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Solubility of β-$FeF_3 \cdot 3H_2O$ in Mixtures of Nitric and Hydrofluoric Acid

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The solubility of β-$FeF_3 \cdot 3H_2O$ has been measured in solutions with different concentrations of nitric acid (0 to 7 *m*) and hydrofluoric acid (1 to 6 *m*) at the temperatures of (30, 40, and 50) °C. The total iron concentration at equilibrium was measured with inductively coupled plasma (ICP) spectroscopy. The solubility was evaluated in terms of the stepwise complexation of iron by fluoride ions at different ionic strength and temperature. The solubility of β-$FeF_3 \cdot 3H_2O$ increases with decreasing concentration of HF and HNO_3 and increasing temperature.

Introduction

Pickling is used to clean and condition metal surfaces. During the finishing of stainless steel, the steel is typically rolled and then annealed to achieve the desired structure and material properties. Since the annealing heat treatment is carried out in the presence of air, an adherent oxide scale layer forms on the surface. Chromium migrates to the oxide layer to a greater extent than iron, and a zone that is depleted of chromium is normally formed under the oxide film. To remove the scale and the chromium-depleted layer, the stainless steel is pickled in a solution containing approximately (1 to 3) $mol \cdot L^{-1}$ nitric acid and (1 to 3) $mol \cdot L^{-1}$ hydrofluoric acid, at about (40 to 60) °C. During pickling the acid migrates to the steel surface through cracks in the oxide layer and oxidizes the metal surface. In the reaction, NO_x gases are formed, which helps the adherent oxide layer to fall off the surface. Fresh acid has to be added to keep the acid concentration approximately constant. The metal content of the mixed acid pickling solution increases during pickling. The pickling acid must be replaced before metal fluoride salts begin to crystallize out of the solution since it is a very time-consuming, messy, and hazardous task to regularly empty the pickling tank and clean the strongly adhering sludge from the tank.

Several different regeneration and purification systems have been proposed in order to be able to reuse the acid. The two principle processes developed for purification are acid retardation and diffusion dialysis. In Sweden, acid retardation systems are employed for the major coil and plate pickling operations. The waste acid is neutralized with lime; a process that reduces the metal and fluoride content by precipitation, and metal hydroxide sludge is obtained. Pickling processes generate about 18000 t/yr of metal hydroxide sludge in Sweden. At present the sludge is put into deposits. Commercial processes in use today to recover components from spent pickling baths are the OPAR (Outokumpu Pickling Acid Recovery) process, the Kawasaki process, and the Pyromars process.[1] In the OPAR process, sulfuric acid is added to the spent pickling solution, and the metals are recovered as metal sulfates. The Kawasaki process recovers the acid by solvent extraction. In the Pyromars process, the acids evaporate, and the metal fluorides and nitrates decompose at high temperatures (i.e., 400 °C) into metal oxides. All these processes have very high installation and running costs.[1]

The aim of this project is to develop a method to separate the metals from spent HF + HNO_3 pickle liquors by crystallization of metal fluorides. The metal fluorides can then be thermally hydrolyzed into hydrofluoric acid and metal oxides. In this approach, both acids and metals will be recovered and reused, and the consumption of neutralization agents will be eliminated. The crystallization of iron, chromium, and nickel fluoride hydrates is however not well-investigated.

Iron fluorides are the most abundant metal species in spent HF + HNO_3 pickle liquors. During pickling of stainless steels in mixed acid, the pH is below the range for hydroxide precipitation. Experiments have shown that trivalent iron crystallizes as $FeF_3 \cdot 3H_2O$ and $(FeCr)F_3 \cdot 3H_2O$ at the temperature interval of interest, (20 to 60) °C.[1,2] Iron fluoride trihydrate precipitates from mixed acid in the two polymorphic forms: α-$FeF_3 \cdot 3H_2O$ and β-$FeF_3 \cdot 3H_2O$.[3] The β-form is the stable form at the temperature interval studied here, (30 to 50) °C. In the temperature range (30 to 50) °C, no solubility data of β-$FeF_3 \cdot 3H_2O$ or α-$FeF_3 \cdot 3H_2O$ in hydrofluoric acid solutions with varying nitric acid concentrations have been found in the literature. Tananaev and Deichman[32] have reported solubility measurements of $FeF_3 \cdot 3H_2O$ in (0.5 to 35) $mol \cdot L^{-1}$ hydrofluoric acid at 25 °C.[4] Solubility of $FeF_3 \cdot 3H_2O$ in hydrofluoric and nitric acid mixtures have been reported by Kaneko et al.[5] at 20 °C for (0.2 to 4) $mol \cdot L^{-1}$ HF and (3 to 6) $mol \cdot L^{-1}$ HNO_3 and by Takahari et al.[6] at 60 °C for (0.3 to 8) $mol \cdot L^{-1}$ HNO_3 and (1 to 8) $mol \cdot L^{-1}$ HF. The solubility of $FeF_3 \cdot 3H_2O$ at 150 $g \cdot L^{-1}$ HNO_3 (2.4 $mol \cdot L^{-1}$) and different amounts (0 to 40) $g \cdot L^{-1}$ of "excess HF" has been determined by Kreppler at (20 to 90) °C.[7] In all these papers the authors have not been specific about the properties of the solid phase. From the results of Takahari et al.,[6] only approximate solubilities can be deduced. The structure of ferric fluoride hydrate crystals have been investigated,[8−12] especially due to their unusual magnetic behavior. Solution chemistry of HF + HNO_3 + Fe(III) solutions has been investigated by different chemical analysis methods and by computer simulation.[2,13−18]

