CHAPTER III

EXPERIMENTAL PROCEDURE

3.1 Reagents

3.1.1 Organic solvents.

The organic solvents were purified by first drying overnight using anhydrous calcium chloride as a dehydrating agent then fractionally distilled at the atmospheric pressure. The purity of the solvents was tested using the Packard gas chromatography and the following results obtained.

Solvents	Boiling point (C^{o})	Literature value C^{o}
n-Amyl acetate	148	$148.4^{737\ mm}$
B-Methyl butyl acetate	140	141-2
n-Butyl acetate	124	126.1
n-Propyl acetate	98	101.6
Benzene	79	80.1

3.1.2 Standard solutions.

The Analar grade chemicals were used throughout this work. Further purification was not carried out.

3.1.2.1 The sodium hydroxide solutions. About 200 gm of the solid sodium hydroxide was dissolved in carbon dioxide free distilled water and diluted to litre. The solution of about 5.00M-sodium hydroxide was obtained. The solution was allowed to stand then was filtered and collected in a polyethylene bottle. This was standardised by a standard solution of potassium hydrogen phthalate. The sodium hydroxide solutions of other concentrations were prepared in a similar manner or by the dilution of a more concentrated standard sodium hydroxide solution.

3.1.2.2 The hydrochloric acid solutions. Hydrochloric acid solutions of various concentrations were prepared. Their exact concentrations were determined by titration withastandard sodium hydroxide solution to the phenolphthalein end-point.

3.1.2.3 The solutions of ferric chloride in hydrochloric acid. The standard solutions of ferric chloride at the concentration range 0.02-0.0001 M-ferric chloride in about 1.00 M-hydrochloric acid were prepared by dissolving dried ferric oxide* in concentrated hydrochloric acid and diluting with distilled water to a desired concentration. For example,in order to prepare a0.02 M-ferric chloride in about 1.00 M-hydrochloric acid,0.1596 gm of ferric oxide* was dissolved in 8.70 ml of concentrated hydrochloric acid and diluted with distilled water to a mark in a 100 ml-volumetric flask. This solution was used in the preparation of the calibration curve for iron (III)concentration by the thiocyanate method.

* prepared by neutralizing ferric chloride in hydrochloric acid solution with ammonium hydroxide.

The stock solution of about 0.2 M-ferric chloride in 6.00 M-hydrochloric acid was prepared from ferric chloride hexahydrate and was used for preparing a more diluted solution of ferric chloride in the various concentrations of hydrochloric acid. The diluted solutions were analyzed colorimetrically for iron(III)with thiocyanate and by titration with standard sodium hydroxide solutions of about 1.00 and 5.00 M for total acid.

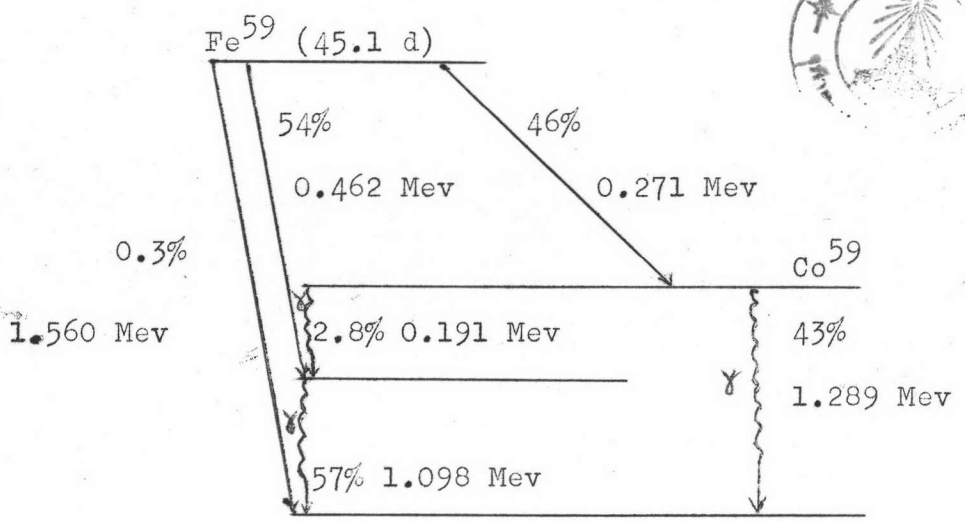
3.1.2.4 The solution of potassium thiocyanate in hydrochloric acid. 4.5 gm of dried potassium thiocyanate was dissolved in 1.00 M-hydrochloric acid and was diluted to 250 ml to give a 0.18 M-solution.

3.1.2.5 Solutions of the various concentrations of n-amyl acetate in benzene. They were prepared by the addition of the desired amount of the ester into benzene in a volumetric flask, the volume was then adjusted accordingly with benzene.

