

## CHAPTER V

### RESULTS AND CALCULATIONS



#### 5.1 Preliminary works

5.1.1 Volumetric titration Percentage oxidation at various quantities of furfural and its relation with standing time were obtained and shown in Tables 5.1.1.1 and 5.1.1.2

#### 5.1.2 Viscometry

5.1.2.1 Effect of ferric chloride hexahydrate on one reactant at 25°C When 0.2M furfural was mixed with 5%  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  at  $25 \pm 0.5^\circ\text{C}$ , a clear solution was obtained without any other observable changes although it had been left standing upto 18 hours. However, with 0.7M phenol instead of furfural, a violet solution of a complex nature instantly occurred and yielding some deep brown precipitates after 18 hour-standing. Because of the complex formation, the ferric chloride could not be used as a catalyst in the kinetic study of the phenol-furfural reaction. Hydrochloric acid was the next choice from the selection list of the catalysts (๑๑).

5.1.2.2 Effect of hydrochloric acid on one reactant and both reactants at 25°C Using concentrated hydrochloric acid in the same manner as in 5.1.2.1, it was found that at the beginning

Table 5.1.1.1

Relation between milligrams of furfural and % furfural oxidized

cm <sup>3</sup> . of 2.002% furfural	mg. furfural	% furfural oxidized
0.2	4	100.00
0.5	10	86.91
1.0	20	83.92
1.5	30	78.91
2.0	40	75.67
2.5	50	72.33

Table 5.1.1.2

Relation between standing time and ~~milli~~volume of sodium thiosulfate, using 4 mg. of furfural

Standing time, min	volume of S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , cm <sup>3</sup>
10	8.80
15	8.75
20	8.80
25	8.78
30	8.80
35	8.80

of mixing the solution containing both phenol and furfural remained colourless but that of furfural changed into pale brown one while that of phenol remained colourless after 18 hour-standing. Consequently, more details about the effect of hydrochloric acid on furfural and the mixture of both furfural and phenol were studied and given in Tables 5.1.2.2.1 and 5.1.2.2.2

5.1.2.3 Kinetic data for the furfural-hydrochloric acid reaction In accordance with 4.3.1.2.4, kinetic data for the furfural-hydrochloric acid reaction at  $30.4 \pm 0.1^{\circ}\text{C}$  was obtained and given in Tables 5.1.2.3.1 and 5.1.2.3.2

5.1.2.4 Study of the phenol-furfural reaction at various temperatures With reference to 4.3.1.2.5, viscosity data for the phenol-furfural reaction in the presence of conc. HCl at temperatures 30, 40 and  $50^{\circ}\text{C}$  were obtained and given in Tables 5.1.2.4.1, 5.1.2.4.2 and 5.1.2.4.3 respectively.

5.1.3 Spectrophotometry Spectra of products, reactants, both in absence and in presence of conc. HCl, are shown in Figures 5.1.3.1, 5.1.3.2, 5.1.3.3 and 5.1.3.4. The reproducibility check in the presence of phenol and furfural and reproducibility check of furfural-conc. HCl system were also made. The results are shown in Tables 5.1.3.1 and 5.1.3.2

Effect of hydrochloric acid on the phenol-furfural mixture was studied spectrophotometrically and its spectrum is shown in Figure 5.1.3.5. After these, the UV absorption in the kinetic study of the phenol-furfural reaction in the presence of conc. HCl was

Table 5.1.2.2.1

Effect of hydrochloric acid on furfural at 25°C

Time, min	Color of solution
0	Colorless
30	Colorless
60	Pale pink
90	Pink
120	Pink
150	Deep pink
180	Deep pink
18 hrs.	Pale brown

Table 5.1.2.2.2

Effect of hydrochloric acid on both reactants at 25°C

ml HCl \ Time, min	0.0	0.2	0.4	0.6	0.8	1.0	2.0	3.0
0	CL	CL	CL	CL	CL	CL	CL	CL
30	"	"	"	"	"	"	"	"
60	"	"	"	"	"	"	BK	BK
90	"	W	W	W	W	W	"	"
120	"	"	"	PB	PB	"	"	"
150	"	"	"	"	"	"	"	"
180	"	"	"	B	B	BK	"	"
18 hrs	"	PB	BN	BN	BK	"	"	"

CL = Colorless, W = White, PB = Pale blue, B = Blue, BK = Black, BN = Brown

Table 5.1.2.3.1

Kinetic data for the reaction between furfural and concentrated hydrochloric acid

Reaction time, min	Efflux time, sec		
	First reading	Second reading	Average
15	257.1	257.3	257.2
30	257.1	256.9	257.0
75	256.9	256.7	256.8
105	257.0	256.8	256.9
150	256.9	256.9	256.9
18 hrs.	256.7	257.3	257.0

Table 5.1.2.3.2

Efflux time of doubly distilled water

Reading	Efflux time, sec
1	254.0
2	254.0
Average	254.0

Table 5.1.2.4.1

Efflux time of the reaction solution at 30°C

Reaction time, min	Efflux time, sec		
	First reading	Second reading	Average
15	255.6	255.5	255.55
30	-	-	-
45	-	-	-
60	256.0	256.1	256.15
75	-	-	-
90	-	-	-
105	-	-	-
120	256.0	255.6	255.8
150	-	-	-
180	256.5	256.4	256.45
20 hrs.	256.1	255.7	255.9

Table 5.1.2.4.2

Efflux time of the reaction solution at 40°C

Reaction time, min	Efflux time, sec		
	First reading	Second reading	Average
15	-	-	-
30	255.9	256.0	255.95
45	-	-	-
60	255.9	255.7	255.8
75	-	-	-
90	-	-	-
105	-	-	-
120	-	-	-
150	-	-	-
180	256.0	256.4	256.2
20 hrs.	255.0	255.2	255.1

Table 5.1,2.4.3

Efflux time of the reaction solution at 50°C

Reaction time, min	Efflux time, sec		
	First reading	Second reading	Average
15	254.1	254.4	254.25
30	-	-	-
45	-	-	-
60	255.6	256.2	255.8
75	-	-	-
90	-	-	-
105	-	-	-
120	-	-	-
150	-	-	-
180	254.3	253.8	254.05
20 hrs.	256.1	256.7	256.4



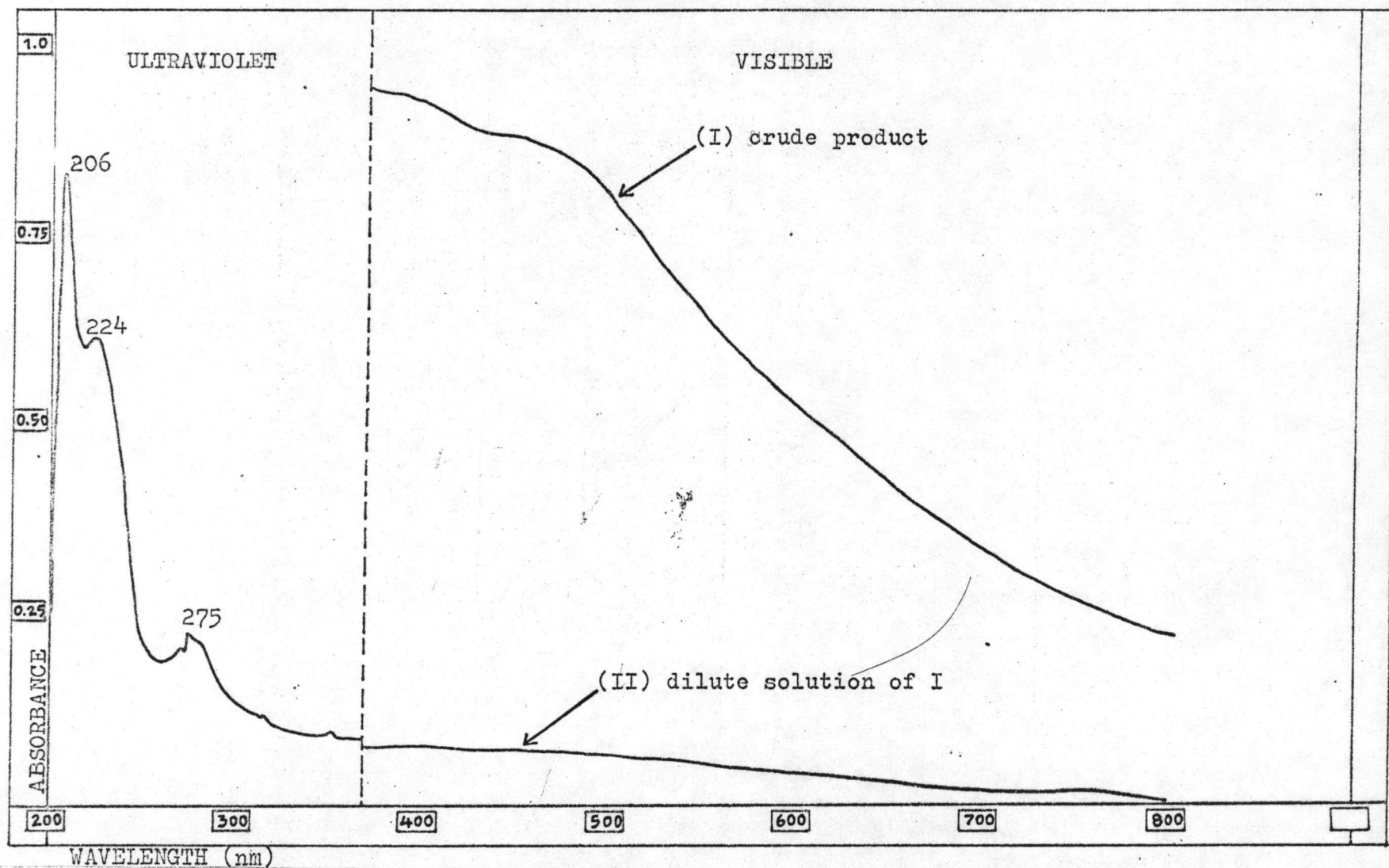


Fig.5.1.3.1 The ultra violet and visible spectra of the reaction product in ethyl alcohol

