

## KINETICS OF PRECIPITATION OF FERRIC DIBUTYLPHOSPHATE FROM AQUEOUS HNO<sub>3</sub> SOLUTIONS\*

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(Received 8 March 1968)

**Abstract**—The kinetics of the precipitation of iron(III) dibutylphosphate in 1, 3, and 5 M HNO<sub>3</sub> were studied at an initial Fe<sup>3+</sup> concentration of 231 mg/l. (4.14 mM) and at initial dibutylphosphoric acid (HDBP) concentrations of 3.06 and 1.53 g/l. (14.56 and 7.28 mM). The experimental data on Fe<sup>3+</sup> concentration (C, moles/l.) were used to obtain the nonlinear parameters of the integrated form of the rate equation

$$dC/dt = -k(C - S_{Fe})^n.$$

This equation is obtained from a more general expression of the form

$$dC/dt = -k'(C - S_{Fe})^p(C_D - S_D)^q.$$

where C<sub>D</sub> and S<sub>D</sub> are, respectively, instantaneous and final (i.e. its solubility) concentrations of dibutylphosphate, and S<sub>Fe</sub> is the final (solubility) concentration of Fe<sup>3+</sup>.

The assumed reaction, Fe<sup>3+</sup> + 3 HDBP ⇌ Fe(DBP)<sub>3</sub> + 3H<sup>+</sup>, appears to have a combined order n(= p + q) of approximately 2; the rate constant (k) is of the order of 10<sup>-3</sup>–10<sup>-2</sup> when time is expressed in minutes. The value of the solubility product increases from about 2 × 10<sup>-13</sup> to 2 × 10<sup>-12</sup> (moles/l.)<sup>4</sup> as the nitric acid concentration increases from 1 to 5 M.

### INTRODUCTION

SIGNIFICANT quantities of dibutylphosphoric acid (HDBP), monobutylphosphoric acid (H<sub>2</sub>MBP) and orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>) will be produced in the processing of fast-reactor fuels by extraction with tributyl phosphate (TBP). These quantities will exceed those currently being produced in the processing of thermal reactor fuels because of the higher radiation levels that will be associated with fast reactors. Furthermore, the high burn-ups expected for fuels from these reactors will result in the formation of large quantities of fission products which might precipitate as the ortho, monobutyl, and dibutyl phosphates in the aqueous phase, the TBP phase, or in both phases. Iron corrosion products will also be encountered in fuel processing.

Davis [1] has measured the solubility of iron(III) dibutylphosphate in aqueous nitric acid solutions by agitating suspensions in Fe(DBP)<sub>3</sub> for periods as long as forty days. In addition, three kinetic experiments on the system HDBP-HNO<sub>3</sub>-Fe<sup>3+</sup>-H<sub>2</sub>O have been reported [2]. It is evident that more information is needed

\*Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

1. W. Davis, Jr., *Solubilities of Uranyl and Iron(III) Dibutyl and Monobutyl Phosphates in TBP Solvent Extraction Solutions*, ORNL-3084, April 19 (1961).
2. *Semiannual Report of the Department of Chemistry, November 1965 through May 1966*, Centre d'Études Nucléaires, Fontenay-aux-Roses, CEA-N-616, December (1966).

about the conditions under which butyl phosphates precipitate in TBP solvent extraction systems and about the kinetics of such precipitation. The purpose of the work reported here was to study the kinetics of precipitation of  $\text{Fe}(\text{DBP})_3$  in solutions of 1, 3, and 5 M  $\text{HNO}_3$  using tracer methods of analysis. Qualitative observations concerning the precipitation process and the nature of the precipitate are also presented.

## EXPERIMENTAL

### Procedure

An aqueous solution (50 ml) of HDBP and an aqueous solution (50 ml) of  $\text{Fe}^{3+}$  in  $\text{HNO}_3$  were prepared from stock solutions. Approximately  $1-2 \mu\text{c}$  of  $^{59}\text{Fe}$  tracer (specific activity  $1-2 \mu\text{c}/\text{ml}$ ) was added to the iron solution. The HDBP solution was then poured into the  $\text{Fe}^{3+}$  solution at reference time  $t = 0$ , and 2-ml samples were withdrawn at various times thereafter. The combined solution was mixed well before and after sampling, but generally was not stirred otherwise. Each sample was filtered, and the filtrate was collected in a 1-oz sample bottle (which was subsequently placed in a lead castle for gamma-ray counting). The precipitate was washed with 2 ml of water, and this wash liquid was also collected in the sample bottle. (In nearly all cases, solids formed in this bottle after the filtration process.) This entire operation required about 10–15 sec. Therefore, the sampling process for each sample was started about 5 sec before, and completed about 5 sec after, the desired reaction time. All but one of the experiments were conducted at room temperature ( $25 \pm 2^\circ\text{C}$ ).