3.1.3 Radioactive material.

Iron-59 was obtained from the Radiochemical Centre, Amersham England in the form of ferric chloride. The specific activity was 6.85 μc/μgm Fe^{59}. The stock solution was made up by injection the iron-59 tracer solution from the glass ampoule using a calibrated micropipette (100 λ)into a 10-ml volumetric flask containing a solution of known concentration of ferric chloride in hydrochloric acid giving 0.08 μgm Fe^{59}/10 ml of solution.

Decay scheme of iron-59 is as follows :



3.2 Procedure

3.2.1 The phase diagram study of the water-hydrochloric acid-n-amyl acetate system.

The objective of this study is to obtain the limit of the compositions of the three components distributed in two phases from which the constant distribution ratio and the maximum per cent extraction could be calculated. Another piece of information taken from the phase diagram is the qualitative information involving possible variation in behaviour in the non-ideal system.

The ferric chloride-water-hydrochloric acid-n-amyl acetate equilibrium phase diagram was also studied. The latter diagram (Fig3.2) obtained does not differ from that of the three component system, showing that if $C_M \ll C_{HCl}$ the behaviour of the system as a whole will be essentially that of the two phase condensed system of three components. The procedure for the determination of the phase diagram is outlined below .

The various compositions of water and n-amyl acetate were titrated with concentrated hydrochloric acid until the turbidity produced when shaken disappeared. In order to complete the phase diagram, the two extreme concentrations were included i.e., the saturated aqueous solution of n-amyl acetate and the n-amyl acetate solution saturated with water. The per cent of each component in each solution was calculated. A suitable number of the tie lines was established by equilibrating the equal volumes of aqueous acid solution and

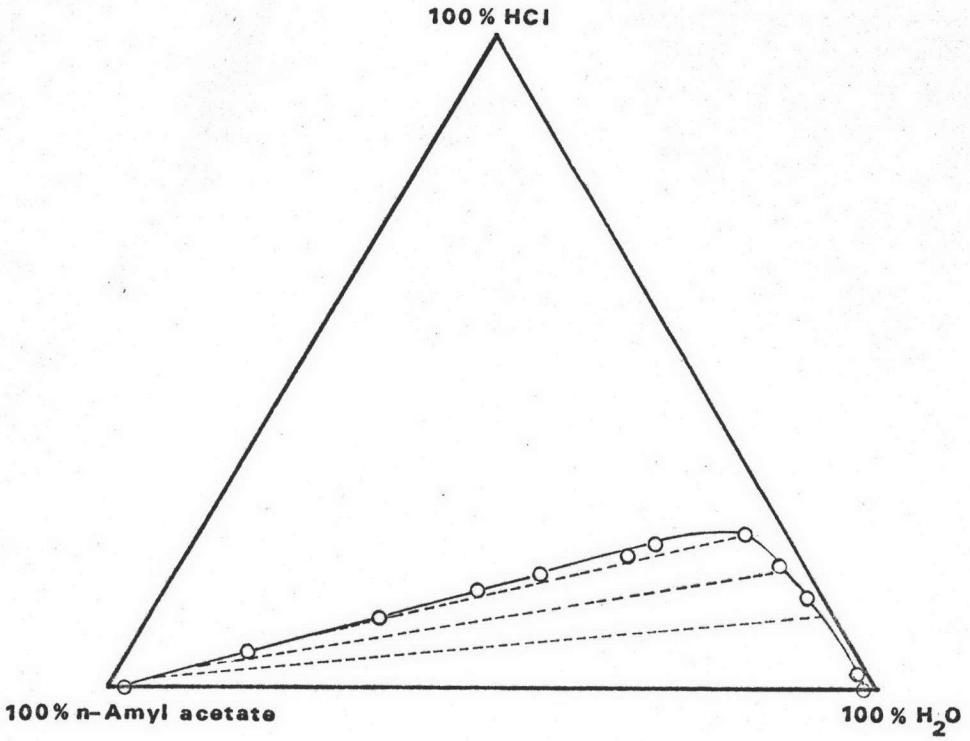


FIG. 3.1 The phase diagram of water–hydrochloric acid–n-amyl acetate.