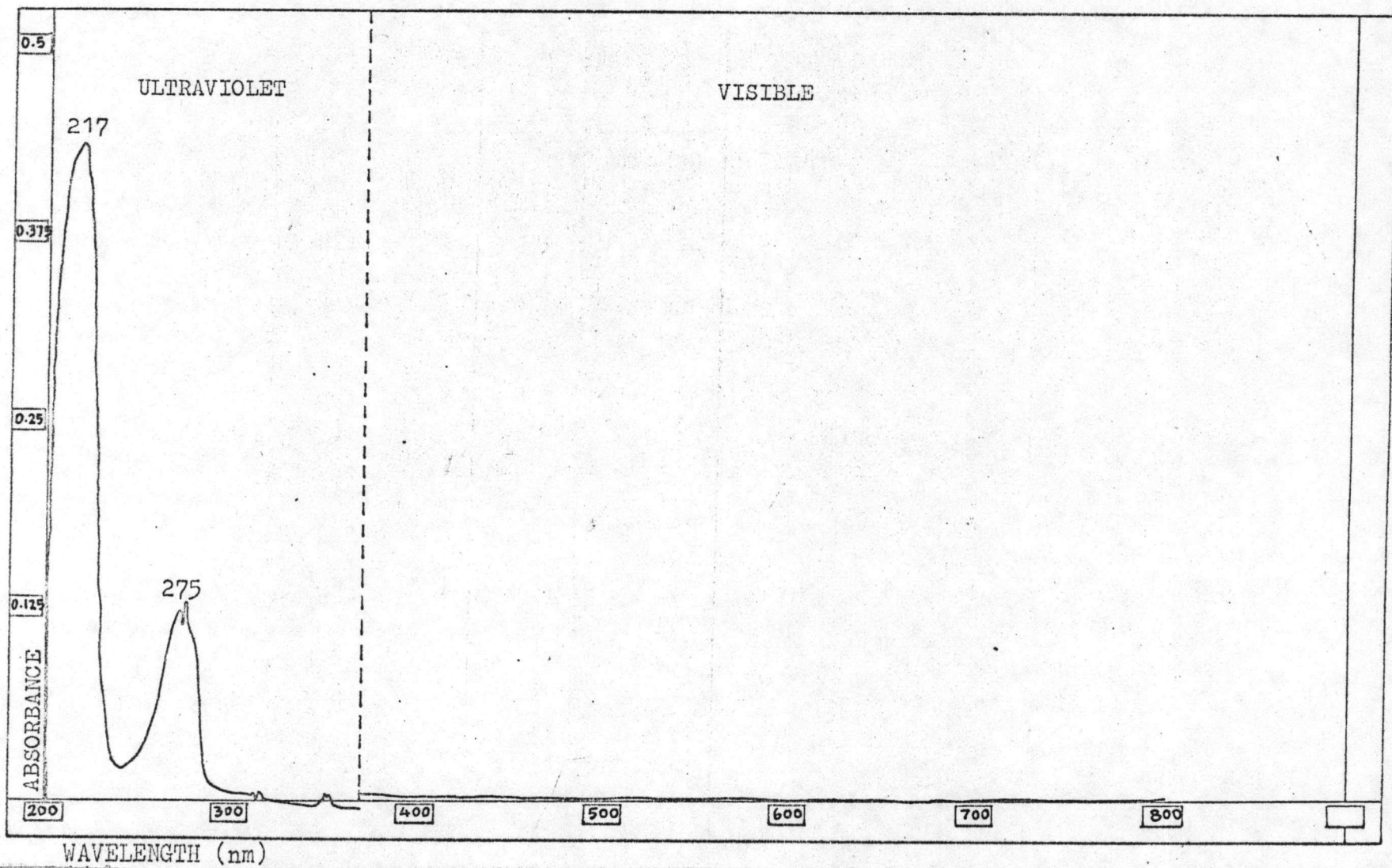


Fig.5.1.3.2 The ultra violet and visible spectra of phenol in ethyl alcohol

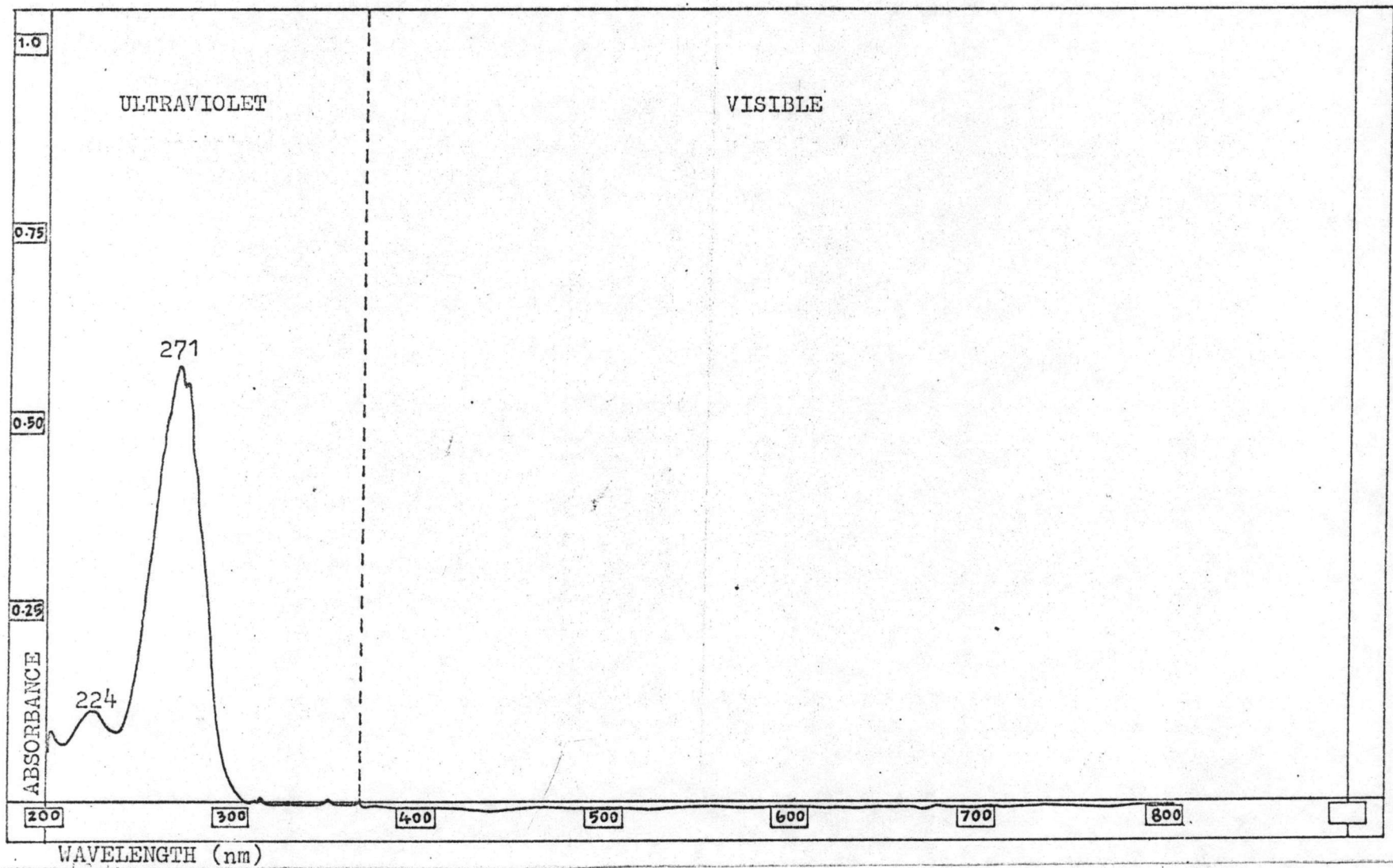


Fig.5.1.3.3 The ultra violet and visible spectra of furfural in ethyl alcohol

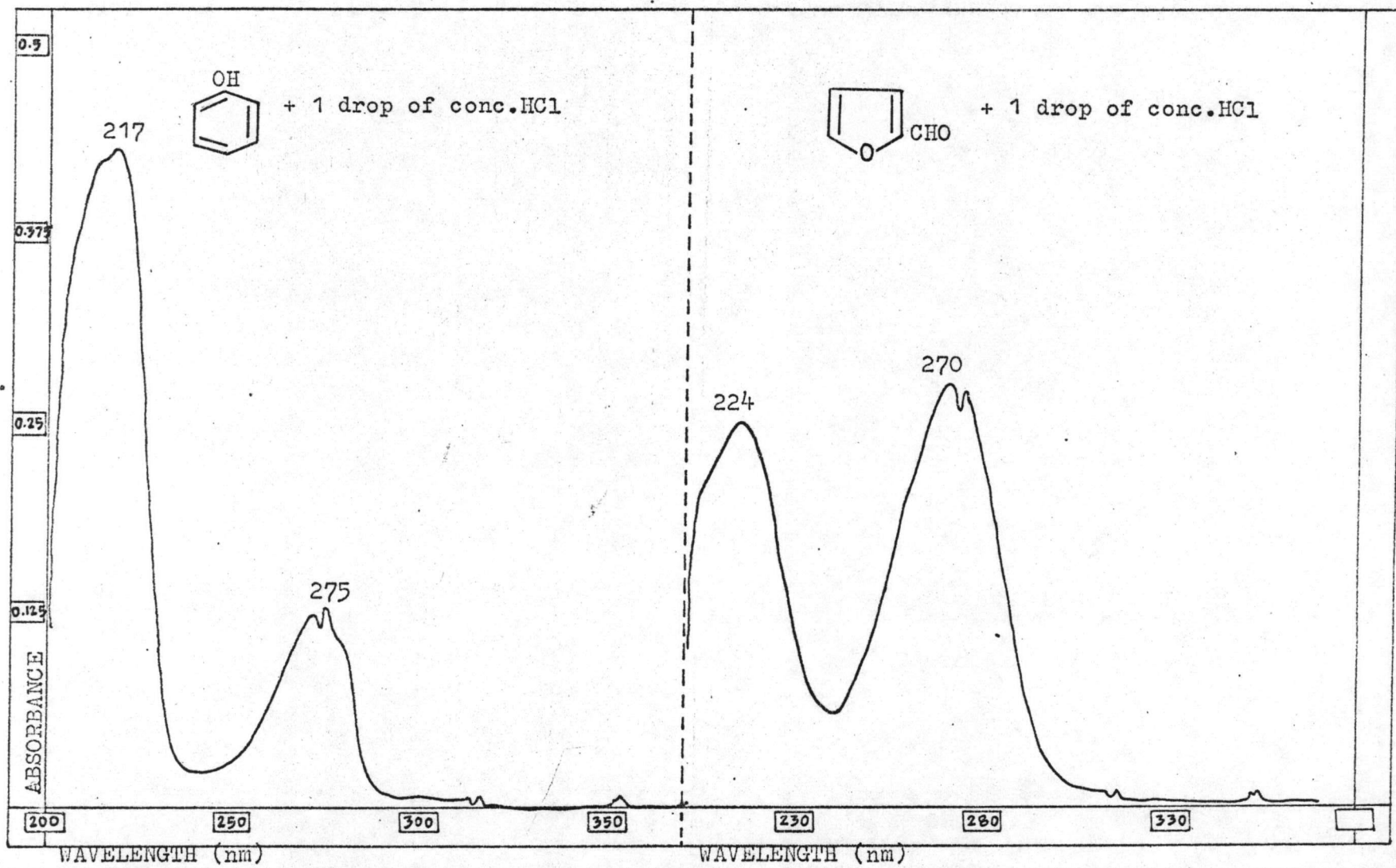


Fig.5.1.3.4 The ultra violet spectra of reactants in the presence of conc.HCl

Table 5.1.3.1

Variation of reaction time with absorbance of phenol-furfural mixture at wavelengths of 206, 217, 224, 270, and 275 nm

Reaction time, min	A <sub>206</sub>	A <sub>217</sub>	A <sub>224</sub>	A <sub>270</sub>	A <sub>275</sub>
5	0.310	0.399	0.344	0.737	0.693
15	0.313	0.406	0.339	0.735	0.703
30	0.313	0.409	0.342	0.740	0.702
45	0.307	0.406	0.342	0.734	0.699
60	0.309	0.408	0.341	0.738	0.701
75	0.313	0.411	0.342	0.738	0.702
90	0.326	0.423	0.354	0.738	0.701
105	0.314	0.415	0.348	0.744	0.704
120	0.313	0.415	0.344	0.744	0.705
135	0.319	0.416	0.347	0.743	0.704
150	0.318	0.418	0.347	0.743	0.706
165	0.335	0.428	0.355	0.743	0.706
180	0.335	0.428	0.355	0.747	0.706

A = Absorbance

Table 5.1.3.2

Variation of reaction time with absorbance of furfural-conc.HCl system at wavelengths of 215, 224, and 270 nm

Reaction time, min	A <sub>215</sub>	A <sub>224</sub>	A <sub>270</sub>
5	0.228	0.200	0.455
15	0.229	0.203	0.460
30	0.229	0.204	0.463
45	0.227	0.203	0.463
60	0.226	0.202	0.464
75	0.225	0.200	0.466
90	0.224	0.202	0.466
105	0.223	0.201	0.465
120	0.223	0.200	0.467
135	0.222	0.200	0.467
150	0.221	0.198	0.467
165	0.220	0.198	0.468
180	0.220	0.199	0.468

