Journal of Fluorine Chemistry, 10 (1977) 63 – 73

Received: January 31, 1977

THE REACTION OF AlF_3 SOLUTION WITH ALUMINIUM HYDROXIDE AND SOME REACTIONS OF THE ALUMINIUM HYDROXYFLUORIDE OBTAINED

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SUMMARY

AlF_3 solution (150 g/l) reacts with $Al(OH)_3$ in the m.ratio 2:1 in excess of ca. 115°C to produce $Al(OH,F)_3.H_2O$ with an F/Al at. ratio > 2. At lower temperatures, e.g. 110°C, or at higher reactants ratios, e.g. 3-11, formation of $Al(OH,F)_3.H_2O$ may be accompanied by crystallization of AlF_3-hydrates as $AlF_3.3H_2O$ and/or β-$AlF_3.H_2O$. When crystallization of β-$AlF_3.H_2O$ occurs to a greater extent, $Al(OH,F)_3.H_2O$ may vary in its F/Al at.ratio from ca. 2.5 to 1, during the reaction.

$Al(OH)F_2.H_2O$ reacts readily with NaOH, NaF and NH_4F solutions to give sodium and ammonium cryolite. Reactions with $NaHF_2$ and H_2SiF_6 were unsuccessful, while with AlF_3 solution an increase of the F/Al ratio in the Al basic fluoride used resulted.

INTRODUCTION

As was reported earlier [1], crystallization of AlF_3 at temperatures above ca. 115°C results in precipitation of β-$AlF_3.H_2O$ along with some Al basic fluoride, due to hydrolysis. The amounts are greater the lower the initial concentration of the solute. Because of the very low solubility of the latter there is an interest in the recovery AlF_3 from its supersaturated solutions in the form of an $Al(OH,F)_3$ phase. In this connection a study was made of the reaction between AlF_3 solution (150 g/l) and $Al(OH)_3$ at elevated temperatures under autoclave conditions.

In addition, a preliminary study on the reactivity of the $Al(OH,F)_3.H_2O$ phase was performed. The chemistry of this compound is, as yet, almost unknown except that it can be utilized in producing HF and $(NH_4)_3AlF_6$ [2, 3]. So far, the reaction of AlF_3 solution with $Al(OH)_3$ has not been the object of any report. Recently it was proposed for the recovery of Al and F values from diluted solutions [4].

EXPERIMENTAL

Materials used in experiments concerning the title reaction were:

- AlF_3 solution (150 g/l, pH 3.5), freshly prepared in the reaction of H_2SiF_6 (1 M) with stoichiometric amounts of $Al(OH)_3$,
- aluminium hydroxide, dry, commercial grade.

Experiments were made with AlF_3 : $Al(OH)_3$ (F/Al) molar (atomic) ratios: 11.0 (2.75), 5.0 (2.50), 3.0 (2.25) and 2.0 (2.0) at temperatures and pressures (^oC/at.): 112/1.2, 122/2, 132/3 and 143/5. The apparatus (laboratory autoclave) and technique of the measurements employed were as described earlier [1, 5]. Chemical analysis involved the determination of Al by the EDTA method and of F by the alizarine method. For the qualitative X-ray analysis of the solid phases standard patterns of particular compounds were used. Studies were made by the X-ray method on $Al(OH)_3$, β-$AlF_3.H_2O$ and $Al(OH,F)_3.H_2O$ in their mixtures. For this purpose calibration curves were utilized for the systems: $Al(OH)_3$-$Al(OH,F)_3.H_2O$ (Fig. 1) and $Al(OH,F)_3.H_2O$ - β-$AlF_3.H_2O$ [5].

Atomic ratio F/Al = x in the $Al(OH,F)_3.H_2O$ - phase obtained in the reaction under study was calculated from the balance equation:

$$x = \frac{100\,u - a \cdot v}{b} \qquad (1)$$

where:

a, b = contributions of β-$AlF_3.H_2O$ and/or $AlF_3.3H_2O$ and $Al(OH,F)_3.H_2O$ in admixture (mole %),

u, v = F/Al atomic ratios in solids admixture and in AlF_3 hydrates, respectively.

