
CHAPTER - II

EXPERIMENTAL TECHNIQUES



EXPERIMENTAL

Reagent grade chemicals were used and double distilled water was used throughout the work. The stock solution of Au(III) was prepared by dissolving 1gm. of chloroauric acid (JMC) in 100 ml of 1.0 mol dm^{-3} hydrochloric acid (BDH, AR).

The pyridinium chlorochromate was prepared⁵⁰ by adding 100 gm. of CrO_3 to 184 ml of 6 M HCl rapidly with stirring. After 5 minutes the homogeneous solution was cooled to 0° and 79.1 gm of pyridine was added carefully over 10 minutes. Recooling to 0° gave yellow orange solid which was collected on sintered glass funnel and dried for one hour in vacuum. The solutions were obtained by dissolving the pyridinium chlorochromate in water.

The thallium(I) solutions were obtained by dissolving thallium (I) chloride (BDH) in distilled water and standardising⁵¹ against potassium bromate solution using methyl orange as indicator in 6 M HCl.

Thallium (III) chloride was prepared by dissolving thallic oxide (BDH) in 1.0 M hydrochloric acid and standardised iodometrically⁵² by titrating with 0.002 M thiosulphate solution.

To maintain ionic strength, sodium perchlorate was used which was prepared by dissolving equivalent quantities of sodium carbonate (Loba GR) and perchloric acid (E. Merck, 70%) in water.

BEER'S LAW VERIFICATION

The Beer's law for both oxidants, tetrachloroaurate(III) (0.5×10^{-4} to 5.0×10^{-4} M) in 3.0 M hydrochloric acid and pyridinium chlorochromate (0.578×10^{-4} to 6.94×10^{-4} M) in 2 M hydrochloric acid was verified at 360 nm making use of Bausch & Lomb spectronic-20 spectrophotometer. The data are given in Table 2.1 and 2.2 and the respective Beer's law plots are shown in Figures 2.1 and 2.2 for tetrachloroaurate(III) and pyridinium chlorochromate respectively. The molar absorptivity was found to be 464 for tetrachloroaurate(III) and 700 for pyridinium chlorochromate.

KINETIC STUDIES

The ionic strength was maintained at 3.1 M and 2.1 M using sodium perchlorate for tetrachloroaurate(III) - thallium(I) and pyridinium chlorochromate-thallium(I) reactions respectively. In a typical run oxidant and reductant are taken in separate conical flasks along with required quantities of hydrochloric acid and sodium perchlorate and are kept in a thermostat at $25 \pm 0.1^\circ$ C for half an

Table 2.1 : Beer's law verification for Au(III) at 360 nm in 3.0 M HCl

Volume of Au(III) 0.002 m	Volume of HCl 12 M	Volume of water	[Au(III)]x10 ⁵	O.D.
0.5	5.0	14.5	5.0	0.025
1.0	4.9	14.1	10.0	0.049
1.5	4.9	13.6	15.0	0.069
2.0	4.8	13.2	20.0	0.089
2.5	4.8	12.7	25.0	0.119
3.0	4.8	12.2	30.0	0.135
3.5	4.7	11.8	35.0	0.160
4.0	4.7	11.3	40.0	0.230
5.0	4.6	10.4	50.0	0.240

Figure 2.1: Beer's law verification for tetrachloroaurate (III) (conditions as in Table 2.1)

