ANION-EXCHANGE PROPERTIES OF HYDROTALCITE-LIKE COMPOUNDS

Shigeo Miyata

Kyowa Chemical Industry Co., Ltd., 305 Yashimanishi-machi
Takamatsu, Kagawa, 761-01, Japan

Abstract—Ion-exchange isotherms between hydrotalcite-like compounds (HT) of the NO_3^-, Cl-, and SO_4-forms and F^-, Cl^-, Br^-, I^-, OH^-, SO_4^{2-}, CO_3^{2-}, and Naphthol Yellow S (NYS^{2-}) ions were determined, and the spacing and the width of the 003 reflection were measured as a function of HT composition. The ion-exchange equilibrium constant for HTs of monovalent anions are in the sequence $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$, those for divalent anions are in the sequence $CO_3^{2-} > NYS^{2-} > SO_4^{2-}$. The ion-exchange equilibrium constants tend to increase as the diameters of the anions decrease, and the crystallite size in the 001 direction tends to increase with anions having higher selectivity. The OH-form of HT has the smallest basal spacing and the largest crystallite size in the 001 direction.

Key Words—Anion exchange, Anion selectivity, Crystallite size, Hydrotalcite, Naphthol Yellow S, X-ray powder diffraction.

INTRODUCTION

Hydrotalcite-like compounds (HT) can be represented by the following formula: $[Mg_{1-x}Al_x(OH)_2]^{x+}$ $[A_{x/n}^{n-} \cdot mH_2O]^{x-}$, wherein $0 < x < 0.33$, and A^{n-} is an exchangeable anion having a valence of n. These compounds are similar to the mineral hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ (Miyata and Kumura, 1973; Taylor, 1973; Miyata, 1975). HT consists of positively charged brucite-like layers $[Mg_{1-x}Al_x(OH)_2]^{x+}$ alternating with disordered, negatively charged interlayers $[A_{x/n}^{n-} \cdot mH_2O]^{x-}$. Mg and Al are randomly distributed among the octahedral positions, and the OH layer sequence is –BC–CA–AB–BC– (Allmann, 1968).

HT is stable to 400°C, but transforms into a $MgO-Al_2O_3$ solid solution ($Mg_{1-3x/2}Al_xO$) by heating to 500°–800°C. This solid solution rehydrates and combines anions to form HT in the presence of water and anion (Miyata and Okada, 1977; Miyata, 1980). Consequently, both HT and heat-treated HT are capable of capturing anions and are therefore useful as halogen scavengers for polyolefines produced by Ziegler catalyst or Fridel-Craft catalyst and thermal stabilizers for polyvinylchloride etc. (Miyata and Kuroda, 1981a, 1981b). Accordingly, the ion-exchange properties of hydrotalcite-like compounds are important. The present article of hydrotalcite reports the synthesis of the NO_3^-, Cl-, and SO_4-forms and the ion-exchange isotherms and ion selectivity for these compounds and F^-, Cl^-, Br^-, I^-, OH^-, SO_4^{2-}, CO_3^{2-}, and Naphthol Yellow S^{2-} anions.

EXPERIMENTAL

Hydrotalcite-like compounds corresponding to the above mentioned formula in which x is about 0.3 and A^{n-} is NO_3^-, Cl^-, or SO_4^{2-} were prepared by the method described by Miyata (1975) and Miyata *et al.* (1977). At x = about 0.3, the ion-exchange capacity of the products was high, and by-products did not form. A small amount of CO_3^{2-} was incorporated into the products, but because the CO_3^{2-} is highly selected by these compounds as compared with other anions, the ion-exchange reaction of CO_3^{2-} was ignored.

Determination of ion-exchange isotherm

An amount of each HT calculated to give an ion-exchange capacity of 2 to 5 meq was placed in a flask with a ground glass stopper and an appropriate amount of a 0.1 N aqueous solution of each the aforementioned anions was added. The flask was placed in a constant temperature vessel (25°C) and shaken overnight. The contents of the flask were then filtered and the anion concentration in the filtrate determined. The anion solutions used were prepared by using NaF, NaBr, KI, NaOH, Na_2CO_3, Na_2SO_4, and Naphthol Yellow S (analytical grade made by Wako Pure Chemical Co., Ltd., chemical formula $C_{10}H_4N_2Na_2O_8S \cdot 3H_2O$).

