6.

KINETICS OF EXCHANGE WITH CINCHONA ALKALOID SULPHATES :

6.1 Ion exchange kinetics (1 - 24) :

For the effective use of ion exchange resins, the understanding of the rate of exchange is essential, in addition to that of exchange equilibria. The factors, which in general, increase the exchange rates are

(i) decrease in the particle size,
(ii) increase in the rate of stirring,
(iii) increase in the concentration of solution,
(iv) increase in temperature,
(v) decrease in the ionic size,
and (vi) decrease in the relative degree of cross-linking of the resin,

When a resin bead is placed in a solution, as an approximation, it is plausible to assume that the bulk of the solution is being instantaneously mixed by stirring, but in the vicinity of the solid surface, there is a thin film of immobile solution, in which diffusion is the only transport process. The ion exchange reaction is, hence, governed by (a) diffusion through the Nerst film and (b) diffusion through the resin bead. The two extreme cases are those in which one or the other of the diffusion processes is mainly operative.

Film diffusion is favoured by highly swollen resins, small ions, small particle size, inefficient stirring and dilute solutions. Particle diffusion is favoured by, higher cross-linked resins, large ions, large particle size, efficient mixing, and stronger solutions.

The mathematical treatment has been worked out for various cases of simple nature, making plausible assumptions. Still, the actual rate equations are quite complex.

Although no chemical activation is involved in ion-exchange reactions, the rate of exchange is increased to some extent by rise in temperature, because of the effect on the diffusion coefficients and film thickness. The value of the calculated apparent activation energy is usually small. This suggests that the liquid in the pores of the resin is similar in structure, to the aqueous solution. The slowing down of the diffusion in the resin particle is a consequence of the hindered path, the ion has to travel through the tangle of the polymer chains.

On the other hand, the diffusion of the large organic ions in resins, requires a higher energy of activation than in water and should be due to steric obstruction of the network and the need for a local distortion of the structure to allow the ion to pass from pore to pore.

The interpretation of diffusion data for different types of ions is complicated by the differences of water content which are usually involved.

Most practical operations of ion exchange resins, whether in the laboratory, or on a large scale, can be operated more effectively on the column principle than by the batch method. The usual methods of operating columns can be divided into : (A) displacement, in which the ion on the

column is sharply displaced by another, more strongly sorbed, and (B) elution, in which the ion is more gradually moved down the column by treatment with a more weakly sorbed element. (A) leads to sharp bands travelling at a rate determined by the flow of the incoming solution. (B) leads to bands somewhat diffuse at the boundaries, travelling at a rate dependent on the relative affinity of the resin for the two ions. (A) is useful in dealing with large quantities, while (B) is the preferred process for obtaining optimum separation of substances, but in small quantities.

In either case, the highest efficiency would be reached, if the liquid passing down the column, came to full equilibrium with each layer of resin bed. However, this would require an infinitesimally slow rate of flow. In practice, non-equilibrium conditions would prevail with reduced efficiency. The essence of column operation is to choose an appropriate compromise between efficiency and speed compatible with the required result. It is possible to calculate the performance of the column under conditions where film or particle diffusion are rate determining. A more practical approach, which covers any type of non-equilibrium, is to apply the plate theory. According to this, the column is considered to consist of a number of sections ('theoretical plates') in each of which overage concentration of the solution in the pores can be considered as effectively in equilibrium with the average amount of solute sorbed by the resin. The effectiveness of the column can be judged from the

number of theoretical plates, it appears to contain and thus the elution curve may be predicted.

6.2. Exchange kinetics of cinchona alkaloid sulphates with resins.

6.2.a. Introduction :

In the previous chapters, the equilibrium uptake of cinchona alkaloids by resins had been considered. This section deals with the study of the rates of exchange (cf. section 1.3.b.) from the aqueous solutions of alkaloid sulphates by the resins. The study includes the effect of (a) the relative degree of cross-linking of the resin (b) the concentration of the external solution (c) the size of the alkaloid molecule (d) temperature (e) the particle size and (f) the structure of the resin.

6.2.b. Experimental :

Resins and chemicals : These were from the same stocks as used earlier.

Solutions : The procedure for the preparation and estimation of the aqueous solutions of the alkaloid sulphates was the same as described earlier.

Procedure for rate studies : A known weight of the air-dry resin (concentration of resin in meq. / litre, on the basis of effective capacity = the concentration of the aqueous alkaloid sulphate solution in meq. / litre.) was kept in a

clean, dry, three necked pyrex flask (capacity 500 cc.) clamped in a thermostat (Townson and Mercer model, constancy of temperature being $\pm$ 0.02 ^{o}C). The central opening of the flask was closed with a quickfit metallic stopper with a glass stirrer and a regulator on the stirrer motor to control the speed. The other two openings of the flask were closed with quickfit glass stoppers.

450 cc. of the aqueous alkaloid sulphate solution of known concentration were poured into the flask (with the help of a short stem, clean, dry funnel) through the side opening and the stop-watch was started when about half the volume of the solution had been added. The stirrer was switched on as soon as the addition of the solution was complete (complete addition required about 20 seconds.). After a definite time, the stirrer was switched off and 15 or 10 seconds (depending on the particular resin) were allowed for the settling down of the resin particles. A suitable volume was quickly pipetted out (the pipette end just dipping in the solution to avoid the sucking up of the resin particles) into well stoppered clean, dry test-tubes and stirring re-started. Further samples were taken out similarly.

Usually, 30 cc. of the reaction mixture was pipetted out (six samples, each of 5 cc.) or 40 cc. (four samples, each of 10 cc.) depending on the initial alkaloid sulphate concentration from an initial total volume of 450 cc. of the added solution, during one run.

The contents of the test tubes were suitably diluted by adding known volume of distilled water with a pipette and the optical density, Do, was noted at the invarient wave-length (296.5 mμ for quinine sulphate and quinidine sulphate and 294.5 mμ for cinchonine sulphate and cinchonidine sulphate). The original aqueous solution of the alkaloid sulphate was diluted to the same extent and the optical density, Di , measured at the respective invarient wave-lengths.

Then, (Di - Do / Do) represents the value of x / (b - x), where b = the concentration of the alkaloid sulphate at time t = zero and x = the concentration of the alkaloid sulphate at any time t = t.

Preliminary work was done with different speeds of stirring (400 r.p.m. to 1000 r.p.m.) and it was observed that after a rate of stirring of about 700 r.p.m., the rate of the reaction was practically independent of the stirring rate. Hence throughout this work, the spped of the stirrer was kept at $\sim$ 800 - 900 r.p.m. It was also observed that when the stirrer was switched off, 15 seconds were quite sufficient for settling down of the resin particles (10 seconds , in case of IR-120, IR-200 and Amb-15).

Runs were carried out with different concentrations of the same alkaloid sulphate solution with the corresponding calculated weights of the resin, at 35°C and 45°C. The runs were always checked for reproducibility.

The values of x / (b - x) obtained with different concentrations of the four alkaloid sulphates with different resins at 35°C and 45°C are given in the following tables.

6.2.c. RESULTS :

Tables (6.01 to 6.16) give the data for the exchange rate (at 35°C and 45°C) of the quinine sulphate, quinidine sulphate, cinchonine sulphate and cinchonidine sulphate, of different concentrations, with resins from X 1 to X 20 .

Figures (6.01 to 6.07) give the plots of x/(b-x) against t, for quinine sulphate (of different concentrations) with resins X 1 to X 20, at 35°C and 45°C, as an illustration of the similar plots for the other alkaloid sulphates.

Tables (6.17 to 6.30) give the data for the exchange rate (at 35°C and 45°C) of the quinine sulphate, quinidine sulphate, cinchonine sulphate and cinchonidine sulphate, of different concentrations, with resins IR-200, IR-120 and Amb-15, of different particle diameters.

Figures (6.08 to 6.10) illustrate the plots of x/(b-x) against t, for the four alkaloid sulphates (of different concentrations) with resins IR-200,IR-120 and Amb-15 (of different particle diameters) at 35°C and 45°C.

Tables (6.31 to 6.34) give the data for the slope from the plot of x/(b-x) against t (the intercept, in all cases = zero) and values of K at different concentrations for the four alkaloid sulphates with resins X 1, X 2 and X 4 and IR-200 and Amb-15, of different particle diameters, at 35°C and 45°C.

Tables (6.35 to 6.38) give the data for the slope and intercept from the plot of x/(b-x) against t , at different concentrations, at 35°C and 45°C, for the four alkaloid sulphates with resins X 8 to X 20 and IR-120 of different particle diameters.

Tables (6.39 and 6.40) give the values of K in $(\text{minute})^{-1} \cdot (\text{gram-equivalent per litre})^{-1}$ at 35°C and 45°C for the four alkaloid sulphates with resins from X 1 to X 20 and resins IR-200, IR-120 and Amb-15(of different particle diameters).

Table (6.41) gives the slopes and intercepts of the plots of log K against X, at 35°C and 45°C, for the four alkaloid sulphates (from figures 6.11 to 6.14).

Tables (6.48 and 6.49) give the experimental and calculated (from figures 6.11 to 6.14) values of log K at 35°C and 45°C, for the four alkaloid sulphates with resins X 1 to X 20 .

Table (6.42) gives the slope and intercept of the plot of E against X for the four alkaloid sulphates (from figures 6.15 and 6.16).

Tables (6.43 and 6.44) give the slope and intercept of the plot of K against 1 / a for the four alkaloid sulphates at $35^{\circ}C$ and $45^{\circ}C$ with resins IR-200 and Amb-15 (from figures 6.17 to 6.20) and values of γ and E .

Table (6.45) gives the slope and intercept of the plot of K against 1 / a for the four alkaloid sulphates at $35^{\circ}C$ and $45^{\circ}C$ with resin IR-120(from figures 6.21 to 6.24).

Table (6.46) gives the slopes and intercepts of the plot of E against a, for the four alkaloid sulphates with resin IR-120 (from figures 6.25 and 6.26).

Table (6.47) gives the experimental and calculated (from figures 6.21 to 6.24) values of K for the four alkaloid sulphates with resin IR-120 of different particle diameters.

