ISSN 1070-4272, Russian Journal of Applied Chemistry, 2011, Vol. 84, No. 8, pp. 1319–1323. © Pleiades Publishing, Ltd., 2011.
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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Preparation and Examination of the Properties of Complex Scandium Fluorides

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Received December 6, 2010

Abstract—Precipitation of scandium with sodium fluoride from an ammonium hydrogen difluoride solution was examined at the molar ratios of Na to Sc within 1–14 and different initial concentrations of scandium in solution. The composition of the resulting precipitate was determined by X-ray phase analysis method. The solubility of the scandium compounds synthesized was examined.

DOI: 10.1134/S1070427211080040

The available published data on the properties of complex scandium fluorides are mostly concerned with the solid state. The phase diagrams of the $MF–ScF_3$ ($M =$ Li, Na, K, Rb, Cs, NH_4, Ag, Tl) and other systems are presented in [1].

Data concerning the occurrence and properties of complex scandium fluorides in solution are scarce. In the early twentieth century Meyer [2] discovered solubility of scandium(III) fluoride in solutions of alkali-metal and ammonium fluorides. Sterba–Bohm [3] described the synthesis of $(NH_4)_3ScF_6$ and its decomposition into a number of compounds when dissolved in water. A more recent study of the solubility isotherm of $(NH_4)_3ScF_6$ in an ammonium fluoride solution at 25°C showed that incongruent dissolution of the complex salt at the fluoride ion concentrations under 1.8 M leads to formation of congruently soluble ammonium tetrafluoroscandate NH_4ScF_4 (solubility in water at 25°C 1.29 g l^{-1}, or 9.28×10^{-3} mol l^{-1}). At the fluoride ion concentrations above 1.8 M scandium occurs in solution as hexafluoroscandate ion [4, 5].

Tananaev and Golubev [6, 7] examined the $ScCl_3–KF–H_2O$ system [6, 7] and, based on the optical density and molar electrical conductivity data for the solutions characterized by molar ratio of F to Sc n ranging from 1 to 10, presumed that ScF_3 ($n = 3$) and K_3ScF_6 ($n = 6$) are formed, and at higher n values, $KScF_4·0.1H_2O$ and $K_{2.5}ScF_{5.66}·H_2O$ (in the presence of 0.2 M KF in solution). The X-ray diffraction data reported in those studies do not correspond to the currently known parameters for $KScF_4$, KSc_2F_7, $K_5Sc_3F_{14}$, and K_3ScF_6 (prepared by solid-phase syn-thesis procedure) [1, 8], i.e., most likely refer to solid solutions. We studied the interaction of a scandium(III) chloride solution with crystalline KHF_2 and revealed formation of scandium(III) fluoride at $n = 2–3$, of a mixture of ScF_3 with KSc_2F_7 at $n = 4$, of KSc_2F_7 at $n = 5–7$, and of $K_5Sc_3F_{14}$ at $n = 10–12$ [9]. A relatively low degree of precipitation of scandium (80%) in preparation of scandium(III) fluoride, as well as the formation of a KSc_2F_7 gel, prevent the use of the above-mentioned system for quantitative recovery of scandium from solution.

Complex scandium fluorides were prepared by the reaction between scandium(III) chloride and sodium fluoride solutions [10]. The conditions for preparation of scandium fluoride were determined (solid phase had the composition $ScF_3·0.16\ H_2O$), as well as those for the synthesis of sodium tetrafluoroscandate in the form of $NaScF_4·H_2O$. As to the occurrence of Na_3ScF_6, whose preparation was reported in that study, this fact should not be taken as proved. The maximal F/Sc ratio obtained for the precipitate was 5.76, and the X-ray phase analysis data reported in that study are inconsistent with the currently known characteristics of Na_3ScF_6. Consequently, those findings need clarification.

Here, we explored the conditions for the synthesis of complex scandium fluorides from scandium solution in ammonium hydrogen difluoride with the use of sodium fluoride.

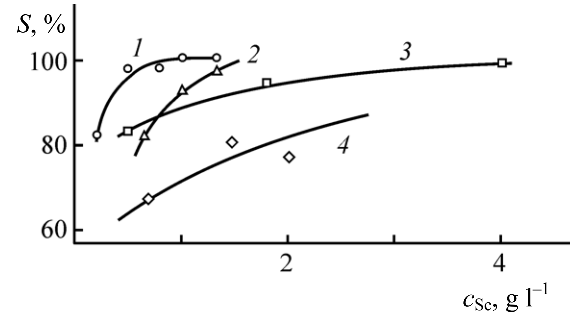

Fig. 1. Degree of precipitation S of Sc(III) from 10% NH_4HF_2 solution vs. Sc(III) concentration in the initial solution. m: (*1*) 3, (*2*) 1.5, (*3*) 1, and (*4*) 0.5.

