

CHAPTER II

PRELIMINARY WORK

The chloro complexes of trivalent iron from hydrochloric acid solutions have been studied via a method of solvent extraction using weakly basic solvents such as the ethers and the esters. The formula of chloro complexes in organic layers has been determined to be FeCl_4^- (vide infra) and the mechanism of the complex formation was suggested. In some cases the distribution coefficients, the hydration numbers, and the solvation numbers of extracted species were determined. The ultraviolet absorption spectra of solutions of FeCl_4^- in organic solvents were also studied. They are summarised below.

2.1 The Distribution Coefficient of Iron (III)

in Various Organic Solvents

The comparison of extractions using isopropyl ether and diethyl ether as solvents was made in the work of Dodson and coworkers.⁴ Since the efficiency of the extraction with diethyl ether is generally known to be very dependent on the acid concentration, hence the acid dependence of the extraction efficiency in the medium of isopropyl ether was of interest. The extraction of iron into isopropyl ether was carried out with 125 and 250 mg of iron over a wide range of acid concentration. With these amounts of iron, three phases appear at hydrochloric acid concentration above 7.5 molar. It was found by Laurene and coworkers⁵ that water is the controlling factor in the formation of a third phase.

The upper two layers are ether phases. The volumes of these two phases at acid concentration of 7.5-8.0 molar approximately equal and the distribution ratio for iron between them varies from about 2.5 to 7.5, the ratio favoring the bottom layer of the two and increases with increasing in hydrochloric acid concentration. While system involving small amounts of iron was determined colorimetrically with thiocyanate⁶, that of larger amounts was carried out either by the Zimmermann-Reinhardt method or by the iodometric method.⁷

The extractions of ferric ions into isopropyl ether were re-examined by Nachtrieb and Fryxell.⁸ The interesting alternative to the hypothesis of polymerization of the ethereal iron complex was considered here. The hypothesis has been suggested by the unpublished work of Dodson in the attempt to explain the dependence of the distribution ratio upon the concentration of iron. Nachtrieb and Fryxell proposed that the cause of the anomalous extraction of ferric chloride into isopropyl ether (i.e., the efficiency of extraction being a direct proportion to the total iron concentration) is a self-salting out effect of ferric chloride. Since they found that the thermodynamic activity of ferric chloride in high concentration of aqueous hydrochloric acid increases much more rapidly than the concentration of ferric chloride. The distribution curves, i.e. the logarithmic plots of iron concentration in ether versus that in aqueous solution from 3.00, 4.00, 5.00, 6.00 and 7.00 molar hydrochloric acid are straight lines of unit slope. It is seen that the prediction of constant distribution ratio for a particular hydrochloric acid concentration is fulfilled for sufficiently dilute ferric chloride solution.

The effect of the presence of aluminium chloride was found to increase the efficiency of the extraction at the low iron concentration. The distributions of ferric ions with a fixed hydrochloric acid concentration were repeated and the similar results to those obtained in (8) were reported.

The distribution of ferric ions in the hydrochloric acid-ether-water system has also been re-examined by Chalkley and Williams¹⁰. They concluded that this system is apparently "non ideal". They also studied the effect on the distribution of hydrochloric acid and ferric ions as the result of the addition of methanol to this system. It was found that as the amount of methanol increases the thermodynamic activity of the aqueous phase falls and that of the organic phase rises. Thus the extracting power of one solvent can be adjusted by adding different amounts of the third component.

The extraction of ferric ions from hydrochloric acid solutions into bis(2-chloroethyl)ether was studied by Axelrod and coworkers¹¹. Their results suggested that this ether can be used for the quantitative extraction of iron from a solution of acid with a concentration greater than 7N-HCl. However, the time required for the separation of the two phases is longer than for either diethyl or isopropyl ether, being 30-60 minutes at 25°C for the equilibration time when the equal volumes of the aqueous solution and the ether are used.

Under the ordinary conditions used in the solvent extraction method, the degree of dissociation of the halo-metallic acid complexes in the organic phase is very small and the behavior of the systems can be interpreted without consideration of this dissociation as Irving and Rossotti¹² (1956) have shown. However, the complex halo acids such as HFeCl_4 are very strong acid, so that at some sufficiently low concentration of the solute the degree of dissociation will become appreciable, this was confirmed experimentally.¹³⁻¹⁵ This dissociation should produce an increase in the over-all metal extraction coefficient at very low ferric concentration.

2.2 The Empirical Formula of the Iron (III) Chloro

Complexes in the Organic Phases

It has been shown by the conventional chemical analysis that^{16,17} the extracted species in diethyl ether is $\text{FeCl}_3 \cdot n\text{HCl}$ where "n" is unity at a low acid concentration and becomes greater than unity when the acid concentration is increased. When bis(2-chloroethyl) ether is used the empirical formula of the iron complexes is $\text{FeCl}_3 \cdot \text{HCl}$ even it is extracted from 8 molar hydrochloric acid. Nachtrieb and Conway¹⁷ showed that when the initial acid concentration is less than 7 molar the compound extracted in isopropyl ether is $\text{FeCl}_3 \cdot \text{HCl}$. When the acid concentration is higher, however there seem to be more than one hydrogen chloride associated with each iron even a correction for the dissolved hydrogen chloride is made. On the other hand, the ultraviolet absorption spectra remained unchanged regardless of the change of acid concentration. It is therefore conceivable that this additional acid is associated with the co-ordinated water or ether and not directly with the iron. With the aid of the chemical analysis, Gamlen and Jordan¹⁸ confirmed that the highest chloro complexes of iron (III) formed have the formula of FeCl_4^- .