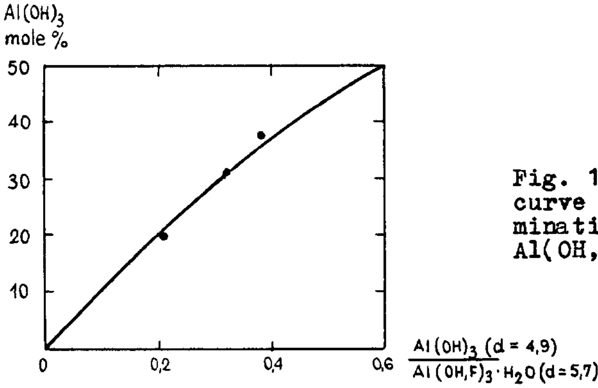

Fig. 1. The calibration curve for $Al(OH)_3$ determination in admixture with $Al(OH,F)_3.H_2O$.

Values of u were determined analytically or calculated from the consumption of AlF_3 (difference between initial and final concentration) and the quantity of $Al(OH)_3$ used in the reaction. For v a value of 2.93 was taken as exhibited by the β -$AlF_3.H_2O$ phase when crystallized out of solution [1].

In studying the chemistry of the $Al(OH,F)_3.H_2O$ obtained, solutions of NaOH (28 g/l, 0.7 M), NaF (36 g/l, 0.86 M), NH_4F (37 g/l, 1 M), AlF_3 (21 g/l, 0.25 M), $NaHF_2$ (62 g/l, 1 M) and H_2SiF_6 (46 g/l, 0.32 M) were used. Reactions were carried out in defined molar ratios of substrates at temperatures ranging from ca. 50 to 150°C and followed by a typical procedure comprising the chemical determinations in the solution concerned and a study of the phase composition of resulting solids by the X-ray method.

RESULTS AND DISCUSSION

Reaction of AlF_3 solution (150 g/l) with $Al(OH)_3$

The experimental data, involving a variety of reaction conditions and phase compositions of the solids obtained, are listed in Table 1. Figure 2 shows curves for the AlF_3 concentration drop during reactions proceeding at different temperatures and molar ratios of the substrates.

The results presented show that when the temperature is as low as 112°C (run 4) or the $AlF_3:Al(OH)_3$ molar ratio is higher than 2, the process gives rise to the formation of both Al

TABLE 1. The effect of reactants ratio (AlF_3 soln. (150 g/l) to $Al(OH)_3$) and temperature on phase composition of the products obtained

Run	Reactant ratio AlF_3/$Al(OH)_3$	Reaction temp./press. °C/at.	Phase compn., m.% I a	II b	III	Atomic ratio F/Al in I+II u	I v	II x
1	2	3	4	5	6	7	8	9
1	11.0	143/5	70	30	0	2.74		2.3
2	5.0	132/3	78	18	4	2.43		0.8
3	3.0	132/3	40	53	7	2.22		2.0
4	2.0	112/1.2	42[c]	35	23	1.96	2.93	2.1
5	2.0	122/2	0	87	13	2.00		2.3
6	2.0	132/3	0	93	7	2.00		2.1
7	2.0	143/5	0	96	4	1.98		2.1

I - β-$AlF_3.H_2O$, II - $Al(OH,F)_3.H_2O$, III - $Al(OH)_3$

c 26% $AlF_3.3H_2O$ + 16% β-$AlF_3.H_2O$

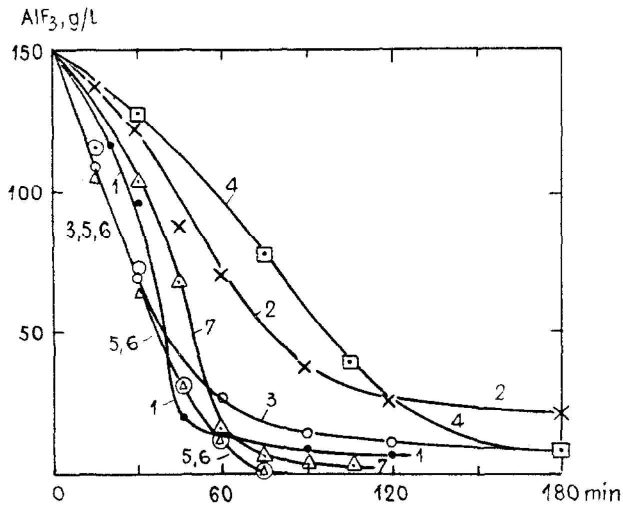

Fig. 2. The course of the reaction of AlF_3 (150 g/l) with different amounts of $Al(OH)_3$ at different temperatures. The reaction conditions are given in Table 1. The final temperature was attained in ca. 30 (run 2-6) and 50 min (run 1 and 7).

basic fluoride and β-$AlF_3.H_2O$. This is reflected in the course of the corresponding curves, in that the AlF_3 concentration does not decrease to zero, but stops at ca. 7 g/l in runs 1, 3 and 4 or at 21 g/l in run 2.