(The apparent energy of activation, E, is given in calories, the average particle diameter, a, is given in mm. in further data, unless otherwise mentioned. γ denotes the temperature coefficient $K\ 45^{\circ} / K\ 35^{\circ}$. The temperature is in $^{\circ}C$.).

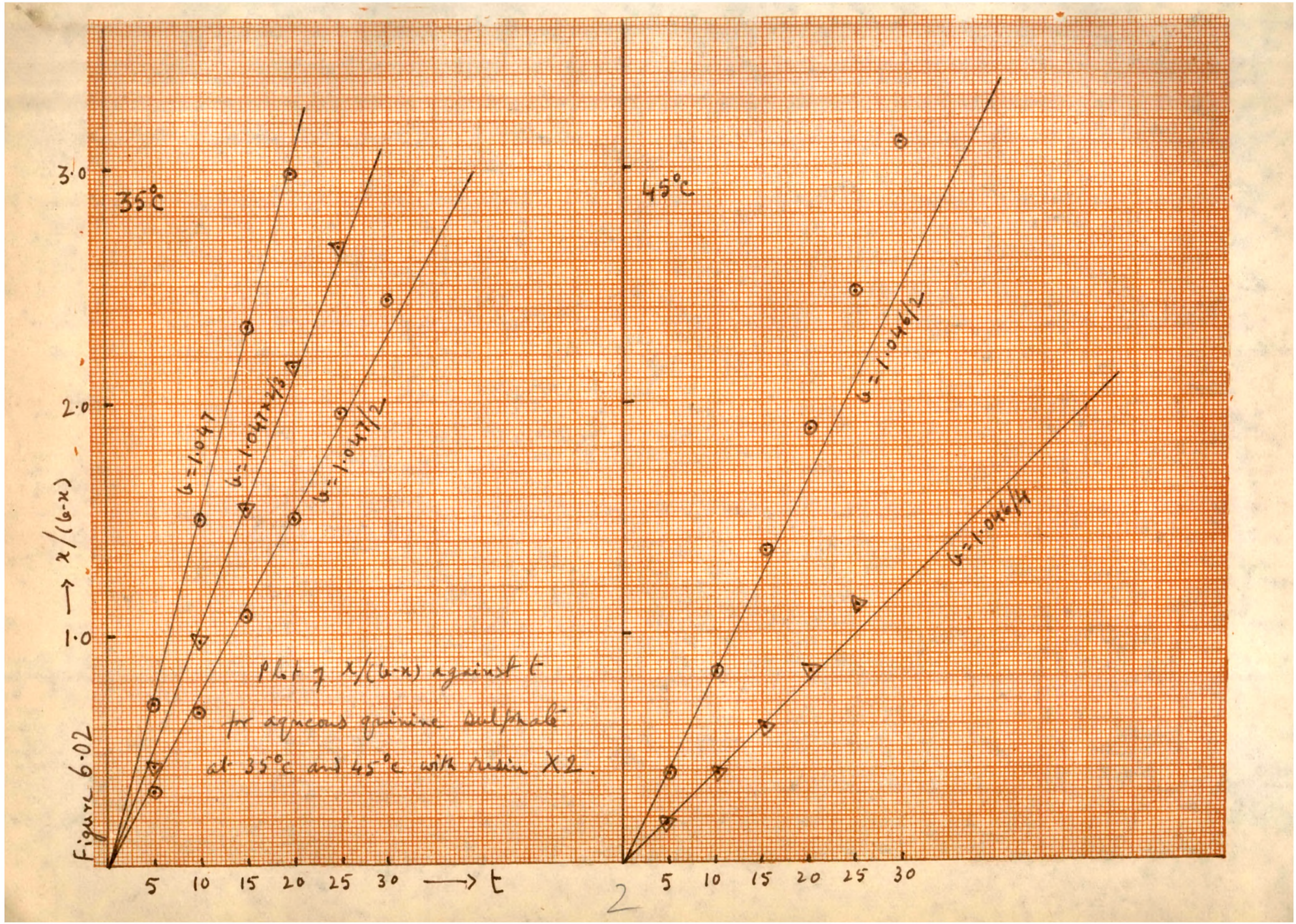

Figure 6·02

Plot of $x/(a-x)$ against t for aqueous quinine sulphate at 35°C and 45°C with resin X2.

Figure 6.01

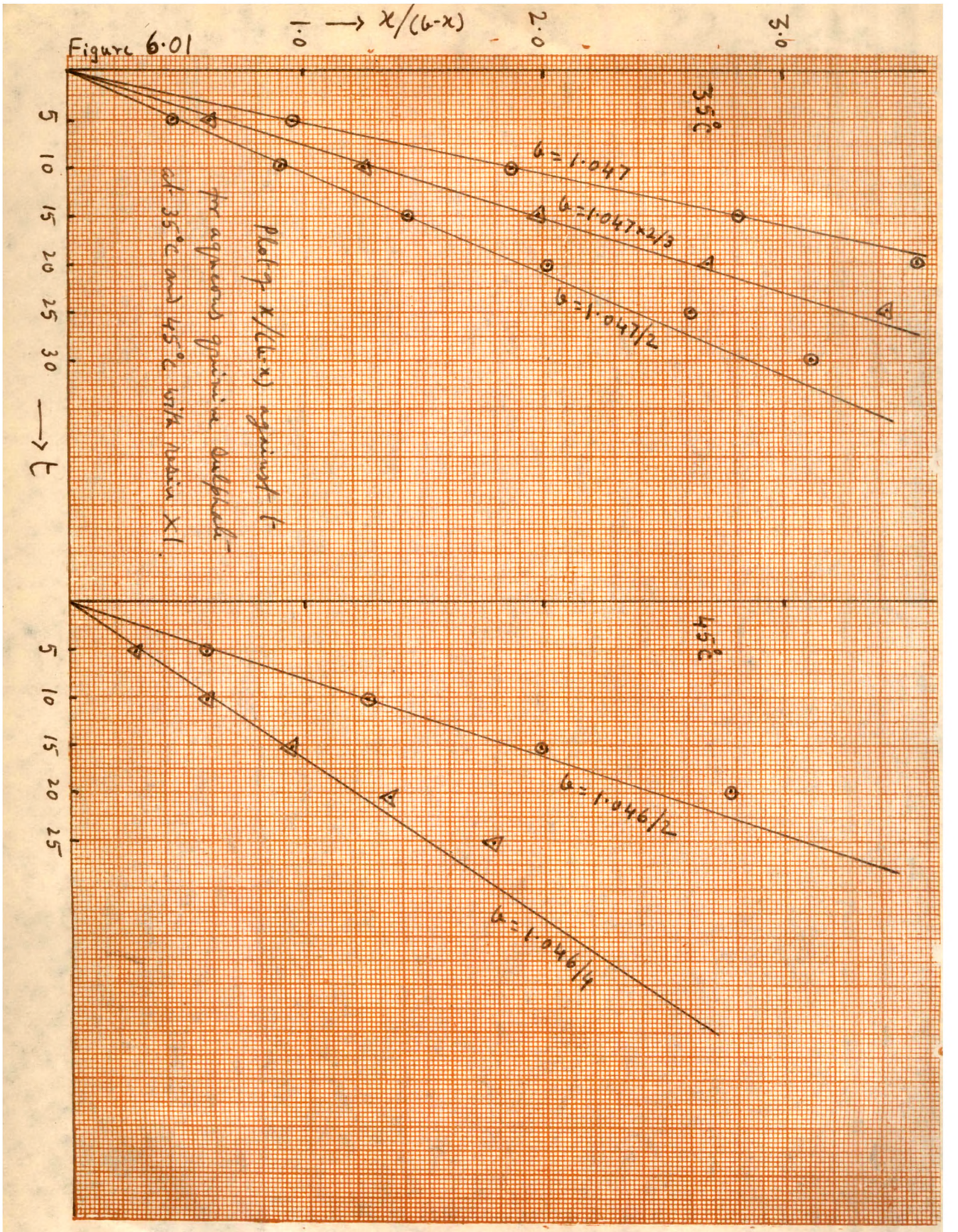
1.0 → x/(b-x) 2.0 3.0
35°C
45°C
t
5 10 15 20 25 30
5 10 15 20 25
b = 1·047
b = 1·047 × 2/3
b = 1·047/2
b = 1·046/2
b = 1·046/4
Plot of x/(b-x) against t for aqueous solution of Amidon at 35°C and 45°C with Resin XI.

Table 6.01

Exchange rate of quinine sulphate with resins X 1 and X 2.

		35°C			45°C	
		Values of x/(b-x) when b =				
Resin	t (min.)	1.047	1.047×2/3	1.047/2	1.046/2	1.046/4
X 1	5	0.95	0.60	0.44	0.58	0.28
	10	1.87	1.24	0.89	1.25	0.58
	15	2.82	1.98	1.43	1.98	0.94
	20	3.57	2.69	2.02	2.78	1.35
	25	4.45	3.45	2.62	3.67	1.78
	30	5.15	4.09	3.13	4.36	-
X 2	5	0.71	0.42	0.32	0.39	0.18
	10	1.50	0.96	0.66	0.83	0.39
	15	2.33	1.54	1.07	1.35	0.59
	20	2.99	2.16	1.50	1.87	0.83
	25	3.57	2.67	1.96	2.46	1.11
	30	4.15	3.37	2.45	3.11	-