The individual anions were quantitatively determined by the following method: OH^-, by titration with 0.1 N HCl; F^- by titration with 0.1 N thorium nitrate using Alizarin Red S as an indicator in accordance with the method of Japan Standard Association (1965a); Cl^-, Br^-, and I^-, by the Volhard method (Nippon Bunseki Kagakukai, 1961); CO_3^{2-} by the method of Japan Standard Association (1965b); NO_3^-, by reducing NO_3^- of the sample with a mixture of NaOH solution and Debalda alloy to form NH_3 and backtitrating excess sulfuric acid having NH_3 absorbed in it with aqueous NaOH; SO_4^{2-}, by the gravimetric analysis of barium sulfate; and Naphthol Yellow S, photometrically by measuring the absorbance at 430 nm using a Hitachi Model 101 Spectrophotometer.
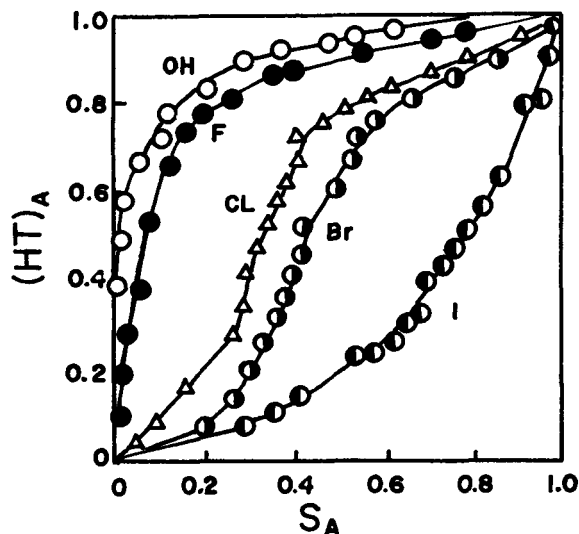
Figure 1. Ion-exchange isotherms for the HT-NO_3–OH^- (O), HT-NO_3–F^- (●), HT-NO_3–Cl^- ($\triangle$), HT-NO_3–Br^- (◑), and HT-NO_3–I^- (◐) systems at 0.1 total normality and 25°C.

Figure 2. Ion-exchange isotherms for the HT-NO_3–SO_4^{2-} (●), HT-NO_3–CO_3^{2-} (O), HT-Cl–NYS^{2-} ($\triangle$), and HT-SO_4–CO_3^{2-} (◑) systems at 0.1 total normality and 25°C.

X-ray powder diffraction (XRD) analyses were carried out using Ni-filtered CuKα radiation with a Philips X-ray diffractometer after drying the products at 60°C for 20 hr.

RESULTS AND DISCUSSION

Three different HT exchangers (HT-NO_3, HT-Cl, HT-SO_4) were prepared. Their chemical compositions are listed in Table 1.

Prior to measuring ion-exchange isotherms the stability of HT-NO_3 in NaF and NaOH solutions was determined by examining the molar ratio of Mg to Al in the HT-NO_3 using the lattice parameter a (Miyata, 1980) before and after contact with the solution. The molar ratio of Mg to Al in HT-NO_3 did not change, and Al was virtually undetectable in the solution. Accordingly, Al in HT does not react with F^- or OH^- anions.

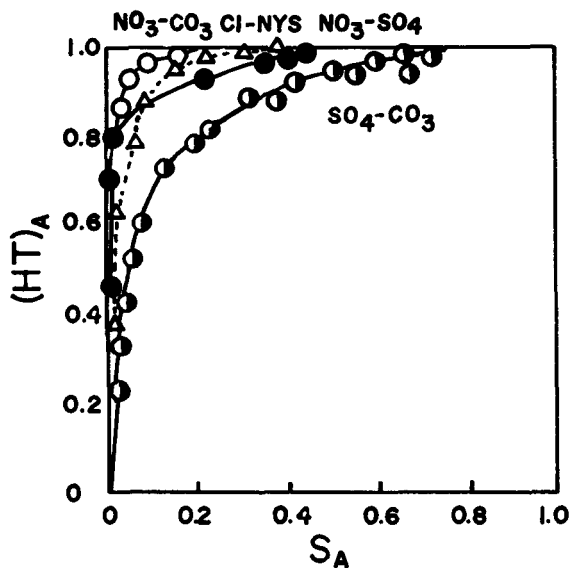Ion-exchange isotherms at 25°C in a total ion concentration of 0.1 N of HT-NO_3–OH^-, HT-NO_3–F^-, HT-

