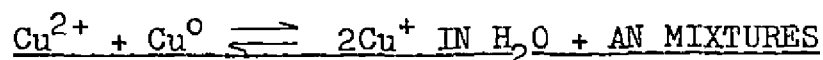


CHAPTER-IV

DISCUSSION - PART 2

(KINETIC STUDIES-I)

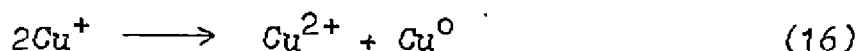
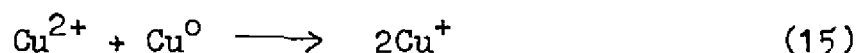
KINETICS OF THE FORWARD REACTION OF THE REVERSIBLE REACTION:

Cu^+ and Ag^+ possess a special type of interaction with ammonia, organic bases, AN and some other organic solvents^{2,3,11,42,46,47,145}. All these organic ligands form $[\text{Ag}(\text{X})_2]^+$ complexes with Ag^+ which like the $[\text{Ag}(\text{NH}_3)_2]^+$ complex are also linear⁴⁸. Similarly, Cu^+ is known to form complexes with AN in $\text{H}_2\text{O} + \text{AN}$ mixtures. These complexes can be $[\text{Cu}(\text{AN})_2]^+$, $[\text{Cu}(\text{AN})_3]^+$ and $[\text{Cu}(\text{AN})_4]^+$ depending upon the concentration of AN taken in the $\text{H}_2\text{O} + \text{AN}$ mixtures². In pure AN, $[\text{Cu}(\text{AN})_4]^+$ complex is known to be formed in sufficient amount^{146,147}. Because of its smaller size, Cu^+ can form complexes with 3 and 4 molecules of AN as compared to Ag^+ which is known to form complexes with only two molecules of AN.

The complex formation tendency of Cu^+ with AN and hence its stabilization in $\text{H}_2\text{O} + \text{AN}$ mixtures forms the basis for the study of the kinetics of reaction (1).

Under certain conditions forward reaction of the reversible reaction: $\text{Cu}^{2+} + \text{Cu}^0 \rightleftharpoons 2\text{Cu}^+$ is much faster than the backward reaction and under other conditions when AN is distilled from the Cu^+ solutions in $\text{H}_2\text{O} + \text{AN}$ mixtures by heating, the backward reaction is significant and copper powder from the solution separates out. When the forward reaction is extremely fast, the

rate of the backward reaction is negligibly small and vice versa. Therefore, for the kinetic studies of the reaction under study i.e. reaction (1), the rate of the backward reaction has been neglected when the rate of the forward reaction is investigated and the rate of the forward reaction has been neglected when the rate of the backward reaction is studied. In other words, it has been assumed that the forward reaction should be represented by reaction (15) and the backward reaction by reaction (16).



In order to discover the optimum conditions under which reactions (15) and (16) in turn become predominant, the rates of the reactions under different conditions have been investigated by following the amount of copper(I) formed (in reaction (15)) or decomposed (in reaction (16)) as a function of time. The kinetics of reaction (15) are reported in this chapter while the kinetics of reaction (16) are given in the next chapter.

The rate of reaction (15) has been measured under nitrogen gas atmosphere at 25°C in 150 cm³ of H₂O + AN mixtures containing 5, 10 and 20% (V/V) AN (also 40% (V/V) AN in cases of 0.032 and 0.064 mol dm⁻³ copper sulphate solutions) together with 0.032, 0.064, 0.16 and 0.32 mol dm⁻³ copper sulphate, 0.07 mol dm⁻³ H₂SO₄

and 1, 4 and 8 g of 2-30 μm in size copper crystals. The amount of copper(I) formed (M) in mol dm^{-3} as a function of time in minutes (t) is reported in TABLES 13 to 24 given in the Appendix of this dissertation. The rate of reaction (15) has also been measured under varying conditions and the results are used to draw interesting conclusions. The effect of H_2SO_4 concentration on copper(I) formation as a function of time has been reported in TABLES 25 and 26. The effect of temperature on copper(I) formation as a function of time has been given in TABLES 27 to 38. In TABLE 39 the effect of the surface area of the copper crystals and in TABLES 40 to 42, the effects of the stirring speed at 25, 35 and 45 $^{\circ}\text{C}$ on the copper(I) formation as a function of time have been presented. In all of these cases the plots of copper(I) formed as a function of time gave parabolic curves passing through the origin at zero time with a steep linear rise at the beginning of the reaction. The plots slowly smoothed out after 50% of the reaction time. For illustration, the plots of 0.16 mol dm^{-3} copper sulphate with 1, 4 and 8 g of copper crystals (2-30 μm) and 5, 10 and 20% AN are shown in FIGS. 1 to 3. Such plot with 8 g copper crystals (2-30 μm), 20% AN and with different copper sulphate concentrations is shown in FIG. 4. The plots of copper(I) formed as a function of time with 0.32 mol dm^{-3} copper sulphate and 8 g copper crystals in 20% AN at various temperatures and at different stirring speeds with same composition as above at

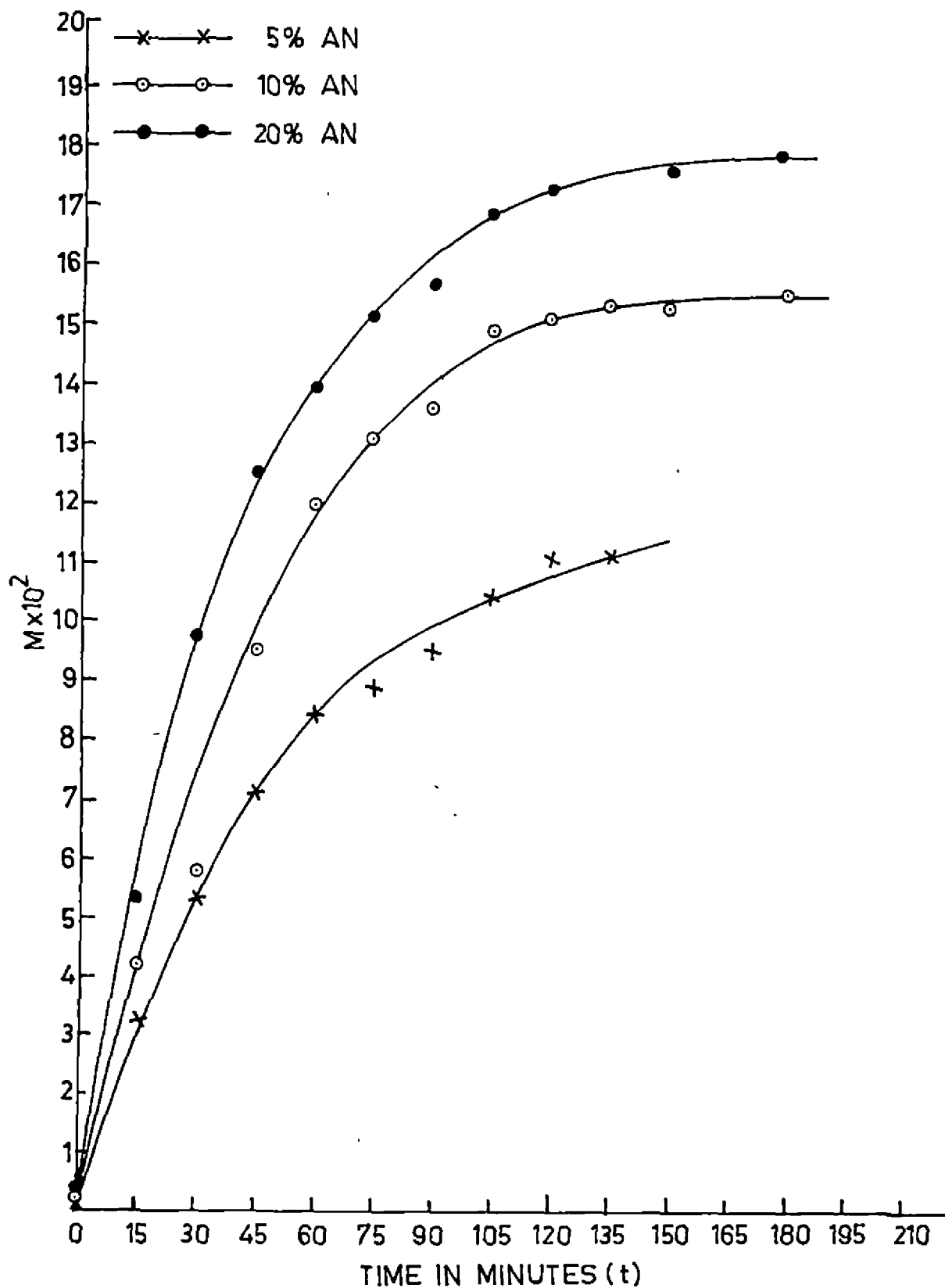


FIG.1. PLOT OF COPPER (I) FORMED AS A FUNCTION OF TIME AT 25°C (0.16 mol dm⁻³ COPPER SULPHATE+1g COPPER CRYSTALS 2-30 μm).