A = Absorbance

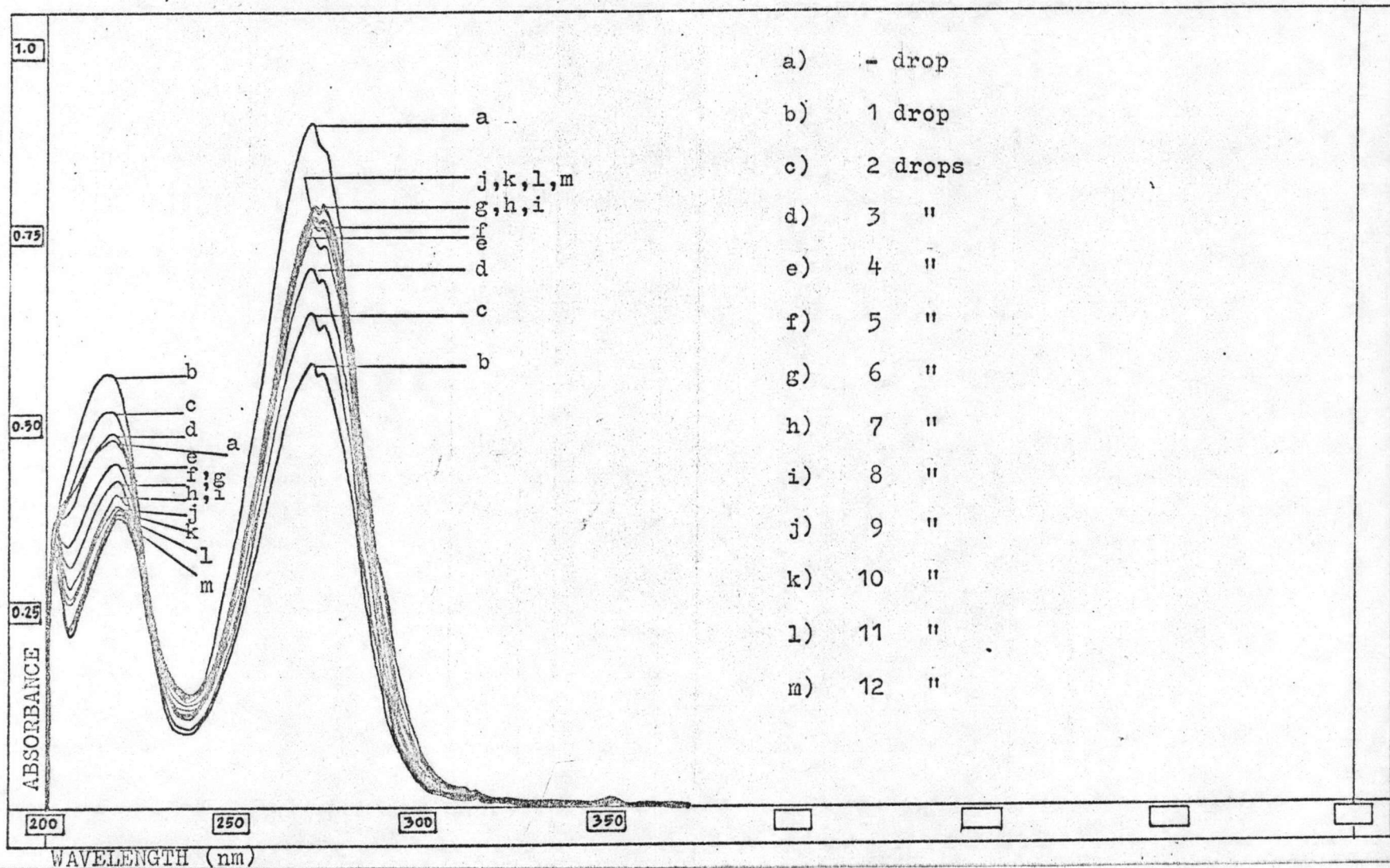


Fig.5.1.3.5 The variation of absorbance in the ultra violet region with various quantity of conc.HCl for the phenol-furfural mixture

obtained and present in Figure 5.1.3.6 and their visible absorbance at several concentrations were recorded and shown in Figure 5.1.3.7

Variation of absorbance with reaction time of phenol-furfural mixture in the presence of 1 and 3 cm<sup>3</sup> of conc. HCl at wavelengths of 217 and 271 nm is shown in Figures 5.1.3.8 and 5.1.3.9 and Tables 5.1.3.4 and 5.1.3.5.

## 5.2 Kinetic study

Kinetic data for the phenol-furfural reaction with conc. HCl as a catalyst at various conditions are given in Tables 5.2.1, 5.2.2, 5.2.3, 5.2.4, 5.2.5, 5.2.6, 5.2.7 and 5.2.8 and Figures 5.2.1, 5.2.2, 5.2.3, 5.2.4, 5.2.5, 5.2.6, 5.2.7 and 5.2.8 respectively.

The data in the above Tables and Figures was used in plotting graphs of absorbance at wavelength of 635 nm ( $A_{635}$ ) against time. All of the resulted graphs are linear as shown in Figures 5.2.9, 5.2.10 and 5.2.11



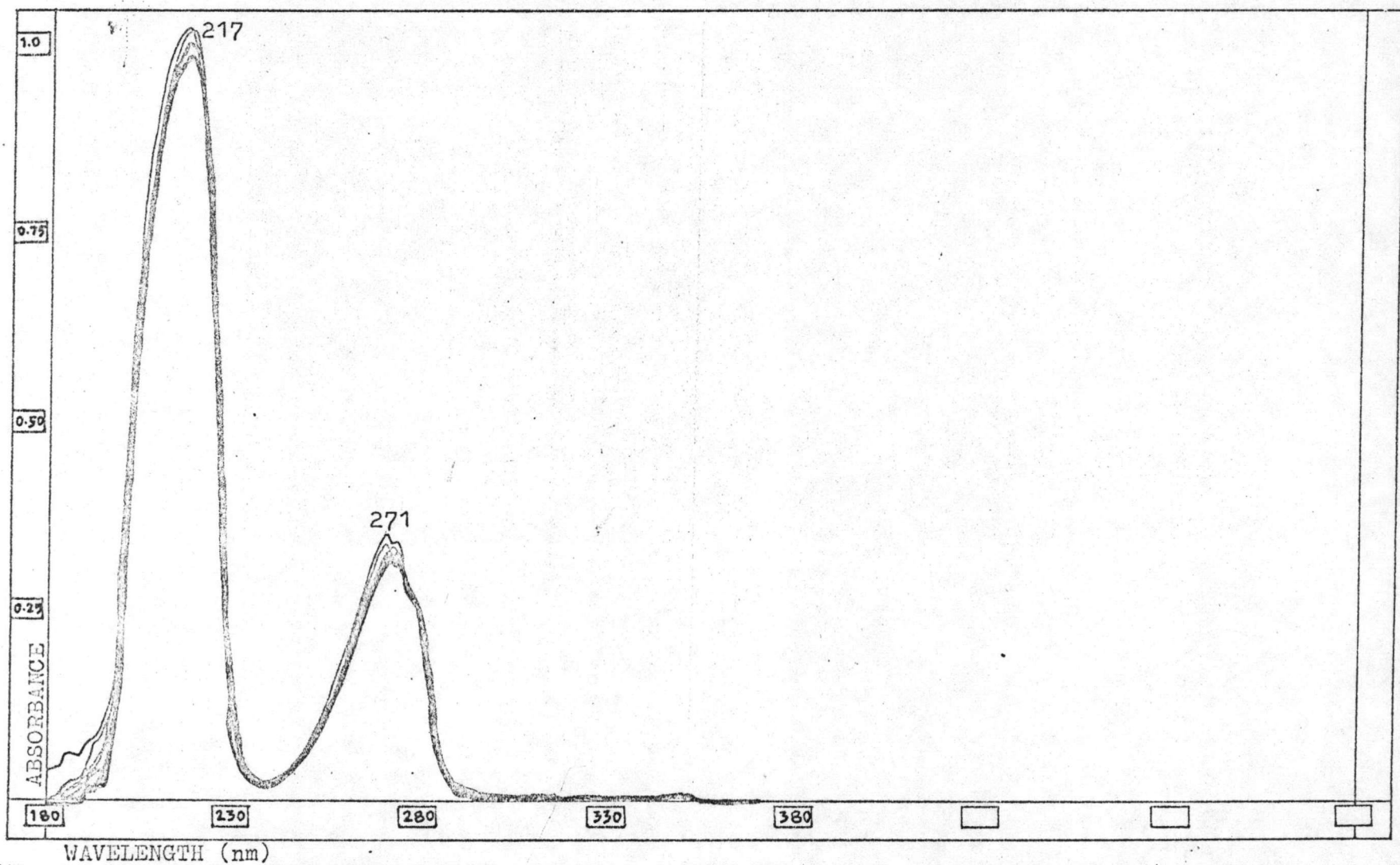


Fig.5.1.3.6 The variation of ultra violet absorbance with reaction time for the phenol-furfural reaction in the presence of conc.HCl

Table 5.1.3.3

Variation of reaction time with ultra-violet absorbance in phenol-furfural reaction with conc HCl as a catalyst at wavelengths of 217 and 271 nm

Reaction time, min	A <sub>217</sub>	A <sub>271</sub>
2	0.993	0.322
30	0.974	0.311
60	0.990	0.319
90	0.978	0.319
120	1.014	0.325
150	0.973	0.312
180	0.993	0.323
240	0.980	0.309
360	1.014	0.334
22 hrs.	1.076	0.335

A = Absorbance

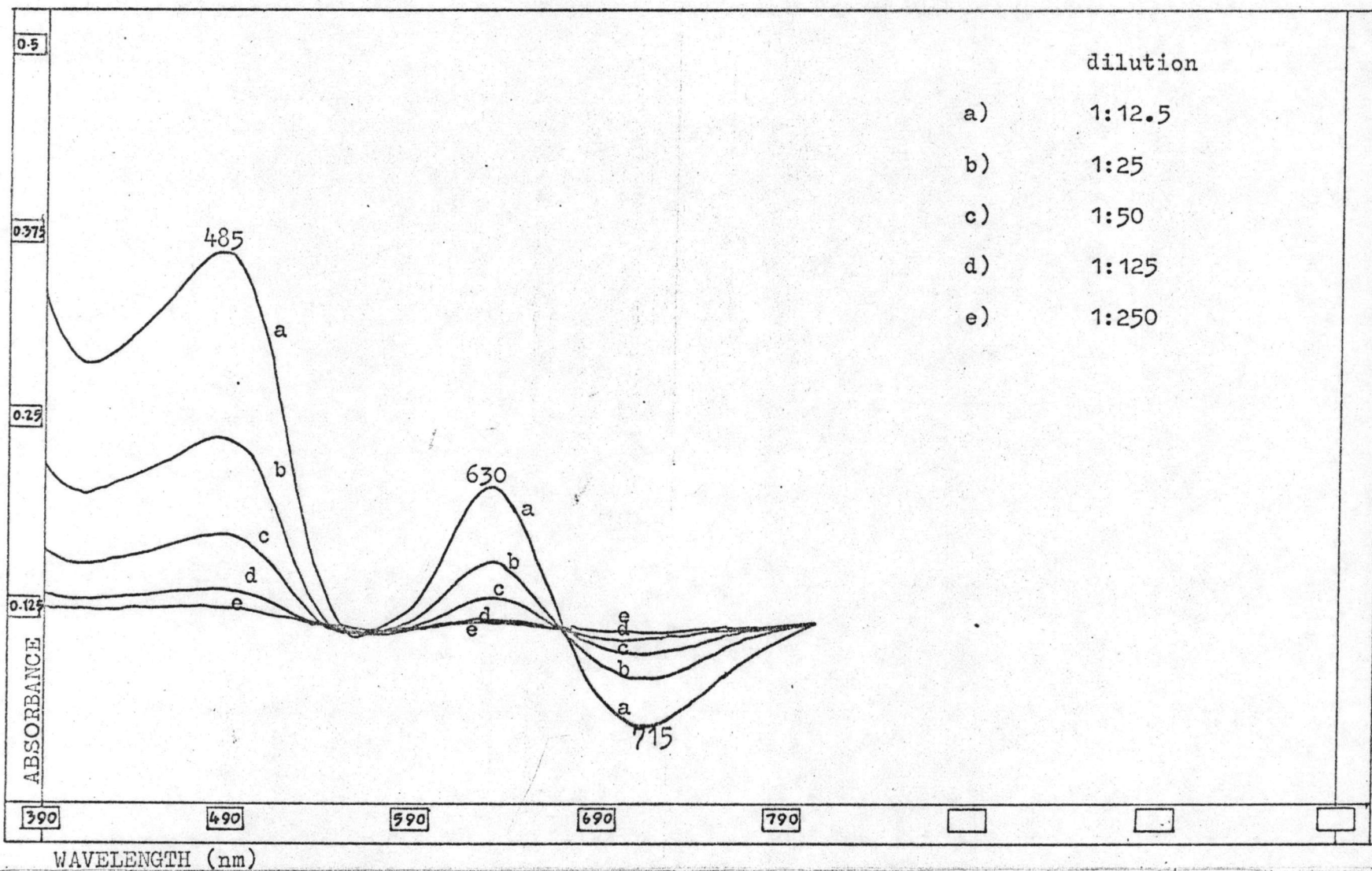


Fig.5.1.3.7 The visible absorbance of the reaction product at various concentrations.