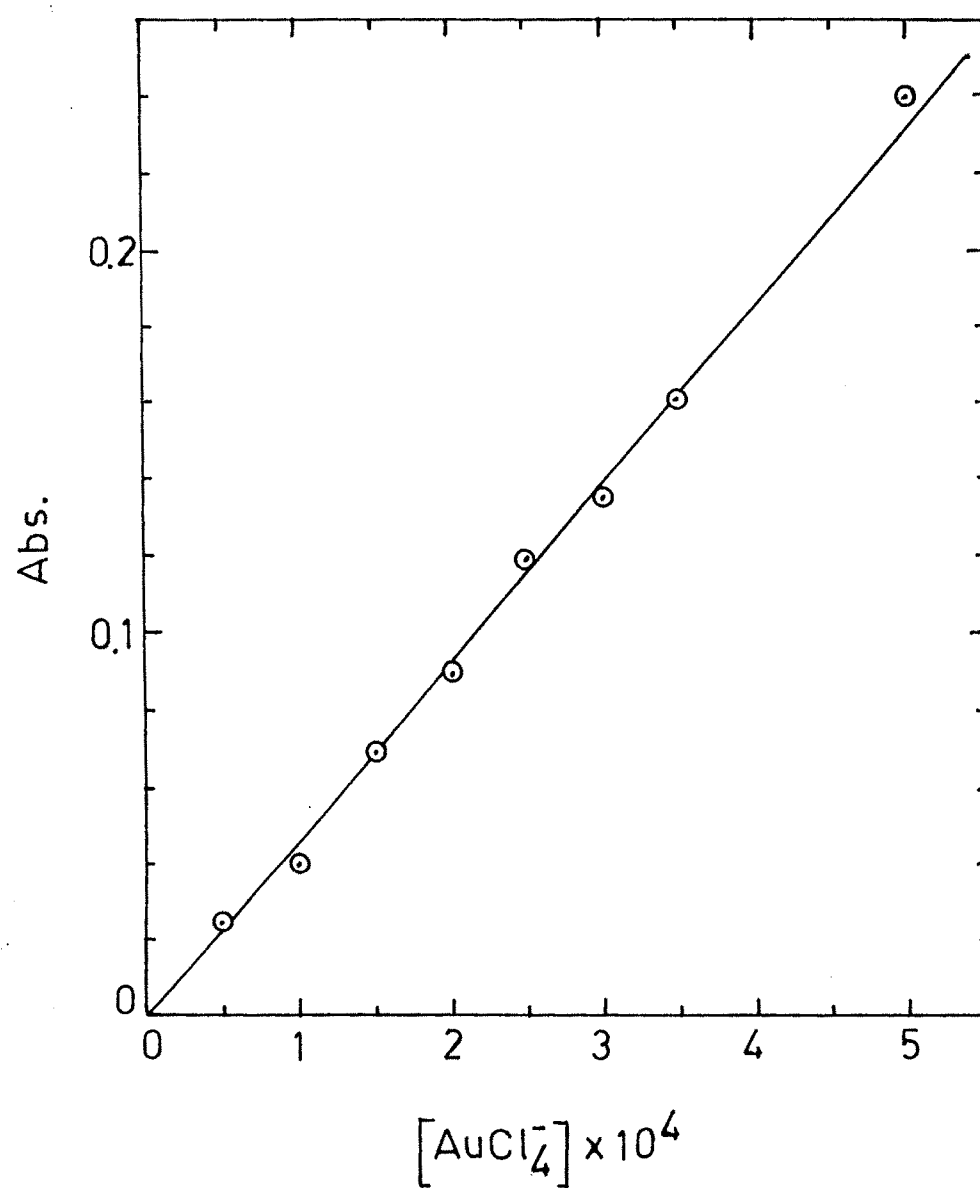
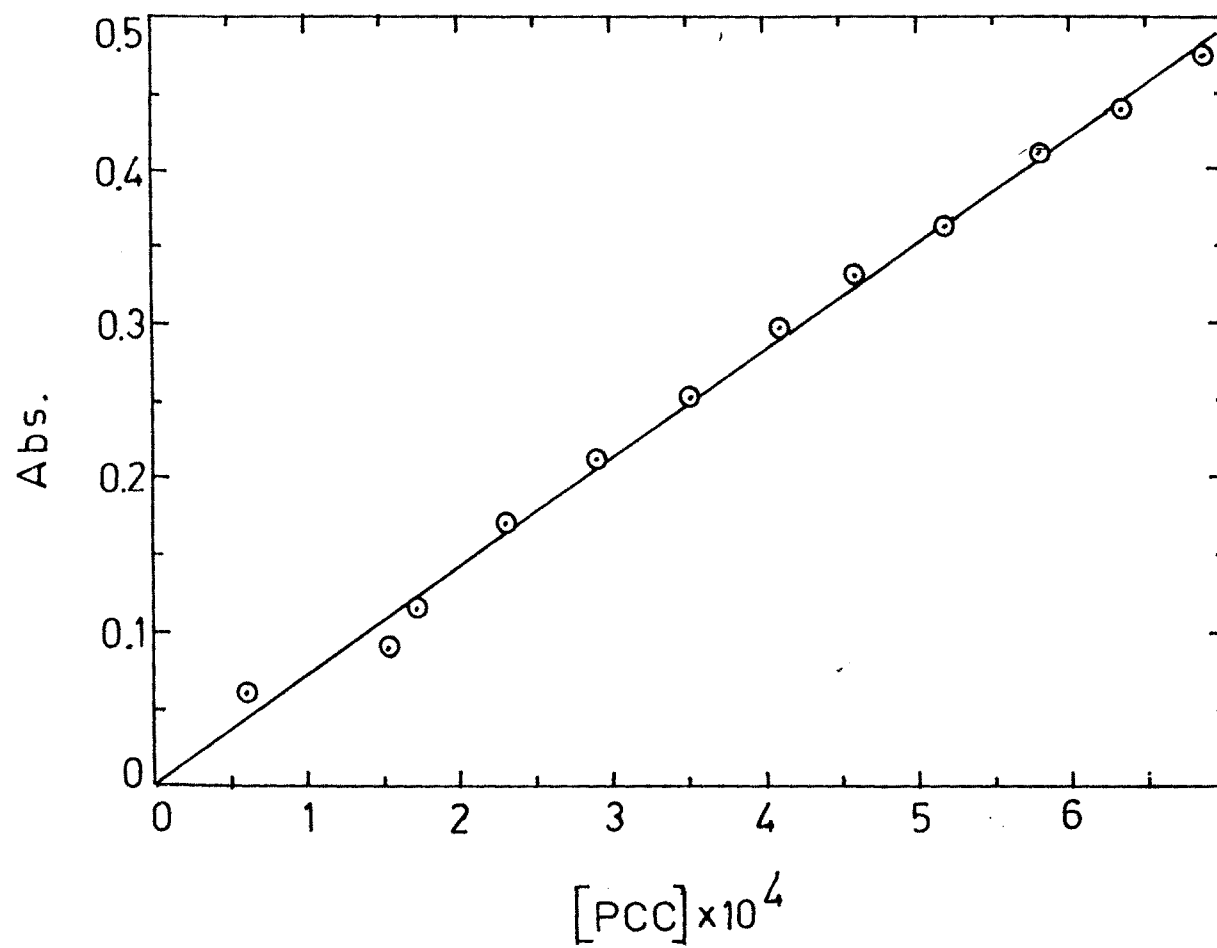


