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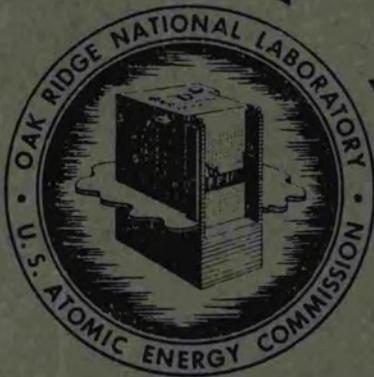
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## THE EXTRACTION OF IRON(III) FROM ACIDIC SULFATE SOLUTIONS BY DI-n-DECYLAMINE SULFATE IN BENZENE

C. F. Baes, Jr.



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THE EXTRACTION OF IRON(III) FROM  
ACIDIC SULFATE SOLUTIONS BY DI-n-DECYL-  
AMINE SULFATE IN BENZENE

C. F. Baes, Jr.

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## ABSTRACT

Iron(III) extraction coefficients have been measured at 25°C in the liquid-liquid extraction system di-n-decylamine sulfate (DDAS) - benzene, aqueous sulfuric acid - sodium sulfate as a function of acid, sulfate, iron(III) and DDAS concentrations. The results are consistent with the extraction of the hydrolyzed complex  $\text{FeOHSO}_4$  to form both monomeric and dimeric iron(III) species in the benzene phase. The limiting mole ratio,  $\text{Fe(III)} : (\text{R}_2\text{NH}_2)_2\text{SO}_4$ , appears to be unity. The iron(III) extraction results and results of the extraction of sulfuric acid by DDAS are discussed in terms of association of DDAS molecules in the benzene phase.

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INTRODUCTION

In describing the ability of certain long-chain aliphatic amines dissolved in organic solvents to extract acids from aqueous solution, Smith and Page<sup>(1)</sup> suggested the possibility that metals such as chromium and vanadium in their higher oxidation states might be extracted by these reagents. Ellenburg, Leddicotte and Moore<sup>(2)</sup> confirmed this view by demonstrating the separation of niobium(V) and tantalum(V) using high molecular weight tertiary amines. In a later publication<sup>(3)</sup>, Mahlman, Leddicotte and Moore described the amine extraction behavior of the first transition series elements in hydrochloric acid solution.

The use of such reagents in the extraction of uranium and other metals from acidic sulfate solutions has been reported by Brown et al.<sup>(4)</sup>, and Crouse and Denis<sup>(5)</sup>. These extensive investigations have shown that a variety of metals (e.g., uranium(IV), uranium(VI), thorium(IV), vanadium(V), molybdenum(VI), zirconium(IV), cerium(IV) and iron(III)) are appreciably extracted with a suitable choice of amine type (i.e., primary, secondary or tertiary) and structure, organic solvent and aqueous solution composition.

It has been noted<sup>(4)</sup> that certain of these extraction measurements indicate association of the amine sulfate molecules in the organic phase. This is supported by Allen's measurements of extraction by tri-n-octylamine<sup>(6)</sup> and by

other, as yet unpublished, results. Such associatio behavior has been observed for certain long chain quaternary ammonium salts<sup>(7,8)</sup>, ionic and non-ionic detergents<sup>(9-12)</sup>, and organophosphorus acids<sup>(13)</sup> in low dielectric-constant media.

Another interesting feature of the acidic sulfate solution results is that the majority of the metals which show appreciable extraction by amines presumably are present in these aqueous solutions as oxygenated ions. A notable exception is iron(III) which evidently is present principally as simple sulfate complexes<sup>(14-16)</sup>. Accordingly, while the selection of iron(III) for detailed study in the present investigation was made primarily because of its importance in uranium processing, it is of additional interest in the general study of amine extraction processes.

In virtually all the previous investigations of amine extraction, a parallelism with anion exchange sorption has been noted. It is of particular interest, therefore, that Kraus and Nelson<sup>(17)</sup> have found iron(III) to be appreciably adsorbed from sulfuric acid solutions by Dowex-1, a strong-base anion exchange resin. In general, the present results are qualitatively in agreement with their observations.

Di-n-decylamine (DDA) was chosen for this investigation because it exhibits conveniently high extraction coefficients for iron(III) and shows no appreciable distribution to acidic sulfate solutions<sup>(4)</sup>. Preliminary acid extraction measurements have shown this amine to be a stronger base in benzene

solution than tri-n-octylamine<sup>(6)</sup>, the equivalence point for amine sulfate formation occurring at pH ca. 3 when it is titrated with pure aqueous sulfuric acid. From these measurements it is estimated that at the lowest acid concentration used in the present investigation (0.01 M H<sub>2</sub>SO<sub>4</sub> - 0.49 M Na<sub>2</sub>SO<sub>4</sub>) the free amine concentration in the equilibrated benzene phase was ca. 0.0001 M. Accordingly, the free amine concentration is assumed negligible in all the measurements. As in the case of tri-n-octylamine<sup>(6)</sup>, DDA in the sulfate form (DDAS) extracts additional sulfuric acid with increasing aqueous acidity, presumably to form the amine bisulfate. At aqueous acid concentrations greater than ca. 0.2 M, the amine precipitates as a white solid (presumably bisulfate) from the 0.5 M sulfuric acid - sodium sulfate solutions, which were used in all but one series of extractions. The extraction measurements, therefore, were limited to the range 0.01 - 0.18 M sulfuric acid.

#### EXPERIMENTAL

Preparation of Di-n-decylamine. - Armeen-10D (a mixture of straight chain primary amines, predominantly n-decylamine) was fractionated in a five foot Podbielniak-type column at atmospheric pressure under argon, yielding n-decylamine with the boiling range 217-219°C. This purified starting material was reacted in the presence of Raney nickel according to the procedure given by Hoerr, Harwood and Ralston<sup>(18)</sup>.

The product was distilled from the reaction mixture at 20 mm. pressure under argon in the boiling range 226-230°C. A 54% yield, based on the purified n-decylamine, was obtained. The molecular weight of the product based on several acidimetric titrations varied from 300 to 304, presumably as a result of hydration and CO<sub>2</sub> absorption upon exposure to the air (Theo. M.W. = 297.6). The m.p. of the freshly prepared material (41.5 - 42.5°C) was in agreement with that reported by Ralston<sup>(19)</sup>. Differential analysis indicated 95% secondary and 5% primary amine\*.

Reagent Solutions. - A 0.1036 N stock solution of DDA in thiophene-free benzene was prepared and analyzed by potentiometric titration in chloroform against a standard solution of perchloric acid in dioxane\*\*. A 1.064 M stock solution of iron(III) sulfate was prepared from the reagent grade salt and analyzed by the volumetric dichromate method<sup>(23)</sup>. Stock solutions of sulfuric acid and sodium sulfate were also prepared from reagent grade chemicals.

Procedure. - The liquid-liquid extraction equilibration measurements were performed as follows: 20 ml. volumes of aqueous solutions containing known amounts of iron(III) sulfate, sulfuric acid and sodium sulfate were delivered into 60 ml. separatory funnels and contacted with equal volumes of

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\*This analysis, performed by John G. Moore, Materials Chemistry Division, ORNL, was based on the publication of J. S. Fritz<sup>(20)</sup>.

\*\*This procedure (supplied by J. G. Moore, Materials Chemistry Division, ORNL) was based on several publications<sup>(20-22)</sup>.

benzene solutions of DDAS. These were prepared by first contacting a portion of the 0.1 M DDA stock solution with sufficient aqueous sulfuric acid to convert the free amine to the amine sulfate and then washing the resulting solution several times with an aqueous sulfuric acid-sodium sulfate solution of the same composition as that to be used in each equilibration.\* The separatory funnels were mounted on a mechanical shaker in a  $25.0 \pm 0.1^{\circ}\text{C}$  thermostat and shaken for one hour. Upon separation of the two equilibrated phases, which was rapid in all cases, a portion of each phase was taken for analysis.

Several extraction rate measurements indicated that equilibrium was reached with less than one minute of shaking in most cases. The longest equilibration time encountered in these measurements was ca. 16 minutes for an 0.03 M sulfuric acid solution sufficiently concentrated in iron(III) to nearly saturate the benzene phase.

Two aqueous iron(III) solutions, 0.03 and 0.18 M in sulfuric acid, were left in contact with equilibrated 0.1 N DDA benzene solutions overnight and then tested for the presence of iron(II), which conceivably could have been produced by reducing action of the amine. Potentiometric measurements and direct titration indicated that no appreciable iron reduction took place.

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\*Typical wash solutions were tested for water-soluble amine impurities (presumably n-decylamine sulfate) by shaking a neutralized aliquot with benzene, adding a few drops of conc. hydrochloric acid to the separated benzene phase, evaporating to dryness and weighing the residue. The results averaged  $< 0.1 \text{ mg/ml}$  of solid ( $< 5 \times 10^{-4}$  N as decylamine sulfate).

No measurable amount of either iron(III) or sulfuric acid was found to be extracted by pure benzene contacted with ca. 0.2 M iron(III) sulfate solutions, 0.03 M and 0.18 M in sulfuric acid. Spectrometric sodium analyses of various DDAS solutions which had been equilibrated with aqueous 0.18 M sulfuric acid - 0.32 M sodium sulfate solutions indicated sodium sulfate concentrations of ca.  $10^{-4}$  M, which could have resulted from mechanical entrainment.