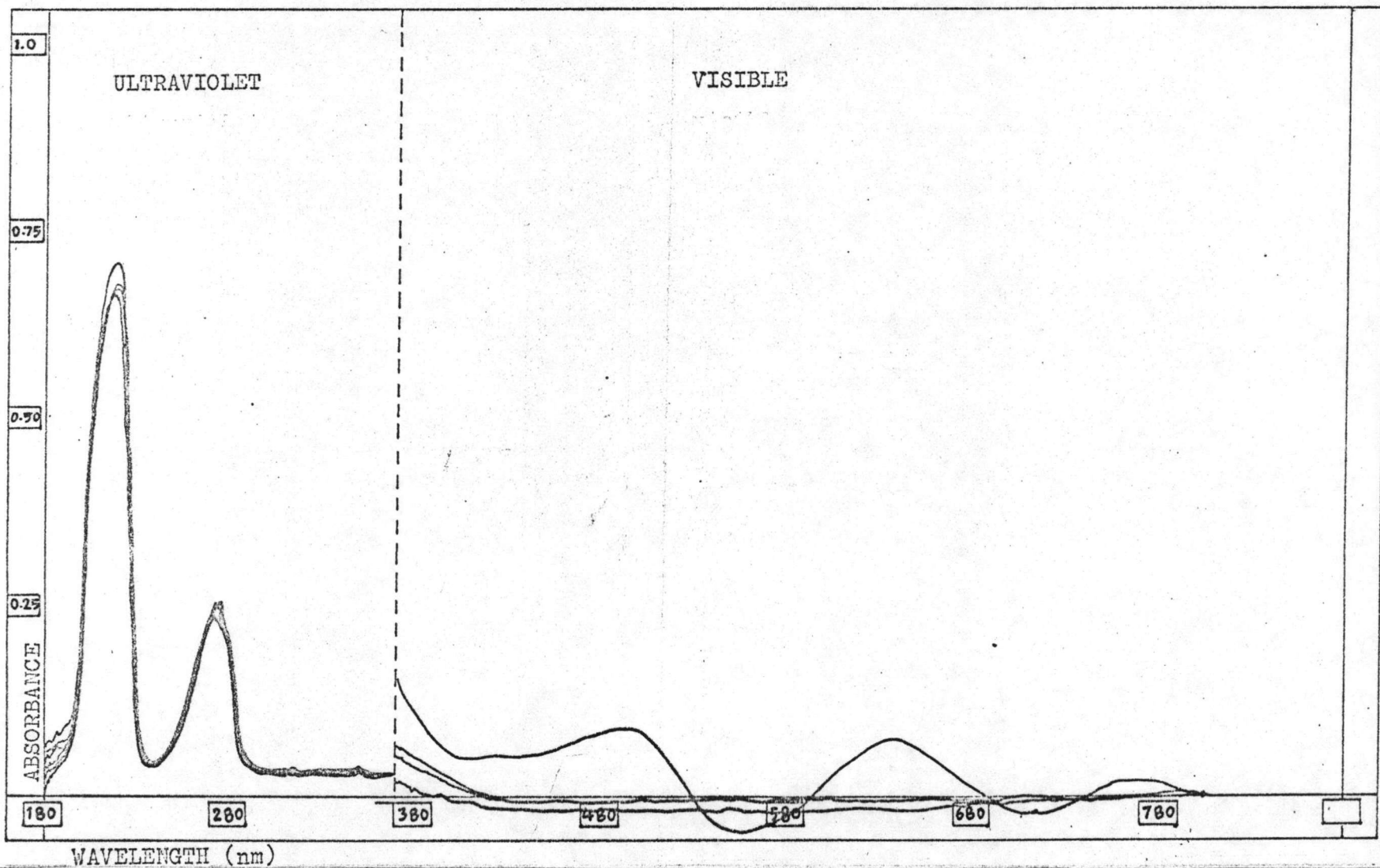


Fig.5.1.3.8 The variation of absorbance with reaction time for the phenol-furfural reaction in the presence of 1 cm<sup>3</sup> conc.HCl

Table 5.1.3.4

Variation of absorbance with reaction time in phenol-furfural mixture in the presence of 1 cm<sup>3</sup> conc HCl at wavelengths of 217 and 271 nm

Reaction time, min	A <sub>217</sub>	A <sub>271</sub>
2	0.671	0.245
60	0.698	0.254
120	0.698	0.250
180	0.663	0.242
240	0.654	0.240
22 hrs.	0.698	0.247

A = Absorbance

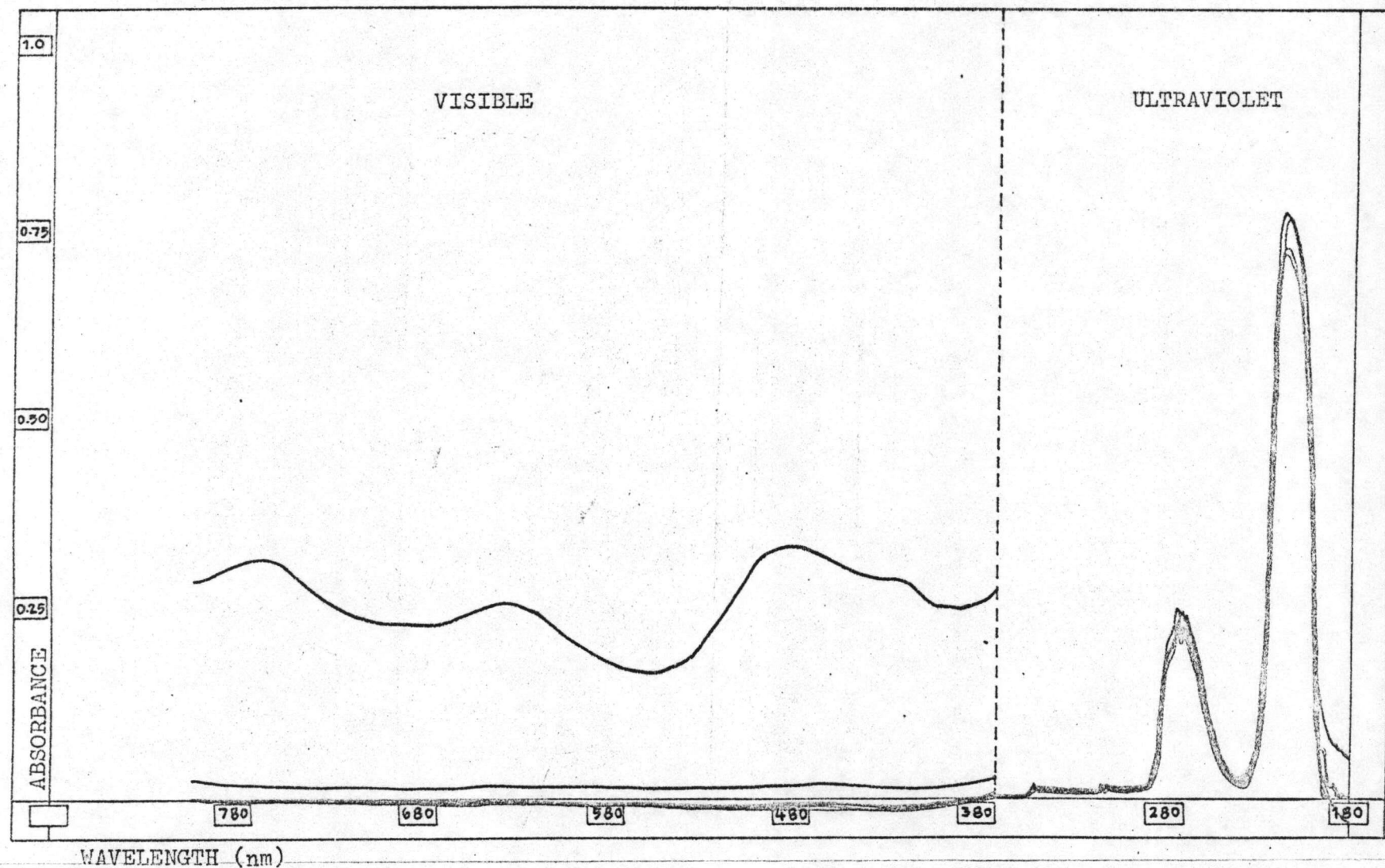


Fig.5.1.3.9 The variation of absorbance with reaction time for the phenol-furfural reaction in the presence of 3 cm<sup>3</sup> conc.HCl

Table 5.1.3.5

Variation of absorbance with reaction time in phenol-furfural mixture in the presence of  $3\text{cm}^3$  conc HCl at wavelengths of 217 and 271 nm

Reaction time, min	$A_{217}$	$A_{271}$
2	0.710	0.211
60	0.715	0.213
120	0.764	0.237
180	0.709	0.220
240	0.717	0.218
22 hrs.	0.761	0.238

A = Absorbance

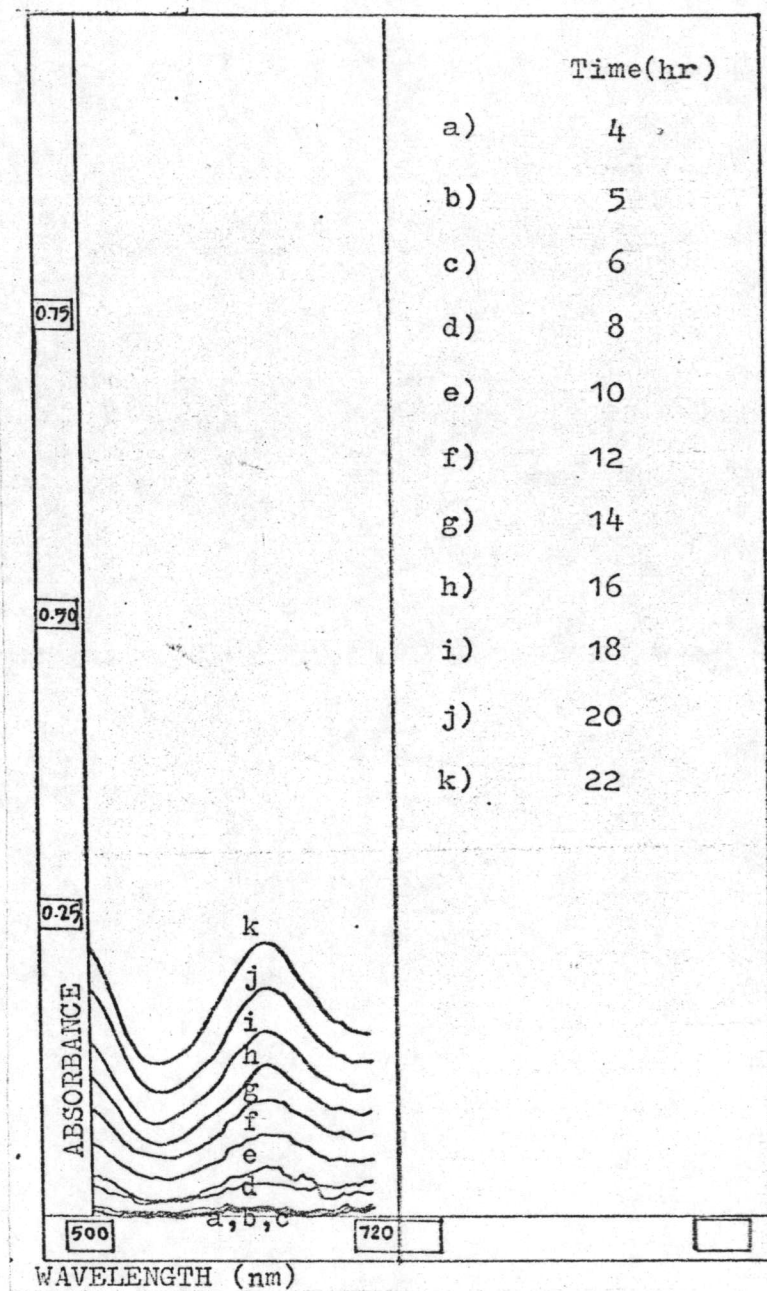


Fig.5.1.3.10 The variation of visible absorbance with reaction time for the phenol-furfural reaction in the presence of conc.HCl