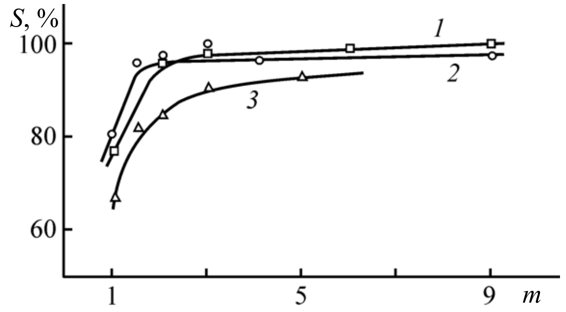

Fig. 2. Degree of precipitation S, %, of Sc(III) from 10% NH_4HF_2 solution vs. molar ratio of Na to Sc m. c_{Sc}, g l^{-1}: (*1*) 1.8, (*2*) 1.5, and (*3*) 0.67.

EXPERIMENTAL

The initial solutions of scandium in ammonium hydrogen difluoride were obtained by the reaction of 0.1–0.2 g of scandium oxide (OS-99.0 grade) with 100 ml of 10% NH_4HF_2 at 80–90°C. The insoluble residue was separated from the solution by filtration. The precipitation of scandium from NH_4HF_2 solution was examined with solutions containing 0.6–2 g l^{-1} scandium as an example.

The Sc(III) and Na(I) concentrations in the solutions were determined by the inductively coupled plasma emission spectrometry on a Labtam V-310 Plasma Spectrometer and a Perkin-Elmer AAnalyst 300 atomic absorption spectrometer. The lower determination limit of the elements was 10^{-6} %, and the determination error did not exceed 20%. The F^- and NH_4^+ concentrations in the solutions were determined with an ANION-410 pH-meter/ion meter and ELIS-131 F and ELIS-121 NH_4 ion-selective electrodes. The X-ray phase analysis was carried out on a DRON-3 automated X-ray diffractometer with monochromatized CuK_α radiation. The resulting spectra were processed using a software package for X-ray analysis of polycrystalline solids [11]. We determined the phase composition of the samples, as well as the lattice constants (the latter, with the accuracy $\Delta a/a$ = 0.0015).

Ivanov–Emin et al. [5] reported that, in NH_4F solution, Sc(III) occurs in the form of hexafluoroscandate ion, which is apparently true for NH_4HF_2 solution as well. Introduction of sodium fluoride, either solid or in the form of solution, into an ammonium hydrogen difluoride solution containing the hexafluoroscandate ion causes formation of a scandium-containing precipitate.

We examined the degree of precipitation of scandium with crystalline sodium fluoride in relation to the initial concentration of Sc(III) in solution and to the molar ratio of Na to Sc m. Figures 1 and 2 show respectively how the degree of precipitation of scandium from 10% NH_4HF_2 solution with sodium fluoride varies with the Sc(III) concentration in the initial solution at different molar ratios m and with the molar ratio m at different Sc(III) concentration in the initial solution.

It is seen that, at Sc(III) concentrations under 0.5 g l^{-1}, scandium precipitation is incomplete; in the concentration range 0.5–1.5 g l^{-1} precipitation requires a considerable amount of the precipitation agent; and at the Sc(III) concentration of 1.5 g l^{-1} and above the degree of precipitation from the NH_4HF_2 solution reaches 96% even at m = 1.5.

The precipitates resulted from introduction into solution of Sc(III) in 10% NH_4HF_2 of solid NaF under stirring and of a NaF solution have different compositions, specifically, within the m = 1–14 range they are represented by a mixture of ScF_3, Na_3ScF_6, and $Na(NH_4)_2ScF_6$ (Table 1). Figure 3 shows the line diagram of the powder patterns for the components of the mixture obtained in experiment no. 4.

These results suggest proceeding of the following reactions upon introduction of sodium fluoride into an NH_4HF_2 solution:

$$(NH_4)_3ScF_6 + NaF = Na(NH_4)_2ScF_6 + NH_4F, \quad (1)$$

$$(NH_4)_3ScF_6 + 3NaF = Na_3ScF_6 + 3NH_4F. \quad (2)$$

A variable number of phases obtained under close precipitation conditions is evidently associated with high local supersaturations occurring both during introduction of solid sodium fluoride and in solution.

