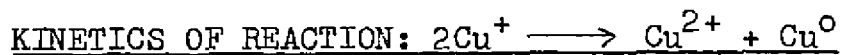


CHAPTER-V

DISCUSSION - PART 3

(KINETIC STUDIES-II)



IN  $\text{H}_2\text{O} + \text{AN}$  MIXTURES

In the previous chapter, the kinetics of the reaction:  $\text{Cu}^{2+} + \text{Cu}^0 \longrightarrow 2\text{Cu}^+$  i.e. reaction (15) have been investigated and the optimum conditions for this reaction are reported. It has also been mentioned in that chapter that when AN is removed from the  $\text{Cu}^+$  solutions in  $\text{H}_2\text{O} + \text{AN}$  mixtures by heating, the reaction:  $2\text{Cu}^+ \longrightarrow \text{Cu}^{2+} + \text{Cu}^0$  i.e. reaction (16) becomes extremely fast and copper powder from the reaction solution separates out. In order to establish optimum conditions for reaction (16), kinetic measurements for this reaction have been carried out at  $80 \pm 2^\circ\text{C}$  by distilling AN from  $\text{Cu}_2\text{SO}_4$  solutions in  $\text{H}_2\text{O} + \text{AN}$  mixtures at a constant temperature.

The rate of reaction (16) has been measured in  $\text{H}_2\text{O} + \text{AN}$  mixtures using 0.40, 0.30, 0.20 and 0.10 mol  $\text{dm}^{-3}$   $\text{Cu}_2\text{SO}_4$  in 10, 20, 30 and 40% (V/V) AN, 0.60 mol  $\text{dm}^{-3}$   $\text{Cu}_2\text{SO}_4$  in 20, 30 and 40% (V/V) AN, 1.12 mol  $\text{dm}^{-3}$   $\text{Cu}_2\text{SO}_4$  in 40% (V/V) AN, 1.45, 1.57 and 1.93 mol  $\text{dm}^{-3}$   $\text{Cu}_2\text{SO}_4$  in 50% (V/V) AN and 1.82 mol  $\text{dm}^{-3}$   $\text{Cu}_2\text{SO}_4$  in 60% (V/V) AN in the presence of 0.07 mol  $\text{dm}^{-3}$   $\text{H}_2\text{SO}_4$  in all the cases by following the change of copper(I) concentration as a function of time. The change in copper(I) concentration as a function of time for various systems has been reported in TABLES 43 to 47 given in the Appendix of this dissertation.

Copper in the +1 state is preferentially solvated by AN in  $H_2O + AN$  mixtures and is known to form a 1:4 complex with  $AN^{2,3}$  when AN concentration in the solvent mixture is sufficiently large. This implies that the amount of AN more than four times the amount of  $Cu^+$  remains unbound and starts immediately distilling over when the temperature of the solution is raised to the boiling point of AN. The temperature at which the unbound AN started distilling over in Shimla (54 cm of Hg pressure) was  $69^\circ C$ . After the whole amount of the unbound AN had distilled over at  $69^\circ C/54$  cm, the temperature of the reaction solution rose to  $80^\circ C$  when bound AN started distilling over. This temperature remained practically constant  $80 \pm 2^\circ C$  till whole of bound AN was distilled over. When unbound AN started distilling over, the amount of  $Cu^+$  in the solution increased linearly upto a certain period (which was different for each  $H_2O + AN$  mixtures) and thereafter  $Cu^+$  concentration decreased linearly when whole of the unbound AN had distilled over. The linear decrease in  $Cu^+$  concentration was observed upto a sufficiently long time (50 to 60 minutes) and finally this decrease became non-linear as a function of time. A typical plot showing change of copper(I) concentration  $[Cu^+]$  as a function of time using  $0.40 \text{ mol dm}^{-3} Cu_2SO_4$  in 40, 30, 20 and 10% AN in  $H_2O + AN$  mixtures is shown in FIG. 14. The point from which  $Cu^+$  concentration started decreasing was taken as the initial  $Cu^+$  concentration i.e.  $C_0$  and the time corresponding to

