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Ionic Equilibria in Mixed Solvents. V. Intermediates of Polymerization of Aluminum Ion in a 0.2 Mole Fraction Dioxane-Water Mixture

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Formation of highly polymerized hydroxo-complexes of aluminum ions proceeded so slowly in a dioxane-water mixture that less polymerized intermediates were detected by means of the usual emf titration techniques. The titrations were performed at 25° in solutions of total aluminum concentrations of 0.00500, 0.0100, 0.0200, 0.0399, 0.0400 and 0.0798M in a 0.2 mol fraction (55.01 % w/w) dioxane-water mixture containing 3M $LiClO_4$ as an ionic medium. The emf data obtained can be explained in terms of the formation $Al_2(OH)_2^{4+}$ ($\log {}^*\beta_{2,2}=-6.95\pm0.07$) and $Al_2(OH)_3^{3+}$ ($\log {}^*\beta_{3,2}=-10.02\pm0.03$) assuming equilibrium conditions. It was observed that these complexes proceed further slowly to form highly polymerized complexes.

Several works have been made on the hydrolysis reaction of aluminum ion, and various conclusions have been reported on the formulae of the species formed. In dilute solutions a series of mononuclear complexes, $Al(OH)_n^{(3-n)+}$, may be formed. However, in more concentrated solutions formation of polynuclear complexes is certain. Treadwell and Zürcher[1] have found a dimerized species, $Al_2(OH)_5^+$, at room temperature. Formation of another dimer complex, $Al_2O(NO_3)_3^+$, and a highly polymerized complex, $(AlONO_3)_{\sim 8}$, has been reported by Jander and Jahr[2] by a diffusion method. Formation of a dimerized $Al_2(OH)_2^{4+}$ complex, which has recently been confirmed by some workers, was first suggested by Faucherre[3] in 1948 and he determined the formation constant of the species.[4] The same complex has been found by Jahr and Brechlin[5] at 0°C, Kenttämaa,[6] Kubota[7] and Aveston[8] at 25°C. In a crystalline state of a basic aluminum sulfate or selenate, a group of $Al_2(OH)_2(H_2O)_8^{4+}$ was found to construct a unit cell of the crystals.[9] For higher complexes several authors have described the formation of cationic trimers,[10,11] tetramers[5,6] and sometimes octamers.[12]

After X-ray analysis of another basic aluminum sulfate ($13Al_2O_3\cdot6SO_3\cdot xH_2O$)[13] and the corresponding selenate ($Na[Al_{13}O_4\cdot(OH)_{24}\cdot(H_2O)_{12}](SeO_4)_4\cdot xH_2O$)[14] had been carried out by Johansson, Sillén[15] reexamined his results[16] in order to explain the data[16] in terms of the formation of the $Al_{13}(OH)_{34}^{5+}$ complex together with the $Al_7(OH)_{17}^{4+}$ complex. From the results obtained by ultracentrifugal methods and by emf measurements, Aveston[8] concluded that the highly polymerized cationic species has the formula $Al_{13}(OH)_{32}^{7+}$.

As has been pointed by Brosset[17] and Aveston,[8] diverse formulae of species hitherto reported may mainly be due to a slow reaction rate of the hydrolysis reaction of aluminum ions. Different conclusions may also have resulted from different accuracies of measurements by different authors. For such a complicated system of the complex formation, accuracy of measurements substantially affects the ratio of OH/Al in the complexes.

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1) W. D. Treadwell and Zürcher, *Helv. Chim. Acta*, **15**, 980 (1932).

2) G. Jander and K. F. Jahr, *Kolloid-Beih.*, **43**, 296 (1936).

3) J. Faucherre, *Compt. Rend.*, **227**, 1367 (1948).

4) J. Faucherre, *Bull. Soc. Chim. France*, **1954**, 253.

5) K. F. Jahr and A. Brechlin, *Z. anorg. Chem.*, **270**, 257 (1952).

6) J. Kenttämaa, *Suomen Kem.*, **28B**, 172 (1955).

7) H. Kubota, Thesis, Univ. Wisconsin, 1956, University Microfilms 16182.

8) J. Aveston, *J. Chem. Soc.*, **1965**, 4438.

9) G. Johansson, *Acta Chem. Scand.*, **16**, 403 (1962).

10) L. K. Leptin and A. Ya. Vaidave, *Zhur. fiz. Khim.*, **27**, 217 (1953).

11) H. Tanabe, *J. Pharm. Soc. Jap.*, **74**, 866 (1954).

12) E. Matijevic, K. G. Mathai, R. H. Ottewill and M. Kerker, *J. Phys. Chem.*, **65**, 826 (1961).

