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Solubility of Boron Trifluoride in Liquid Hydrogen Fluoride

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MIXTURES of boron trifluoride in hydrogen fluoride have been used to catalyze a variety of Friedel-Crafts reactions including alkylation, isomerization, and disproportionation; they have also been used to effect separation and purification processes (*6*). Despite these varied uses, little has been reported about the composition of the catalyst phase.

The acidic nature of these catalysts depends largely on the concentration of BF_3. Such highly acidic systems are susceptible to deactivation and to dilution by the solution of basic material during the course of the reaction. These effects make the definition of the catalyst composition highly involved, and the determination of the solubility of BF_3 in HF then represents only a starting point.

In previous studies (*2, 3, 4*), the solubility of BF_3 was calculated by performing a mass balance; the experimental conditions ranged between 0° and 43° C. and 0 and 180 p.s.i. of BF_3. The present work involves the chemical analysis of the acid phase formed at 24°, 49°, and 98° C. and between 0 and 1000 p.s.i. of BF_3. Most practical catalysts would be formed under these conditions.

EXPERIMENTAL

The HF was anhydrous and of 99.9 mole % minimum purity; the BF_3 was of 99.0 mole % minimum purity. The solutions were prepared in a Hastelloy-B stirred autoclave.

To the closed reactor was added about 200 cc. of undistilled HF. The vessel was brought to temperature and the vapor pressure of HF was recorded. Boron trifluoride was added and the mixture was stirred 20 to 30 minutes to establish equilibrium. The difference between the total pressure and the vapor pressure of HF gave the BF_3 pressure. A small quantity of the liquid phase was withdrawn through a metering valve at the bottom of the reactor into methanol chilled in solid CO_2 and acetone; the sample was stored at this temperature until it was analyzed. The reactor was then pressured with more BF_3 or depressured by venting, and the stirring and sampling procedure was repeated. Usually, five or six samples were obtained in this manner from one charge of HF.

Determination of the mole fraction of BF_3 was based on hydrolysis in the presence of calcium:

$$2BF_3 + 6H_2O + 3Ca^{+2} \rightarrow 6H^+ + 2H_3BO_3 + 3CaF_2\downarrow$$

This reaction produces three hydrogen ions and one molecule of boric acid for each molecule of BF_3. The HF content of the sample is equivalent to the strong-acid titer, *A*, minus three times the boric acid titer, *B*; the BF_3 content is equivalent to the boric acid titer. The mole fraction of BF_3 is then given by $B/(A-2B)$.

The analysis was started by transferring a small sample of the alcoholic $HF\text{-}BF_3$ solution to a 150-ml. beaker containing 70 ml. of 1*M* calcium chloride, which had been cooled to 0° C. and adjusted to the methyl red end point. The resulting solution was titrated back to the methyl red end point with 0.5*M* potassium hydroxide; this neutralization established part of the strong-acid titer. The temperature was then raised and maintained at 95° C. to hydrolyze the BF_3 more rapidly. During the hydrolysis, the pH was maintained between one and four, which required neutralization to the methyl red end point at 10-minute intervals