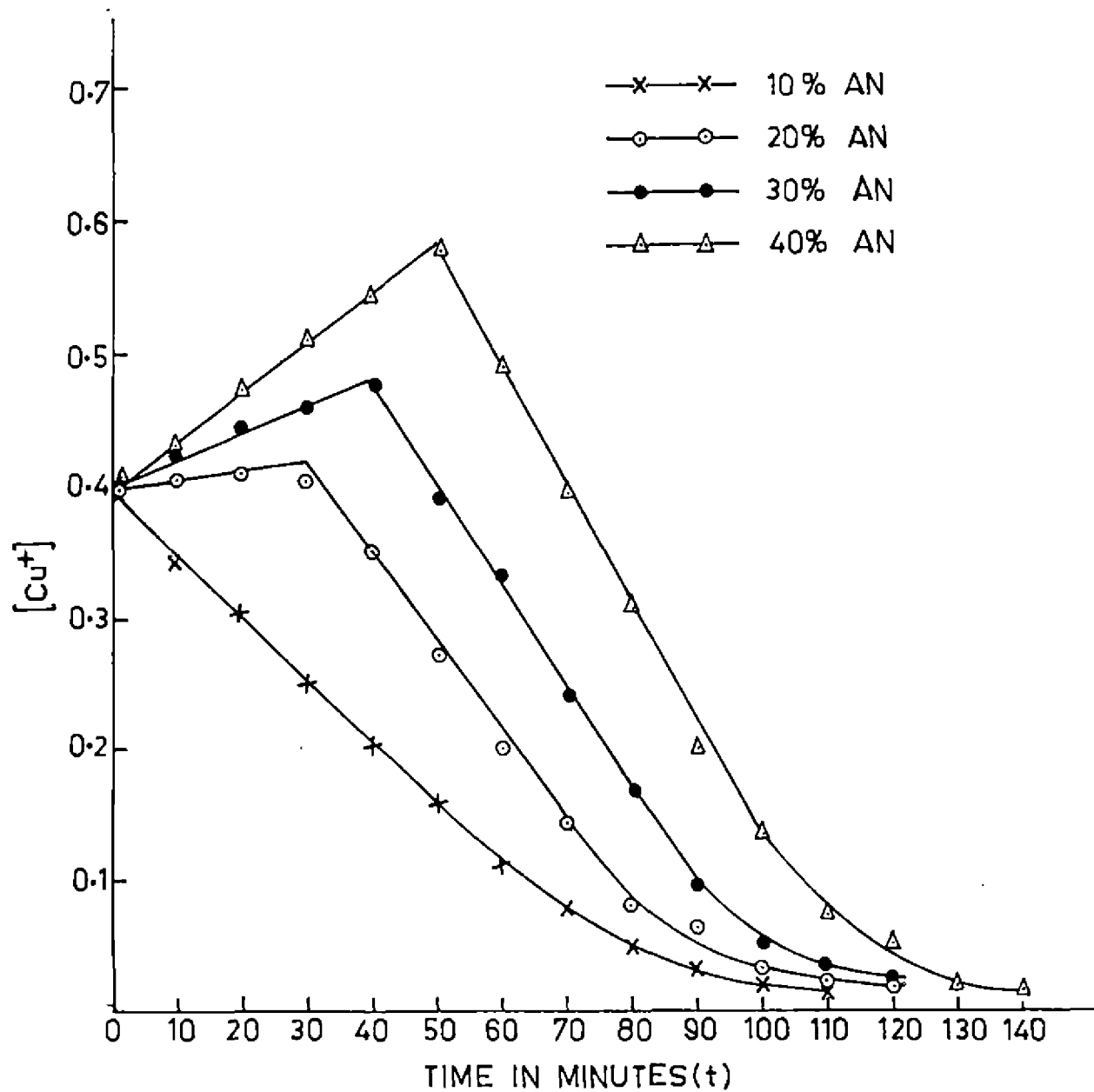


FIG.14. PLOT OF CHANGE OF COPPER (I) CONCENTRATION  $[Cu^+]$  AS A FUNCTION OF TIME FROM  $0.40 \text{ mol dm}^{-3} \text{ Cu}_2\text{SO}_4$  SOLUTION.

this initial concentration was taken as the zero time for the reaction in all the cases. The rate of the reaction in each case was calculated from the linear part of the plots by evaluating the slopes of the lines in FIG. 14. The values of the rate of reaction (16) in different  $H_2O + AN$  mixtures are presented in TABLE 12.