13) G. Johansson, *Arkiv Kemi*, **20**, 321 (1963).

14) G. Johansson, *ibid.*, **20**, 305 (1963).

15) L. G. Sillén, "Hydrolytic Aqueous Species," Lecture, Houston, Texas, November 1962.

16) C. Brosset, G. Biedermann and L. G. Sillén, *Acta Chem. Scand.*, **8**, 1917 (1954).

17) C. Brosset, *ibid.*, **6**, 910 (1952).

Schwarzenbach and Wenger[18] also reported that the hydrolysis reaction of aluminum ion proceeds rather slowly. Yotsuyanagi and Aoyama[19] reported that it reaches equilibrium after two to three years in aqueous solutions.

Although Brosset[17] pointed out that equilibrium potentials might be obtained on standing a solution tens of hours after the addition of an alkaline solution, no intermediate could be detected during the course of the formation of highly polymerized complexes of aluminum ion in aqueous solutions. However, in the aqueous dioxane solution the rate of polymerization reactions was so slow that some intermediates could be found and the data obtained could be treated assuming equilibrium conditions.

The present study deals with the hydrolysis reactions of aluminum ion in a 0.2 mol fraction dioxane-water (55.01% w/w dioxane) mixture containing 3M $LiClO_4$ as an ionic medium.

The hydrolysis reaction of aluminum ion may be written as

$$q\mathrm{Al}^{3+} + p\mathrm{H_2O} = \mathrm{Al}_q(\mathrm{OH})_p{}^{(3q-p)+} + p\mathrm{H}^+ \qquad (1)$$

In Eq. (1) solvated dioxane and water molecules are omitted,[20] and $*\beta_{p,q}$ was calculated, which is defined by

$$*\beta_{p,q} = [\mathrm{Al}_q(\mathrm{OH})_p{}^{(3q-p)+}][\mathrm{H}^+]^p/[\mathrm{Al}^{3+}]^q = [\mathrm{Al}_q(\mathrm{OH})_p{}^{(3q-p)+}]h^p/b^q \qquad (2)$$

Here the brackets denote the concentration of the relevant species.

Symbols

h	Hydrogen ion concentration at equilibrium
H	Concentration of analytical excess of hydrogen ions$=[\mathrm{ClO_4}^-]-3B-[\mathrm{Li}^+]$
B	Total concentration of aluminum
b	Concentration of free aluminum ions
Z	Average number of hydrogen ion set free per aluminum atom$=(h-H)/B$
p	Number of OH groups bound to hydrolyzed species
q	Number of Al atoms present in hydrolyzed species
$*\beta_{p,q}$	Equilibrium constant of the formation of $\mathrm{Al}_q(\mathrm{OH})_p{}^{(3q-p)+}$
E	Emf

Experimental

Reagents. Aluminum perchlorate was prepared from aluminum chloride and perchloric acid as follows. Reagent grade aluminum chloride was recrystallized three times from aqueous solution by bubbling dry hydrogen chloride, The aluminum chloride crystals were dissolved in a small amount of water and then an excess of perchloric acid was added. Hydrochloric acid thus liberated was evaporated repeatedly under an infrared lamp. Aluminum perchlorate crystals prepared were recrystallized from water. Neither chloride nor iron(III) was detected.

The concentration of aluminum ion in the stock solution was determined as Al_2O_3 by igniting aluminum hydroxide at about 1100°C.

The concentration of free acid in the aluminum perchlorate solution was determined in a similar way to that employed in the preceding works;[21-24] that is, aliquot of a dilute solution of aluminum perchlorate, which contained a known amount of the stock solution, was titrated with a standard perchloric acid, and then, the amount of free acid present was estimated from a plot of $V_{\mathrm{tot}}.10^{E/59.15}$ *vs.* volume of the perchloric acid added (Gran plot[25]), where V_{tot} denotes the total volume of the solution in a titration vessel.

Lithium Perchlorate was prepared as described by Biedermann and Ciavatta.[26]

Dioxane was purified by the method described elsewhere.[21]

Apparatus. *Glass Electrodes and pH Meter.* Beckman Nos. 40498 and 41263 glass electrodes were used in combination with a Beckman 101900 Research pH Meter.

The Wilhelm-type Half-cell described by Forsling, Hietanen and Sillén[27] was used for emf measurements.

All emf measurements were performed at 25.00± 0.01°C in a paraffin oil thermostat in a room thermostated at 25±1°C. Air in a titration vessel was replaced by nitrogen gas free from carbon dioxide during the titration.