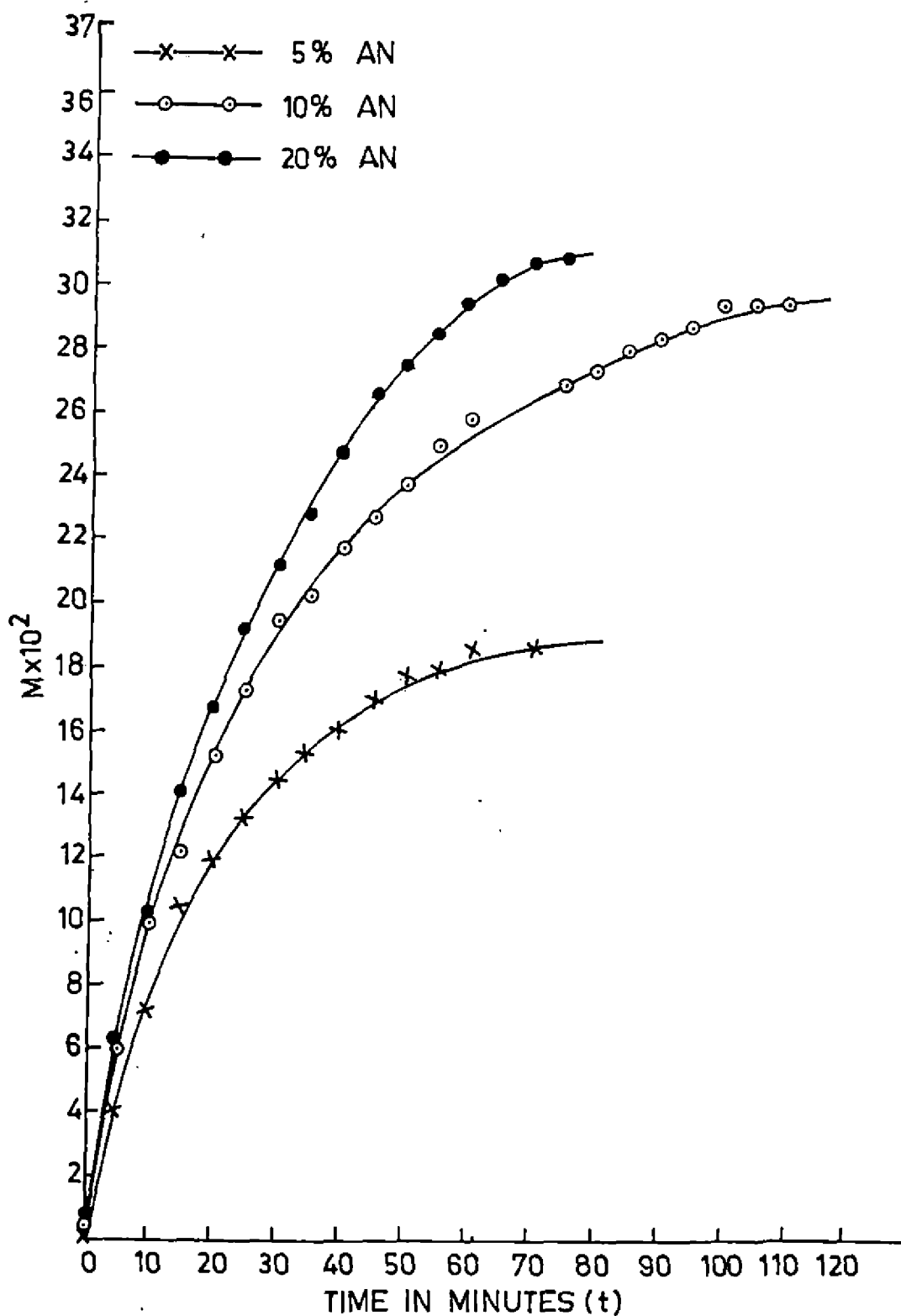


FIG.2. PLOT OF COPPER (I) FORMED AS A FUNCTION OF TIME AT 25°C (0.16 mol dm⁻³ COPPER SULPHATE+4g COPPER CRYSTALS 2-30 μm).

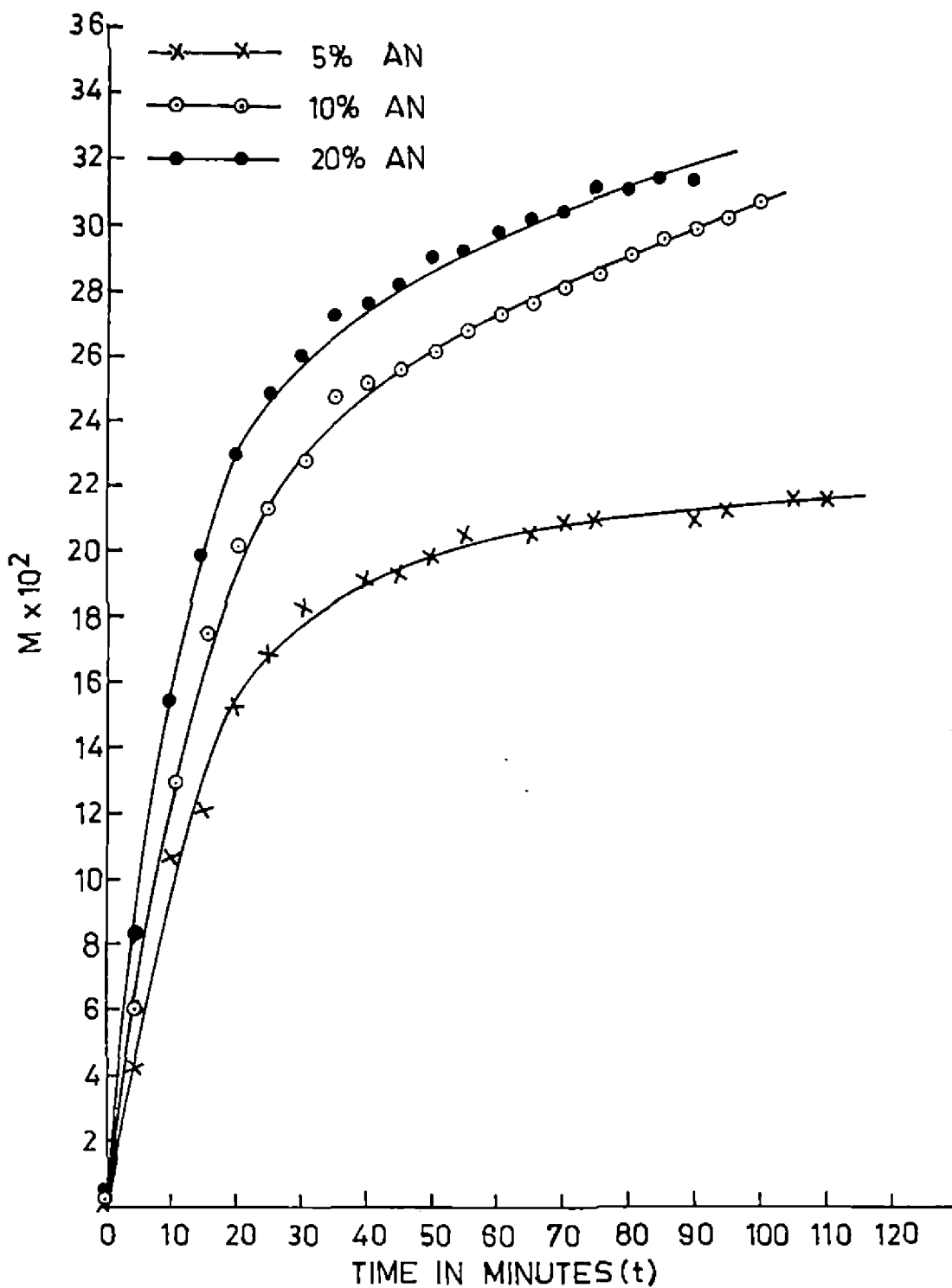


FIG.3. PLOT OF COPPER (I) FORMED AS A FUNCTION OF TIME AT 25°C (0.16 mol dm⁻³ COPPER SULPHATE+8g COPPER CRYSTALS 2-30 μm).

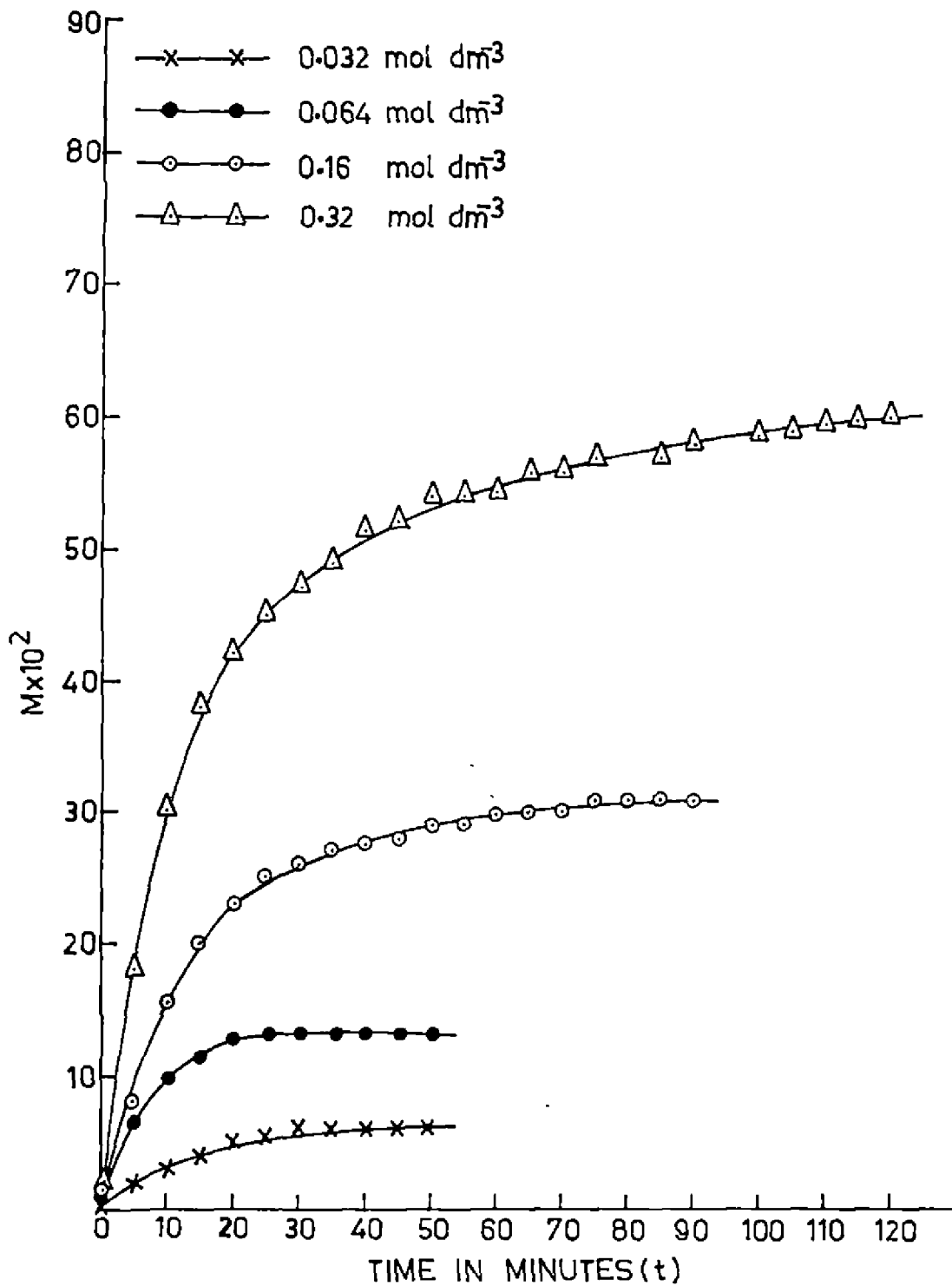


FIG. 4. PLOT OF COPPER (I) FORMED AS A FUNCTION OF TIME AT 25°C FOR DIFFERENT COPPER SULPHATE CONCENTRATION (8g COPPER CRYSTALS 2-30 μm IN 20% AN).