Methods of Analysis. - The aqueous solutions resulting from extraction equilibrations were analyzed for iron by an o-phenanthroline colorimetric method\* with an accuracy of about  $\pm 1\%$  relative error. The iron concentration in the corresponding benzene solutions was similarly determined after first stripping a 15 ml. portion with three successive 10 ml. portions of 0.5 M nitric acid in a small separatory funnel, collecting the aqueous solution in a 50 ml. volumetric flask and diluting to volume.

In one series of measurements (Table III) these nitric acid strip solutions were analyzed gravimetrically for sulfate with an estimated relative error of  $\pm 2\%$ .

The sulfuric acid concentration of several equilibrated aqueous iron(III) solutions was determined by direct titration against standard base to an indicated pH of 7.0 (using a Beckman Model G pH meter). The acid molarity was calculated on the assumption that the iron(III) was precipitated

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\*This procedure was supplied by J. C. White, Analytical Chemistry Division, ORNL.

quantitatively as hydrous ferric hydroxide. The accuracy of this procedure was checked using known solutions and found to be comparable to similar titrations of iron-free solutions.

For the two series of iron-free equilibrations in which the distribution of sulfuric acid was measured, the total acid concentration in the benzene phase was determined by the following procedure: A volume of the benzene solution (up to 10 ml.) was pipetted into 50 ml. of ethanol, 3 drops of thymol blue were added, and the solution was titrated with a standard 0.1 M sodium ethoxide solution in 1:1 benzene-ethanol. The blank was found to be 0.08 ml. The sodium ethoxide solution was standardized against benzoic acid, using the same procedure. A precision of about  $\pm 0.01$  ml. was usually obtained in duplicate determinations\*.

## RESULTS

The aqueous sulfuric acid activity as it appears herein is defined

$$a_{\text{H}_2\text{SO}_4} = [\text{H}^+]^2 [\text{SO}_4^{=}] g_{\text{H}^+}^2 g_{\text{SO}_4^{=}} = 4C_{\text{H}_2\text{SO}_4}^2 C_{\text{SO}_4^{=}} = (\gamma_{\pm})^3_{\text{H}_2\text{SO}_4} \quad (1)$$

in which  $C_{\text{H}_2\text{SO}_4}$  and  $C_{\text{SO}_4^{=}}$  are, respectively, the total sulfuric acid and the total sulfate ( $C_{\text{H}_2\text{SO}_4} + C_{\text{Na}_2\text{SO}_4}$ ) molarities;  $g_{\text{H}^+}$  and  $g_{\text{SO}_4^{=}}$  are the ionic activity coefficients. Values of  $(\gamma_{\pm})_{\text{H}_2\text{SO}_4}$  have been taken from the curve in Fig. 1.

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\*This method, based on the publication of Fritz<sup>(20)</sup>, was developed by W. J. McDowell, Materials Chemistry Division, ORNL.

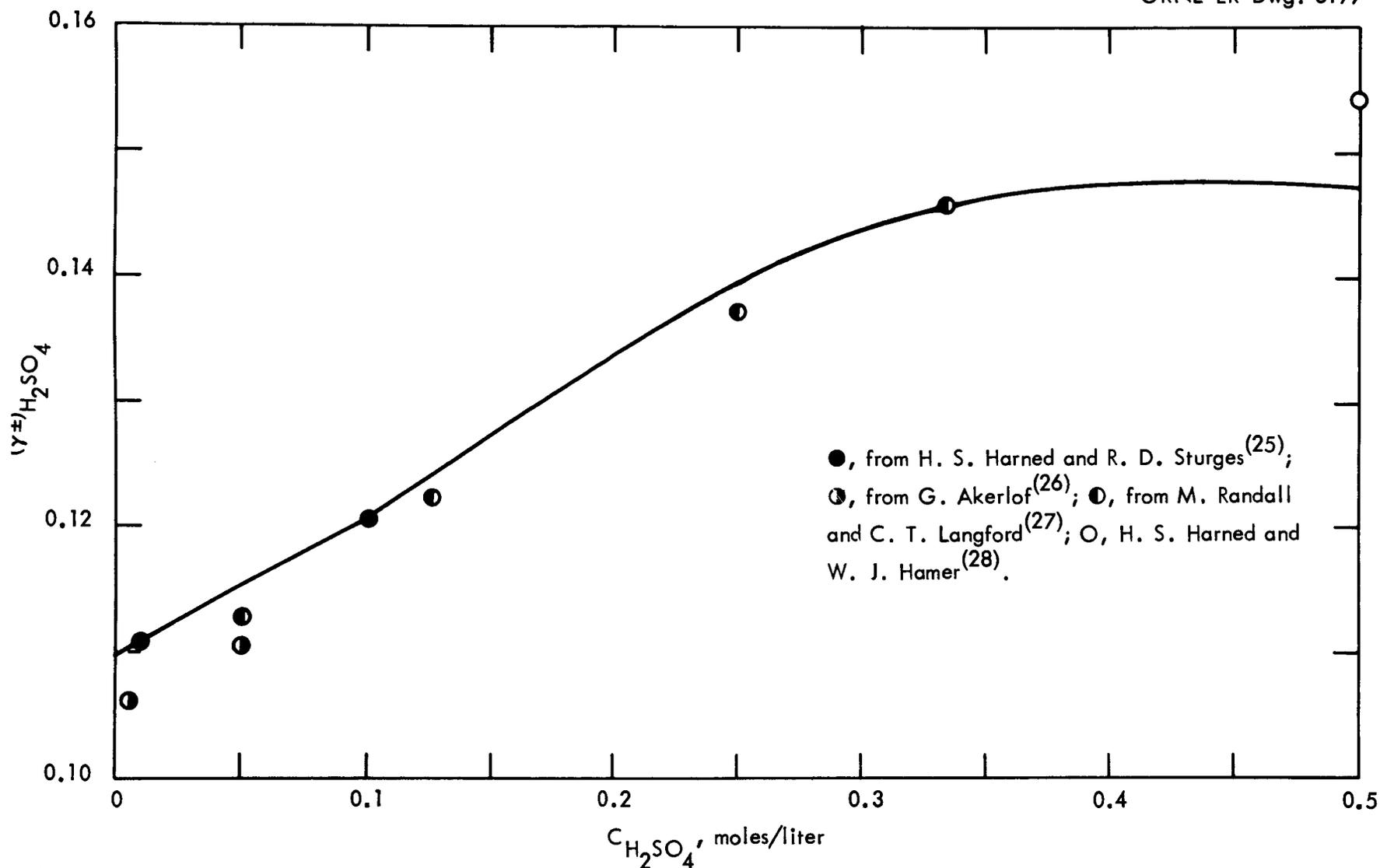


Fig. 1. The Mean Activity Coefficient of Sulfuric Acid in  $H_2SO_4 - Na_2SO_4$  Mixtures at Constant Total Concentration of  $0.5 \underline{M}$ ,  $25^\circ C$ . The  $(\gamma^\pm)_{H_2SO_4}$  Values (Except That at  $0.5 \underline{M}$   $H_2SO_4$ ) Were Calculated from Published e.m.f. Data for the Cell,  $H_2 | H_2SO_4 (C), Na_2SO_4 (0.5-C) | Hg_2SO_4 - Hg$ , Using  $E^\circ = 0.61515 \text{ v.}$ <sup>(24)</sup>

This curve, based on the data of Harned and Sturges<sup>(25)</sup> at  $C_{H_2SO_4} = 0.01 \underline{M}$  and  $0.1 \underline{M}$ , was calculated assuming

$$K_2^a = \frac{[H^+][SO_4^{=}]}{[HSO_4^-]} = 0.066 \text{ moles/liter}^*; g_{H^+}^2 g_{SO_4} = 0.09735 \quad (2)$$

The assumption of a constant  $K_2^a$  seems reasonable over the acid range of the present measurements ( $C_{H_2SO_4} = 0.01 - 0.18 \underline{M}$ ) and provides a useful means of smoothing out the literature values of  $(\gamma_{\pm})_{H_2SO_4}$ . Since the difference between the molar and molal scales is small in this range, it has been neglected in the calculation.

While the equilibrated DDA-benzene solutions which were used in the extraction measurements presumably contain both amine sulfate and amine bisulfate, they will be referred to simply as DDAS solutions. Their concentrations,  $C_R$ , will be expressed as normality; i.e.,  $C_R(N) = 2C_{R_2S} + C_{RHS}$ , in which  $C_{R_2S}$  and  $C_{RHS}$  are respectively the amine sulfate and bisulfate molarities.