Experimental Section

β-$FeF_3 \cdot 3H_2O$ was prepared by dissolving freshly precipitated ferric hydroxide in 20 % mass fraction hydrofluoric acid followed by evaporation at 50 °C.[3,12] The ferric hydroxide was

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precipitated from an iron nitrate solution, prepared from $Fe(NO_3)_3\cdot 9H_2O$ (p.a., > 99 %), by dropwise addition of ≈25 % mass fraction ammonium hydroxide solution (p.a.) at room temperature. The precipitate was vacuum filtered and washed with deionized water to eliminate the ammonia excess. The ferric hydroxide was added to high-density polyethylene (HDPE) wide-mouth bottles filled with 20 % mass fraction hydrofluoric acid held at 50 °C. The ferric hydroxide easily dissolved in less than 5 min mixing time leaving a clear solution. The solutions were then concentrated by evaporation at (50 ± 0.01) °C in a thermostatic water bath (Julabo MD), which by the time yielded a precipitation of pink crystals. The pink precipitate was vacuum filtered and washed with water at 50 °C and dried by leaving the crystal mass for several days in an open bottle in the water bath at 55 °C or in an incubator at 60 °C. The crystals were identified by single-crystal X-ray diffraction (Bruker-Nonius KappaCCD single-crystal diffractometer).

Different acid mixtures consisting of HF from (1 to 6) $mol\cdot kg^{-1}$ and HNO_3 from (0 to 7) $mol\cdot kg^{-1}$ were used in the solubility measurements. Two parallel series of experiments were performed at each temperature, using the same set of a total of 16 different acid mixtures; thus resulting in two measurements (two different test tubes) for each acid mixture. In addition, at 50 °C a total of 19 more experiments using a second set of nine different acid mixtures was performed. The different acid mixtures were added to 14 mL polypropylene (PP) test tubes filled with β-$FeF_3\cdot 3H_2O$ crystals. The test tubes were closed with stoppers and also sealed up with Parafilm to prevent evaporation losses. The test tubes were placed in a water bath (Julabo MD, ± 0.01 °C). Each solution was stirred with a magnetic stir bar. The $HF + HNO_3$ solutions were prepared in 125 mL HDPE wide-mouth bottles by weighing appropriate volumes of 65 % mass fraction HNO_3 (Merck, Gr. for analysis, ISO), 40 % mass fraction HF (Sigma-Aldrich, Reag. ISO, Reag. Ph. Eur.), and filtered water (0.2 μm, Schleicher & Schuell) using a balance with a sensitivity of ± 0.1 mg (Mettler AE 260). The acid concentration given in the certificate of analysis for the particular batches of HNO_3 (65.4 % mass fraction) and HF (40.1 % mass fraction) was used in calculating solution concentrations. All the solutions were kept in a dark hood to prevent decomposition of the nitric acid.

All the samples were equilibrated for at least 7 d. Analyses after up to 14 d gave equal solubility curves as after 7 d. After equilibration, the solutions were left without stirring, and the solutions and solids were separated by settling overnight. The next day a clear saturated solution was carefully drawn out of each test tube using a preheated syringe (heated in an incubator to the same temperature as the solution). A number of samples were also filtered through preheated 0.2 μm PVDF syringe filters (Acrodisc). However, no difference in the iron concentrations was observed using unfiltered or filtered solutions. The samples were immediately diluted in two steps with deionized water to a concentration range of (1 to 10) mg/L Fe(III). The samples were analyzed for total iron using inductively coupled plasma atomic emission spectroscopy (ICP-AES JY 24, Jobin Yvon). The measurements were made at 239.204 nm. Calibration curves for the ICP measurements were made using an iron standard solution of Fe(III) in 0.5 $mol\cdot L^{-1}$ HNO_3 (Merck, CertiPUR).

