

CHAPTER V

DISCUSSION AND CONCLUSION

5.1 Spectrophotometric Studies of Iron(III)Chloro Complexes.

Gamlen and Jordan¹⁸ calculated the molecular extinction coefficient (ϵ) at various wavelengths for the species FeCl_4^- , FeCl_3 , FeCl_2^+ , FeCl^{2+} , and Fe^{3+} and presented diagrammatically as shown overleaf in Fig.5.2. The values of ϵ_{FeCl_3} and $\epsilon_{\text{FeCl}_2^+}$ obtained by Gamlen and Jordan are in agreement with those calculated by Rabinowitch and Stockmayer³² even the different assumptions were used. The values of $\epsilon_{\text{FeCl}^{2+}}$ and $\epsilon_{\text{Fe}^{3+}}$ used were obtained from the Olerup's results.³³ The spectra for the species FeCl^{2+} , FeCl_2^+ , and FeCl_3 give the similar broad band at 340 nm whereas the species FeCl_4^- shows the spectrum with the absorption peaks at 362, 312, and 242 nm. Gamlen and Jordan also showed that the species FeCl_3 and FeCl_4^- are in equilibrium in 8.00-11.35 M-hydrochloric acid with FeCl_4^- being the principal species.

If the ultraviolet absorption spectra obtained in this work like that shown in Fig.4.1 are inspected the qualitative interpretation concerning the effects of the hydrochloric acid concentration on the formations of various chloro complexes of iron(III) in aqueous phase can be given. The spectra of complexes in low hydrochloric acid concentrations at about 2-4 M give the broad band at about 340 nm whereas those in higher hydrochloric acid concentrations at about 7-9 M give the absorption peaks at 362 and 312 nm.

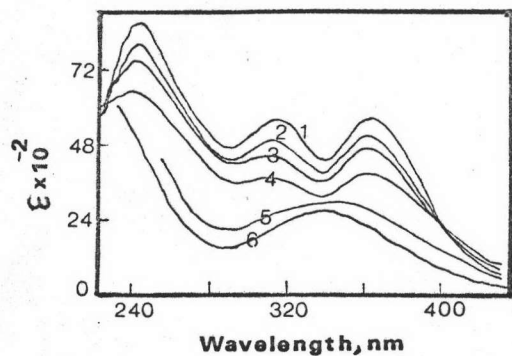


Fig. 5.1 Variation of extinction coefficient with wavelength for various concentrations of hydrochloric acid at constant concentration of ferric chloride, 0.002 M. 1- 11.35 M; 2- 10.60 M; 3- 9.86 M; 4- 8.65 M; 5- 5.08 M; 6- 3.33 M.

/ Gamlen and Jordan's work /

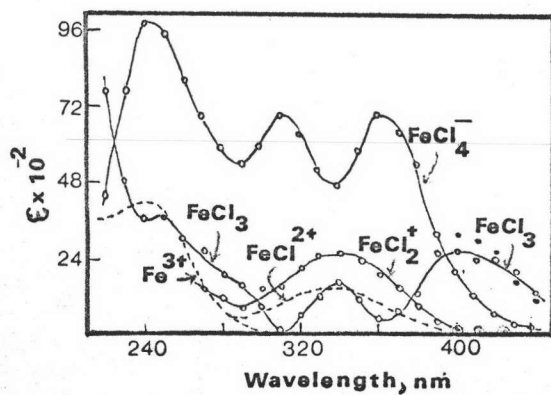


Fig. 5.2 Molecular extinction coefficients at various wavelengths for the species FeCl_4^- , FeCl_3 , FeCl_2^+ , FeCl^+ , and Fe^{3+} . \circ Values calculated from results in Fig. 5.1 by Gamlen and Jordan. \bullet Rabinowitch and Stockmayer's results. Broken line: Olerup's data.

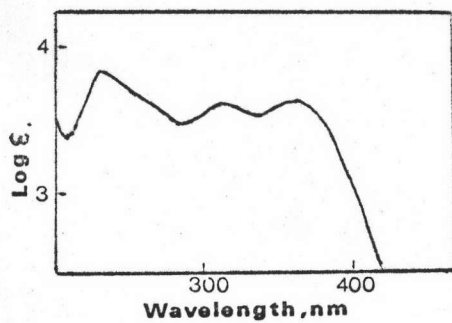


Fig. 5.3 The ultraviolet absorption spectrum of KFeCl_4 in diethyl ether.