In contrast, processes running with AlF_3 : $Al(OH)_3$ = 2 but at temperatures higher than ca. 120°C provide only the $Al(OH,F)_3.H_2O$ phase along with some unreacted $Al(OH)_3$ in proportions decreasing from 13 to 7 and 4% when passing from a reaction temperature of 122 to 132 and 143°C, respectively. In these cases a rapid drop of AlF_3 concentration to zero follows with time, within ca. 75 min (runs 5-7).

Variations in the course of the reaction and in the composition of the solids obtained, may be explained in terms of the kinetics of particular processes involved. Under the conditions used, higher temperatures apparently favour hydrolysis of AlF_3 and a neutralization reaction of the liberated HF with $Al(OH)_3$ over crystallization of AlF_3-hydrates. On the other hand, lower temperatures, e.g., ca. 112°C favour the precipitation of the AlF_3-hydrates, $AlF_3.3H_2O$ and β-$AlF_3.H_2O$. Decrease in the concentrations of the reactants slows down all the processes, crystallization being stopped before neutralization, viz. when AlF_3 solution becomes no more supersaturated(below ca. 18 g/l). Such solution may, however, react further, due to hydrolysis, with $Al(OH)_3$ to give $Al(OH,F)_3.H_2O$ phase. It seems therefore probable that in sufficient long reaction times, all the unreacted $Al(OH)_3$, present in samples 2-6, would turn into the Al basic fluoride phase, especially in the systems containing AlF_3-hydrates (sample 2-4).

The reaction of AlF_3 with $Al(OH)_3$ can be considered as proceeding in two successive steps:

hydrolysis: $AlF_3 + (1+x)\ H_2O \longrightarrow Al(OH)_xF_{(3-x)}.H_2O + x\ HF$ (2)

reaction: $x\ HF + Al(OH)_3 \longrightarrow Al(OH)_{(3-x)}F_x + x\ H_2O$ (3)

These reactions are reflected in variations of pH, which initially decreases to ca. 1.5 when the temperature is raised to a definite level, and then increases to ca. 2.8 owing to the neutralization reaction (3).

Balance calculation show that irrespective of reaction conditions, the resulting Al basic fluoride has substantially the same final composition with an F/Al ratio of 2.0-2.3. An unexpected case is represented by the reaction product with an F/Al atomic ratio as low as 0.8 obtained in run 2, despite the fact that the starting mixture was characterized by as high F/Al ratio as 2.5. This run, presented in Fig. 2, curve 2, was also examined by investigation the solids.

Variations in phase composition with time, parallel to changes in solution, are shown in Fig. 3. As is seen, the progressive drop of $Al(OH)_3$ content in solids mixture from initial 100% to a final value of 4% is attended by a rise of the β-$AlF_3.H_2O$ phase from 0 to 77 mole %. The plot illustrating the content of $Al(OH,F)_3.H_2O$ is more sophisticated. It displays a maximum corresponding to the highest operating temperature, 132°C, similar in nature to that observed earlier during the hydrothermal decomposition of $AlF_3.3H_2O$ [5]. Balance calculations according to equation (1) show that the $Al(OH,F)_3.H_2O$ phase varies in its F/Al atomic ratio from an initial value of ca. 2.5 to the final value of 0.8.

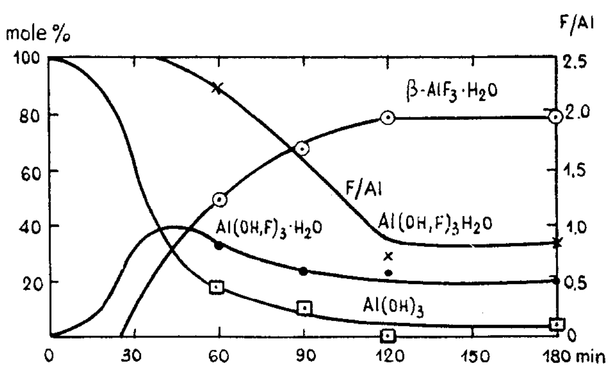

Fig. 3. Variations in solid phase composition during the reaction of AlF_3 soln. (150 g/l) with $Al(OH)_3$ at 5:1 m.r. and 132°C (3 at.) (run 2).