Figure 6.03

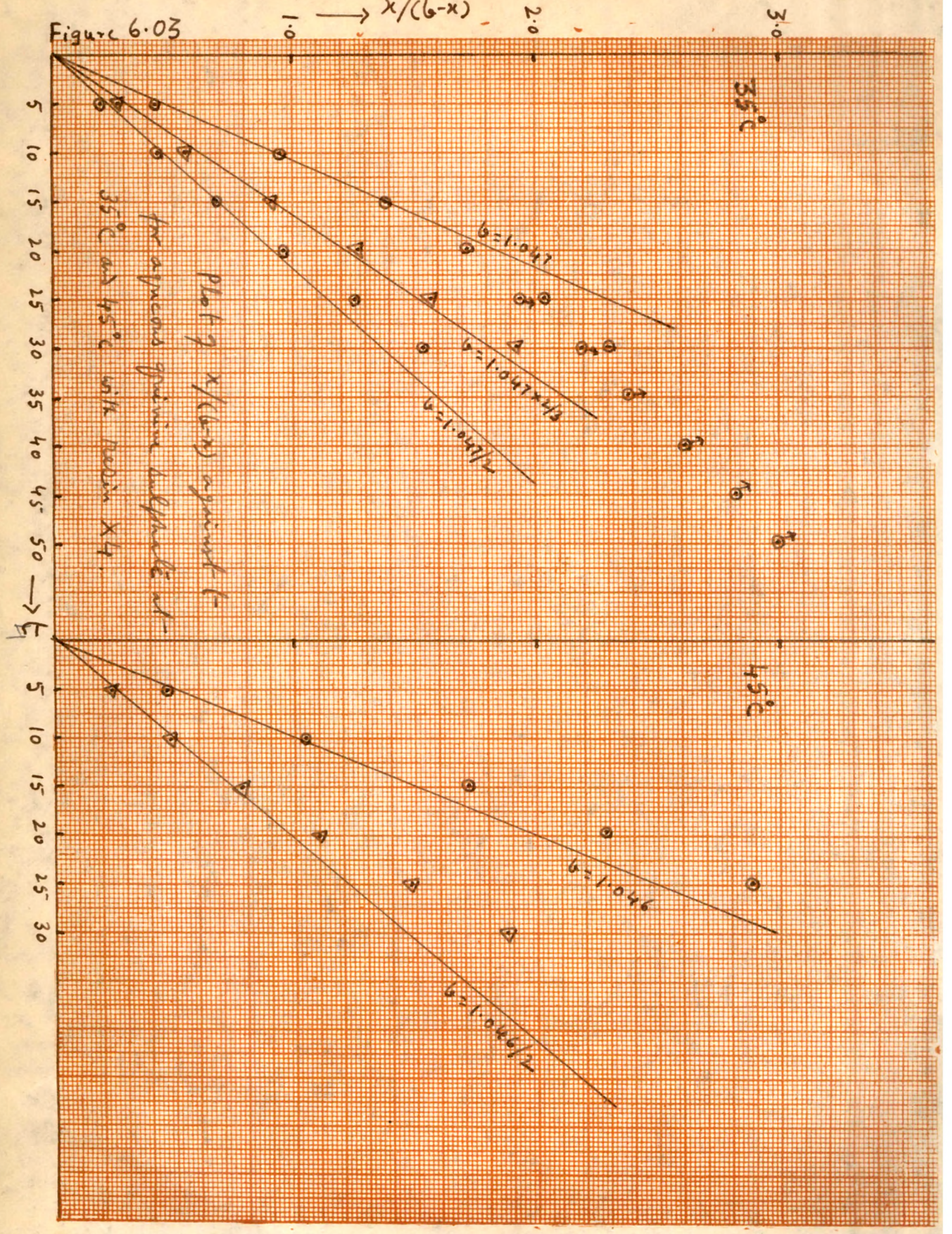
x/(6-x)
1.0
2.0
3.0
35°C
45°C
5 10 15 20 25 30 35 40 45 50
5 10 15 20 25 30
b=1.047
b=1.047 x 4/3
b=1.047/2
b=1.046
b=1.046/2
Plot of x/(6-x) against t for aqueous glucose solutions at 35°C and 45°C with resin X4.

Table 6.02.a.

Exchange rate of quinine sulphate with resin X 4.

		35°C			45°C	
	t	Values of x / (b - x) when b =				
Resin	(min.)	1.047	1.047 x 2/3	1.047/2	1.046	1.046/2
X 4	5	0.42	0.26	0.20	0.46	0.23
	10	0.94	0.54	0.44	1.03	0.48
	15	1.37	0.91	0.68	1.71	0.78
	20	1.71	1.26	0.96	2.28	1.09
	25	2.03	1.56	1.25	2.87	1.47
	30	2.29	1.93	1.53	3.36	1.86

Table 6.02.b.

Repetition of the exchange rate of quinine sulphate with resin X 4, at 35°C, when b = 1.047 meq./litre.

t (min.)	25	30	35	40	45	50
x/(b-x)	1.93	2.19	2.38	2.61	2.82	2.99

Figure 6.04

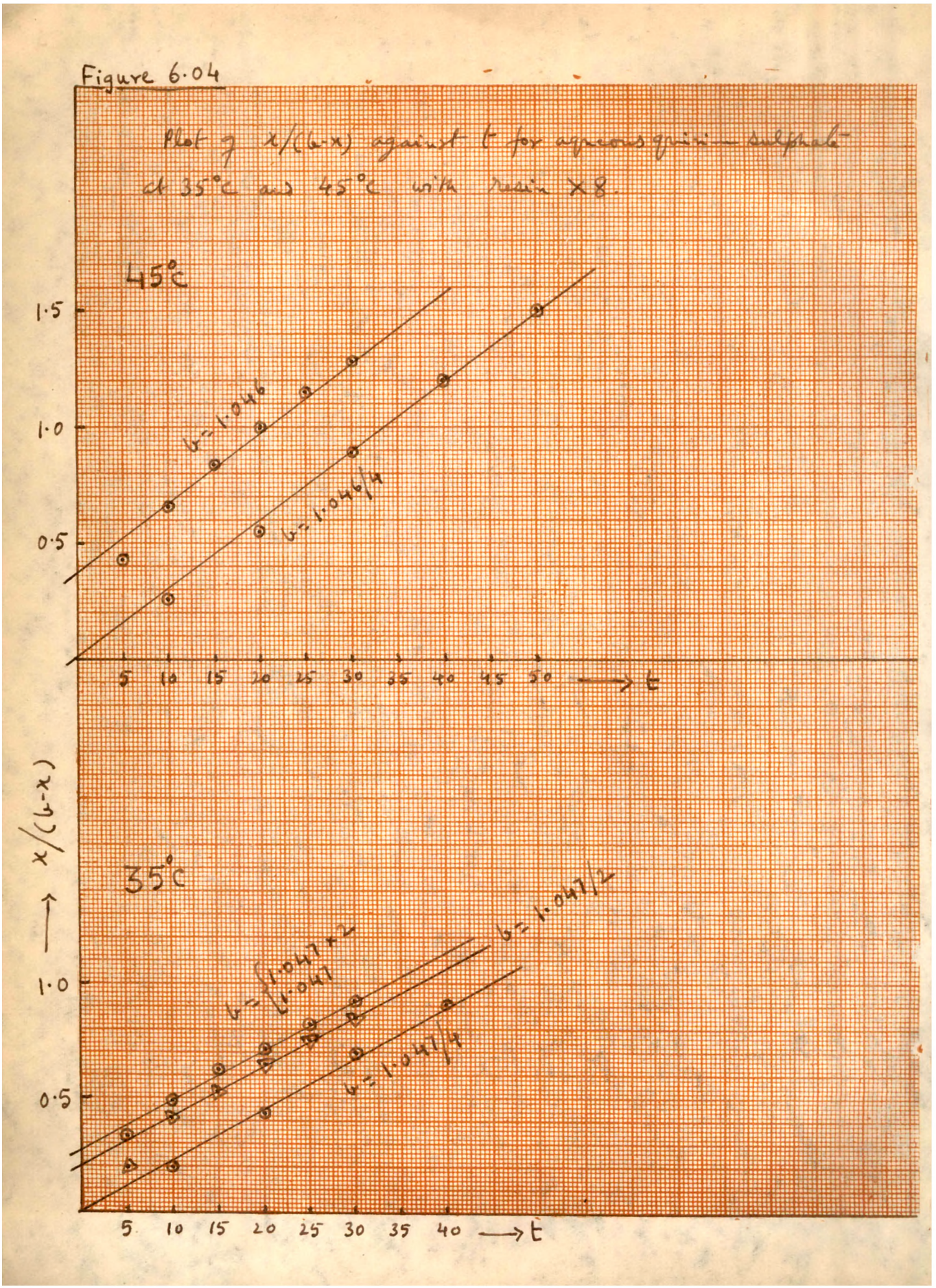
Plot of x/(b-x) against t for aqueous grain-sulphate at 35°C and 45°C with resin ×8.
45°C
1·5
1·0
0·5
b=1·046
b=1·046/2
5 10 15 20 25 30 35 40 45 50 → t
x/(b-x) →
35°C
1·0
0·5
b=[1·047×2]/[1·047]
b=1·047/2
b=1·047/4
5 10 15 20 25 30 35 40 → t

Table 6.02.

Exchange rate of quinine sulphate with resin X 8.

Resin	t (min.)	35°C				45°C	
		Values of x / (b-x) when b =					
		1.047x2	1.047	1.047/4	1.047/2	1.046	1.046/4
X 8	5	0.33	0.32	-	0.19	0.42	-
	10	0.48	0.47	0.20	0.41	0.64	0.25
	15	0.62	0.59	-	0.54	0.83	-
	20	0.71	0.69	0.43	0.66	1.00	0.54
	25	0.81	0.80	-	0.76	1.14	-
	30	0.91	0.88	0.69	0.84	1.27	0.89
	40	-	-	0.91	-	-	1.20
	50	-	-	-	-	-	1.49

