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# Complexation Processes in KF–$SbF_3$–$H_2O$ System Studied by Calorimetric Titration

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**Abstract**—Complexation in a KF–$SbF_3$–$H_2O$ system is studied in a range of molar ratios of fluorides KF : $SbF_3$ = (0.1–2) : 1 by calorimetric titration. The equilibrium formation constants of complexes $KSb_2F_7$, $KSbF_4$, and $K_2SbF_5$ ($5.8 \times 10^5 \pm 800$, $3.3 \times 10^4 \pm 500$, and $1.9 \times 10^6 \pm 950$, respectively) and the changes in enthalpy ($-31.75 \pm 0.74$, $-28.15 \pm 0.44$, and $-25.5 \pm 0.64$ J mol$^{-1}$, respectively) and entropy ($4 \pm 7$, $-8 \pm 5$, and $-35 \pm 9$ J mol$^{-1}$ K$^{-1}$, respectively) are determined. The thermodynamic stability of the antimony(III) fluoride complexes is found to increase on going from $KSb_2F_7$ to $K_2SbF_5$.

## INTRODUCTION

In this work, we continued the systematic study of the physicochemical properties of the antimony(III) fluoride complexes [1–4]. Complexation in a KF–$SbF_3$–$H_2O$ system was studied by calorimetric titration. The equilibrium constants ($\boldsymbol{K_c}$) and the changes in enthalpy ($\Delta H$) and entropy ($\Delta S$) of formation of $KSb_2F_7$, $KSbF_4$, and $K_2SbF_5$ complexes were determined.

## EXPERIMENTAL

Potassium and trivalent antimony fluorides (reagent grade) served as the starting substances. Complexation in the KF–$SbF_3$–$H_2O$ system was studied by calorimetric titration at 298.15 K in an interval of KF to $SbF_3$ molar ratios of (0.1–2) : 1. A solution of KF with concentration 1.3–1.45 mol/l was placed in a dosing vessel, and a solution of $SbF_3$ with concentration 0.003–0.008 mol/l was poured into a calorimetric cell. Solid substances isolated by crystallization from a solution with a specified molar ratio of the starting components KF : $SbF_3$ (0.6 : 1, 1.1 : 1, and 1.9 : 1) were identified after calorimetric titration by thermogravimetric analysis.

Calorimetric titration was carried out on a differential automated calorimeter designed for measuring low thermal effects of endo- and exothermic processes. The method is described in detail in [5]. All experimental data were compiled and processed on a computer. First, from experimental titration curves we determined single thermal effects, which corresponded to a response of the system to the introduction of particular doses, as a product of the surface area of the corresponding peak by a cell constant $\alpha$. The obtained single thermal effects were corrected taking into account the results of a "blank" experiment in each titration step. The "blank" experiment (titration of a pure solvent with a solution of a titrant) made it possible to take into account thermal effects caused by the introduction of the titrant and dilution of a solution with the titrant.

The thermodynamic characteristics of the processes under study were calculated using a KALORY computer program [6, 7]. The program is based on a graphical method for the determination of numerical values of $K_c$ and $\Delta H$. For these values, the calculated function ($\boldsymbol{Q_n^{calcd}}$) almost coincides with the experimental curve ($Q_n^{exp}$) ($Q_n$ is the amount of heat evolved upon the addition of the $n$th dose of the titrant) due to varying the equilibrium constant and the enthalpy change and reducing to minimum the sum of quadratic deviations $\Sigma(Q_n^{exp} - Q_n^{calcd})^2$. The coincidence of the experimental and calculated curves and the presence of inflection points corresponding to the composition of a solution with the molar ratio KF : $SbF_3$ = 1 : 1 (see below) indicates that the model (formation of the $KSbF_4$ complex) was chosen correctly. If the $Q_n^{calcd}$ function unsatisfactorily describes the experimental plot $Q_n^{exp}$ and the inflection point corresponded to the other composition of fluorides (1 : 2 or 2 : 1) in a solution, the thermodynamic characteristics of formation of complexes of the respective composition were calculated.

