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Abstract

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ON THE COMPOSITION OF HYDROLYSIS PRODUCTS IN ALUMINUM CHLORIDE SOLUTIONS

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Hydrolysis of aluminum chloride is treated in the literature as a typical case of stepwise hydrolysis of a salt containing a polyvalent cation

$$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+ \tag{1}$$

and then

$$AlOH^{2+} + H_2O \rightleftharpoons Al(OH)_2^+ + H^+. \tag{2}$$

This interpretation has become classical and is cited in numerous manuals as an obvious example of stepwise hydrolysis ([1,2]). A large number of basic aluminum chlorides have been described. In the course of studying these compounds, the idea was developed according to which the system $AlCl_3$—$Al(OH)_3$ is a continuous series of basic chlorides bounded by these compounds

$$AlCl_3 \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} AlOHCl_2 \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} Al(OH)_2Cl \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} Al_2(OH)_5Cl \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} Al_n(OH)_{(3n-1)}Cl \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} Al(OH)_3. \tag{3}$$

However, analysis of the extensive literature that has accumulated on this question forces one to doubt the truth of the interpretation set forth above. This material contains a number of experimental data indicating the existence, in the pH range 2–6, not of a series of compounds

$$AlCl_3 \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} AlOHCl_2 \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} Al(OH)_2Cl \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} Al_2(OH)_5Cl, \tag{4}$$

but only of the two end members: $AlCl_3$ and $Al_2(OH)_5Cl$. In accordance with this, hydrolysis of aluminum chloride may be described by the reaction

$$2Al^{3+} + 5H_2O \rightleftharpoons Al_2(OH)_5^+ + 5H^+, \tag{5}$$

and the basic chlorides of lower basicity are mixtures

$$5AlOHCl_2 = 3AlCl_3 + Al_2(OH)_5Cl; \quad (6)$$

$$5Al(OH)_2Cl = AlCl_3 + 2Al_2(OH)_5Cl. \quad (7)$$

Below, data will be considered that make it possible to put forward a hypothesis on the hydrolysis of aluminum chloride according to reaction (5).

1. The existence of a basic salt in solution is unambiguously proved by the presence of an inflection (potential jump) on the curve of potentiometric titration of the salt solution with alkali. On the curves of potentiometric titration of aluminum chloride solutions in the pH range 2–6 there is only one such jump, corresponding to the ratio OH : Al = 2.5, i.e. to 5/6-basic chloride $Al_2(OH)_5Cl$ (^{3,4}).
2. The curves of back titration of hydrolyzed solutions with hydrochloric acid have an analogous character. For solutions with a ratio

At OH : Al > 2.5, a bend in the curve is clearly observed at the point OH : Al = 2.5; in solutions alkalized to OH : Al < 2.5, the back-titration curve shows no jumps in potential (^{3}).

3. In the study of solutions with the same Al concentration it was found that their specific electrical conductivity, with increasing basicity, decreases linearly from $AlCl_3$ to $Al_2(OH)_5Cl$. The optical properties of the solutions also change just as smoothly with increasing degree of basicity (^{5}).
4. In studying solutions alkalized to OH : Al < 2.5, a number of properties were revealed that are not explicable from the standpoint of classical concepts of the hydrolysis of aluminum chloride.

Thus, in solutions of composition $Al(OH)_2Cl$ the presence of the cation $Al_2(OH)_5^+$ is clearly detected (both from the bend in the curve of potentiometric titration with alkali solution (^{3}), and upon titration with salts containing a polyvalent anion, for example $C_2O_4^{2-}$, SO_4^{2-}). It is known that upon titration of aluminum sulfate with alkali, sparingly soluble basic salts of the most varied basicity are formed (^{6}). Therefore one might expect that when sulfate ion is added to a solution of $Al(OH)_2Cl$ (for example, a solution of Na_2SO_4), a precipitate $[Al(OH)_2]_2SO_4$–2/3-basic sulfate–would form. In reality, however, a precipitate of composition $[Al_2(OH)_5]_2SO_4$–5/6-basic aluminum sulfate –always separates (^{4,7}). Similar results are observed upon titration, with salts containing polyvalent anions, of solutions of basic aluminum chlorides whose composition ranges over OH : Al = 1.5-2.5. Experimental proof of the hypothesis that compounds intermediate in composition between $AlCl_3$ and $Al_2(OH)_5Cl$ are absent from the hydrolysis products of aluminum chloride is associated with a number of difficulties. Separation of the components in aqueous solution is practically impossible, since they are in equilibrium with one another and, when one of them is removed from the system, the hydrolytic equilibrium shifts toward its formation.

However, this question can also be considered from another side. If intermediate compounds exist and hydrolysis in the pH range 2–6 proceeds by a stepwise mechanism, then, irrespective of differences in the magnitudes of the hydrolysis constants of these compounds, partially alkalized solutions can contain only products of a definite degree of basicity. Thus, in a solution with $OH : Al > 1$, 1/3-basic chloride $AlOHCl_2$ and more basic compounds (products of its hydrolysis) may be present; the possibility of the existence of $AlCl_3$ in such solutions is excluded. If it turns out that preparations of basic chloride with $OH : Al > 1$ contain $AlCl_3$, the classical theory of stepwise hydrolysis as applied to this system loses its meaning.