Figure 6.05

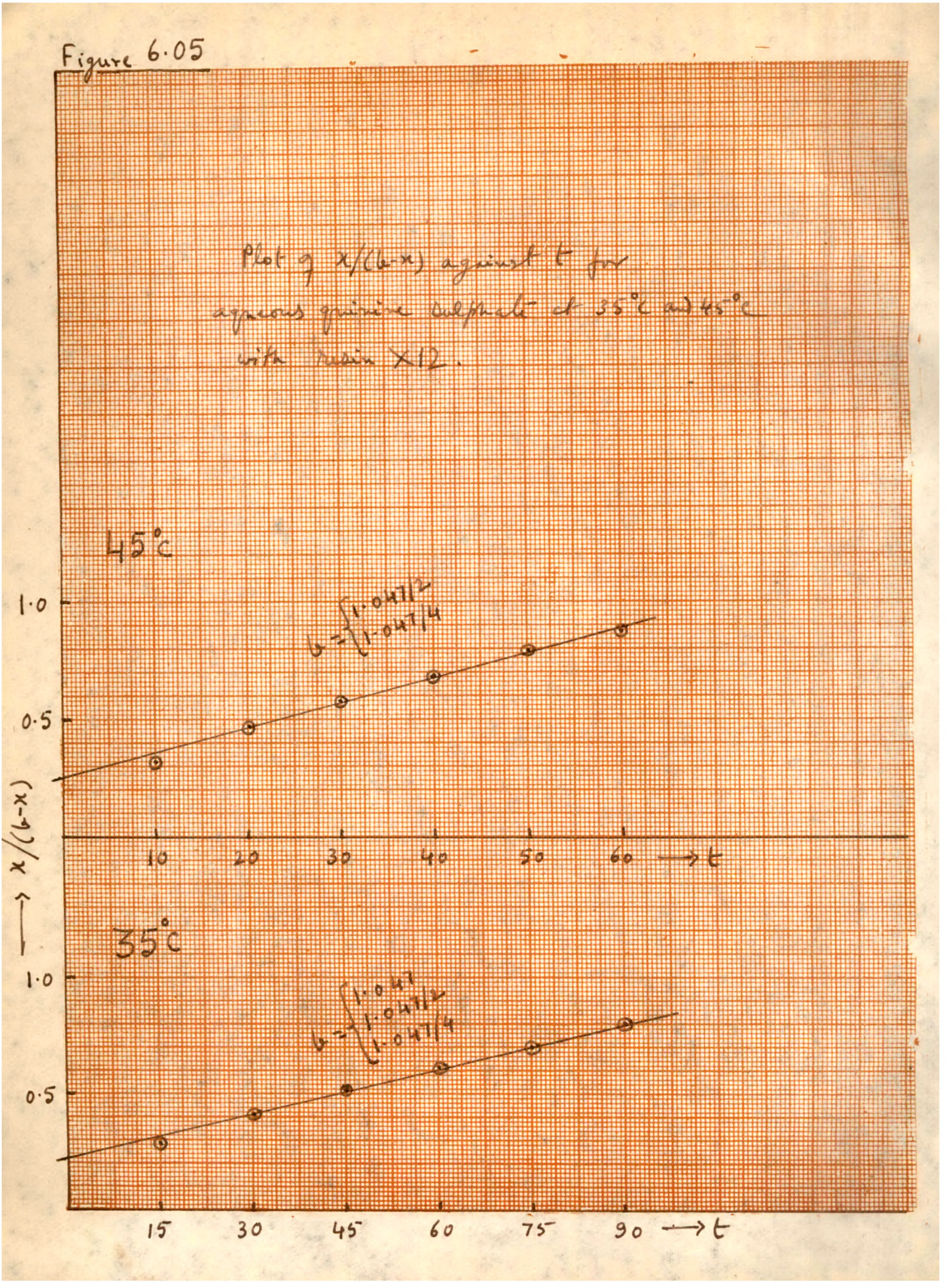
Plot of x/(b-x) against t for aqueous quinine sulphate at 35°C and 45°C with resin ×12.
45°C
35°C
1·0
0·5
1·0
0·5
x/(b-x) ⟶
10
20
30
40
50
60 ⟶ t
15
30
45
60
75
90 ⟶ t

Figure 6.06

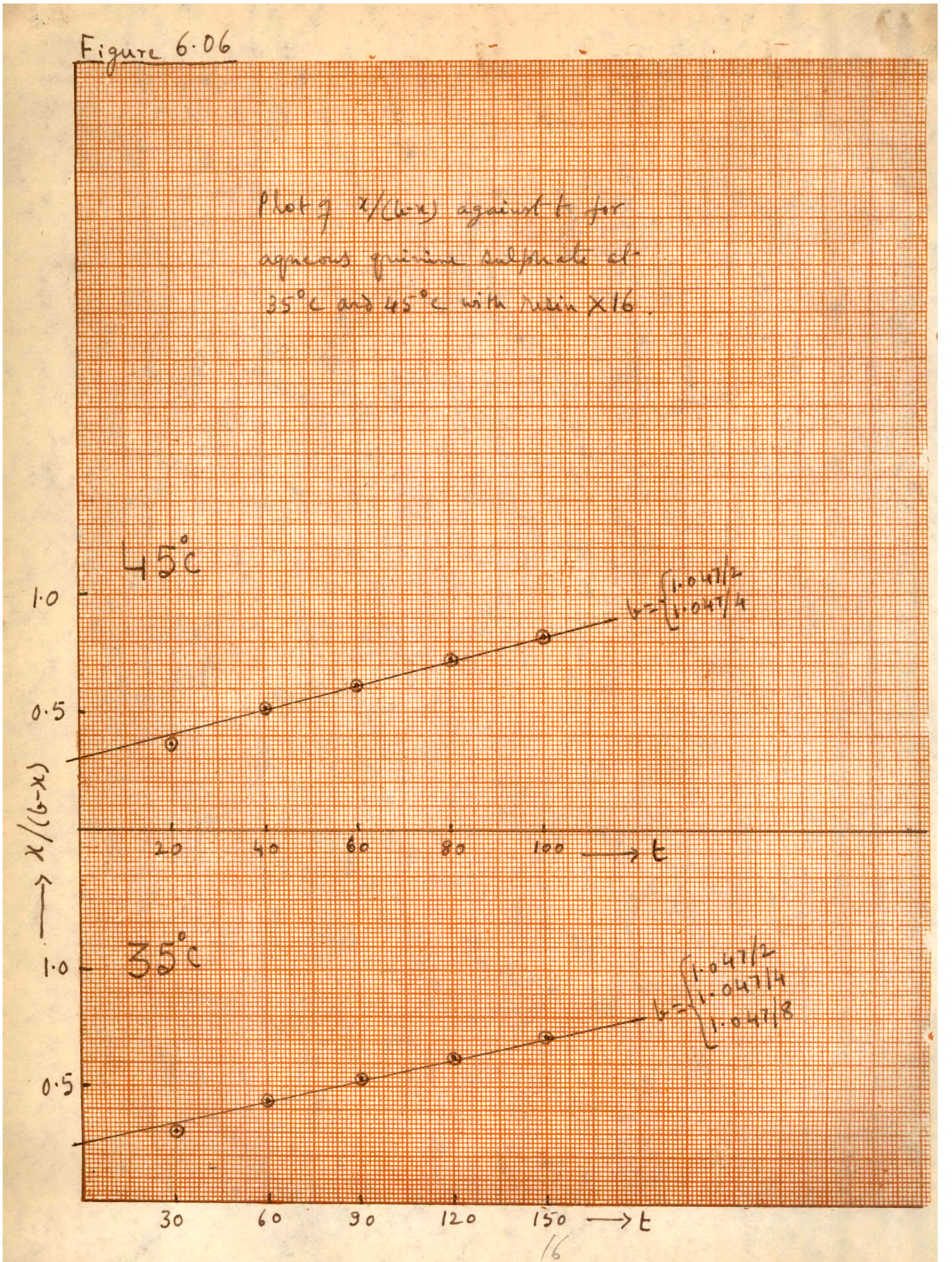
Plot of x/(b-x) against t for aqueous purine sulphate at 35°C and 45°C with ratio X16.
45°C
1.0
0.5
x/(b-x) ⟶
20
40
60
80
100
⟶ t
k = 1.047/2
1.047/4
35°C
1.0
0.5
30
60
90
120
150
⟶ t
k = 1.047/2
1.047/4
1.047/8

Table 6.04

Exchange rate of quinine sulphate with resins X 12 and X 16.

		35°C				45°C	
		Values of x / (b-x) when b =					
Resin	t (min.)	1.047	1.047/2	1.047/4	1.047/8	1.046/2	1.046/4
X 12	10	-	-	-	-	0.32	0.30
	15	0.30	0.29	0.30	-	-	-
	20	-	-	-	-	0.46	0.46
	30	0.41	0.42	0.42	-	0.57	0.57
	40	-	-	-	-	0.69	0.68
	45	0.51	0.52	0.53	-	-	-
	50	-	-	-	-	0.76	0.78
	60	0.62	0.62	0.63	-	0.84	-
	75	0.71	0.70	-	-	-	-
	90	0.80	0.76	-	-	-	-
X 16	20	-	-	-	-	0.35	0.36
	30	-	0.29	0.29	0.29	-	-
	40	-	-	-	-	0.50	0.50
	60	-	0.42	0.44	0.41	0.58	0.62
	80	-	-	-	-	0.71	0.70
	90	-	0.53	0.54	0.52	-	-
	100	-	-	-	-	0.82	-
	120	-	0.62	0.64	0.59	-	-
	150	-	0.70	-	-	-	-