/ Friedman's work /

It can be seen that the ultraviolet absorption spectra of ferric chloride in various concentrations of hydrochloric acid (Fig. 4.1) are similar to those shown in Fig. 5.1 for Gamlen and Jordan's work.

Attention should be drawn to the spectra of medium acid concentrations i.e., 5 M and 6 M-hydrochloric acid. Here, small humps showed up at the middle of the formerly broad band spectra obtained at a lower acid concentration. It is suspected that a higher chloro complex of iron(III) of the type HFeCl_4 begins to form in a trace quantity.

The ultraviolet absorption spectra of ferric chloride of various concentrations, ranging from 3×10^{-5} to 3×10^{-4} M in the presence of 6 M-hydrochloric acid are shown in Fig. 4.2. They are all identical with respect to the positions of the peaks but different in their height regardless of the iron concentration. Hence, the formations of any species of iron (III) chloro complexes in hydrochloric acid solution depend on chloride concentration but not on iron (III) concentration. Moreover, the sources of chloride are not important in the formations of the chloro complexes. This belief is supported by the resemblance of Fig. 4.1 and Fig. 4.3 (curve B) where different chloride sources are used, the former being hydrochloric acid alone the latter hydrochloric acid plus sodium chloride.

There are 3 variables in this study namely concentration of chloride ions ; concentration of ferric ions and the nature of the

extractant. It is interesting to see whether the type of the complexes formed is a function of those variables. All good investigations should be carried out with a control. Here spectra of ether extract of chloro complexes of iron(III)^{19,20} and of anhydrous ether solution of KFeCl_4 as prepared by Friedman¹⁹ (Fig. 5.3) are used as the "control". Results of this part of the work are summarized in Fig. 4.4, Fig. 4.5, and Fig. 4.6. Each of these figures shows the spectra of species extracted into non-aqueous phase by keeping a different set of two variables constant in each case. There are all three peaks, the first two of the spectra are all identical being at 362 and 312 nm and are in good agreement with the control and also with those obtained in aqueous phase at high acid concentration (Fig. 4.1). The third peak in ester solutions, except that in β -methyl butyl acetate, exhibits a marked shift (Fig. 4.5). In the control as well as in the aqueous phase at a high acid concentration, the third peak is at 242 nm whereas results shown in Fig. 4.4, Fig. 4.5, and Fig. 4.6 exhibit the shift to the right being at 255 nm. It is not quite clear about the cause of this shift, although tentative explanation may be given by taking into account the nature of the solvent which may limit the performance of the instrument at low wavelengths. In spite of this discrepancy, it is still reasonable that the principal iron(III) species formed in aqueous solutions of high hydrochloric acid concentration and extracted into the esters is HFeCl_4 .

5.2 The Distribution Coefficient of Iron(III) in Hydrochloric Acid - Amyl Acetate System

The distribution coefficients of iron(III) in hydrochloric acid-n-amyl acetate system under different conditions were studied using 1×10^{-4} M-ferric chloride labelled with iron-59. Similar study was also carried out using iron-59 tracer in the form of ferric chloride of very high specific activity. When 1×10^{-4} M-ferric chloride labelled with iron-59 was used the extraction of iron(III) from about 2 M-hydrochloric acid into n-amyl acetate phase is negligible. The distribution coefficient increases with increasing the hydrochloric acid concentration until the maximum distribution coefficient was just obtained at approximately 8 M-hydrochloric acid (Fig.4.7). On the other hand, when a high specific activity of iron-59 as ferric chloride was present the maximum distribution coefficient was obtained at a lower acid concentration i.e., about 7 M-hydrochloric acid, and the extraction of iron(III) into a non-aqueous phase can also be observed even at as a low concentration as 2-M hydrochloric acid (Fig.4.7).

When these experiments were duplicated in β -methyl butyl acetate similar results as discussed in the above paragraph were obtained and were represented graphically in Fig. 4.8 .

The results indicate that the iron concentration affects the distribution coefficient in such a way that the distribution coefficient increases with decreasing the iron concentration.

Although the optimum concentration of acid or of chloride ions which facilitate the extraction of species of iron(III)chloro complex into a non-aqueous phase was obtained by independent work i.e., spectrophotometric study of the complex and the study of the distribution coefficient of iron(III)chloro complex, the results coincide. For example, the extraction of a complex into a non-aqueous layer was not observed (by counting radioactivity) at lower acid concentration than 3M-hydrochloric acid, exactly the same acid concentration dependence was experienced in the spectrophotometric measurement for the presence of the iron(III)chloro complex in a non-aqueous phase.

