Extraction of Group VIII Metals by Long-Chain Alkyl Amines. IV. Studies on the Extraction of Iron(II), Iron(III), Cobalt(II), Cobalt(III), and Nickel(II) from Aqueous Sulfate Media[1]
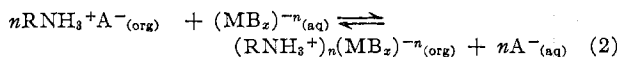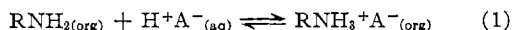
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The extraction of the Fe, Co, and Ni ions from aqueous sulfate solutions by long-chain alkyl amines has been investigated. The extraction efficiency of the amine solutions for the metal ions has been studied as a function of amine type, organic diluent, acid pretreatment of the amine, and composition of the aqueous solution. Appreciable extraction was obtained in the case of the Fe(III) solutions only. This extraction system was studied in detail and on the basis of the results obtained the stoichiometry of the extracted species is postulated.

Introduction

Previous papers in this series have dealt with the extraction of Fe, Co, and Ni (as the chlorides or oxalates) by long-chain alkyl amines.[2-4] In all of the cases where appreciable extraction was observed, it was postulated that the extraction process occurred by "liquid anion exchange" since the metallic anionic complex could be identified in the organic phase. The over-all reaction might be represented by (assuming a primary amine)

$$RNH_{2(org)} + H^+A^-_{(aq)} \rightleftharpoons RNH_3^+A^-_{(org)} \quad (1)$$

$$nRNH_3^+A^-_{(org)} + (MB_x)^{-n}_{(aq)} \rightleftharpoons$$
$$(RNH_3^+)_n(MB_x)^{-n}_{(org)} + nA^-_{(aq)} \quad (2)$$

However, an alternative solvent extraction model might be one of "ion pair absorption" which could be represented as

$$nRNH_{2(org)} + nH^+A^-_{(aq)} + (MB_x)^{-n}_{(aq)} \rightleftharpoons$$
$$(RNH_3^+)_n(MB_x)^{-n}_{(org)} + nA^-_{(aq)} \quad (3)$$
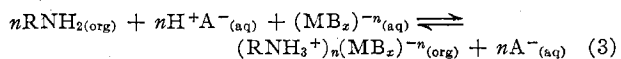
or as in the case of the chloride complexes extracted from hydrochloric acid solutions

$$nRNH_{2(org)} + nH^+Cl^-_{(aq)} + M^{+v}_{(aq)} \rightleftharpoons$$
$$(RNH_3^+)_n(MCl_{v+n})^{-n}_{(org)} \quad (4)$$
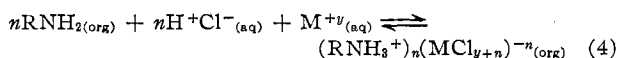
Previous work[5] on the extraction of Fe(III) from sulfate solutions indicated that the extracted species did not contain a simple metallic anion of Fe(III) and SO_4^{-2}. Baes postulated that the Fe(III) moiety was extracted as $FeOHSO_4$ to give an extraction species of $[R_2NH_2^+]_2SO_4^{-2} \cdot FeOHSO_4$ in the organic phase. However, no conclusive evidence for the stoichiometry of the extracted species or the extraction mechanism was presented. Thus the present work was undertaken in an attempt to further clarify the extraction of metal ions from sulfate media by long-chain alkyl amines. Our results are most easily interpreted in terms of an anion-exchange model [such as described in eq. 1 and 2] although our data do not provide a discriminating test to identify the true mechanism.