Chemical Speciation

The goal with the speciation calculations was to find the solubility constants for β-$FeF_3\cdot 3H_2O$ at different temperatures and ionic strength. The computer program SSPEC was used in the speciation calculations. SSPEC is a computer program developed at U.S. Bureau of Mines to calculate chemical speciation in mixed acid pickle bath solutions.[15] The program uses 17 equilibrium equations together with mass and charge balance equations for given total mass concentrations of nitrate, fluoride, iron(III), chromium(III), and nickel(II) ions. There are no solid-phase equilibria incorporated in the program. SSPEC performs the speciation according to the conditional stability constants and total concentrations of the components in the solution, which are given by the user. The SSPEC program itself do not estimate activity coefficients or introduce corrections for ionic strength. Hence, we use conditional stability constants that have been determined at the same temperature and in the same medium[19] and effective ionic strength as the solutions of interest or have been recalculated to these conditions. For the evaluation of the solubility data, the needed conditional stability constants could be found as a function of ionic strength, except for iron nitrate where only two conditional stability constant values were found. Stepwise stability constants for the iron complexes are given as follows:

$$FeF_{n-1}^{+3-(n-1)} + F^- \leftrightarrows FeF_n^{+3-n}$$

$$K_n(FeF_n^{+3-n}) = \frac{[FeF_n^{+3-n}]}{[FeF_{n-1}^{+3-(n-1)}] \times [F^-]} \quad 1 \le n \le 6 \qquad (1)$$

In SSPEC, overall stability constants are used. The overall stability constant (β) is the product of the stepwise constants. By using the total iron, fluoride, and nitrate concentrations for the solutions at equilibrium in the speciation calculations with SSPEC, the concentrations of the species at equilibrium were obtained. The results of the speciation calculations for the solubility measurements were then evaluated in terms of the following equilibria involving the solid phase:

$$FeF_3(s) + (3-n)H^+ \leftrightarrows FeF_n^{+(3-n)} + (3-n)HF$$

$$K_{sn} = \frac{[FeF_n^{+(3-n)}] \times [HF]^{(3-n)}}{[H^+]^{(3-n)}} \quad 1 \le n \le 3 \qquad (2)$$

In the experiments, solid crystals of β-$FeF_3\cdot 3H_2O$ are used, which is the thermodynamically stable phase of $FeF_3\cdot 3H_2O$ in the temperature range studied.[9] Therefore, the activity of the solid phase is assumed to remain constant as the solution composition varies.

In equilibrium with the solid phase, the concentration of $FeF_3(H_2O)_3(aq)$ is constant for different total iron and fluoride concentrations if changes in ionic strength and medium effects are neglected. The solubility constants can be obtained by taking the average of the $FeF_3(H_2O)_3(aq)$ concentration or as the slope in a plot of the concentration of $[FeF_n^{+(3-n)}]$ against $[H^+]^{(3-n)}/[HF]^{(3-n)}$ for $n = 1$ or 2 (eq 2) in solutions at equilibrium with β-$FeF_3\cdot 3H_2O$ crystals at specific temperatures and ionic strengths.

By using conditional stability constants in SSPEC taken at the same ionic strength as the nitric acid concentration for each series of solubility data, the distribution of species could be approximately evaluated. The effective ionic strength was then calculated, and SSPEC was run again with conditional stability constants corresponding to this ionic strength. The procedure was repeated until a difference in ionic strength of less than 0.1 $mol\cdot kg^{-1}$ was obtained. The solubility data were evaluated using two different sets of conditional stability constants. In the first set (set 1), the conditional stability constants for HF at

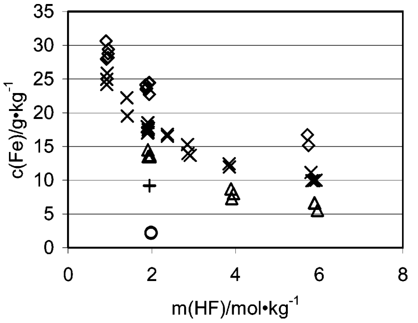

Figure 1. Solubility of β-FeF_3·$3H_2O$ at 50 °C, $m(HNO_3)$/mol·kg^{-1}: ◇, 1; ×, 2; △, 3; +, 4; ○, 7.