Table 5.1.3.6

The variation of reaction time with absorbance at wavelength of 635 nm ( $A_{635}$ ) for the phenol-furfural reaction at 50°C in the presence of conc.HCl

Reaction time, hr	$A_{635}$
4	0.000
5	0.000
6	0.000
8	0.018
10	0.040
12	0.065
14	0.095
16	0.122
18	0.150
20	0.188
22	0.225

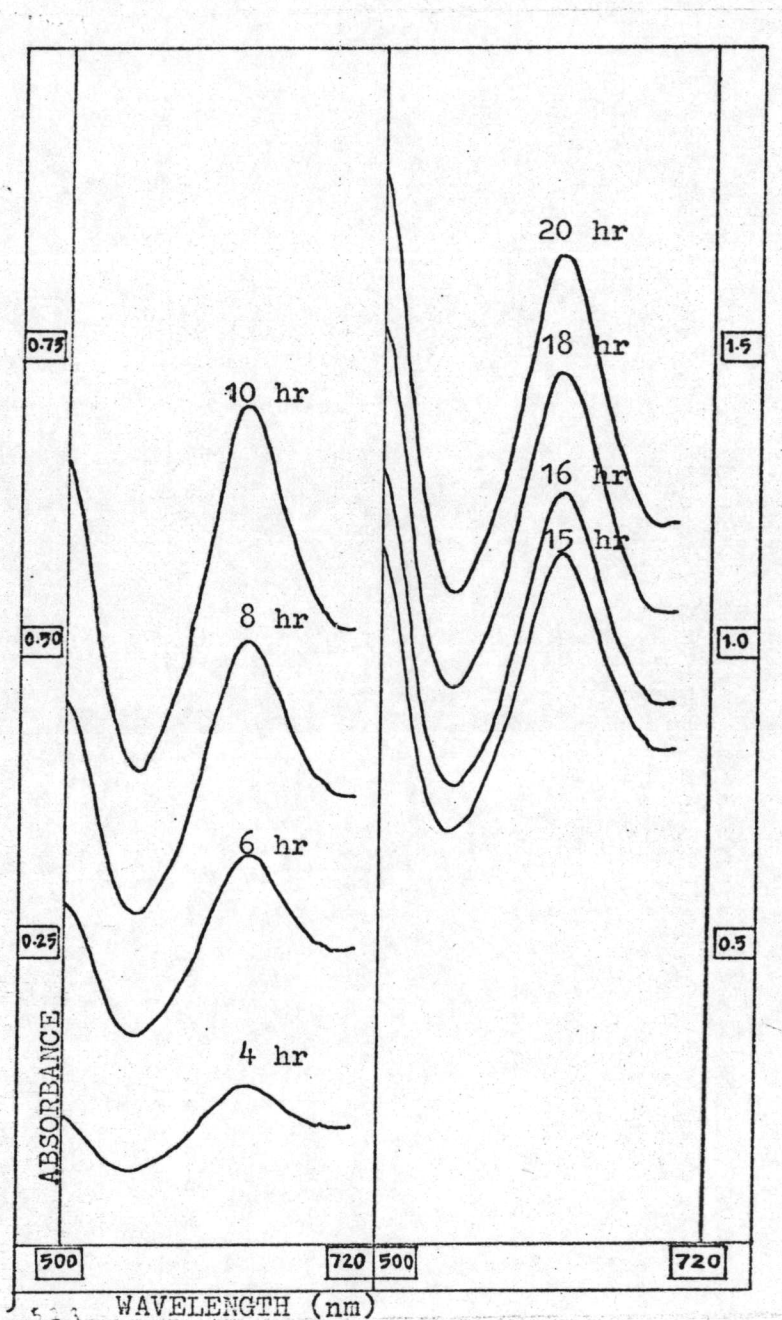


Fig.5.2.1 The variation of reaction time with absorbance at wavelength of 635 nm for the reaction between 0.7M phenol ( $45 \text{ cm}^3$ ) and 0.2M furfural ( $15 \text{ cm}^3$ ) in the presence of conc.HCl ( $3 \text{ cm}^3$ ) at  $53^\circ \text{C}$

Table 5.2.1

The variation of reaction time with absorbance at wavelength of 635 nm ( $A_{635}$ ) for the reaction between 0.7M phenol ( $45\text{cm}^3$ ) and 0.2M furfural ( $15\text{cm}^3$ ) in the presence of conc.HCl ( $3\text{cm}^3$ ) at  $53^\circ\text{C}$

Reaction time, hr	$A_{635}$	$X = 2A_{635}$
4	0.138	0.276
6	0.335	0.670
8	0.515	1.030
10	0.720	1.440
15	1.160	2.320
16	1.265	2.530
18	1.482	2.964
20	1.710	3.420
		$k = 0.193 \text{ hr}^{-1}$

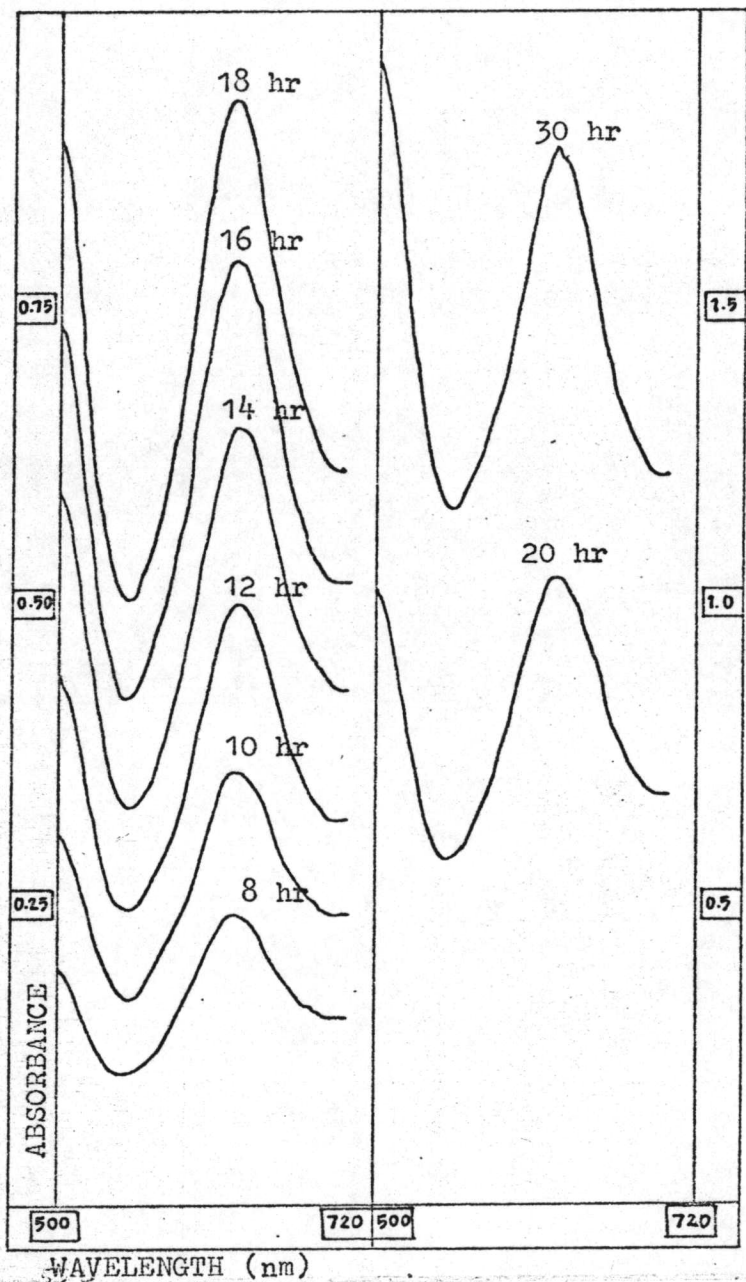


Fig.5.2.2 The variation of reaction time with absorbance at wavelength of 635 nm for the reaction between 0.7M phenol ( $45 \text{ cm}^3$ ) and 0.2M furfural ( $15 \text{ cm}^3$ ) in the presence of conc.HCl ( $3 \text{ cm}^3$ ) at  $50^\circ \text{C}$

Table 5.2.2

The variation of reaction time with absorbance at wavelength of 635 nm ( $A_{635}$ ) for the reaction between 0.7M phenol ( $45 \text{ cm}^3$ ) and 0.2M furfural ( $15 \text{ cm}^3$ ) in the presence of conc.HCl ( $3 \text{ cm}^3$ ) at  $50^\circ \text{C}$

Reaction time, hr	$A_{635}$	$X = 2A_{635}$
8	0.240	0.480
10	0.365	0.730
12	0.502	1.004
14	0.658	1.316
16	0.810	1.620
18	0.950	1.900
20	1.118	2.236
		$k = 0.147 \text{ hr}^{-1}$

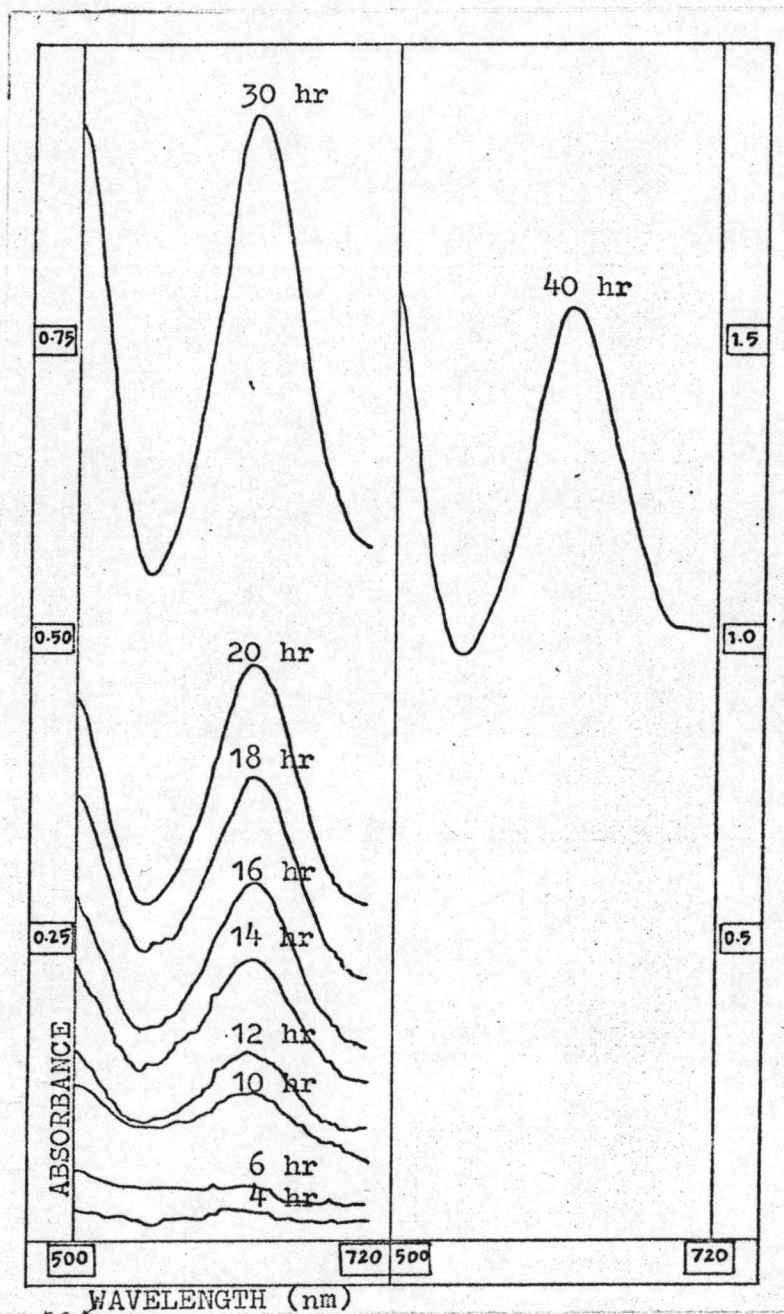


Fig.5.2.3 The variation of reaction time with absorbance at wavelength of 635 nm for the reaction between 0.7M phenol ( $45 \text{ cm}^3$ ) and 0.2M furfural ( $15 \text{ cm}^3$ ) in the presence of conc.HCl ( $3 \text{ cm}^3$ ) at  $45^\circ \text{C}$