Experimental

Materials. Fe(III), Fe(II), Co(II), and Ni(II).—Solutions were prepared from the corresponding Analytical Reagent grade metal sulfate with the excess sulfate added as Analytical Reagent grade sulfuric acid. The iron was determined volumetrically using potassium permanganate, the sulfate was determined gravimetrically as barium sulfate, the hydrogen ion concentration was titrated with standard sodium hydroxide, the cobalt was determined volumetrically using EDTA, and the nickel was determined gravimetrically with dimethylglyoxime. In those cases where the acid content of the organic amine solution is reported, values were obtained volumetrically by titrating with standard sodium ethoxide in a benzene–ethyl alcohol mixture.[6]

Co(III)–Sulfate Solutions.—$Co_2(SO_4)_3$ was prepared by electrolytic oxidation of $CoSO_4$ by a method described by Swann, *et al.*,[7] using an electrolysis cell similar to one described by Bricker, *et al.*[8] To obtain a Co^{58} labeled compound, an appropriate quantity of Co^{58} (Oak Ridge stock solution) was added to the $CoSO_4$ solution before electrolysis. The resulting $Co_2(SO_4)_3$ was very unstable and had to be stored at a temperature of $-5°$ or lower. Spectra obtained on the resulting solutions showed no evidence of Co(II) contamination.

Amine Solutions.—All amines used in this study have been described in previous papers.[2-4] Reagent grade organic solvents were used without further purification. In those cases where the amine salt was desired, the amine solution was equilibrated with a 3.0 N solution of the appropriate acid.

Procedure.—Extraction data were obtained for the Fe(III) and Co(II) systems by a tracer method described previously.[2,3] In the case of the Co(III) system, the Co^{58} labeled compound was used to make up the solutions and the extraction data were determined as described previously for several oxalate complexes.[4] The distribution of Fe(II) between the aqueous sulfate system and the organic amine solution was followed by volumetric determination of the Fe(II) solutions before and after extraction. The results reported for the Ni(II) systems were obtained by comparing the spectra of the aqueous solution before and after extraction and also testing a nitric acid stripping solution for Ni(II) with dimethylglyoxime.

Results

No significant extraction of Fe(II), Co(II), or Ni(II) was found over a wide range of varying H_2SO_4 and total sulfate concentrations for any of the amines or amine salts studied. Solutions of $Co_2(SO_4)_3$ in concentrated H_2SO_4 were reduced to Co(II) when extraction was attempted.

(1) Presented in part before the Joint Southeast–Southwest Regional Meeting of the American Chemical Society, New Orleans, Louisiana, December 7, 1961.

(2) M. L. Good and S. E. Bryan, *J. Am. Chem. Soc.*, **82**, 5636 (1960).

(3) M. L. Good and S. E. Bryan, *J. Inorg. Nucl. Chem.*, **20**, 140 (1961).

(4) S. E. Bryan and M. L. Good, *ibid.*, **21**, 339 (1961).

(5) C. F. Baes, Jr., USAEC, ORNL-1930 (1955).

(6) J. S. Fritz and N. M. Lisicki, *Anal. Chem.*, **23**, 589 (1951).

(7) S. Swann, Jr., and T. S. Xanthakos, *J. Am. Chem. Soc.*, **53**, 400 (1931).

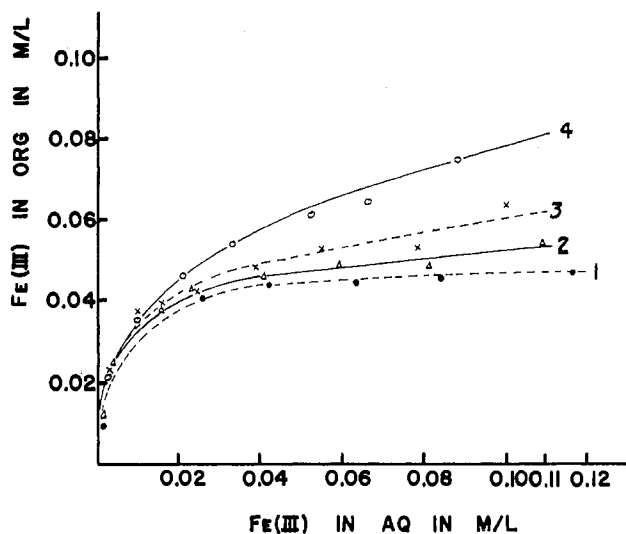(8) C. E. Bricker and L. J. Loeffler, *Anal. Chem.*, **27**, 1419 (1955).