25°C have been shown in FIGS. 5 and 6 respectively. In all of the cases the amount of copper(I) formed in a fixed time was maximum with 20% AN and decreased in the order: 20% > 10% > 5%. In cases of 0.032 and 0.064 mol dm⁻³ copper sulphate solutions where 40% AN in the mixture was also used, the amount of copper(I) formed in case of 40% AN was maximum and decreased in the order: 40% > 20% > 10% > 5% AN. With 0.16 and 0.32 mol dm⁻³ copper sulphate the reaction kinetics could not be studied in H₂O + AN mixture with 40% AN because in this mixture the required amount of copper sulphate did not dissolve.

The rate of the reaction R (= dM/dt) was determined in all cases by the empirical differentiation method, i.e. by evaluating the slope of the linear parts of the plots of M against t at the initial stage of the reaction. The values of the rate thus obtained for various systems studied are reported in TABLES 7 to 11. The uncertainty in these rate values is ± 5%.

From the results of TABLES 7 to 11 it can be found that the rate of reaction (15) depends upon the following factors:

1. The concentration of Cu²⁺ taken in the solution.
2. The concentration of AN in H₂O + AN mixtures.
3. The concentration of H₂SO₄ taken.
4. The temperature of the reaction.
5. The amount and particle size of copper crystals and hence the surface area of the copper crystals.
6. The rate of stirring of the reaction solutions.

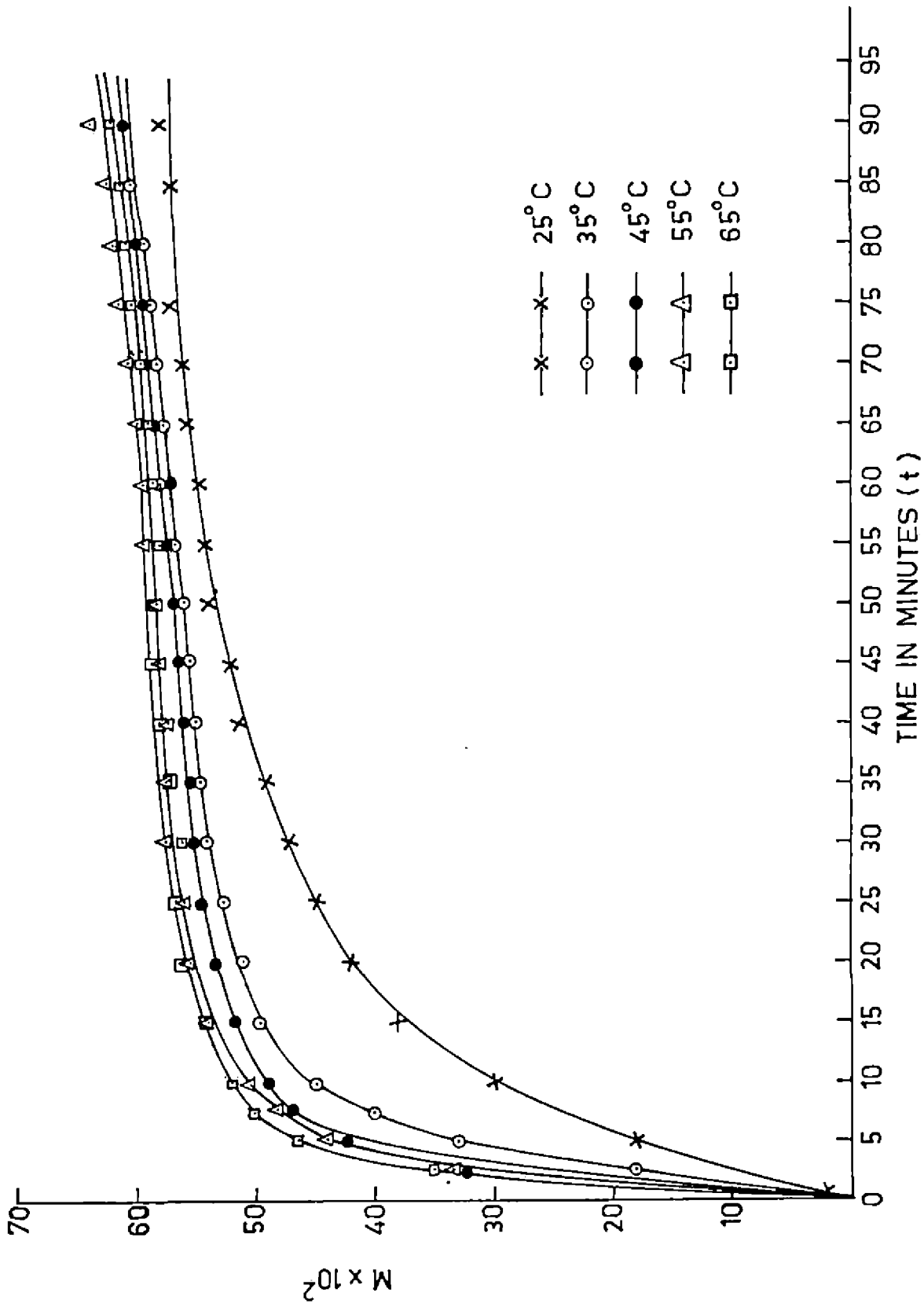


FIG.5. PLOT OF COPPER (I) FORMED AS A FUNCTION OF TIME AT DIFFERENT TEMPERATURES (0.32 mol dm⁻³ COPPER SULPHATE+8g COPPER CRYSTALS 2-30 μm IN 20 % AN).

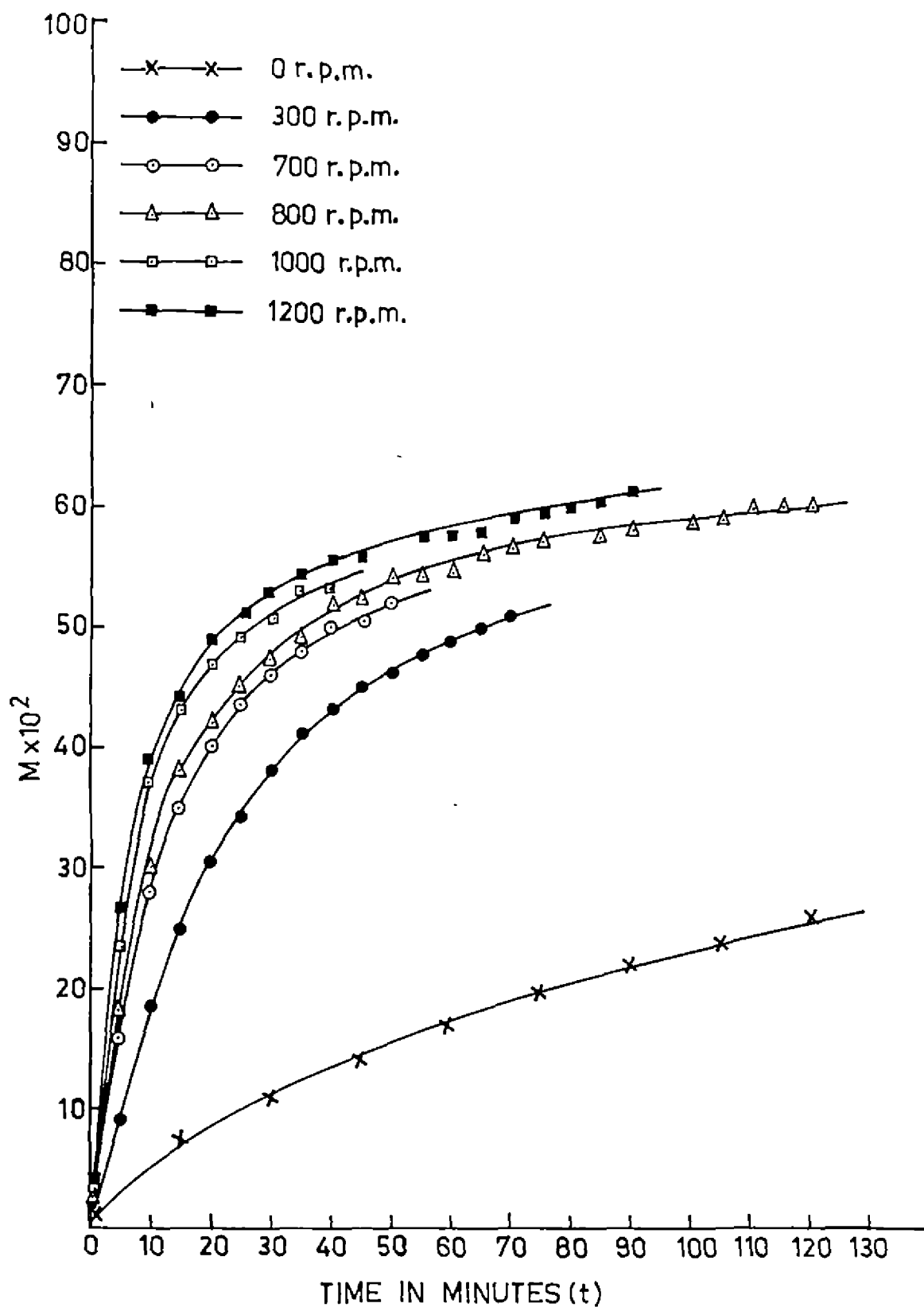


FIG.6. PLOT OF COPPER (I) FORMED AS A FUNCTION OF TIME AT 25°C WITH DIFFERENT STIRRING SPEEDS (0.32 mol dm⁻³ COPPER SULPHATE+8g COPPER CRYSTALS 2-30 μm IN 20% AN).