Methods of Investigation. The hydrolysis reactions were studied from the measurements of the hydrogen ion concentration of a series of aluminum perchlorate solutions at 25°C using a glass electrode. During the potentiometric titration B was kept constant. The values of B studied were 0.00500, 0.0100, 0.0200, 0.0399, 0.0400 and 0.0798M. All solutions were prepared with a 0.2 mol fraction dioxane-water mixture (55.01% w/w dioxane).

Emf Measurements. The general composition of a test solution may be described as: $B\,\mathrm{Al}^{3+}$, $H\,\mathrm{H}^+$, $(3-3B-H)\,\mathrm{Li}^+$, 3M $\mathrm{ClO_4}^-$, where H, the analytical excess of hydrogen ion, is either positive or negative depending on the degree of hydrolysis of aluminum ion. The original composition of the test solution, S_1, has a composition, $S_1=B\,\mathrm{Al(ClO_4)_3}$, $H_0\,\mathrm{HClO_4}$, $(3-3B-H_0)$ $\mathrm{LiClO_4}$. Values of H_0, the initial concentration of acid in the solution taken in a titration vessel, were controlled to fall in the range from 0.01 to 0.03M, where the acidity

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[18] G. Schwarzenbach and H. Wenger, Proceedings of the 11th International Conference on Coordination Chemistry, Haifa and Jerusalem, September, 1968.

[19] T. Yotsuyanagi and K. Aoyama, Annual Meetings of the Chemical Society of Japan, Osaka, April, 1968.

[20] J. F. Hinton, L. S. McDowell and E. S. Amis (*Chem. Commun.*, **1966**, 776) reported solvation of dioxane in aqueous dioxane solutions of $Al(ClO_4)_3$.

[21] H. Ohtaki, *Inorg. Chem.*, **6**, 808 (1967).

[22] H. Ohtaki and H. Kato, *ibid.*, **6**, 1935 (1967).

[23] H. Ohtaki, *ibid.*, **7**, 1205 (1968).

[24] C. Bercki-Biedermann, *Arkiv. Kem.*, **9**, 175 (1956).

[25] G. Gran, *Analyst*, **77**, 661 (1952).

[26] G. Biedermann and L. Ciavatta, *Acta Chem. Scand.*, **15**, 1347 (1961).

[27] W. Forsling, S. Hietanen and L. G. Sillén, *ibid.*, **6**, 901 (1952).

of the solution is sufficiently high to prevent any appreciable hydrolysis of aluminium ion.

Compositions of titransts were as follows: $T_1=A$ LiOH, $(3-A)$ LiClO$_4$: and $T_1'=2B$ Al(ClO$_4$)$_3$, X HClO$_4$, $(3-6B-X)$ LiClO$_4$. Equal volumes of T_1 and T_1' were added to S_1 in order to keep B constant during the course of titration. Concentration of the added hydroxide ion was calculated from the difference of A and X.

The concentration of hydrogen ion was measured by means of the cell

$$(-)\mathrm{GE}\,|\,\mathrm{solution}\,|\,\mathrm{Ref}(+) \qquad (3)$$

where GE denotes a glass electrode and Ref the reference half-cell,

3.00M LiClO$_4$ in 0.2 mol fraction aqueous dioxane	2.99M LiClO$_4$ and 0.01M AgClO$_4$ in aqueous solution	AgCl-Ag

The emf of the cell (3) at 25°C may be written as

$$E = E^\circ - 59.15 \log h - 59.15 \log f_\mathrm{H} - E_j(h,B) \qquad (4)$$

where E° is a constant and f_H represents the activity coefficient of hydrogen ion. As described in the previous works,[21–23] the standard state is defined so that f_H, as well as the activity coefficients of the other reacting species, tends toward unity as the composition of the solution approaches 3M LiClO$_4$ in 0.2 mol fraction of aqueous dioxane. During the course of titration Z varied from zero to 0.3 at the lowest B and to 0.08 at the highest. Nevertheless, we assume that the activity coefficients of the reacting species to be constant as long as B is maintained constant and the ionic medium in the solution is sufficiently high.

The liquid-junction potential at the junction, test solution | 3M LiClO$_4$ in 0.2 mol fraction of aqueous dioxane, is described as $E_j(h,B)$ in Eq. (4). At $B=0$ it was found in a cell of similar design that $E_j(h,0)=-8.3h$ mV.[21] In the present study $E_j(h,B)$ can be assumed to be equal to $E_j(h,0)$ without causing any appreciable error in the evaluation of the hydrogen ion concentration from emf measurements.

A glass electrode is calibrated against a perchloric acid through a Gran plot.[25] The value, $E^0-59.15\cdot\log f_\mathrm{H}$, in Eq. (4) thus obtained is assumed to be kept constant throughout titration.

