

## CHAPTER IV

## RESULTS

Table 4.1

The standard electrode potential  $E^\circ$  of the calomel electrode

HCl (molarity)	E.M.F. of the cell Pt, $H_2/HCl(c)/Hg_2Cl_2/Hg$ (volt)	$E^\circ$ electrode (volt)
0.004897	0.543864	
0.010151	0.508794	
0.029920	0.455837	0.2677
0.049968	0.431180	
0.079910	0.408243	

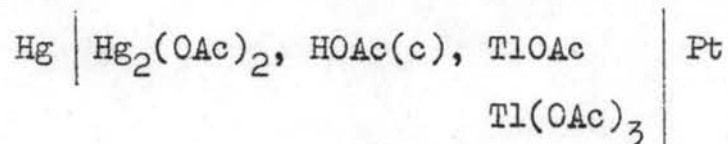
Table 4.2

The standard electrode potential  $E^\circ$  of the  
mercury-mercurous acetate electrode

HOAc (molarity)	E.M.F. of the cell Pt, H <sub>2</sub> /HOAc(c)/Hg <sub>2</sub> (OAc) <sub>2</sub> /Hg (volt)	$E^\circ$ electrode (volt)
0.0496	0.868650	0.5072
0.0794	0.856040	
0.5352	0.805462	
1.0556	0.790810	
1.6604	0.780512	
3.3451	0.772404	

Table 4.3

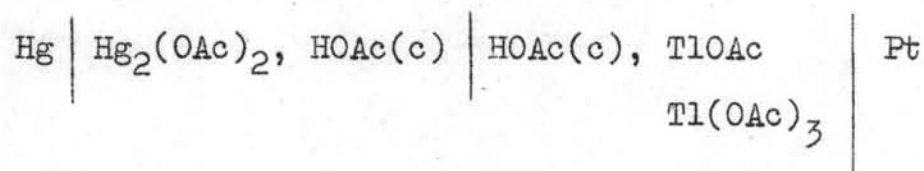
The redox potential of the Tl(III)/Tl(I) electrode in various acetic acid concentrations using cell (AI)



Concentrations (molarity)		E.M.F. (volt)	
Tl(I)/Tl(III)	HOAc	$E_{\text{cell}}$ (obsd.)	$E^{\circ}_{\text{electrode}}$
1.358288	1.996	0.268604	0.946075
1.227786	3.941	0.254036	0.932026
1.710920	7.271	0.240957	0.935845
1.621478	8.430	0.233406	0.937129
1.687356	10.775	0.224066	0.941687

Table 4.4

The redox potential of the Tl(III)/Tl(I) electrode in various acetic acid concentrations using cell (A II)



Concentrations (molarity)		E.M.F. (volt)	
Tl(I)/Tl(III)	HOAc	$E_{\text{cell}}$ (obsd.)	$E_{\text{electrode}}^{\circ}$
1.285213	0.863	0.333203	1.001936
1.596712	1.996	0.282193	0.947141
0.048827	3.941	0.252623	0.885221
1.769231	4.702	0.225293	0.892091
1.710920	7.271	0.225706	0.902437
1.621478	8.430	0.224663	0.907931
1.687356	10.775	0.219116	0.915240
1.486391	13.114	0.206333	0.932880

Table 4.5

The redox potential of the Tl(III)/Tl(I) electrode  
in glacial acetic acid using cell (B)

Concentrations (molarity)		E.M.F. (volts)	
Tl(I)/Tl(III)	HCl	$E_{\text{cell}}$ (obsd.)	$E^{\circ}_{\text{electrode}}$
1.841399	0.010151	0.392359	1.048963
1.841399	0.029920	0.416946	1.048782
1.657711	0.049968	0.435013	1.048695
			Average = 1.048813

Table 4.6

Changes in composition of  $Tl(OAc)_3$  with time and strength of acetic acid

%acetic acid Time (days)	100	90	80	70	60	50	40	30	20	10
0	0.01495	0.01920	0.01720	0.01840	0.01960	0.01870	0.01870	0.01980	0.01895	0.01870
3	0.01530	0.01675	0.01675	0.01820	0.01900	0.01795	0.01835	0.01795	0.01860	0.01860
6	0.01515	0.01530	0.01635	0.01840	0.01910	0.01760	0.01840	0.01760	0.01815	0.01840
9	0.01520	0.01520	0.01625	0.01895	0.01925	0.01780	0.01820	0.01770	0.01795	0.01805
12	0.01510	0.01540	0.01605	0.01855	0.01995	0.01775	0.01840	0.01790	0.01815	0.01830
14	0.01525	0.01505	0.01630	0.01840	0.01940	0.01770	0.01840	0.01815	0.01815	0.01815
17	0.01550	0.01515	0.01615	0.01850	0.01945	0.01775	0.01840	0.01800	0.01815	0.01830