The effect of all these factors on the reaction rate has been discussed in detail under separate headings in the following sections:

1. EFFECT OF COPPER SULPHATE CONCENTRATION ON THE REACTION RATE

A perusal of TABLE 7 shows that the rate of reaction (15) is strongly influenced by the concentration of copper sulphate. The increased concentration of copper sulphate and hence of Cu^{2+} , increases the rate of the reaction. It is, however, not possible to prepare copper sulphate solution of very high concentration in $\text{H}_2\text{O} + \text{AN}$ mixtures because of solubility reasons. The maximum copper sulphate concentration which can be prepared in $\text{H}_2\text{O} + \text{AN}$ mixture with 20% AN is 0.32 mol dm^{-3} at 25°C . At higher AN concentrations in water, copper sulphate solutions even upto 0.32 mol dm^{-3} cannot be prepared because of decreased solubility in such mixtures. With less than 20% AN in water, although, copper sulphate solutions more concentrated than 0.32 mol dm^{-3} can be prepared but with such solutions the rate of reaction (15) has been found to be much less than that with 0.32 mol dm^{-3} copper sulphate in 20% AN. Therefore, the optimum copper sulphate concentration which can give the maximum rate of reaction (15) is 0.32 mol dm^{-3} in 20% AN.

The dependence of rate on Cu^{2+} concentration $[\text{Cu}^{2+}]$ has been determined by plotting $\log(\text{rate})$ from TABLE 7 against

TABLE 7

Effect of copper sulphate concentration on the rate (R) of reaction (15) in
 $H_2O + AN$ mixtures at $25^\circ C$

Concentration of copper sulphate ($mol\ dm^{-3}$)	$R/10^{-3}\ mol\ dm^{-3}\ min^{-1}\ ^d$											
	5% AN			10% AN			20% AN			40% AN		
	1 ^a	2 ^b	3 ^c	1 ^a	2 ^b	3 ^c	1 ^a	2 ^b	3 ^c	1 ^a	2 ^b	3 ^c
0.032	0.5	1.4	1.9	0.6	1.7	2.4	0.7	1.7	3.0	0.7	2.6	3.9
0.064	0.6	3.0	4.6	0.8	4.7	6.2	1.9	6.1	11.7	2.4	6.3	12.5
0.16	1.9	6.7	8.3	2.8	8.0	11.6	4.2	9.5	17.6	-	-	-
0.32	2.4	8.6	12.9	4.1	14.0	17.0	6.7	20.0	31.3	-	-	-

^a With 1 g copper crystals (2-30 μm); ^b with 4 g copper crystals (2-30 μm);

^c with 8 g copper crystals (2-30 μm)

^d All these rate values have an uncertainty of $\pm 5\%$.

$\log [\text{Cu}^{2+}]$ for 1, 4 and 8 g of copper crystals in $\text{H}_2\text{O} + \text{AN}$ mixtures containing 5, 10 and 20% AN. In all cases the plots were linear and the slope of these plots gave an average value of 1.0 ± 0.05 as the dependence of rate on $[\text{Cu}^{2+}]$.

PLOTS USING DIMENSIONLESS PARAMETERS

Plots using dimensionless parameters in the form recommended by Powell and extended by Frost and Pearson¹⁴⁸ were made by plotting α versus $\log t$ in all cases. The relative concentration, α , for the dimensionless parameter plots was calculated in each case from the ratio of the concentration of Cu^{2+} remaining at a particular time, i.e. $C_0 - x$, to the initial concentration of Cu^{2+} taken in the beginning, i.e. C_0 . The values of x were calculated at various times from the amount of copper(I) formed using the relation $[\text{Cu}^{2+}] = \frac{1}{2} [\text{Cu}^+]$. For a given amount of copper crystals (1, 4 and 8 g respectively) with 5, 10 and 20% AN (including 40% in cases of 0.064 and 0.032 mol dm^{-3} copper sulphate solutions) for each concentration of the copper sulphate solution studied, the plots using dimensionless parameters were all of the same type and comparable to the theoretical curve for the first order reaction¹⁴⁸. For illustration the plots using dimensionless parameters for 0.32 mol dm^{-3} copper sulphate, 1, 4 and 8 g copper crystals (2-30 μm) with 5, 10 and 20% AN are shown in FIGS. 7 to 9.

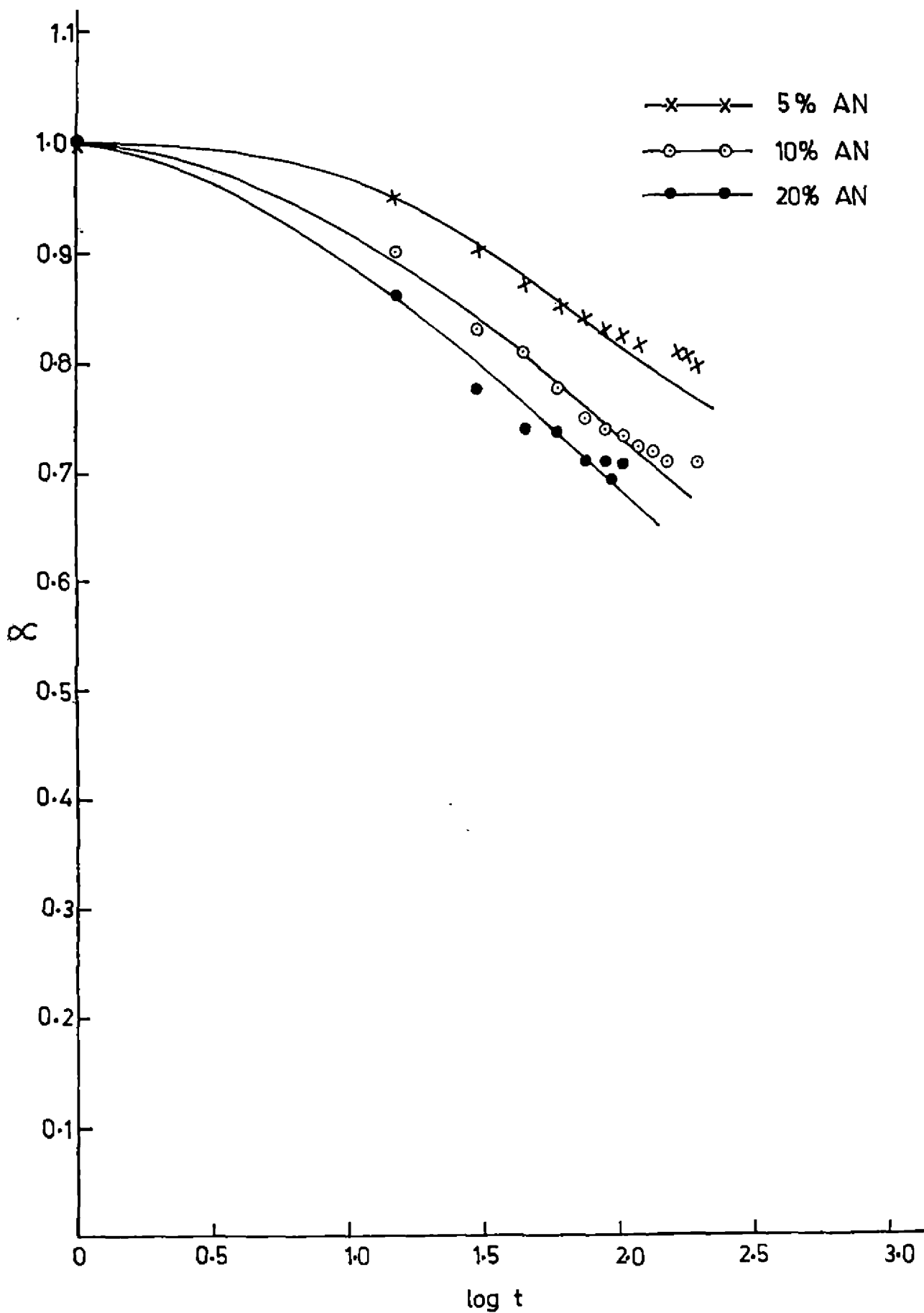


FIG. 7. FRACTION OF Cu^{2+} REMAINING (α) AS A FUNCTION OF TIME PARAMETER ($\log t$) AT 25°C (0.32 mol dm^{-3} COPPER SULPHATE+1g COPPER CRYSTALS $2\text{-}30 \mu\text{m}$).