At a sufficiently low pH range where no appreciable hydrolysis occurred, a stable potential was established within 5 to 10 min after addition of the titrants. However, in the range where the hydrolysis occurred, reactions seemed to progress rather slowly. At lower Z ($Z\lesssim 0.1$) and relatively low pH range, stable emf's were obtained only after two to three hours. When Z increased($Z>0.1$), the reaction seemed to be so accelerated that the stable potential was established more rapidly (within half an hour or less). Finally the solution was distinctly turbid and the potential was nearly unchanged in systems of lower B. When the solution was clear and the emf remained unchanged for at least an hour, we recorded the emf value as the final one. In fact the emf was still maintained constant within an accuracy of ±0.1 mV for at least 5 hr thereafter.

Titration in the reverse way was demonstrated as follows: A test solution was prepared by the addition of LiOH solution into an aluminum perchlorate solution until precipitates formed. The solution was left for two months in a thermostated room at 25°C with occasional shaking. The precipitates were separated by centrifugation and a portion of the supernatant was subjected to gravimetric determination of the concentration of aluminum ion in the test solution. Another portion of the supernatant was used for emf measurements, in which the solution was gradually acidified by adding a titrant, whose composition was $T_2=B$ Al(ClO$_4$)$_3$, X' HClO$_4$ (back titration). In the present case $B=0.02913$M and $X'=0.1032$M.

All processes of preparation of the test solution and of transfer of solutions were performed in a glove box which was filled with air free from carbon dioxide.

The maximum Z value found was 0.6 which was almost three times as large as that expected from the ordinary forward titrations. At lower Z less than 0.3, reactions between the hydrogen ions added and the hydrolyzed aluminum species present in the solution progressed very slowly and no stable potential was obtained even after more than 24 hr. However, in a strong acid solution having pH lower than 1.9, all the hydrolysis products were decomposed and a stable emf was obtained within 5—10 min.

Table 1. Survey of experimental data

$B=0.00500$M		$B=0.0100$M		$B=0.0200$M	
$-\log h$	Z	$-\log h$	Z	$-\log h$	Z
2.979	0.00320	3.134	0.01807	2.746	0.00100
3.092	0.00378	3.305	0.03957	2.881	0.00435
3.212	0.01292	3.381	0.05414	3.038	0.01333
3.342	0.02859	3.451	0.07036	3.172	0.02944
3.466	0.05362	3.513	0.09859	3.261	0.05087
3.567	0.08653	3.569	0.1271	3.329	0.07412
3.647	0.1238	3.609	0.1561	3.300	0.09783
3.702	0.1647	3.645	0.1846	3.432	0.1221
3.750	0.2063	3.679	0.2248	3.464	0.1458
3.784	0.2557	3.699	0.2642	3.501	0.1690
3.819	0.2912			3.520	0.1925
				3.544	0.2154
				3.571	0.2377

$B=0.0399$M		$B=0.0400$M		$B=0.0798$M	
$-\log h$	Z	$-\log h$	Z	$-\log h$	Z
2.649	0.00272	2.626	0.00368	2.531	0.00440
2.786	0.00594	2.739	0.00563	2.678	0.00820
2.925	0.01281	2.866	0.00929	2.833	0.01408
3.035	0.02389	2.947	0.01337	2.937	0.02342
3.102	0.03783	3.008	0.01950	3.016	0.03392
3.165	0.05208	3.087	0.02985	3.063	0.04483
3.217	0.06657	3.151	0.04585	3.101	0.05563
3.270	0.08611	3.209	0.06224		
3.300	0.1058	3.261	0.08298		
3.334	0.1251	3.303	0.1034		
3.359	0.1476	3.322	0.1281		
		3.361	0.1509		
		3.383	0.1732		
		3.407	0.2019		