### Apparatus

Rapid sample filtration was achieved with Millipore vacuum filtration units connected to a vacuum pump with manifold. A "mixed esters of cellulose" filter paper (Millipore No. HAWG 04700) of  $0.45\text{-}\mu$  pore size was used. Rapid clogging of the filter was prevented by use of a prefilter (Millipore No. HP 2003500). An automatic pipetting apparatus, set to deliver 2-ml samples, was used to speed up the sampling process. Background and sample activities were determined with a  $^{137}\text{Cs}$ -standardized scintillation counter employing an NaI detector ( $3 \times 3$ -in. crystal).

### Reagents

Analytical-grade  $\text{HNO}_3$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were used. A solution containing  $^{59}\text{Fe}^{3+}$  (radiochemical purity, 99.4%) was obtained from Nuclear Science and Engineering Corporation. HDBP (Victor Chemical Company) analyzed as follows:

density at $27.4^\circ\text{C}$	0.9581 g/ml
m-equiv. HDBP/g	4.290
m-equiv./ml	4.11
mg/m-equiv. HDBP	233.0
theoretical mg/m-equiv. HDBP· $\text{H}_2\text{O}$	228.2
theoretical mg/m-equiv. HDBP	210.0.

These results are indicative of an approximately 50 mole %  $\text{H}_2\text{O}$ -HDBP solution.

The purity of the HDBP was also determined by an established methylation technique[3]. Subsequent gas chromatographic analysis showed >97 mole % methyl dibutylphosphate, 0.9 mole % dimethyl monobutylphosphate (from  $\text{H}_2\text{MBP}$ ), < 0.1 mole % trimethyl phosphate (from  $\text{H}_3\text{PO}_4$ ), and ~ 0.9 mole % butanol.

## RESULTS AND DISCUSSION

Pertinent data concerning the various experiments are summarized Table 1. Some of the  $\text{Fe}^{3+}$  concentrations are shown as functions of sampling time in Figs. 1 and 2. Duplicate experiments were conducted, using 1, 3, and 5 M  $\text{HNO}_3$ , with initial  $\text{Fe}^{3+}$  concentrations of 231 mg/l. and HDBP concentrations of 3.06

3. C. J. Hardy, *J. Chromatogr.* **13**, 372 (1964).

Table 1. Kinetic parameters and solubility products for precipitation of  $\text{Fe}(\text{DBP})_3$  from  $\text{HNO}_3$  solutions\*

Experiment number	Initial HDBP concentration (g/l.)	$\text{HNO}_3$ Concentration (M)	Final measured concentration of $\text{Fe}^{3+}$ in solutions (mg/l.†)	Final time (min)	Least-squares parameters‡			Solubility product, $K_{sp} \times 10^{10}$ , (moles/l.) <sup>4</sup>	
					$k \times 10^3$	$n$	$S_{Fe}$	Based on last $^{59}\text{Fe}$ activity measurement	
								Based on activity measurement	Based on $S_{Fe}$
Fe-9	3.06	1.0	1.22	330	1.58	2.05	0.72	2.4	1.4
Fe-10	3.06	1.0	1.86	300	2.45	2.03	(0.80)§	3.7	
Fe-11	3.06	1.0	1.05	1680	2.78	2.00	0.88	2.0	1.7
Fe-19	3.06	1.0	1.95	1338	11.05	1.77	1.10	4.0	2.1
Fe-15	3.06	3.0	2.84	1380	6.07	1.76	4.20	6.2	10.1
Fe-16	3.06	3.0	3.45	1405	1.96	1.95	5.47	7.8	14.2
Fe-18	3.06	5.0	6.64	2895	4.44	1.89	8.07	18.6	24.8
Fe-22	3.06	5.0	7.60	11270	1.93	1.95	8.69	22.8	27.7
Fe-12	1.53	1.0	83.4	1324	12.3	1.70	(84.0) <sup>¶</sup>		
Fe-13	1.53	1.0	84.5	1445	1.96	2.17	84.0		
Fe-20	1.53	3.0	102.0	1395	15.0	1.51	105.3		
Fe-21	1.53	3.0	109.0	1530	38.6	1.04	114.3		
Fe-23	1.53	5.0	109.7	8658	24.3	1.59	115.1		
Fe-24	1.53	5.0	108.0	4218	93.8	1.15	110.2		
Fontenay-aux-Roses (Ref. [2])	3	1	3.1	1250	2.09	2.14	2.26	5.0	
	3	2	10.5	1250	3.38	1.94	10.8	28.7	
	3	3	36.3	1250	20.30	1.28	36.8	57.8	