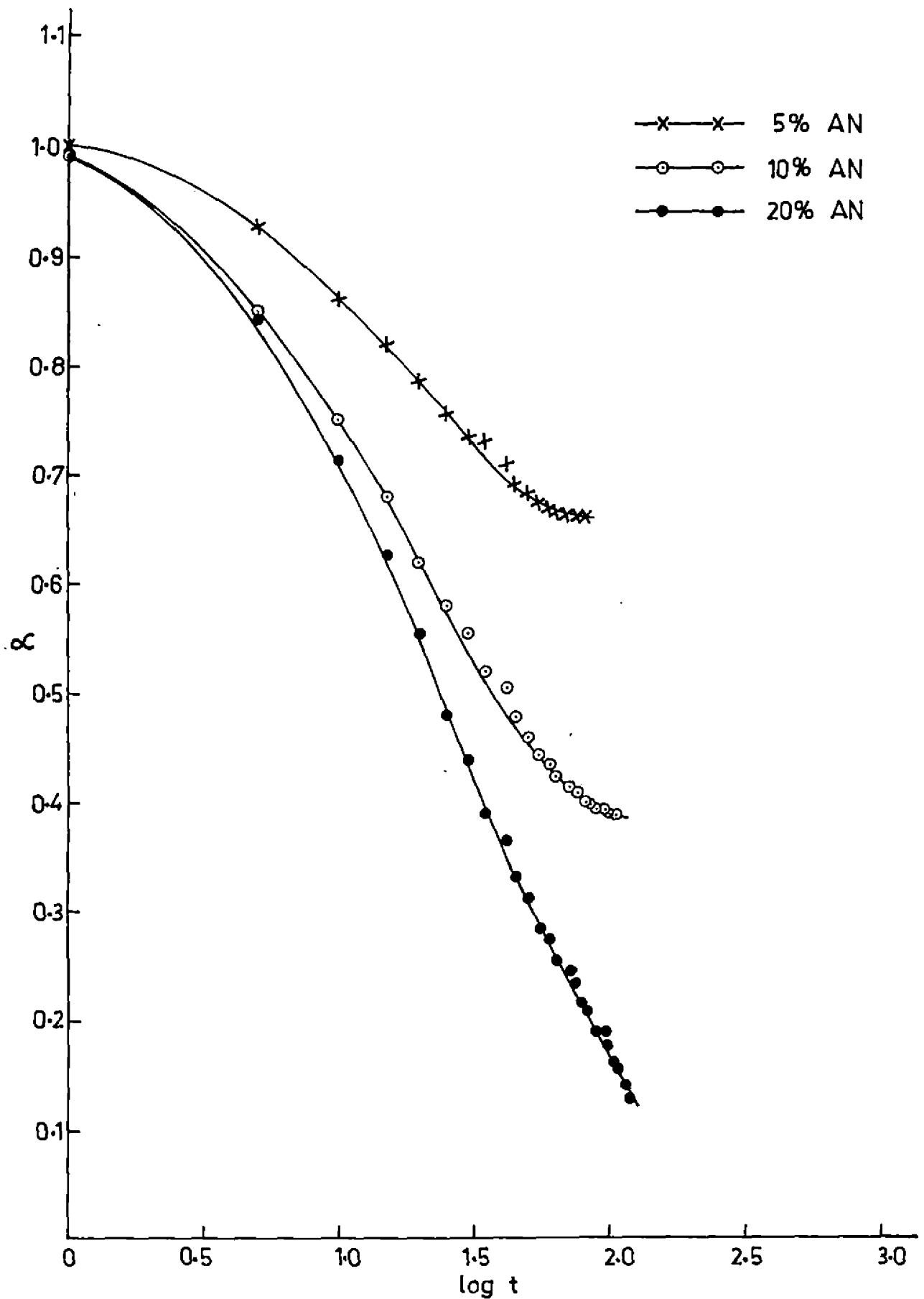


FIG.8. FRACTION OF Cu^{2+} REMAINING (α) AS A FUNCTION OF TIME PARAMETER ($\log t$) AT 25°C (0.32 mol dm^{-3} COPPER SULPHATE + 4g COPPER CRYSTALS $2\text{-}30 \mu\text{m}$).

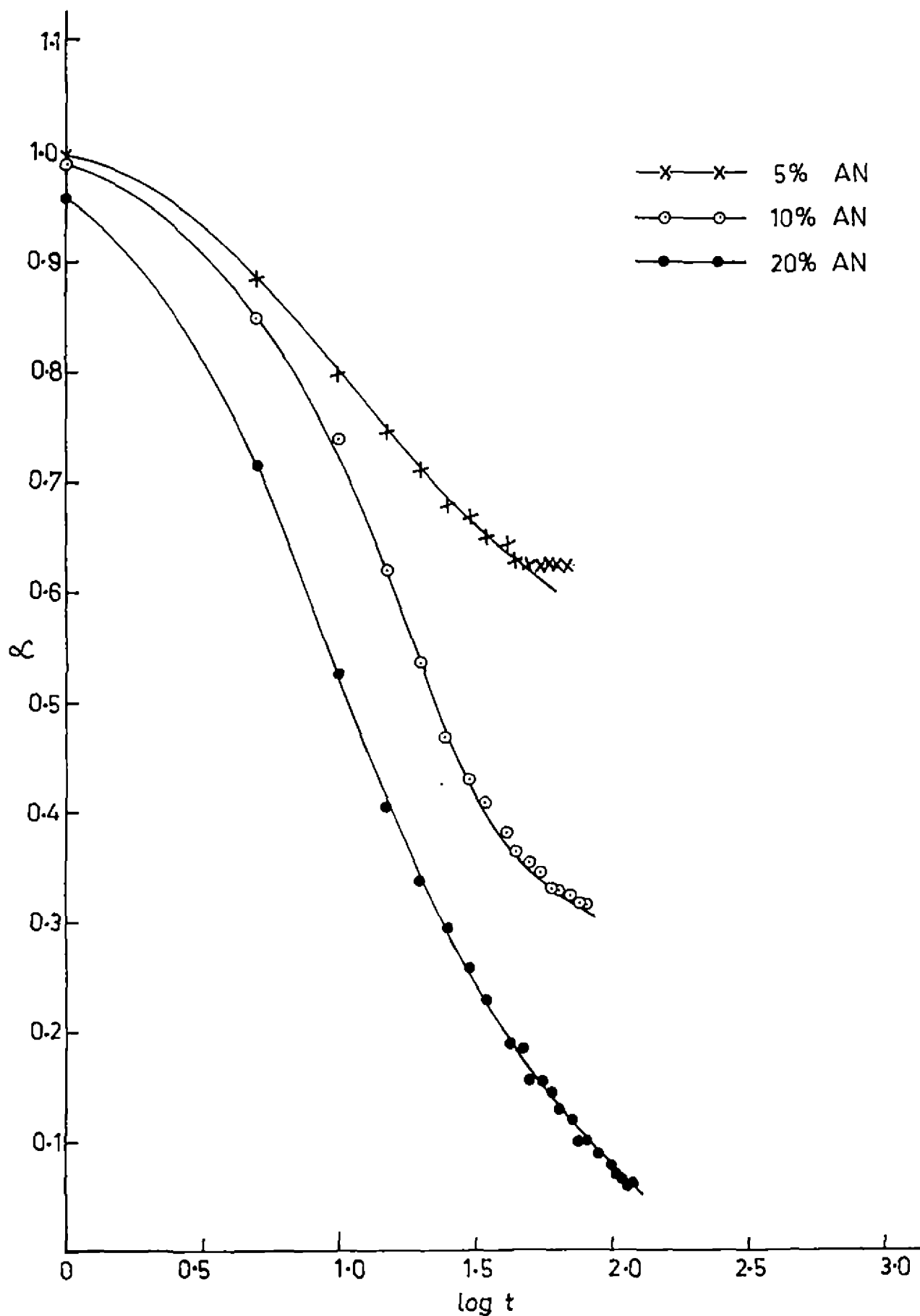


FIG. 9. FRACTION OF Cu^{2+} REMAINING (α) AS A FUNCTION OF TIME PARAMETER ($\log t$) AT 25°C (0.32 mol dm^{-3} COPPER SULPHATE+8% COPPER CRYSTALS $2\text{-}30 \mu\text{m}$).

2. EFFECT OF ACETONITRILE CONCENTRATION ON THE REACTION RATE

Results of TABLES 7 and 9 show that the increased amount of AN increases the rate of the reaction in all cases. The maximum rate has been observed with the maximum amount of AN. The plots using dimensionless parameters (FIGS. 7 to 9) show that the basic type of the curve and hence the order of the reaction has not been affected by the increasing amount of AN concentration. It can, however, be emphasised that for a given concentration of Cu^{2+} and a given amount of copper crystals, an increase in the rate of reaction with increasing AN concentration in $\text{H}_2\text{O} + \text{AN}$ mixtures (TABLES 7 and 9) can only be due to the changes in the solvent composition i.e. the medium effects¹⁴⁹. The medium effects influence the rate of the reaction either by change in the dielectric constant of the medium or by the changes in the solvation effects^{150,151}. With an increase in AN concentration the dielectric constant of $\text{H}_2\text{O} + \text{AN}$ mixtures decreases¹⁰² and one expects the formation of more ion-pairs, leading to a decrease in free Cu^{2+} concentration. This would lead to a decrease in the rate of the reaction. There is actually an increase in the rate with increasing AN concentration (TABLES 7 and 9). Therefore, the increase in the rate is possibly due to the increased solvation effects¹⁵⁰. Studies by Parker and coworkers² confirm this assumption. They have reported that Cu^{2+} is preferentially hydrated and Cu^+ is

preferentially solvated by AN in $H_2O + AN$ mixtures². Their studies have also shown that the free energy of transfer for Cu^+ from pure water to $H_2O + AN$ mixtures becomes more negative while for Cu^{2+} it becomes more positive as the amount of AN in the mixture increases, and the effects for Cu^+ are much more pronounced than the effects for Cu^{2+} . This indicates that the increasing concentration of AN in the mixture increases the solvation effects for Cu^+ much more strongly than it decreases the hydration of Cu^{2+} . The increased solvation effects for Cu^+ stabilize these ions much more in $H_2O + AN$ mixtures with higher AN concentration and hence there is an increase in the rate of the reaction. Single-ion solvent activity coefficients for SO_4^{2-} , Cu^{2+} , Cu^+ and the activated complex formed in the present reaction are not available in the literature for $H_2O + AN$ mixtures and, therefore, a quantitative account of the changes of the solvation effects in terms of the solvent activity coefficients could not be made. But from the work reviewed by Parker¹⁵¹ it has been reported that due to the increased solvation effects the rate of reaction is usually faster in dipolar aprotic solvents and in protic + dipolar aprotic solvent mixtures as compared with the rate in protic solvents.

With 0.32 mol dm^{-3} copper sulphate concentration, the optimum AN concentration to give the maximum rate was found to be 20%.

3. EFFECT OF THE CONCENTRATION OF H_2SO_4 ON THE REACTION RATE

Copper(I) salts are easily hydrolysed by water in neutral medium. The possibility of hydrolysis in acidic medium, however, is eliminated. Therefore, the kinetic study of the present reaction was made in the presence of an acid; dilute H_2SO_4 was found to be the most suitable. In some cases kinetic studies were tried without H_2SO_4 and in all those cases precipitation occurred after a few minutes and the experiments were discarded. The effect of varying concentrations of H_2SO_4 on the rate of the reaction is shown in TABLE 8.

In case of $0.064 \text{ mol dm}^{-3}$ copper sulphate solutions under nitrogen gas, the rate of the reaction within the experimental error is not significantly affected by the concentration of H_2SO_4 . In case of 0.32 mol dm^{-3} copper sulphate, however, some effect of H_2SO_4 concentration has been observed on the rate of the reaction. The rate of the reaction in that case increases with the increase of H_2SO_4 concentration upto 0.47 mol dm^{-3} and then decreases at higher H_2SO_4 concentrations (TABLE 8). The minimum concentration of H_2SO_4 which avoided the hydrolysis of Cu^+ in solution and was sufficient to check precipitation was 0.07 mol dm^{-3} . Therefore, this concentration of H_2SO_4 was taken as the optimum concentration and was used in almost all the kinetic measurements. Dilute H_2SO_4 has been found not to react with copper metal in the absence of oxygen^{1,152}. In the present

TABLE 8

Rate (R) of reaction (15) at different concentrations of H_2SO_4 in H_2O + AN mixtures containing 5 and 20% AN using 0.064 and 0.32 mol dm^{-3} copper sulphate with 4 and 8 g of copper crystals (2-30 μm) at 25°C respectively

Concentration of H_2SO_4 (mol dm^{-3})	R/ 10^{-3} mol dm^{-3} min $^{-1}$	
	0.064 mol dm^{-3} copper sulphate + 4 g copper crystals in 5% AN	0.32 mol dm^{-3} copper sulphate + 8 g copper crystals in 20% AN
0.07	3.0	31.3
0.18	3.0	33.0
0.28	3.5	35.8
0.47	3.3	40.4
0.70	-	39.4
0.94	-	34.4

measurements, therefore, all the dissolved oxygen was removed by bubbling oxygen-free nitrogen gas through the reaction solution. By performing the kinetic measurements in an atmosphere of nitrogen gas, the chances of a side reaction of copper metal with H_2SO_4 were eliminated.