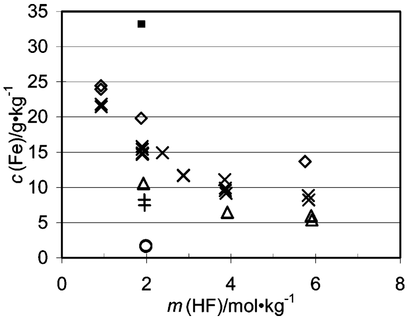

Figure 2. Solubility of β-FeF_3·$3H_2O$ at 40 °C, $m(HNO_3)$/mol·kg^{-1}: —, 0; ◇, 1; ×, 2; △, 3; +, 4; ○, 7.

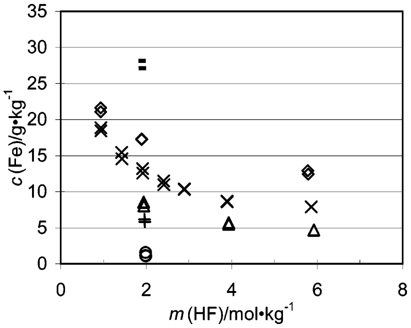

Figure 3. Solubility of β-FeF_3·$3H_2O$ at 30 °C, $m(HNO_3)$/mol·kg^{-1}: —, 0; ◇, 1; ×, 2; △, 3; +, 4; ○, 7.

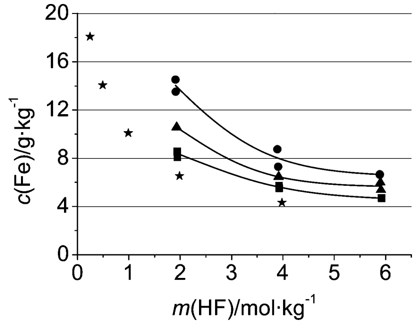

Figure 4. Comparison of solubility in 3 mol·kg^{-1} HNO_3 solutions at different temperatures with data reported by Kaneko et al.[5] at 3.1 mol·kg^{-1} HNO_3 at 20 °C. *T*/°C: ●, 50; ▲, 40; ■, 30; ★, 20.

different ionic strengths were obtained by interpolation of values reported in IUPAC chemical data series critical review of fluoride conditional stability constants prepared by Bond and Hefter.[20] In this way the conditional stability constant for HF at 2 mol·L^{-1} became similar to the conditional stability constants given in SSPEC for which Fernando[15] found the best agreement with measured concentrations at an ionic strength of about 2 mol·L^{-1}. In the second set (set 2), conditional stability constants for HF were obtained by interpolation of conditional stability constant data as a function of ionic strength for measurements in $NaNO_3$ solutions at 25 °C reported by Hammer.[17] The conditional stability constants for HF_2^- in sets 1 and 2 were obtained by interpolation of all the recommended data reported in the IUPAC chemical data series above an ionic strength of 1 mol·L^{-1}. For the chemical equilibria of nitric acid in both sets 1 and 2, the mean activity coefficients were calculated as a function of ionic strength and temperature using the method of Pitzer and co-workers,[21,22] employing the Pitzer parameters obtained by Kobylin[13,14] and the nitric acid thermodynamic stability constant -1.204 *m*, calculated using $G°(HNO_3) = -251049.5$ J·mol^{-1} and $G°(NO_3^-) = -250588.6$ J·mol^{-1} at 298.15 K.[14] Stability constants $K_1(FeF^{+2})$ and $K_2(FeF_2^+)$ were calculated by the method of Gallagher,[23] using values of the average number of fluorides associated with iron ions and HF/H^+ given by Hammer[17] in 0.96 mol·L^{-1} HNO_3 and 2.88 mol·L^{-1} HNO_3 solutions at 45 °C and 60 °C. From these values the stability constant values (K_n, eq 1, $n = 1, 2$) in the present study were interpolated. Values of $K_3(FeF_3)$, $K_4(FeF_4^-)$, and $K_5(FeF_5^{-2})$ were obtained by using a general correlation,[24] which states that the logarithm of the successive ratios decreases by a constant value. All the conditional stability constants for which enthalpy data could be found were adjusted to the current temperature by means of the van't Hoff equation or directly in the Pitzer activity coefficient calculations. The enthalpy data for the iron fluoride complexes were taken from the IUPAC chemical data series. For HF and HF_2^-, the following values were employed: $\Delta H_r(HF) = 13.2$ kJ·mol^{-1} and $\Delta H_r(HF_2^-) = 3$ kJ·mol^{-1}.[20]

