

CHAPTER-II

EXPERIMENTAL

E X P E R I M E N T A L

The experimental section of this dissertation consists of the following five parts:

1. Purification of solvents
2. Preparation/purification of salts
3. Selection and purification of copper crystals for the kinetic measurements
4. Conductance measurements
5. Kinetic measurements

1. Purification of solvents

Water: Water of high purity was needed for the kinetic measurements and for the determination of cell constant for the conductance measurements. The ordinary tap water was treated with acidified (with H_2SO_4) potassium permanganate and distilled through a long fractionating column packed with glass beads. The singly distilled water was once more treated with acidified $KMnO_4$ and redistilled under the same conditions. The doubly distilled water with specific conductance $6-20 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$, viscosity 0.890 cP and density 0.9970 g cm^{-3} at 25°C was used for the preparation of solutions.

Acetonitrile: Acetonitrile (AN) of 99% purity (E. Merck, Bombay) was further purified by fractional distillation (twice) over P_2O_5

(E. Merck, Bombay) through a long vertical column. The middle fraction was collected. The purified solvent had specific conductance $1.4 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$, viscosity 0.341 cP and density 0.7766 g cm^{-3} , all at 25°C . These physical constants were in good agreement with the literature values⁹⁶ and also with the values already reported from this laboratory⁹⁷. The purified solvent was immediately used after distillation.

2. Preparation/purification of salts

Tetrabutylammonium tetraphenylboride: Tetrabutylammonium tetraphenylboride (Bu_4NBPh_4) was prepared by mixing aqueous solutions of tetrabutylammonium iodide (>98% purity from Sisco Research Laboratories, Bombay) and sodium tetraphenylboride (99.5% pure from Sisco Research Laboratories, Bombay) in 1:1 molar ratio. The precipitate formed was filtered, redissolved in acetone, again filtered and reprecipitated by adding excess of water. This process of recrystallization was repeated thrice. The salt was dried at 50°C under vacuum over P_2O_5 for several days. The purity of the salt was checked by determining its melting point. The melting point of the salt agreed very well with the literature value of $223\text{-}225^{\circ}\text{C}$ ⁹⁸.

Tetrabutylammonium perchlorate: Tetrabutylammonium perchlorate (Bu_4NClO_4) was prepared by mixing aqueous solutions of silver perchlorate monohydrate (99.8% pure from Sisco Research

Laboratories, Bombay) with aqueous acetone solutions of tetrabutylammonium iodide in 1:1 molar ratio. The solution was filtered, concentrated by evaporation, again filtered and heated to dryness. The residual mass was recrystallised twice from acetone and dried to a constant weight in vacuum over P_2O_5 at $60^\circ C$ for two days.

Copper perchlorate: Copper(I) perchlorate ($CuClO_4 \cdot 4AN$) was prepared by a method similar to that reported by Hathaway and coworkers⁹⁹. Copper(II) perchlorate was first prepared by reacting equivalent proportion of copper(II) carbonate with 70% aqueous perchloric acid. The solution was heated to boil off CO_2 completely. When the reaction was complete, excess of AN was added and the solution was heated again. Excess of copper powder (99.9% pure) was then added and the solution was vigorously stirred. When whole copper(II) perchlorate got converted into copper(I) perchlorate, the solution became colourless. The solution was quickly filtered while hot. On cooling, white crystals of copper(I) perchlorate separated out. The salt was recrystallised from anhydrous AN and dried under vacuum. The analysis of the salt (dissolved in $H_2O + AN$ mixture) by $KMnO_4$ titration gave the composition as $CuClO_4 \cdot 4AN$. The attempts to remove AN from the salt led to immediate conversion of copper(I) perchlorate into copper(II) perchlorate which was bluish in colour.

Copper sulphate: Cupric sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) extra pure (99.5% pure) from Sarabhai Merck Chemicals, Baroda was used as received.