Initially the fastest reaction is the process associated with the formation of Al hydroxyfluoride with an F/Al ratio of ca. 2.5 during the first 30 minutes, when the system is continuously heated from 100°C to the final operation temperature 132°C. Then, crystallization of β-$AlF_3.H_2O$ becomes the dominant process and while this compound is progressively formed, the Al hydroxyfluoride phase loses F and gives ultimately after 120 min a composition with the F/Al ratio ~ 1. This fact allows the tentative conclusion to be drawn that Al hydroxyfluoride can under favoured conditions disproportionate during crystallization of β-$AlF_3.H_2O$, as for example:

$$2\ Al(OH)F_2.H_2O \longrightarrow \beta\text{-}AlF_3.H_2O + Al(OH)_2F.H_2O \qquad (4)$$

It may be that $Al(OH)_3$ present in the system leads to the same result:

$$Al(OH)F_2.H_2O + Al(OH)_3 + H_2O \longrightarrow 2\ Al(OH)_2F.H_2O \qquad (5)$$

To confirm these reactions and determine the conditions under which they proceed, a further study is required.

Some reactions of Al basic fluoride

Investigations included reactions of $Al(OH)F_2.H_2O$ contaminated by 4 % $Al(OH)_3$ (sample 7) with solutions of NaOH, NaF, NH_4F, AlF_3, $NaHF_2$ and H_2SiF_6.

The reaction with NaOH (28 g/l, 0.7 M) at atomic ratio Na/Al = 2 proved not to occur at ambient temperature, but at 45°C proceeded as shown in Fig. 4 with the formation of cryolite and $Al(OH)_3$ in the course of 90 min.

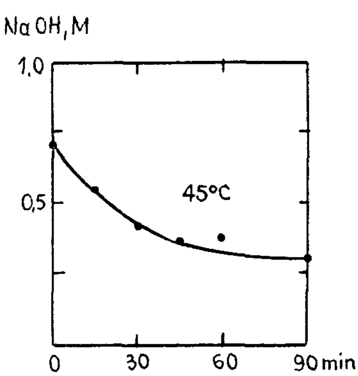

Fig. 4. The course of the reaction between NaOH soln. (0.7 M) and $Al(OH)F_2.H_2O$ at at.r. Na/Al = 2, at 45°C

Taking into account that ca. 50 % of the NaOH used initially was reacted, it gives the equation:

$$3\ NaOH + 3\ Al(OH)F_2.H_2O \longrightarrow Na_3AlF_6 + 2\ Al(OH)_3 + 3\ H_2O \qquad (6)$$

The reaction with NaF (36 g/l, 0.86 M) in the atomic ratio Na/Al = 1, 2 and 3 at 95°C was essentially over in ca. 30 min. In all cases the reaction followed the equation:

$$6\ NaF + 3\ Al(OH)F_2.H_2O \longrightarrow 2\ Na_3AlF_6 + Al(OH)_3 + 3\ H_2O \qquad (7)$$

When Na/Al = 1, excess Al basic fluoride was also present, whereas at Na/Al = 3 appropriate amounts of NaOH were formed:

$$18\ NaF + 6\ Al(OH)F_2.H_2O \longrightarrow 5\ Na_3AlF_6 + Al(OH)_3 + 3\ NaOH + 6\ H_2O \qquad (8)$$

After 60 min the parent solutions exhibited the following composition:

NaF : $Al(OH)F_2.H_2O$	Composition of soln., M		pH
	NaF	NaOH	
1	0.03	0.00	7.75
2	0.06	0.06	9.85
3	0.13	0.13	10.9

The data in the Table demonstrate a progressive increase in F and NaOH concentrations as well as pH value. Alkalinity in case 2 is ascribable to the presence of some $Al(OH)_3$ in Al basic fluoride, which reacts with NaF to give some NaOH.

The chemical composition of the precipitate obtained in the reaction (8), after neutralization of the NaOH by HCl to pH 6-7, filtration of the solids and drying at ca. 100°C, is (%): Na 29.9, Al 13.2, F 49.0, OH calcd. 2.7, balance 5.2. It corresponds to a mixture of Na_3AlF_6 and $Al(OH)_3$ with the molar ratio 5 : 0.6.