Sulfuric Acid Extraction Results. - Measurements of the distribution of sulfuric acid from  $0.5 \underline{M}$  sulfate solution as

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\*This  $K_2^a$  may be compared to the following values in the literature:  $0.075$  ( $\mu = 1 \underline{M}$ ,  $25^\circ C$ , Whiteker and Davidson<sup>(14)</sup>);  $0.082$  ( $\mu = 2 \underline{M}$ ,  $25^\circ C$ , E. L. Zebroski, H. W. Alter and F. K. Heuman<sup>(29)</sup>);  $0.084$  ( $\mu = 1 \underline{M}$ ,  $20^\circ C$ , S. Fronaeus<sup>(30)</sup>). In so calculating the curve in Fig. 1, the limiting slope as  $C_{H_2SO_4} \rightarrow 0$  is determined by the choice of  $K_2^a$ . Accordingly, approximately the same value of this equilibrium quotient would result if the data of Akerlof or of Randall and Langford in the region below  $C_{H_2SO_4} = 0.14 \underline{M}$  were used to determine the curve.

a function of total amine concentration and as a function of sulfuric acid concentration are presented in Tables I and II and in Fig. 2. Values of the amine sulfate concentration and the amine bisulfate concentration were calculated from the total sulfate concentration in the benzene phase ( $C_{SO_4} =$ )<sub>bz</sub>, and  $C_R$ , according to the equations

$$C_{R_2S} = C_R - (C_{SO_4} =)_{bz}; \quad C_{RHS} = 2(C_{SO_4} =)_{bz} - C_R \quad (3)$$

These were derived from material balance relations assuming the reaction



for the extraction process in this range of acidity.

The approximate constancy of the ratio  $C_{RHS}/C_{R_2S}$  independent of  $C_R$  at constant acidity (Table I) and the conformity of the points above  $C_{RHS}/C_{R_2S} > 0.2$  to a straight line of 0.5 slope on the  $\log (C_{RHS}/C_{R_2S})$  vs.  $\log a_{H_2SO_4}$  plot (Fig. 2) suggests the empirical relation,

$$K = \frac{C_{RHS}}{C_{R_2S} a_{H_2SO_4}^{1/2}} = 97 \pm 6 \quad (5)$$

The negative deviations of the two lowest points in Fig. 2 from this relationship are of the same magnitude as their estimated uncertainties and so are not necessarily real\*.

\*While the expression

$$K = \frac{C_{RHS}^2}{2C_R C_{R_2S} a_{H_2SO_4}^{2/3}}$$

which Allen<sup>(6)</sup> has applied to the tri-n-octylamine sulfate-bisulfate results fits the present results for  $C_{RHS}/C_{R_2S} > 0.5$  quite well, appreciably greater deviations occur at lower values of this ratio than in the case of equation 5.

Table I  
THE EXTRACTION OF SULFURIC ACID BY DDAS  
AS A FUNCTION OF TOTAL AMINE CONCENTRATION

$C_{\text{Na}_2\text{SO}_4} = 0.320 \text{ M}$ ;  $C_{\text{H}_2\text{SO}_4} = 0.180 \text{ M}$  (pH = 1.0); 25°C

$\frac{C_R}{N}$	$\frac{(C_{\text{SO}_4})_{bz}}{M}$	$\frac{C_{R_2S}}{M}$	$\frac{C_{RHS}}{M}$	$\frac{C_{RHS}}{C_{R_2S}}$
0.1036	0.07022	0.03338	0.03684	1.10
.06216	.04247	.01969	.02278	1.16
.04144	.02837	.01307	.01530	1.17
.02072	.01428	.00644	.00784	1.22
.01036	.00714	.00322	.00392	1.22
.006216	.00419	.00203	.00216	1.06
				Ave. 1.15

Table II  
THE EXTRACTION OF SULFURIC ACID BY DDAS AS  
A FUNCTION OF ACIDITY

$$C_{H_2SO_4} + C_{Na_2SO_4} = 0.500 \text{ M}; C_R = 0.1036 \text{ N}; 25^\circ\text{C}$$

$C_{H_2SO_4}$ <u>M</u>	${}^a H_2SO_4$ $\times 10^6$ <u>M<sup>3</sup></u>	pH	$(C_{SO_4})_{bz}$ <u>M</u>	$C_{R_2S}$ <u>M</u>	$C_{RHS}$ <u>M</u>	$C_{RHS}/C_{R_2S}$
0.01032	0.290	2.47	0.05229	0.05131	0.00098	0.0191
.02047	1.174	2.17	.05373	.04987	.00386	.0774
.05062	7.85	1.72	.05836	.04524	.01312	.290
.1013	36.7	1.39	.06396	.03964	.02432	.614
.1523	96.7	1.11	.06792	.03568	.03224	.904
.180	147	1.00	.07022	.03338	.03684	1.10
.235	355	0.80	.03509 <sup>a</sup>			

(a) A white solid, presumably the amine bisulfate, was formed upon equilibration.

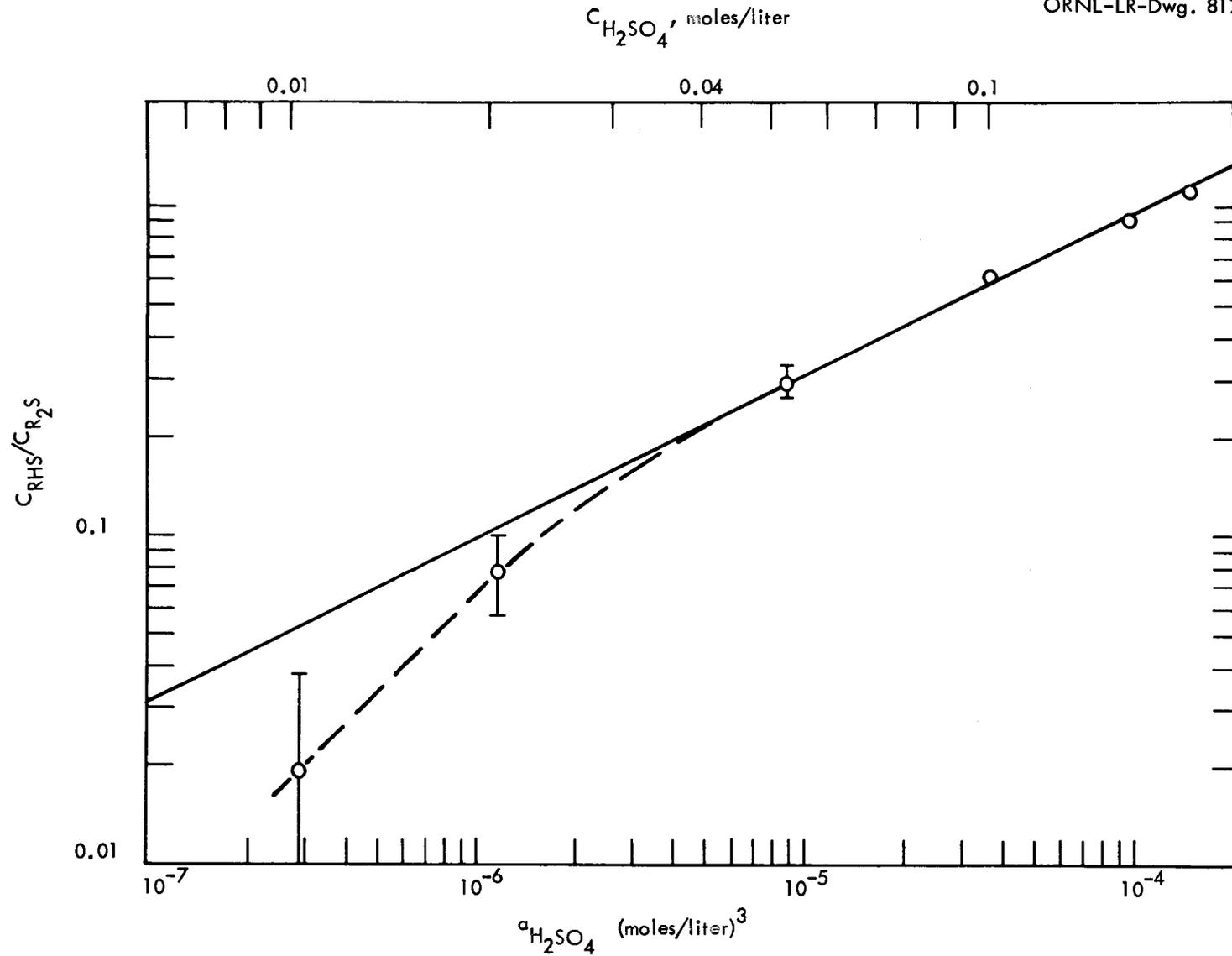


Fig. 2. The Acidity Dependence of Sulfuric Acid Extraction from 0.5 M Sulfate Solution by 0.1036 N DDAS, 25°C. The indicated uncertainties show the effect of  $\pm 1\%$  relative error in  $(C_{SO_4^{=}})_{bz}$  on the ratio  $C_{RHS}/C_{R_2S}$ .