NO_3–Cl^-, HT-NO_3–Br^-, HT-NO_3–I^-, HT-NO_3–SO_4^{2-}, HT-NO_3–CO_3^{2-}, HT-Cl–NYS^{2-}, and HT-SO_4–CO_3^{2-} systems are shown in Figures 1 and 2. In the ion-exchange isotherms, S_F, for example, on the abscissa represents the equivalent fraction of a F^- ion based on the total anion concentration in an aqeous solution at equilibrium, and $(HT)_F$, for example, on the ordinate represents the equivalent fraction of the F^- ion exchanged onto HT.

The selectivity coefficients ($K_{NO_3}^A$) of HT with re-

Table 1. Chemical analyses and formulae for hydrotalcite-like compounds studied.

	HT-NO_3 (wt. %)	HT-Cl (wt. %)	HT-SO_4 (wt. %)
Al_2O_3	17.5	18.4	17.6
MgO	32.5	36.1	34.1
CO_2	1.05	0.77	0.77
NO_3	17.0		
Cl		12.3	
SO_4			15.7
x	0.299	0.287	0.290

HT-NO_3: $Mg_{0.702}Al_{0.298}(OH)_2(NO_3)_{0.268}(CO_3)_{0.618} \cdot mH_2O$.
HT-Cl: $Mg_{0.713}Al_{0.287}(OH)_2Cl_{0.275}(CO_3)_{0.014} \cdot mH_2O$.
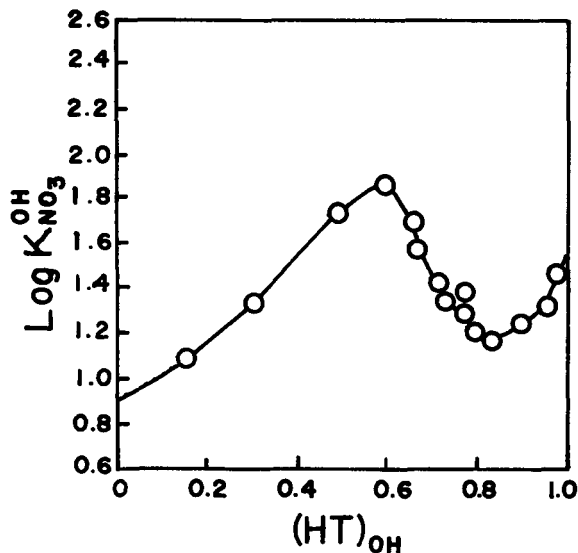HT-SO_4: $Mg_{0.710}Al_{0.290}(OH)_2(SO_4)_{0.137}(CO_3)_{0.015} \cdot mH_2O$.

Figure 3. Selectivity coefficient for the HT-NO_3–OH^- system as a function of HT composition.

