# CHAPTER-II

## EXPERIMENTAL

## CHAPTER - II

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

Calibrated weights were used for weighing the substances. Calibrated and certified burettes, pipettes and volumetric flasks were used for preparation of solutions. All solutions were prepared in double distilled water.

Substituted anilines, viz. Ortho-toluidine (o-T), meta-toluidine (m-T) were from Thomas Baker and Co. (London). They were distilled under reduced pressure before use. The boiling points and refractive indices were compared with literature values.

For this purpose amines were — accurately weighed and dissolved in requisite amount of double distilled alcohol. The stock solution thus prepared was used for 24 hours only to avoid the change in concentration due to oxidation of amines. The amines and their solutions were protected from direct light.

**ETHANOL :**

All reactions were carried out in 50% (v/v) ethanol medium. The ethanol was purified, dried and double distilled before use.

**CHLORAMINE-B-(CAB) :**

CAB from Sisco Chem Industries was used for preparation of solutions. To prepare the solution, appropriate amount of chloramine-B — was dissolved in required quantity of double distilled water.

stock solution of CAB of 0.02M was prepared in double distilled water and used for 24 hours.

**HYDROCHLORIC ACID SOLUTION :**

Hydrochloric acid solution was prepared by taking 85.4ml (B.D.H AR) concentrated hydrochloric acid and diluting it to one litre using distilled water and it was standardised with standard sodium hydroxide solution.

**SODIUM THIOSULPHATE SOLUTION :**

0.01M sodium thiosulphate solution was prepared by dissolving 2.480 gms of pure sodium thiosulphate (B.D.H.AR) in double distilled water and the solution was diluted to one litre and was standardised. For actual experimental work 0.0005M sodium thiosulphate solution was prepared by diluting the stock solution and used.

**SODIUM PERCHLORATE SOLUTION :**

$NaClO_4$ G.R. grade (Riedel) sample was used without any purification. A standard solution of 3.6N sodium perchlorate was prepared in double distilled water. 12.5ml of this solution was always used to keep the ionic strength at 0.5M of the reaction medium.

**SULPHURIC ACID :**

2N sulphuric acid was used and was prepared by taking 56 ml (B.D.H.AR) concentrated sulphuric acid and diluting it to one

litre using distilled water and was standardised.

**POTASSIUM IODIDE :**

5% potassium iodide solution was prepared in distilled water from B.D.H.,A.R. grade potassium iodide.

**INDICATOR :**

Fresh starch solution was the indicator in iodometric titration.

**KINETIC MEASUREMENTS :**

All experiments were carried out under pseudo-first order conditions by keeping amine concentration in excess over the concentration of CAB. The amine solution of exact concentration was prepared in double distilled ethyl alcohol and 25ml of it was transferred to a 250ml well stoppered flask and 12.5ml of 0.4M HCl, 12.5ml of 3.6N $NaClO_4$ were then added to it. The flask was then maintained at constant temperature by keeping it in thermostat. The solution of CAB ( 4 times the concentration required) was prepared from stock solution using 50% (V/V) ethanol at $30^{o}C$. 50ml of this solution was transferred to 250ml flask. The flask was maintained at constant temperature by keeping it in the same thermostat. After thermal equilibrium was attained the amine solution was transferred quickly to the CAB solution. The reaction was then followed by withdrawing 5ml of the reaction mixture and quenching it in freshly prepared potassium iodide solution (5%,5ml ). To the

quenched solution 10ml of 2N sulphuric acid was added and the liberated iodine was titrated against standard (0.0005M ) sodium thiosulphate solution using starch solution as an indicator to determine the amount of unreacted CAB at that particular instant.

A blank experiment was performed under identical conditions without the amine. Thus the zero time reading was found. The first order rate constants were calculated by graphical as well as numerical method using integrated rate expression.

At constant hydrogen ion concentration (0.05M) and CAB (0.002M) rate dependance on the concentration of amine was noted. From the plot of log $k_{obs}$ against log [Amine] the order dependance on amine concentration was calculated.