Table 1. Precipitation of Sc(III) from 10% NH_4HF_2 solution with sodium fluoride at 20°C. The precipitate composition was determined by X-ray phase analysis accurately to within 0.1%, except for experiment nos. 1, 3, and 7

Exp. no.	Initial concentration of Sc, g l^{-1}	m	Precipitate composition,[a] %				Precipitated Sc, %
			ScF_3	Na_3ScF_6	$Na(NH_4)_2ScF_6$	NaF	
1	0.67	1	~20	~25	~55	–	Not determined
2	1.0	1.3	11.9	20.3	67.8	–	″
3	0.67	1.5[a]	~45	~45	~10	–	82.1
4	1.0	1.5	7.2	6.2	86.6	–	Not determined
5	1.5	1.5	100	–	–	–	95.7
6	1.8	1.5	5	8	87	–	Not determined
7	0.67	3	~20	~22	~58	–	91.0
8	1.5	3	30.4	46.0	23.6	–	99.4
9	1.5	4.5	3.9	10.1	84.2	1.9	95.1
10[b]	1.5	9	24.5	28.8	10.8	28.4	96.9
11[b]	1.5	14	6.2	24.4	7.3	59.6	99.4

[a] Precipitated with 4% solution of sodium fluoride. [b] The rest is sodium fluorosilicate from ammonium hydrogen difluoride and sodium fluoride.

Table 2. Degree of decomposition of complex scandium fluoride with water at different liquid to solid ratios ($T = 20°C$)

l/s, ml g^{-1}	Degree of salt decomposition, %	Na/Sc molar ratio in the precipitate
150	24.0	2.7 (mixture of $NaScF_4$ with Na_3ScF_6)[a]
250	68.7	1.1 (mixture of $NaScF_4$ with Na_3ScF_6)
300	73.5	1.0 ($NaScF_4$)
400	75.2	0.9 (mixture of $NaScF_4$ with ScF_3)
500	89.5	0.4 (mixture of $NaScF_4$ with ScF_3)

[a] Given in parentheses is the composition of the compounds, determined by X-ray phase analysis.

At $m \geq 4.5$ the precipitate contains sodium fluoride, which is due to the achievement of the salt solubility limit.

The presence of scandium(III) fluoride in the mixture may be associated with involvement of the most stable ScF^{2+} ion (stability constant 10^7 [12]) into interaction by the following scheme:

$$ScF^{2+} + HF_2^- \rightarrow ScF_3 + H^+ \qquad (3)$$

or with incongruent dissolution of the resulting complex salts.

To determine the conditions conducive to decomposition of complex fluoride Na_3ScF_6 we examined the interaction of a mixture of Na_3ScF_6 and NaF (it was obtained by the reaction of a scandium(III) chloride solution with an overstoichiometric amount of sodium fluoride, the total composition being 3.2 $NaF \cdot ScF_3$) with water at different liquid to solid ratios. The time of establishment of equilibrium was identified from a constant concentration of the F^- ion in solution. The degree of decomposition of the salt was determined from the loss in the precipitate weight during the experiment.

Our results (Table 2) suggest incongruent dissolution of Na_3ScF_6 in water with formation of sodium

