)$ soaked in solutions of 0.1 *M* LiCl and LiOH to investigate the effect of prior intercalated alkylammonium. The reaction rates of both complexes were very rapid. The amount of lithium was about 26% of total exchangeable cations in methylammonium complex soaked in 0.1 *M*

LiCl solution for 1 day at 60°C. It was 29% in 3 days and 28% in 5 days. In LiOH solution, it was 53% in 1 day, 55% in 3 days, and 50% in 5 days. In the case of the *n*-propylammonium complex, it was 28% in 1 day, 33% in 3 days, and 32% in 5 days in 0.1 *M* LiCl solution. In LiOH solution, it was 53% in 1 day, 49% in 3 days, and 53% in 5 days. Thus each reaction attained an equilibrium in 1 day under these conditions. Lithium uptake could not be observed on $\text{H}_2\text{Ti}_3\text{O}_7$ itself in 0.1 *M* LiCl aqueous solution as can be imagined from our previous studies (8, 9). However, lithium could be taken into the interlayer of the alkylammonium complexes even in 0.1 *M* LiCl.

Reaction rate of $(n\text{-C}_3\text{H}_7\text{NH}_3)_{0.81}\text{H}_{1.19}(\text{Ti}_3\text{O}_7)$ was also studied in 0.1 *M* NaCl solution. The sample (500 mg) was soaked in 30 cm^3 of the solution at 23°C. Sodium concentration in solution was measured by a Na^+ ion-selective electrode (Na-115B supplied by TOA Electronics Ltd.). It rapidly decreased with a duration of 60 sec and attained the value of 0.047 *M* in 210 sec as shown in Fig. 1. The loss of sodium in solution can be calculated as $(0.100 - 0.047) \times 30/1000 = 1.6 \times 10^{-3}$ mole and corresponds to about 48% of total exchangeable cations in 500 mg of $(n\text{-C}_3\text{H}_7\text{NH}_3)_{0.81}\text{H}_{1.19}(\text{Ti}_3\text{O}_7)$. The exchange reac-

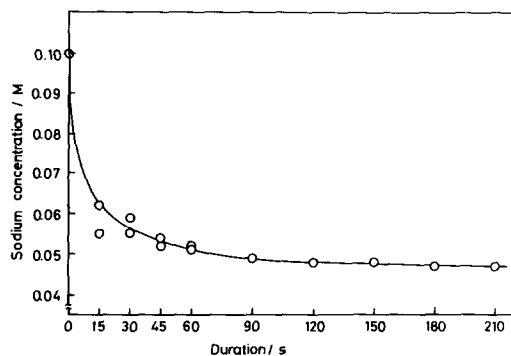


FIG. 1. Reaction of $(n\text{-C}_3\text{H}_7\text{NH}_3)_{0.81}\text{H}_{1.19}(\text{Ti}_3\text{O}_7)$ with sodium ion measured by ion-selective electrode.

tions finished in a few minutes at room temperature.

Exchanged products were preliminarily characterized. They were equilibrated respectively with 0.1 M ACl and AOH, where A is Li, Na, or K for 3 days at 60°C. The kinds of solutions, estimated chemical formulae of the products, and their interlayer distances are summarized in Table I. The amounts of alkali were 27–36% of total exchangeable cations in methylammonium complex immersed in 0.1 M ACl solution for 3 days at 60°C. They were 50–55% in case of 0.1 M AOH. Intercalated water contents of the products were calculated by weight loss of TG below 150°C. The exchanged products in chloride solution showed small exotherms due to combustion of alkylammonium on their DTA. However, ammonium was not detected in the products exchanged in 0.1 M AOH. The interlayer distance decreased from 1.20 nm of the original methylammonium complex to the values listed in Table I during the reactions. It was almost the same whether the sample was wet or dry. In the case where propylammonium complex was used as ion-exchanger, the absorbed alkali amount was 27–35% in 0.1 M ACl. It was 39–55% in 0.1 M AOH. The interlayer distances decreased from 1.55 nm to the same values listed in Table I for methylammonium complexes.

The original alkylammonium complexes did not have interlayer water, but their exchanged products had 0.5–1.8 mole of interlayer water. The alkylammonium ions were exchanged with hydrated alkali metal ions.