Iron(III) Extraction Results. - The dependence of the iron(III) extraction coefficient  $E_{Fe}$  on the total amine concentration is shown in Table III and Fig. 3. The dependence of  $E_{Fe}$  on the aqueous iron(III) concentration  $(C_{Fe})_{aq}$  and on acidity is shown in Table IV and plotted for low values of  $(C_{Fe})_{aq}$  in Fig. 4. The results at 0.18 M and 0.03 M acid (Curves I and V) conform adequately to linear plots. The uniform positive deviation of the lowest points at 0.18 M acid is too small to be accepted as a real effect. In addition, the less extensive results at intermediate acidities are consistent with linearity. The straight lines which have been drawn for the data in Fig. 4 are defined by

$$E_{Fe} = E_1 + E_2(C_{Fe})_{aq} \quad (6)$$

The values of  $E_1$  and  $E_2$  at each acidity are given in Table V. Since  $E_{Fe}$  approaches a limiting value,  $E_1$ , as  $(C_{Fe})_{aq}$  approaches zero, then from the curves in Fig. 3 it appears that for infinitely dilute iron(III) solutions at constant acidity

$$K = \frac{(C_{Fe})_{bz}}{(C_{Fe})_{aq}(C_R)^p} = \frac{E_1}{C_R^p}; \quad p = 1/2 - 2/3 \quad (7)$$

The considerable increase in  $E_{Fe}$  with decreasing acidity (Fig. 5) indicates the extraction of a hydrolyzed complex. This conclusion is supported by the following acid titration results for one of the runs

Table III

THE EXTRACTION OF IRON(III) BY DDAS AS  
A FUNCTION OF TOTAL AMINE CONCENTRATION

$$C_{H_2SO_4} + C_{Na_2SO_4} = 0.500 \text{ M}; 25^\circ C$$

<u>C<sub>R</sub></u> <u>N</u>	<u>(C<sub>Fe</sub>)<sub>aq</sub></u> <u>M</u>	<u>(C<sub>Fe</sub>)<sub>bz</sub></u> <u>M</u>	<u>E<sub>Fe</sub></u>
<u>C<sub>H<sub>2</sub>SO<sub>4</sub></sub> = 0.0300 M, pH = 2.00</u>			
0.1036	0.001017 <sup>a</sup>	0.001333 <sup>a</sup>	1.31 <sup>a</sup>
.06216	.001208	.001223	1.012
.04144	.001267	.001164	0.919
.02072	.001421	.001036	.729
.01036	.001590	.000846	.532
.006216	.001752	.000693	.396
.004144	.001894	.000599	.316
<u>C<sub>H<sub>2</sub>SO<sub>4</sub></sub> = 0.180 M, pH = 1.00</u>			
0.1036	0.00206 <sup>a</sup>	0.000283 <sup>a</sup>	0.137 <sup>a</sup>
.06216	.002115 <sup>b</sup>	.000235	.111
.04144	.002163 <sup>b</sup>	.000187	.0865
.02072	.002226 <sup>b</sup>	.000124	.0557
.01036	.002266 <sup>b</sup>	.0000836	.0369
.006216	.002288 <sup>b</sup>	.0000622	.0272
.004144	.002306 <sup>b</sup>	.0000440	.0191

a) These values were obtained by interpolation of the data in Table IV.

b) These values were obtained by material balance. In general, they are in satisfactory agreement with the analytical results.

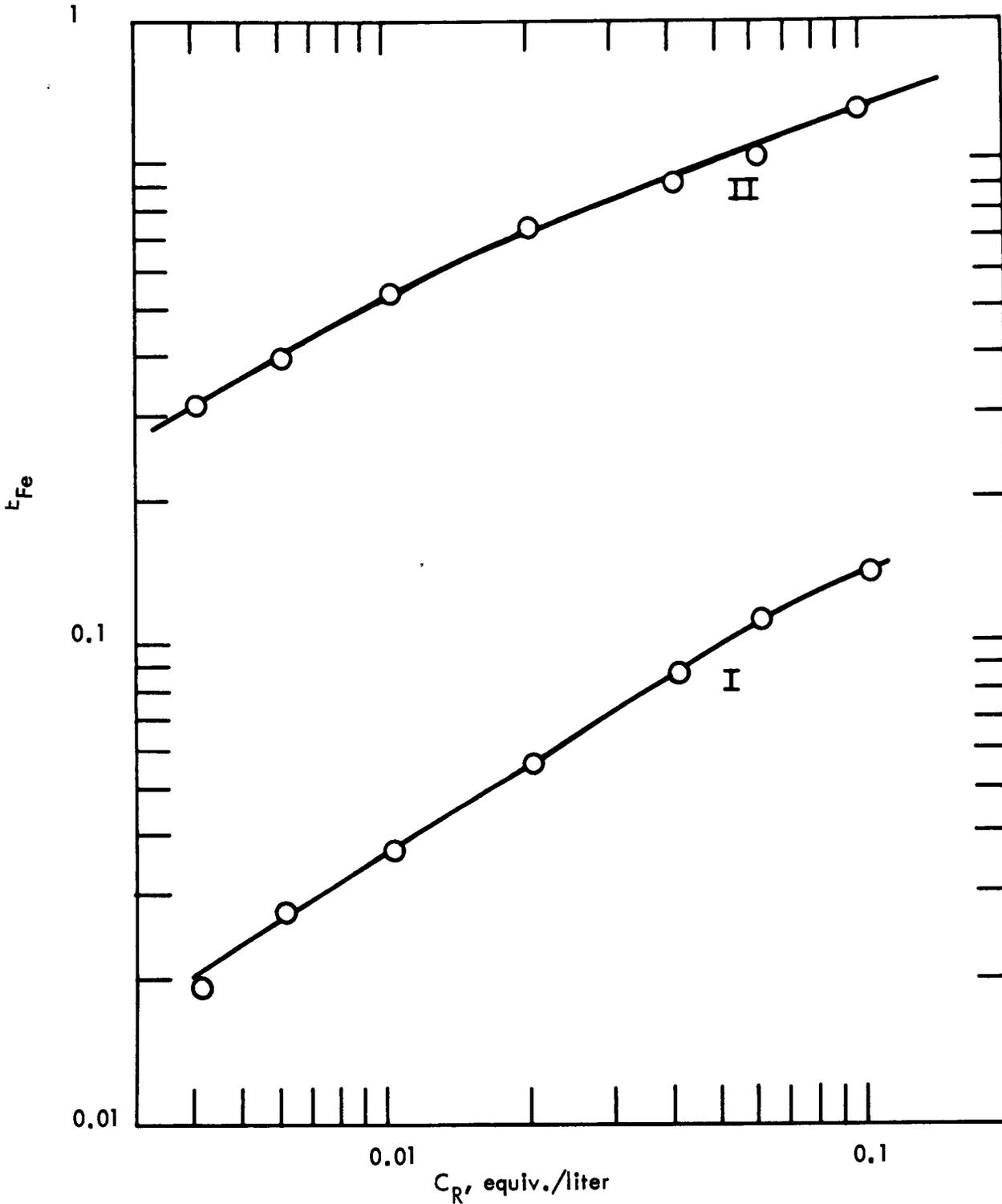


Fig. 3. The Total Amine Concentration Dependence of Iron(III) Extraction from 0.5 M Sulfate Solution, 25°C: I, 0.180 M  $H_2SO_4$  (pH = 1.0); II, 0.0300 M  $H_2SO_4$  (pH = 2.0). The total iron(III) concentration in all cases was 0.00235 M.

Table IV

THE EXTRACTION OF IRON(III) BY DDAS AS A  
FUNCTION OF ACIDITY AND IRON(III) CONCENTRATION

$$C_{H_2SO_4} + C_{Na_2SO_4} = 0.500 \text{ M}; C_R = 0.1036 \text{ N}; 25^\circ C$$

$C_{H_2SO_4}$ <u>M</u>	pH	$(C_{Fe})_{aq}$ <u>M</u>	$(C_{Fe})_{bz}$ <u>M</u>	$E_{Fe}$	$C_{H_2SO_4}$ <u>M</u>	pH	$(C_{Fe})_{aq}$ <u>M</u>	$(C_{Fe})_{bz}$ <u>M</u>	$E_{Fe}$
0.00964	2.50	0.000684	0.001677	2.45	0.0889	1.42	0.000440	0.000156	0.355
							.000859	.000327	.381
0.01806	2.23	0.000897	0.001472	1.64			.001678	.000681	.406
0.0300	2.00	0.000116	0.0000818	0.707	0.135	1.19	0.000973	0.000213	0.219
		.000224	.000168	.750			.001897	.000453	.239
		.000394	.000307	.779					
		.000629	.000673	1.070	0.180	1.00	0.000351 <sup>a</sup>	0.0000496	0.141
		.001083	.001456	1.344			.000660 <sup>a</sup>	.0000925	.140
		.001487	.00239	1.607			.00165 <sup>a</sup>	.000232	.141
		.00209	.00418	2.00			.00275 <sup>a</sup>	.000385	.140
		.00334	.00919	2.75			.00544 <sup>a</sup>	.000829	.1524
		.00705	.0243	3.45			.00803 <sup>a</sup>	.001368	.1704
		.0225	.0402	1.79			.01309 <sup>a</sup>	.00258	.1971
		.1097	.0470	0.428			.0253 <sup>a</sup>	.00598	.236
		.267	.0464	0.174			.0326 <sup>a,b</sup>	.00894	.274
0.0439	1.80	0.000358	0.000235	0.656			.0541 <sup>a,b</sup>	.0151	.279
		.000684	.000502	.734			.0771 <sup>a,b</sup>	.0197	.256
		.001279	.001090	.852			.1123 <sup>a,b</sup>	.0260	.232
							.1751 <sup>a,b</sup>	.0324	.185
							.308 <sup>a,b</sup>	.0375	.122

a) These values were obtained by material balance. In general, they are in satisfactory agreement with the analytical results.

b) In these runs, an additional amount of sodium sulfate equal to one-half of the iron(III) molarity was added to the aqueous phase.