The plots using dimensionless parameters showed that the order of reaction was not affected by H_2SO_4 concentration.

4. EFFECT OF TEMPERATURE

In order to study the effect of temperature on the rate of reaction (15) and to find out the optimum temperature, kinetic measurements were also carried out using 150 cm^3 of the reaction solution containing 0.32 mol dm^{-3} copper sulphate, 5, 10 and 20% AN, 0.07 mol dm^{-3} H_2SO_4 and 1, 4 and 8 g of copper crystals (2-30 μm in size) at 35, 45, 55 and $65^\circ \pm 0.1^\circ\text{C}$ respectively.

The rate of reaction (15) at 35, 45, 55 and 65°C using 0.32 mol dm^{-3} copper sulphate in 5, 10 and 20% AN with 1, 4 and 8 g of copper crystals (2-30 μm) determined from the initial stages of reaction by the method given before are reported in TABLE 9. The corresponding reaction rates at 25°C taken from TABLE 7 are also included in TABLE 9. It is observed from TABLE 9 that for a given AN concentration and for a given amount of copper crystals the rate of reaction at 35°C is more than double the

TABLE 9

Rate (R) of reaction (15) with copper sulphate concentration of 0.32 mol dm^{-3}
in $\text{H}_2\text{O} + \text{AN}$ mixtures at different temperatures

Temperature (°C)	$R/10^{-3} \text{ mol dm}^{-3} \text{ min}^{-1}$ ^d								
	5% AN			10% AN			20% AN		
	1 ^a	2 ^b	3 ^c	1 ^a	2 ^b	3 ^c	1 ^a	2 ^b	3 ^c
25*	2.4	8.6	12.9	4.1	14.0	17.0	6.7	20.0	31.3
35	5.4	18.8	25.0	8.3	30.0	40.0	13.7	50.0	70.0
45	10.0	35.0	50.0	16.4	58.0	82.5	25.7	90.0	138.0
55	10.5	36.0	50.5	17.0	58.5	84.0	26.5	92.0	140.0
65	11.0	37.0	51.0	17.8	60.0	85.0	27.0	93.0	140.6

^a With 1 g copper crystals, 45 cm^2 surface area; ^b With 4 g copper crystals, 150 cm^2 surface area;

^c With 8 g copper crystals, 210 cm^2 surface area.

^d All these values are at stirring speed of 800 r.p.m. and have maximum uncertainty of $\pm 5\%$.

* Values from TABLE 7.

rate at 25°C and the rate at 45°C is almost double the rate at 35°C. The rates of reaction at 55 and 65°C within the experimental uncertainty are, however, practically equal to the rate at 45°C in each case. This establishes the optimum temperature for this reaction to be 45°C. At temperature $> 45^{\circ}\text{C}$, AN starts evaporating out from the solution and the stability of the complex of Cu^+ formed with AN starts decreasing. The increase in the reaction rate by the increased thermal agitation is perhaps off set by a decrease in the reaction rate by the evaporation of AN. At temperature $> 65^{\circ}\text{C}$ when most of AN has evaporated off, the rate of reaction (15) becomes negligibly small and the backward reaction becomes significant with the result that copper powder starts separating out from the solution.

In order to find out if the increased temperature, only increased the rate of the reaction or it brought about any change in the mechanism of the reaction, plots using dimensionless parameters in the same form as discussed before in the previous sections were constructed at all temperatures. These plots shown in FIGS. 10 and 11 for 35 and 55°C with 4 g copper crystals (2-30 μm) respectively, as an illustration, are of the same type and comparable to the corresponding plot at 25°C (FIG. 8) and also to the theoretical curves for the first order reaction¹⁴⁸. This showed that the basic reaction mechanism was not affected by the change in temperature.

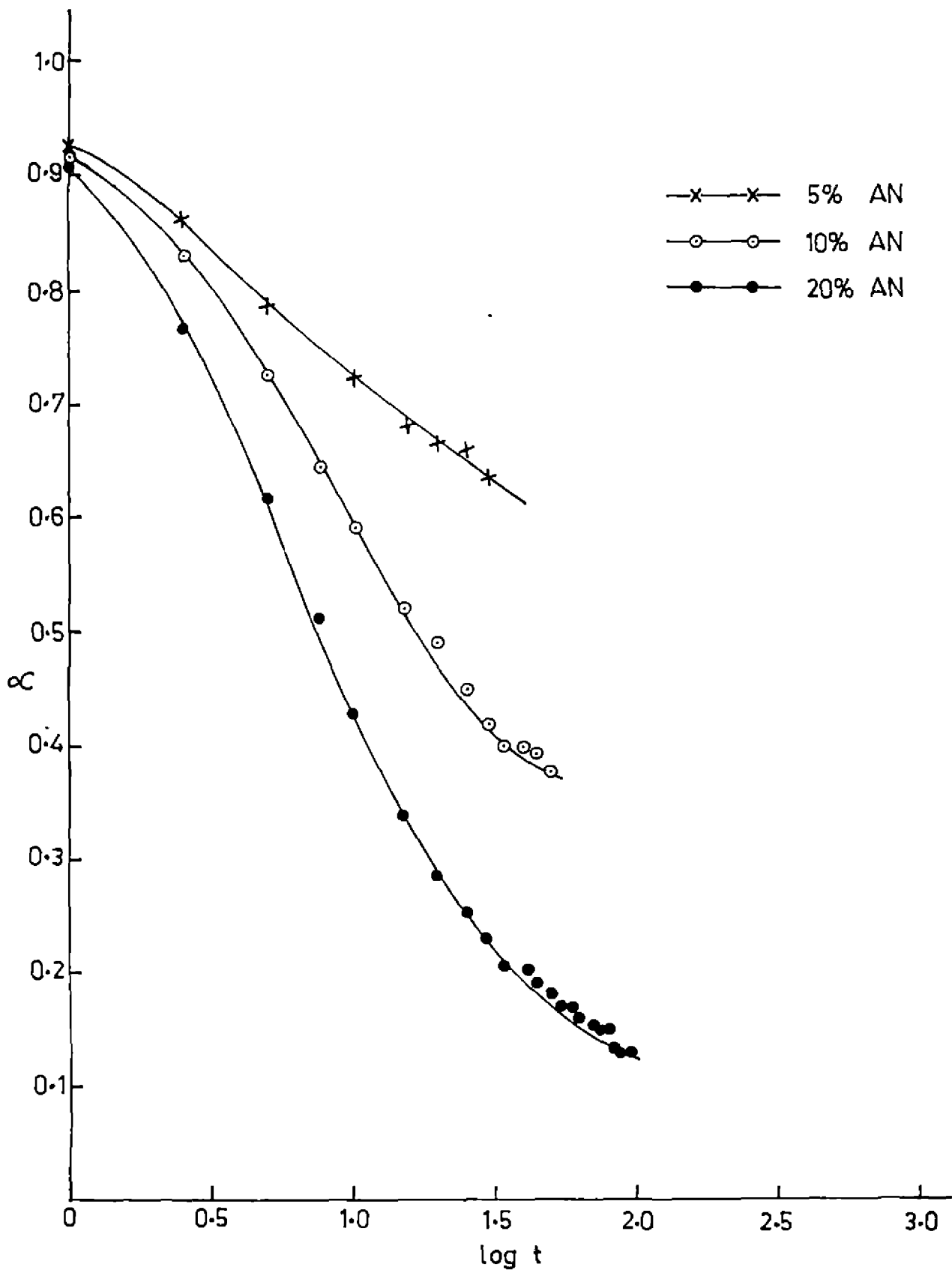


FIG.10. FRACTION OF Cu^{2+} REMAINING (ρ_c) AS A FUNCTION OF TIME PARAMETER ($\log t$) AT 35°C (0.32 mol dm^{-3} COPPER SULPHATE + 4g COPPER CRYSTALS $2\text{-}30 \mu\text{m}$).

