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**PHYSICOCHEMICAL ANALYSIS  
OF INORGANIC SYSTEMS**

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## To the Properties of Fluorosilicic Acid: Evolution of Views on the State in Aqueous Solutions (Overview)

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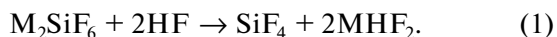
**Abstract**—The views of different authors on equilibria in solutions of fluorosilicic acid are discussed. The model of the acid as an equilibrium system involving hexacoordinated complexes  $[\text{SiF}_6 - n(\text{H}_2\text{O})_n]^{n-2}$  ( $n = 0-2$ ) is believed to be the most adequate.

**Keywords:** fluorosilicic acid, aqueous solutions, hexafluorosilicate anion, hydrolysis

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Fluorosilicic acid (FSA) holds a special place in the chemistry and technology of inorganic fluorides [1]. As is known, FSA is a large-scale by-product of processing of phosphate raw materials (production of phosphate fertilizers, phosphoric acid, and elemental phosphorus), is currently considered to be the basic alternative source of fluorine for the chemical industry [1–5]. This circumstance stimulates the interest of researchers in various aspects of the chemistry of FSA, including issues related to the expansion of the assortment of products of processing and utilization of FSA [1, 3, 6–9]. The latter is all the more topical because, for example, judging by the estimates [4], the US industry, the largest producer of FSA, utilizes only about 1% of the FSA formed during the processing of phosphate ores (the fluorine content in phosphorites and apatites is 3.5–4.2%, which corresponds to 630 million tons available for recovery of fluorine). Obviously, when developing chemical aspects of the processes of FSA utilization, it is necessary to take into account the component composition and properties of its aqueous solutions; these issues have been repeatedly discussed in the literature [1, 7, 10–16]. In this article, an attempt is made to systematize and generalize publications reflecting the views of various authors and their evolution on the problem of chemistry of equilibria in aqueous solutions of FSA.

Prior to discussing the problem of the state of FSA in aqueous solutions, we note that the FSA does not exist in an individual state. The interaction of excess liquid anhydrous HF with alkali metal hexafluorosilicates [17, 18] is accompanied by an almost quantitative displacement of  $\text{SiF}_4$  according to the scheme:



In turn, the attempt of authors [18] to isolate  $\text{H}_2\text{SiF}_6$  by co-condensing  $\text{SiF}_4$  and excess HF in a sapphire tube at  $-78^\circ\text{C}$  followed by heating the reaction mixture to  $25^\circ\text{C}$  led to identification of only the initial compounds in both the gas and liquid phases.

The existence of unstable of solid FSA “crystal hydrates”  $\text{H}_2\text{SiF}_6 \cdot n\text{H}_2\text{O}$  ( $n = 1, 2, 4$ ) was discussed in [17]; in the absence of structural data at the time of publication [16], the structure of oxonium salts of FSA ( $n = 2, 4$ ) and  $\text{SiF}_4$  crystal hydrate ( $n = 1$ ) was proposed for them. Much later, the authors of [19] isolated crystal hydrates of composition  $\text{H}_2\text{SiF}_6 \cdot n\text{H}_2\text{O}$  ( $n = 4, 6, 9.5$ ; mp  $20, -12, \text{ and } -54^\circ\text{C}$ , respectively) when studying the  $\text{H}_2\text{SiF}_6\text{--H}_2\text{O}$  system by the low-temperature DTA method; according to the X-ray diffraction data, these crystal hydrates were oxonium salts  $(\text{H}_3\text{O})_2\text{SiF}_6$ ,  $(\text{H}_3\text{O})_2\text{SiF}_6 \cdot 2\text{H}_2\text{O}$ , and  $(\text{H}_3\text{O})_2\text{SiF}_6 \cdot 4.5\text{H}_2\text{O}$ . In addition, the unstable dihydrate  $\text{H}_2\text{SiF}_6 \cdot 2\text{H}_2\text{O}$  was isolated, which decomposed at a temperature “slightly above room temperature” [19]. When attempting to react 45% FSA with nitrilotriacetic acid hydrazide, a colorless crystalline compound melting with decomposition at  $T \geq 60^\circ\text{C}$  and identified by X-ray diffraction as oxonium hexafluorosilicate  $(\text{H}_3\text{O})_2\text{SiF}_6$  was obtained in low yield. “Dihydrate”  $\text{H}_2\text{SiF}_6 \cdot 2\text{H}_2\text{O}$  (more precisely, oxonium hexafluorosilicate) can apparently exist in different crystalline modifications, and a more stable form of the compound was characterized in [20].