It is observed from TABLE 12 that for a given  $H_2O + AN$  mixture, the rate of the reaction is strongly influenced by the  $Cu_2SO_4$  concentration. Reaction mixtures containing higher initial  $Cu^+$  concentration showed higher rates. It is significant to note that the plot of the rate (R) of reaction (16) from TABLE 12 versus  $C_o$ , irrespective of the composition of  $H_2O + AN$  mixture taken in the beginning, was linear passing through the origin (FIG. 15). This indicated that corresponding to the initial copper(I) concentration at which unbound AN had distilled over in each case, the nature of the copper(I) complex formed with AN remained the same and the decomposition of this complex by further distillation of AN beyond the point at which bound AN started distilling followed the same mechanism in all the cases.

#### PLOTS USING DIMENSIONLESS PARAMETERS

As mentioned before in the previous chapter, plots using dimensionless parameters provide information regarding the order

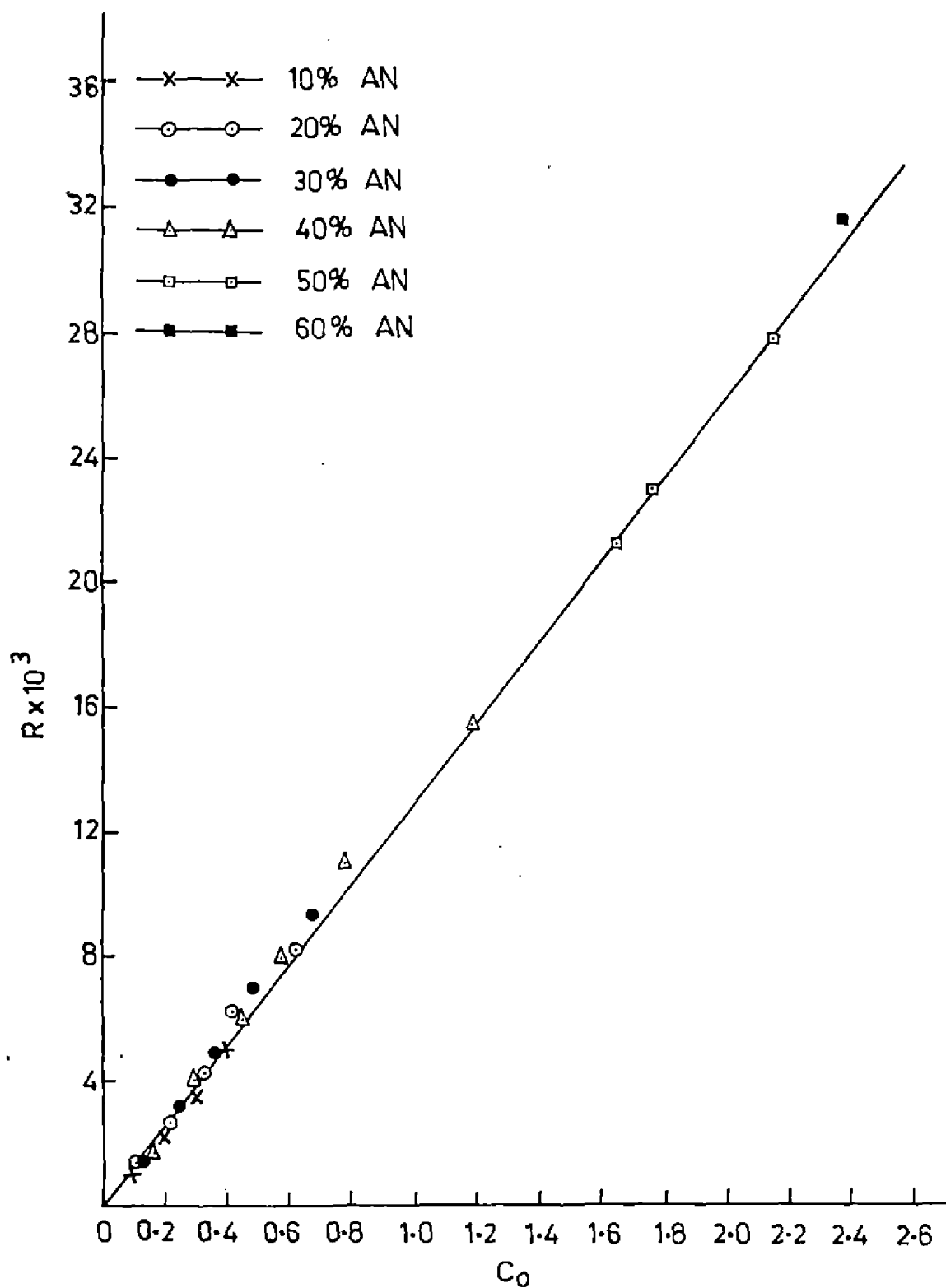


FIG. 15. PLOT OF RATE (R) OF REACTION (16) AS A FUNCTION OF INITIAL  $Cu_2SO_4$  CONCENTRATION  $C_0$ .

TABLE 12

Initial copper(I) concentration,  $C_0$  ( $\text{mol dm}^{-3}$ ) and the rate<sup>a</sup>  
 ( $R$ , in  $\text{mol dm}^{-3} \text{min}^{-1}$ ) of reaction (16) in  $\text{H}_2\text{O} + \text{AN}$   
 mixtures of different composition at  $80 \pm 2^\circ\text{C}$

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10% AN	$C_0$	0.40	0.30	0.20	0.10		
	$R/10^{-3}$	5.0	3.6	2.2	1.0		