Figure 4.   Selectivity coefficient for the HT-NO_3–F^- system as a function of HT composition.
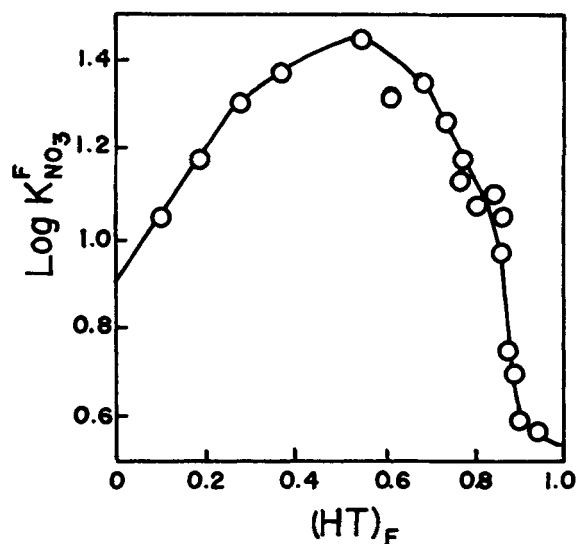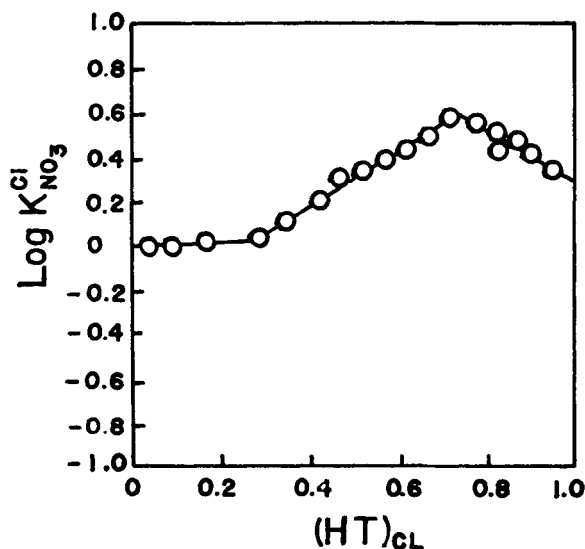

Figure 6.   Selectivity coefficient for the HT-NO_3–Br^- system as a function of HT composition.

spect to NO_3 were calculated from the ion-exchange isotherms in Figures 1 and 2 in accordance with the following equations.

When n = 1,

$$K_{NO_3}^A = (HT)_A S_{NO_3}/(HT)_{NO_3} S_A,$$

When n = 2,

$$K_{NO_3}^{A_{0.5}} = (HT)_A^{0.5} S_{NO_3}/(HT)_{NO_3} S_A^{0.5}.$$

According to Figures 1 and 2, ion-exchange isotherms of HT-NO_3–OH^-, HT-NO_3–F^-, HT-NO_3–SO_4^{2-}, HT-NO_3–CO_3^{2-}, HT-Cl–NYS^{2-}, and HT-SO_4–CO_3^{2-} sys-

tems are nearly of the Langmuir type. The ion-exchange isotherms of the HT-NO_3–I^- system are not of the Langmuir type.

Figures 3 to 9 show the logarithm of selectivity coefficients as a function of the mole fraction of anion A on the HT. The equilibrium constant (Ke) was calculated by using the method of Gaines and Thomas (1953) from the following equation

$$\log Ke = \int_{(HT)_A=0}^{(HT)_A=1} \log K_{NO_3}^A \ d(HT)_A,$$

in which $(HT)_A$ is the mole fraction of anion A on the HT. The integral in the above equation was graphically
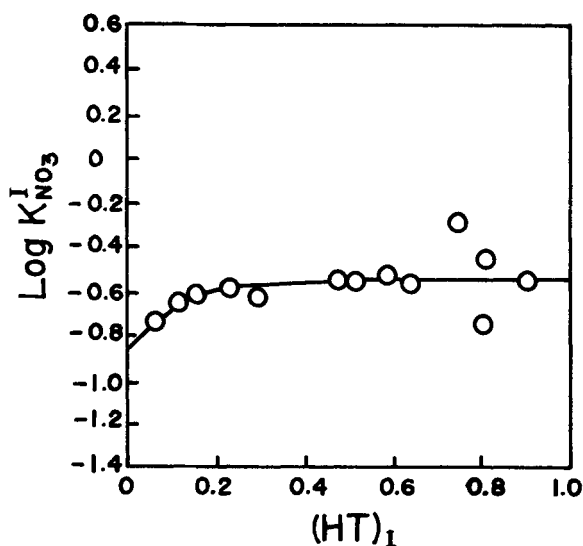