The reaction with NH_4F (37 g/l, 1 M) in the molar ratio NH_4F/Al = 2 was examined at 60 and 100°C for 4 and 1.5 hr, respectively. The reaction proceeds according to the curves in Figure 5 with evolution of NH_3 which increase the pH of the solution to ca. 8. The reaction at 100°C may be considered as

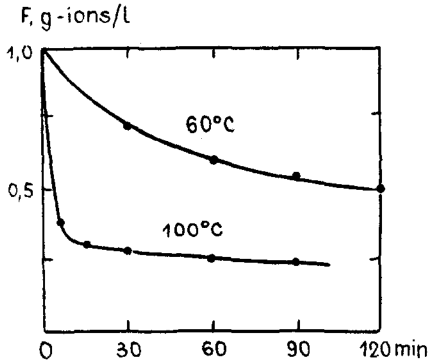

Fig. 5. The course of the reaction of NH_4F soln. (1 M) with $Al(OH)F_2.H_2O$ at m.r. NH_4F/Al = 2 at 60 and 100°C.

complete because of the solubility of $(NH_4)_3AlF_6$, which amounts to ca. 7.6 g/l [6], corresponding to 0.23 g-ions of F. X-ray analysis reveals major amounts of $(NH_4)_3AlF_6$ and $Al(OH,F)_3.H_2O$, along with some $Al(OH)_3$ in the residues. It indicates, that the **reaction proceeds predominantly according to an equation given by Kidde [4] :**

$$4\ NH_4F + Al(OH)F_2 \longrightarrow (NH_4)_3AlF_6 + NH_3 + H_2O \qquad (6)$$

In part, a side reaction must be assumed to explain the formation of aluminium hydroxide:

$$6\ NH_4F + 3\ Al(OH)F_2.H_2O \longrightarrow 2(NH_4)_3AlF_6 + Al(OH)_3 + 3\ H_2O \qquad (10)$$

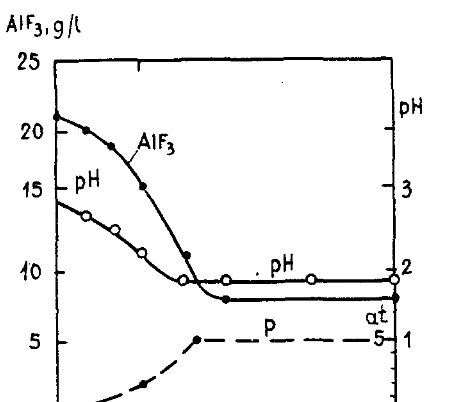

Fig. 6. The course of the reaction of AlF_3 soln. (0.25 M) with $Al(OH)F_2.H_2O$ at 1:1 m.r. at 143°C (5 at.).

The reaction with AlF_3 (21 g/l, 0.25 M) was carried out at a 1:1 molar ratio at 143°C (5 at) :

$$AlF_3 + Al(OH)F_2 \cdot H_2O \longrightarrow 2\ Al(OH)_{0.5}F_{2.5} \cdot H_2O \qquad (11)$$

The reaction proceeded as shown in Figure 6. As is seen, it stopped when the final temperature/pressure conditions were approached after 50 min, AlF_3 concentration decreasing to ca. 8 g/l. Chemical analysis of the solid product for F and Al content gave an F/Al at. ratio of 2.22, whereas balance calculations based on the material consumption and composition gave a value of 2.40. It could be inferred from this that further increase of temperature would decrease the AlF_3 concentration and give the Al basic fluoride with even higher F/Al ratio.

The attempted reaction with $NaHF_2$ (62 g/l, 1 M) in the atomic ratio Na/Al = 3 was intended to give cryolite according to equation:

$$3\ NaHF_2 + Al(OH)F_2 \cdot H_2O \longrightarrow Na_3AlF_6 + 2\ HF + 2\ H_2O \qquad (12)$$

It proved to be completely inert even under such forcing conditions as 100 and 150°C (6 at) for 2 hr. The original concentration of $NaHF_2$ remained unchanged in both cases.

The attempted reaction with H_2SiF_6 (46 g/l, 0.32 M) in the at. ratio F/Al = 3, to give aluminium fluoride according to:

$$H_2SiF_6 + 6\ Al(OH)F_2 \cdot H_2O \longrightarrow 6\ AlF_3 + SiO_2 + 10\ H_2O \qquad (13)$$

failed to proceed. After 2 hr, the pH of the solution remained at below 1, whereas corresponding amounts of $Al(OH)_3$ reacted completely in ca. 15 min with formation of AlF_3 solution and an increase of pH to ca. 4. Even after prolonged heating with a large excess of 80 % Al basic fluoride, the reaction was not complete. The observed drop of H_2SiF_6 concentration was from 46 to 18 g/l, from which about 50 % is to ascribe to $Al(OH)_3$ present as contaminant in the substrate.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to A.Hałat for performing experiments, M.Czakłosz for chemical analyses and A.Krüger for X-ray diffraction patterns.

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