20% AN	$C_0$	0.62	0.42	0.32	0.22	0.11	
	$R/10^{-3}$	8.2	6.2	4.2	2.6	1.2	
30% AN	$C_0$	0.68	0.48	0.37	0.25	0.13	
	$R/10^{-3}$	9.4	7.1	5.0	3.2	1.4	
40% AN	$C_0$	1.20	0.79	0.58	0.44	0.30	0.16
	$R/10^{-3}$	15.8	11.3	8.1	6.1	4.0	1.9
50% AN	$C_0$	1.65	1.76	2.15			
	$R/10^{-3}$	21.0	23.1	28.8			
60% AN	$C_0$	2.40					
	$R/10^{-3}$	31.6					

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<sup>a</sup> The maximum uncertainty of the rate values in this TABLE is  $\pm 5\%$ .

of the reaction<sup>148</sup>. Such plot between  $\alpha = \frac{C}{C_0}$ , where  $C_0$  and  $C$  are the initial concentration and the concentration of  $\text{Cu}^+$  remained in the solution at a particular time respectively versus  $\log t$  with different initial  $\text{Cu}_2\text{SO}_4$  concentrations ( $C_0$ ) in  $\text{H}_2\text{O} + \text{AN}$  mixtures with 10% AN has been shown in FIG. 16. The general shape of the curve of this plot is matchable to the theoretical curve<sup>148</sup> for the first order reaction. In FIG. 16 the curve corresponding to each of the  $\text{Cu}_2\text{SO}_4$  concentration could not be drawn because of the overlap of the points of one curve with another. Therefore, the single curve drawn in this FIG. is the theoretical curve for the first order reaction. The theoretical curve in FIG. 16 fit to most of the points for each  $\text{Cu}_2\text{SO}_4$  concentration and indicate the general shape of the curve to be alike in all the cases. These results indicate that the reaction under investigation is first order in  $\text{Cu}^+$  concentration.