To test this proposition, samples with the ratio $OH : Al = 0$–2.5 were prepared. The samples were prepared by dissolving very pure metallic aluminum in titrated hydrochloric acid according to the method described by Denck (^{7}). Dissolution was intensified by adding a catalyst (a drop of mercury). The solutions obtained were evaporated and dried first in air at room temperature, and then in a vacuum desiccator successively over sulfuric acid and P_2O_5. All samples obtained were examined by X-ray phase analysis.* Using Cu radiation from a BSV tube, X-ray powder patterns were taken for preparations having the following gross composition: $Al(OH)_{1.06}Cl_{1.94}$; $Al(OH)_{1.53}Cl_{1.47}$; $Al(OH)_{2.03}Cl_{0.97}$, as well as $AlCl_3 \cdot 6H_2O$ and $Al_2(OH)_5Cl \cdot 3.8H_2O$.

As can be seen from the line diagram obtained from the calculated interplanar spacings (Fig. 1), on the X-ray powder patterns of preparations having an intermediate composition between $AlCl_3 \cdot 6H_2O$ and $Al_2(OH)_5Cl \cdot 3.8H_2O$, composition, lines are found that belong only to hexahydrate aluminum chloride. In the photograph of a preparation having the composition $Al(OH)_{2.03}Cl_{0.97}$, owing to strong background it was possible to identify only nine lines; all of them coincide with the corresponding lines of $AlCl_3 \cdot 6H_2O$. This apparently agrees with the data of Kohlschütter (^{4}), who found only weak $AlCl_3 \cdot 6H_2O$ lines in photographs of samples of composition $Al(OH)_2Cl$. 5/6-basic aluminum chloride is X-ray amorphous.

Thus, X-ray phase analysis has shown the presence in preparations with basicity $OH : Al = 0$–2 of appreciable amounts of aluminum chloride. This quite clearly indicates the untenability of the classical interpretation of the hydrolysis process of aluminum chloride in the pH range 2–6 by a stepwise mechanism. It is just as obvious that these results do not yet prove the truth of the proposed hypothesis concerning the formation, upon hydrolysis of $AlCl_3$ under the

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* The X-ray examination of the samples was carried out at the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR by Yu. N. Mikhailov, to whom the authors express their sincere gratitude.

Fig. 1. Line diagram calculated from X-ray powder patterns of aluminum chloride and hydrolyzed products. *I*—$AlCl_3 \cdot 6H_2O$; *II*—$Al(OH)_{1.06}Cl_{1.34}$; *III*—$Al(OH)_{1.53}Cl_{1.47}$; *IV*—$Al(OH)_{2.30}Cl_{0.97}$.

Figure 1: Fig. 1. Line diagram calculated from X-ray powder patterns of aluminum chloride and hydrolyzed products. *I*—$AlCl_3 \cdot 6H_2O$; *II*—$Al(OH)_{1.06}Cl_{1.34}$; *III*—$Al(OH)_{1.53}Cl_{1.47}$; *IV*—$Al(OH)_{2.30}Cl_{0.97}$.

indicated conditions, of only the 5/6-basic chloride $Al_2(OH)_5Cl$. To test this hypothesis, a method was used for separating the components in a nonaqueous medium, where displacement of the hydrolytic equilibrium upon removal of one of the substances should not occur.

Fig. 1. Line diagram calculated from X-ray powder patterns of aluminum chloride and hydrolyzed products.
I—$AlCl_3 \cdot 6H_2O$; *II*—$Al(OH)_{1.06}Cl_{1.34}$;
III—$Al(OH)_{1.53}Cl_{1.47}$; *IV*—$Al(OH)_{2.30}Cl_{0.97}$.

Absolute ethyl alcohol was chosen as the solvent; $AlCl_3 \cdot 6H_2O$ is readily soluble in it, whereas $Al_2(OH)_5Cl \cdot 3.8H_2O$ is practically insoluble. Preliminary experiments showed that substances intermediate in composition between $AlCl_3$ and $Al_2(OH)_5Cl$ dissolve incompletely in absolute ethanol. A weighed portion of the substance was shaken for 10 min with 30 ml of alcohol; the suspension was then filtered through a glass porous filter No. 4, the precipitate was washed with alcohol on the filter, the alcoholic fraction was collected, and the precipitate on the filter was treated with distilled water. The aqueous and alcoholic fractions were then analyzed (by the gravimetric method) for chlorine and aluminum.

