CHAPTER 5

DISCUSSION AND CONCLUSION

There are two problems which must be considered in the discussion of the result of this work. These are the problems involved in the method of determination of various quantities effectively and the problem as to the behaviour of the ionic species in the system as a function of concentration of various components. Hence for the sake of simplicity and clearity, the discussion will confine to two areas, the practical and the theoretical aspects of the work.

Practical Aspects

Since in this work two secondary reference electrodes were used namely, calomel electrode and mercury-mercurous acetate electrode. Both were standardised against the hydrogen electrode by using cells without liquid junction.

$$\text{Pt, } H_2/HCl(c)/Hg_2Cl_2/Hg$$

and $$\text{Pt, } H_2/HOAc(c)/Hg_2(OAc)_2/Hg$$

Two series of measurement with varying concentration of acids were made and the Hitchcock extrapolation (13) was applied which yield E° as the intercept of the rectilinear plot (see Fig.3.2 and 3.3) The E° values of both calomel and mercury-mercurous acetate electrode are recorded regardless of the concentration of acid. But the conductivity data of acetic acid as a function of a wide range of concentrations like that covered in this work is scarce and those available in the Hand book (15) are the approximate ones, it was thought advisable to use our own data in the subsequent computation of the E° values.

The technique adopted here is to measure the conductivity of acetic acid at various concentrations from which the corresponding pK values were calculated. A plot of pK values and concentrations is presented graphically in Fig.5.3 . The dissociation constant of acetic acid at any concentration thus can be readily obtained for the pK values read off from this graph.

The reproducibility of the e.m.f. readings are high and every set of data reported in this thesis is taken from the measurements which performed in duplicate. Usually it took about half a day for cell I, II and III to reach equilibrium after which the equilibrium attained for further half a day.