2. pH Dependence

Cation exchange was studied on $H_2Ti_3O_7$, $(CH_3NH_3)_{0.78}H_{1.22}(Ti_3O_7)$, and $(n-C_3H_7NH_3)_{0.58}H_{1.42}(Ti_3O_7)$ in solutions having various pH values. Molar percentage of lithium in the product was calculated for total amounts of exchangeable cations. It was plotted against pH values of starting solutions as shown in Fig. 2. It was less than 3% in the products prepared from $H_2Ti_3O_7$ below pH = 11.0 and rapidly increased with pH in the region of pH \geq 11.5, attaining a value of 51% at pH = 12.8. On the other hand, it was about 25% in the products prepared from $(CH_3NH_3)_{0.78}H_{1.22}(Ti_3O_7)$ and $(n-C_3H_7NH_3)_{0.58}H_{1.42}(Ti_3O_7)$ below pH = 11.0 and increased with pH in the region of pH > 11.0, attaining the value of 55% at pH = 12.8. TG-DTA was performed on the products prepared from $(CH_3NH_3)_{0.78}H_{1.22}(Ti_3O_7)$ in the temperature range up to 800°C. The products obtained below pH = 12.0 showed two exotherms with weight loss due to a combustion of methylammonium at about 380 and 570°C. These

TABLE I
ION EXCHANGE OF $(CH_3NH_3)_{0.66}H_{1.34}(Ti_3O_7)$ WITH ALKALI METAL IONS

Solution (0.1 M)	Interlayer distance (nm)	Product
LiCl	1.05 (1.06) ^a	$Li_{0.54}(CH_3NH_3)_iH_{1.46-i}(Ti_3O_7) \cdot 0.7H_2O$
NaCl	1.09 (1.11)	$Na_{0.70}(CH_3NH_3)_iH_{1.30-i}(Ti_3O_7) \cdot 1.1H_2O$
KCl	0.97 (0.98)	$K_{0.72}(CH_3NH_3)_iH_{1.28-i}(Ti_3O_7) \cdot 0.6H_2O$
LiOH	1.04 (1.09)	$Li_{1.10}H_{0.90}(Ti_3O_7) \cdot 1.2H_2O$
NaOH	1.08 (1.16)	$Na_{1.07}H_{0.93}(Ti_3O_7) \cdot 1.8H_2O$
KOH	0.98 (1.06)	$K_{1.00}H_{1.00}(Ti_3O_7) \cdot 0.5H_2O$

^a The interlayer distance in parentheses represents the value for the exchanged wet product.

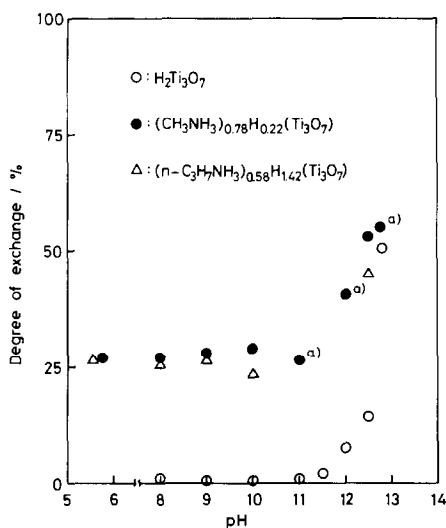


FIG. 2. Effect of pH on cation exchange of $\text{H}_2\text{Ti}_3\text{O}_7$ and its alkylammonium complexes with lithium ion. a) The value of propylammonium complex overlapped with that of methylammonium complex.

exotherms were not observed on the products prepared above $\text{pH} = 12.5$.

The contents of lithium and methylammonium were represented as shown in Table II in the products equilibrated at various pH. The original compound contained 0.78 molar methylammonium. The lithium contents agree well with the decrease of methylammonium during the