Potassium permanganate: Potassium permanganate (KMnO_4) GR of 99.5% purity from Sarabhai Merck Chemicals, Baroda required for the purification of water and for the preparation of standard solutions for the kinetic measurements was used without further purification.

Sulphuric acid: Sulphuric acid (H_2SO_4) (AnalaR, 98% pure) from Glaxo Research Laboratories, Bombay was used for all the kinetic measurements.

3. Selection and purification of copper crystals for the kinetic measurements

Copper crystals of three different sizes were used for the kinetic studies. 200 mesh copper crystals (copper powder) of 99.5% purity from Sisco Research Laboratories, Bombay were used as received. Copper crystals between $2\text{-}30\ \mu\text{m}$ and between $40\text{-}180\ \mu\text{m}$ particle size, however, were selected from a sample having a large range of sizes of copper crystals by the following method.

A sample containing varying sizes of copper crystals was washed thoroughly with distilled water to remove dust and soluble impurities. The sample was then washed with dilute nitric acid

followed by 4 to 5 washings with distilled water and finally dried at 60°C under nitrogen gas. It was sieved through an iron sieve of appropriate hole size to get copper crystals between 2-30 μm in size. Similarly copper crystals between 40-180 μm size were also obtained by sieving the sample through a sieve with bigger holes. In most of the kinetic measurements, copper crystals between 2-30 μm size were used. In some measurements, however, copper crystals of 200 mesh size and between 40-180 μm size were used. To avoid oxidation by air, the selected copper crystals were stored under dry nitrogen gas.

4. Conductance measurements

Conductance of the electrolyte solutions was measured at 1000 Hz frequency with a calibrated Digital Conductivity Meter Model NDC-732 supplied by Naina Electronics, Chandigarh. All the conductance measurements were carried out in a water thermostat bath maintained at $25.00 \pm 0.01^\circ\text{C}$. The conductivity cell similar in design to that reported by Shedlovsky¹⁰⁰ with bright platinum electrodes was used. The cell constant of the conductivity cell 0.755 cm^{-1} was determined using aqueous potassium chloride solutions in the concentration range $6-70 \times 10^{-4} \text{ mol dm}^{-3}$ by the method reported by Fuoss and coworkers¹⁰¹. Before use the conductivity cell was thoroughly cleaned with distilled water, rinsed with pure acetone and dried by blowing warm air. $\text{H}_2\text{O} + \text{AN}$ mixtures were prepared by weight and a known

amount of the solvent or solvent mixture was taken in the conductivity cell. A range of concentrations (between $1-50 \times 10^{-4} \text{ mol dm}^{-3}$ of the salts) was produced by adding stock solutions of appropriate concentrations from a weight pipette to a known quantity of the solvent or solvent mixture taken in the conductivity cell. In all cases the measurements were repeatedly made with at least two different stock solutions to get reproducible results. The reproducibility of the conductance measurements was about $\pm 0.2\%$.

5. Kinetic measurements

a) Forward reaction: For all of the kinetic measurements of the forward reaction: $\text{Cu}^{2+} + \text{Cu}^0 \rightleftharpoons 2\text{Cu}^+$, 150 cm^3 of the reaction solution was used. This solution was prepared by adding AN, corresponding to 5, 10, 20 and 40% (V/V) and $0.07 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ to the balance of distilled water. The amount of copper sulphate required to obtain 0.032, 0.064, 0.16 and 0.32 mol dm^{-3} solutions was accurately weighed and dissolved in the appropriate $\text{H}_2\text{O} + \text{AN}$ mixtures. In order to remove the dissolved air from the solutions, purified nitrogen gas (saturated with the same $\text{H}_2\text{O} + \text{AN}$ mixture) was bubbled through the solution for 20-30 minutes before the kinetic measurements were started. A slow current of nitrogen gas was, however, continued till the kinetic measurements in each kinetic run was over. Kinetic measurements were made with 1, 4 and 8 g of