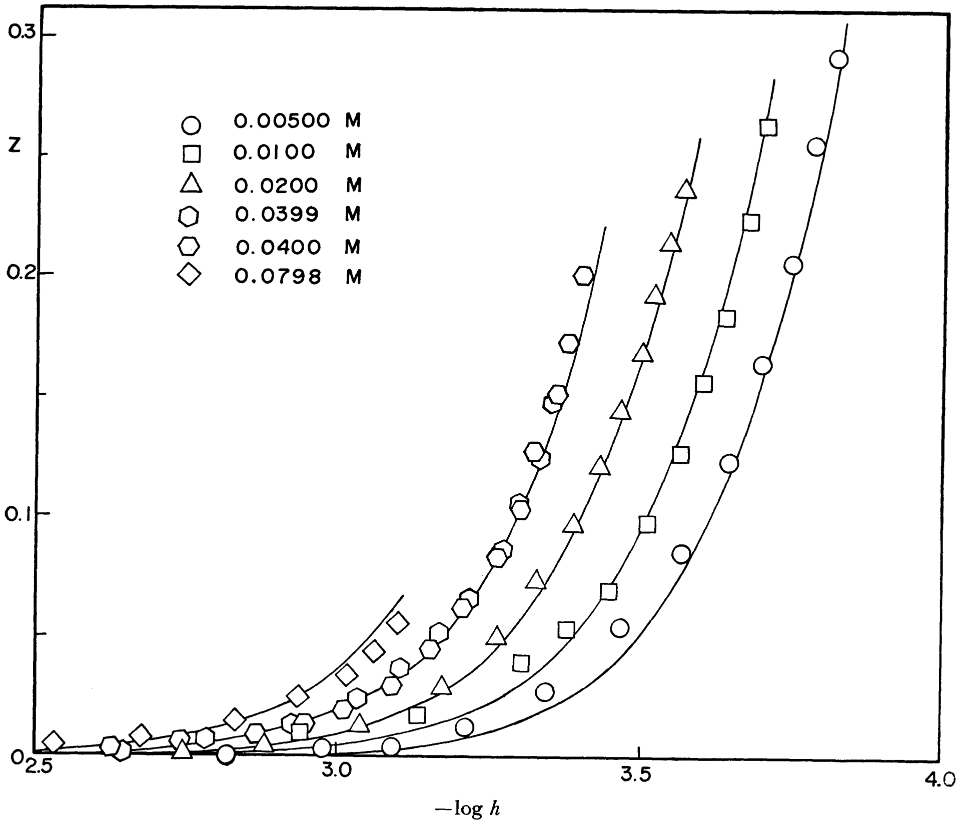

Fig. 1. Z as a function of $-\log h$. Curves were calculated with ${}^*\beta_{2,2}=1.16\times10^{-7}$ and ${}^*\beta_{3,2}=9.55\times10^{-11}$.

Results

Results obtained by means of forward titrations were treated with the assumption of the equilibrium condition. Values of $-\log h$ and Z at each series of B were calculated from the emf data obtained. They are shown in Table 1 and also represented graphically in Fig. 1.

The concentration of hydrogen ion set free by hydrolysis, BZ, is given by the general formula

$$BZ = \sum_p\sum_q p[\mathrm{Al}_q(\mathrm{OH})_p{}^{(3q-p)+}] = \sum_p\sum_q p{}^*\beta_{p,q}h^{-p}b^q \qquad (5)$$

and B is given as

$$\begin{aligned} B &= b + \sum_p\sum_q q[\mathrm{Al}_q(\mathrm{OH})_p{}^{(3q-p)+}] \\ &= b + \sum_p\sum_q q{}^*\beta_{p,q}h^{-p}b^q \qquad (6) \end{aligned}$$

Plots of $\log B$ against $-\log h$ gave a set of straight lines with a slope of 2.7—3.0, which approximately corresponds to t in the formula $[\mathrm{Al}(\mathrm{Al}(\mathrm{OH})_t)_n]$ according to the core-link treatment.[28]

As a preliminary consideration, simple assumptions were made as follows: only a complex, $\mathrm{Al}_Q(\mathrm{OH})_P{}^{(3Q-P)+}$, is mainly formed and an approximation of $B\approx b$ is applied. Thus,

$$Z \approx P{}^*\beta_{P,Q}h^{-P}B^{Q-1} \qquad (7)$$

or

$$\log Z \approx \log P{}^*\beta_{P,Q}B^{Q-1} - P\log h \qquad (8)$$

An examination was made for the assumption of the formation of $\mathrm{Al}_{13}(\mathrm{OH})_{32}{}^{7+}$ which has been proposed by Aveston.[8] In the formula of this complex t is described as $32/12=2.667$ which is fairly close to that found in the present case. The following relations can be derived:

$$BZ = 32{}^*\beta_{32,13}h^{-32}b^{13} \qquad (9)$$

$$B = b + 13{}^*\beta_{32,13}h^{-32}b^{13} \qquad (10)$$

Then,

$$Z = 32{}^*\beta_{32,13}\{B(1-0.406Z)^{13/12}\cdot h^{-32/12}\}^{12} \qquad (11)$$

All points obtained in this work fell on a straight line of $\log Z$ plotted against $\log B + 13/12 \log(1-13/32 \cdot Z) - 32/12 \log h$. However, the slope of the line was not 12 but only 1. From this observation the main complex was not $\mathrm{Al}_{13}(\mathrm{OH})_{32}{}^{7+}$ but the formation of dimerized species ($q=2$) might be expected.