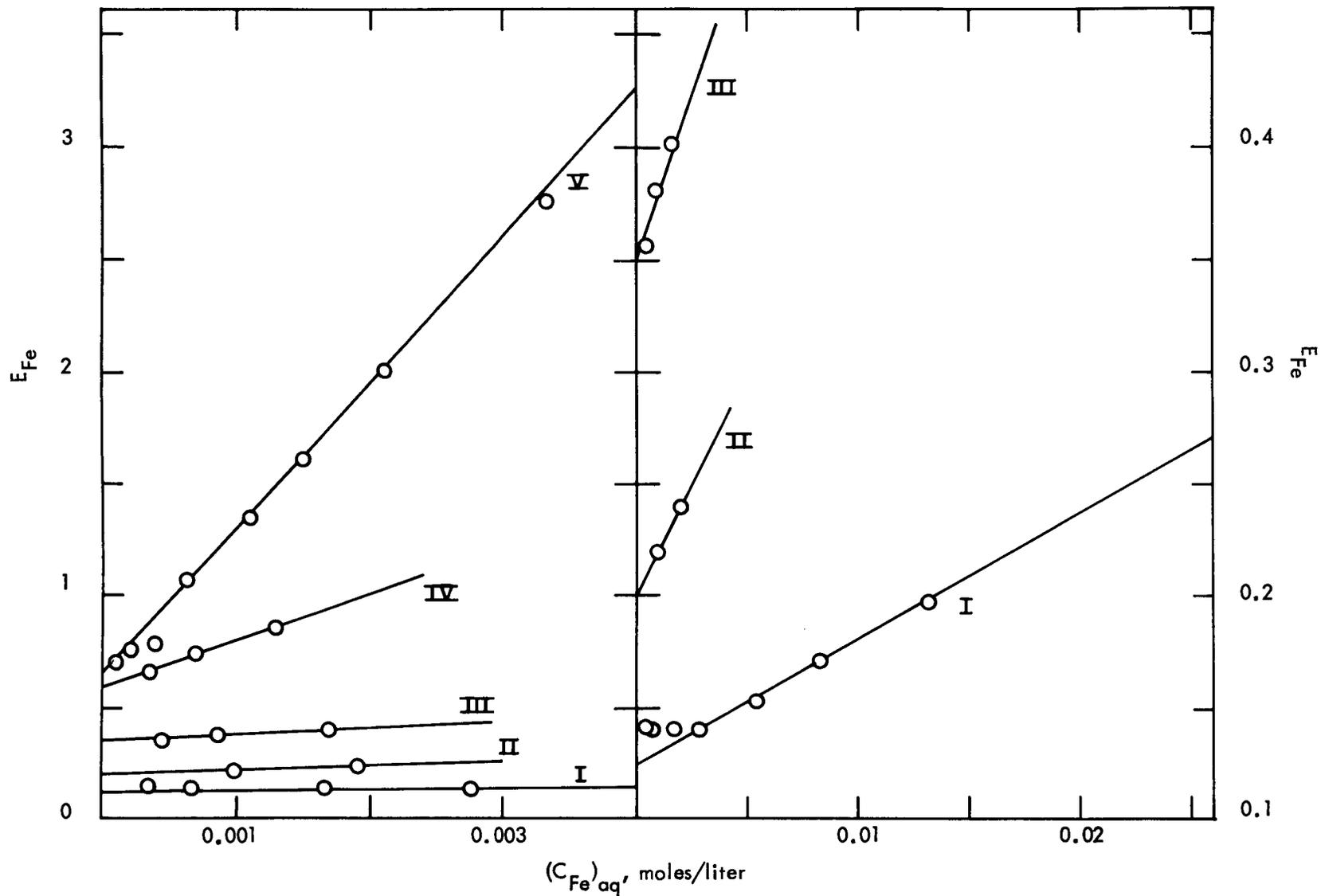


Fig. 4. The Iron(III) Concentration Dependence of Iron(III) Extraction from 0.5 M Sulfate Solution by 0.1036 N DDAS, 25°C: I, 0.180 M  $H_2SO_4$ ; II, 0.135 M  $H_2SO_4$ ; III, 0.0889 M  $H_2SO_4$ ; IV, 0.0439 M  $H_2SO_4$ ; V, 0.0300 M  $H_2SO_4$ .

Table V

PARAMETERS IN THE EQUATION  $E_{Fe} = E_1 + E_2(C_{Fe})_{aq}$

$C_{H_2SO_4} + C_{Na_2SO_4} = 0.500 \underline{M}$ ,  $C_R = 0.1036 \underline{N}$ ,  $25^\circ C$

$\frac{C_{H_2SO_4}}{\underline{M}}$	$\underline{E_1}$	$\frac{E_2}{\underline{M}^{-1}}$	$\frac{E_1/\sqrt{E_2}}{\underline{M}^{1/2}}$
0.0300	0.62	680	0.0238
.0439	.59	210	.0407
.0889	.35	28	.0662
.135	.20	20	.0446
.180	.125	5.6	.0526

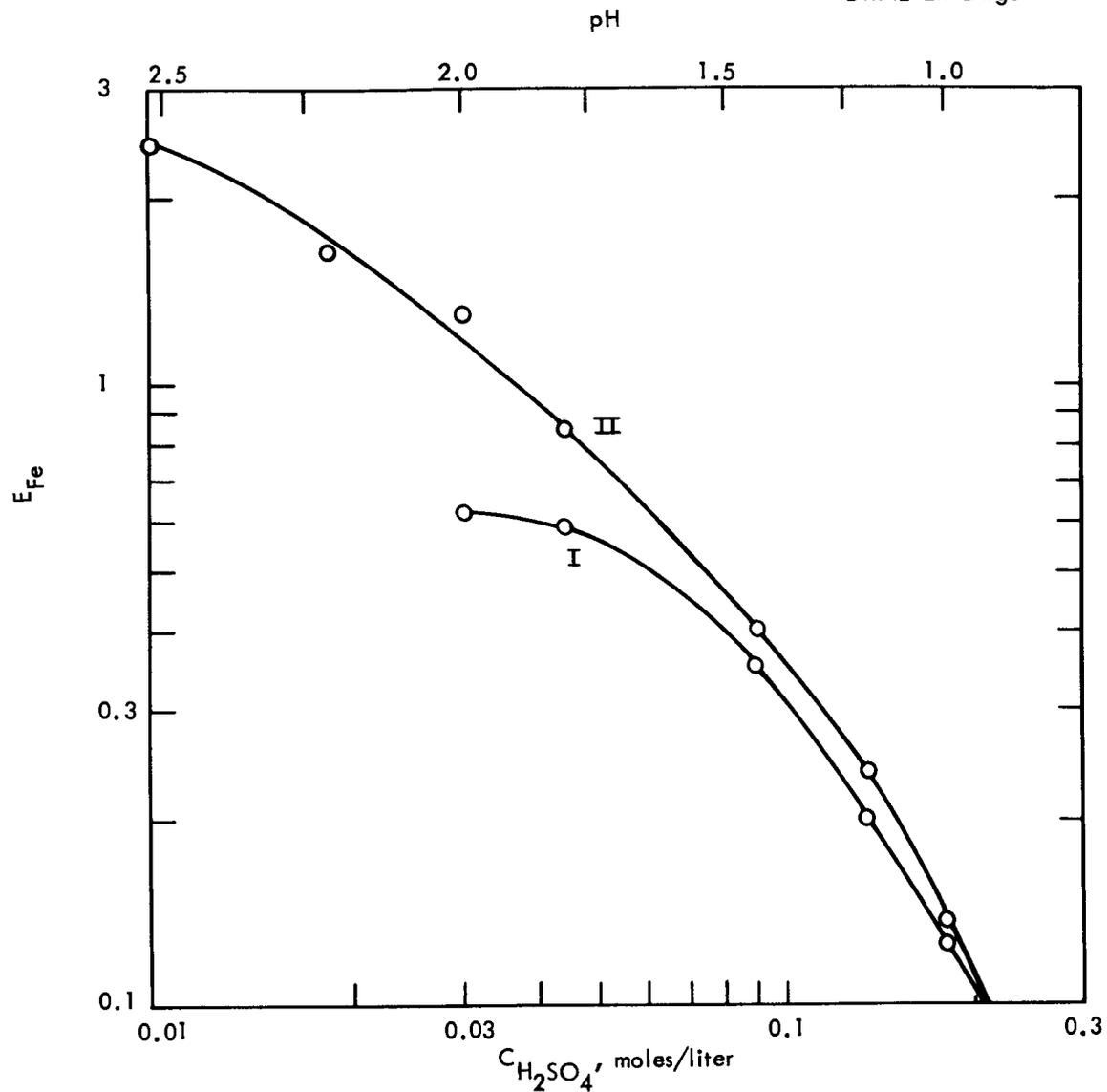
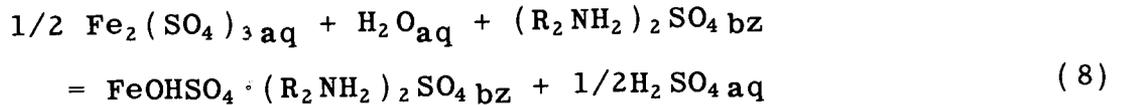


Fig. 5. The Acidity Dependence of Iron(III) Extraction from 0.5 M Sulfate Solution by 0.1036 N DDAS, 25°C: I, at Infinite Dilution of Iron(III); II, at Constant Total Iron(III) Concentration of 0.00235 M.