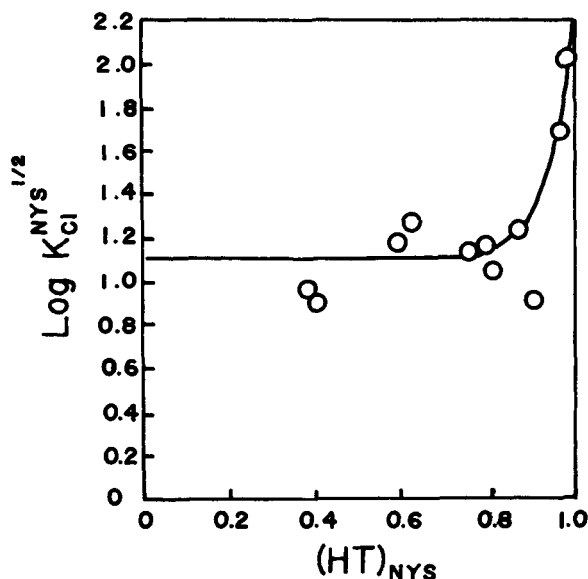Figure 5.   Selectivity coefficient for the HT-NO_3–Cl^- system as a function of HT composition.

Figure 7.   Selectivity coefficient for the HT-NO_3–I^- system as a function of HT composition.

Figure 8. Selectivity coefficient for the HT-Cl–NYS^{2-} system as a function of HT composition.

Figure 9. Selectivity coefficient for the HT-SO$_4$–CO$_3^{2-}$ system as a function of HT composition.

evaluated by calculating the area under the curve in Figures 3 to 9. The calculated Gaines and Thomas equilibrium constants are listed in Table 2.

These data show that the ion selectivities of monovalent anions are in the order of OH$^-$ > F$^-$ > Cl$^-$ > Br$^-$ > NO$_3^-$ > I$^-$, and that divalent anions have higher ion selectivities than monovalent anions. Of the monovalent anions tested, OH$^-$ and F$^-$ have particularly high ion selectivities, and CO$_3^{2-}$ is the most selective of the divalent anions. Figures 10 and 11 show the basal spacing, d(003), and the width of the 003 reflection, B(003), as a function of the mole fraction of anion A in the HT. The basal spacing decreases almost continuously below that of HT-NO$_3$ (d(003) = 8.79 Å). In the HT-Cl–NYS^{2-} system, however, two basal spacings corresponding to the HT-Cl and HT-NYS were observed at HT$_{NYS}$ mole fractions of 0.4 to 0.75. When the mole fraction of HT$_{NYS}$

is less than about 0.6, the diffraction intensity of the 003 reflection corresponding to HT-Cl is stronger than that corresponding to HT-Naphthol Yellow S, and conversely, the former is weaker than the latter when the mole fraction of HT$_{NYS}$ is more than about 0.7.

Thus, where no great difference in radius exists between two anions in question, the XRD patterns of the 003 reflection of the two HTs corresponding to the two anions overlap and are seen as one diffraction pattern; however, where the difference in radius between two anions is relatively large, as in the HT-NO$_3$–OH$^-$, HT-NO$_3$–F$^-$, HT-NO$_3$–CO$_3^{2-}$ systems, the XRD pattern of the 006 reflection is split into two. This split of the 006 reflection is 4.44 Å and 4.00 Å for the HT-NO$_3$–OH$^-$ system, 4.44 Å and 4.07 Å for the HT-NO$_3$–F$^-$ system, and 4.44 Å and 4.04 Å for the HT-NO$_3$–CO$_3^{2-}$ system. In each split, the former corresponds to HT-NO$_3$ and the latter corresponds to HT-OH, HT-F, HT-CO$_3$, respectively.

On the other hand, the width of the 003 reflections, B(003), which is nearly inversely proportional to the

Table 2. The Gaines-Thomas equilibrium constant for hydrotalcite-like compounds and the selectivity coefficient for Dowex[1] anion-exchange resins.

Anion (A^{n-})	log Ke	log K$_{NO_3}^{A_{1/n}^{n-1}}$			
		Dowex 1	Loading	Dowex 2	Loading
OH$^-$	1.42	−1.62	0.23	−0.70	0.6
F$^-$	1.19	−1.62	0.82	−1.40	0.30
Cl$^-$	0.263	−0.58	—	−0.52	—
Br$^-$	0.082	−0.13	0.60	−0.16	0.64
NO$_3^-$	0	0	0.62	0	—
I$^-$	−0.60	0.36	0.73	0.35	0.73
CO$_3^{2-}$	1.84	—	—	—	—
NYS^{2-}	1.46	—	—	—	—
SO$_4^{2-}$	1.39	—	—	−0.11	0.55

[1] Peterson (1954).