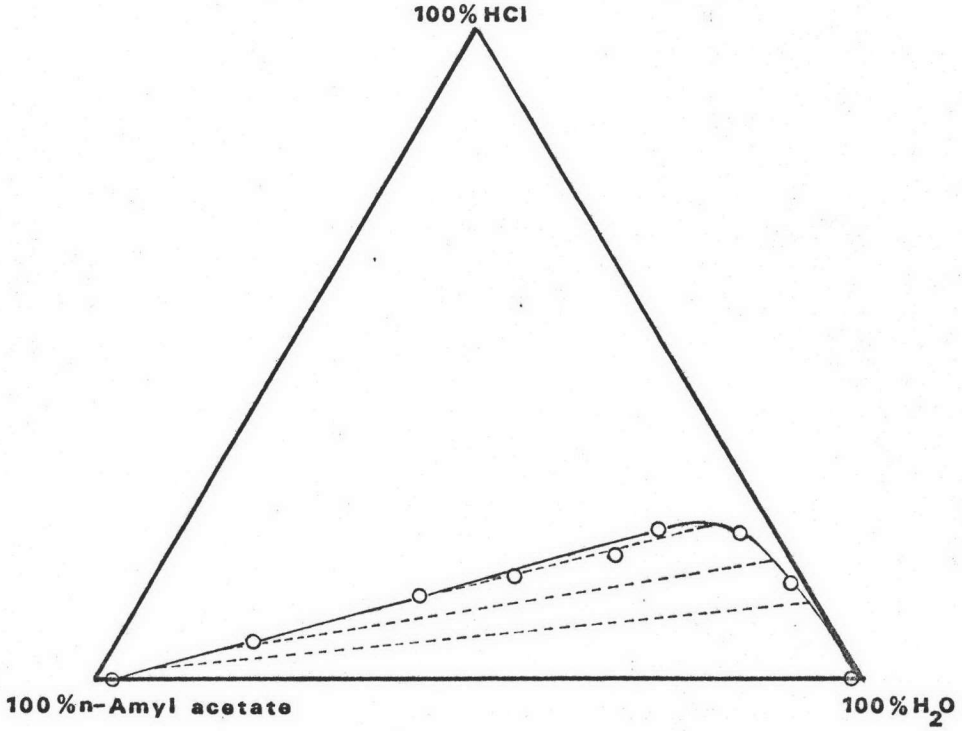


FIG. 3.2 The phase diagram of water–hydrochloric acid with a little amount of ferric chloride– n-amyl acetate.

n-amyl acetate until the thermal equilibrium reached at the room temperature ($30 \pm 2^{\circ}C$) and the atmospheric pressure. The per cent of hydrochloric acid in each phase of each solution was determined by titration with a standard sodium hydroxide.

Three component phase diagram with tie lines showing regions of miscibility and immiscibility was illustrated on triangular co-ordinates as shown in Fig. 3.1

3.2.2 Solvent extraction techniques.

The apparatus used for the extractions of iron (III) chloro complexes into amyl acetate in this experiment was the separatory funnel. The equilibrium time required is about $1\frac{1}{2}$ hrs by manual shaking at the room temperature ($30 \pm 2^{\circ}C$) and the atmospheric pressure. The content was left to stand for at least 20 minutes then the two phases were separated by drawing off the bottom layer via the tap. Each separated phase was kept for the u.v. spectrophotometric and radiometric studies from which the formula of iron(III) chloro complex, the distribution of iron (III) in the aqueous acid and the amyl acetate, and the solvation number of the iron (III) chloro complexes with n-amyl acetate were proposed.

The distribution coefficient depends upon the temperature only to a certain extent. Temperature control was not exercised here since the room temperature is in the limited range of $30 \pm 2^{\circ}C$. The effect of this size of temperature variation was not noticeable in the study of the distribution coefficient.

3.2.3 Spectrophotometric studies of iron (III)chloro complexes

The Perkin Elmer,model 124,double beam,grating spectrophotometer with a pair of matching silica cells of 1-cm light path was used throughout this work.

The ultraviolet absorption spectra of iron (III)chloro complexes in hydrochloric acid solution before being extracted and those of iron (III)chloro complexes in the organic extracts were recorded in the region of 420-200 nm on the chart for electronic recorder no 159-1003. The solutions were carried out for the spectra by the following process.

As a beam of violet light from deuterium lamp was passed through the sample,the other beam passed through the reference which was the identical solvent without iron (III). The absorption of light in the ultraviolet regions of the spectra involves the displacement of electrons within the molecules. The grating disperses the light beam to produce the spectrum.

The extent of absorption depends upon the probability that the quantum energy will be absorbed by a molecule where it can effect a chemical reaction or where it is dissipated eventually as heat. The probability of absorption is directly proportion to the concentration of absorbing molecules,it can be expressed mathematically by the equation.

$$\frac{dI}{I} = -kcdt \qquad (3.1)$$

where I is the intensity of light, photon/cm^2-sec,

dI is the change in light intensity produced by absorption in a thin layer of thickness dt and concentration c ,provided that the thickness and fraction absorbed are small.

k is the proportionality constant varying with the wavelength of light used and the temperature

Integrate the equation(3.1)between the limits I_o (incident intensity) when t=0 and I at length t.

$$\int_{I_o}^{I} \frac{dI}{I} = -kc \int_{0}^{t} dt \qquad (3.2)$$

$$\ln \frac{I}{I_o} = 2.303 \log \frac{I}{I_o} = -kct \qquad (3.3)$$

$$\log \frac{Io}{I} = As = Ect \qquad (3.4)$$

where $\log \frac{I_o}{I}$ is referred as the absorbancy (As) of the sample.