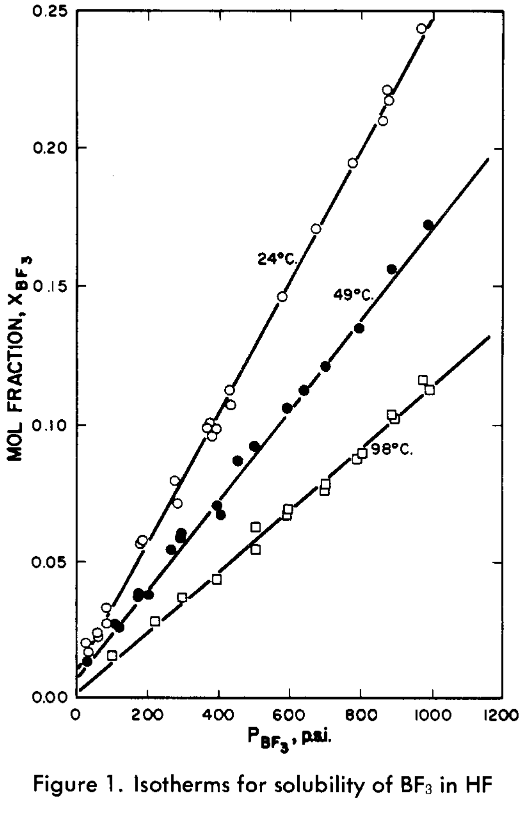

Figure 1. Isotherms for solubility of BF_3 in HF

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during the first hour, and at 30- minute intervals for 2 hours. Finally the samples were left on a steam bath overnight to ensure complete hydrolysis. At the completion of the hydrolysis, the solution was again adjusted to the methyl red end point; the strong acid was represented by the total volume of potassium hydroxide used for the neutralizations. Added mannitol (*5*) allowed the boric acid to be titrated to a pH of 8.4 with phenolphthalein.

Two tests were used to confirm the accuracy of the analytical method. In the first, a BF_3-methanol solution was analyzed in the absence and in the presence of known amounts of HF; the titer of the strong acid due to the hydrolysis was always within 3% of three times the titer of the boric acid. In the second, the method was compared with a thorium-chloranilate method (*1*) for fluoride by again hydrolyzing and analyzing a BF_3-methanol solution; differences averaged only 1.5%.

RESULTS

Results of the solubility determinations are plotted in Figure 1. The mole fraction of BF_3 depends linearly on the partial pressure of BF_3 at all three temperatures.

A least-squares analysis describes the data by:

$$x^{24}{}_{\mathrm{BF}_3} = (9.07 \times 10^{-3}) + (2.36 \times 10^{-4})P_{\mathrm{BF}_3}$$

$$x^{49}{}_{\mathrm{BF}_3} = (7.02 \times 10^{-3}) + (1.70 \times 10^{-4})P_{\mathrm{BF}_3}$$

$$x^{98}{}_{\mathrm{BF}_3} = (1.77 \times 10^{-3}) + (1.11 \times 10^{-4})P_{\mathrm{BF}_3}$$

where the mole fractions of solute BF_3 are given in terms of the pressure of BF_3 in pounds per square inch. The data may be considered as obeying Henry's law, if a subtractive adjustment is made for the intercepts.

DISCUSSION

Coordination between boron trifluoride and hydrogen fluoride is normally assumed to lead to fluoboric acid. However, the acid is not known in the free state, although its hydrate and many salts do exist (*4*). A large negative temperature coefficient of the solubility of boron trifluoride below 0° C. (*1*) gives a basis for assuming the formation of an unstable coordination compound (*6*), but the applicability of Henry's law would indicate no such formation. Complexing, if it occurred, would lead to negative deviations from the linearity shown in Figure 1. The system may therefore be considered as a simple solution and treated by the principles of vapor-liquid equilibria.

The influence of temperature on the solubility may be interpreted thermodynamically in either of two ways. For an ideal two-component system, the differential heat of solution can be calculated from the relationship between the mole fraction of solute and the absolute temperature at constant total pressure. On the other hand, if the system is treated as though BF_3 were the only component involved, the heat of vaporization can be determined from the Clausius-Clapeyron equation by relating the partial pressure to the absolute temperature at constant mole fraction. If both interpretations are valid, the differential heat of solution and the heat of vaporization should differ only in sign.

In accordance with the first interpretation, Figure 1 has been replotted as isobars with respect to BF_3 partial pressures in Figure 2. Using them instead of total-pressure isobars leads to more convenient interpolation. The differential heat of solution can best be obtained from the slope of the 1000-p.s.i. isobar, which gives a value of −2.3 kcal. per mole.