Figure 6.07

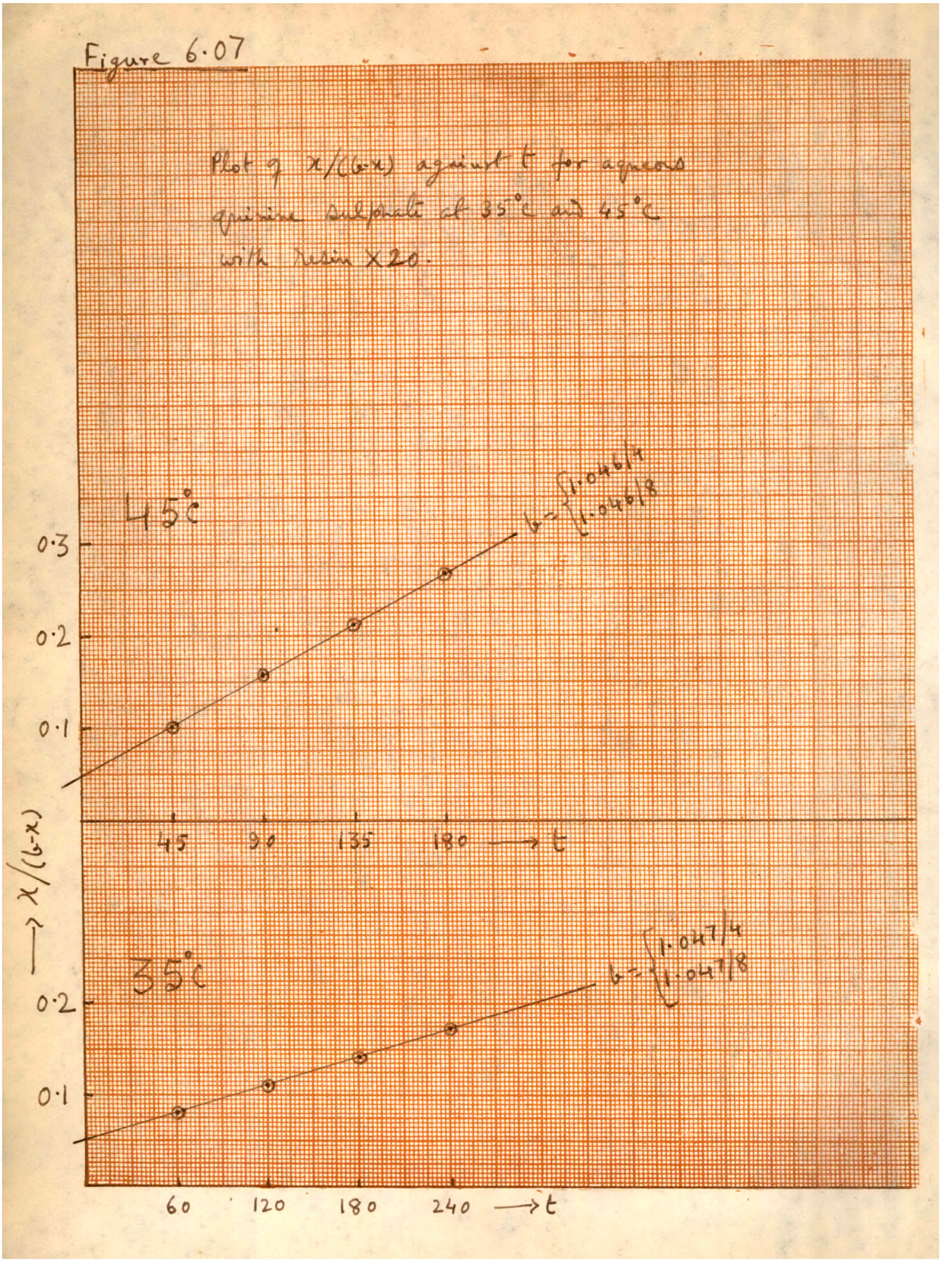
Plot of x/(b-x) against t for aqueous quinine sulphate at 35°C and 45°C with Resin ×20.
45°C
35°C
0·3
0·2
0·1
0·2
0·1
45
90
135
180
60
120
180
240
t
x/(b-x)

Table 6.05

Exchange rate of quinine sulphate with resin X 20.

		35°C		45°C	
	t	Values of x / (b - x) when b =			
Resin	(min.)	1.047/4	1.047/8	1.046/4	1.046/8
X 20	45	-	-	0.100	0.100
	60	0.077	0.079	-	-
	90	-	-	0.155	0.148
	120	0.108	0.111	-	-
	135	-	-	0.211	0.208
	180	0.141	0.144	0.264	0.264
	240	0.178	0.172	-	-

Table 6.06

Exchange rate of quinidine sulphate with resins X 1 and X 2.

		35°C		45°C	
	t	Values of x / (b - x) when b =			
Resin	(min.)	1.000	1.000/2	$1.005 \times \frac{2}{3}$	1.005/2
X 1	5	0.95	0.46	0.72	0.48
	10	2.12	0.96	1.56	1.02
	15	3.11	1.39	2.48	1.66
	20	3.80	1.94	3.42	2.25
	25	4.31	2.43	4.25	2.73
	30	-	-	5.00	3.27
X 2	5	0.67	0.30	0.52	0.38
	10	1.38	0.60	1.17	0.81
	15	2.02	0.95	1.88	1.30
	20	2.59	1.28	2.62	1.80
	25	2.93	1.66	3.33	2.28
	30	-	-	4.12	2.87

Table 6.07

Exchange rate of quinidine sulphate with resins X 4 and X 8.

Resin	t (min.)	35°C			45°C		
		Values of x / (b-x) when b =					
		1.000	1.00/2	1.00/4	1.000	1.00/2	1.00/4
X 4	5	0.38	0.17	-	0.47	0.22	-
	10	0.84	0.36	-	1.06	0.45	-
	15	1.27	0.57	-	1.64	0.71	-
	20	1.61	0.80	-	2.15	1.00	-
	25	1.86	1.08	-	2.59	1.34	-
X 8	5	0.29	-	-	0.38	-	-
	10	0.42	-	0.21	0.57	-	0.25
	15	0.54	-	-	0.73	-	-
	20	0.62	-	0.44	0.86	-	0.52
	25	0.71	-	-	1.01	-	-
	30	-	-	0.65	1.12	-	0.83
	40	-	-	0.80	-	-	1.08
	50	-	-	0.92	-	-	1.29

Table 6.08

Exchange rate of quinidine sulphate with resins X 12 and X 16

		35°C			45°C		
	t	Values of x / (b-x) when b =					
Resin	(min.)	1.005	1.005/2	1.005/4	1.005	1.005/2	1.005/4
X 12	10	0.21	0.20	-	0.30	0.27	-
	20	0.30	0.31	-	0.44	0.41	-
	30	0.37	0.38	-	0.55	0.51	-
	40	0.43	0.44	-	0.65	0.60	-
	50	0.48	0.49	-	0.73	0.67	-
	60	0.54	0.54	-	0.83	0.74	-
X 16	30	-	0.27	0.28	-	0.38	0.38
	60	-	0.41	0.41	-	0.55	0.54
	90	-	0.49	0.48	-	0.69	0.67
	120	-	0.57	0.56	-	0.81	0.78
	150	-	0.64	0.64	-	-	-

Table 6.09

Exchange rate of quinidine sulphate with resin X 20 .

		35°C		45°C	
	t	Values of x / (b - x) when b =			
Resin	(min.)	1.00/4	1.00/8	1.00/4	1.00/8
X 20	45	0.104	-	0.148	-
	60	-	0.081	-	0.124
	90	0.154	-	0.223	-
	120	-	0.129	-	0.196
	135	0.194	-	0.303	-
	180	0.233	0.160	0.377	0.269
	240	-	0.194	-	0.345

Table 6.10

Exchange rate of cinchonine sulphate with resins X 1 and X 2.

Resin	t (min.)	35°C Values of x / (b - x) when b = 0.957 x 2/3	35°C 0.957/2	45°C 0.957 x 2/3	45°C 0.957/2
X 1	5	0.63	0.45	0.76	0.55
	10	1.43	1.01	1.69	1.19
	15	2.32	1.66	2.88	2.02
	20	3.36	2.36	4.20	2.94
	25	4.43	3.07	5.55	3.83
	30	5.72	3.89	7.18	4.96
X 2	5	0.46	0.30	0.57	0.40
	10	1.01	0.64	1.26	0.86
	15	1.65	1.04	2.10	1.39
	20	2.41	1.51	3.13	1.98
	25	3.29	1.98	4.29	2.68
	30	4.23	2.60	5.69	3.50

Table 6.11

Exchange rate of cinchonine sulphate with resins X 4 and X 8.

		35°C			45°C		
		Values ov x / (b-x) when b =					
Resin	t (min.)	0.957	$0.957 \times \frac{2}{3}$	0.957/2	0.957	$0.957 \times \frac{2}{3}$	0.957/2
X 4	5	-	0.25	0.16	-	0.33	0.22
	10	-	0.52	0.38	-	0.71	0.46
	15	-	0.87	0.60	-	1.14	0.74
	20	-	1.26	0.87	-	1.67	1.05
	25	-	1.68	1.15	-	2.31	1.41
	30	-	2.18	1.46	-	3.09	1.83
X 8	5	0.36	-	0.18	0.48	-	0.22
	10	0.69	-	0.39	0.96	-	0.48
	15	0.91	-	0.59	1.28	-	0.78
	20	1.14	-	0.85	1.59	-	1.12
	25	1.27	-	1.04	1.86	-	1.43
	30	1.43	-	1.24	2.14	-	1.75

Table 6.12

Exchange rate of cinchonine sulphate with resin X 12.

		35°C		45°C	
	t	Values of x / (b - x) when b =			
Resin	(min.)	0.957	0.957/2	0.957	0.957/2
X 12	5	-	-	0.36	0.33
	10	0.38	0.34	0.55	0.52
	15	-	-	0.70	0.65
	20	0.56	0.52	0.82	0.77
	25	-	-	0.95	0.90
	30	0.66	0.64	1.08	1.04
	40	0.84	0.77	-	-
	50	0.97	0.87	-	-
	60	1.08	0.98	-	-

Table 6.13

Exchange rate of cinchonine sulphate with resins X 16 and X 20.

		35°C		45°C	
	t	Values of x / (b - x) when b =			
Resin	(min.)	0.957/4	0.957/8	0.957/4	0.957/8
X 16	15	-	-	0.40	0.30
	30	0.40	0.37	0.57	0.51
	45	-	-	0.71	0.63
	60	0.54	0.53	0.80	0.73
	75	-	-	0.92	0.80
	90	0.65	0.63	1.01	-
	120	0.73	0.71	-	-
	150	0.80	0.78	-	-
X 20	60	0.09	0.10	0.17	0.18
	120	0.15	0.16	0.29	0.29
	180	0.20	0.21	0.43	0.42
	240	0.26	0.26	0.55	0.54

Table 6.14

Exchange rate of cinchonidine sulphate with resins X 1 and X 2.

Resin	t (min.)	35°C Values of x / (b-x) when b = 1.091	1.091 × 2/3	1.091/2	45°C Values of x / (b-x) when b = 1.077	1.077 × 2/3	1.077/2
X 1	5	0.94	0.68	0.45	1.23	0.82	0.62
	10	2.18	1.51	0.98	2.83	1.90	1.40
	15	3.51	2.47	1.64	4.57	3.10	2.26
	20	4.90	3.45	2.37	6.44	4.28	3.28
	25	6.27	4.31	3.03	7.89	5.42	4.18
	30	7.72	5.38	3.92	9.32	6.50	5.18
X 2	5	0.72	0.46	0.30	0.97	0.58	0.43
	10	1.68	1.01	0.68	2.24	1.30	0.94
	15	2.84	1.68	1.12	3.69	2.12	1.52
	20	4.21	2.44	1.65	5.47	3.06	2.19
	25	5.70	3.12	2.14	6.86	4.10	2.90
	30	7.18	4.08	2.80	8.87	5.10	3.71

Table 6.15

Exchange rate of cinchonidine sulphate with resins X 4 and X 8.