Variation of concentration of hydrochloric acid medium was studied at constant [CAB] and [amine]. The order dependance on [HCl] was determined from the plot of $\log k_{obs}$ vs log[HCl].

At constant chloride ion concentration (kept at 0.12M by adding NaCl) variation of $[H^+]$ was studied. The order dependance on the concentration of hydrogen ions was calculated from the plot of log $k_{obs}$ against log $[H^+]$.

Keeping the hydrogen ion concentration at 0.05M variation of chloride ion concentration was studied by adding NaCl (0.06 to 0.13M) and from the plot of log $k_{obs}$ vs log [Cl] the order with respect to chloride ion concentration was determined. Finally, effect

of variation of ethanol and of ionic strength (0.5 to 0.1M) was studied.

**STOICHIOMETRY :**

Reaction mixture containing excess of CAB over amine was kept for 30 hours at 30$^{o}$C and unreacted CAB was estimated using standard sodium thiosulphate solution. From the unreacted CAB the stoichiometry was established.

**END PRODUCT ANALYSIS :**

One of the products benzene sulphonamide was identified by paper chromatography. The solvent used was 90% ethanol and developed in iodine chamber. The Rf value was 0.38.

The n-haloamines were detected by TLC.

TABLE 2.1.1

Chlorination of ortho-toluidine by chloramine-B

Effect of concentration of chloramine-B

$[o\text{-}T] = 2.0 \times 10^{-2}M$; $[HCl] = 0.05M$

$[Na_2S_2O_3] = 5.0 \times 10^{-4}M$; Ionic strength $= 0.5M$

Temp $= 303^{o}K$

| Conc of CAB X $10^{3}$M | | 1.5 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|---|
| Sr.No. | Time(min) | (a-x) | (a-x) | (a-x) | (a-x) |
| 1. | 0 | 11.3 | 15.9 | 20.1 | 22.9 |
| 2. | 10 | 9.1 | 12.5 | 15.9 | 17.7 |
| 3. | 20 | 6.7 | 9.7 | 12.3 | 13.4 |
| 4. | 30 | 5.6 | 7.8 | 9.9 | 10.5 |
| 5. | 40 | 4.5 | 5.9 | 7.7 | 8.2 |
| 6. | 50 | 3.4 | 4.7 | 6.1 | 6.3 |
| 7. | 60 | 2.7 | 3.5 | 4.9 | 5.3 |
| 8. | 70 | 2.4 | 3.2 | 4.0 | 4.2 |
| $k(min^{-1}) \times 10^{2}$ | | 2.39 | 2.46 | 2.44 | 2.46 |
| $k(sec^{-1}) \times 10^{4}$ | | 3.99 | 4.10 | 4.08 | 4.10 |

TABLE 2.2.1

Chlorination of meta-toluidine by chloramine-B

Effect of concentration of chloramine-B

$[m.T] = 2.0 \times 10^{-2}M$; $[HCl] = 0.05M$

$[Na_2S_2O_3] = 5.0 \times 10^{-4}M$; Ionic strength = 0.5M

Temp = $303^{o}K$

| Conc of CAB X $10^3$M | | 2.0 | 2.5 | 3.0 | 3.5 |
|---|---|---|---|---|---|
| Sr.No. | Time (min) | (a-x) | (a-x) | (a-x) | (a-x) |
| 1. | 0 | 15.3 | 21.0 | 22.2 | 23.5 |
| 2. | 10 | 12.3 | 16.5 | 17.9 | 19.1 |
| 3. | 20 | 9.8 | 13.6 | 14.5 | 14.7 |
| 4. | 30 | 7.7 | 10.9 | 11.5 | 13.0 |
| 5. | 40 | 6.0 | 8.7 | 9.4 | 10.3 |
| 6. | 50 | 4.9 | 7.0 | 7.5 | 8.5 |
| 7. | 60 | 3.9 | 5.7 | 6.0 | 7.1 |
| 8. | 70 | 3.1 | 4.7 | 4.8 | 5.6 |
| $k(min^{-1}) \times 10^2$ | | 2.26 | 2.16 | 2.17 | 2.13 |
| $k(sec^{-1}) \times 10^4$ | | 3.77 | 3.60 | 3.62 | 3.56 |