To exclude possible local minima in the $\Sigma(Q_n^{exp} - Q_n^{calcd})^2$ function, we plotted and analyzed the profile of this function for each system under study. For all systems studied, the $\Sigma(Q_n^{exp} - Q_n^{calcd})^2$ function has only

**Table 1.** Molar ratios of potassium and antimony(III) fluorides in an aqueous solution, the compositions of crystalline antimony(III) fluorides formed upon crystallization from an aqueous solution, and the temperatures of phase transitions and melting

| Molar ratio KF : $SbF_3$ in water | Composition of the main compound in solid phase [1]* | Structure of complex, references | Temperature, °C | | References |
|---|---|---|---|---|---|
| | | | polymorphous transformation | melting | |
| (0.01–0.03) : 1 | $Sb_3O_2F_5$ | [9] | | | |
| (0.03–0.04) : 1 | $KSb_4F_{13}$ ($Sb_3O_2F_5$, $KSb_2F_7$) | [10] | | | |
| (0.05–0.65) : 1 | $KSb_2F_7$ ($Sb_3O_2F_5$, $KSb_4F_{13}$, $K_2Sb_3F_{11}$) | [11] | Absent | 270 | [16] |
| (0.55–0.68) : 1 | $K_2Sb_3F_{11}$ ($KSb_2F_7$, $K_3Sb_4F_{15}$, $KSbF_4$) | [12] | 160–165<br>180–185 | | [2] |
| (0.69–0.78) : 1 | $K_3Sb_4F_{15}$ ($KSb_2F_7$, $K_2Sb_3F_{11}$, $KSbF_4$) | | 180–185 | | [2] |
| (0.65–1.4) : 1 | $KSbF_4$ ($KSb_2F_7$, $K_2Sb_3F_{11}$, $K_3Sb_4F_{15}$, $K_2SbF_5$) | [13] | –83<br>167–177 | 315 | [16–21] |
| (1.5–5) : 1 | $K_2SbF_5$ ($KSbF_4$) | [14, 15] | 555 | 575 | [16] |

* Compounds that can crystallize as an admixture at boundary molar ratios of the components are given in parentheses.

one minimum, which is confirmed by the shape of the profile of the corresponding function (the profile was obtained by varying only one of the desired parameters). In this case, the dispersion minimum characterizes the best agreement between the calculated and experimental single thermal effects. The presence of one minimum indicates its global character and confirms reliability of thermodynamic characteristics determined by the program.

The thermogravimetric study of precipitates obtained from solutions of antimony(III) and potassium fluorides was carried out on a 1000D derivatograph (MOM, Hungary) in a temperature interval of 20–500°C in air flow. A weighed sample (50–80 mg) was placed in a platinum crucible. The sensitivity of a galvanometer for recording a DTG signal was 1 mV, and those for DTA and thermobalance were 250 μV and 100 mg/250 mm of scale, respectively; heating rate was 1.25 K/min. The accuracies of measuring the temperatures of a sample and intraphase polymorphous conformation transitions in the studied temperature interval were checked by the characteristic temperatures of reference substances according to [8].

## RESULTS AND DISCUSSION

The formation of the hydrolysis product of antimony trifluoride $Sb_3O_2F_5$ and six fluoride complexes $KSb_4F_{13}$, $KSb_2F_7$, $K_2Sb_3F_{11}$, $K_3Sb_4F_{15}$, $KSbF_4$, and $K_2SbF_5$ (Table 1) in the synthesis of antimony(III) fluoride complexes with the potassium cation in an aqueous solution in an interval of molar ratios KF : $SbF_3$ (0.01–5) : 1 was reliably established by the preparative chemical method [1, 2, 9–21]. Compounds with the same compositions were obtained by the solidphase synthesis [22]. The crystal structures were determined for all compounds, except for $K_3Sb_4F_{15}$ (unfortunately, we could not obtain a crystal appropriate for X-ray diffraction analysis). Similar structures of complexes with $Cs^+$ and $NH_4^+$ cations are known [23]. The thermal properties of the antimony(III) fluoride complexes with the $K^+$ cation were studied in several works (Table 1).