Results

X-ray diffraction analyses identified β-FeF_3·$3H_2O$ to be the solid phase used as a starting material in the solubility experiments.[12] The solubility was measured as the total iron concentration at equilibrium. Figures 1 to 4 show the solubility of β-FeF_3·$3H_2O$ in different acid mixtures at 50 °C, 40 °C, and 30 °C, respectively. Figure 4 shows the solubility of β-FeF_3·$3H_2O$ at the different temperatures for 3 mol·kg^{-1} HNO_3. The hydrofluoric acid concentration in Figures 1 to 4 is the concentration in which β-FeF_3·$3H_2O$ was dissolved, corrected for the dissolved crystal mass as c_{HF} [mol/(kg of solvent)]·1000/(1000 + $m_{FeF_3\cdot 3H_2O}$ [kg]). The hydrofluoric acid and nitric acid concentrations are given as mol/(kg of solution). Solubility data by Kaneko et al.[5] have been recalculated from mol/(kg of H_2O) to mol/(kg of solution) and are included in Figure 4 for comparison. The solubility of β-FeF_3·$3H_2O$ increases with increasing temperature and decreases with increasing concentration of hydrofluoric acid and nitric acid.

All the conditional stability constants used in the chemical speciation calculations are presented in Table 1. A linear relationship was always found when plotting $[FeF_n^{+(3-n)}]$ against $[H^+]^{(3-n)}/[HF]^{(3-n)}$ for both sets of conditional stability constants (Table 1). By small changes in $K_2(FeF_2^+)$ (eq 1), within the range of reported values, the slopes at 30 °C were adjusted so that the lines passed through the origin. In the evaluation of the data at 40 °C and 50 °C, the obtained value of K_2 at 30 °C was used, corrected to the current temperature as described above. Observe that the ionic strength is assumed to be constant although the hydrofluoric acid concentration varies. This is acceptable since hydrofluoric acid is a weak acid and poorly dissociated ($pK_a \approx 3$). The results of the evaluation are presented in Figures 5 to 7 and in Tables 2 and 3. In Tables 2 and 3, solubility constants expressed by eq 2 ($n = 2$) obtained

Table 1. Conditional Stability Constants at 25 °C Used in the Speciation Calculations[a]

species	log *K* at *I*/mol·kg^{-1} 1.0	1.8	2.7
	Set 1		
HF	2.95	3.10	3.26
HF_2^-	0.644	0.758	0.872
FeF^{2+}	5.085	5.095	5.150
FeF_2^+	3.82	3.90	4.10
FeF_3	2.56	2.71	3.05
FeF_4^-	1.29	1.51	2.00
FeF_5^{2-}	0.025	0.315	0.950
HNO_3	−1.455	−1.414	−1.355
$FeNO_3$	0.76	1.00	1.00
	Set 2		
HF	2.93	2.94	3.05
HF_2^-	0.644	0.758	0.872
FeF^{2+}	5.085	5.095	5.150
FeF_2^+	3.81	3.85	4.00
FeF_3	2.535	2.605	2.850
FeF_4^-	1.26	1.36	1.70
FeF_5^{2-}	−0.015	0.115	0.550
HNO_3	−1.455	−1.414	−1.355
$FeNO_3$	0.76	1.00	1.00

[a] All the values are tabulated as stepwise constants. In SSPEC, overall stability constants (β) are used.

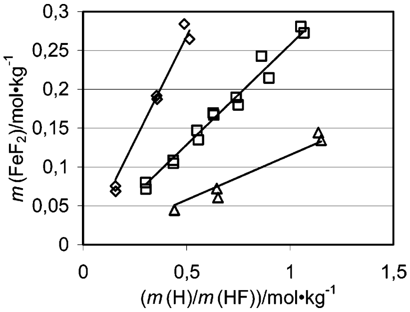

Figure 5. Graphical evaluation of solubility constants, K_{s2}, at 50 °C (set 1) evaluated at three different ionic strengths *I*/mol·kg^{-1}: ◇, 1.0; □, 1.8; △, 2.7.

by the first and second set of conditional stability constant data respectively at 30 °C, 40 °C, and 50 °C are summarized.

The total iron concentration at equilibrium can be calculated as a function of free fluoride concentration from the following expression:

$$\mathrm{Fe_{tot}} = \frac{K_{s2}}{K_{HF}\beta_2}\left(\frac{1}{F^3} + \frac{\beta_1}{F^2} + \frac{\beta_2}{F} + \beta_3 + F\beta_4 + F^2\beta_5\right) \qquad (3)$$

where the overall stability constants for the iron fluoride complexes β_n are used, expressed as follows:

$$\beta_n = \frac{[\mathrm{FeF}_n^{+(3-n)}]}{[\mathrm{Fe}^{3+}][\mathrm{F}^-]^n} \quad 1 \le n \le 6$$

Figure 8 shows the measured total iron concentration plotted at the corresponding free fluoride concentrations calculated by SSPEC together with calculated values of the total iron concentration as a function of free fluoride concentration using eq 3. The figure shows how the equation (with the constants obtained from the experimental data) fits the data at 30 °C. The stepwise stability constants for iron fluoride in Table 1 from set 1 were changed to overall constants and used in the calculations together with the solubility constants from Table 2. The nitric acid concentrations (1, 2, and 3) mol·kg^{-1} corresponds to the ionic strength (1.0, 1.8, and 2.7) mol·kg^{-1}, respectively.