	<u>Initial</u>	<u>Final</u>	<u>Change</u>
$(C_{Fe})_{aq}$ :	0.0627 <u>M</u>	0.0225 <u>M</u>	-0.0402 <u>M</u>
$C_{H_2SO_4}$ :	0.0300	0.0502	+0.0202

in which one equivalent of acid is liberated by the extraction of one mole of iron(III). The extraction results at higher  $(C_{Fe})_{aq}$  values, plotted as  $(C_{Fe})_{bz}/C_R$  vs.  $(C_{Fe})_{aq}$  in Fig. 6, indicate that the limiting mole ratio of iron(III) to  $C_R$  is 0.5; accordingly, the molecular reaction is suggested



This gives the material balance relation

$$(C_{SO_4=})_{bz} = C_{R_2S} + C_{RHS} + 2FeOHSO_4 \cdot (R_2NH_2)_2SO_4_{bz} \quad (9)$$

Values of  $(C_{SO_4=})_{bz}$  calculated from this expression are compared with analytical results in Table VI, for several of the runs at 0.18 M acid\*. The agreement between the calculated and found  $(C_{SO_4=})_{bz}$  values is satisfactory.

Results which show the dependence of  $E_{Fe}$  on the aqueous sulfate concentration are shown in Table VII and Fig. 7.

## DISCUSSION

Sulfuric Acid Extraction Results. - The constancy of the ratio  $C_{RHS}/C_{R_2S}$  (Table I), independent of the total amine

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\*From the results in Table I, the ratio  $C_{RHS}/C_{R_2S}$  was taken to be 1.15 in these calculations.

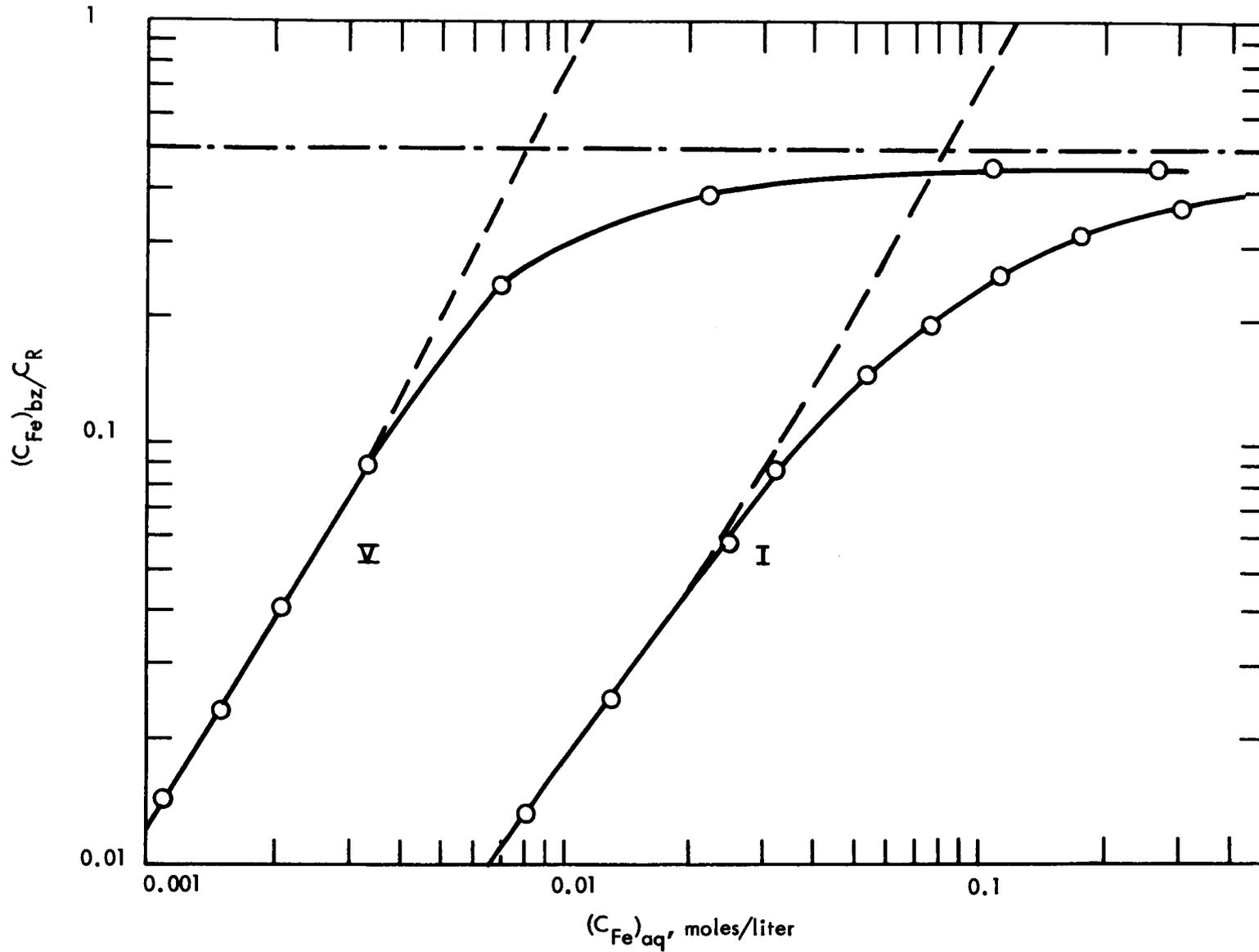


Fig. 6. The Dependence of the Mole Ratio Fe(III)/DDA on the Aqueous Iron(III) Concentration in 0.5 M Sulfate Solution for 0.1 N DDAS, 25°C: I, 0.180 M  $H_2SO_4$ ; V, 0.0300 M  $H_2SO_4$ ; ---, Calculated from Curves in Fig. 4; -.-.-, Fe(III)/DDA = 0.5.

Table VI

COMPARISON OF CALCULATED AND FOUND ( $C_{SO_4=}$ ) bz

$C_{H_2SO_4} = 0.180 \underline{M}$ ,  $C_{Na_2SO_4} = 0.320 \underline{M}$ ,  $C_R = 0.1036 \underline{N}$ ,  $25^\circ C$

$(C_{Fe})_{bz}$ <u>M</u>	$C_{R_2S}$ <u>M</u>	$C_{RHS}$ <u>M</u>	$(C_{SO_4=})_{bz}$ , <u>M</u>	
			Calc.	Found
0.0197	0.02035	0.0235	0.0833	0.0829
.0260	.01636	.01888	.0872	.0874
.0324	.01230	.01420	.0913	.0906
.0375	.00907	.01046	.0945	.0909

Table VII

THE EXTRACTION OF IRON(III) BY DDAS  
AS A FUNCTION OF SULFATE CONCENTRATION

$C_R = 0.1036 \underline{N}$ ;  $pH = 2.0$ ,  $25^\circ C$

$C_{H_2SO_4}$ <u>M</u>	$C_{Na_2SO_4}$ <u>M</u>	$(C_{Fe})_{aq}$ <u>M</u>	$(C_{Fe})_{bz}$ <u>M</u>	$E_{Fe}$
0.00573	-----	0.000460	0.001890 <sup>a</sup>	4.11
.00690	0.00800	.000455	.001895 <sup>a</sup>	4.16
.00770	.01678	.000478	.001872 <sup>a</sup>	3.92
.00990	.03906	.000533	.001817 <sup>a</sup>	3.41
.01340	.08512	.000630	.001720 <sup>a</sup>	2.73
.01849	.1794	.000780	.001570 <sup>a</sup>	2.01
.0300	.470	.001017 <sup>b</sup>	.001333 <sup>b</sup>	1.31 <sup>b</sup>

a) These values were obtained by material balance. In general, they are in satisfactory agreement with the analytical results.

b) This value was obtained by interpolation of the data in Table IV.