TABLE 2.1.2

Chlorination of ortho-toluidine by chloramine-B

Effect of concentration of substrate

$[CAB] = 2.0 \times 10^{-3}M$; $[HCl] = 0.05M$

$[Na_2S_2O_3] = 5.0 \times 10^{-4}M$; Ionic strength = 0.5M

Tamp = $303^{O}K$.

| $[o-T]$ = | | 0.020M | 0.030M | 0.035M | 0.040M |
|---|---|---|---|---|---|
| Sr.No. | Time (min) | (a-x) | (a-x) | (a-x) | (a-x) |
| 1. | 0 | 15.8 | 15.8 | 15.8 | 15.8 |
| 2. | 10 | 12.9 | 12.3 | 12.2 | 12.0 |
| 3 | 20 | 10.3 | 9.9 | 9.7 | 9.6 |
| 4. | 30 | 8.1 | 7.8 | 7.3 | 7.2 |
| 5. | 40 | 6.7 | 6.2 | 5.5 | 5.4 |
| 6. | 50 | 5.3 | 4.8 | 4.1 | 4.0 |
| 7. | 60 | 4.2 | 3.9 | 3.2 | 2.9 |
| 8. | 70 | 3.4 | 3.0 | 2.5 | - |
| $k(min^{-1}) \times 10^{2}$ | | 2.06 | 2.62 | 3.03 | 3.23 |
| $k\ (sec^{-1}) \times 10^{4}$ | | 3.44 | 4.38 | 5.05 | 5.39 |

TABLE 2.2.2

Chlorination of meta-toluidine by chloramine-B

Effect of concentration of substrate

$[CAB] = 2.0 \times 10^{-3}M$; $[HCl] = 0.05M$

$[Na_2S_2O_3] = 5.0 \times 10^{-4}M$; Ionic strength = 0.5M

Temp = $303^{o}K$

| [m-T] = | | 0.020M | 0.025M | 0.035M | 0.040M |
|---|---|---|---|---|---|
| Sr.NO. | Time (min) | (a-x) | (a-x) | (a-x) | (a- x) |
| 1. | 0 | 15.8 | 15.8 | 15.8 | 15.8 |
| 2. | 10 | 13.4 | 12.8 | 12.5 | 10.6 |
| 3. | 20 | 10.9 | 9.7 | 9.4 | 7.8 |
| 4. | 30 | 8.8 | 8.0 | 6.9 | 5.6 |
| 5. | 40 | 7.2 | 6.3 | 5.3 | 4.0 |
| 6. | 50 | 5.9 | 4.7 | 4.1 | 2.9 |
| 7. | 60 | 4.7 | 3.8 | 3.1 | 2.1 |
| 8 | 70 | 3.9 | 3.1 | 2.1 | - |
| $k\ (min^{-1}) \times 10^2$ | | 2.05 | 2.36 | 2.88 | 3.22 |
| $k\ (sec^{-1}) \times 10^4$ | | 3.42 | 3.93 | 4.80 | 5.37 |