Fig. 1.—Extraction isotherms for the extraction of Fe(III) by 0.2 M Primene 81-R in various solvents (aqueous solution was 0.1 M H_2SO_4 and 0.5 M total sulfate): 1, chloroform; 2, hexane; 3, trichloroethylene; 4, benzene.

The extraction of Fe(III) was studied as a function of the amine type and organic solvent used (data shown in Table I); pH of the aqueous solution (data shown in Table II); and total sulfate concentration in the aqueous solution (data shown in Table III). Also, acid pretreatment of the amines had an effect which was strongly dependent upon the nature of the acid. Typical results for different acid pretreatment of Primene 81-R in chloroform show distribution coefficients as follows: $HClO_4$ pretreatment, $D = 0.42$; HNO_3, 0.43; HCl, 0.76; H_2SO_4, 8.4; $HC_2H_3O_2$, 10.6; and H_2-C_2O_4, 20.3. The mole ratios of hydrogen ion to amine in the H_2SO_4-pretreated solutions were determined. For a 1.5 M H_2SO_4 pretreating solution, the ratio for Primene 81-R and for 2,2'-diethyldihexylamine was 1.7. For tri-n-hexylamine the ratio was 1.9. This indicates that at this relatively high acid concentration,
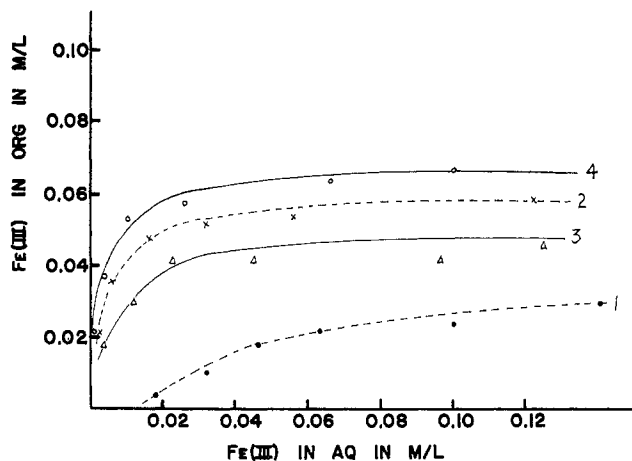

Fig. 2.—Extraction isotherms for the extraction of Fe(III) by secondary and tertiary amines in various solvents (aqueous solution was 0.1 M H_2SO_4 and 0.5 M total sulfate): 1, 0.2 M tri-n-hexylamine in benzene; 2, 0.2 M 2,2'-diethyldihexylamine in chloroform; 3, 0.2 M 2,2'-diethyldihexylamine in trichloro-ethylene; 4, 0.2 M 2,2'-diethyldihexylamine in benzene.

TABLE I

VARIATION OF DISTRIBUTION COEFFICIENT[a] WITH AMINE TYPE IN THE EXTRACTION OF Fe(III) FROM AQUEOUS SULFATE SOLUTIONS[b]

| | Solvent | |
Amine	Chloroform	Benzene
Primene 81-R	250	500
Primene JM-T	250	250
2,2'-Diethyldihexyl	15	39
LA-2	2.6	12
Di-n-decyl	6.4	2.8
XE-204	0.004	...
Tri-n-hexyl	...	...