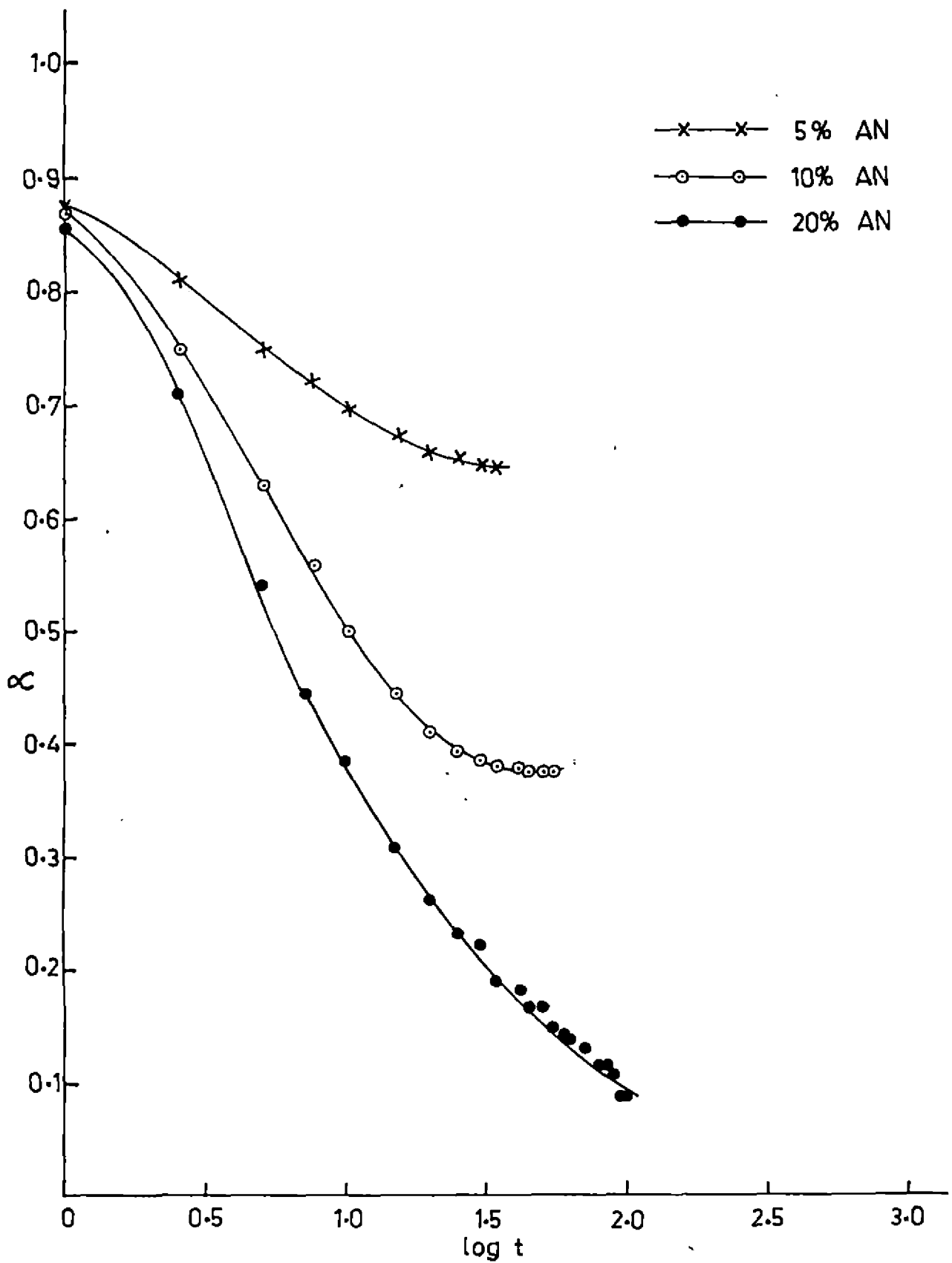


FIG.11. FRACTION OF Cu^{2+} REMAINING (α) AS A FUNCTION OF TIME PARAMETER ($\log t$) AT 55°C (0.32 mol dm^{-3} COPPER SULPHATE + 4g COPPER CRYSTALS $2\text{-}30 \mu\text{m}$).

5. EFFECT OF THE PARTICLE SIZE AND THE SURFACE AREA OF COPPER CRYSTALS ON THE REACTION RATE

The increased amount of copper crystals increased the rate of reaction (15) in all $H_2O + AN$ mixtures and at all the temperatures. The rate with 8 g of copper crystals in each $H_2O + AN$ mixture was more than with 4 g of copper crystals and with 1 g of copper crystals the rate was the lowest (TABLES 7 and 9). This is expected because in heterogeneous surface reactions the rate of the reaction depends upon the surface area of the solid phase and the larger the surface area, the faster is the reaction^{153,154}.

In order to study the effect of the particle size of copper crystals on the reaction rate, kinetic measurements, in addition, were also made under similar conditions using 200 mesh as well as between 40 and 180 μm in size copper crystals. In TABLE 10 are reported the rates of the reaction with $0.064 \text{ mol dm}^{-3}$ copper sulphate and $0.07 \text{ mol dm}^{-3} H_2SO_4$ in 150 cm^3 of the reaction solution in 5, 20 and 40% AN in $H_2O + AN$ mixtures using 4 g of 40-180 μm , 2-30 μm and 200 mesh copper crystals respectively.

The rate of the reaction with 200 mesh copper crystals is about 6 times the rate with 2-30 μm copper crystals and about 30 times the rate with 40-180 μm copper crystals (TABLE 10).

The total surface area of 1, 4 and 8 g of copper crystals

TABLE 10

Rate (R) of reaction (15) using $0.064 \text{ mol dm}^{-3}$ copper sulphate, $0.07 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ in 150 cm^3 of the reaction solution in $\text{H}_2\text{O} + \text{AN}$ mixtures containing 5, 20 and 40% AN with 4 g of copper crystals of $40\text{-}180 \mu\text{m}$, $2\text{-}30 \mu\text{m}$ and 200 mesh in size at 25°C

$(\text{V/V})\% \text{ AN}$	$R/10^{-3} \text{ mol dm}^{-3} \text{ min}^{-1}$		
	$40\text{-}180 \mu\text{m}$ copper crystals	$2\text{-}30 \mu\text{m}$ copper crystals	200 mesh copper crystals
5	0.6	3.0	17.4
20	1.2	6.1	35.7
40	1.3	6.3	38.0

2-30 μm in size equal to 45, 150 and 210 cm^2 respectively was determined by comparing the rate of reaction (15) at 25°C with the corresponding rate obtained under the similar conditions with the copper crystals of known total surface area and then fitting the data in the well known relation¹⁵⁵ (17):

$$\frac{R_1}{R_2} = \frac{A_1}{A_2} \quad (17)$$

A_1 and A_2 are the known surface area and the surface area to be evaluated respectively and R_1 and R_2 are the corresponding rates of the reaction. The known total surface area A_1 was evaluated by selecting a known quantity (8 g) of copper crystals 40-180 μm in size (75 cm^2 surface area) and determining the area of each crystal separately by measuring the dimensions with the help of vernier callipers and the screw gauge.

For a given AN concentration in $\text{H}_2\text{O} + \text{AN}$ mixtures and at a given temperature, the rate of reaction (15) increased as the surface area of the copper crystals increased (TABLE 9). With 1, 4 and 8 g of copper crystals 2-30 μm in size (45, 150 and 210 cm^2 surface area respectively) the average ratio of the rates of reaction (15) at all temperatures was found to be 1:3.3:4.7 respectively (TABLE 9).

The plots using dimensionless parameters (FIG. 12) show that the basic type of the curve was not affected when copper

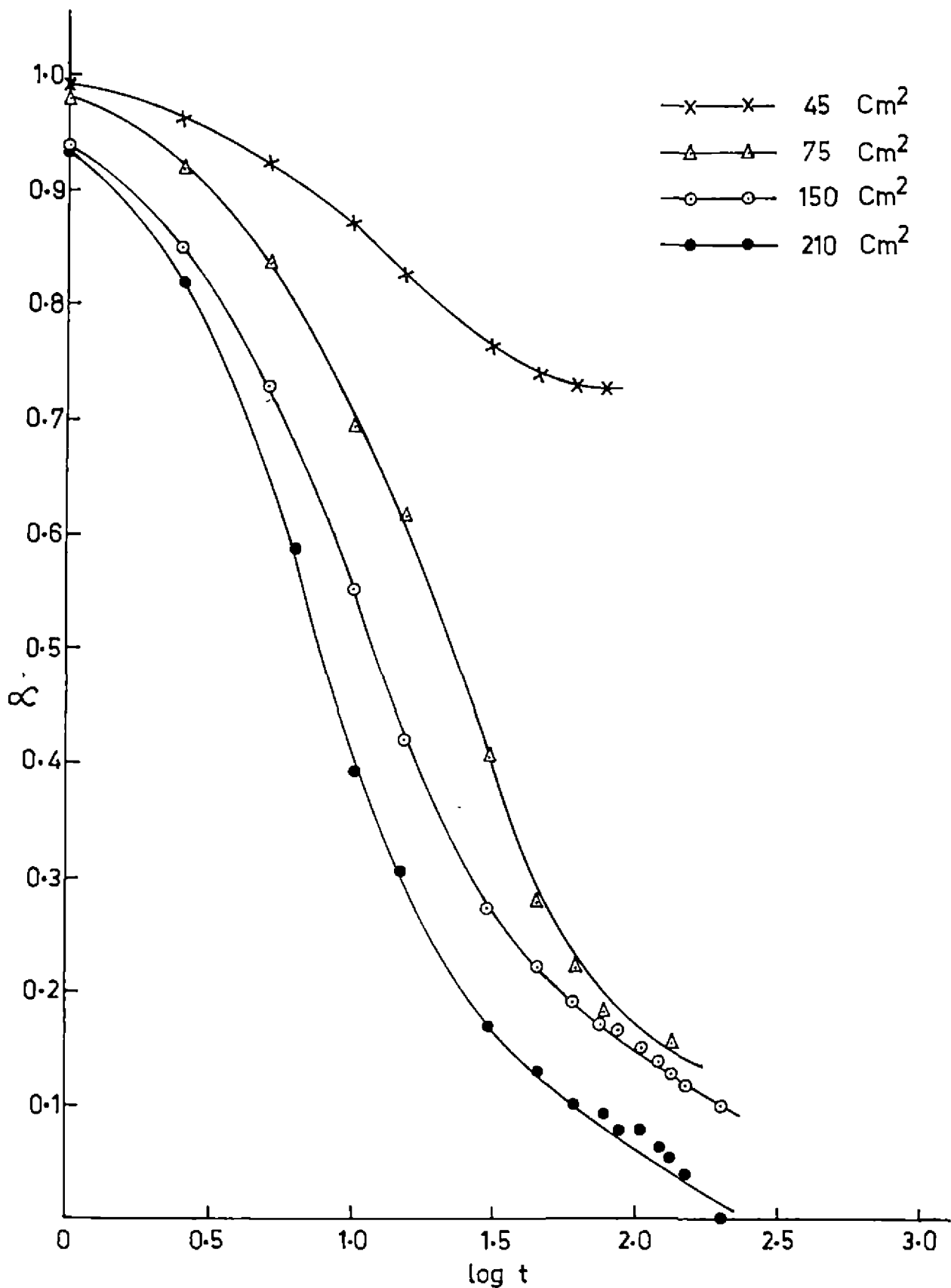


FIG.12. FRACTION OF Cu^{2+} REMAINING (α) AS A FUNCTION OF TIME PARAMETER ($\log t$) AT 25°C FOR DIFFERENT VALUES OF SURFACE AREAS (0.32 mol dm^{-3} COPPER SULPHATE IN 20% AN).

crystals of different surface area were used. In all these cases the plots were also comparable to the theoretical curve for the first order reaction. This showed that the increase of the surface area of the copper crystals did not effect the order of reaction, though it did increase the rate of the reaction.