TABLE II
LITHIUM AND METHYLAMMONIUM CONTENTS OF
THE PRODUCTS REACTED IN SOLUTIONS HAVING
VARIOUS pH VALUES

pH	Lithium (mole)	Methylammonium (mole)	Decrease of methylammonium (mole)
5.8	0.54	0.26	0.52
8.0	0.54	0.25	0.53
9.0	0.56	0.25	0.53
10.0	0.58	0.25	0.53
11.0	0.59	0.25	0.53
12.0	0.81	0.19	0.59
12.5	1.06	0	0.78
12.8	1.10	0	0.78

exchange below $\text{pH} = 11.0$. This methylammonium was exchanged with lithium in this pH region. Lithium ions can be incorporated into $\text{H}_2\text{Ti}_3\text{O}_7$ above $\text{pH} = 11.0$ as shown in Fig. 2. Both methylammonium and proton in $(\text{CH}_3\text{NH}_3)_{0.78}\text{H}_{1.22}(\text{Ti}_3\text{O}_7)$ can be exchanged with lithium in this pH region. Cation exchange was observed on $\text{H}_2\text{Ti}_3\text{O}_7$ only in the high pH region because of its Brønsted acidic nature. The prior intercalation of alkylammonium in the interlayer region made the exchange reaction possible even in chloride solution.

3. Cation Exchange in Mixed Alkali Solution

The cation exchange reactions of $(\text{CH}_3\text{NH}_3)_{0.78}\text{H}_{1.22}(\text{Ti}_3\text{O}_7)$ and $(n\text{-C}_3\text{H}_7\text{NH}_3)_{0.50}\text{H}_{1.50}(\text{Ti}_3\text{O}_7)$ were studied in 0.1 M mixed chloride solution containing equal amounts of Li, Na, K, and Cs. Molar ratios of Li:Na:K:Cs in the exchanged products are summarized in Table III, which compares the results in mixed hydroxide solution.

A sharp preference for lithium among alkali metal ions had been observed on the cation exchange of $\text{H}_2\text{Ti}_3\text{O}_7$ as shown in Table III (8). The interlayer cations were not hydrated in the exchanged products prepared from $\text{H}_2\text{Ti}_3\text{O}_7$ even if the samples were in equilibrium with a solution of 0.1 M AOH (8). On the other hand, there was no clear selectivity in the exchange of alkylammonium complexes in ACl aqueous solution. Alkylammonium in the starting complex was assumed to be exchanged with hydrated alkali ions in ACl solution as described in the previous section. Any kinds of hydrated alkali metal ions may be able to diffuse equally in the expanded interlayer region substituting alkylammonium.

In hydroxide solution, lithium content was the largest in the exchanged products of alkylammonium complexes. However, the lithium preference was not so remark-

TABLE III
CATION EXCHANGE OF $H_2Ti_3O_7$ AND ITS ALKYLAMMONIUM COMPLEXES
IN MIXED ALKALI SOLUTION

Exchanger	Solution (0.1 M)	Molar ratios of alkali in the products Li : Na ^a : K : Cs
$(CH_3NH_3)_{0.78}H_{1.22}(Ti_3O_7)$	(LiCl + NaCl + KCl + CsCl)	1.00 : 1.87 : 2.00 : 1.97
	(LiOH + NaOH + KOH + CsOH)	1.00 : 0.23 : 0.85 : 0.23
$(n-C_3H_7NH_3)_{0.50}H_{1.50}(Ti_3O_7)$	(LiCl + NaCl + KCl + CsCl)	1.00 : 1.95 : 1.82 : 1.86
	(LiOH + NaOH + KOH + CsOH)	1.00 : 0.20 : 0.60 : 0.26
$H_2Ti_3O_7$	(LiOH + NaOH + KOH + CsOH)	1.00 : 0.34 : 0.04 : 0.01 ^b

^a The starting material contained a small amount of sodium. The value is an increase of sodium content during the exchange.

^b From Ref. (8).

able as in the case of $H_2Ti_3O_7$. Alkali metal ions were taken up into $H_2Ti_3O_7$ by substituting for its proton. Both alkylammonium and proton in the starting complexes were exchanged with alkali metal ions in the present exchange in hydroxide solution. The substitution of alkylammonium made the cation exchange selectivity less remarkable.

4. Cation Exchange with Alkaline Earth Metal Ions

Cation exchange reactions with alkaline earth metal ions were studied on $H_2Ti_3O_7$,

$(CH_3NH_3)_{0.78}H_{1.22}(Ti_3O_7)$, and $(n-C_3H_7NH_3)_{0.81}H_{1.19}(Ti_3O_7)$. The samples were soaked respectively in solutions of 0.1 M $MgCl_2$, $CaCl_2$, and $SrCl_2$ for 3 days at 60°C. $H_2Ti_3O_7$ scarcely reacted with alkaline earth metal ions in their chloride solutions. The exchanged products contained very small amounts of alkaline earth metal and their interlayer distances agreed with that of $H_2Ti_3O_7$, 0.79 nm, as shown in Table IV. The alkaline earth metals were adsorbed only on the $H_2Ti_3O_7$ surface.