[a] Distribution coefficient = $[Fe(III)]_{org}/Fe(III)]_{aq}$ = (act. of Fe^{59} in counts/min. per ml.)$_{org}$/(act. of Fe^{59} in counts/min. per ml.)$_{aq}$. [b] The aqueous solution was 0.012 M $Fe_2(SO_4)_3$ in 0.192 N H_2SO_4, all amine solutions were 0.2 M, and equal volumes of aqueous and organic phases were used.

TABLE II

VARIATION OF DISTRIBUTION COEFFICIENT WITH pH IN THE EXTRACTION OF Fe(III) FROM AQUEOUS SULFATE SOLUTIONS

pH	Soln. A[a]	Soln. B[b]
0.1	0.90	3.5
0.5	5.8	10
1.0	8.7	23
1.5	16	88
2.0	16[c]	...

[a] Soln. A: Primene 81-R in benzene *vs.* 0.0128 M Fe(III) in 0.5 M SO_4^{-2} solution. [b] Soln. B: Primene 81-R in chloroform *vs.* 0.012 M Fe(III) in 0.2 M SO_4^{-2} solution. [c] Small amount of solid formed.

TABLE III

VARIATION OF DISTRIBUTION COEFFICIENT WITH TOTAL SULFATE ION CONCENTRATION IN THE EXTRACTION OF Fe(III) FROM AQUEOUS SULFATE SOLUTIONS[a]

Total [SO_4^{-2}]	Soln. C[b]	Soln. D[c]	Soln. E[d]
0.17	500	9.6	0.012
.20	330	6.6	.010
.30	340	9.9	.004
.40	500	15	.002
.50	20	8.2	.005

[a] 0.011 M $Fe_2(SO_4)_3$ in 0.1 M H_2SO_4 and excess Na_2SO_4 (pH 1.1–1.5). [b] Soln. C, 0.2 M Primene 81-R in $CHCl_3$. [c] Soln. D, 0.2 M 2,2'-diethyldihexylamine in $CHCl_3$. [d] Soln. E, 0.2 M XE-204 in $CHCl_3$.

the tertiary amine is converted almost quantitatively to the bisulfate salt ($R_3NH^+HSO_4^-$) while the primary and secondary amines are converted to a mixture of the bisulfate and the sulfate [$(RNH_3^+)_2SO_4^{-2}$] with the bisulfate predominating.

Extraction isotherms as a function of amine type and organic solvent were determined, as shown in Fig. 1 and 2. A reverse loading curve is shown in Fig. 3, where the Fe(III) concentration remains constant and the amine concentration in the organic phase is varied. In all experiments done, equilibrium between the two phases was reached rapidly. Three-minute shaking times were more than adequate. These data agree in general with those obtained by Baes[5] from a similar study of the extraction of Fe(III) from sulfate media by di-n-decylamine in benzene. However, there are

some significant differences. The distribution co-efficients for various amines in chloroform do not de-crease with increasing sulfate ion concentration as is reported for di-*n*-decylamine in benzene. We have not pursued our study in benzene solutions because of non-reproducible distribution coefficients. This may be due, at least in part, to an anomalous solvent extraction equilibrium resulting from the type of agitation. This anomalous effect, found in the extraction of uranyl sulfate from acidic sulfate media when benzene solu-tions of tri-*n*-octylamine or di-*n*-decylamine were used as extractants, has been reported by Allen and McDowell.[9]

In an attempt to ascertain the stoichiometry of the extracted Fe(III) species, the aqueous solutions, be-fore and after extraction, were analyzed for H$^+$, total sulfate, and Fe(III). Also, blank extractions [no added Fe(III)] were analyzed to determine the H$_2$SO$_4$ distribution. Representative data are given in Table IV. The results indicate for the extraction reactions

Fig. 3.—Reverse loading curve for the extraction of Fe(III) by primary and secondary amines (aqueous solution composi-tion: 0.011 M Fe$_2$(SO$_4$)$_3$; 0.1 M H$_2$SO$_4$; 0.5 M SO$_4^{-2}$): 1, Primene 81-R in chloroform; 2, 2,2'-diethyldihexylamine in benzene.