\* In all of our experiments the initial  $\text{Fe}^{3+}$  concentration was 231 mg/l.; in the Fontenay-aux-Roses experiments [2], it was 230 mg/l. 230 mg/l.

† By  $\gamma$ -ray counting.

§  $S_{Fe}$  was fixed at 0.80.

¶  $S_{Fe}$  was fixed (because of poor data) at the value calculated for experiment 13.

‡ Time in min;  $\text{Fe}^{3+}$  concentration in mg/l.

and 1.53 g/l. In each case white  $\text{Fe}(\text{DBP})_3$  particles (particle size, 0.1–0.5 mm) formed rapidly (1–5 min after contact) on the surface of the solution. The initial precipitation was followed by the slow formation of a milky dispersion, which began to settle after 2–3 hr.

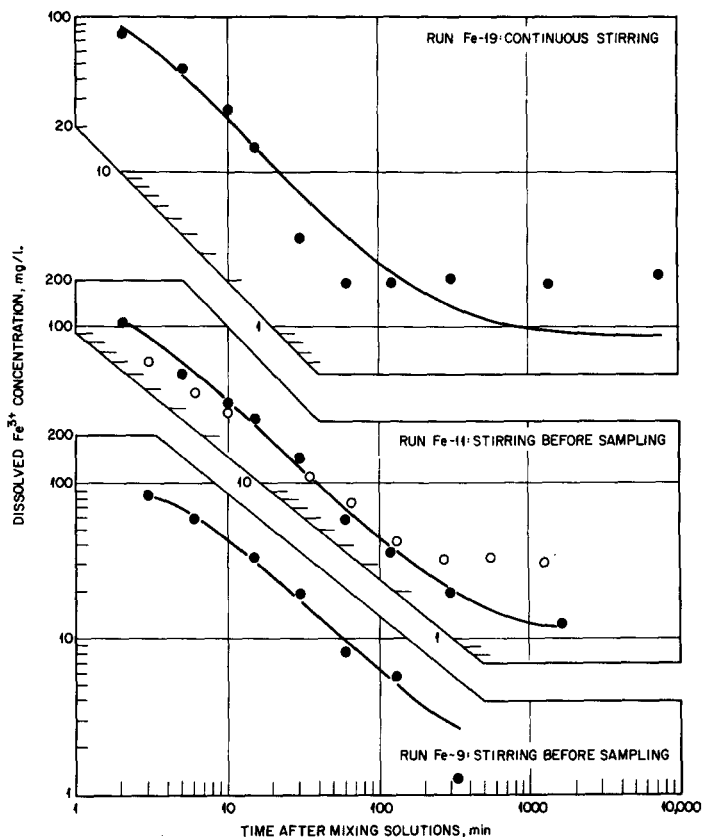


Fig. 1. The residual concentration of dissolved  $\text{Fe}^{3+}$  decreases as iron precipitates as  $\text{Fe}(\text{DBP})_3$ . Each curve is calculated from Equation 8 and parameters of Table 1. Initial conditions: 231 mg  $\text{Fe}^{3+}$ /l.; 3.06 g HDBP/l.; 1 M  $\text{HNO}_3$ . ●— Our data. ○— Data from [2].

Several trends are readily observable from Table 1. When the HDBP concentration is initially 3.06 g/l., the final concentration of  $\text{Fe}^{3+}$  in solution increases from  $\sim 1$  mg/l. to  $\sim 7$  mg/l. as the  $\text{HNO}_3$  concentration increases from 1 to 5 M. When the initial concentration of HDBP is reduced from 3.06 to 1.53 g/l. (compare Figs. 1 and 2), the final  $\text{Fe}^{3+}$  concentration (that is, the solubility) increases from  $\sim 84$  mg/l. in 1 M  $\text{HNO}_3$  to  $\sim 110$  mg/l. in 5 M  $\text{HNO}_3$ . Davis [1] has reported a similar increase in the solubility of  $\text{Fe}(\text{DBP})_3$  as the  $\text{HNO}_3$  concentration increases.