Table 5.2.3

The variation of reaction time with absorbance at wavelength of 635 nm ( $A_{635}$ ) for the reaction between 0.7M phenol ( $45\text{cm}^3$ ) and 0.2M furfural ( $15\text{cm}^3$ ) in the presence of conc.HCl ( $3\text{cm}^3$ ) at  $45^\circ\text{C}$

Reaction time, hr	$A_{635}$	$X = 2A_{635}$
4	0.020	0.040
6	0.040	0.080
10	0.110	0.220
12	0.157	0.314
14	0.235	0.470
16	0.300	0.600
18	0.368	0.772
20	0.480	0.960
		$k = 0.057 \text{ hr}^{-1}$

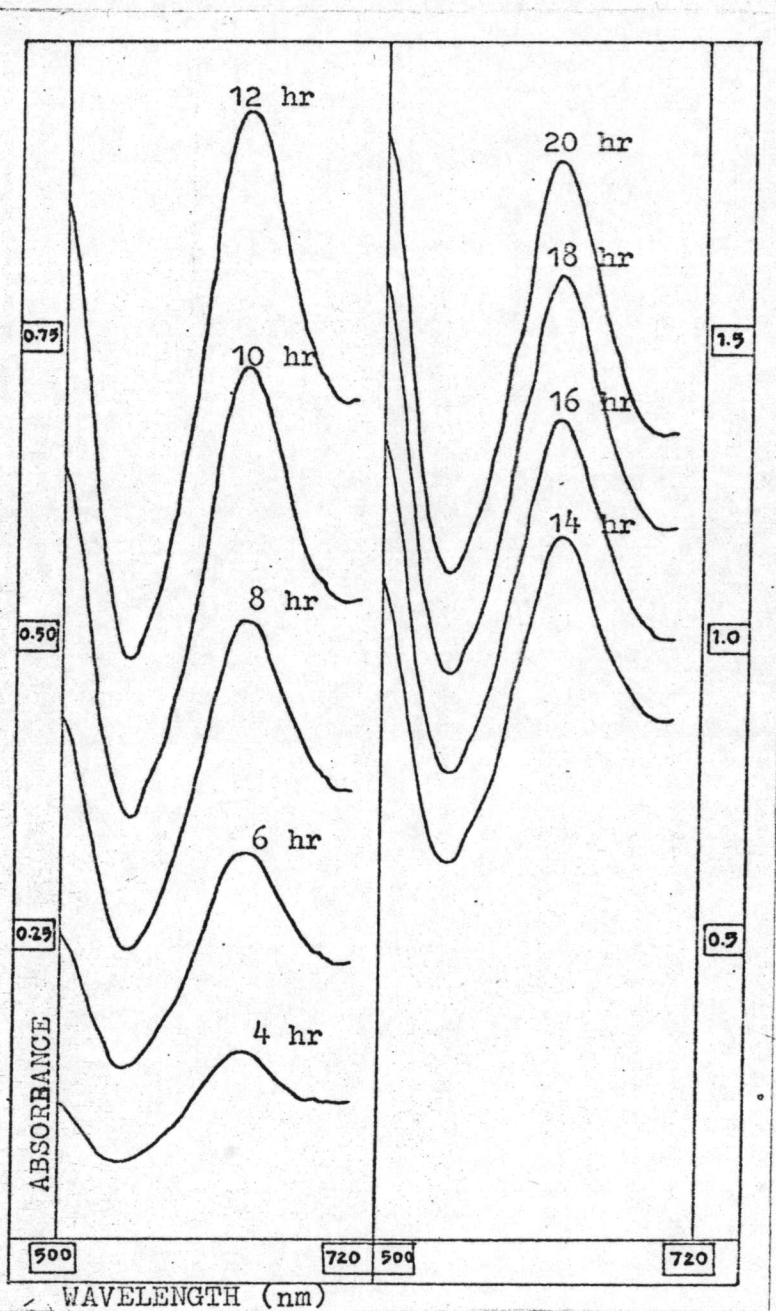


Fig.5.2.4 The variation of reaction time with absorbance at wavelength of 635 nm for the reaction between 0.7M phenol ( $45 \text{ cm}^3$ ) and 0.2M furfural ( $15 \text{ cm}^3$ ) at  $50^\circ \text{C}$  in the presence of  $6 \text{ cm}^3$  conc.HCl



Table 5.2.4

The variation of reaction time with absorbance at wavelength of 635 nm ( $A_{635}$ ) for the reaction between 0.7M phenol ( $45\text{cm}^3$ ) and 0.2M furfural ( $15\text{cm}^3$ ) at  $50^\circ\text{C}$  in the presence of  $6\text{cm}^3$  conc.HCl

Reaction time, hr	$A_{635}$	$X = 2A_{635}$
4	0.158	0.316
6	0.324	0.648
8	0.521	1.042
10	0.738	1.476
12	0.970	1.940
14	1.180	2.360
16	1.398	2.796
18	1.640	3.280
20	1.845	3.690
		$k = 0.215 \text{ hr}^{-1}$

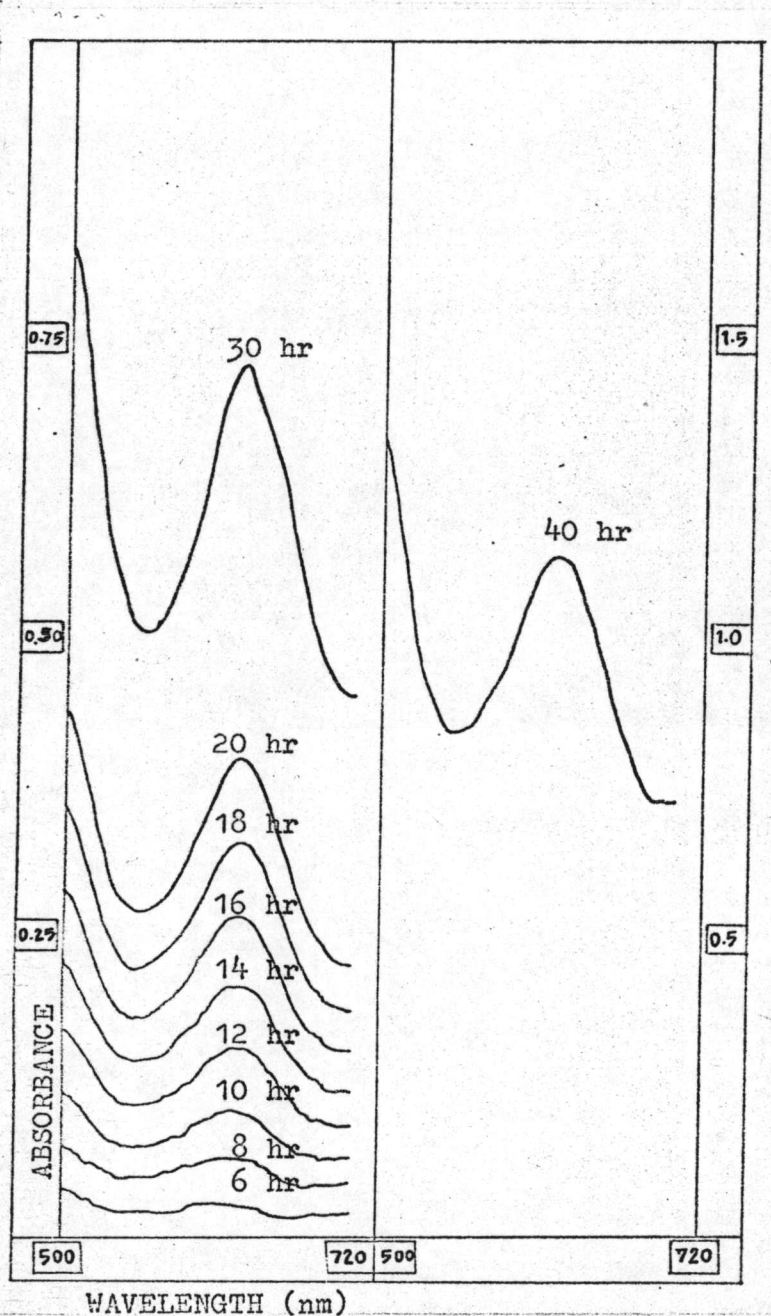


Fig.5.2.5 The variation of reaction time with absorbance at wavelength of 635 nm for the reaction between 0.7M phenol ( $45 \text{ cm}^3$ ) and 0.2M furfural ( $15 \text{ cm}^3$ ) at  $50^\circ \text{C}$  in the presence of  $1 \text{ cm}^3$  conc.HCl

Table 5.2.5

The variation of reaction time with absorbance at wavelength of 635 nm ( $A_{635}$ ) for the reaction between 0.7M phenol ( $45\text{ cm}^3$ ) and 0.2M furfural ( $15\text{ cm}^3$ ) at  $50^\circ\text{C}$  in the presence of  $1\text{ cm}^3$  conc.HCl

Reaction time, hr	$A_{635}$	$X = 2A_{635}$
6	0.035	0.070
8	0.070	0.140
10	0.112	0.224
12	0.166	0.332
14	0.220	0.440
16	0.278	0.556
18	0.340	0.680
20	0.408	0.816
		$k = 0.054\text{ hr}^{-1}$

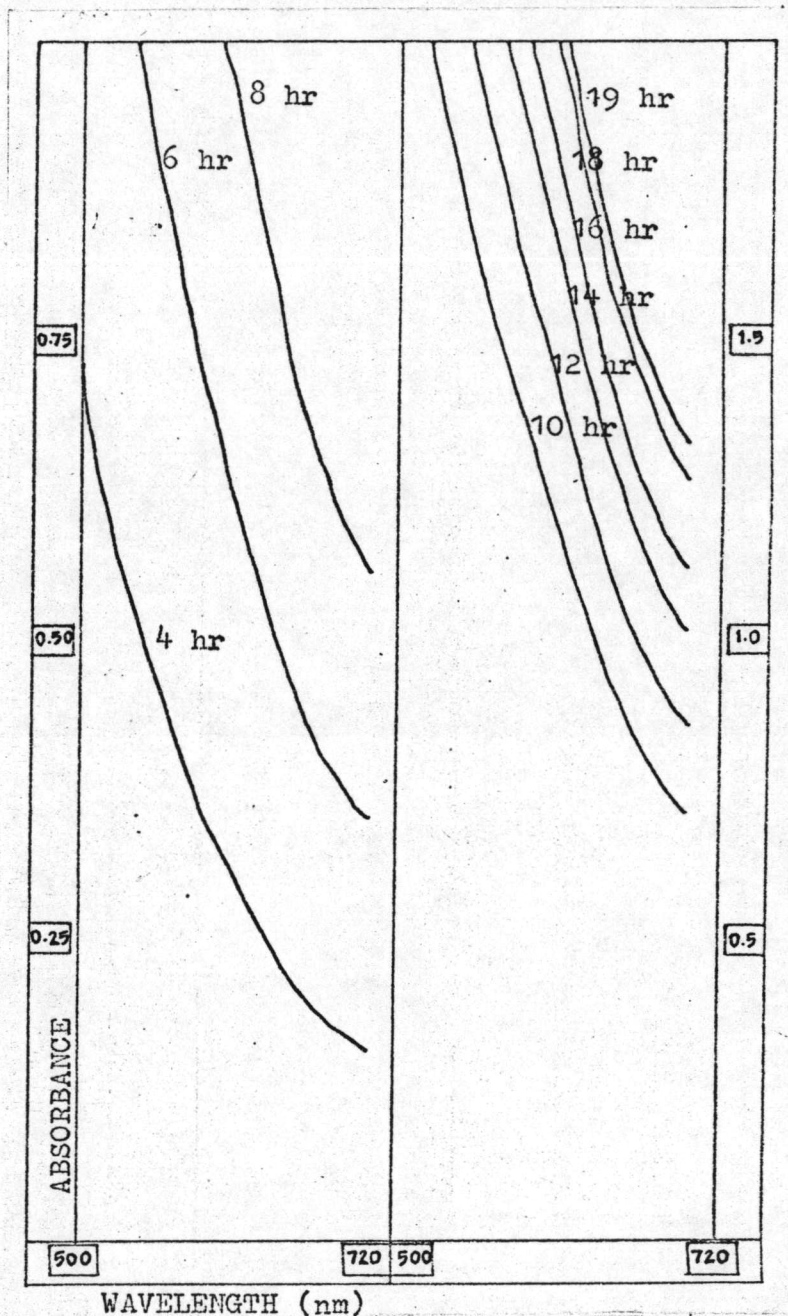


Fig.5.2.6 The variation of reaction time with absorbance at wavelength of 635 nm for the reaction between 0.7M furfural ( $45\text{cm}^3$ ) and 0.2M phenol ( $15\text{cm}^3$ ) in the presence of conc.HCl ( $3\text{cm}^3$ ) at  $55^\circ\text{C}$