Table 3. Basal spacing d(003) and the width of the 003 reflection at (HT)$_A$ = 0.9–1.0.

Anions	Basal spacing (Å)	003 width (°2θ)
OH$^-$	7.55	0.64
F$^-$	7.66	0.88
Cl$^-$	7.86	0.77
Br$^-$	7.95	0.92
NO$_3^-$	8.79	1.13
I$^-$	8.16	1.45
CO$_3^{2-}$	7.65	0.69
NYS^{2-}	13.00	0.96
SO$_4^{2-}$	8.58	1.40

Figure 10. Basal spacing (○) and the width of the 003 reflection (◑) for the HT-NO$_3$–OH$^-$ system as a function of HT composition.
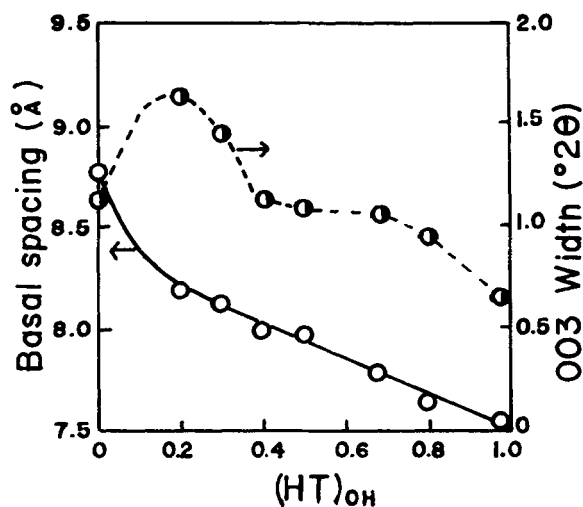

Figure 11. Basal spacing (○) and width of the 003 reflection (◑) for the HT-Cl–NYS^{2-} system as a function of HT composition.

crystallite size, increases when (HT)$_A$ is relatively small, and subsequently decreases progressively until finally it is smaller than that of the original material.

Table 3 summarizes the basal spacing and the widths of the 003 reflection for various HTs with (HT)$_A$ of 0.9 to 1.0. The relationship between the basal spacing and the equilibrium constant in an ion-exchange equilibrium of monovalent anions is plotted in Figure 12. Figure 12 demonstrates that except for HT-NO$_3$, the equilibrium constant of HT increases with decreasing basal spacing, and the rank of the basal spacing agrees with the rank of the ionic radii, i.e., F$^-$ (1.36 Å) < Cl$^-$ (1.81 Å) < Br$^-$ (1.95 Å) < I$^-$ (2.16 Å). These results also agree with the conclusion of Miyata (1975) in that the basal spacing is substantially determined by the sum of the thickness of the basic layer (which decreases with an increase in x but at a smaller rate than that of the interlayer) and the size of the anion in the interlayer. Therefore, a main factor that determines the selectivity of the anion-exchange of HT is the diameter of a bare, non-hydrated anion.

The equilibrium constant of HT is just opposite to that of the anion-exchange resins Dowex-1 and Dowex-2, also listed in Table 2 (Peterson, 1954); i.e., the ion selectivity of the latter depends upon the diamter of a *hydrated* anion.