		35°C			45°C		
	t	Values of x / (b-x) when b =					
Resin	(min.)	1.091	1.091×⅔	1.091/2	1.077	1.077×⅔	1.077/2
X 4	5	0.41	0.26	0.19	0.54	0.32	0.25
	10	0.94	0.56	0.42	1.20	0.71	0.53
	15	1.58	0.93	0.67	2.01	1.14	0.85
	20	2.28	1.33	0.97	3.00	1.70	1.21
	25	3.07	1.78	1.28	4.09	2.27	1.62
	30	4.08	2.31	1.67	5.19	3.01	2.10
X 8	5	0.38	-	0.17	0.51	-	0.23
	10	0.70	-	0.37	0.97	-	0.50
	15	0.91	-	0.58	1.31	-	0.80
	20	1.11	-	0.83	1.56	-	1.14
	25	1.27	-	1.03	1.83	-	1.44
	30	1.44	-	1.24	2.07	-	1.78

Table 6.16

Exchange rate of cinchonidine sulphate with resin X 12.

		35°C		45°C	
	t	Values of x / (b - x) when b =			
Resin	(min.)	1.091	1.091/2	1.077	1.077/2
X 12	5	-	-	0.34	0.30
	10	0.35	0.32	0.51	0.49
	15	-	-	0.65	0.63
	20	0.52	0.49	0.76	0.74
	25	-	-	0.87	0.83
	30	0.65	0.62	0.98	0.95
	40	0.76	0.73	-	-
	50	0.87	0.82	-	-
	60	0.98	0.93	-	-

Table 6.17

Exchange rate of cinchonidine sulphate with resins X 16 and X 20.

		35°C		45°C	
	t	values of x / (b - x) when b =			
Resin	(min.)	1.091/4	1.091/8	1.077/4	1.077/8
X 16	15	-	-	0.37	0.30
	30	0.39	0.39	0.56	0.52
	45	-	-	0.67	0.63
	60	0.57	0.56	0.78	0.72
	75	-	-	0.85	-
	90	0.69	0.67	-	-
	120	0.79	0.77	-	-
	150	0.87	-	-	-
X 20	60	0.145	0.106	0.213	0.245
	120	0.212	0.171	0.368	0.371
	180	0.266	0.236	0.494	0.490
	240	0.322	0.391	0.641	0.610

Table 6.18

Exchange rate of quinine sulphate with resin IR-200 of different particle diameters.

		35°C		45°C	
a	t	Values of x / (b - x) when b =			
(mm.)	(min.)	1.046/2	1.046/4	1.046/2	1.046/4
0.37	5	0.17	0.09	0.22	0.10
	10	0.37	0.18	0.48	0.22
	15	0.57	0.29	0.75	0.35
	20	0.83	0.40	1.07	0.49
	25	1.04	0.52	1.40	0.66
	30	1.32	-	1.73	-
0.58	5	0.12	0.06	0.14	0.08
	10	0.24	0.11	0.31	0.16
	15	0.36	0.18	0.48	0.25
	20	0.49	0.25	0.63	0.35
	25	0.59	0.33	0.77	0.46
	30	0.70	-	0.93	-
0.84	5	-	-	-	0.05
	10	0.17	0.08	0.21	0.10
	15	-	-	-	0.16
	20	0.31	0.17	0.41	0.21
	25	-	-	-	0.28
	30	0.46	0.28	0.58	-
	40	0.58	0.40	0.78	-
	50	0.69	0.51	0.96	-

Table 6.19

Exchange rate of quinidine sulphate with resin IR-200 of different particle diameters.

a (mm.)	t (min.)	35°C Values of x / (b - x) when b = 1.00/2	35°C 1.00/4	45°C 1.005/2	45°C 1.005/4
0.37	5	0.17	0.10	0.21	0.11
	10	0.35	0.19	0.48	0.24
	15	0.56	0.27	0.76	0.37
	20	0.74	0.37	1.07	0.52
	25	0.93	0.46	1.42	0.68
	30	-	-	1.78	-
		1.004/2	1.004/4	1.004/2	1.004/4
0.58	5	0.10	0.07	0.15	0.08
	10	0.22	0.13	0.29	0.15
	15	0.35	0.19	0.49	0.23
	20	0.46	0.26	0.67	0.32
	25	0.57	0.34	0.82	0.40
	30	0.68	-	0.98	-
0.84	5	0.08	0.05	0.10	0.07
	10	0.16	0.09	0.20	0.12
	15	0.24	0.14	0.31	0.17
	20	0.32	0.18	0.42	0.23
	25	0.40	0.23	0.52	0.29
	30	0.46	-	0.60	-

Table 6.20

Exchange rate of cinchonine sulphate with resin IR-200 of different particle diameters.

		35°C		45°C	
a	t	Values of x / (b - x) when b =			
(mm.)	(min.)	0.957/2	0.957/4	0.957/2	0.957/4
0.37	5	0.14	0.07	0.21	0.10
	10	0.33	0.16	0.44	0.20
	15	0.52	0.23	0.71	0.30
	20	0.74	0.35	1.02	0.42
	25	0.99	0.45	1.37	0.55
	30	1.26	0.56	1.78	0.71
0.58	5	0.10	0.05	0.13	0.07
	10	0.22	0.10	0.29	0.13
	15	0.34	0.16	0.45	0.18
	20	0.48	0.22	0.62	0.25
	25	0.61	0.28	0.83	0.34
	30	0.76	0.35	1.04	0.43
0.84	5	-	-	0.09	0.04
	10	0.13	0.06	0.19	0.10
	15	-	-	0.29	0.15
	20	0.28	0.12	0.36	0.22
	25	-	-	0.51	0.27
	30	0.43	0.19	0.59	0.34
	40	0.59	0.26	-	-
	50	0.74	0.37	-	-
	60	0.90	0.46	-	-

Figure 6·08

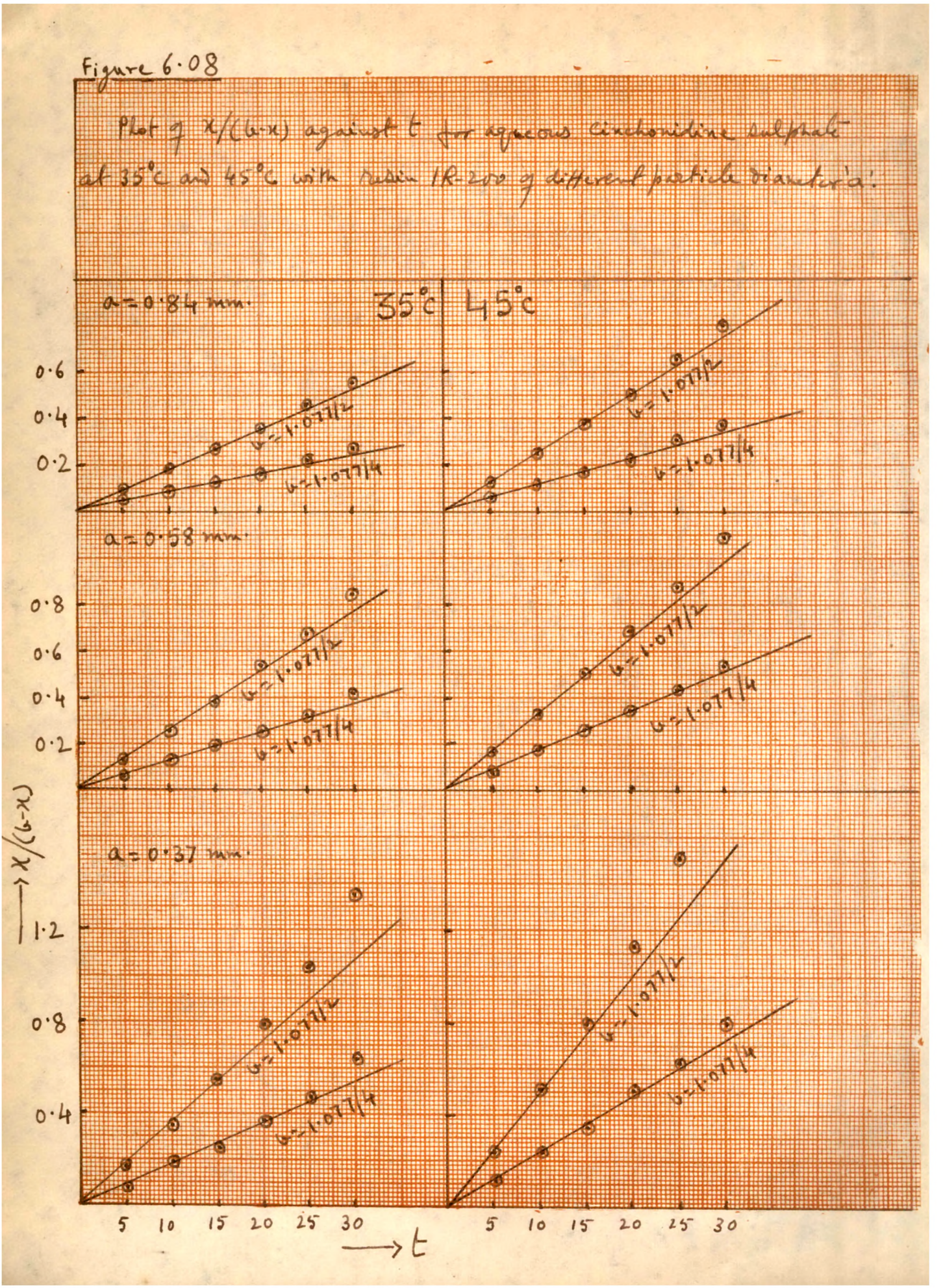
Plot of x/(a-x) against t for aqueous cinchonidine sulphate at 35°C and 45°C with radius 1R-200 g different particle diameter 'a'.
a = 0·84 mm.
35°C
45°C
a = 0·58 mm.
a = 0·37 mm.
b = 1·077/2
b = 1·077/4
0·6
0·4
0·2
0·8
1·2
x/(a-x)
5
10
15
20
25
30
t