When we plotted $\log Z$ against $-\log h$ a set of straight lines with a slope of 2.4—2.6 was obtained, which corresponds to the value of P in Eq. (8).

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[28] L. G. Sillén, *Acta. Chem. Scand.*, **8**, 299 (1954).

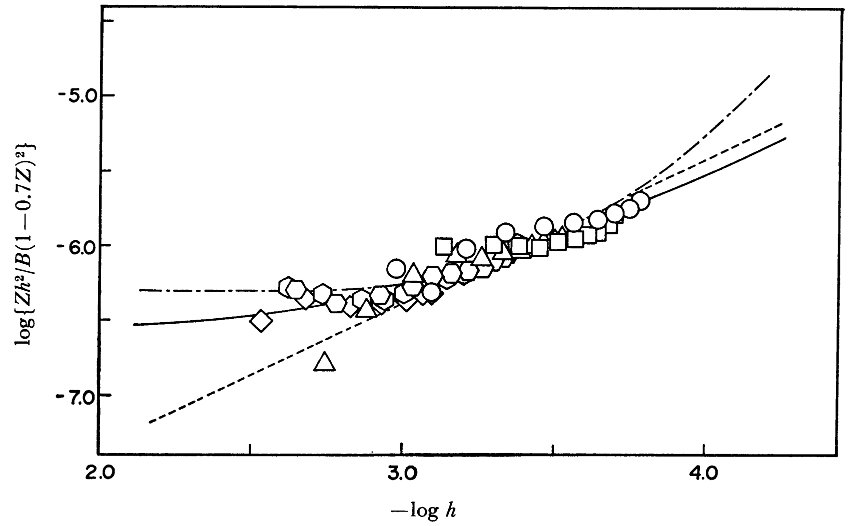

Fig. 2. log $(Zh^2/B(1-0.7Z)^2)$ as a function of $-\log h$.
———— , Assumption of the formation of both $Al_2(OH)_2^{4+}$ and $Al_2(OH)_3^{3+}$;
–·–·–·– , $Al_2(OH)_2^{4+}$ and $Al_2(OH)_4^{2+}$; ------ , $Al_2(OH)_3^{3+}$ only.
Symbols used are the same as those in Fig. 1.

Since P is given as nt in the $[Al(Al(OH)_t)_n]$ complex and t was found to be 2.7—3.0, the value of n should be unity and thus, the main species formed should contain two Al atoms.

The second step of the approximation was made for a nonstoichiometric complex such as $Al_2(OH)_{2.4}^{3.6+}$. A plot of Z against $\log B + 2 \log (1-0.833Z) - 2.4 \log h$ systematically deviated from a normalized curve, $y = x = f(\log x)$, which led to the conclusion that the average value of p ($\bar{p}$) of the complexes must be larger than 2.4. An examination with another assumption that $Al_2(OH)_3^{3+}$ is the unique complex formed led to the conclusion that $\bar{p}$ must be smaller than 3. Thus, the average value of p, *i.e.*, $\bar{p}$, must lie between 2.4 and 3.

It may be natural to assume the formation of two complexes both of which contain two aluminum atoms. An approach was tried for the formation of complexes of $Al_2(OH)_2^{4+}$ and $Al_2(OH)_3^{3+}$. The following approximation was made for calculation of b:

$$b = B(1-\alpha Z) \qquad (12)$$

For the value of α, we put $\alpha = 0.7$ which is a number between 0.667 (for $\bar{p}=3$) and 0.833 ($\bar{p}=2.4$). The variation of α was insensitive to the present calculations. Inserting Eq. (12) into Eqs. (5) and (6), the following equation was readily derived:

$$BZ = 2{}^*\beta_{2,2}B^2(1-0.7Z)^2h^{-2} + 3{}^*\beta_{3,2}B^2(1-0.7Z)^2h^{-3} \qquad (13)$$

TABLE 2. VARIOUS SETS OF COMPLEXES ASSUMED AND ERROR SQUARE SUMS OBTAINED WITH A GENERALIZED LEAST SQUARES METHOD

Complexes assumed (p,q)	U
1,1　2,2　3,2	3.019×10^{-3}
2,2　3,2	3.077×10^{-3}
2,2　3,2　4,2	5.430×10^{-3}
2,2　4,2	7.189×10^{-3}
2,2　5,2	1.391×10^{-2}
1,1　2,2　4,2	1.641×10^{-2}
2,2　6,4	5.709×10^{-2}
2,2　3,3	7.231×10^{-2}
2,2　15,6	1.125×10^{-1}
2,2　32,13	1.290×10^{-1}
2,2　17,7　34,13	8.790
17,7　34,13	15.58