Despite the more than a century and a half history of studying the properties of FSA [17], the questions of its state in aqueous solutions continue to be the subject of discussion. The essence of the polemics is reduced to the choice of one of the four basic models of the

composition of FSA solutions discussed in the literature:

(i) in FSA solutions, the only or dominant silicon fluoro complex is the  $\text{SiF}_6^{2-}$  anion;

(ii) in the FSA solutions, the  $\text{SiF}_6^{2-}$  and  $[\text{SiF}_5(\text{H}_2\text{O})]^-$  anions coexist in comparable amounts;

(iii) polynuclear silicon fluoro complexes like  $\text{H}_2\text{S}_2\text{iF}_{11}$  are present in FSA solutions;

(iv) in FSA solutions, there is a molecular form  $\text{H}_2\text{SiF}_6$ .

According to the ideas of Ryss, stated in the classic monograph [17], there is no molecular form of FSA in aqueous solutions, and the high acidity of such solutions is due to the shift to the right of the equilibrium of dissociation of HF due to the formation of a relatively strong complex anion  $\text{SiF}_6^{2-}$ :

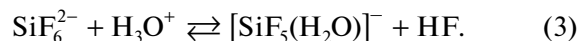


In this case, the possibility of the existence of hydroxy complexes  $[\text{SiF}_5(\text{OH})]^{2-}$  and  $[\text{SiF}_4(\text{OH})_2]^{2-}$  or corresponding aqua complexes in solutions was not taken into account; i.e., the  $\text{SiF}_6^{2-}$  anion was considered as the only silicon fluoro complex in FSA solutions.

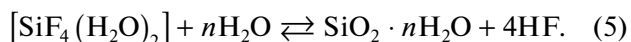
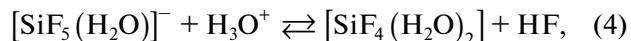
Further development of the ideas about the dominant contribution of the  $\text{SiF}_6^{2-}$  complex to the balance of silicon and fluorine in solutions of FSA is reflected in the publications [21–26] and is presented in the most complete form in the reviews [12, 13] and the thesis [27]. The authors of the cited papers have studied the equilibrium of complexation in acidic silicon fluoride solutions by the fluoride potentiometry method, and it has been shown that the stability of the  $\text{SiF}_6^{2-}$  anion depends significantly on the pH of the medium: the maximum thermodynamic stability of the  $\text{SiF}_6^{2-}$  anion is in the pH range 2.6–2.7, and with increasing acidity of the solution (pH < 2.6), the equilibrium concentration of  $\text{SiF}_6^{2-}$  decreases [10, 12, 13, 27]. An analogous conclusion was made in [28] on the basis of the results of studying the hydrolysis of FSA in the presence of sulfuric acid. According to [12, 13, 21, 27], a tetrafluorosilicon complex accumulates in the solution; it is presumably  $[\text{SiF}_4(\text{H}_2\text{O})_2]$  because of the noticeable Lewis acidity of  $\text{SiF}_4$  [29]. It is essential that, in contrast to earlier publications [17], the existence of a species with the number of fluorine atoms  $N_F < 6$  is already accepted for strongly acidic solutions of FSA, in addition to the anion  $\text{SiF}_6^{2-}$ , whereas in a weak acidic medium, the  $\text{SiF}_6^{2-}$  anion predominates.