Table 6.21

Exchange rate of cinchonidine sulphate with resin IR-200 of different particle diameters.

a (mm.)	t (min.)	35°C		45°C	
		Values of x / (b - x) when b =			
		1.077/2	1.077/4	1.077/2	1.077/4
0.37	5	0.15	0.07	0.23	0.11
	10	0.34	0.19	0.50	0.23
	15	0.54	0.25	0.78	0.33
	20	0.78	0.36	1.13	0.49
	25	1.04	0.47	1.49	0.61
	30	1.34	0.63	1.93	0.78
0.58	5	0.11	0.05	0.15	0.07
	10	0.24	0.12	0.31	0.16
	15	0.36	0.18	0.48	0.24
	20	0.52	0.24	0.67	0.33
	25	0.66	0.31	0.86	0.42
	30	0.83	0.41	1.08	0.53
0.84	5	0.08	0.04	0.11	0.05
	10	0.17	0.06	0.24	0.11
	15	0.25	0.11	0.37	0.16
	20	0.34	0.15	0.49	0.23
	25	0.45	0.22	0.65	0.30
	30	0.54	0.27	0.80	0.36

Table 6.22

Exchange rate of quinine sulphate with resin Amb-15 of different particle daimeters.

a (mm.)	t (min.)	35°C Values of x / (b - x) when b = 1.052/2	45°C Values of x / (b - x) when b = 1.052/2
0.37	5	0.19	0.22
	10	0.39	0.44
	15	0.58	0.66
	20	0.78	0.93
	25	0.96	1.11
	30	1.15	1.40
0.58	5	0.12	0.14
	10	0.24	0.29
	15	0.35	0.44
	20	0.47	0.59
	25	0.58	0.73
	30	0.68	0.88
0.84	5	0.09	0.11
	10	0.18	0.21
	15	0.27	0.32
	20	0.35	0.43
	25	0.42	0.52
	30	0.47	0.61

Table 6.23

Exchange rate of quinidine sulphate with resin Amb-15 of different particle diameters.

a (mm.)	t (min.)	35°C Values of x / (b - x) when b = 1.004/2	45°C Values of x / (b - x) when b = 1.004/2
0.37	5	0.18	0.22
	10	0.33	0.46
	15	0.51	0.69
	20	0.59	0.93
	25	0.85	1.17
	30	0.99	1.37
0.58	5	0.12	0.15
	10	0.24	0.29
	15	0.35	0.44
	20	0.47	0.56
	25	0.58	0.72
	30	0.66	0.85
0.84	5	0.08	0.12
	10	0.17	0.24
	15	0.26	0.35
	20	0.35	0.46
	25	0.41	0.57
	30	0.47	0.68

Figure 6·09

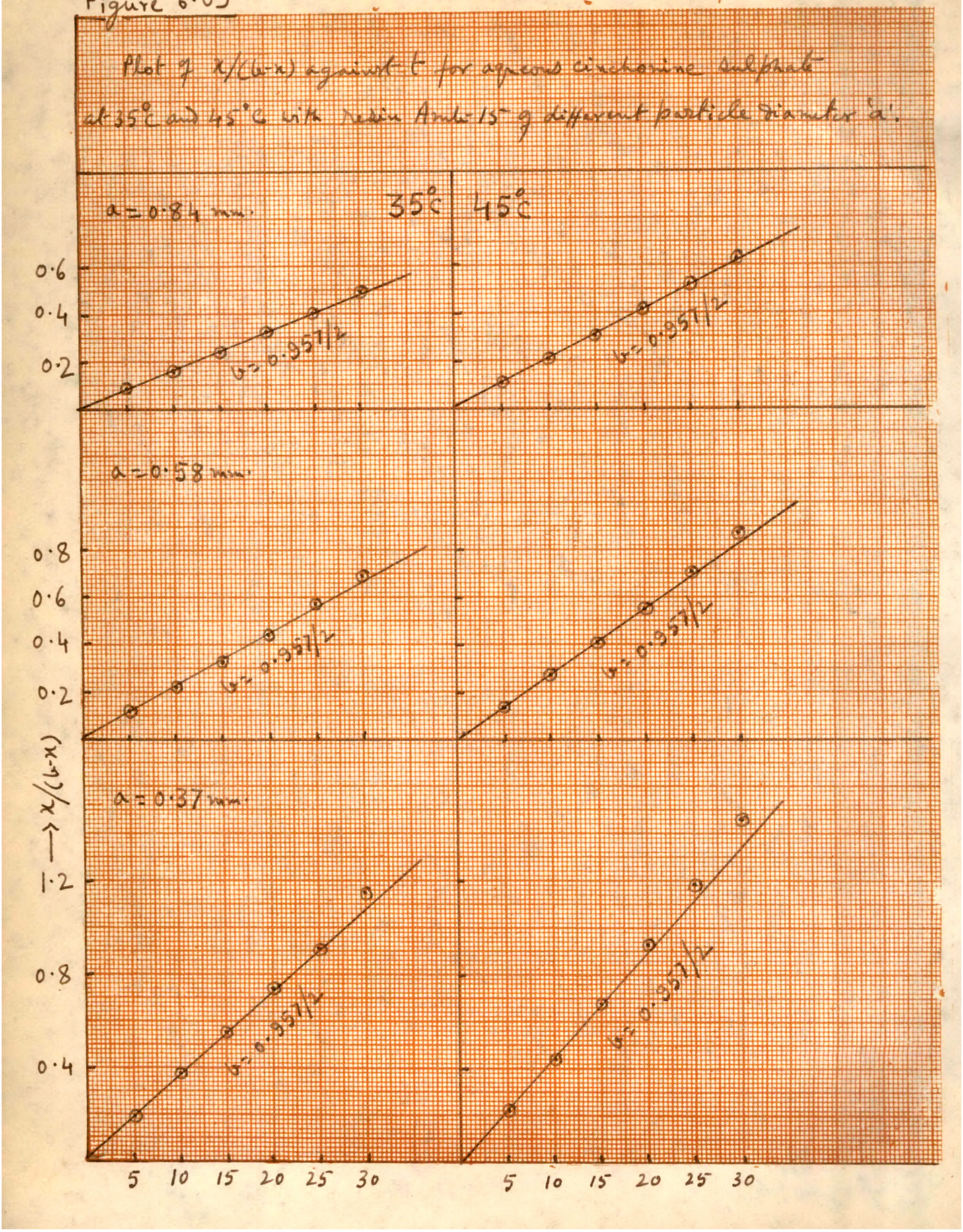
Plot of x/(a-x) against t for aqueous zirchorine sulphate at 35°C and 45°C with Resin Amb-15 of different particle diameter 'a'.
a = 0·84 mm.
35°C
45°C
a = 0·58 mm.
a = 0·37 mm.
x/(a-x) ⟶
0·2
0·4
0·6
0·8
1·2
5
10
15
20
25
30
y = 0·957/x

Table 6.24

Exchange rate of cinchonine sulphate with resin Amb-15 of different particle diameters.

a (mm.)	t (min.)	35°C Values of x/(b-x) when b = 0.957/2	45°C Values of x/(b-x) when b = 0.957/2
0.37	5	0.18	0.21
	10	0.36	0.44
	15	0.53	0.67
	20	0.72	0.93
	25	0.92	1.18
	30	1.14	1.45
0.58	5	0.11	0.12
	10	0.21	0.26
	15	0.31	0.40
	20	0.43	0.54
	25	0.56	0.70
	30	0.68	0.87
0.84	5	0.08	0.10
	10	0.15	0.19
	15	0.23	0.29
	20	0.32	0.41
	25	0.39	0.51
	30	0.49	0.62

Table 6.25

Exchange rate of cinchonidine sulphate with resin Amb-15 of different particle diameters.

		35°C	45°C
a (mm.)	t (min.)	Values of x/(b-x) when b = 1.077/2	1.077/2
0.37	5	0.19	0.22
	10	0.39	0.45
	15	0.59	0.70
	20	0.80	0.95
	25	1.04	1.25
	30	1.26	1.54
0.58	5	0.13	0.15
	10	0.25	0.29
	15	0.37	0.45
	20	0.51	0.63
	25	0.64	0.80
	30	0.78	0.97
0.84	5	0.09	0.10
	10	0.18	0.20
	15	0.27	0.30
	20	0.37	0.42
	25	0.45	0.55
	30	0.55	0.66

Table 6.26

Exchange rate of quinine sulphate with resin IR-120 of different particle diameters.