2.5 Spectrophotometric Studies of Iron (III) Chloro Complexes

The ultraviolet absorption spectra of ferric chloride in various concentrations of hydrochloric acid¹⁸⁻²⁰ and those of the diethyl ether, isopropyl ether, n-butyl acetate, amine extracts¹⁹⁻²² have been compared with that of anhydrous diethyl ether solution of KFeCl_4 and those of anhydrous FeCl_3 in the ethers^{5,20,22} and in n-butyl acetate²². The crystalline anhydrous dietherate of tetrachloroferric acid, $(\text{HFeCl}_4 \cdot 2 \text{ iso-Pr}_2\text{O}$, will be later called DTA) which is very slightly soluble in isopropyl ether was prepared by Laurene, et al⁵, the corresponding acid was obtained upon the addition of water. It was shown that the spectra of the hydrated acid in isopropyl ether, the anhydrous diethyl ether solution of KFeCl_4 , the extracts mentioned above, and FeCl_3 in concentrated hydrochloric acid are all identical, the absorption peaks shown are about 312 and 362 nm, corresponding to the spectrum of FeCl_4^- . A broad band at λ_{max} 340 nm as obtained from the anhydrous ferric chloride sample was understood to be due to a dimer, Fe_2Cl_6 ^{20,22}. By spectrophotometric method, Dragulescu and Pomoje²² have extended their study to cover the effect of the presence of water and also of the dried hydrogen chloride in n-butyl acetate containing the initially anhydrous ferric chloride. They concluded from their results that Fe_2Cl_6 and FeCl_4^- exist in equilibrium.

2.4 The Significance of Water in the Extraction

Several investigators^{5,8,9,11,16,17,19,23-27} displayed interest in the possible significance of the water found in the organic layers when ferric chloride is extracted from hydrochloric acid solutions. It is revealed that most of the water coextracted with HFeCl_4 . With bis(2-chloroethyl)ether, 4.5 molecules of water per mole of HFeCl_4 were found¹¹ and with isopropyl ether, the value of 5 was reported⁵. Fomin and Morgunov²⁴ reported the values between 3 and 4 for ethyl, butyl and isoamyl ethers. It is interesting to note that the number of water molecules coextracting with strong acid decreases with increasing extractant basicity i.e., from 4 with nitrobenzene²⁶ and dibutyl Cellosolve²⁸ (low basicity) to 1 with trioctylphosphine oxide²⁹ (high basicity). Organic phase water determination was done by the titration with Karl Fischer reagent. Alternatively Laurene, et al.⁵ simply added the known amount of water just sufficiently to make DTA soluble in isopropyl ether. The amount of water attached to one molecule of the compound was then calculated. The manner of water coextracting with strong acid will be discussed later.

2.5 The Solvation Number of the Extracted Iron (III)

Chloro Complexes in Organic Solvents

The term solvation has usually been applied to reactions where the solvent molecule remains in contact with the cation, the anion, or a molecule of solute by either the coordination or the hydrogen bonding. The common method of studying solvation in the extraction systems is to follow the change in the distribution coefficient as the extractant is diluted with a second inert solvent,³⁰ all other parameters are held constant.

The equation that applies³¹ is

$$\log D_{S_m} = \log D_{S_a} + \log [1 + K' C_b^{q_b}] \quad (2.1)$$

where S_m signifies the mixture solvents,

S_a , S_b signify the pure solvents A and B respectively,

q_b is the solvation number due to the solvent B,

and C_b is the concentration of the solvent B.

At a very low C_b , unity may be neglected in the second term on the right, as shown by Tuck²⁸ in the case of extraction of chloroauric acid by tri-n-butyl phosphate (TBP) in xylene. However, in most cases C_b and K' are sufficiently large for unity to be neglected and by putting

$$\begin{aligned} K &= D_{S_a} K', \text{ the equation} \\ \log D_{S_m} &= \log K + q \log C_b \end{aligned} \quad (2.2)$$

is obtained, $\log D_{S_m}$ is linear with $\log C_b$, the slope q being the solvation number.

The dibutyl ether solvation number for HFeCl_4 was shown by Fomin,²⁴ et al. to be 3. They studied the change of the distribution coefficient with the concentration of ether in carbon-tetrachloride or benzene, however, Morgunov and Fomin stated in a later paper²⁵ that the same data could be interpreted in terms of a mixture of di and trisolvates. McDonald^{26,27} determined the solvation numbers for HFeCl_4 in nitrobenzene and diethyl ether having benzene as a second inert solvent. The solvation numbers found are 12 at a high nitrobenzene concentration, 6 at a low concentration and 4 when diethyl ether was a solvent. In all determination ferric chloride labelled with iron-59 was used.