The width of 003 reflection, B(003), also decreases with the ion selectivity. In other words, the crystallite size of HT increases with increasing ion selectivity (Tables 2 and 3). In view of the relationship shown in Figure 12, the basal spacing of HT-NO$_3$ is unexpectedly large. To find a cause of this, two different HT-NO$_3$ products in which x was 0.250 and 0.280 were prepared and the basal spacings determined to be 8.34 Å and 8.40 Å, respectively. If these data are considered in con-
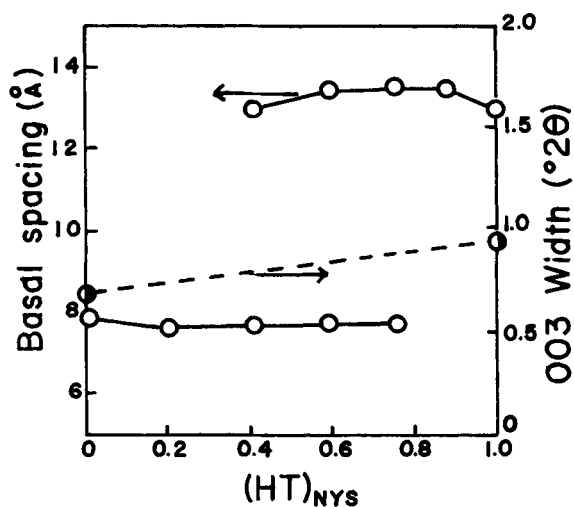
junction with the fact that the basal spacing was 8.79 Å at x = 0.304, the basal spacing of HT-NO$_3$ increases with an increase in x, at higher values of x. Thus, the relationship is inconsistent with the relationship generally observed for HT-CO$_3$, etc., i.e., that x is inversely proportional to the basal spacing. The reason why HT-NO$_3$ has an unexpectedly large basal spacing at higher values of x is presumably due to repulsion be-
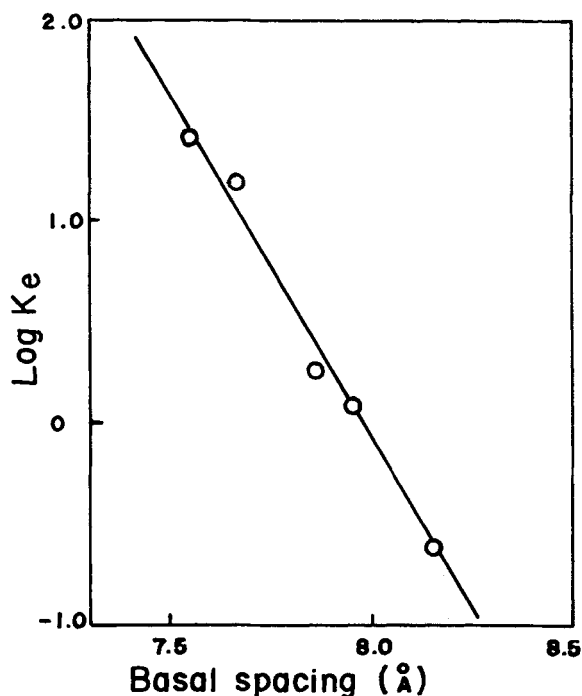

Figure 12. Relationship between the basal spacing and the equilibrium constant log Ke.

tween NO_3^- ions. Because NO_3^- is monovalent and occupies a space corresponding to three oxygens, the space occupied by NO_3^- in the interlayer is greater than that occupied by other anions such as Cl^- and Br^-. When x is small and the repulsion between NO_3^- ions is small, NO_3^- is oriented in the interlayer such that the bond direction of N–O, i.e., the plane formed by NO_3^-, is parallel to the basic layer. But as x increases, the repulsion between NO_3^- ions becomes stronger, such that the N–O bond direction of NO_3^- may be no longer parallel to the basic layer. This orientation change of NO_3^- in the interlayer leads to the increase of interlayer thickness. If the arrangement of NO_3^- ions in the interlayer does not change as a result of the repulsion between NO_3^- ions, the basal spacing at x = 0.304 will be close to 8.12 Å which is anticipated from the relation shown in Figure 12.

It is worth noting that HT-OH shows the smallest basal spacing and the largest crystallite size of the mono- and divalent anion forms studied (Table 3). This small spacing is presumed to be due to the fact that the ionic diameter of OH^- is nearly equal to that of H_2O in the interlayer, and hydrogen bonding is great among OH^-, interlayer water, and OH of basic layers. Accordingly, the crystal structure of HT-OH consists of three oxygen layers derived from two oxygen layers of the basic layer and one oxygen layer of the interlayer. This structure has the closest packing of atoms in the 001 direction.

Table 2 also shows that divalent anions generally have higher ion selectivity than monovalent anions. In particular, NYS^{2-} has high selectivity despite the fact that its ionic diameter is about 1½ times larger than SO_4^{2-}. This is due presumably to the difference in bonding strength to Mg or Al in the basic layer between NYS^{2-} and SO_4^{2-}.