TABLE IV
DETERMINATION OF Fe(III)/SO$_4^{-2}$ FOR THE EXTRACTED SPECIES

| | | ┌───Expt. 2^b───┐ | |
	Expt. 1^a	Blank	Fe(III) soln.
Aq. [SO$_4^{-2}$] before ext.	0.1270	0.1233	0.1265
Aq. [H$^+$] before ext.	.1845	...	...
Aq. [SO$_4^{-2}$] after ext.	.0304	.0565	.0309
Aq. [H$^+$] after ext.	.0512	...	...
Calcd. [SO$_4^{-2}$] lost to org. as H$_2$SO$_4$	.0667	.0668	...
Calcd. [SO$_4^{-2}$] lost to org. as Fe(III)–sulfate species	.0299	...	.0288
Fe(III) extracted	.020	...	.020
[Fe(III)]/[SO$_4^{-2}$] lost to org. by extraction process	$^2/_3$	...	$^2/_3$

^{a} Equal volumes of 0.2 M Primene 81-R in chloroform and an aqueous solution containing Fe$_2$(SO$_4$)$_3$ (as shown in the analyses) were equilibrated, the phases separated, and analyses obtained on aliquots of the aqueous phase. ^{b} Experiment 1 was repeated for a different Fe(III)–sulfate solution and for a blank [no Fe(III)] containing Na$_2$SO$_4$ in place of the Fe$_2$(SO$_4$)$_3$.

a net gain in the organic phase of two Fe(III) ions for every three sulfate ions.

The spectra of several aqueous and organic solutions containing the Fe(III) moiety were obtained. Some representative spectra are shown in Fig. 4. As is indi-cated in curves 1 and 2, the absorption maximum for the aqueous solutions increased as the ratio of sulfate to Fe(III) increased. These aqueous spectra cor-respond closely to those reported by Whiteker and Davidson for the Fe(SO$_4$)$^+$ and the Fe(SO$_4$)$_2^-$ species.[10] However, even at high sulfate to Fe(III) ratios (*i.e.*, 500:1) the apparent extinction coefficients for our solutions were always below that reported for the Fe-(SO$_4$)$_2^-$ species, indicating that complete conversion of the Fe(III) to this species did not occur in the aque-ous solutions. The spectrum shown in Fig. 4 for the extracted Fe(III)–sulfate–amine species in chloro-
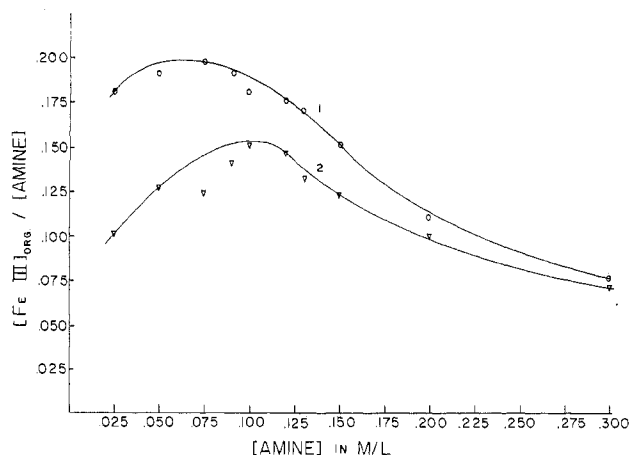
(9) K. A. Allen and W. J. McDowell, *J. Phys. Chem.*, **64**, 877 (1960).