Theoretical Aspects

The e.m.f. of the cells I, II and III are generally given by

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{Ox.}}{a_{Red.}}$$

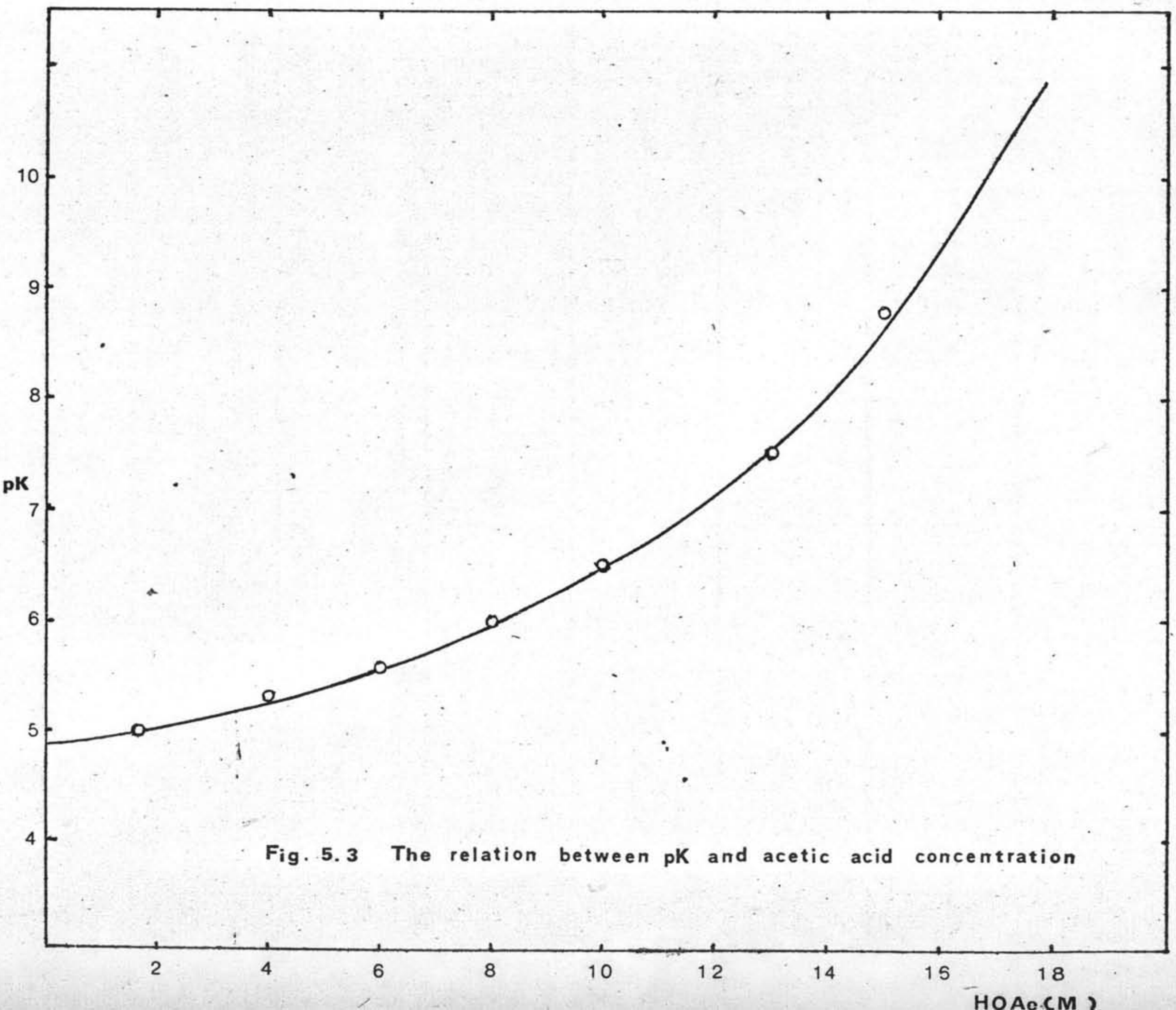

Fig. 5.3 The relation between pK and acetic acid concentration

$$= \quad E^\circ - \frac{RT}{nF} \ln \frac{c_{Ox.}\gamma_{Ox.}}{c_{Red.}\gamma_{Red.}}$$

It is evident that in order to arrive at the E° value the activity coefficient γ of oxidised form and those of reduced form must be known. This proves to be uncomplicated matter for cell I as can be seen from the working equation below.

$$E \quad = \quad E^\circ - \frac{RT}{2F} \ln \frac{c_{Tl^+}}{c_{Tl^{3+}}} \times \frac{1}{c^2_{Cl^-}\gamma^2_{Cl^-}}$$

The γ_{Tl^+}, $\gamma_{Tl^{3+}}$ and γ_{Cl^-} are readily obtained using equation $\log \gamma_i = - \frac{AZ_i^2 I^{1/2}}{1+Ba\ I^{1/2}}$ (for details, see Appendix I) since the electrolyte solutions are glacial acetic acid for the positive electrode and hydrochloric acid for the negative electrode the dielectric constants of both solvents are accurate known, hence A and B in the above formula were calculated directly using the formula given in Appendix I. The value of "a", the distance of closest approach, however was taken from the literature (16). It can be seen that the e.m.f. measurement of cell I is technically feasible but the potentials recorded always including the unknown liquid junction potential which can not be eliminated completely by the use of a salt bridge.

The working equation for evaluation of E° of the Tl(III)/Tl(I) electrodes in cell II and III is somewhat different from that quoted for cell I i.e.,

$$E = E^{\circ} - \frac{RT}{2F} \ln \frac{c_{Tl^{+}}}{c_{Tl^{3+}}} \cdot \frac{\gamma_{Tl^{+}}}{\gamma_{Tl^{3+}}} \times \frac{1}{c^{2}_{OAc^{-}}\ \gamma^{2}_{OAc^{-}}}$$

The concentration of acetate ions ($c_{OAc^{-}}$) varies with the water content in the acid since acetic acid is a weak electrolyte. This called for the knowledge of the dissociation constant of the acetic acid at every concentration employed in the investigation. The same argument is also applicable to the value of dielectric constant of the solvent which appear in "A" and "B". The dielectric constant of pure acetic acid is 6.21 (17) and that water is 78.5 (18). Hence the addition of water to pure acetic acid will result in the increasing of the dielectric constant of the aqueous acid. The extent of which the change occur depends on the amount of water added. Hence the very diluted solution of acetic acid will have a much higher dielectric constant than the concentrated one. The change of dielectric constant with the amount of water added is unfortunatety not linear. Direct conversion cannot be made.