Experiment Fe-19 was conducted with constant stirring. The rate of reaction was somewhat higher than that of the corresponding static test, but there was a 4.5°C temperature increase (above room temperature) due to the heating effect

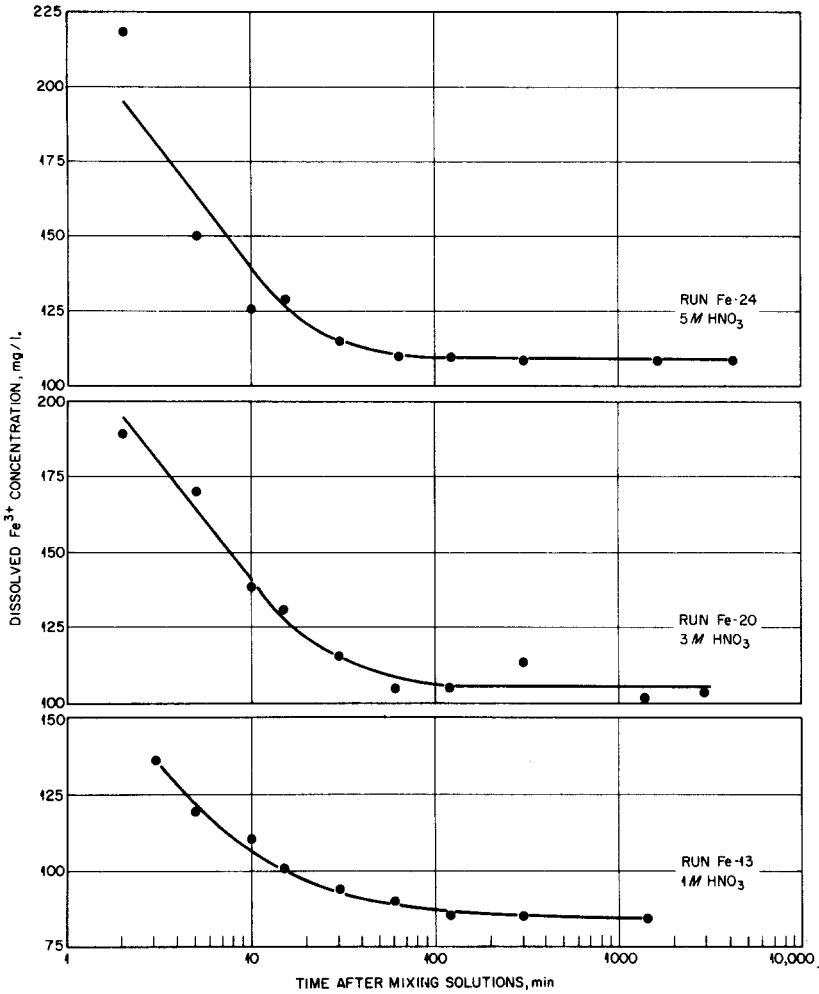


Fig. 2. The residual concentration of dissolved  $\text{Fe}^{3+}$  decreases as iron precipitates as  $\text{Fe}(\text{DBP})_3$ . The final  $\text{Fe}^{3+}$  concentration increases as the  $\text{HNO}_3$  concentration increases. Each curve is calculated from Equation 8 and the parameters of Table 1. Initial conditions: 231 mg  $\text{Fe}^{3+}/\text{l}$ .; 1.53 g HDBP/l.

of the magnetic stirrer. The effect of temperature on the reaction rate may be important; to date, however, it has not been investigated further.

#### *Kinetics of precipitation of $\text{Fe}(\text{DBP})_3$*

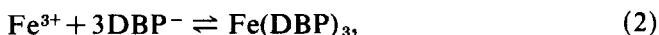
Data on the  $\text{Fe}^{3+}$  concentration versus time were used to obtain a preliminary description of the kinetics of the precipitation of  $\text{Fe}(\text{DBP})_3$  in 1–5 M  $\text{HNO}_3$  solutions.