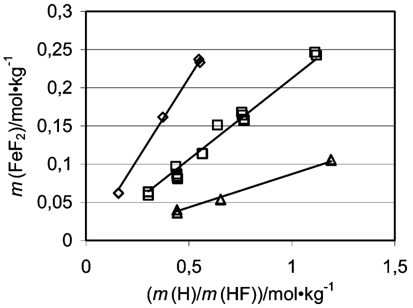

Figure 6. Graphical evaluation of solubility constants, K_{s2}, at 40 °C (set 1) evaluated at three different ionic strengths *I*/mol·kg^{-1}: ◇, 1.0; □, 1.8; △, 2.7.

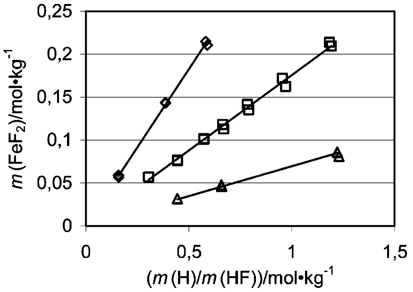

Figure 7. Graphical evaluation of solubility constants, K_{s2}, at 30 °C (set 1) evaluated at three different ionic strengths *I*/mol·kg^{-1}: ◇, 1.0; □, 1.8; △, 2.7.

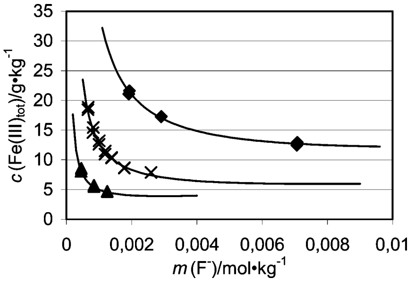

Figure 8. Degree of fit of eq 3 at 30 °C, $m(HNO_3)$/mol·kg^{-1}: ◆, 1; ×, 2; ▲, 3.

Table 2. Set 1, Solubility Constant K_{s2} at Different Temperatures and Ionic Strengths

I/mol·kg^{-1}	K_{s2} at *T*/°C 30	40	50
1.0	0.37	0.43	0.54
1.8	0.18	0.21	0.26
2.7	0.069	0.087	0.12

Table 3. Set 2, Solubility Constant K_{s2} at Different Temperatures and Ionic Strengths

I/mol·kg^{-1}	K_{s2} at *T*/°C 30	40	50
1.0	0.37	0.43	0.54
1.8	0.17	0.20	0.25
2.7	0.072	0.089	0.12

Discussion and Conclusions

Solubility Data. The solubility values obtained in this study are in agreement with those of Kaneko et al.,[5] although Kaneko et al. did not specify the polymorphic form of the solid. The results also agree with those of Krepler at 2.4 mol·L^{-1} HNO_3 (ca. 2.1 mol·kg^{-1} HNO_3) and 0 to 2 mol·L^{-1} HF (ca 0 to 1.7

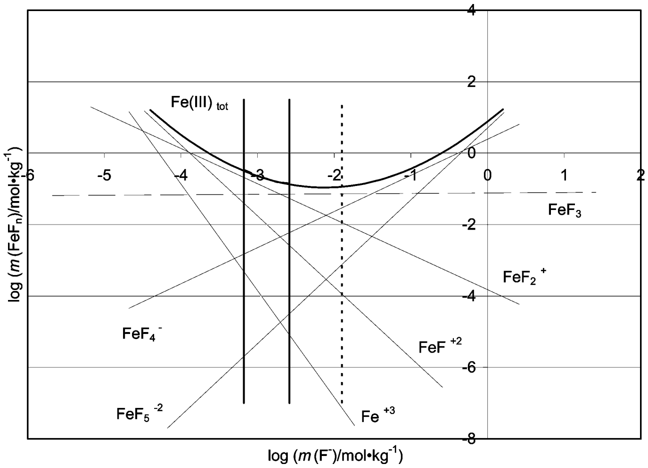

Figure 9. Iron fluoride species distribution ($n = 0$ to 5) with varying free fluoride ion concentration at equilibrium in a 2 mol·kg^{-1} HNO_3 solution at 30 °C and a calculated ionic strength of 1.85 mol·kg^{-1}. The measurement interval is marked with two solid vertical lines. The dotted vertical line marks the fluoride concentration above which $FeF_3·3HF·3H_2O$ might precipitate.