TABLE 2.1.3

Chlorination of ortho-toluidine by chloramine-B

Effect of Temperature

$[o\text{-}T] = 2.0 \times 10^{-2}M$; $[CAB] = 2.0 \times 10^{-3}M$

$[HCl] = 0.05M$; $[Na_2S_2O_3] = 5.0 \times 10^{-4}M$

Ionic strength = 0.5M

| Temperature ($^0K$) | | 298 | 303 | 308 | 313 |
|---|---|---|---|---|---|
| Sr.No. | Time (min) | (a-x) | (a-x) | (a-x) | (a-x) |
| 1. | 0 | 16.1 | 16.1 | 16.1 | 16.9 |
| 2. | 5 | 15.2 | 13.9 | 15.0 | 12.3 |
| 3. | 10 | 14.6 | 12.8 | 13.3 | 10.7 |
| 4. | 15 | 13.5 | 11.5 | 11.4 | 8.7 |
| 5. | 20 | 12.2 | 10.4 | 9.5 | 6.9 |
| 6. | 25 | 11.7 | 9.4 | 8.3 | 6.2 |
| 7. | 30 | 10.9 | 8.4 | 7.0 | 5.0 |
| 8. | 35 | 10.0 | 7.8 | 6.2 | 4.1 |
| 9. | 40 | 9.4 | 7.2 | 5.2 | 3.2 |
| 10 | 45 | 8.6 | 6.3 | 4.7 | 3.0 |
| 11. | 50 | 7.8 | 5.8 | 3.9 | 2.5 |
| k ($min^{-1}$) X $10^2$ | | 1.56 | 2.16 | 2.96 | 3.68 |
| k ($sec^{-1}$ X $10^4$ | | 2.60 | 3.60 | 4.94 | 6.14 |

TABLE 2.2.3

Chlorination of meta-toluidine by chloramine-B

Effect of Temperature

$[m\text{-}T] = 2.0 \times 10^{-2}M$; $[CAB] = 2.0 \times 10^{-3}M$

$[HCl] = 0.05M$; $[Na_2S_2O_3] = 5.0 \times 10^{-4}M$

Ionic strength = 0.5M

| Temperature ($^{o}K$) | | 298 | 303 | 308 | 313 |
|---|---|---|---|---|---|
| Sr.No. | Time(min) | (a-x) | (a-x) | (a-x) | (a-x) |
| 1. | 0 | 15.8 | 15.8 | 15.8 | 15.8 |
| 2. | 5 | - | 15.3 | 13.6 | 11.6 |
| 3. | 10 | 14.2 | 13.8 | 11.8 | 9.6 |
| 4. | 15 | - | 12.6 | 9.9 | 8.1 |
| 5. | 20 | 12.8 | 11.5 | 8.8 | 6.7 |
| 6. | 25 | - | 10.3 | 7.7 | 5.7 |
| 7. | 30 | 11.5 | 9.1 | 6.8 | 4.8 |
| 8. | 35 | - | 8.3 | 6.0 | 4.2 |
| 9. | 40 | 10.3 | 7.8 | 5.3 | 3.5 |
| 10. | 45 | - | 7.1 | 4.7 | 2.9 |
| 11. | 50 | 9.2 | 6.5 | 4.1 | 2.5 |
| k ( $min^{-1}$) X $10^2$ | | 1.21 | 1.93 | 2.56 | 3.39 |
| k ( $sec^{-1}$) X $10^4$ | | 2.02 | 3.22 | 4.27 | 5.65 |