Table 2.2 : Beer's law verification for pyridinium chlorochromate at 360 nm in 2 M HCl

Volume of 0.001156M PCC	Volume of HCl	Volume of water	[PCC] $\times 10^4$	O.D.
1.0	3.4	15.6	0.578	0.060
2.0	3.4	14.6	1.156	0.090
3.0	3.4	13.6	1.734	0.115
4.0	3.4	12.6	2.312	0.170
5.0	3.4	11.6	2.890	0.210
6.0	3.4	10.6	3.470	0.250
7.0	3.4	9.6	4.050	0.295
8.0	3.4	8.6	4.620	0.328
9.0	3.4	7.6	5.200	0.360
10.0	3.4	6.6	5.780	0.410
11.0	3.4	5.6	6.360	0.440
12.0	3.4	4.6	6.940	0.475

Figure 2.2: Beer's law verification for pyridinium chlorochromate (conditions as in Table 2.2)



hour. The kinetics were followed by mixing thermally equilibrated solutions of reactants and transferring the reaction mixture to 1 Cm cuvettes. The absorbance at 360 nm was followed with Bausch and Lomb spectronic 20 spectrophotometer. In case of AuCl_4^- - Tl(I) reaction conical flasks and cuvettes were washed each time with aquaregia⁵³ in order to prevent further reduction of AuCl_2^- to metallic gold. However, in any of the runs precipitation of metallic gold was not observed. Kinetic runs could be reproduced to $\pm 3\%$ or better.

The second order rate constants for the tetrachloroaurate(III)-thallium(I) reaction were obtained by plotting

$$\log \frac{a}{b} \frac{(b-x)}{(a-x)} \text{ Vs time and } \frac{1}{(a-x)} \text{ Vs time}$$

When the concentrations of reactants were different and same respectively.

While for the pyridinium chlorochromate thallium(I) reaction the second order rate constants were determined using equation 1.

$$k_s = \frac{2.303}{t(a - 3b/2)} \log \frac{b(a - 3x/2)}{a(b - x)} \dots\dots(1)$$

by plotting $\log \frac{b(a - 3x/2)}{a(b - x)}$ Vs time

where a and b are concentrations of reductant and oxidant respectively.

STOICHIOMETRY

Several reaction mixtures were prepared in hydrochloric acid of requisite quantity by keeping oxidant in excess over reductant. The reaction mixture was allowed to stand for one day and the amount of oxidant remaining was estimated spectrophotometrically at 360 nm. The results of stoichiometry for tetrachloroaurate(III)-thallium(I) reaction and pyridinium chlorochloramte-thallium(I) reaction are given in Table 2.3 and 2.4 respectively.

The stoichiometry for AuCl_4^- - thallium(I) reaction is found to be 1; 1 and for pyridinium chlorochromate-thallium(I) reaction it is 1; 1.5. The stoichiometric equations are given in equation 1 and 2 respectively.

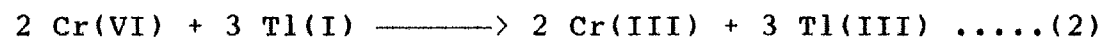


Table 2.3: Stoichiometry of Au(III) - Tl(I) reaction in 3 M HCl

[Au(III)] $\times 10^4$ Taken	[Tl(I)] $\times 10^4$ Taken	[Au(III)] $\times 10^4$ remaining	O.D.	[Au(III)] $\times 10^4$ found
2.0	0.78	1.22	0.057	1.228
2.0	1.17	0.83	0.038	0.819
3.0	1.56	1.44	0.067	1.444
3.0	1.56	1.44	0.066	1.422
3.0	1.95	1.05	0.049	1.056

Table 2.4: Stoichiometry of Pyridinium Chlorochromate -
Thallium(I) reaction in 2 M HCl

[PCC] $\times 10^4$ Taken	[Tl(I)] $\times 10^4$ Taken	[PCC] $\times 10^4$ remaining	O.D. at 360 nm	[PCC] $\times 10^4$ found
5.0	1.0	4.33	0.307	4.380
5.0	2.0	3.66	0.259	3.700
5.0	3.0	3.00	0.213	3.040
5.0	4.0	2.33	0.165	2.360
5.0	5.0	1.66	0.118	1.680
5.0	6.5	0.66	0.046	0.657