Table 5.2.6

The variation of reaction time with absorbance at wavelength of 635 nm ( $A_{635}$ ) for the reaction between 0.7M furfural ( $45\text{cm}^3$ ) and 0.2M phenol ( $15\text{cm}^3$ ) in the presence of conc.HCl ( $3\text{cm}^3$ ) at  $55^\circ\text{C}$

Reaction time, hr	$A_{635}$	$X = 2A_{635}$
4	0.274	0.548
6	0.754	1.508
8	0.875	1.750
10	1.108	2.216
12	1.330	2.660
14	1.552	3.104
16	1.718	3.436
18	1.900	3.800
19	1.980	3.960
		$k = 0.214 \text{ hr}^{-1}$

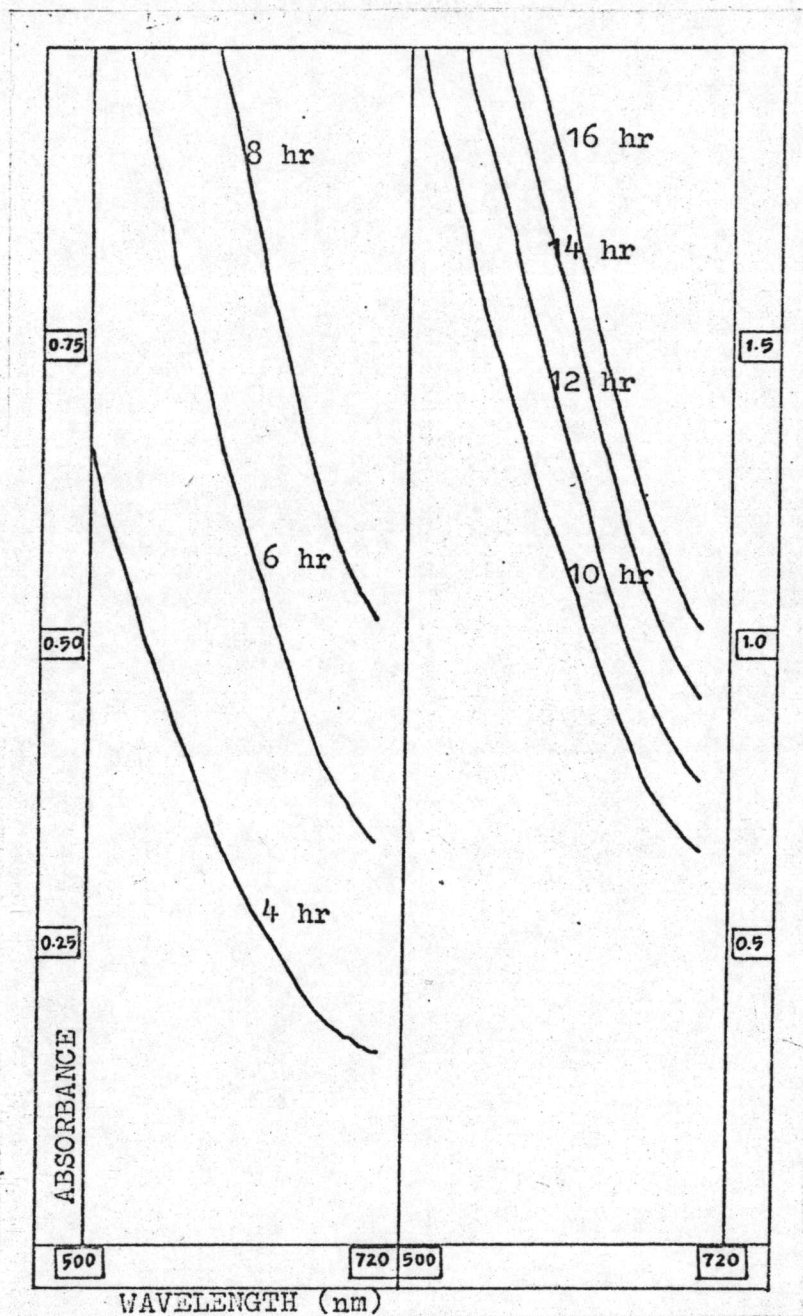


Fig-5.2.7 The variation of reaction time with absorbance at wavelength of 635 nm for the reaction between 0.7M furfural ( $45 \text{ cm}^3$ ) and 0.2M phenol ( $15 \text{ cm}^3$ ) in the presence of conc.HCl ( $3 \text{ cm}^3$ ) at  $50^\circ \text{C}$

Table 5.2.7

The variation of reaction time with absorbance at wavelength of 635 nm ( $A_{635}$ ) for the reaction between 0.7M furfural ( $45 \text{ cm}^3$ ) and 0.2M phenol ( $15 \text{ cm}^3$ ) in the presence of conc.HCl ( $3 \text{ cm}^3$ ) at  $50^\circ \text{C}$

Reaction time, hr	$A_{635}$	$X = 2A_{635}$
4	0.259	0.518
6	0.532	1.064
8	0.812	1.624
10	1.035	2.070
12	1.238	2.476
14	1.445	2.890
16	1.628	3.256
		$k = 0.227 \text{ hr}^{-1}$

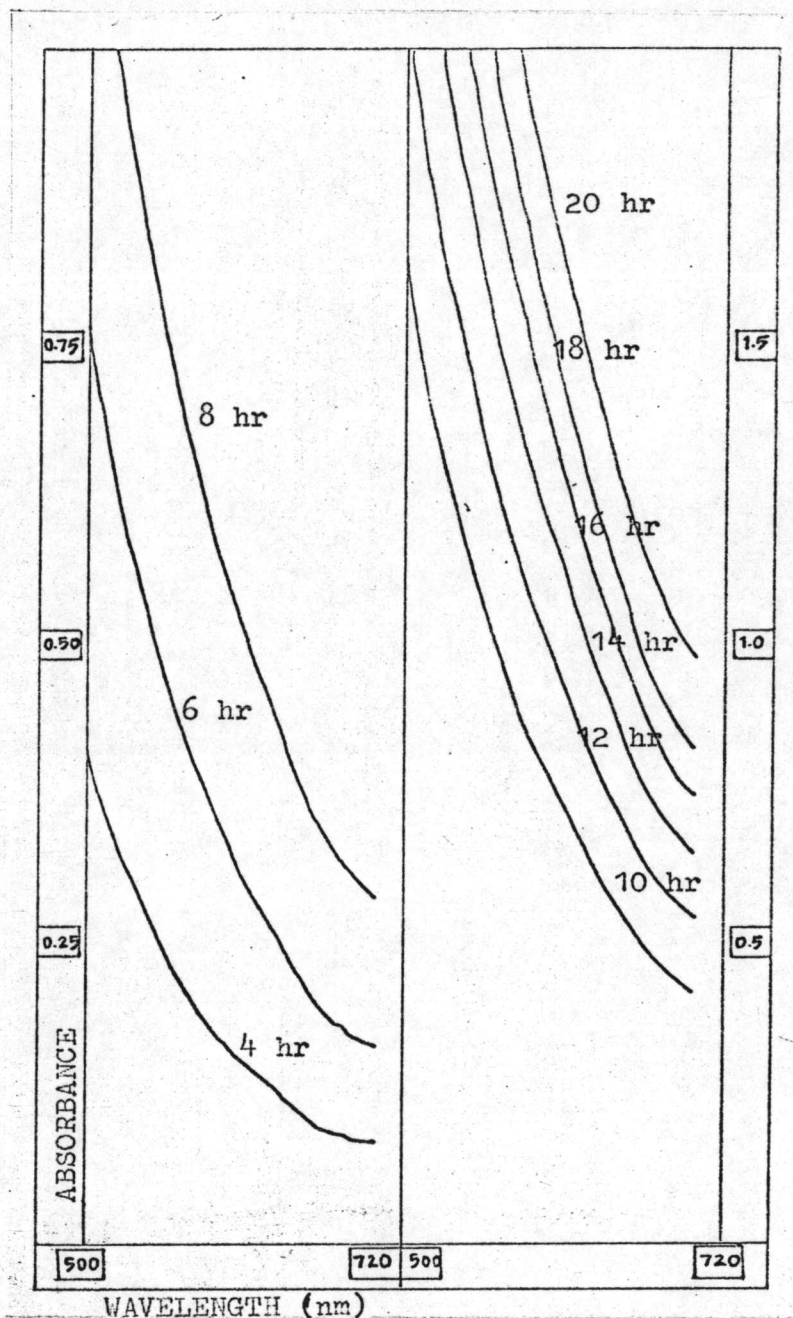


Fig.5.2.8 The variation of reaction time with absorbance at wavelength of 635 nm for the reaction between 0.7M furfural ( $45 \text{ cm}^3$ ) and 0.2M phenol ( $15 \text{ cm}^3$ ) in the presence of conc.HCl ( $3 \text{ cm}^3$ ) at  $47^\circ \text{C}$



Table 5.2.8

The variation of reaction time with absorbance at wavelength of 635 nm ( $A_{635}$ ) for the reaction between 0.7M furfural ( $45\text{cm}^3$ ) and 0.2M phenol ( $15\text{cm}^3$ ) in the presence of conc.HCl ( $3\text{cm}^3$ ) at  $47^\circ\text{C}$

Reaction time, hr	$A_{635}$	$X = 2A_{635}$
4	0.112	0.224
6	0.232	0.464
8	0.392	0.784
10	0.568	1.136
12	0.738	1.476
14	0.862	1.724
16	1.017	2.034
18	1.125	2.250
20	1.258	2.516
		$k = 0.147 \text{ hr}^{-1}$