6. EFFECT OF THE STIRRING SPEED ON THE REACTION RATE

The stirring of the reaction solution was done with a magnetic stirrer and the rate of the reaction was found to be drastically affected by changing the stirring speed.

The rate of reaction (15) obtained at 25, 35 and 45°C at stirring speeds of 0, 300, 700, 800, 1000 and 1200 r.p.m. using 150 cm³ of the reaction solution containing 0.32 mol dm⁻³ copper sulphate, 20% AN, 0.07 mol dm⁻³ H₂SO₄ and 8 g (2-30 μm) of copper crystals (given in TABLE 11) show that the maximum rate of the reaction is produced by the maximum speed of stirring. In most of the transport controlled heterogeneous reactions in solution such an observation has been found to be true¹⁵⁶. In case of 0 r.p.m. i.e. no stirring, a sharp concentration gradient was observed to exist in the solution as a function of distance from the copper surface. In this case the rate of reaction reported in TABLE 11 was obtained by making the reaction solution homogeneous by stirring at 1200 r.p.m. for 5 to 10 seconds before measuring the amount of copper(I) formed as a function of time.

TABLE 11

Rate (R) of reaction (15) using 0.32 mol dm^{-3} copper sulphate,
 8 g of copper crystals ($2\text{-}30 \mu\text{m}$) and 20% AN in $\text{H}_2\text{O} + \text{AN}$
 mixture at 25, 35 and 45°C at different
 rates of stirring

Temperature ($^\circ\text{C}$)	$R/10^{-3} \text{ mol dm}^{-3} \text{ min}^{-1}$					
	0 r.p.m.	300 r.p.m.	700 r.p.m.	800 r.p.m.	1000 r.p.m.	1200 r.p.m.
25	4.1	16.2	29.5	31.3	34.3	37.5
35	7.2	35.5	60.4	70.0	72.8	80.0
45	14.0	72.0	121.8	143.2	145.8	163.0

A power relation of the form:

$$\text{rate} \propto (\text{r.p.m.})^{0.63} \quad (18)$$

was found applicable between the reaction rate and the stirring speed at all temperatures. Most of the transport controlled heterogeneous reactions in solution studied in the literature report such a relation¹⁵⁶ with stirring coefficient between 0.5 and 0.8.

The plots using dimensionless parameters (FIG. 13) also show that the stirring speed changed the rate of the reaction but the order of reaction was independent of the stirring speed.

MECHANISM OF REACTION (15)

As the rate of reaction (15) was drastically increased by increasing the stirring speed, this indicated that reaction under investigation was transport controlled¹⁵⁶. The reaction has been assumed to take place not through a single step but through a number of different steps:

- i) Diffusion of the preferentially hydrated Cu^{2+} from the bulk of the solution to the copper surface.
- ii) Diffusion of the solvated SO_4^{2-} from the bulk of the solution to form the negative side of the solvent-separated electrical double layer near the solid surface¹⁵⁷.

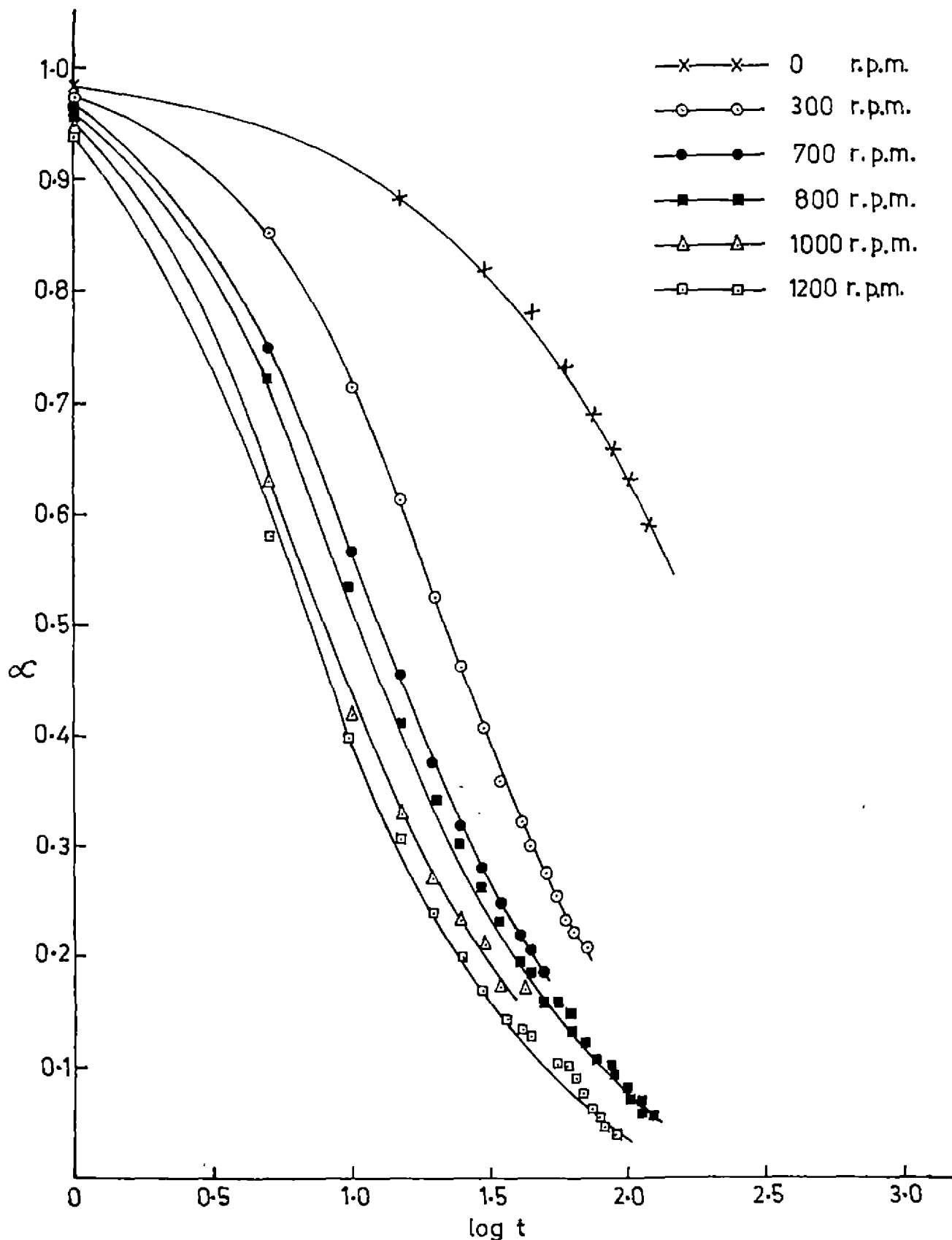


FIG.13. FRACTION OF Cu^{2+} REMAINING (α) AS A FUNCTION OF TIME PARAMETER ($\log t$) AT 25°C WITH DIFFERENT STIRRING SPEEDS (0.32 mol dm^{-3} COPPER SULPHATE+8g COPPER CRYSTALS 2-30 μm IN 20% AN).

- iii) Electron transfer from a copper atom at the surface to a Cu^{2+} to form two Cu^+ cations.
- iv) Solvation of Cu^+ preferentially by AN to form the stable Cu^+ complex.
- v) Diffusion of the preferentially solvated Cu^+ complex out of the electrical double layer to the bulk of the solution.

Steps (iii) and (iv) are fast and should not be affected by changing the stirring speed. It is thus any one or all of the other steps which determine the rate of reaction (15).

The following important conclusions can be drawn from the results of the kinetic measurements of reaction (15):

- i) The increased copper sulphate concentration increased the rate of the reaction. The optimum Cu^{2+} concentration has been found to be 0.32 mol dm^{-3} .
- ii) The increased amount of AN in $\text{H}_2\text{O} + \text{AN}$ mixtures increased the rate of the reaction upto 20% of AN. At higher percentage of AN in the mixture, the rate of the reaction increased slightly but the increase was not significant. With 0.32 mol dm^{-3} copper sulphate, the optimum AN concentration to give the maximum rate was found to be 20%.
- iii) Under nitrogen gas atmosphere the rate of the reaction was found to be slightly dependent on H_2SO_4 concentration i.e. on the pH of the solution. The rate of the reaction, however,

was affected significantly by the pH of the reaction solution when no nitrogen gas was bubbled through the reaction solution.

- iv) Using optimum concentration of copper sulphate (0.32 mol dm^{-3}), 5, 10 and 20% AN in $\text{H}_2\text{O} + \text{AN}$ mixtures and a given amount of copper crystals the rate of the reaction in each $\text{H}_2\text{O} + \text{AN}$ mixture at 35°C was more than double the rate at 25°C and the rate at 45°C was almost double the rate at 35°C . The rate of reaction at 55 and 65°C within the experimental uncertainty was, however, practically equal to the rate at 45°C in each case. This established an optimum temperature for reaction to be 45°C .
- v) The amount and the particle size of the copper crystals strongly affected the rate of the reaction. The smaller the particle size of copper crystals the more was the rate of the reaction. The maximum reaction velocity of reaction (15) was found with 200 mesh copper crystals, intermediate with $2\text{-}30 \mu\text{m}$ copper crystals and minimum with copper crystals between $40\text{-}180 \mu\text{m}$ in size.
- vi) The increased amount of copper crystals increased the rate of the reaction.
- vii) The rate of the reaction was found to be strongly affected by the rate of stirring of the solution. The maximum rate was found with maximum stirring speed. The relation between

the rate of the reaction and the stirring speed was a power law obeying the relation: $\text{rate} \propto (\text{r.p.m.})^{0.63}$.

- viii) The plots using dimensionless parameters showed that the reaction is first order in Cu^{2+} concentration.
- ix) The reaction has been found to be extremely fast to reach almost to the completion within 0.5 to 5 hours. In case of 1 g of copper crystals using 0.32 mol dm^{-3} copper sulphate solutions in all $\text{H}_2\text{O} + \text{AN}$ mixtures studied, the reaction was complete in a relatively short time because whole amount of copper crystals dissolved quickly. The dissolution of 1 g of copper crystals took place even more quickly at higher temperatures. In all these cases, reaction continued only for 30 to 45 minutes. Also with low copper sulphate concentration and with high AN concentration as well as with high copper sulphate concentration and low AN concentration, the time required for the completion of reaction was relatively small.