The calorimetric titration of an aqueous solution of $SbF_3$ with a solution of potassium fluoride in water allowed us to establish that three inflection points corresponding to ratios of 0.65 : 1, 1.1 : 1, and 1.9 : 1 are observed in the calorimetric titration curves in the interval of molar ratios KF : $SbF_3$ = (0.1–2) : 1. When KF is introduced into a solution of $SbF_3$, complexes of different compositions are formed (Table 1), and the thermal effects detected include, undoubtedly, all changes that occur in solution. After the calorimetric experiment was finished, solid phases were isolated from solutions in the inflection points and examined by thermogravimetric analysis in order to refine the composition of the complexation products.

The DTA curve of the sample obtained from a solution with the molar ratio KF : $SbF_3$ = 0.6 : 1 contains one peak at 265°C. Since this peak does not correspond to a weight loss and no changes are observed in the TG and DTG curves, we concluded that it corresponds to

**Table 2.** Characteristics of the formation of potassium fluoroantimonates(III) in water at 298.15 K

| Compound | $K_c$ | $\Delta H$, J mol$^{-1}$ | $\Delta S$, J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| $KSb_2F_7$ | $5.8 \times 10^5 \pm 800$ | $-31.75 \pm 0.74$ | $4 \pm 7$ |
| $KSbF_4$ | $3.3 \times 10^4 \pm 500$ | $-28.15 \pm 0.44$ | $-8 \pm 5$ |
| $K_2SbF_5$ | $1.9 \times 10^6 \pm 950$ | $-25.5 \pm 0.64$ | $-35 \pm 9$ |

melting of the substance. A comparison of the obtained experimental and published data (Table 1) and the absence of other peaks in the DTA curve indicate that only one complex $KSb_2F_7$ is detected in this system within the sensitivity limit of the thermogravimetric method. All the aforesaid makes it possible to assign the thermal effects detected in the calorimetric experiment to the formation of compound $KSb_2F_7$. Based on the experimental curves obtained by calorimetric titration, we calculated the thermodynamic characteristics of $KSb_2F_7$ formation according to [5–7] (Table 2).

The procedure of studying the $KF–SbF_3–H_2O$ systems with achievable molar ratios of fluorides of 1.1 : 1 and 1.9 : 1 is similar: after calorimetric experiment, the solution was evaporated in a vacuum until a crystalline precipitate formed. The solid product was filtered off and identified by thermogravimetry on the basis of the data in Table 1. The formation of the $KSbF_4$ and $K_2SbF_5$ complexes was established, and the thermodynamic characteristics of their complexation were calculated (Table 2).

Thus, according to the data obtained in this work, the formation of three complexes $KSb_2F_7$, $KSbF_4$, and $K_2SbF_5$ in an aqueous solution of a $KF–SbF_3–H_2O$ system was established for the range of molar ratios of fluorides KF : $SbF_3$ = (0.1–2) : 1. These complexes are likely to be thermodynamically most stable in solution of a whole group of the known potassium fluoroantimonate(III) complexes. The highest stability constant belongs to $K_2SbF_5$. This indicates that potassium pentafluoroantimonate(III) (for which the minimum $K_c$ value was determined) has the highest stability in an aqueous solution of the three complexes. The transition from $KSb_2F_7$ to $K_2SbF_5$ is accompanied by a decrease in the thermal exothermic effect, while the character of entropy change indicates an increase in the ordering in the $KF–SbF_3–H_2O$ system with an increase in the molar ratio of the components. The absence of inflection points in the region of $K_2Sb_3F_{11}$ and $K_3Sb_4F_{15}$ formation for the calorimetric titration of fluoride solutions (Table 1) is associated, most probably, with very narrow area of their existence and a low thermodynamic stability of these compounds under conditions studied.