TABLE 3. EQUILIBRIUM CONSTANTS OF THE HYDROLYSIS REACTION OF ALUMINUM ION†

Author	log $^*\beta_{1,1}$	log $^*\beta_{2,2}$	log $^*\beta_{3,2}$	log $^*\beta_{6,15}$	log $^*\beta_{7,17}$	log $^*\beta_{13,32}$	log $^*\beta_{13,34}$
Brosset[17)]				−47			
Kentämaa[6)]	−4.96	−7.55					
Kubota[7)]	−5.03	−6.27					
Sillén[15)]					−48.8		−97.6
Aveston[8)]		−7.07				−10.45	
Present Work		−6.95	−10.02				

† Except for the present work all the measurements were performed in aqueous solutions.

or

$$\frac{Zh^2}{B(1-0.7Z)^2} = 2{}^*\beta_{2,2} + 3{}^*\beta_{3,2}h^{-1} \qquad (14)$$

Plots of log $(Zh^2/B(1-0.7Z)^2)$ against log h^{-1} were compared with a normalized curve, $y=\log(1+x)$ plotted against log x. It is seen from Fig. 2 that all the points examined fall on a single curve which overlapped with the normalized curve. From the position of the best fit of curve we evaluated that log ${}^*\beta_{2,2}=-6.92$ and log ${}^*\beta_{3,2}=-10.02$. Another assumption that complexes formed were $Al_2(OH)_2^{4+}$ and $Al_2(OH)_4^{2+}$ gave a worse agreement. Evidently the assumption of the formation of $Al_2(OH)_3^{3+}$ complex only did not explain the experimental results.

Finally the data have been treated by a generalized least-squares method with the help of an electronic computer HITAC 5020E for various sets of complexes in order to find the best set of the complexes. Calculation of Z_{calc} ($Z_{\text{calc}}=\sum_p\sum_q p{}^*\beta_{p,q}\,h^{-p}b^q/B$ for a particular set of constants ${}^*\beta_{p,q}$) with a set of ${}^*\beta_{2,2}$ and ${}^*\beta_{3,2}$ resulted in a satisfactory agreement with the experimental data. The other sets of ${}^*\beta_{p,q}$ gave more or less worse agreement *i.e.*, larger error square sums, U ($U=\sum(Z-Z_{\text{calc}})^2$) were obtained. Highly polymerized complexes such as $Al_7(OH)_{17}^{4+}$, $Al_{13}(OH)_{32}^{7+}$ or $Al_{13}(OH)_{34}^{5+}$ were thus excluded. Formation of any monomeric complexes was not conclusive in the present work. Various sets of complexes assumed and square sums obtained are listed in Table 2. The final values of the constants obtained by the computer calculation are log${}^*\beta_{2,2}=-6.95\pm0.07$ and log${}^*\beta_{3,2}=-10.02\pm0.03$. They are listed in Table 3 together with values reported by some workers in aqueous solutions.

Discussion

Although we could not estimate the composition of complexes formed after two months of aging, the following conclusions may be drawn from the results obtained by back titration: precipitates of aluminum hydroxide once formed dissolve slowly and, as a result, the value of the maximum Z increases to nearly threefold of that expected from the ordinary forward titration at the same B, and binuclear $Al_2(OH)_2^{4+}$ and $Al_2(OH)_3^{3+}$ complexes may coagulate, releasing some protons to form higher polynuclear complexes which result in the increase of the hydrogen ion concentration at equilibrium. Thus, the hydrolysis reactions of aluminum ion may be schematically described as follows:

$$2Al^{3+} + \begin{Bmatrix} 2H_2O \\ 3H_2O \end{Bmatrix} \overset{{}^*\beta_{p,q}}{\rightleftarrows} \begin{Bmatrix} Al_2(OH)_2^{4+} + 2H^+ \\ Al_2(OH)_3^{3+} + 3H^+ \end{Bmatrix}$$