Cation exchange reactions were observed on the alkylammonium com-

TABLE IV
ION EXCHANGE WITH ALKALINE EARTH METAL IONS

Exchanger	Solution (0.1 M)	Product	Interlayer distance (nm)
$H_2Ti_3O_7$	$MgCl_2$	$Mg_{0.03}H_{1.94}(Ti_3O_7)$	0.79
	$CaCl_2$	$Ca_{0.06}H_{1.88}(Ti_3O_7)$	0.79
	$SrCl_2$	$Sr_{0.07}H_{1.86}(Ti_3O_7)$	0.80
$(CH_3NH_3)_{0.78}H_{1.22}(Ti_3O_7)$	$MgCl_2$	$Mg_{0.44}H_{1.12}(Ti_3O_7) \cdot 1.6H_2O$	1.10
	$CaCl_2$	$Ca_{0.51}H_{0.98}(Ti_3O_7) \cdot 1.3H_2O$	1.04
	$SrCl_2$	$Sr_{0.49}H_{1.02}(Ti_3O_7) \cdot 1.4H_2O$	1.04
$(n-C_3H_7NH_3)_{0.81}H_{1.19}(Ti_3O_7)$	$MgCl_2$	$Mg_{0.45}H_{1.10}(Ti_3O_7) \cdot 1.9H_2O$	1.18
	$CaCl_2$	$Ca_{0.44}H_{1.12}(Ti_3O_7) \cdot 1.4H_2O$	1.08
	$SrCl_2$	$Sr_{0.51}H_{0.98}(Ti_3O_7) \cdot 2.0H_2O$	1.08

plexes as shown in Table IV. No exotherm related to the presence of alkylammonium was detected on DTA of the exchanged products. The amounts of alkaline earth metals were 0.44–0.51 mole per one mole of the products. A part of them, 0.03–0.07 mole, might be adsorbed on the surface as observed in the case of $\text{H}_2\text{Ti}_3\text{O}_7$. Net amounts of exchanged alkaline earth metals were calculated by subtracting these values from the alkaline earth metal contents in the products. They were 0.41–0.45 mole in the products obtained from $(\text{CH}_3\text{NH}_3)_{0.78}\text{H}_{1.22}(\text{Ti}_3\text{O}_7)$. These values agreed with a half of the methylammonium contents in the original complex, $0.78/2 = 0.39$ mole. Similarly, the net values were calculated as 0.38–0.44 mole on the products prepared from $(n\text{-C}_3\text{H}_7\text{NH}_3)_{0.81}\text{H}_{1.19}(\text{Ti}_3\text{O}_7)$. Interlayer distances decreased in both alkylammonium complexes during the reactions as shown in Table IV. The products had 1.3–2.0 moles of interlayer water. Thus two alkylammonium ions were exchanged with one hydrated alkaline earth metal ion in chloride solution.

The reaction rate of $(n\text{-C}_3\text{H}_7\text{NH}_3)_{0.81}\text{H}_{1.19}(\text{Ti}_3\text{O}_7)$ was studied in a solution of 0.1 M SrCl_2 . The amount of strontium was about 47% after 1 hr of soaking at 60°C. It was about 51% in 3 days. Both products showed the same X-ray diffraction diagram, and no exotherm related to combustion of propylammonium was detected in their DTA. The exchange reaction was assumed to be completed within 1 hr.

In summary, the prior expansion of interlayer distance with alkylammonium made the following ion exchange reaction of $\text{H}_2\text{Ti}_3\text{O}_7$ easy. Hydrated alkali and alkaline

earth metal ions could be taken up into the interlayer of the alkylammonium complexes even in chloride solutions where they could not be incorporated into $\text{H}_2\text{Ti}_3\text{O}_7$. The alkylammonium complexes could take in the cations in a wide pH region and enhance the exchange reaction rate. However, the previous intercalation of alkylammonium extinguished a sharp preference for lithium on the cation exchange of $\text{H}_2\text{Ti}_3\text{O}_7$.

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