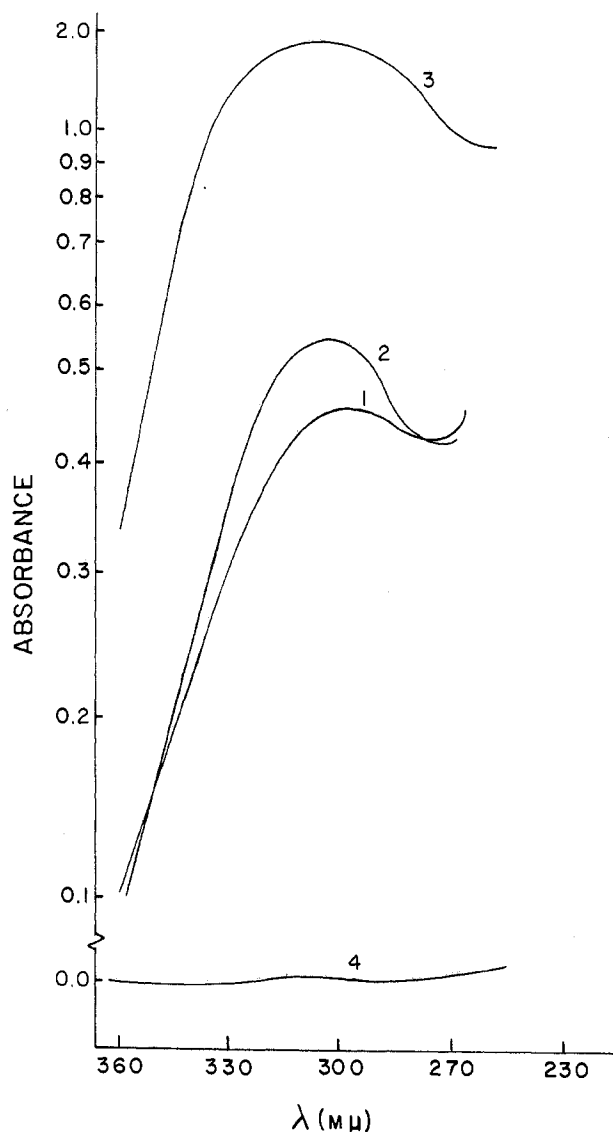(10) R. A. Whiteker and N. Davidson, *J. Am. Chem. Soc.*, **75**, 3081 (1953).

Fig. 4.—Spectra of the Fe(III) sulfate species in aqueous solution and the extracted species in chloroform: 1, 2.2 × 10^{-4} M Fe(III) in 0.006 M SO$_4^{-2}$ and 0.002 H$^+$; 2, 2.2 × 10^{-4} M Fe(III) in 0.13 M SO$_4^{-2}$ and 0.19 H$^+$; 3, 0.2 M Primene 81-R in chloroform extract of aqueous solution shown in 2.

form has a maximum at approximately 300 mμ and an apparent molar extinction coefficient of 7000. The spectrum of the organic solution is reproducible and obeys Beer's law, indicating no dissociation of the absorbing species with dilution. However, the absorption peak is much broader and the extinction coefficient higher than that reported for aqueous Fe(III)–sulfate complexes. This may be due (at least in part) to the change in solvent and the interaction between the amine and the Fe(III)–sulfate complex. In previous studies, we have observed that the spectra of metallic anions extracted into chloroform–amine solutions have higher extinction coefficients than the same anions in aqueous solutions, particularly in the ultraviolet region, although the character and absorption maxima of the spectra remain constant (see ref. 2, Fig. 4).

Discussion

Since no extraction of Fe(II), Co(II), or Ni(II) occurs under the conditions of our experiments, it is reasonable to assume that no extractable sulfate species of these ions are formed in aqueous sulfate solutions. This is in agreement with some work done by Coleman and co-workers[11] on the effect of amine structure on the extraction of metal sulfates. In the case of Co(III)–sulfate, no conclusions can be drawn about the metal sulfate species present in the aqueous solution since reduction of the Co(III) occurs so readily.