A radically different point of view on the character of equilibria in FSA solutions has been presented in [30–34]. On the basis of kinetic [30–33] and

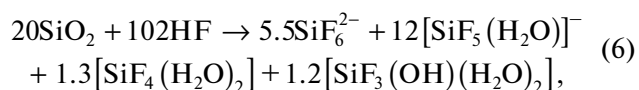
$^{19}\text{F}$  NMR [34–36] data, it has been shown that the basic process in FSA solutions of stoichiometric composition and in acidic solutions of hexafluorosilicates ( $\varphi = \Sigma\text{F}/\Sigma\text{Si} = 6.0$ ) is the hydrolysis equilibrium:



Deeper hydrolytic transformations in FSA solutions are described by equilibria (4) and (5):



For an FSA solution with  $\varphi = \Sigma\text{F}/\Sigma\text{Si} \approx 5$ ,  $^{19}\text{F}$  NMR data [34] indicate the existence of the equilibrium



the  $[\text{SiF}_5(\text{H}_2\text{O})]^-$  complex turns out to be the dominating species in the equilibrium mixture (the distribution of fluorine between the  $[\text{SiF}_5(\text{H}_2\text{O})]^-$ ,  $\text{SiF}_6^{2-}$ ,  $[\text{SiF}_4(\text{H}_2\text{O})_2]$ , and  $[\text{SiF}_3(\text{OH})(\text{H}_2\text{O})_2]$  species is 59, 32, 5, and 3%, respectively).

The idea of the existence in FSA solutions of the aquapentafluoro complex  $[\text{SiF}_5(\text{H}_2\text{O})]^-$  (equilibrium (3)), in addition to  $\text{SiF}_6^{2-}$ , has been structurally confirmed when studying the products of interaction of FSA with azacrown ethers. The  $[\text{SiF}_5(\text{H}_2\text{O})]^-$  aqua anion was stabilized and characterized by single-crystal X-ray diffraction in the host–guest compounds  $(\text{L}^1\text{H})_2[\text{SiF}_5(\text{H}_2\text{O})]_2 \cdot 3\text{H}_2\text{O}$  (**I**,  $\text{L}^1 =$  monoaza-12-crown-4) [37],  $(\text{L}^2\text{H} \cdot \text{H}_2\text{O})[\text{SiF}_5(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}]$  (**II**,  $\text{L}^2 =$  monoaza-18-crown-6), and  $(\text{L}^3\text{H}_2)[\text{SiF}_5(\text{H}_2\text{O})]_2$  (**III**,  $\text{L}^3 =$  1,10-diaza-18-crown-6) [38]. The stabilization of the aquapentafluorosilicon complex in structures **I–III** occurs through systems of H-bonds  $\text{NH} \cdots \text{F}$ ,  $\text{NH} \cdots \text{O}$ ,  $\text{OH} \cdots \text{F}$ , and  $\text{OH} \cdots \text{O}$  (Fig. 1). In turn, the reaction of FSA with *cis-syn-cis* isomer of dicyclohexano-18-crown-6 ( $\text{L}^4$ ) is accompanied by the formation of the host–guest complex  $(\text{L}^4 \cdot \text{H}_3\text{O})\text{SiF}_5$  (**IV**) isolated in the individual state, and its structure has been proved by single-crystal X-ray diffraction data [39]. This result is yet another argument in favor of the existence of a species with  $N_F = 5$  in FSA solutions, which was denied by the authors [12, 13, 21–27].

It is known that the rate-limiting stage of the formation of the  $[\text{SiF}_5(\text{H}_2\text{O})]^-$  anion by scheme (3) is the removal of the first fluoride ion from the  $\text{SiF}_6^{2-}$  anion to give the  $\text{SiF}_5^-$  anion by the dissociative  $\text{S}_{\text{N}}1$  mechanism [33, 40]:

