there is no profound geometric change in going from the ethylene to the trimethylene derivatives, as is borne out by the dipole moment data of McCarthy and Martell[37] who find a difference of ~0.3 D. in two such instances. The effect of non-planarity of the M–O_2N_2 system on the absorption spectrum is not easily assessed. The chelate rings in bis-(acetylacetone)-*cis*-1,2-hexanediimine Cu(II) and Ni(II) are considered to be non-planar,[38] but no important spectral differences in solution compared to the ethylene analogs were observed. Introduction of a tetramethylene bridge produces even larger red shifts and band broadenings, but bis-(salicylaldehyde)-tetramethylenediimine Ni(II) and its higher homologs are diamagnetic though not necessarily strictly planar.[39]

The Ni(II) complex of bis-(formylcamphor)-ethylenediimine possesses the weakest ligand field of any of the nickel complexes, yet contains a two-carbon bridge. Again, the cause of this field weakening is not clear but the position of λ_{max} is relevant to the remarkable magnetic behavior of this complex in solution. Bis-(formylcamphor)-ethylenediimine Ni(II), diamagnetic as a solid, becomes partially paramagnetic in benzene, methylbenzenes and methanol yet is diamagnetic in chloroform and pyridine[17]; bis-(acetylacetone)-ethylenediimine Ni(II) is diamagnetic in chloroform and ethanol.[17] Diamagnetic solid bis-(salicylaldoxime) and bis-(N-methylsalicylaldimine) Ni(II) have λ_{max} in chloroform in the range 610–620 mμ[18,33] and manifest partial paramagnetism in chloroform and benzene, becoming fully paramagnetic in pyridine.[17,18]

If an average ligand field of tetragonal symmetry may be assumed, then the strength of this average field must be very near that at the magnetic cross-over point and small perturbations of field strength, such as the introduction of a weak tetragonal z-component by solvation or association and the removal of intermolecular crystalline fields, are sufficient to decrease the singlet-triplet separation.[33] This is in keeping with Maki's result that as the in-plane components of the ligand field are decreased a smaller axial component is required for partial paramagnetism.[33] The spectral data (Tables I and II) indicate that for *cis*-planar complexes the ligand field is stronger than that in *trans*-planar complexes with apparently equivalent sets of donor atoms, and for this reason stabilization of a triplet state is more difficult to achieve.

Temperature dependent magnetic studies of the *cis*- and *trans*-planar cases in solution are underway.

Acknowledgment.—The author wishes to thank the National Science Foundation for financial support under grant NSF-G12312.

---

[37] P. J. McCarthy and A. E. Martell, THIS JOURNAL, **78**, 2106 (1956).

[38] M. Honda and G. Schwarzenbach, *Helv. Chim. Acta*, **40**, 27 (1957).

[39] Recently a diamagnetic tetracoördinate Ni(II) complex has been partially resolved; *cf.* H. Irving and J. B. Gill, *Proc. Chem. Soc.*, 168 (1958); H. Irving, J. B. Gill, W. R. Cross, *J. Chem. Soc.*, 2087 (1960).

[CONTRIBUTION FROM THE DIVISION OF SCIENCES, LOUISIANA STATE UNIVERSITY IN NEW ORLEANS, LAKE FRONT, NEW ORLEANS, LOUISIANA]

Extraction of Group VIII Metals by Long Chain Alkyl Amines. I. A Tracer Study of Iron(III)–Chloride Systems[1]

BY MARY L. GOOD AND SARA E. BRYAN

RECEIVED APRIL 14, 1960

The distribution of Fe(III) between aqueous hydrochloric acid solutions and various long chain alkyl amines in organic solvents has been investigated using tracer techniques. The effects of HCl concentration, structure of the amine, and type of organic solvent have been extensively studied. The extracted Fe(III) species in the organic phase has been observed spectrophotometrically and evidence is presented to support the conclusion that the extracted species is the tetrachloroferrate(III) ion.

Introduction

The use of alkyl amines as liquid extractants for various anionic species of metal ions has been largely confined to the separation of a few scattered pairs of metal ions[2–5] and to the extraction of uranium, thorium and plutonium.[6–9] In most analytical separations and purifications reported, the successful procedures were determined empirically for the particular system under study. However, some work has been done using the extraction information to elucidate the structures of the anionic species, particularly for uranyl sulfate and ferric sulfate complexes.[10–12] Also, some of the work done at the Oak Ridge National Laboratory has been accumulated and compared, showing that many fac-

---

[1] Presented in part before the Southwest Regional Meeting of the American Chemical Society, Baton Rouge, Louisiana, December 5, 1959.

[2] F. L. Moore, *Anal. Chem.*, **27**, 70 (1955).

[3] H. A. Mahlman, G. W. Leddicotte and F. L. Moore, *ibid.*, **26**, 1939 (1954).

[4] J. Y. Ellenburg, G. W. Leddicotte and F. L. Moore, *ibid.*, **26**, 1045 (1954).

[5] G. W. Leddicotte and F. L. Moore, THIS JOURNAL, **74**, 1618 (1952).

[6] C. F. Coleman, K. B. Brown, J. G. Moore and D. J. Crouse, *Ind. and Eng. Chem.*, **50**, 1756 (1958).

[7] K. B. Brown, C. F. Coleman, D. J. Crouse, C. A. Blake and A. D. Ryon, Paper 509, presented at the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, September 1–13, 1958.

[8] J. B. Rosenbaum, S. R. Borrowman and J. B. Clemmer, Paper 501, *ibid.*

[9] F. L. Moore, presented as paper No. 85 to the Analytical Division at the 136th National Meeting of the American Chemical Society in Atlantic City, New Jersey, September, 1959.

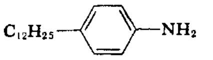
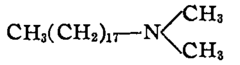
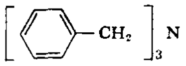
[10] K. A. Allen, THIS JOURNAL, **80**, 4133 (1958).

[11] K. A. Allen, *J. Phys. Chem.*, **60**, 239 (1956).

[12] C. F. Baes, Jr., ORNL-1930, August 1955.

TABLE I

ALKYL AMINES USED AS EXTRACTANTS

Amines	Structure	Mol. wt.	Source
Palmityl	$CH_3(CH_2)_{15}NH_2$	241	General Mills
Primene 81-R	$t\text{-}C_{12-14}H_{25-29}NH_2$	185–213	Rohm and Haas
Alkylaniline C-12		Approx. 260	Monsanto
Di-*n*-decyl	$[CH_3(CH_2)_9]_2NH$	297	Eastman
2,2′-Diethyldihexyl	$[CH_3(CH_2)_3CH(C_2H_5)CH_2]_2NH$	241	Eastman
LA-1	Highly branched chain secondary	351–393	Rohm and Haas
LA-2	Same as LA-1 except more basic	353–395	Rohm and Haas
Tri-*n*-hexyl	$[CH_3(CH_2)_5]_3N$	269	Eastman
N,N′-dimethyloctadecyl	 $CH_3(CH_2)_{17}N(CH_3)_2$	297	Eastman
Tri-benzyl		287	Eastman
XE-204	Long chain (branched) tertiary	406	Rohm and Haas

tors are involved in the successful extraction of a particular anionic species.[6] Some of these factors were: the structure of the amine extractant (both from a steric viewpoint and from basicity considerations); the organic diluent in which the amine is dissolved; and the nature and concentration of the complexing anion in the aqueous phase. However, no systematic study of the extraction of a group of related complex ions has been carried out. It is possible that such a study would lend itself to the elucidation of the extraction process and to the further clarification of the structure of some of the complexes considered. With this in mind the authors have undertaken a study of the extraction of some of the complexes formed by the Group VIII metals. The following paper describes the results obtained from an investigation of one such com-

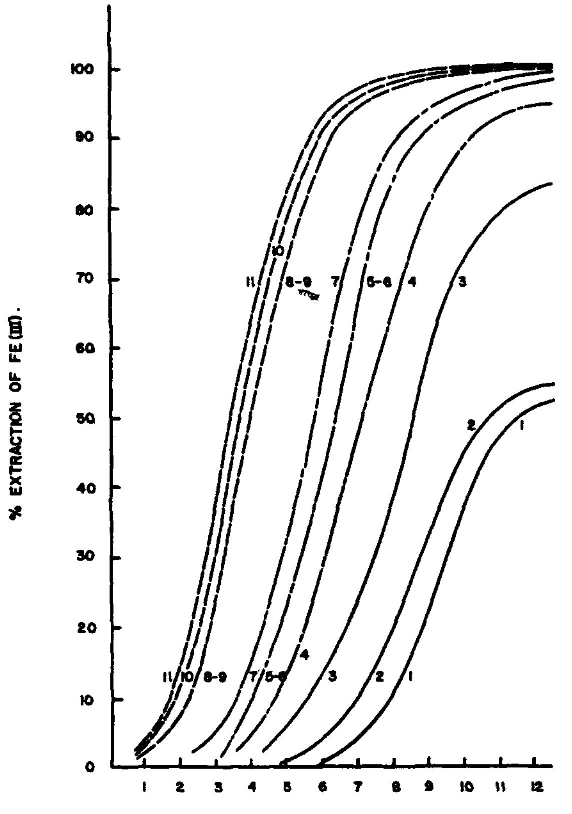


Fig. 1.—Extraction of Fe(III) from HCl solutions by various amines in $CHCl_3$: I, primary amines (—): curve 1, Primene 81-R; curve 2, C-12 alkylaniline; curve 3, palmityl. II, secondary amines (–·–): curve 4, di-*n*-decyl; curve 5, 2,2′-diethyldihexyl; curve 6, LA-2; curve 7, LA-1. III, tertiary amines (---): curve 8, XE-204; curve 9, NN-dimethyloctadecyl; curve 10, tri-*n*-hexyl; curve 11, tribenzyl.

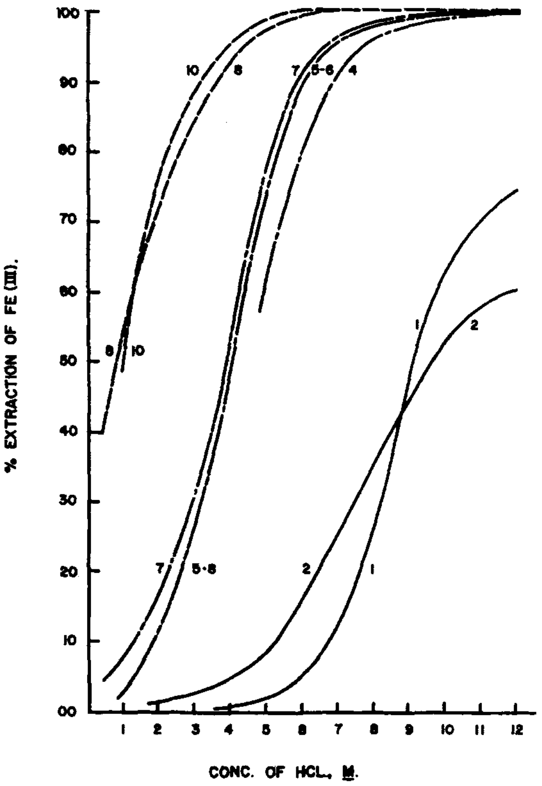


Fig. 2.—Extraction of Fe(III) from HCl solutions by various amines in C_6H_6: I, primary amines (—): curve 1, Primene 81-R; curve 2, C-12 alkylaniline. II, Secondary amines (–·–): curve 4, di-*n*-decyl; curve 5, 2,2′-diethyldihexyl; curve 6, LA-2; curve 7, LA-1. III, tertiary amines (---): curve 8, XE-204; curve 10, tri-*n*-hexyl.

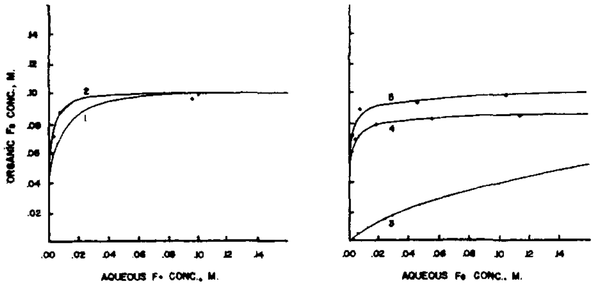


Fig. 3.—Extraction isotherms for Fe(III) in 12 *M* HCl: curve 1, 0.1 *M* LA-2 in $CHCl_3$; curve 2, 0.1 *M* LA-2 in C_6H_6; curve 3, 0.145 *M* aniline C-12 in $CHCl_3$; curve 4, 0.083 *M* XE-204 in $CHCl_3$; curve 5, 0.1 *M* XE-204 in C_6H_6.

plexing system—Fe(III) in hydrochloric acid solutions.

Experimental

Materials.—All inorganic chemicals used were Analytical Reagent Grade. The chloroform solvent was redistilled practical grade. The fraction boiling between 59–60° was used. The hexane was technical grade, pretreated first with sulfuric acid, then with sodium bicarbonate, followed by a water wash. The redistilled fraction boiling between 66 and 67° was used. Reagent grade (thiophene-free) benzene was used without further purification. The alkyl amines used are listed in Table I. They were all practical grade materials, used without further purification. Those listed from Rohm and Haas Company are actually mixtures as indicated by the structures given.

Procedure.—The appropriate alkyl amine was dissolved in the organic solvent (either chloroform, hexane or benzene) to make an approximate 0.2 *M* solution. The water solubility of all of these amines and their salts is known to be essentially zero. The Fe(III) solutions were made up approximately 0.1 *M* Fe(III) chloride in the appropriate HCl solutions. A small, countable amount of Fe-59 activity in the form of Fe(III) chloride was added to each of the Fe solutions. Equal volumes of the organic-amine solution and the aqueous Fe(III) solution were mixed together. The two phase system was shaken on a mechanical shaker or by hand for approximately two minutes. Complete equilibrium was established in that length of time. Equal aliquots of each phase were removed and counted as liquid samples in a well-type scintillation counter. The per cent. extraction was calculated as

$$\%\,\text{extraction} = \frac{\text{activity in the org. phase}}{\text{activity in the org. phase} + \text{activity in aq. phase}}$$

Reproducibility on individual % extraction values was ± 1.5%. To check the accuracy of the isotopic-tracer method several of the distributions were carried out using larger volumes and no activity. The total Fe(III) concentration before extraction and the amount remaining after extraction were determined volumetrically using a standard $KMnO_4$ solution. The % extraction values so obtained agreed with the isotopic tracer values to within 2%.

To obtain extraction isotherms for the various amines the above procedure was repeated except that the total Fe(III) concentration was varied from 0.025 to 0.2 *M*.

The absorption spectra reported were all obtained on a Beckman DU spectrophotometer using standard 1 cm. silica cells. The accompanying Tungsten lamp was used as a light source in the visible and the Beckman hydrogen lamp and power supply were used in the ultraviolet range. All spectra reported were made on organic samples of the amines after they had been equilibrated with the appropriate Fe(III)–chloride solution. The blank in each case consisted of the amine-solvent solution pretreated with the appropriate hydrochloric acid solution.

Results and Discussion

The extent of the extraction of the Fe(III) as a function of the HCl concentration and the structure of the amine is shown in Fig. 1 and Fig. 2. The effect of the solvent is seen by comparing appropriate curves in Fig. 1 with the corresponding ones in Fig. 2. In all cases the extraction efficiency of the benzene solvent system is appreciably better than that of the chloroform system. However, the tendency to form emulsions was much greater in the benzene systems, particularly at the lower HCl concentrations. In some cases it was impossible to sample the layers, thus some of the curves in Fig. 2 do not extend to the lower values of HCl concentration. No curve is shown in Fig. 2 for tribenzyl amine because a precipitate formed at all HCl concentrations when the two phases were mixed.

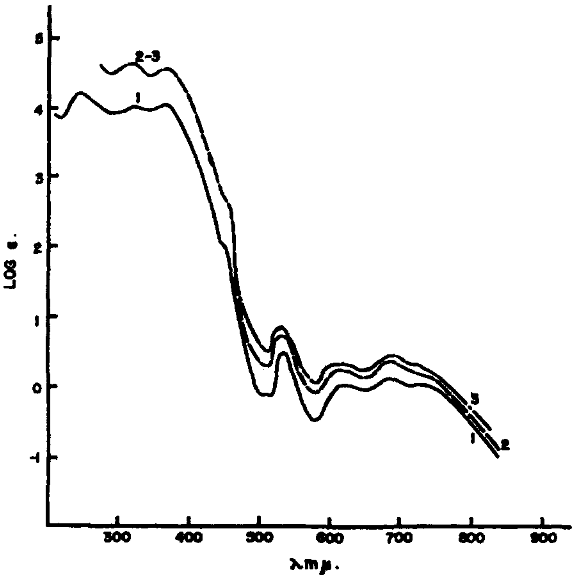


Fig. 4.—Comparison of absorption spectra of Fe(III)-amine extracting species with that of $FeCl_4^-$: curve 1, $KFeCl_4$ in diethyl ether (ref. 14); curve 2, Fe(III)-tri-*n*-hexylamine species in C_6H_6 or $CHCl_3$; curve 3, Fe(III)-N,N-dimethyloctadecylamine species in C_6H_6 or $CHCl_3$.

It is also obvious from these plots that the extraction efficiency increases from primary to secondary to tertiary amines. For a given amine class, *i.e.*, the tertiary amines, it seems that it makes little difference whether the carbon atoms are divided equally among the chains or not. However, it seems that the extraction efficiency of the branched chain secondary amines is greater than that for the unbranched chain secondary amines of comparable molecular weight.

The same technique was applied to the extraction of Fe(III) by *n*-hexane solutions of the amines. For all of the amines studied a third phase separated out between the hexane and the aqueous phase. All other volumes being equal, the volume of the third phase depended on the individual amine. By separating the layers and counting equivalent volumes of each it was possible to determine the fraction of Fe(III) activity in each phase. The extraction data for two typical systems are given in Table II. Apparently the Fe(III)-amine extraction species in these cases are not soluble either in hexane or in HCl solutions. Again it appears that the Fe(III)-amine species is formed more readily with the tertiary amine than with the secondary. Also at the higher HCl concentrations all of the Fe(III) is tied up with amine in the newly formed third layer. Some further work on the exact nature of this third layer is planned.

TABLE II

Fe^{+++} EXTRACTION FROM Cl^- SOLUTIONS BY AMINES IN HEXANE SOLUTIONS

I. LA-1, 0.2 *M* in hexane, volume of 3rd phase = 0.8 ml.

Phase	HCl: 1 *M*	2 *M*	3 *M*	9 *M*	11 *M*
Aq.	87.2	62.8	64.4	2.9	1.1
Org.	12.8	37.2	9.4	3.4	4.2
"3rd"	2 phases only	2 phases only	26.2	93.6	94.6

II. Tri-*n*-hexylamine, 0.2 *M* in hexane, volume of 3rd phase = 0.4 ml.

Phase	HCl: 1 *M*	2 *M*	3 *M*	9 *M*	11 *M*
Aq.	25.0	..	2.3	2.4	0.4
Org.	21.9	..	2.5	2.8	0.7
"3rd"	53.1	..	95.2	94.8	98.8

In order to be able to say something definite about the nature of the Fe(III)-amine extracting species, some extraction isotherms were made to determine the stoichiometry of the species, and the spectra of the extracted species in the organic phase were determined. Some typical extraction isotherms are shown in Fig. 3. All of the amines studied, with the exception of Aniline C-12, approached a limiting Fe(III)-amine mole ratio of 1:1 very rapidly. Apparently the Aniline C-12 amine does not extract in the same manner as do the other amines studied. This is not unreasonable since the nitrogen atom is bonded directly to the aromatic ring in this case. One would expect some effect of the ring's aromatic character on the reaction potential of the nitrogen atom.

Some typical spectra of the extracted organic solutions are given in Fig. 4. Also in Fig. 4, the spectra of $KFeCl_4$ in diethyl ether as determined by Friedman[13] is shown. The spectra are similar enough to convince the authors that the absorbing species in each case are the same. Friedman's work seems to be fairly conclusive that his spectra is that of the $FeCl_4^-$ ion. Thus we feel confident that the metallic anion involved in the extraction process is $FeCl_4^-$.

The above data are consistent with either of these mechanisms

I. $Fe^{+++}(aq) + 4Cl^-(aq) \rightleftarrows FeCl_4^-(aq)$

$R_3N{:}(org) + H^+(aq) + Cl^-(aq) \rightleftarrows R_3NH^+Cl^-(org)$

$R_3NH^+Cl^-(org) + FeCl_4^-(aq) \rightleftarrows$
$R_3NH^+FeCl_4^-(org) + Cl^-(aq)$

II. $Fe^{+++}(aq) + 4Cl^-(aq) \rightleftarrows FeCl_4^-(aq)$

$R_3N{:}(org) + H^+(aq) + FeCl_4^-(aq) \rightleftarrows$
$R_3NH^+FeCl_4^-(org)$

In either case the resulting extracting species would be the same.

Since the free base amines have been shown to be fairly good acid extractants,[14,15] it seems probable that the first mechanism is correct. If so, the amines in this case are behaving as liquid anion exchangers as has been previously suggested. This explanation is further augmented by the reported behavior of Fe(III) on anion exchange resins.[16] The distribution curves obtained on Dowex-1 greatly resemble the extraction curves in Fig. 1 and Fig. 2.

A further application suggested by the above study is the possibility of using this extraction method to separate other relatively unstable complex anions from their aqueous equilibrium mixtures, thus enabling the spectra of the complex anion to be determined free from interfering materials.

Acknowledgments.—We are grateful to Dean A. R. Choppin of the College of Chemistry and Physics, Louisiana State University in Baton Rouge, for the loan of the basic counting equipment used. We would also like to thank Mr. Marc Rieth and Mr. Ferdinand Holland for their assistance in some of the laboratory work. We are indebted to the following companies for their generosity in providing us with samples of some of the amines: General Mills, Rohm and Haas and Monsanto Chemical Company. A major part of this investigation has been supported by the United States Atomic Energy Commission under Contract No. At-(40-1)-2576.

---

(13) H. L. Friedman, THIS JOURNAL, **74**, 5 (1952).

(14) E. L. Smith and J. E. Page, *J. Soc. Chem. Ind.* (*London*), **67**, 48 (1948).

(15) F. L. Moore, *Anal. Chem.*, **29**, 1660 (1957).

(16) G. E. Moore and K. A. Kraus, THIS JOURNAL, **72**, 5792 (1950).