The extraction of Fe(III) from aqueous sulfate media is influenced significantly by the amine type, the pH of the aqueous solution, and the nature of the amine salt. Any attempt at writing an equation for the overall extraction reaction must take cognizance of the fact that the aqueous solubilities of the amines and the amine salts used in this study are essentially zero. Thus the extraction reaction must be either one which allows for the reaction between the amine (or amine salt) and the Fe(III)–sulfate species at the interface between the two phases or one which postulates the extraction of a neutral Fe(III)–sulfate species which can react with the amine or amine salt in the organic phase. One reaction which is in agreement with the data presented is

$$(RNH_3{}^+)_2SO_4{}^{-2}{}_{(org)} + 2Fe(SO_4)_2{}^-{}_{(aq)} \rightleftharpoons$$
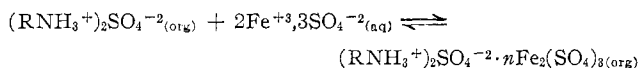$$2RNH_3{}^+Fe(SO_4)_2{}^-{}_{(org)} + SO_4{}^{-2}{}_{(aq)}$$
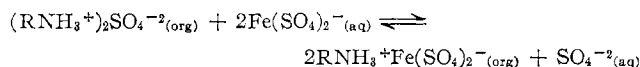
The net change of one Fe(III) extracted for every 1.5 sulfate ions is consistent with the data presented in Table IV. The effect of pH as shown in Table II is

understood if one remembers that the excess H_2SO_4 will cause conversion of the amine sulfate to the bisulfate, thus reducing the sulfate sites available in the organic phase. This may very well account for the poor extraction properties of the tertiary amines in this study since they appear to extract the bisulfate preferentially, to the exclusion of the sulfate ion. The presence of the bisulfate salt in the organic phase could also account for the fact that the extraction isotherms (Fig. 1 and 2) do not approach a plateau at an amine to Fe(III) ratio of one, but instead indicate an amine loading well below this point.

The idea of an ion-exchange reaction is also enhanced by the analogy of the results reported here to those obtained for basic anion-exchange resins. Kraus and co-workers[12,13] have shown that the adsorbability of Fe(III) by the sulfate form of a strong base anion-exchange resin decreases as the H_2SO_4 content of the Fe(III) solution increases. The excess H_2SO_4 converts the sulfate form of the resin to the bisulfate, thus inhibiting the exchange reaction. Also, the results in Table IV indicate the dependence of the distribution coefficient on the nature of the anion of the amine salt and the order of increasing distribution coefficient is the same as the order of preference shown by anion-exchange resins, *i.e.*, $ClO_4{}^- < Cl^- < SO_4{}^{-2} <$ acetate $<$ oxalate.[11] Furthermore, the fact that Primene 81-R is the best extractant studied and 2,2′-diethyldihexyl amine is second agrees very well with the anion-exchange studies on the oxalate complexes of Fe, Co, and Ni.[4]

It should be pointed out that the data presented here do not exclude other possible extraction reactions. The spectra presented are suggestive of the existence of the $Fe(SO_4)_2{}^-$ entity rather than proof of its existence in the organic phase. Thus a solvent extraction reaction such as

$$(RNH_3{}^+)_2SO_4{}^{-2}{}_{(org)} + 2Fe^{+3}, 3SO_4{}^{-2}{}_{(aq)} \rightleftharpoons$$
$$(RNH_3{}^+)_2SO_4{}^{-2} \cdot nFe_2(SO_4)_{3(org)}$$

would be consistent with the data presented (with the exception perhaps of the analogy to ion-exchange resin studies).

(11) C. F. Coleman, K. B. Brown, J. G. Moore, and K. A. Allen, Paper No. 510, Second United Nations International Conference on the Peaceful Uses of Atomic Energy, June, 1958.

(12) K. A. Kraus and F. Nelson, *J. Am. Chem. Soc.*, **75**, 3273 (1953).

(13) K. A. Kraus, F. Nelson, and J. F. Baxter, *ibid.*, **75**, 2768 (1953).