mol·kg^{-1} HF). The solubility data at 60 °C obtained by Takahari et al.[6] are scattered; therefore, no reliable comparison could be made with these data. The β-phase is the thermodynamically stable form of $FeF_3·3H_2O$ in the temperature interval studied here, (30 to 50) °C, and also at room temperature,[9] although the α-$FeF_3·3H_2O$ will usually precipitate first in a supersaturated solution at temperatures below about 30 °C. Often the product is a mixture of α-$FeF_3·3H_2O$ and β-$FeF_3·3H_2O$ due to precipitation of the α-phase if the temperature falls during filtration.[9] To prevent precipitation during filtration, the crystal samples were washed with water and filtered and dried at 50 °C. Furthermore, in preparation of the saturated solution a large amount of crystal mass was dissolved in each test tube, and it is very probable that possible traces of α-$FeF_3·3H_2O$, having a higher solubility than the stable β-phase, would have dissolved completely leaving only the stable β-phase in equilibrium with the solution.

The solubility of β-$FeF_3·3H_2O$ increases with increasing temperature and decreases with increasing concentration of hydrofluoric acid and nitric acid within the experimental range (Figures 1 to 4). In the range studied, the total iron concentration at equilibrium ranges from about (1 to 35) g/kg solution depending on temperature and acid concentration. In a solution of 2 mol·kg^{-1} HF and 3 mol·kg^{-1} HNO_3 at 50 °C, the decrease in solubility from increasing the nitric acid concentration 1 mol·kg^{-1} is comparable to the decrease in solubility by lowering the temperature by 15 K. The solubility is more sensitive to temperature changes at higher temperatures and at lower hydrofluoric acid concentration. The solubility is more sensitive to changes in nitric acid concentration at lower HNO_3 and HF concentrations. The decrease in solubility as a result of increased acid concentrations can be explained by examining the chemical speciation in the solutions. In Figure 9, the concentration of iron complexes is plotted as a function of the concentration of free fluoride at equilibrium expressed using iron complexes up to $FeF_5(H_2O)$, neglecting variations in ionic strength and activity of β-$FeF_3·3H_2O$ with variations in hydrofluoric acid concentration. The figure shows the distribution of iron fluoride complexes at different free fluoride ion concentrations in a solution at equilibrium with β-$FeF_3·3H_2O$ crystals at 30 °C.

As can be seen, the total iron concentration forms a U-shaped curve. The total iron concentration decreases as the free fluoride concentration increases up to a point where negatively charged iron complexes are extensively formed, and then the total iron concentration starts to increase as the fluoride concentration increases. Under the conditions of this work, no significant amount of anionic species was formed, and only one side of the U-shaped dependence was observed.

As the nitric acid concentration increases, the free FeF_3(aq) concentration decreases and the total solubility is lowered. The solubility increases with increasing temperature.

In Figure 9, it can be recognized that the total iron solubility starts to increase at 13 mol·kg^{-1} HF ($\log(c(F^-)/mol·kg^{-1}) = -2.2$). This is approximately the same hydrofluoric acid concentration as where the total iron solubility starts to increase in the experiments reported by Tananaev and Deichman.[32] The results should be comparable at least at the lower fluoride concentrations due to the small variation in the first three iron fluoride stability constants (K_1−K_3) with ionic strength. The extrapolated curve ($Fe(III)_{tot}$) drawn at free fluoride concentrations above 10^{-2} mol·kg^{-1} might not express the total iron solubility since the solid phase at such high hydrofluoric acid concentrations might be $FeF_3·3HF·3H_2O$ and not β-$FeF_3·3H_2O$.[32]