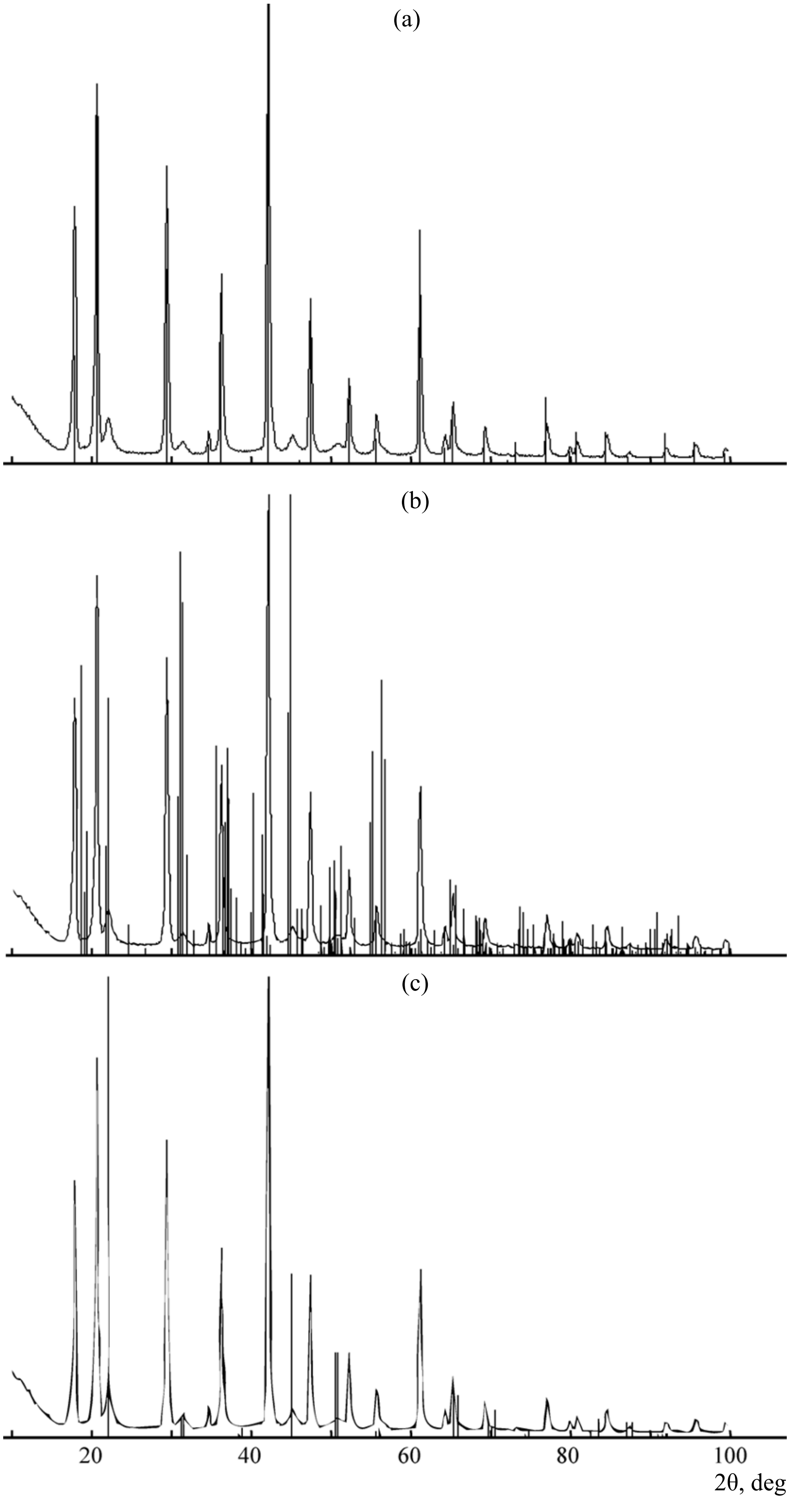

Fig. 3. Line diagrams of the X-ray powder diffraction patterns of (a) $Na(NH_4)_2ScF_6$ (structural type cF72/5), (b) Na_3ScF_6 (structural type mP20/13), and (c) ScF_3 (structural type hR4/10). (2θ) Bragg's angle.

tetrafluoroscandate, as well as its decomposition by the following schemes:

$$Na_3ScF_6 \rightleftarrows NaScF_4 + 2NaF, \qquad (4)$$

$$NaScF_4 \rightleftarrows ScF_3 + 2NaF. \qquad (5)$$

However, even at large liquid to solid ratios we obtained a mixture of $NaScF_4$ with ScF_3.

Treatment of the initial mixture of scandium fluorides with 1% HCl solution at 70°C at the liquid to solid ratio of ca. 50 (w/w) for 30 min led to a two-step formation of scandium(III) fluoride. A similar result (under identical conditions) was obtained upon treatment of the salt mixture with 1% nitric acid solution. Treatment of the precipitates obtained in experiment nos. 7–9 (Table 1) with dilute solutions of the same mineral acids also resulted in formation of scandium(III) fluoride. These findings suggest that Na_3ScF_6, $NaScF_4$, and $Na(NH_4)_2ScF_6$ show incongruent dissolution in an acid medium by schemes (4)–(6):

$$Na(NH_4)_2ScF_6 \rightleftarrows ScF_3 + 2NH_4F + NaF. \qquad (6)$$

Apparently, the equilibrium of reactions (4)–(6) in an acid medium shifts to the right because of a decrease in the concentration of the free fluoride ion due to formation of hydrogen difluoride ion HF_2^-.

Our results allow interpreting the data reported in [10] as due to partial decomposition of the resulting sodium hexafluoroscandate because of incongruent dissolution of this compound with formation of a mixture of sodium hexafluoroscandate, sodium tetrafluoroscandate, and possibly scandium(III) fluoride.

CONCLUSIONS

(1) It was found that introduction of sodium fluoride into a solution of ammonium hexafluoroscandate in NH_4HF_2 at molar ratios of F to Sc within 1–14 leads to formation of the precipitate consisting of a mixture of ScF_3, Na_3ScF_6, and $Na(NH_4)_2ScF_6$ in different ratios.

(2) It was shown that Na_3ScF_6 undergoes incongruent dissolution in water with formation of sodium tetrafluoroscandate.

(3) Incongruent solubility in water and dilute solutions of mineral acids with formation of scandium(III) fluoride was revealed for $NaScF_4$ and $(NH_4)_2NaScF_6$.

ACKNOWLEDGMENTS

The authors are grateful to V.G. Miskar'yants from GIREDMET Federal State Unitary Enterprise and T.A. Sviridova from the Center for Composite Materials, Moscow Institute of Steel and Alloys, National Research Technological University, for assistance in conducting the studies.

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