#### OPTIMUM CONCENTRATION OF $\text{Cu}_2\text{SO}_4$ FOR INDUSTRIAL APPLICATION

When reaction (16) proceeds, pure copper powder from the reaction solution separates out. This reaction, therefore, can have industrial application for the recovery of pure copper from  $\text{Cu}_2\text{SO}_4$  solutions. It has already been shown above that more concentrated  $\text{Cu}_2\text{SO}_4$  solutions give relatively higher rates of reaction (16). This implies that more concentrated  $\text{Cu}_2\text{SO}_4$  solutions are expected to yield more copper powder in a given



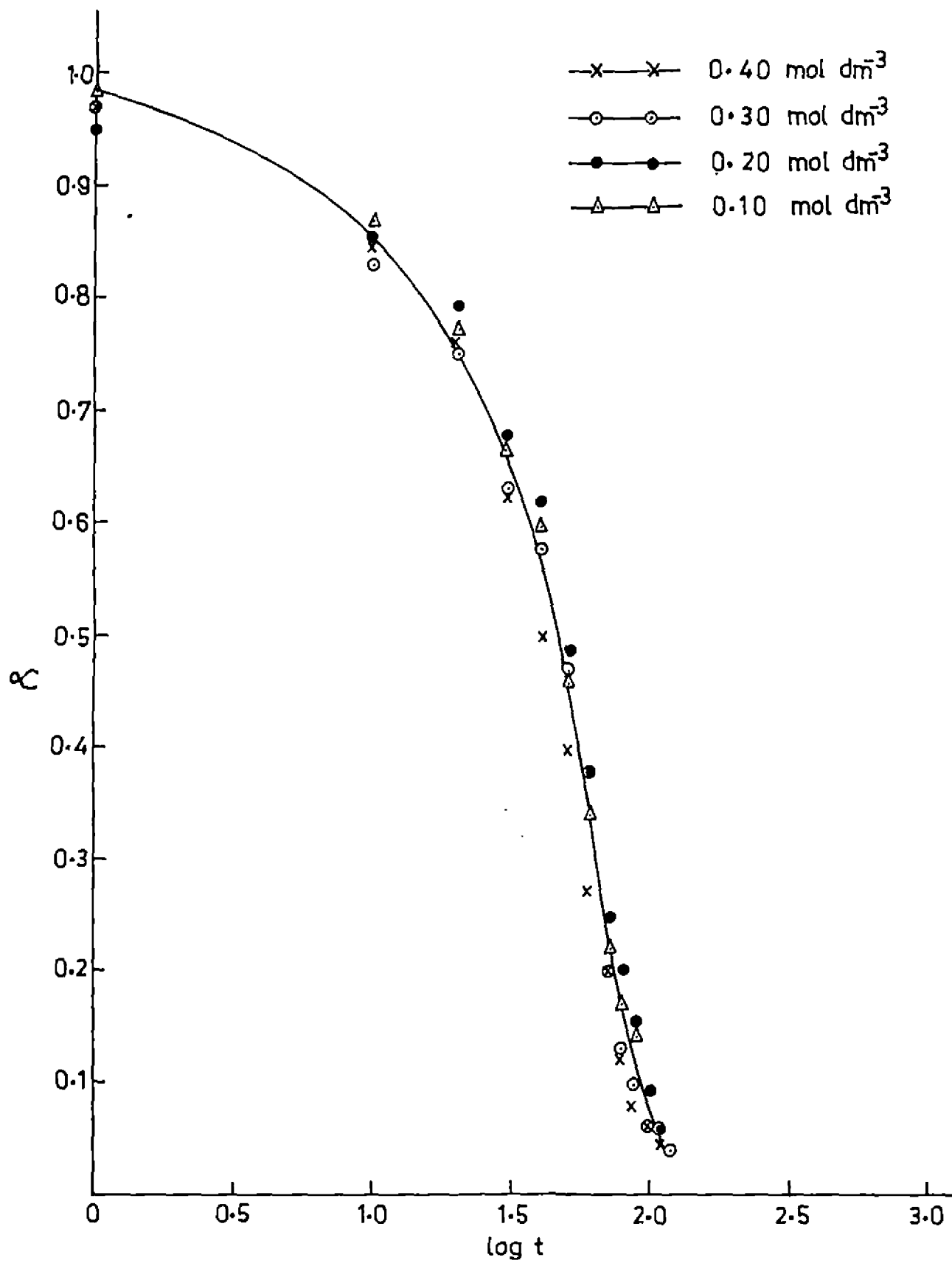


FIG.16. FRACTION OF  $\text{Cu}^+$  REMAINING ( $\alpha C$ ) AS A FUNCTION OF TIME PARAMETER ( $\log t$ ) FOR DIFFERENT INITIAL  $\text{Cu}_2\text{SO}_4$  CONCENTRATIONS ( $C_0$ ) IN 10% AN.