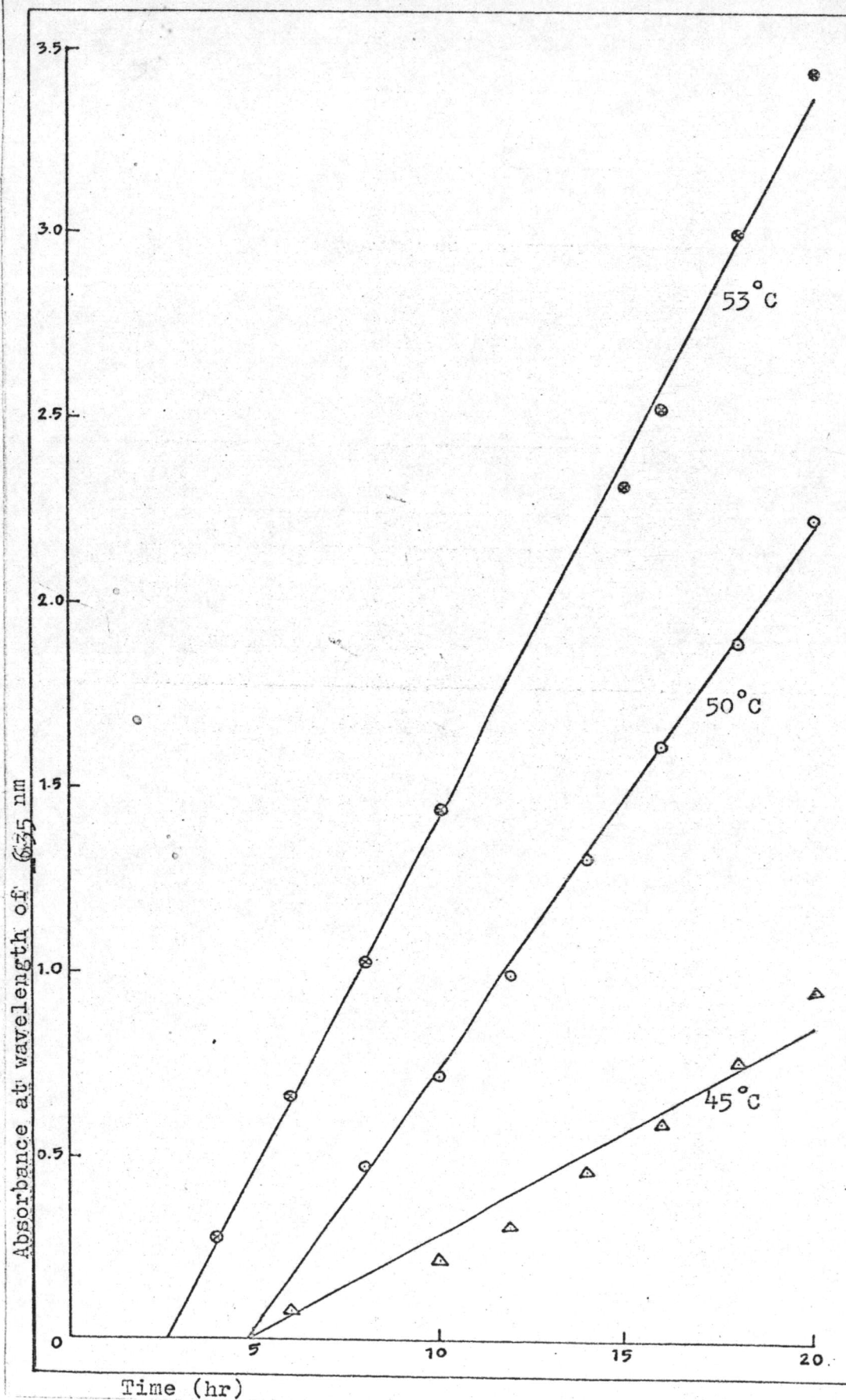


Fig.5.2.9 The absorption-time plots of the phenol-furfural reaction with hydrochloric acid as catalyst at 45, 50 and 53°C when phenol was present in excess amount.

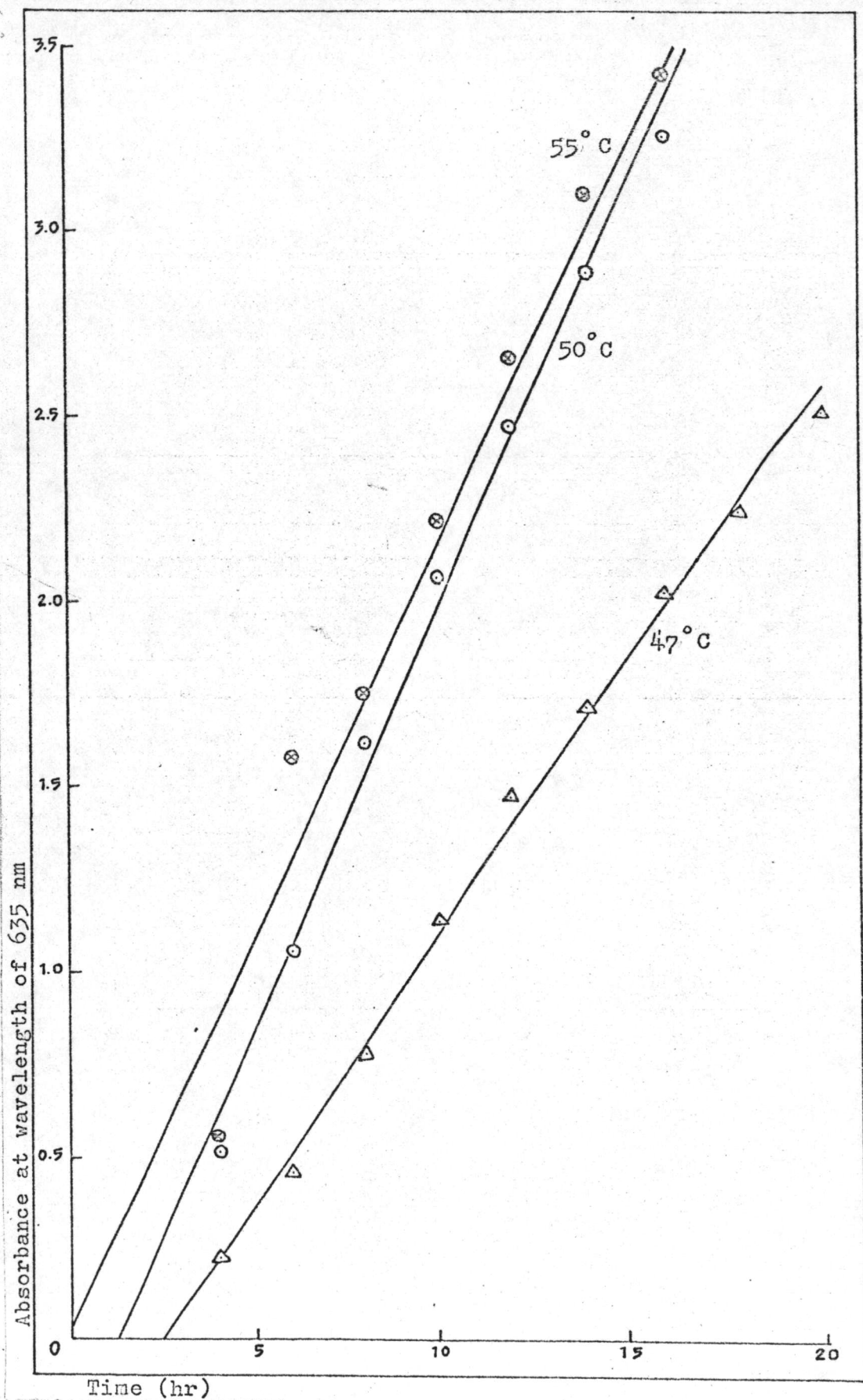


Fig.5.2.10 The absorption-time plots of the phenol-furfural reaction with hydrochloric acid as catalyst at 47, 50 and 55°C when

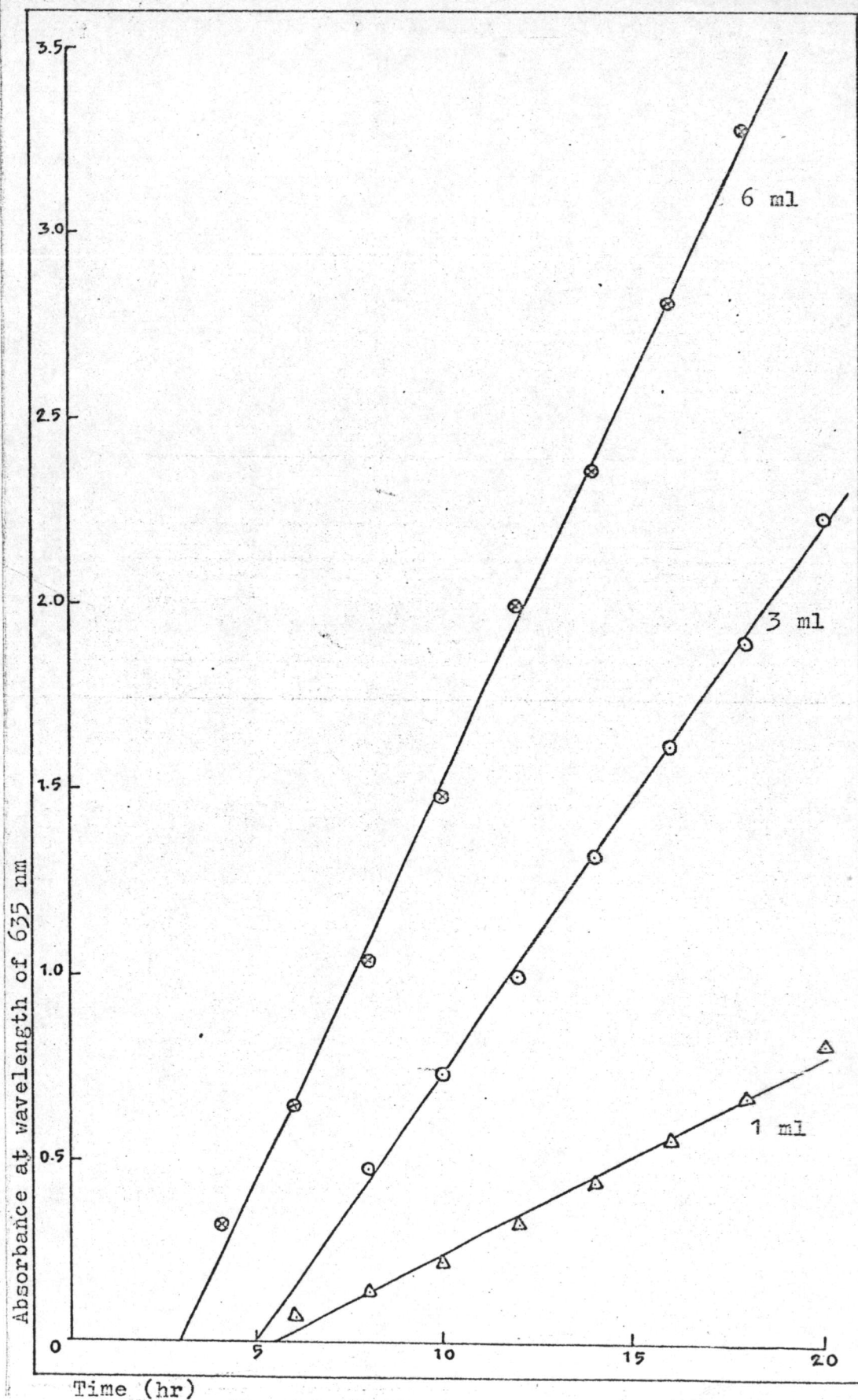


Fig.5.2.11 The absorption-time plots of the phenol-furfural reaction at 50°C when 1, 3 and 6 cm<sup>3</sup> of catalysts were present

### 5.3 Determination of specific rate constant, k and reaction order

The specific rate constant of the reaction was obtained from the slope of the rectilinear plot of X vs time as shown in the same Tables and Figures as section 5.2 and from the plots, the order of the reaction was found. The values for k are given in Tables 5.3.1, 5.3.2 and 5.3.3.

### 5.4 Calculation of activation energy, $E_a$ and frequency factor, A

Based on Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

$$\text{or } \ln k = -\frac{E_a}{RT} + \ln A \dots\dots\dots(5.1)$$

Let  $k = k_1$  at  $T = T_1$  and  $k = k_2$  at  $T = T_2$

substitution of k's and T's into equation 5.1 yields

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{T_1 - T_2}{T_1 T_2} \right) \dots\dots\dots(5.2)$$

Substituting the values of k and T from Table 5.3.1 into equation 5.2, the activation energy,  $E_a$  could be calculated and substitution of k, T, and  $E_a$  in equation 5.1, the frequency factor, A is finally obtained.

In this case,

$$k_1 = 0.147 \text{ hr}^{-1}, \quad T_1 = 323^\circ \text{ K}$$

$$k_2 = 0.193 \text{ hr}^{-1}, \quad T_2 = 326^\circ \text{ K}$$

using  $R = 8.314 \text{ joule deg}^{-1} \text{ mole}^{-1}$ , thus

$$E_a = 8.01 \times 10^4 \text{ joule mole}^{-1}$$

$$\text{and } A = 1.32 \times 10^{12} \text{ hr}^{-1}$$

Table 5.3.1

The variation of  $k$  with temperature when an excess of phenol and  $3 \text{ cm}^3$  of conc.HCl were present

$T, ^\circ\text{K}$	$k, \text{hr}^{-1}$
318	0.057
323	0.147
326	0.193

Table 5.3.2

The variation of  $k$  with temperature when an excess of furfural and  $3 \text{ cm}^3$  of conc.HCl were present

$T, ^\circ\text{K}$	$k, \text{hr}^{-1}$
320	0.147
323	0.227
328	0.214

Table 5.3.3

The variation of  $k$  with volume of conc.HCl when an excess of phenol was present and the reaction temperature was fixed at  $50^{\circ}\text{C}$

$\text{cm}^3$ conc.HCl	$k, \text{hr}^{-1}$
1	0.054
3	0.147
6	0.215