$$\xrightarrow[k]{\text{slow}} \text{High polymers}$$

The rate constant k is so small that the formation

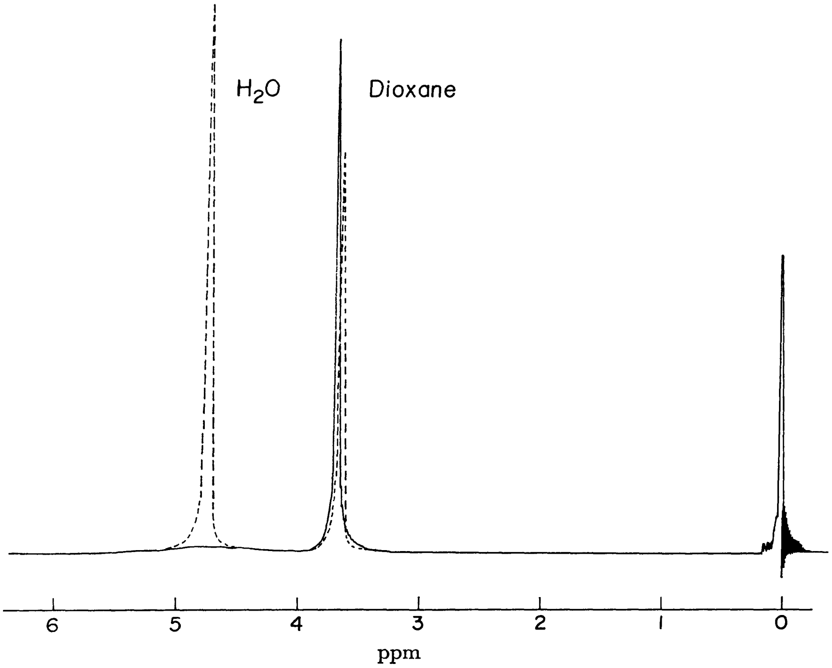

Fig. 3. Proton NMR spectra of water and dioxane in pure water (-----), pure dioxane (-----) and in 80% w/w dioxane-water mixture containing 0.35M $Al(ClO_4)_3$ (————).

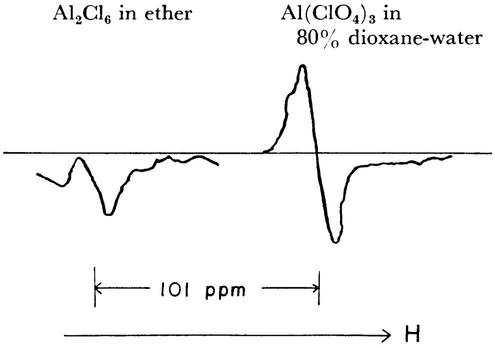

Fig. 4. NMR spectra of ^{27}Al of Al_2Cl_6 in ether and of $Al(ClO_4)_3$ in 80% w/w dioxane-water mixture.

reaction of higher polymers does not noticeably proceed during measurements. Thus, the formation constant obtained in the present work, $*\beta_{p,q}$ are for the intermediates on the way to higher polymers.

The solvent effect on the formation constants of hydrolysis reactions of aluminum ion may be seen from a comparison of $\log *\beta_{2,2}$ found in various media. In aqueous solutions at zero ionic strength the value of $\log *\beta_{2,2}$ spread from -7.55[6] to -6.27[7] at 25°C. In 1 M sodium perchlorate solution $\log *\beta_{2,2}$ is evaluated to be -7.07,[8] which differs only slightly from that in 0.2 mol fraction (55.01% w/w) dioxane-water mixture.

NMR spectra of protons and aluminum ions (^{27}Al) in an acid aqueous dioxane (80% w/w dioxane) solution were measured and are shown in Fig. 3 and 4, respectively. In Fig. 3 a peak caused by protons in water becomes broad but no apparent shift in position compared with the peak in pure water (dotted line) was observed. On the other hand, a peak caused by hydrogen atoms in dioxane molecules remained almost unchanged both in shape and in position. Thus, it may be concluded that even in the aqueous dioxane solution with fairly high dioxane concentration, aluminum ions are surrounded only by water molecules.

The NMR spectra of ^{27}Al (Fig. 4) showed that a peak caused by the aluminum ion in the aqueous dioxane solution is located at about 101 ppm higher side of the magnetic field compared with that in Al_2Cl_6 in ether. We concluded that, at least in acid aqueous dioxane solution, aluminum ion has an octahedral configuration which is so in aqueous solutions. If we assume that the aluminum ions still keep the octahedral configuration even in hydrolyzed complexes, the structure of the $Al_2(OH)_2^{4+}$ complex may be similar to that depicted in Fig. 5, which has been determined by X-ray analysis of a basic aluminum sulfate crystal.[9] The $Al_2(OH)_3^{3+}$ complex may be formed by releasing another proton from one water molecule which occupies an apex of an octahedron of aluminum atom.

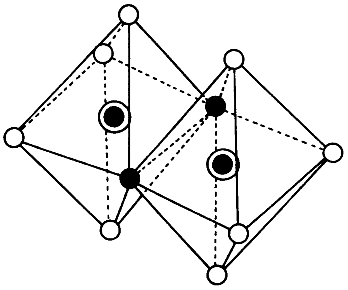

Fig. 5. A model proposed for the $Al_2(OH)_2^{4+}$ complex.

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