time. Kinetic measurements with highly concentrated  $\text{Cu}_2\text{SO}_4$  solutions, however, have shown that a useful hydrometallurgical method for the recovery of pure copper using reaction (16), does not require the maximum  $\text{Cu}_2\text{SO}_4$  concentration which can be prepared in a suitable  $\text{H}_2\text{O} + \text{AN}$  mixture but an optimum concentration of  $\text{Cu}_2\text{SO}_4$  is required because of the following reasons:

- i) To prepare  $\text{Cu}_2\text{SO}_4$  solutions in  $\text{H}_2\text{O} + \text{AN}$  mixtures, the minimum quantity of AN required should be at least 4 times the  $\text{Cu}^+$  concentration. For preparing highly concentrated  $\text{Cu}_2\text{SO}_4$  solutions the amount of AN in  $\text{H}_2\text{O} + \text{AN}$  mixtures should be in major quantity. When reaction (16) proceeds by distillation of AN, the copper sulphate ( $\text{Cu}^{2+}$ ) concentration starts increasing. In  $\text{H}_2\text{O} + \text{AN}$  mixture with relatively more amount of AN, the quantity of water may not be sufficient to dissolve whole amount of copper sulphate formed and hence copper sulphate alongwith copper powder may also separate out from the solution. This has actually been observed in cases of solutions containing  $2.15 \text{ mol dm}^{-3}$   $\text{Cu}_2\text{SO}_4$  in 50% AN and  $2.40 \text{ mol dm}^{-3}$   $\text{Cu}_2\text{SO}_4$  in 60% AN during the present investigation.
- ii) Highly concentrated  $\text{Cu}_2\text{SO}_4$  solutions are easily affected by atmospheric oxygen and disproportionate rapidly on storing. By incorporating the above mentioned difficulties, the

optimum  $\text{Cu}_2\text{SO}_4$  concentration for industrial use has been found to be  $\approx 1.80 \text{ mol dm}^{-3}$  in 50% AN.

The following important conclusion can be drawn from the results of the kinetic measurements of reaction (16):

The rate of the reaction increased almost linearly with the increase in  $\text{Cu}^+$  concentration in the concentration range 0.10 to  $2.40 \text{ mol dm}^{-3}$  showing that the reaction is first order in  $\text{Cu}^+$  concentration. As the reaction proceeds pure copper powder separates out from the solution and the reaction has been found to reach completion in a fairly short time.

#### IMPORTANCE OF THE PRESENT INVESTIGATION

Electrochemical studies by Parker and coworkers<sup>2,3,9,53</sup> have shown that electrorefining of copper by the electrolysis of copper(I) salts involves less consumption of electricity and hence less cost as compared to the electrolysis of copper(II) salts. The electrorefining method for the purification of copper is basically expensive. A simpler, quicker and cheaper hydrometallurgical method for the purification of copper, however, can be developed by utilizing the results of the present kinetic measurements of the reversible reaction (1) in  $\text{H}_2\text{O} + \text{AN}$  mixtures in the following way:

The forward reaction of reversible reaction (1) can be made

extremely fast by selecting the optimum conditions for this reaction. When forward reaction is extremely fast, crude copper taken for purification dissolves to form concentrated  $\text{Cu}^+$  solutions which are stabilized by AN because of strong preferential solvation. The mud and the metal impurities like Pb, Sb, Bi and Ag present in crude copper remain undissolved and can be removed by filtration. Other metal impurities like Fe, Ni and Sn present in crude copper, however, react with dilute  $\text{H}_2\text{SO}_4$  (used to stabilize  $\text{Cu}_2\text{SO}_4$ ) and pass into the solution alongwith  $\text{Cu}_2\text{SO}_4$ . The distillation of AN from this solution makes backward reaction of the reversible reaction (1) extremely fast and pure copper powder from the solution separates out. The impurities like Fe, Ni and Sn remain dissolved in solution. The amount of AN can also be recovered almost completely. The present investigation is thus very useful for developing a novel, cheap and quick hydrometallurgical method for the purification of copper from crude samples in large scale.