E is called the absorbancy index or the extinction coefficient being a characteristic of the solute and depending upon the wavelength of light,the solvent,and the temperature. When the concentration c is in moles per litre and t in centimetres the term molar absorbancy index or molar absorptivity, ε is used

3.2.4 Radiochemical technique

The Abacus G.M. Scaler Model 1234 manufactured by Messr. Baird Atomic was used to detect the beta radiation of iron-59 . Since this work involved in the analysis of a liquid phase, a liquid G.M. tube type MX 124/01 was used. The operating voltage used was determined by plotting the counting rates versus the high voltage values and chosen as the midpoint in the region of "plateau" when counting rate is independent of the high voltage value. The voltage applied in all experiments was fixed at 450 volts and was periodically checked for the performance of the tube and of the mechanical parts of the setup.

The radiochemical technique was used to determine the distribution coefficient of iron(III)in various concentrations of hydrochloric acid in the amyl acetate phase.

Two sets of experiments were carried out in the determination of the distribution coefficients, the difference being the amount of ferric chloride in the solutions i.e., 1×10^{-4} and 2×10^{-4}M-ferric chloride with iron-59 as tracer in 1-9 M-hydrochloric acid in one set and iron-59 as tracer alone in 1-9 M-hydrochloric acid in the other one.

The 10 ml portion of ferric chloride solution was shaken together with the 12 ml of the organic solvent in a separatory funnel until the thermal equilibrium reached. The two equal volumes(10 ml)of the solution from each phase were detected for the activity of iron-59 via its β-radiation. The counting time was usually about 5 minutes or whenever possible was long enough to get total 10,000 counts or more. Background was determined accurately for each count and was usually approximately 15 counts per minute. Results tabulated in ChapterIV,were calculated from counting rates which have been corrected for lost counts and background. The distribution coefficients were calculated using the formula.

$$D = \frac{\text{Counts per minute (organic phase)}}{\text{Counts per minute (the same volume of aqueous phase)}}$$

A typical calculation for the distribution coefficients is given below.

	Counts per minute		
	Background	Source plus background	Corrected countrate (less background)
Aqueous phase	$15 \pm 1.73^{*}$	4330 ± 29.42	4444 ± 29.93
Organic phase	$15 \pm 1.73^{*}$	1173 ± 15.31	1167 ± 15.46

*standard deviation calculated from the countrate recorded as a single measurement over 5 minutes accumulate counting time.

$$D = \frac{\text{Countrate of 10 ml sample (organic phase)}}{\text{Countrate of 10 ml sample (aqueous phase)}}$$

$$= \frac{1167}{4444} \pm \frac{1167}{4444} \sqrt{\left(\frac{15.46}{1167}\right)^2 + \left(\frac{2993}{4444}\right)^2}$$

$$= 0.2626 \pm 0.00389$$

N.B The standard deviation for counting rates N counts being recorded in t minutes has been taken as $\frac{1}{t} N^{\frac{1}{2}}$.

The standard deviation of

$$(A \pm a) + (B \pm b) = \pm \sqrt{a^2 + b^2}$$

$$(A \pm a) - (B \pm b) = \pm \sqrt{a^2 + b^2}$$

$$(A \pm a)(B \pm b) = \pm AB \sqrt{\left(\frac{a}{A}\right)^2 + \left(\frac{b}{B}\right)^2}$$

$$\frac{A \pm a}{B \pm b} = \pm \frac{A}{B} \sqrt{\left(\frac{a}{A}\right)^2 + \left(\frac{b}{B}\right)^2}$$

where A is the counting rate with standard deviation a

and B is the counting rate with standard deviation b

These formulae were used for all the calculations in this thesis.

Because of the hazard of the radiation the experiments were taken carefully in the confined area. The liquid and solid waste were collected in the labelled bottle and were sent to the Thai Atomic Energy Authority for disposal.

3.2.5 The solvation number

Since benzene is an inert solvent for the extraction of iron (III) chloro complexes from hydrochloric acid it was used as a diluent in this experiment. The solvent extraction technique in combination with an application of radioactive tracer (iron-59) was employed. The process involved the observation of changes in the distribution coefficient upon the dilution of n-amyl acetate with benzene as a second inert solvent. This technique is sometimes called the dilution technique.