Table 4.7

The conductivities and related parameters of acetic acid

HOAC (molarity)	L (microhm <sup>-1</sup> cm <sup>-1</sup> )	$\wedge$ (ohm <sup>-1</sup> cm <sup>2</sup> ./equivalent)	K
1.673	1700	1.0174	1.134 X 10 <sup>-5</sup>
3.362	1900	0.5669	7.079 X 10 <sup>-6</sup>
5.062	1750	0.3465	3.981 X 10 <sup>-6</sup>
6.788	1430	0.21180	1.995 X 10 <sup>-6</sup>
8.525	1040	0.12202	8.318 X 10 <sup>-7</sup>
10.281	671	0.0654	2.884 X 10 <sup>-7</sup>
12.053	369	0.03064	7.413 X 10 <sup>-8</sup>
14.952	74.8	0.00501	2.455 X 10 <sup>-9</sup>



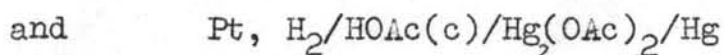
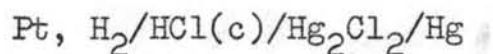
## CHAPTER 5

## 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 clarity, the discussion will be confined 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.



Two series of measurement with varying concentration of acids were made and the Hitchcock extrapolation (13) was applied which yield  $E^\circ$  as the intercept of the rectilinear plot (see Fig. 3.2 and 3.3). The  $E^\circ$  values of both calomel and mercury-mercurous acetate electrode are



in good agreement with the literature values as can be seen from table 5.1. This provides a proof that the methods chosen for the preparation of the two reference electrodes are suitable and reliable in producing electrodes which function reversibly and reproducibly.

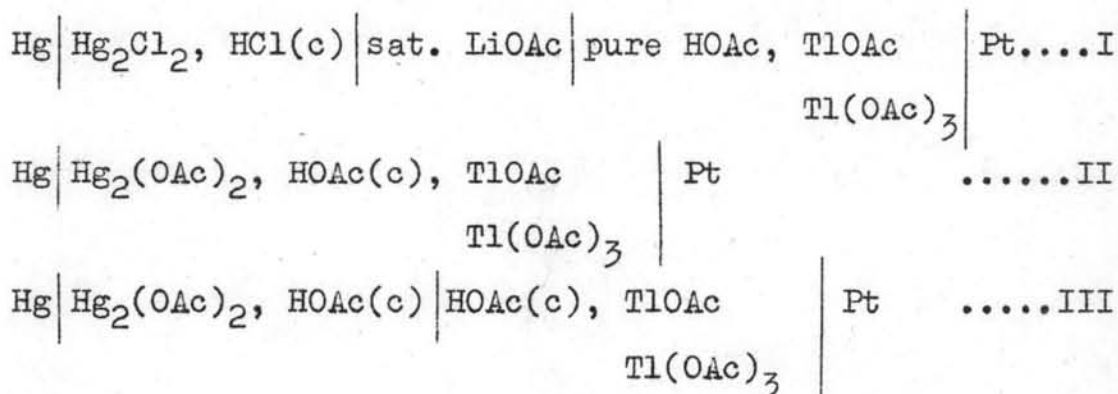
Table 5.1

The standard electrode potential  $E^\circ$  at 25°C of the mercury-mercurous ion electrodes

Electrode	$E^\circ$ electrode in this work (volt)	$E^\circ$ electrode from reference (volt)
calomel	0.2677	0.2678 (13)
mercury-mercurous acetate	0.5072	0.5109 (14)

It should be noted here that the small discrepancy between the  $E^\circ$  value of the mercury-mercurous acetate electrode obtained in this work and that from the work reported in reference (14) should result from the fact that Larson and Tomsicek (14) measured the cell potential in 0.5 to 1.0 M acetic acid solution. In their calculations, they used a single value of dissociation constant

i.e.,  $1.754 \times 10^{-5}$  for the whole range of the concentration of acetic acid and assumed that  $\delta_{\text{HOAc}}$  equal to unity on the molarity scale whereas in this work a wider concentration range of acetic acid was covered and the K value was not considered as a constant throughout. It varies from  $\sim 10^{-5}$  for a very diluted solution to  $\sim 10^{-9}$  for glacial acetic acid (see Table 4.7), it is unreasonable to take  $\delta_{\text{HOAc}}$  as unity. The calculation of the E' value in the present work therefore involving the use of activity coefficient  $\gamma$  whose values vary with the acid concentration (see Appendix I). As far as the e.m.f. measurement is concerned, a Tinsley potentiometer is reliable, it can measure the potential to within  $\pm 0.0001$  volt. The problem encountered in this kind of potential measurement seems to be arisen from the choice of the cell design which should be responsible in giving a cell e.m.f. with or without liquid junction potential. Attempts have been made to measure the potential of the cell without or with minimum junction potential as shown below.