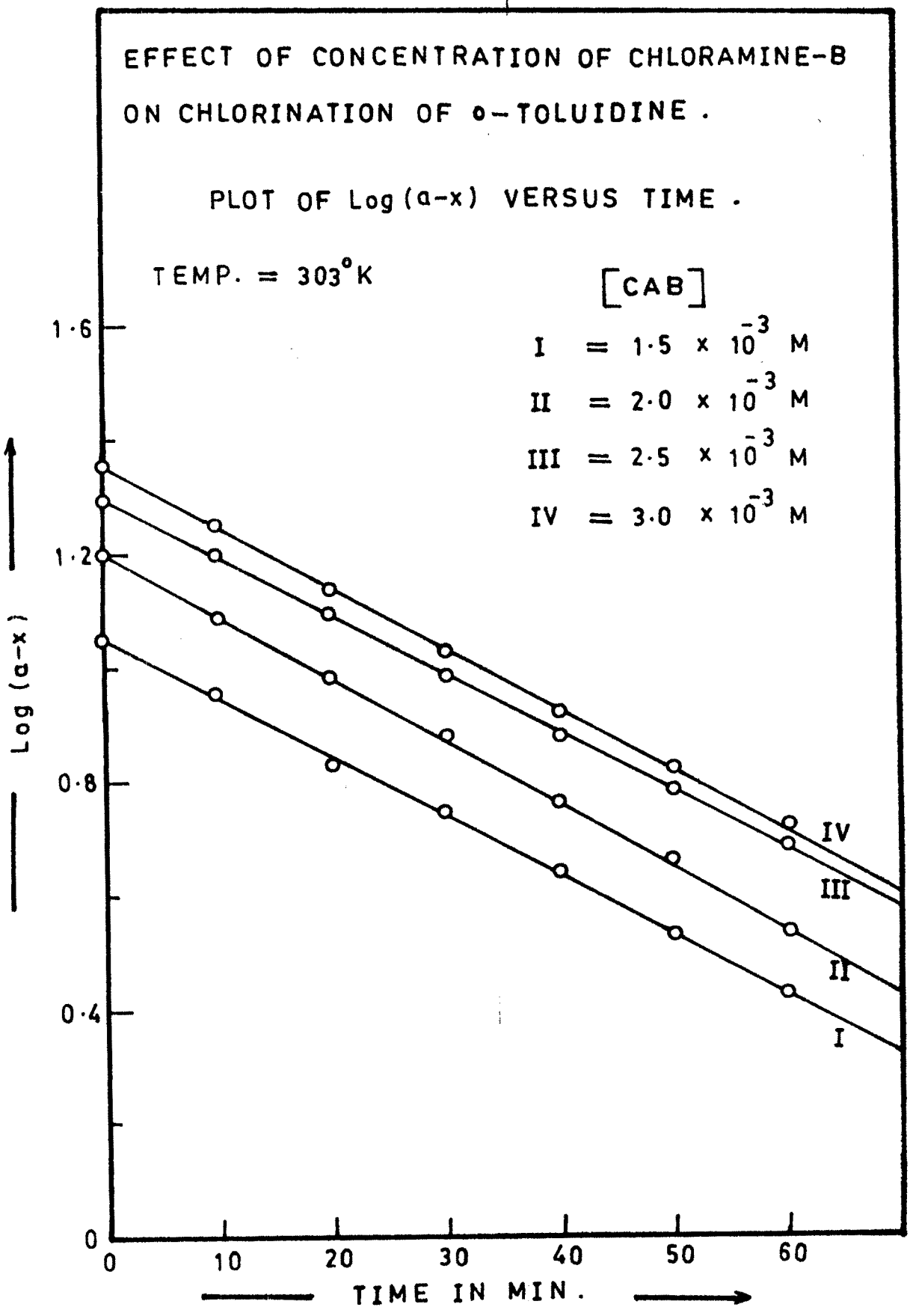
EFFECT OF CONCENTRATION OF CHLORAMINE-B
ON CHLORINATION OF o-TOLUIDINE .
PLOT OF Log (a-x) VERSUS TIME .
TEMP. = 303°K
[CAB]
I = 1·5 x 10⁻³ M
II = 2·0 x 10⁻³ M
III = 2·5 x 10⁻³ M
IV = 3·0 x 10⁻³ M
Log (a-x)
1·6
1·2
0·8
0·4
0
0
10
20
30
40
50
60
TIME IN MIN.
IV
III
II
I