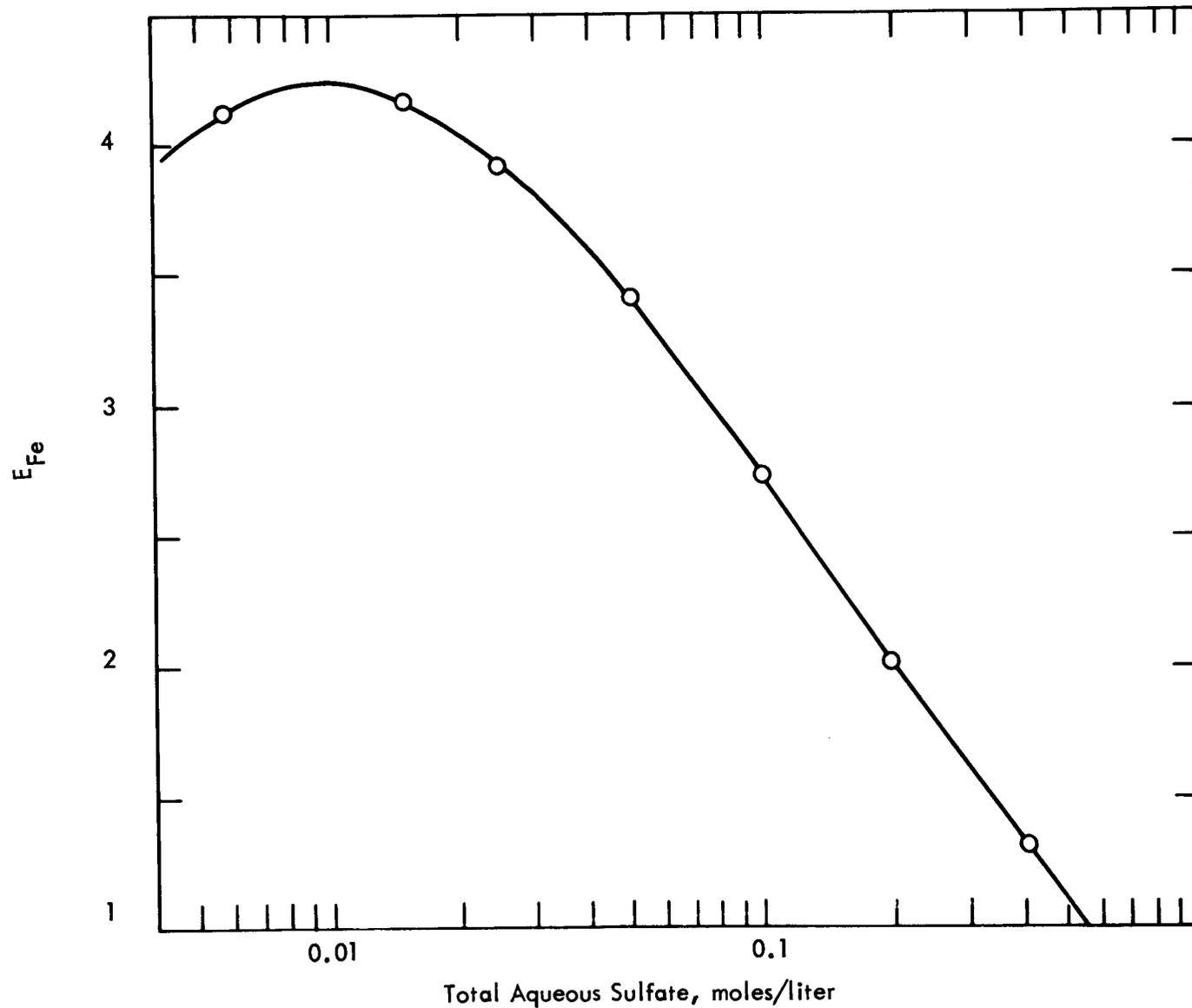
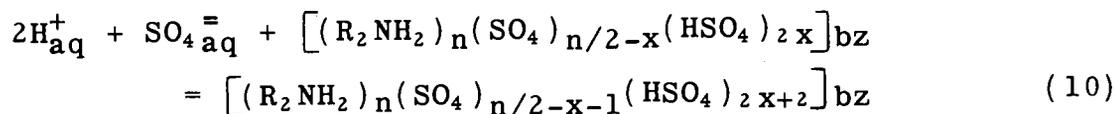


Fig. 7. The Sulfate Dependence of Iron(III) Extraction by 0.1036 N DDAS at pH = 2.0, 25°C. The total iron(III) concentration in all cases was 0.00235 M.

concentration  $C_R$  is consistent with association of amine sulfate molecules in the benzene phase. For example, viewing this extraction process as the incorporation of successive molecules of sulfuric acid into amine sulfate aggregates,



it is reasonable to expect that the composition of the aggregate phase will be independent of its apparent concentration in the benzene phase. If the activities of the amine bisulfate and the amine sulfate in the associated amine phase are related to the respective equivalent fractions  $C_{RHS}/C_R$  and  $2C_{R_2S}/C_R$ , then the equilibrium constant for this reaction may be written

$$K = \frac{C_{RHS}^2}{2C_R C_{R_2S} a_{H_2SO_4}} \cdot \frac{\gamma_{RHS}^2}{\gamma_{R_2S}} \quad (11)$$

This expression is consistent with the empirical relation in equation 5 if  $\gamma_{RHS}^2 / \gamma_{R_2S} = 2C_R / C_{R_2S}^*$ .

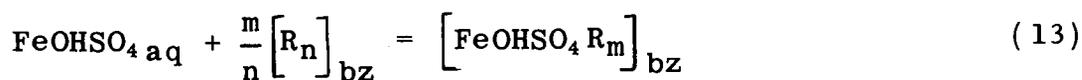
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\*Other interpretations of these acid extraction results assuming monomeric or dimeric species have been unsuccessful. Thus, for monomeric amine sulfate and bisulfate species in the benzene phase, the expected equilibrium quotient is,  $K = C_{RHS}^2 / (C_{R_2S} a_{H_2SO_4})$ . Similarly, if the amine bisulfate is assumed to be dimeric,  $K = C_{RHS} / (C_{R_2S} a_{H_2SO_4})$ . While the second expression implies the required constancy of  $C_{RHS} / C_{R_2S}$  at constant acidity, the predicted acidity dependence is inconsistent with the present results.

Iron(III) Extraction Results. - Rearranging equation 7, which appears to describe the extraction behavior of iron(III) at infinite dilution, constant acidity and 0.5 M sulfate,

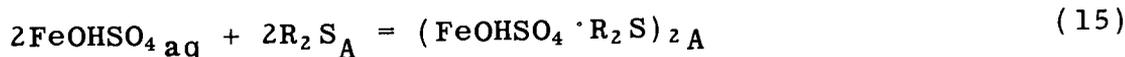
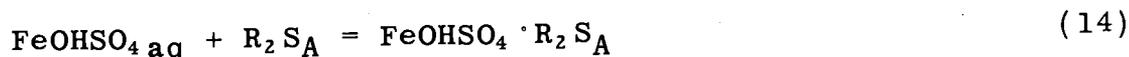
$$\frac{(C_{Fe})_{bz}}{C_R} = K(C_{Fe})_{aq} C_R^{(p-1)}; \quad p = 1/2 - 2/3 \quad (12)$$

It is evident in this case that the composition of the assumed aggregate phase is dependent on the total amine concentration. Assuming that  $FeOHSO_4$  is the extracted iron(III) species, equation 7 suggests the reaction



in which  $R_n$  represents the amine-sulfate-bisulfate aggregate. If activity coefficients are constant,  $m/n = p$ , and the extraction of iron results in a 1.5 - 2 fold increase in the association number of the aggregate. While such a conclusion is not unreasonable, it must be considered quite tentative in view of the present limited knowledge of such extraction processes. In particular, it is possible that the association number of the amine sulfate changes with concentration and that this in turn effects the relative number of favorable iron(III) adsorption sites. In any case, it appears that the iron(III) extraction and the sulfuric acid extraction processes involve different mechanisms.

The extraction results at a constant total amine concentration,  $C_R = 0.1$  N, 0.5 M sulfate, and low iron(III) concentrations (Fig. 4) are consistent with the reactions



in which monomeric and dimeric iron(III) species are formed in the associated DDAS phase (indicated by the subscript A). Their respective total concentrations in the organic layer,  $C_1$  and  $C_2$  (which at constant  $C_R$  are proportional to their concentrations in the associated phase), may be related to the aqueous concentration of the complex  $\text{FeOHSO}_4$  by

$$K_1 = \frac{C_1 G_1}{[\text{FeOHSO}_4]_{\text{aq}}} ; \quad K_2 = \frac{C_2 G_2}{[\text{FeOHSO}_4]_{\text{aq}}^2} \quad (16)$$

in which  $G_1 = \gamma_1 / \gamma_{\text{R}_2 \text{S}}$  and  $G_2 = \gamma_2 / \gamma_{\text{R}_2 \text{S}}^2$  at constant  $C_R$  (the subscripts 1 and 2 again referring to the monomeric and dimeric iron(III) species, respectively). The aqueous activity coefficient of  $\text{FeOHSO}_4$  is taken as constant. Combining the expressions for  $K_1$  and  $K_2$  with the material balance relation,  $(C_{\text{Fe}})_{\text{bz}} = C_1 + 2C_2$

$$E_{\text{Fe}} = \frac{(C_{\text{Fe}})_{\text{bz}}}{(C_{\text{Fe}})_{\text{aq}}} = \frac{K_1}{G_1} \left\{ \frac{[\text{FeOHSO}_4]_{\text{aq}}}{(C_{\text{Fe}})_{\text{aq}}} \right\} + \frac{2K_2}{G_2} \left\{ \frac{[\text{FeOHSO}_4]_{\text{aq}}}{(C_{\text{Fe}})_{\text{aq}}} \right\}^2 (C_{\text{Fe}})_{\text{aq}} \quad (17)$$

Since  $K_1$ ,  $K_2$ ,  $G_1$ ,  $G_2$  and the ratio\*  $[\text{FeOHSO}_4]_{\text{aq}} / (C_{\text{Fe}})_{\text{aq}}$  all may be assumed constant for each series of measurements at constant acidity in Fig. 4, this equation is equivalent to equation 6, and

---

\*Cf. Equation 27.

$$E_1 = \frac{K_1}{G_1} \frac{[\text{FeOHSO}_4]_{\text{aq}}}{(C_{\text{Fe}})_{\text{aq}}}; \quad E_2 = \frac{2K_2}{G_2} \left\{ \frac{[\text{FeOHSO}_4]_{\text{aq}}}{(C_{\text{Fe}})_{\text{aq}}} \right\}^2 \quad (18)$$

In addition

$$\frac{E_1}{\sqrt{E_2}} = \frac{K_1}{\sqrt{2K_2}} \left[ \frac{\sqrt{G_2}}{G_1} \right] \quad (19)$$

From the approximate constancy of  $E_1/\sqrt{E_2}$  (Table V) at the various aqueous acidities, it may be concluded that within the validity of the present interpretation,  $\sqrt{G_2}/G_1$  does not vary greatly with changing amine bisulfate content of the associated amine phase.