The model we used is given by the equation:

$$\frac{dC}{dt} = -k'(C - S_{\text{Fe}})^p (C_D - S_D)^q, \quad (1)$$

where  $C^\circ$ ,  $C$ , and  $S_{Fe}$  are the initial, instantaneous, and final (solubility) concentrations of  $Fe^{3+}$ , respectively, and  $C_D^\circ$ ,  $C_D$ , and  $S_D$  are the corresponding values for HDBP. The exponents  $p$  and  $q$  are the kinetic orders with respect to the degrees of supersaturation of the solution with regard to  $Fe^{3+}$  and  $DBP^-$ .

From the stoichiometry of the reaction



we find that

$$C_D^\circ - C_D = 3(C^\circ - C) \quad (3)$$

and

$$C_D^\circ - S_D = 3(C^\circ - S_{Fe}). \quad (4)$$

By subtracting Equation (3) from Equation (4), we obtain:

$$C_D - S_D = 3(C - S_{Fe}), \quad (5)$$

which, on substitution into Equation (1), yields the simpler equation

$$\frac{dC}{dt} = -k' (3)^q (C - S_{Fe})^{p+q} = -k (C - S_{Fe})^n, \quad (6)$$

where

$$n = p + q.$$

Thus the two rate orders,  $p$  and  $q$ , of the present kinetic model cannot be determined separately; only their sum can be determined.

Integration of Equation (6) gives the following results:

$$\frac{1}{(C - S_{Fe})^{n-1}} - \frac{1}{(C^\circ - S_{Fe})^{n-1}} = (n-1) kt \quad (7)$$

or

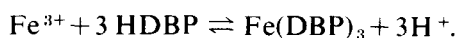
$$C = S_{Fe} + [(C^\circ - S_{Fe})^{-n+1} + (n-1) kt]^{-1/(n-1)}. \quad (8)$$

Equation (8) was used in a least-squares analysis of the various experiments. In this analysis the initial  $Fe^{3+}$  concentration ( $C^\circ$ ) was fixed at 231 mg/l., a more accurate value (based on chemical analysis) than we expected to obtain for  $S_{Fe}$ ,  $k$ , or  $n$ . Table 1 lists the calculated values of these three constants. This table also contains a summary of our calculations of the same constants for data reported from Fontenay-aux-Roses[2].

The present study was not extensive enough to allow us to draw more than a few firm conclusions. One is that Equations (1) through (8) satisfactorily describe our data within the known experimental uncertainties; they also describe the Fontenay-aux-Roses[2] (FAR) data with standard deviations of 0.8, 1.5, and 5.7 mg  $Fe^{3+}$ /l. for the experiments using 1, 2 and 3 M  $HNO_3$ , respectively. Furthermore, a consistent set of values of  $k$ ,  $n$ , and  $S_{Fe}$  is obtained for our experiments, as well as for those at FAR in which the initial concentration of HDBP was  $\sim 3$  g/l. This concentration corresponds to only a small excess of  $Fe^{3+}$  over the stoichiometric value. Less reproducibility in calculated parameters was obtained when the initial HDBP concentration was only 1.53 g/l., which is somewhat less than half the stoichiometric quantity for reaction with all the  $Fe^{3+}$

present. Finally, although  $k$  and  $n$  were treated as independent variables, the nonlinear correlation coefficient showed a strong correlation between  $k$  and  $n$  for both our data and those from FAR. The reason for this inverse relationship (which may be seen in Table 1) is not known, but the rapid initial rate of precipitation and the associated precipitation in the sampling pipette may make an important contribution both to this correlation and to the variation in these calculated parameters from one experiment to another.

While Equations (1) through (8) describe our and the FAR data within reasonable limits, we emphasize that these equations are not meant to imply a *mechanism* as simple as



We have not proved the stoichiometry to correspond to  $\text{Fe}(\text{DBP})_3$ , although in a previous report [1] we described the preparation of a white (as in the present study) ferric dibutylphosphate whose composition was found by analyses to be quite close to that for  $\text{Fe}(\text{DBP})_3$ .

Within the uncertainties posed by the factors mentioned above, the rate of precipitation is approximately proportional to the square of the instantaneous degree of supersaturation  $[(C - S_{\text{Fe}})^2]$  with respect to iron when the initial HDBP concentration is 3.06 (or 3) g/l. and the initial  $\text{Fe}^{3+}$  concentration in 1–5 M  $\text{HNO}_3$  solutions is 231 (or 230) mg/l. At the lower HDBP concentration (1.53 g/l.), neither the rate nor the order is as well defined, although the order is probably nearer 1.5 than 2.