FIG. 2·1·1

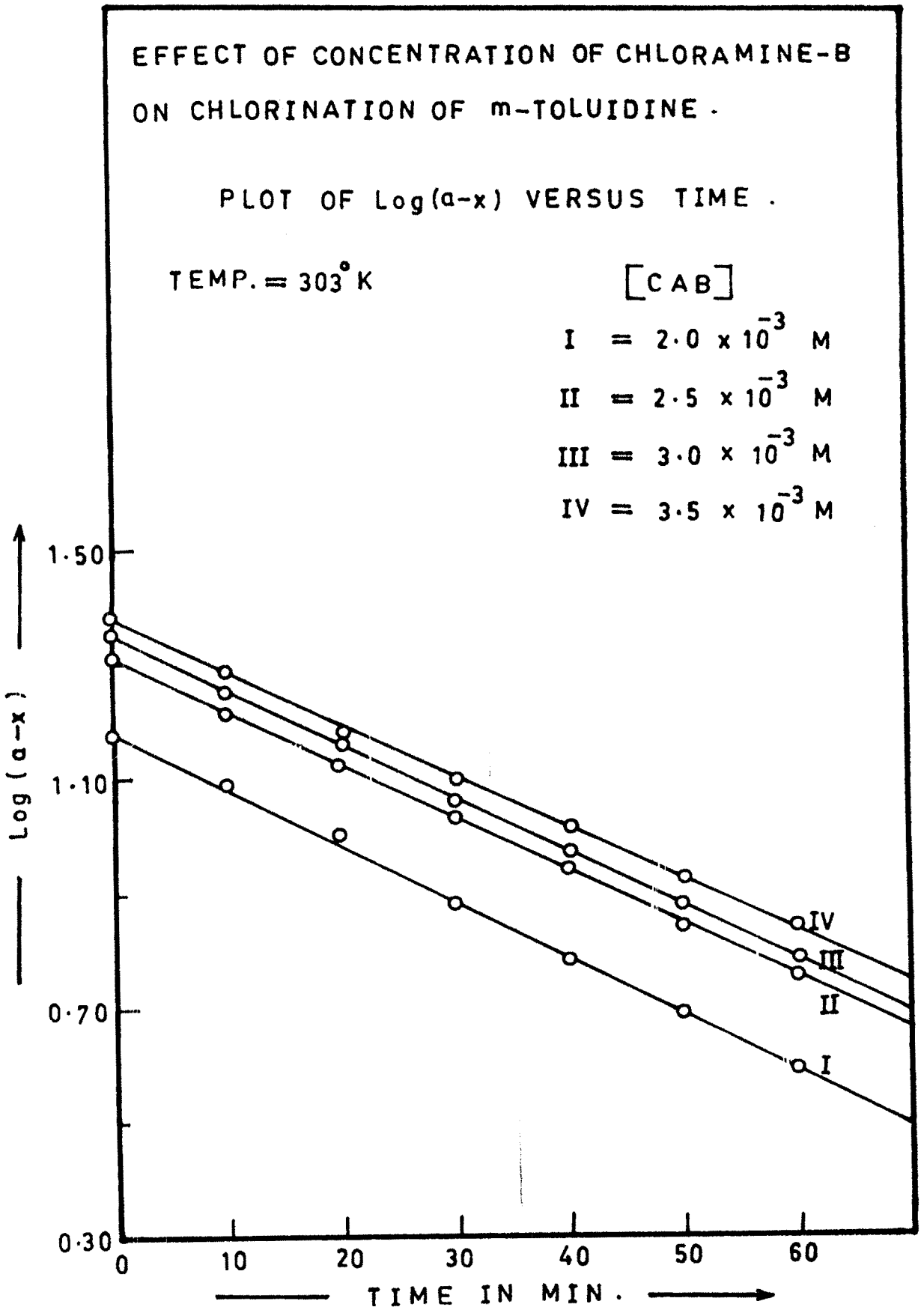
EFFECT OF CONCENTRATION OF CHLORAMINE-B
ON CHLORINATION OF m-TOLUIDINE.
PLOT OF Log(a-x) VERSUS TIME.
TEMP. = 303° K
[CAB]
I = 2·0 x 10⁻³ M
II = 2·5 x 10⁻³ M
III = 3·0 x 10⁻³ M
IV = 3·5 x 10⁻³ M
Log (a-x)
1·50
1·10
0·70
0·30
0
10
20
30
40
50
60
TIME IN MIN.
IV
III
II
I