5.3 The Solvation Number of HFeCl_4 in n-Amyl Acetate.

It is well known that the extracted strong acid such as HClO_4 , HReO_4 , HInBr_4 and HFeCl_4 are hydrated and solvated^{26-31,34,35} when they are extracted into the organic solvents. The values of hydration number and solvation number of each compound are not definite they vary from extractant to extractant.

Irving, Rossotti and Williams³ developed a comprehensive treatment of partition equilibria in inorganic systems by combining the argument of the Nernst Partition Isotherm³⁶. Irving, et al. considered the partition of a species represented by the general formula $\text{H}_h \text{M}_m \text{L}_n (\text{H}_2\text{O})_w \text{S}_s$.

In an aqueous solution saturated with organic solvent where H, M, L, and S represent proton, metal ions, ligand, and organic solvent molecules respectively, general partition equation was derived between the average composition of the species in each phase and can be presented as

$$\begin{aligned} \log D &= \log \frac{\bar{p} \bar{P}_o}{\bar{P}_a} + \log(\bar{m}_o / \bar{m}_a) + (\bar{m}_o \bar{h}_o - \bar{m}_a \bar{h}_a) \log [H] \\ &+ (\bar{m}_o \bar{n}_o - \bar{m}_a \bar{n}_a) \log [L] \\ &+ (\bar{m}_o \bar{w}_o - \bar{m}_a \bar{w}_a) \log [H_2O] + (\bar{m}_o \bar{s}_o - \bar{m}_a \bar{s}_a) \log [S] \end{aligned} \quad (5.1)$$

where \bar{p} = the partition coefficient for the average species,

\bar{P} = the stability constant for the average species,

\bar{m} = the polymerisation number, i.e., the average number of metal atoms per molecular species,

$\bar{h}, \bar{n}, \bar{w}$ and \bar{s} = the average numbers of hydrogen, ligand atoms, water, and organic solvent molecules, attached per atom of metal respectively,

the subscript o and a refer organic and aqueous phase respectively.

Since the possible species believed to be present in the systems under investigation and in the related ones are $FeCl^{2+}$, $FeCl_2^+$, $FeCl_3$ and $HFeCl_4$ (see section 5.5) then the average numbers of iron atom per molecular species, \bar{m}_o and \bar{m}_a are obviously unity. The second term on the right of equation 5.1 can therefore be left out in this case.



Partial differentiation of the general partition equation of Irving, et al. with respect to organic solvent molecules at constant concentration parameters, except that of extractant yields the derivative

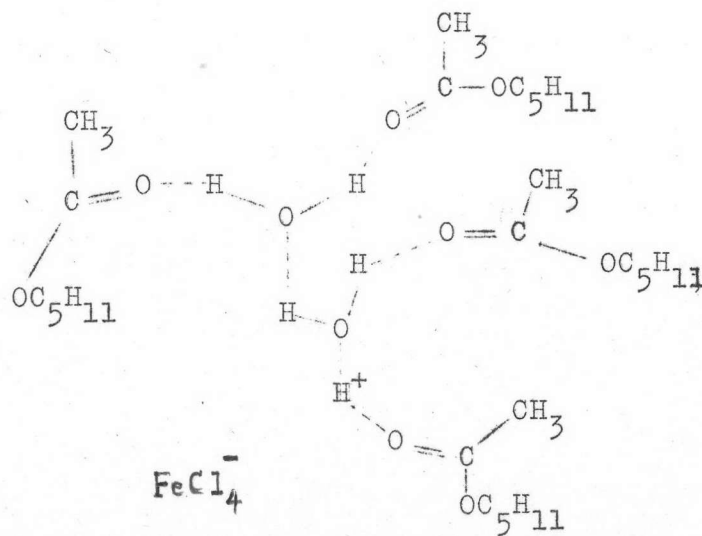
$$\left(\frac{\partial \log D}{\partial \log [n\text{-amyl acetate}]} \right)_{[Fe], [H], [Cl], [H_2O]} = \bar{s}_o - \bar{s}_a \quad (5.2)$$

Since the solubility of n-amyl acetate in the aqueous phase is small the \bar{s}_a may be approximate to zero. Hence the theoretical plot of $\log D$ versus $\log [n\text{-amyl acetate}]$ should yield a straight line with \bar{s}_o , solvation number in an organic phase as a slope.

The experimental plot of the above parameters in Fig.4.9 shows the simple linear relationship between $\log D$ and $\log [n\text{-amyl acetate}]$ as expected by equation 5.2 if the mole fraction concentration of n-amyl acetate in the n-amyl acetate-benzene mixture is not less than 0.20. The deviation from linearity of this plot as may be noticed in Fig.4.9 in the region of the low n-amyl acetate concentration, can be explained that the constancy of the first term on the right of equation 5.1 is valid only in the certain range of extractant concentration.