copper crystals added to 150 cm^3 of the reaction solution prepared in each case. All the kinetic measurements were made in a water thermostat bath maintained at the appropriate temperature within a temperature variation of $\pm 0.1^\circ\text{C}$. The Erlenmeyer flask containing reaction solution was kept in the thermostat bath for half an hour to attain constant temperature. When constant temperature was attained, the reaction was initiated by adding copper crystals to the reaction solution and the solution was vigorously stirred with a magnetic stirrer operating at 800 r.p.m. When the copper crystals were added into the solution, the stop watch was started. After one minute of the initiation of reaction, 5 cm^3 of the reaction solution was drawn out and pipetted out into a conical flask containing 2 cm^3 of $3.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. This solution was titrated against standard aqueous KMnO_4 solution (standardized with oxalic acid solutions) to obtain the amount of Cu^+ formed. 5 cm^3 of the reaction solution was then drawn out at regular time intervals to determine the concentration of Cu^+ formed as a function of time. The reaction kinetics in all cases with 1 g of copper crystals was studied at 15 minutes time intervals while with 4 and 8 g of copper crystals, 5 minutes time intervals were used because the reaction in these two cases was relatively faster.

In order to study the effect of the rate of stirring of the solutions, the effect of temperature and the effect of H_2SO_4

on the rate of the forward reaction, kinetic studies were also made using 0.32 mol dm^{-3} copper sulphate solutions in $\text{H}_2\text{O} + \text{AN}$ mixtures at different rates of stirring, different temperatures and different H_2SO_4 concentrations.

b) Backward reaction: Kinetic measurements of reaction:

$2\text{Cu}^+ \longrightarrow \text{Cu}^{2+} + \text{Cu}^0$ in $\text{H}_2\text{O} + \text{AN}$ mixtures in all the cases were carried out at $80 \pm 2^\circ\text{C}$ by taking 150 cm^3 of Cu_2SO_4 solution in a distillation unit fitted with a vertical fractionating column (length = 50 cm and internal diameter = 1.5 cm). Concentrated Cu_2SO_4 solutions were prepared by the reaction of copper sulphate with 200 mesh copper powder in $\text{H}_2\text{O} + \text{AN}$ mixtures containing 10, 20, 30, 40, 50 and 60% (V/V) AN and $0.07 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. The Cu_2SO_4 solutions in 10, 20, 30 and 40% aqueous AN were diluted with the corresponding $\text{H}_2\text{O} + \text{AN}$ mixtures containing $0.07 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ to obtain 0.40 , 0.30 , 0.20 and $0.10 \text{ mol dm}^{-3} \text{ Cu}_2\text{SO}_4$ solutions in each case. Concentrated solutions containing $0.60 \text{ mol dm}^{-3} \text{ Cu}_2\text{SO}_4$ in 20, 30 and 40% AN, $1.12 \text{ mol dm}^{-3} \text{ Cu}_2\text{SO}_4$ in 40% AN, 1.45 , 1.57 and $1.93 \text{ mol dm}^{-3} \text{ Cu}_2\text{SO}_4$ in 50% AN and $1.82 \text{ mol dm}^{-3} \text{ Cu}_2\text{SO}_4$ in 60% AN were also prepared and used for the kinetic measurements. The reaction solution in each case was heated at the same uniform rate under exactly identical conditions to distil AN from the solution. The distilled AN was collected in a burette and a record of the amount collected as a function of time was maintained in each case. When AN started

distilling over, aliquots (2 cm^3 each) from the reaction solution in the distillation flask were withdrawn and analyzed for Cu^+ concentration by titrating against standard aqueous KMnO_4 solutions. The withdrawal of the aliquot for the first reading was made after one minute and for the subsequent readings at an interval of 10 minutes in each case.

In both forward and backward reactions of the reversible reaction (1), kinetic measurements were repeated at least twice to check the reproducibility of the results. The reproducibility from two independent sets of experiments was within $\pm 5\%$.