The dielectric constants of a series of various concentrations of acetic acid are needed in the computation of the ionic activity coefficients. In this work a direct measurement of the dielectric constants have not been made but a rough estimation of the dielectric constants from a tentative data of the only literature (17) existed at present were used instead.

As a result, the reported standard redox potential is subjected to some uncertainty which can be eliminated when more accurate data of the dielectric constant and the conductivity of acetic acid at various concentrations can be obtained. The extrapolation method seems to provide an unambiguous E° value. This is suggested by the good straight line of Fig. 5.1 and Fig. 5.2 .

The complete understanding of the behavior of cell II & III in the presence of glacial acetic acid is not attainable. However, tentative explanation can be offered as follows. The unability of such cells to give any e.m.f. when glacial acetic acid was used is clearly resulted from an obvious cause i.e. there is no electron flows from the negative electrode to the positive electrode. This phenomenon may be caused by the insufficient availability of the acetate ions from glacial acetic acid in cell III and perhaps by the fact that electrons occured were used up by the thallic ions in cell II. The last mentioned process is likely to occur but at the lower concentration of acetic acid more acetate ions are available and hence more electrons produced whereas the Tl(III) ions stay more or less constant in number. The flow of electrons from the negative electrode to the positive electrode can occur and will initiate the reaction in the vicinity of the positive electrode gives rise to the e.m.f. reading on the instrument.

Conclusion

The possible redox potential of the Tl(III)/Tl(I) electrode in glacial acetic acid seems to lie between 0.9518 volt and 1.0488 volts. The exact value cannot be given at present. Almost complete lack of the experimental data on the behaviour of acetic acid at various concentrations, from a very diluted one to glacial acetic acid, has restricted the calculated E° to a low confident limit. However it should be pointed out here that the cell design, the method of preparation of electrodes, the instrument used for the e.m.f. measurement are all proved to work satisfactorily.

Table 5.2 gives the comparison of the redox potential obtained in this work with those obtained from the previous one.

Those of the previous work are higher than that obtained in this thesis indicating that Tl(III) ions are stabilized by acetate ion more than by perchlorate, nitrate and sulphate ions. Hence thallic acetate is the least powerful oxidising agents in comparison to the sulphate, nitrate and perchlorate.

Table 5.2

The standard electrode potential of Tl(III)/Tl(I) in various anions solutions

Anion present	$E^\circ_{Tl(III)/Tl(I)}$ (volts)
perchlorate	1.260 (7)
nitrate	1.2303 (8)
sulphate	1.2207 (6)
acetate	0.9518-1.0488 (present work)

The mechanism of the electron transfer process of thallic and thallous ion is thought to be two electrons transfer process.

$$Tl^{3+} \longrightarrow Tl^{+} + 2\,e$$

This has been confirmed in the course of the experimental part of the work reported here by potentiometric titration of hydroquinone with thallic acetate solution. The potential of the platinum electrode which immersed in the reacting solution was measured against the calomel reference electrode after each addition of the titrant. The number of electrons involved can be obtained from the slope of the straight line whose equation is as follows:

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{t_c - t}{t}$$

Here t_c is the volume of the titrant added when the sudden change of potential occurs, t is the amount of the titrant added at any point and $\frac{RT}{nF}$ is the slope of the straight line when E is plotted against ln $\frac{t_c - t}{t}$.

From the slope of the graph, it was found that n = 2 (see Fig. 5.4).