Table 1

Separation in absolute ethanol

No.	Initial preparation: Cl content, g	Initial preparation: Cl content, g-at.$\cdot 10^{-3}$	Initial preparation: Al content, g	Initial preparation: Al content, g-at.$\cdot 10^{-3}$	Initial preparation: Cl(g-at.)/Al(g-at.)	Ethanol fraction: Cl content, g	Ethanol fraction: Cl content, g-at.$\cdot 10^{-3}$	Ethanol fraction: Al content, g	Ethanol fraction: Al content, g-at.$\cdot 10^{-3}$	Ethanol fraction: Cl(g-at.)/Al(g-at.)	Aqueous fraction: Cl content, g	Aqueous fraction: Cl content, g-at.$\cdot 10^{-3}$	Aqueous fraction: Al content, g	Aqueous fraction: Al content, g-at.$\cdot 10^{-3}$	Aqueous fraction: Cl(g-at.)/Al(g-at.)
1	0.5012	15.15	0.1362	5.04	3.0	0.5012	15.15	0.1362	5.04	3.0	–	–	–	–	–
2	0.4601	12.95	0.1776	6.58	1.94	0.4341	12.22	0.1425	5.28	2.31	0.0280	0.79	0.0351	1.32	0.60
3	0.2878	8.10	0.2258	8.36	0.97	0.2290	6.46	0.1595	5.90	1.10	0.0521	1.46	0.0667	2.47	0.59
4	1.3260	37.40	1.0411	38.52	0.97	0.7432	20.95	0.2122	7.81	2.68	0.5764	16.26	0.8273	30.64	0.53
5	0.0701	1.97	0.1060	3.92	0.5	–	–	–	–	–	0.0701	1.97	0.1060	3.92	0.5

The results of the experiments are given in Table 1, from which it is seen that in all cases a fairly clear separation is observed: in comparison with the initial preparation, the Cl : Al ratio increases in the alcoholic fraction and decreases in the aqueous fraction. At the same time, if the Cl : Al ratio in the aqueous fraction is close to 0.5 (i.e., the fraction consists of $Al_2(OH)_5Cl$), then obtaining a Cl : Al = 3 ratio in the alcoholic fraction is associated with a number of difficulties. The reason for this is contamination of the alcoholic fraction with the 5/6-basic chloride,

both as a result of breakthrough of part of the precipitate through the filter during separation and as a result of moistening of the absolute alcohol by water absorbed from the air and extracted from the oxychloride preparation. Elimination of the influence of these factors in experiment No. 4 (see Table 1) made it possible sharply to increase the Cl : Al ratio in the alcoholic fraction (from 1.1 in experiment No. 3 to 2.68 in experiment No. 4).

The experiments carried out showed that substances intermediate in composition between $AlCl_3$ and $Al_2(OH)_5Cl$ are not individual compounds, but mechanical mixtures of aluminum chloride and 5/6 basic aluminum chloride. In absolute alcohol these mixtures are separated into fractions consisting of the individual compounds that formed the mixture.

Thus, in the hydrolysis of aluminum chloride in the pH range 2-6, not all theoretically possible basic salts are formed, but only 5/6 basic aluminum chloride, $Al_2(OH)_5Cl$ (5). The proposed scheme for the hydrolysis of aluminum chloride through 5/6 basic chloride (5) makes it possible to explain a number of the phenomena mentioned above, the interpretation of which is impossible from the standpoint of classical concepts.

It is obvious that if a solution with basicity $OH : Al < 2.5$ is a mixture of $AlCl_3$ and $Al_2(OH)_5Cl$, then the cation $Al_2(OH)_5{}^+$ must be detected in this solution (for example, from the inflection of the potentiometric titration curve). It is also obvious that upon addition of polyvalent anions (for example, $SO_4{}^{2-}$) to a hydrolyzed solution of aluminum chloride, a precipitate of precisely 5/6 basic aluminum sulfate should be formed. In an earlier published work (^{8}) the ability of 5/6 basic aluminum chloride to form products of polymeric structure was shown. In this connection it seems possible to regard the so-called "higher" basic chlorides as polymeric varieties of 5/6 basic chloride, $Al_2(OH)_5Cl$.

Thus, there are grounds for asserting that in the hydrolysis of aluminum chloride only one intermediate soluble compound is formed—5/6 basic chloride, $Al_2(OH)_5Cl$. The equilibrium of the hydrolysis reactions in this system is expressed by the scheme:

$$2\left(AlCl_3 \underset{5H^+}{\overset{5OH^-}{\rightleftarrows}} Al_2(OH)_5Cl \underset{H^+}{\overset{OH^-}{\rightleftarrows}} 2Al(OH)_3\right). \tag{8}$$

In conclusion, we note that the regularity revealed (the absence of a series of theoretically possible stages of hydrolysis in the series $AlCl_3$–$Al(OH)_3$) apparently is not a property inherent only in this system. Apart from the obviousness of the hydrolysis of certain soluble aluminum salts (for example, $Al(NO_3)_3$) ([9],[3]) by the same mechanism, one should expect the manifestation of an analogous regularity in a number of polyvalent cations (in particular, Ce^{3+} and the rare-earth metals) ([10]).

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