The configuration of FeCl_4^- has been studied to be sp^3 or tetrahedral because iron in the complex of FeCl_4^- has 5 unpaired electrons. This was first shown by the magnetic susceptibility²⁰ and later by electron paramagnetic resonance spectrophotometric³⁷ studies, regardless of the type of the medium.

Due to the saturation of chloride coordinating with iron in HFeCl_4 there is no primary solvation on hydration of metal anion. The association of n-aryl acetate molecules with HFeCl_4 by hydrogen bonding may be represented by



Results obtained from the present work show that the hydrochloric acid concentration has a great effect on the distribution within the system. The distribution coefficient of iron(III) increases with increasing acid concentration. The maximum distribution coefficient of iron(III) into the organic phase was found to change with the change in the extractant i.e., this value is 6.7×10^2 in n-nyl acetate and is 1.1×10^3 in β -methyl butyl acetate, both at the same hydrochloric acid concentration ranging from 7 to 8 M. The incorporation of iron-59 as traces in the study of the distribution coefficient of iron(III) in the organic phase offers a number of advantages. In general speed and the ease of the manipulation are the basic need, the simplicity of the calculation due to no correction need be made for the amount of the ligand tied up by the ion being studied is also desirable in such a study like this. The use of a labelled compound enables all these requirements to be met. On the other hand, this method suffers from the disadvantage that the amount of iron present was so small that spectrophotometric study could not be performed concurrently with the distribution study. Hence no direct correlation between distribution coefficient obtained and the type of the complex species in the organic phase can be made. There is an indication however that the complex is formed in the aqueous and is extracted into an organic phase at even a low acid concentration as 2 M-hydrochloric acid.

It is noteworthy that in the past a wide range of organic solvents had been incorporated in this type of study but there were only few cases that employed ester in their work, although most of the esters are cheap, readily available and easily to purify. The main reason being that ester undergoes hydrolysis in the presence of hydrochloric acid, the more concentrate the acid the better hydrolysis taking place. This presents considerable problems in the attempt to introduce chemical analysis of the complex for the confirmation of the spectrophotometric results. Although the analysis of each constituent of this complex is simple, the proton concentration thus determined by titration is not the concentration of the individual acid but the total concentration. Differentiation between the contribution of these protons from tetrachloroferric acid can not be made from those from acetic acid and from free hydrochloric acid. It is suggested that more work in this line should be continued to eliminate all of these uncertainties and if these problems are overcome, the chemical analysis for the constituents of the complex should yield an empirical formula of the complex and thus provide an important confirmation of the postulation, concerning the type of the complex, being made through spectrophotometric work.

Because of the limitation of time this work is considered as only partially completed. For the sake of completeness few more investigations are worth trying, for example the determination of the hydration number, the variation of metal concentration in the case of solvation number determination in order to study whether the solvation number depends on the iron concentration, which is one of the variables

in this study. In order to confirm that there is only one species being extracted into a non-aqueous phase, the extracted iron(III) concentration in non-aqueous phase should be determined and be plotted versus the absorbance at the fixed wavelength i.e., 362, 312 and 255 nm. The straight line through the origin which is normal for the system that obeys the Beer's law then be obtained.

During the course of the experiment, changes in volumes of the two phases upon the addition of hydrochloric acid and ferric chloride were observed. However the difference in the extent of the volume changes seems to be unnoticeable with and without the presence of ferric chloride as can be seen from the phase diagram shown in Fig. 3.1 and Fig. 3.2. The volume changes can be attributed to the changes in the solvent properties. This is one of the requirements for the system categorised as a non-ideal system by Irving, et al's postulation.

Since Irving, et al's postulation for ideality is too general the more specific criteria are needed for it to be more useful and this should form an interesting theoretical research in this area.

It is also quite interesting to inspect whether a higher chloro complex than HFeCl_4 exists and also whether the tetrachloroferrate can be formed in the anhydrous organic solvent which is different from the scope of the present work. Here, it is assumed that the preformed HFeCl_4 is extracted from an aqueous phase into the organic phase. In order to perform such a study an aqueous solution of hydrochloric acid is not suitable as a chloride source, a

new source which is soluble and forms a strong electrolyte in the organic solvent has to be introduced. It is therefore recommended that further work on the iron system should include an investigation of the chemical properties of various chloro compounds in organic solvent.