#### *Solubility product*

Solubility products calculated from the data in Table 1 are presented in Fig. 3. These include values based on the final  $^{59}\text{Fe}$  measurement, those based on  $S_{\text{Fe}}$  from the least-squares analysis of Equation (8), and values calculated from the data previously reported [1]. There is considerable scatter, but it is apparent that the data previously presented for solubilities of  $\text{Fe}(\text{DBP})_3$  in 1 and 3 M  $\text{HNO}_3$  solutions are in good agreement with the more extensive data of the present study. Obviously, the solubility products calculated from the FAR data exceed our values by a factor of about 3–4. In terms of the solubility of  $\text{Fe}(\text{DBP})_3$ , the FAR data are 30–40% higher than ours, however, we consider this agreement to be quite satisfactory.

#### SUMMARY AND CONCLUSIONS

This study of the kinetics of precipitation of  $\text{Fe}(\text{DBP})_3$  from aqueous nitric acid solutions and the rather good degree of reproducibility show that the experimental techniques are satisfactory and that they should apply to other precipitation systems. In each experiment the initial concentration of  $\text{Fe}^{3+}$  was 231 mg/l. while that of HDBP was either 3.06 or 1.53 g/l. At the higher HDBP concentration the rate of precipitation of  $\text{Fe}(\text{DBP})_3$  from 1 to 5 M  $\text{HNO}_3$  solutions is approximately second order with respect to the instantaneous degree of supersaturation of the solution with regard to  $\text{Fe}^{3+}$ ; at the lower HDBP concentration the order may be more nearly 1.5. The dependence of the precipitation

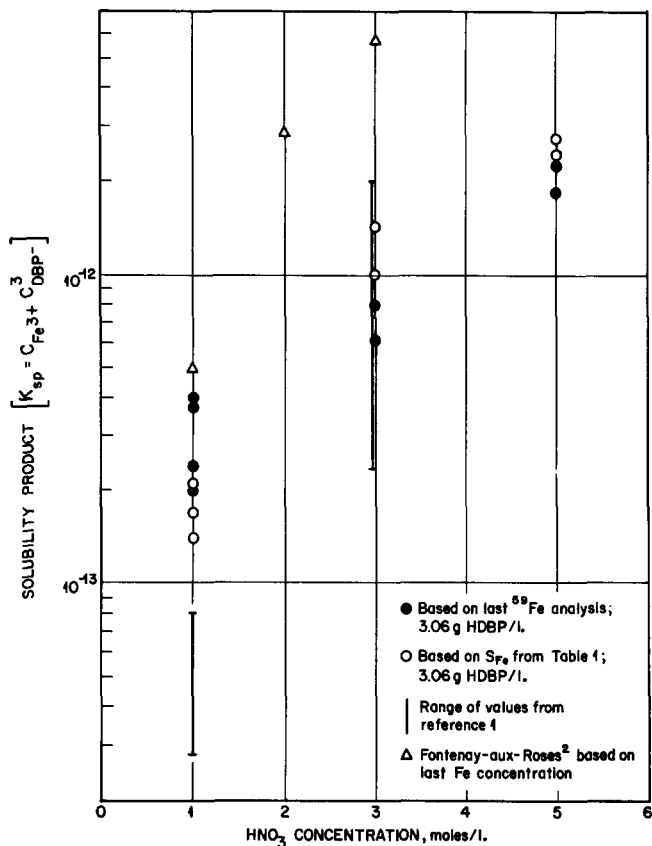


Fig. 3. The solubility product of  $\text{Fe}(\text{DBP})_3$  in aqueous  $\text{HNO}_3$  solutions increases as the  $\text{HNO}_3$  concentration increases.

rate on HDBP concentration has not been determined since the individual exponents,  $p$  and  $q$  of Equation (1), enter the mathematical analysis only as a sum.

Solubility values and solubility products, which are based either on the last measurement of  $^{59}\text{Fe}$  gamma-ray activity (5–190 hr after mixing  $\text{Fe}^{3+}$  and  $\text{DBP}^-$  solutions) or on an extrapolation of a kinetic equation are in good agreement with data previously presented [1]. We find satisfactory agreement between our results and those reported from the Fontenay-aux-Roses laboratory [2].