FIG. 2·2·1

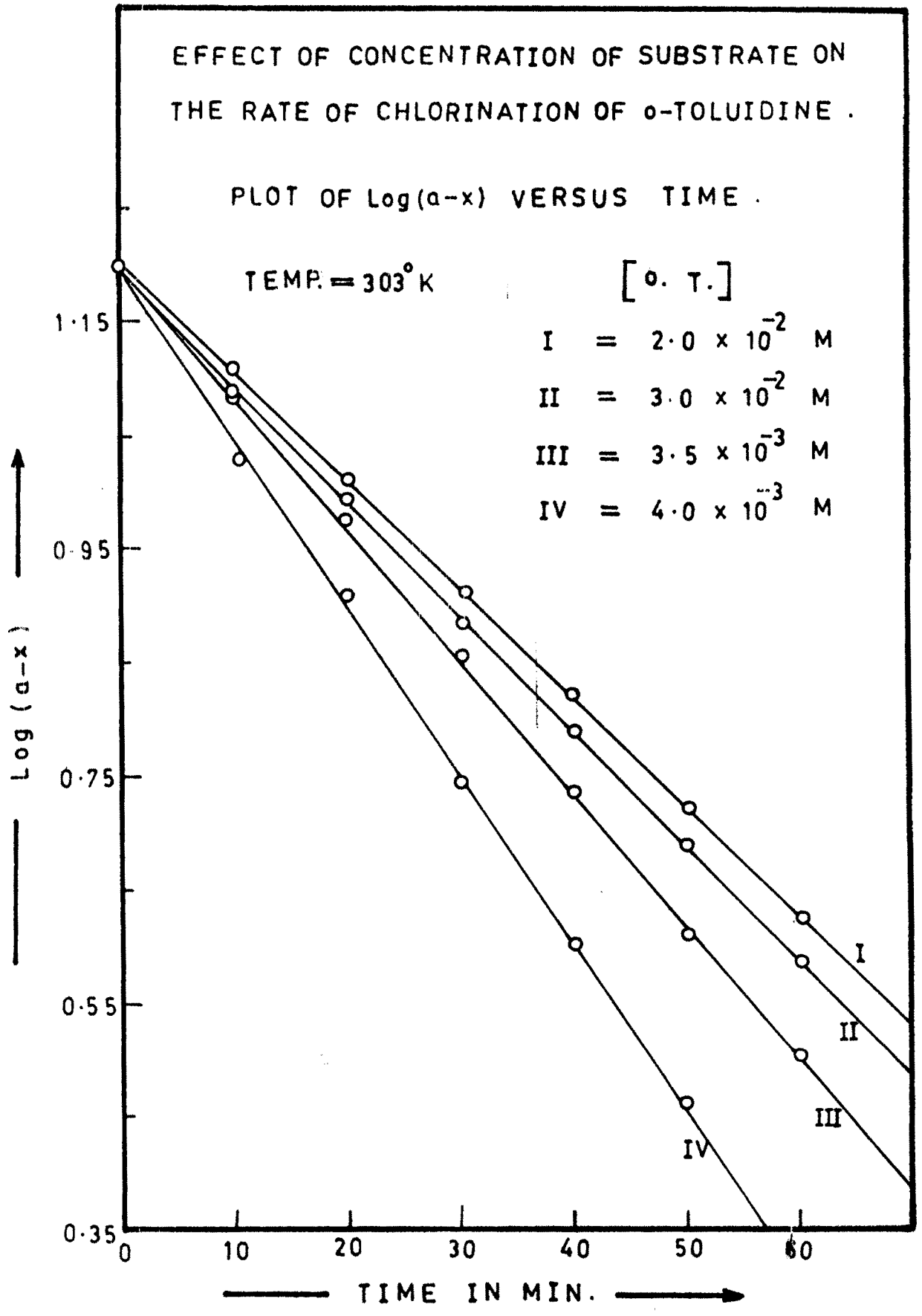
EFFECT OF CONCENTRATION OF SUBSTRATE ON
THE RATE OF CHLORINATION OF o-TOLUIDINE .
PLOT OF Log(a-x) VERSUS TIME .
TEMP. = 303° K
[o. T.]
I = 2·0 x 10⁻² M
II = 3·0 x 10⁻² M
III = 3·5 x 10⁻³ M
IV = 4·0 x 10⁻³ M
Log (a-x)
1·15
0·95
0·75
0·55
0·35
0
10
20
30
40
50
60
TIME IN MIN.
I
II
III
IV