Chemical Speciation. The goal with the speciation evaluation was to determine solubility constants in order to be able to find an expression for the solubility that is applicable to solutions where several additional fluoride equilibria, for example, chromium fluoride equilibria, exist. To get correct speciations using SSPEC, it is necessary to use conditional stability constants valid in the solution to be specified. Many authors have studied the chemical speciation in pickle bath solutions.[2,13−16] However, only two studies with measurements of iron fluoride conditional stability constants in solutions of nitric acid and hydrofluoric acid have been found.[17,18] In the present study, data reported by Hammer[17] was used to obtain conditional stability constants for the iron fluoride complexes. Initial iron fluoride stability constant values in this study were obtained by interpolation using the conditional stability constants obtained from Hammers data. The values in Table 1 were obtained by fitting the model to the solubility data by correcting the K_2 values and then calculating the K_3−K_5 values using a general correlation,[24] which states that the logarithm of the successive ratios decreases by a constant value. The values of $K_1(FeF^{+2})$ measured by Eriksson and Lunner[18] agree very well with Hammers data while the values of $K_2(FeF_2^+)$ are much lower. All the conditional stability constants for the iron complexes were also compared with values determined in other media found in the literature.[20,25,26] The logarithm of the iron fluoride conditional stability constants found in the literature decreased by a constant value.[24] This confirms that there is no major change in the structure and bonding at the metal center for higher order iron fluoride complexes. Since fluoride has almost no bridging properties,[24,29] possible polynuclear Fe−F species in the solution are neglected. Many authors have reported conditional stability constants for hydrofluoric acid at different ionic strength. Only one report of measurements in $NaNO_3$ solutions at higher ionic strength was found.[17]

It is possible to use the methods of Kusik and Meissner[27] and Bromley[28] in order to adjust stability constants for ionic strength. However, the methods of Kusik and Meissner and Bromley are developed for the treatment of strong electrolytes, and much care must be taken when trying to apply these theories for systems with weak electrolytes as HF and iron fluoride complexes.[19,21,30] Belaustegi et al.[19] developed a modified Bromley methodology and determined interaction parameters for equilibrium of iron(III) and the halide ligands Cl^-, Br^-, and F^- in aqueous solution. However, the parameters for FeF_2^+ could not be calculated since there are not enough conditional stability constant data for this complex.[19]

Unfortunately the conditional stability constants for the iron complexes and hydrofluoric acid equilibria are reported in molar units. In the evaluation, no density correction was made, and the solubility values in molal units were used together with the molar stability constants. Further the data presented by Hammer used in the iron fluoride stability constant calculations are given at constant nitric acid concentrations. The way the data are presented it is impossible to calculate the ionic strength in these solutions, thus the ionic strength has been taken to be equal to the nitric acid concentration. This approximation is acceptable since the metal ion concentration in Hammers experiments is low (generally 0.01 $mol \cdot L^{-1}$ or less) and hydrofluoric acid is a weak acid while nitric acid is a strong acid and present at high concentration. Thus, the ionic strength is approximately corresponding to the nitric acid concentration.

The free HF concentration has not been measured in the present work, but the speciation model can be compared with the measured free HF concentrations in pickle liquors reported by Fernando.[15] It turns out that the present speciation model predicts too high free HF concentrations. However, the difficulties involved in measurement of free HF concentration and the variation of measurement results depending on the analytical method have been treated in a number of papers.[6,31] The speciation calculations of Fernando predict approximately the same free HF concentrations as the present speciation model, but the scatter in the predicted concentrations is much stronger. Fernando used two sets of conditional stability constants, all taken from literature data. The constants are determined in different media and are valid at different ionic strengths between about (0.5 to 3) $mol \cdot L^{-1}$. In addition, the stability constants in the second case as written by Fernando were not consistent with the model equilibrium constant definitions. Fernando assumed that the conditional stability constants for the multiligand complexes are too low but concludes that the model (with the first set of data) generally reflects the chemistry in pickle bath solutions although further refinements are needed.

The determined solubility constants vary with ionic strength and temperature (se Tables 2 and 3). The difference in the solubility constants determined using set 1 and set 2 is larger at higher ionic strengths. This is expected because the stability constants for HF and HF_2^- used in the two sets deviate at higher ionic strengths (see Table 1). The magnitude of the solubility product K_{sn} is not greatly affected by temperature.

Equation 3 expresses the total iron solubility concentration as a function of free fluoride which can be measured by fluoride selective electrodes. It would be interesting to measure total iron concentration and free fluoride concentration in saturated solutions to check the model. However accurate measurements of free fluoride in pickle bath solutions are not easily obtained, which has been discussed in many papers[31] and been the object of many recent patents. This is why our model could be of great interest for people working with these solutions (e.g., to plan the recycling of the acid solutions or to see when there is a risk for precipitation of iron fluoride hydrate during pickling). We hope that the model will be improved by more measurements of different kinds.

Solution chemistry and phase equilibrium play a very important role in design, synthesi,s and analysis of crystallization-based separation processes involving electrolytes. To investigate the mechanisms and kinetics of crystallization, it is necessary to know the concentrations of the crystallizing species in solution. The results from the present work will be used in evaluating the results from our study of β-$FeF_3 \cdot 3H_2O$ crystallization from mixtures of hydrofluoric and nitric acid.

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