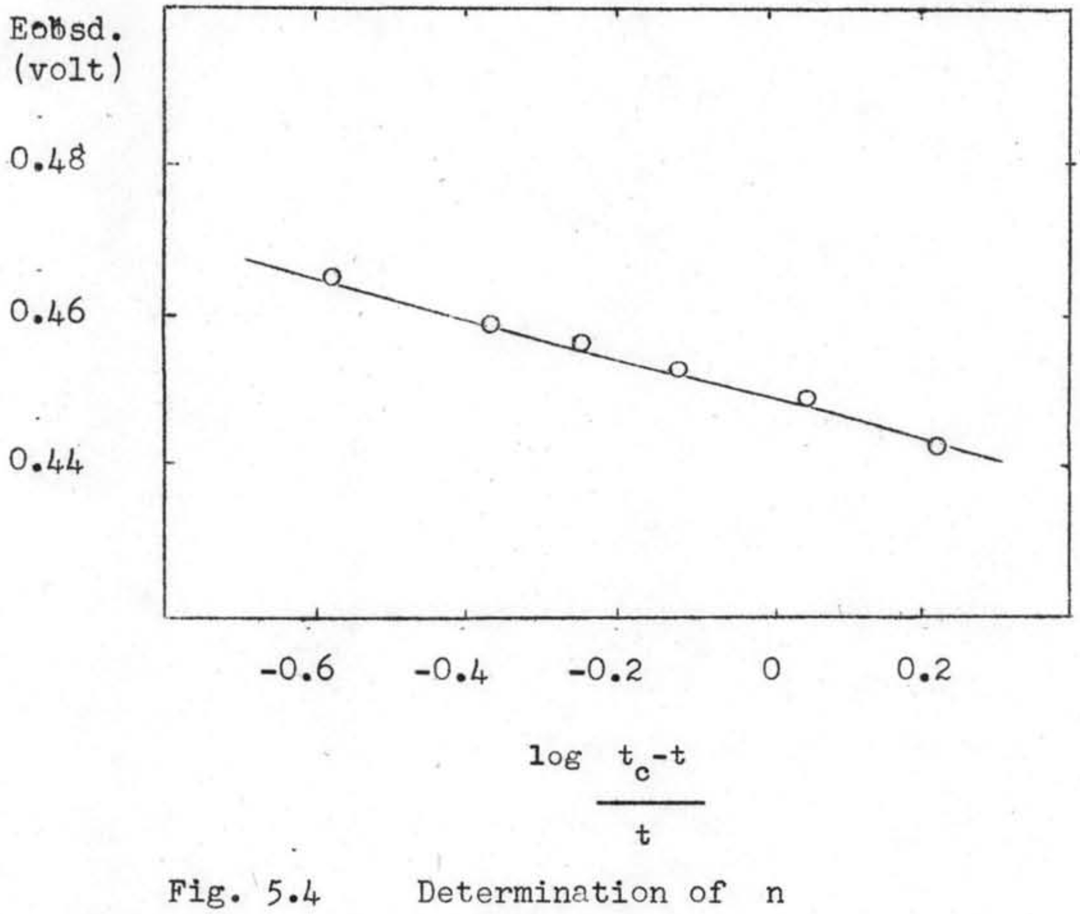

Fig. 5.4 Determination of n

Suggestion for the further work

There are still more interesting problems to be investigated, for example, the value of dielectric constant ε , the specific conductance L of acetic acid should be measured covering a wide range of acid concentration. The activity coefficients should be re-calculated using the new and more reliable values of the dielectric constant and specific conductance, this should enable a more certain value of the redox potential of Tl(III)/Tl(I) electrode to be obtained. The determination of the "a" value (distance of closest approach) by the method shown in Appendix III and especially by the method suggested by Bjerrum (19) using an electrostatic model will yield an information that may lead to a better understanding of the nature of ionic interaction in acetic acid. The liquid junction potential may be found if a suitable internal standard is used. By this it means that e.m.f. measurements are performed on a triple electrodes cell with the third one being an oxidation-reduction electrode with a known redox potential in glacial acetic acid.