CONCLUSIONS

Hydrotalcite-like compounds are some of the few inorganic anion exchangers that have relatively high capacities of about 3 meq/g. Anion-exchanger resins induce an ion-exchange reaction with a hydrated anion, whereas, HT-compounds induce ion-exchange reactions with bare, non-hydrated anions. Accordingly, the ion-exchange equilibrium constants for HTs are in the sequence $OH^- > F^- > Cl^- > Br^- > I^-$ for monovalent anions, and in the sequence $CO_3^{2-} > NYS^{2-} > SO_4^{2-}$ for divalent anions. By utilizing their characteristic ion selectivity, HTs are expected to find application in the removal of acid dyes, HPO_4^{2-}, CN^-, CrO_4^{2-}, AsO_4^{3-}, $(Fe(CN)_6)^{4-}$, etc. from waste waters, as well as in the neutralization and thermal stabilization of halogen-containing polymers.

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Резюме—Были определены ионо-обменные изотермы между гидротальките-подобными соединениями (ГТ) типа NO_3, Cl и SO_4 а ионами F^-, Cl^-, Br^-, I^-, OH^-, SO_4^{2-}, CO_3^{2-}, и желтого нафтола S ($ЖHS^{2-}$), а также были измерены промежуток и ширина 003 отражений как функции состава ГТ. Постоянные ионо-обменного равновесия для соединений ГТ моновалентных анионов были в следующем порядке: $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$, а для дивалентных анионов—в следующем порядке: $CO_3^{2-} > ЖHS^{2-} > SO_4^{2-}$. Постоянные ионо-обменного равновесия увеличивались при уменьшении диаметров анионов, а размер кристаллитов в 001 направлении увеличивался для анионов с высокой селективностью. ОН тип ГТ имел наименьший промежуток и наибольший размер кристаллитов в 001 направлении. [E.G.]

Resümee—Die Ionenaustauschisotherme zwischen Hydrotalkit-ähnlichen Verbindungen (HT) der NO_3^-, Cl-, und SO_4- Form und F^-, Cl^-, Br^-, I^-, OH^-, SO_4^{2-}, CO_3^{2-}, sowie Naphtolgelb S (NYS^{2-})-Ionen wurden bestimmt, und der Abstand und die Breite des 003 Reflexes wurde als Funktion der HT-Zusammensetzung gemessen. Die Ionenaustauschgleichgewichtskonstanten für die HTs mit einwertigen Anionen haben die Reihenfloge $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$; die mit zweiwertigen Anionen die Reihenfolge $CO_3^{2-} > NYS^{2-} > SO_4^{2-}$. Ihre Ionenaustauschgleichgewichtskonstanten haben die Tendenz mit abnehmendem Durchmesser des Anions zuzunehmen. Die Kristallitgröße in der 001 Richtung hat bei Anionen mit höherer Selektivität die Tendenz zuzunehmen. Die OH-Form von HT hat den kleinsten Basisabstand und die größte Kristallitgröße in der Richtung 001. [U.W.]

Résumé—Des isothermes d'échange d'ions entre des composés semblables à l'hydrotalcite (HT) de forme NO_3^-, Cl-, et SO_4-, et les ions F^-, Cl^-, Br^-, I^-, OH^-, SO_4^{2-}, CO_3^{2-}, et Naphthol Yellow S (NYS^{2-}) ont été déterminées, et l'espacement et la largeur de la réflection 003 ont été mesurés en fonction de la composition d'HT. La constante d'équilibre d'échange d'ions pour des HT d'anions monovalents sont dans la séquence $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$, ceux pour des anions divalents sont dans la séquence $CO_3^{2-} > NYS^{2-} > SO_4^{2-}$. Les constantes d'équilibre d'échange d'ions ont tendance à augmenter proportionnellement à une diminution de diamètre des anions, et la taille du cristallite dans la direction 001 a tendance à accroitre avec les anions ayant un plus grand selectionnement. La forme OH^- d'HT a l'espacement basal le plus petit et la taille de cristallite la plus grande dans la direction 001. [D.J.]