The second interpretation leads to calculation of the heat of vaporization of BF_3 at any given mole fraction. The heat was +2.2 kcal. per mole at 0.2 mole fraction BF_3 and +2.5 kcal. per mole at 0.05. These numerical values agree well with the differential heat of solution.

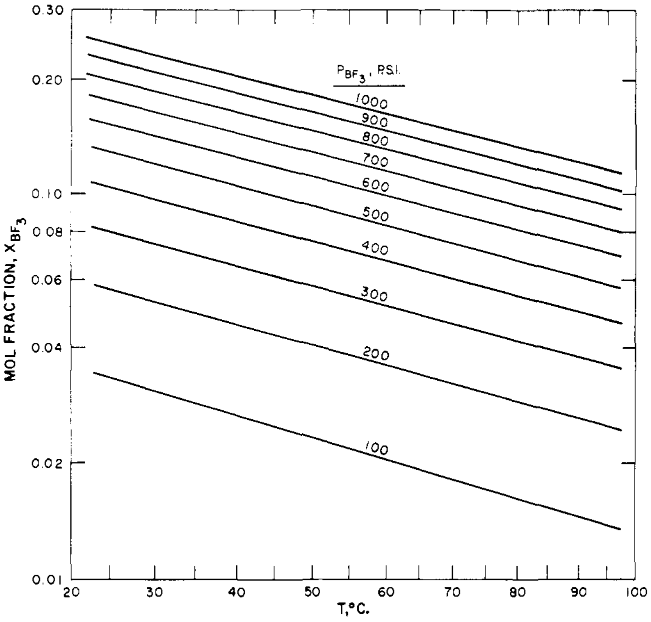

Figure 2. Isobars for solubility of BF_3 in HF

In order to draw a comparison between this work and the published data, Figure 2 can be used to obtain equations for appropriate isotherms. A comparison with the literature shows:

Temp., ° C.	Isotherm Equation, $x_{\mathrm{BF}_3} =$	Ref.
4.4	$(2.8 \times 10^{-3}) + (3.28 \times 10^{-4})P_{\mathrm{BF}_3}$	(*1*)
4.4	$(1.6 \times 10^{-2}) + (3.10 \times 10^{-4})P_{BF_3}$	This work
19	$(2.10 \times 10^{-4})P_{\mathrm{BF}_3}$	(*2*)
19	$(1.1 \times 10^{-2}) + (2.52 \times 10^{-4})P_{\mathrm{BF}_3}$	This work
20.5	$(4.6 \times 10^{-2}) + (2.36 \times 10^{-4})P_{\mathrm{BF}_3}$	(*1*)
20.5	$(1.0 \times 10^{-2}) + (2.47 \times 10^{-4})P_{\mathrm{BF}_3}$	This work
43	$(1.6 \times 10^{-3}) + (1.96 \times 10^{-4})P_{\mathrm{BF}_3}$	(*1*)
43	$(4.5 \times 10^{-3}) + (1.90 \times 10^{-4})P_{\mathrm{BF}_3}$	This work

There is satisfactory agreement among the slopes of the isotherms. Extrapolation of the data to obtain the 4.4° isotherm represents the limit of such an extrapolation due to a large change in the temperature coefficient of solubility below 0° C. (*2*).

The intercepts of the isotherms are probably due to small amounts of impurities, such as hydrates arising from water present in the HF or metal fluoborates due to corrosion of the reactor. These impurities, analyzed as BF_3, are merely additive to the BF_3 concentrations throughout the pressure range; at lower temperatures they are more stable and lead to greater intercepts.

The data of Kilpatrick and Luborsky at 19° C. (*3*), obtained after stringent purification of both the HF and BF_3, define a line passing through the origin in full accord with Henry's law. In a practical catalyst system, such ideality would not be observed. However, the error involved in establishing the composition of the catalyst phase is small compared with the ideal solubility of BF_3.

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