FIG. 2·1·2

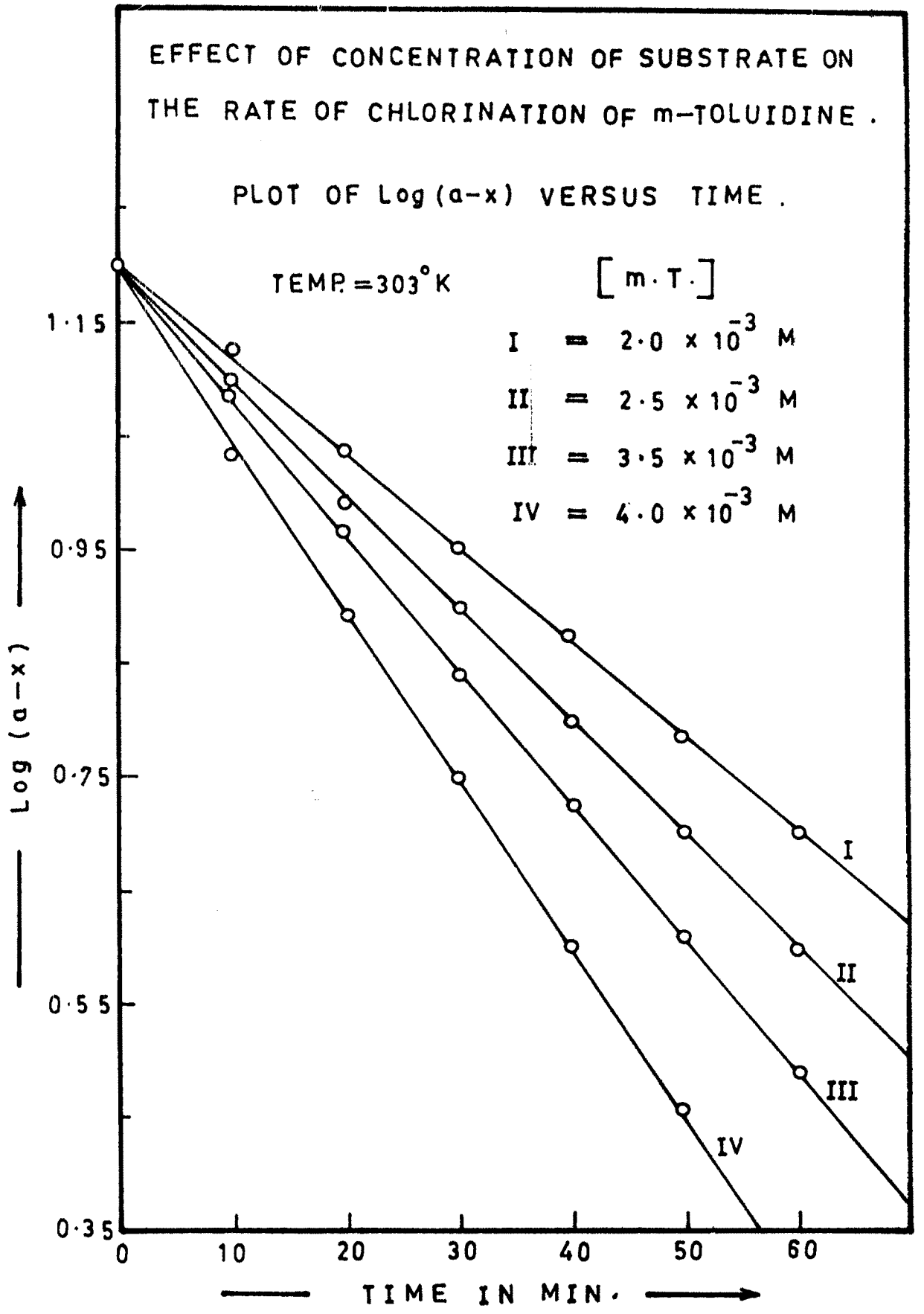
EFFECT OF CONCENTRATION OF SUBSTRATE ON
THE RATE OF CHLORINATION OF m-TOLUIDINE .
PLOT OF Log (a-x) VERSUS TIME .
TEMP. =303°K
[m.T.]
I = 2·0 x 10⁻³ M
II = 2·5 x 10⁻³ M
III = 3·5 x 10⁻³ M
IV = 4·0 x 10⁻³ M
Log (a-x)
1·15
0·95
0·75
0·55
0·35
0
10
20
30
40
50
60
TIME IN MIN.
I
II
III
IV

FIG. 2·2·2