It remains to consider the increase in  $E_1$  and  $E_2$  with decreasing acidity and the sulfate dependence of  $E_{\text{Fe}}$ . For the 0.5 M sulfate solutions it is evident that the ratio  $[\text{FeOHSO}_4]_{\text{aq}}/(C_{\text{Fe}})_{\text{aq}}$  which appears in the expressions for  $E_1$  and  $E_2$  will increase with decreasing acidity. The extent of this increase can be estimated as follows: Whiteker and Davidson<sup>(14)</sup> give for  $\mu = 1$  M perchloric acid-sulfuric acid solutions,



From the results of Milburn and Vosburgh<sup>(16)</sup> for  $\mu = 1.5$  M perchlorate solutions,



Since the affinity of the bipoisitive  $\text{FeOH}^{++}$  for sulfate is expected to be less than that of  $\text{Fe}^{+++}$ , then



Combining equations 20, 22 and 24



If these  $K_3$ ,  $K_4$  and  $K_5$  values are approximately correct for the present 0.5 M sulfate solutions, then the only iron(III) species in appreciable abundance at low  $(C_{\text{Fe}})_{\text{aq}}$  values are  $\text{FeSO}_4^+$  and  $\text{Fe}(\text{SO}_4)_2^-$ . In such a case

$$\frac{[\text{FeSO}_4^+]}{(C_{\text{Fe}})_{\text{aq}}} = \frac{1}{1 + K_4 [\text{SO}_4^-]} \quad (26)$$

and

$$\frac{[\text{FeOHSO}_4]_{\text{aq}}}{(C_{\text{Fe}})_{\text{aq}}} = \frac{K_5}{(1 + K_4 [\text{SO}_4^-]) [\text{H}^+]} \quad (27)$$

Introducing this into equation 18,

$$E_1 = \frac{K_1 K_5 / G_1}{(1 + K_4 [\text{SO}_4^-]) [\text{H}^+]}; \quad E_2 = \frac{2K_2 K_5^2 / G_2}{(1 + K_4 [\text{SO}_4^-])^2 [\text{H}^+]^2} \quad (28)$$

This is qualitatively consistent with the increase in  $E_{\text{Fe}}$  with decreasing sulfate concentration shown in Fig. 7\*.

---

\*Since these measurements were performed at approximately constant pH, then according to equation 27 the concentration of the extracted species,  $[\text{FeOHSO}_4]$ , will vary directly with  $[\text{FeSO}_4^+]$ . Accordingly, the curve in Fig. 7 may be accounted for qualitatively as follows: as the sulfate concentration decreases from 0.5 M,  $[\text{FeSO}_4^+]/C_{\text{Fe}}$  increases as a result of the dissociation of  $\text{Fe}(\text{SO}_4)_2^-$ . In the vicinity of 0.01 M sulfate,  $[\text{FeSO}_4^+]/C_{\text{Fe}}$  levels off and subsequently decreases because of the dissociation of  $\text{FeSO}_4^+$ .

From the points at 0.2 M and 0.5 M sulfate,  $K_4$  (equation 21) was estimated by means of equation 28 to be ca. 2. Considering the ionic strength variation involved, this value is not necessarily inconsistent with Whiteker and Davidson's value of 9.4<sup>(14)</sup>.

From the above expression for  $E_1$  (equation 28), the activity coefficient function  $G_1$  is proportional to  $1/\{E_1(1+K_4 [SO_4^{=}] [H^+])\}$ . This expression is evaluated at each acidity for the 0.5 M sulfate data in Table VIII, using  $K_4 = 2$  and  $K_4 = 10$ . In both cases, the resulting values are reasonably constant in the range 0.044 - 0.18 M acid, there being no apparent systematic variation with changing amine-bisulfate content in the associated amine phase. This result along with the approximate constancy of the ratio  $\sqrt{G_2}/G_1$  suggests that the acidity dependence of  $E_1$  and  $E_2$  can be accounted for fairly well solely in terms of the expected variation of the ratio  $[FeOHSO_4]_{aq}/(C_{Fe})_{aq}$ . This must be considered a tentative conclusion, however, in the absence of direct measurements of iron(III) hydrolysis in such sulfate solutions.

The formation of a binuclear complex  $(FeOHSO_4)_2$  in the aqueous phase, which is suggested by equation 23, may become appreciable as  $(C_{Fe})_{aq}$  increases, contributing to the negative deviations which occur if the  $E_{Fe}$  vs.  $(C_{Fe})_{aq}$  plots are extended above  $(C_{Fe})_{aq} = 0.004$  M at 0.03 M acid and 0.03 M at 0.18 M acid. However, this effect cannot be separated from others such as increasing ionic strength and saturation which become important at these higher iron concentrations.

Table VIII

VARIATION OF THE ACTIVITY COEFFICIENT FUNCTION  $G_1$  WITH ACIDITY

$$C_{H_2SO_4} + C_{Na_2SO_4} = 0.500 \text{ M}, C_R = 0.1036 \text{ N}, 25^\circ\text{C}$$

$C_{H_2SO_4}$ <u>M</u>	$C_{RHS}/C_{R_2S}$ <sup>a</sup>	$[H^+]$ <sup>b</sup> <u>M</u>	$[SO_4^{=}]$ <sup>b</sup> <u>M</u>	$G_1 = \frac{1}{E_1(1+K_4[SO_4^{=}]) [H^+]}$ <sup>c</sup>	
				$K_4 = 2$	$K_4 = 10$
0.0300	0.16	0.00774	0.447	110	38.1
.0439	.23	.01188	.424	77.2	27.2
.0889	.51	.0283	.350	59.4	22.4
.135	.81	.0574	.267	56.8	23.7
.180	1.17	.0829	.222	66.8	30.0

a) These values were obtained using equation 5.

b) These concentrations were calculated assuming  $K_2^a = 0.066$  moles/liter.

c) Cf. equation 28.

The assumption of  $\text{FeOHSO}_4$  as the extracted species is consistent with the observation that the majority of metals which are strongly extracted from acidic sulfate solutions by amines are present as oxygenated aqueous ions and so probably are extracted as oxygenated species. However, in view of the present lack of knowledge of the physical nature of amine sulfate solutions in organic diluents and, therefore, the manner in which extracted metal species are held, other possible interpretations of the present results certainly are not excluded.

#### SUMMARY

Results of an investigation of iron(III) extraction from sulfuric acid-sodium sulfate solutions by di-n-decylamine sulfate (DDAS) in benzene are described.

(1) The extraction of sulfuric acid from 0.5 M sulfate solutions by DDAS (presumably forming the amine bisulfate) conforms to the empirical relation,

$$K = \frac{C_{\text{RHS}}}{C_{\text{R}_2\text{S}} a_{\text{H}_2\text{SO}_4}^{1/2}} = 97 \pm 6$$

in which  $C_{\text{RHS}}$  and  $C_{\text{R}_2\text{S}}$  are, respectively, the molarity of amine bisulfate and amine sulfate in the benzene phase and  $a_{\text{H}_2\text{SO}_4}$  is the aqueous sulfuric acid activity.

(2) The extraction of iron(III) from 0.5 M sulfate solutions at constant acidity and infinite dilution of iron(III) appears to obey the relation,

$$K = \frac{(C_{Fe})_{bz}}{(C_{Fe})_{aq} C_R^p} = \frac{E_1}{C_R^p}; \quad p = 1/2 - 2/3$$

in which  $C_R$  is the total amine concentration

(3) At constant  $C_R$  and constant acidity for 0.5 M sulfate solutions the extraction coefficient  $E_{Fe} = (C_{Fe})_{bz}/(C_{Fe})_{aq}$  at first increases from its infinite-dilution value  $E_1$  with  $(C_{Fe})_{aq}$  according to the relation

$$E_{Fe} = E_1 + E_2 (C_{Fe})_{aq}$$

The limiting ratio  $(C_{Fe})_{bz}/C_R$  as  $(C_{Fe})_{aq}$  is further increased appears to be 0.5.

(4)  $E_{Fe}$  increases (both  $E_1$  and  $E_2$  increase) with decreasing acidity over the range 0.18 - 0.03 M  $H_2SO_4$  in 0.5 M sulfate.

(5)  $E_{Fe}$  increases with decreasing aqueous sulfate concentration at pH = 2.0 in the range 0.5 M - 0.01 M sulfate.

(6) Acid titration results indicate that one equivalent of acid is liberated for each mole of iron(III) extracted.

(7) The results (3), (4), (5) and (6) are consistent with the extraction of  $FeOHSO_4$  from aqueous solution to form a mononuclear and a binuclear iron(III) - DDAS species in the benzene phase. All the results are discussed in terms of association of DDAS in the benzene phase.

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