Investigations have already been carried out by Miss Suda Kiatkamjornwong on the oxidising power of thallic acetate and reducing power of thallous acetate on some organic compounds in comparison to other thallic and thallous salts.

Appendix I

Nernst equation:

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_{Ox.}}{a_{Red.}}$$

$$= E^{\circ} - \frac{RT}{nF} \ln \frac{c_{Ox.} \, \gamma_{Ox.}}{c_{Red} \, \gamma_{Red}}$$

where a = activity

c = concentration in molarity scale

γ = activity coefficient

Debye-Hückel formula for the activity coefficient

$$\log \gamma_i = - \frac{A Z_i^2 \, I^{1/2}}{1 + Ba \, I^{1/2}}$$

where $A = \left(\frac{2 \ N}{1000}\right)^{1/2} \cdot \frac{e^3}{2.303 \ k} \cdot \frac{1}{(\varepsilon T)^{3/2}}$

$= \frac{1.8426 \times 10^6}{(\varepsilon T)^{3/2}}$ mole.$^{-1}$ l.$^{1/2}$ (deg. K)$^{3/2}$

$B = \left(\frac{8 \ Ne^2}{1000 \ k}\right)^{1/2} \cdot \frac{1}{(\varepsilon T)^{1/2}}$

$= \frac{50.29 \times 10^8}{(\varepsilon T)^{1/2}}$ cm.$^{-1}$ mole.$^{-1/2}$ l.$^{1/2}$ (deg. K)$^{1/2}$

$I = \frac{1}{2} \sum c_i Z_i^2$

The meanings of the notation used for A, B & I are as follows:

e = protonic charge

= 4.80298×10^{-10} c.g.s. e.s.u. of charge

ε = dielectric constant

N = Avogadro's number

= 6.02252×10^{23} mol.$^{-1}$

k = Boltzmann's constant

= 1.38054×10^{-16} erg degree^{-1} molecule^{-1}

T = Absolute temperature

Z_i = Valence of ith ion

Appendix II

Formula used for determining the dissociation constants of 1:1 electrolyte

$$K = \frac{\alpha^2 c}{1-\alpha}$$

and

$$\alpha = \frac{\Lambda}{\Lambda_o}$$

where K = dissociation constant

α = degree of dissociation

Λ = equivalent conductance at concentration c molar

Λ_o = equivalent conductance at infinite dilution

N.B. The degree of dissociation can also be calculated using the following relation.

$$\alpha = \frac{\Lambda}{\Lambda_\ell}$$

where Λ_ℓ = the equivalent conductance of the completely dissociated acid at concentration c.

This formula takes into account the ionic interaction in a very dilute solution of weak electrolyte.

Appendix III

Formula used for determining the distance of closest approach "a"

The individual "a" value may be approximately calculated by different methods.

(1) Bonino's equation (20)

$$10^8 a_i/Z_i = 0.9 \times 10^8 r_i/10^{24}\alpha_i + 2$$

where Z_i = Valence of i

r_i = crystal radius

α_i = deformability

(2) using ionic mobilities

$$10^8 a_i = 18\,\alpha\, Z_i/l_\infty$$

where l_∞ = ionic mobility at infinite dilution

(3) Brull's equation (21)

$$10^8 a_i = 216\, Z_i^{1/2}/l_\infty$$

The distance of closest approach "a" of the inorganic univalent ions are most frequently of the order of 3 to 4A°, the values for divalent ones are between 4 to 6 A°, for the trivalent ones are about 9 A° and the tetravalent ions acquire the value of 11 A° .

The "a" values of some ions are tabulated below (16)

Ions	"a" values (A°)
H^+	9
Tl^+	2.5
Cu^{2+}	6
Cr^{3+}	9
OH^-	3.5
OAc^-	4.5