In cell I, a salt bridge was used, the e.m.f. of this cell could be measured with a high certainty in the medium of glacial acetic acid, which is in contrast to the other two cells, cell II and III, which will be discussed presently. As it happened the instrument became insensitive to the potential difference between the two electrodes when measurement was performed on cell II and III in the presence of glacial acetic acid. It was therefore necessary to obtain the  $E^{\circ}_{\text{Tl(III)/Tl(I)}}$  in glacial acetic acid indirectly. The method of extrapolation was used. Here the  $E^{\circ}$  values were plotted against the appropriate concentration of acetic acid and the resulted straight line was extrapolated to glacial acetic acid (see Fig. 5.1 and 5.2.) The corresponding intercept was taken as the standard redox potential of  $\text{Tl(III)/Tl(I)}$  in glacial acetic acid.

The practical problem encountered in the conductivity measurement of the electrolyte solutions used in this work though is similar to that of the e.m.f. measurement with respect to the failure in recording any readings in the presence of glacial acetic acid differs in the efficiency of the instrument employed. In the case of the conductivity measurement, the conductivity bridge available in the laboratory is of so low sensitivity that some uncertainties are attached to the values

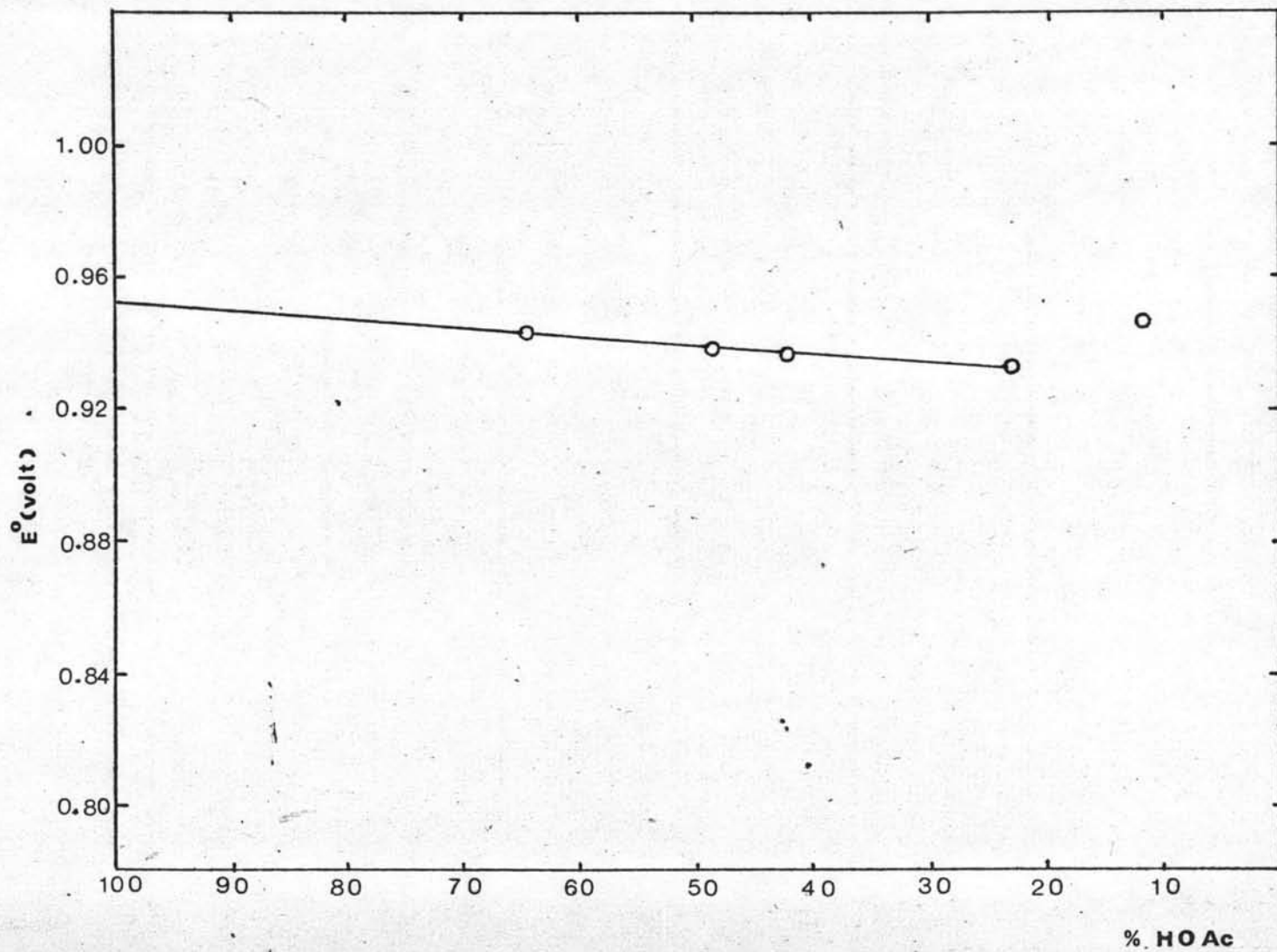


Fig. 5.1 The extrapolation of cell A (I) data

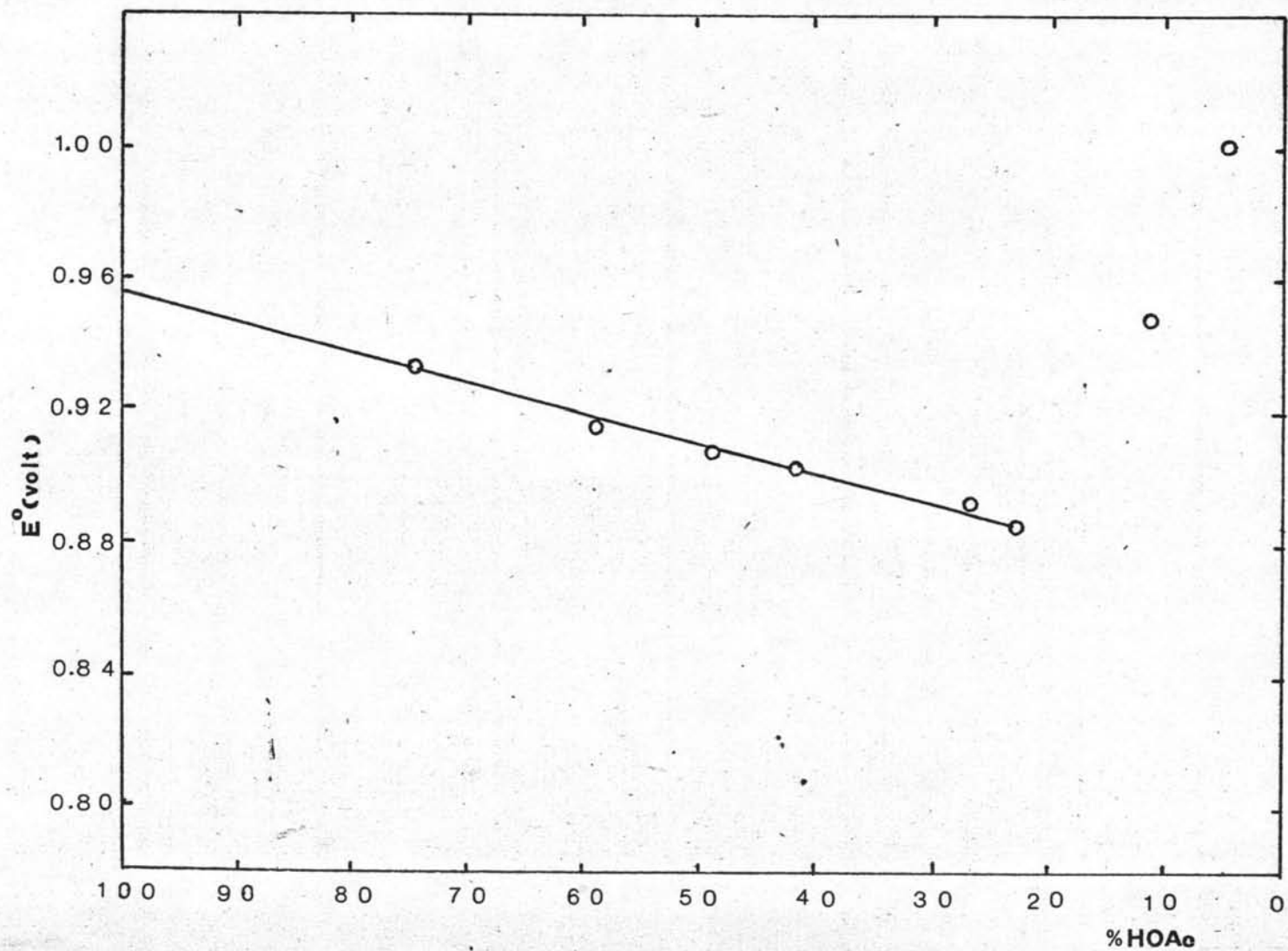


Fig. 5.2 The extrapolation of cell (AII) data