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## REFERENCES

1. Zemnukhova, L.A., *Doctoral (Chem.) Dissertation*, Vladivostok: Inst. of Chemistry, Far-East Division of the RAS, 1998.
2. Kavun, V.Ya., *Doctoral (Chem.) Dissertation*, Vladivostok: Inst. of Chemistry, Far-East Division of the RAS, 2003.
3. Uvarov, N.F., Kavun, V.Ya., and Zemnukhova, L.A., *Trudy I Mezhdunarodnogo sibirskogo seminara "Intersibfluorine"* (Proc. I Int. Siberian Seminar "Intersibfluorine"), Novosibirsk, 2003.
4. Kovaleva, E.V., Zemnukhova, L.A., and Kon'shin, V.V., *Koord. Khim.*, 2002, vol. 28, no. 11, p. 809.
5. Lebedeva, N.Sh., Mikhailovskii, K.V., and V'yugin, A.I., *Zh. Fiz. Khim.*, 2001, vol. 75, no. 6, p. 1140.
6. Lebedeva, N.Sh., Mikhailovskii, K.V., and V'yugin, A.I., *Koord. Khim.*, 2001, vol. 27, no. 10, p. 795.
7. Lebedeva, N.Sh., Vyugin, A.I., Pavlycheva, N.A., *et al.*, *Thermochim. Acta*, 2002, vol. 390, nos. 1–2, p. 179.
8. Zhong, Z. and Callagher, P.R., *Thermochim. Acta*, 1991, vol. 186, p. 199.
9. Udovenko, A.A., Volkova, L.M., Davidovich, R.L., *et al.*, *Koord. Khim.*, 1985, vol. 11, no. 8, p. 1132.
10. Ducourant, B., Fourcade, R., Philippot, E., and Masherpa, G., *Rev. Chim. Min.*, 1975, vol. 12, no. 7, p. 553.
11. Mastin, S.H. and Ryan, R.R., *Inorg. Chem.*, 1971, vol. 10, no. 8, p. 1757.
12. Ducourant, B. and Fourcade, R., *C. R. Acad. Sci., Ser. III*, 1976, vol. 282, no. 16, p. 741.
13. Habibi, N., Ducourant, B., Bonnet, B., and Fourcade, R., *J. Fluorine Chem.*, 1978, vol. 12, no. 1, p. 63.
14. Udovenko, A.A. and Volkova, L.M., *Koord. Khim.*, 1981, vol. 7, no. 12, p. 1763.
15. Udovenko, A.A., Eiberman, M.F., Ivanov, S.B., *et al.*, *Kristallografiya*, 1992, vol. 37, no. 3, p. 729.
16. Davidovich, R.L. and Zemnukhova, L.A., *Koord. Khim.*, 1975, vol. 1, no. 4, p. 477.
17. Yamada, K., Ohnuki, Y., Ohki, H., and Okuda, T., *Chem. Lett.*, 1999, no. 7, p. 627.
18. Borzenkova, M.P., Kalinchenko, F.V., Novoselova, A.V., *et al.*, *Zh. Neorg. Khim.*, 1984, vol. 29, no. 3, p. 703.
19. Davidivich, R.L., Gordienko, P.S., Grigas, J., *et al.*, *Phys. Status Solidi A*, 1984, vol. 84, p. 387.
20. Kavun, V.Ya., Uvarov, N.F., Sergienko, V.I., *et al.*, *Elektron. Zh. "Issledovano v Rossii"*, 2003, no. 13. p. 130. (httr:,Zhurnal.Are.Relarn.Ru/Artisles/2003/013.pdf).
21. Zemnukhova, L.A. and Davidovich, R.L., *Z. Naturforsch., A: Phys. Sci.*, 1998, vol. 53, no. 5, p. 573.
22. Kalinchenko, F.V., *Cand. Sci. (Chem.) Dissertation*, Moscow: Moscow State Univ., 1982.
23. Udovenko, A.A., Gorbunova, Yu.E., Zemnukhova, L.A., *et al.*, *Koord. Khim.*, 2001, vol. 27, no. 7, p. 514.