		35°C			45°C		
a	t	Values of x / (b-x) when b =					
(mm.)	(min.)	1.047x2	1.047	1.052/2	1.046x2	1.046	1.052/2
0.23	5	-	-	0.15	-	-	0.19
	10	-	-	0.26	-	-	0.36
	15	-	-	0.35	-	-	0.48
	20	-	-	0.42	-	-	0.57
	25	-	-	0.48	-	-	0.68
	30	-	-	0.53	-	-	0.77
0.37	5	0.16	0.16	-	0.24	0.22	-
	10	0.24	0.23	-	0.38	0.34	-
	15	0.30	0.30	-	0.46	0.42	-
	20	0.36	0.36	-	0.54	0.51	-
	25	0.41	0.41	-	0.62	0.58	-
	30	0.45	0.45	-	0.70	0.66	-

Table 6.27

Exchange rate of quinine sulphate with resin IR-120 of different particle diameters.

a (mm.)	t (min.)	35°C: Values of x / (b - x) when b = 1.047 x 2	35°C: 1.047	45°C: 1.046 x 2	45°C: 1.046
0.58	5	0.12	0.11	0.17	0.15
	10	0.17	0.16	0.25	0.23
	15	0.21	0.21	0.31	0.30
	20	0.26	0.25	0.37	0.35
	25	0.29	0.29	0.42	0.41
	30	0.32	0.32	0.47	0.46
0.84	5	0.10	0.09	0.14	0.14
	10	0.15	0.14	0.22	0.22
	15	0.20	0.18	0.29	0.29
	20	0.24	0.22	0.34	0.33
	25	0.27	0.25	0.39	0.38
	30	0.30	0.29	0.43	0.42

Figure 6.10

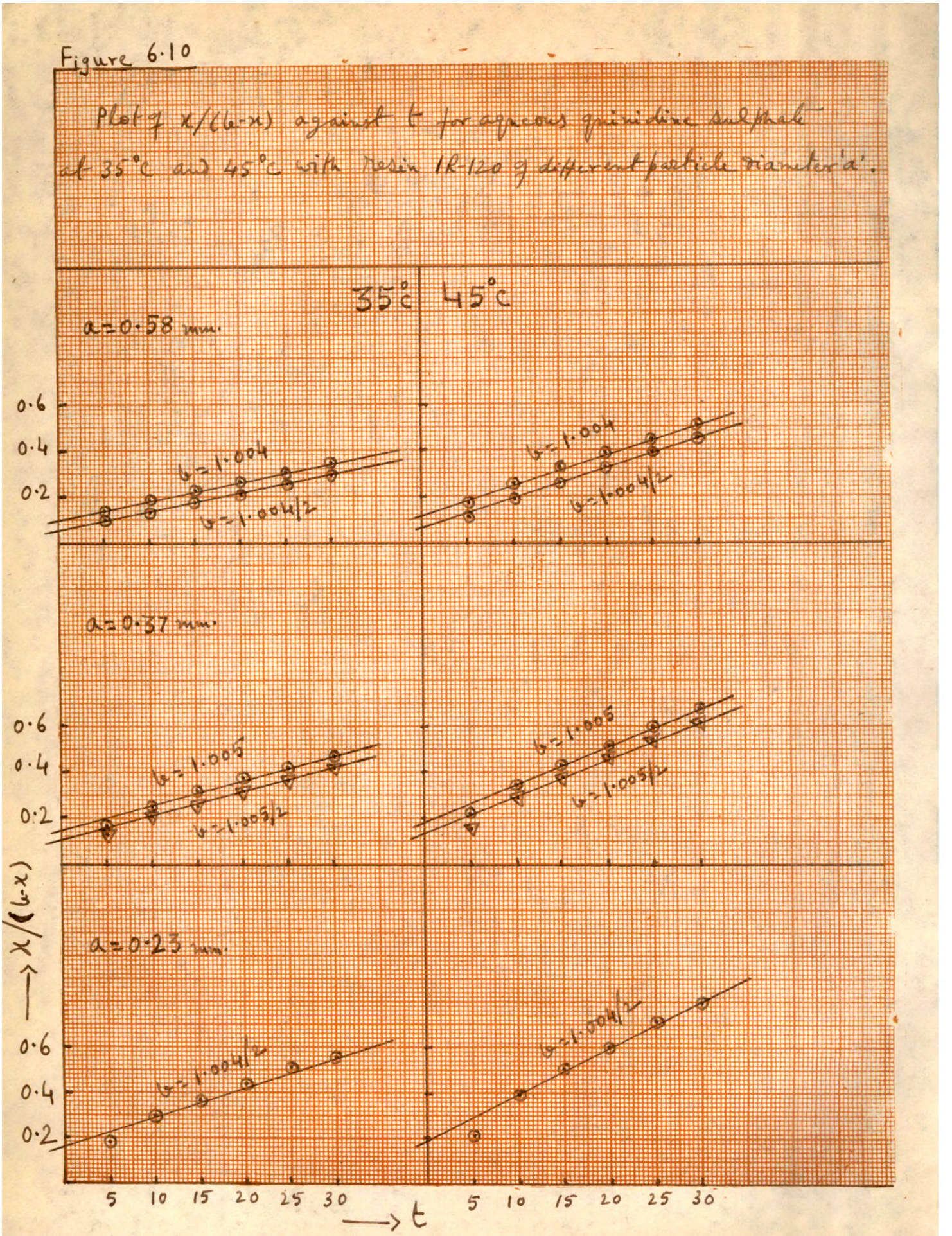
Plot of x/(a-x) against t for aqueous quinidine sulphate at 35°C and 45°C with resin IR-120 of different particle diameter 'a'.
35°C
45°C
a=0.58 mm.
a=0.37 mm.
a=0.23 mm.
b=1.004
b=1.004/2
b=1.005
b=1.005/2
0.6
0.4
0.2
x/(a-x)
5
10
15
20
25
30
t

Table 6.28

Exchange rate of quinidine sulphate with resin IR-120 of different particle diameters.

a (mm.)	t (min.)	35°C		45°C	
		Values of x/(b-x) when b =			
		1.004	1.004/2	1.004	1.004/2
0.23	5	-	0.17	-	0.21
	10	-	0.28	-	0.38
	15	-	0.36	-	0.50
	20	-	0.43	-	0.59
	25	-	0.49	-	0.71
	30	-	0.54	-	0.78
		1.005	1.005/2	1.005	1.005/2
0.37	5	0.15	0.11	0.20	0.14
	10	0.23	0.20	0.33	0.29
	15	0.30	0.26	0.42	0.38
	20	0.36	0.31	0.50	0.46
	25	0.40	0.36	0.57	0.53
	30	0.44	0.40	0.65	0.60
		1.004	1.004/2	1.004	1.004/2
0.58	5	0.12	0.09	0.16	0.10
	10	0.17	0.13	0.24	0.18
	15	0.21	0.16	0.32	0.27
	20	0.24	0.21	0.38	0.33
	25	0.29	0.25	0.43	0.39
	30	0.32	0.29	0.49	0.45

Table 6.29

Exchange rate of cinchonine sulphate with resin IR-120 of different particle diameters.

a (mm.)	t (min.)	35°C Values of x/ (b-x) when b = 0.957	35°C Values of x/ (b-x) when b = 0.957/2	45°C Values of x/ (b-x) when b = 0.957	45°C Values of x/ (b-x) when b = 0.957/2
0.23	5	-	0.14	-	0.17
	10	-	0.27	-	0.34
	15	-	0.41	-	0.53
	20	-	0.54	-	0.72
	25	-	0.64	-	0.88
	30	-	0.73	-	1.03
0.37	5	0.18	0.10	0.25	0.13
	10	0.30	0.20	0.43	0.25
	15	0.41	0.29	0.57	0.38
	20	0.48	0.38	0.70	0.52
	25	0.55	0.47	0.80	0.64
	30	0.62	0.53	0.92	0.75
0.58	5	0.14	0.08	0.18	0.10
	10	0.22	0.15	0.30	0.19
	15	0.29	0.21	0.41	0.30
	20	0.35	0.28	0.52	0.39
	25	0.39	0.33	0.58	0.48
	30	0.45	0.38	0.65	0.55

Table 6.30

Exchange rate of cinchonidine sulphate with resin IR-120 of different particle diameters.

a (mm.)	t (min.)	35°C		45°C	
		Values of x / (b - x) when b =			
		1.077	1.077/2	1.077	1.077/2
0.23	5	-	0.16	-	0.20
	10	-	0.31	-	0.40
	15	-	0.47	-	0.63
	20	-	0.63	-	0.85
	25	-	0.75	-	1.08
	30	-	0.87	-	1.27
0.37	5	0.21	0.11	0.28	0.15
	10	0.35	0.22	0.49	0.31
	15	0.46	0.32	0.65	0.47
	20	0.56	0.43	0.80	0.63
	25	0.64	0.53	0.92	0.76
	30	0.71	0.59	1.06	0.89
0.58	5	0.15	0.08	0.21	0.11
	10	0.24	0.17	0.35	0.21
	15	0.32	0.25	0.46	0.34
	20	0.38	0.32	0.57	0.45
	25	0.44	0.37	0.67	0.56
	30	0.49	0.43	0.76	0.65

6.2.d. Discussion :

The uptake of cations from dilute aqueous solution of cinchona alkaloid sulphate salts has been considered earlier to occur, in general, by two mechanisms, the exchange mechanism and the (molecular) sorption mechanism. The value of P_R , obtained by extrapolating the plot of P_R against (100 - P_A) to (100 - P_A) = 0 , and termed as P_{Ro} , has been considered as the contribution of the exchange mechanism to the experimental value of P_R .

If C denotes the capacity of the resin in meq. per gram of air-dry resin, C. P_{Ro} / 100 is termed as the effective exchange capacity of the resin and is denoted by C_{ef}. If b denotes the concentration of the alkaloid sulphate in meq. per litre, and g the weight of the air-dry resin in grams per litre used in the rate experiment, then g was always kept equal to b / C_{ef} . This means that the concentration of the alkaloid sulphate in aqueous solution per litre was always kept equal to the concentration of the resin per litre, the effective capacity being used, instead of the actual air-dry capacity of the resin, in the calculation of the concentration of the resin in meq. / litre. This condition was observed in all the runs which have been carried out.

The rate of exchange may be determined by film diffusion or particle diffusion or both, depending on the particular experimental conditions. The mathematical solutions have been worked out in literature for some simple cases

involving simple inorganic cations. However, even those calculations are difficult and the application to the large organic cations would be more so. Hence a simplified procedure, involving the application of the second order law, similar to that used by Nachod and Wood (18) for simple cations, has been applied to obtain relative rate constants and their co-relation to other variables.

For the condition, when the concentration of the salt solution, b , in meq. / litre is equal to the concentration of the resin, in meq. / litre, the effective capacity being used instead of air-dry capacity, the second order rate constant K is given by

$$K = \frac{10^3}{b \cdot t} \cdot \frac{x}{(b - x)}$$

where x is the concentration in meq. / litre when time $t = t$. Hence the plot of $x/(b-x)$ against t should be linear, pass through the origin and the slope, S , is given by $b.K/10^3$. Therefore the slope should be proportional to b , and the slope divided by $b/10^3$ gives the value of K in $(\text{minute})^{-1}$. $(\text{gram-equivalents per litre})^{-1}$.

When the data for resins X 1, X 2 and X 4 are considered, it is observed that (tables 6.01 and 6.02, 6.06 and 6.07, 6.10 and 6.11, 6.14 and 6.15 and figures 6.01 to 6.03) the above conditions are applicable upto atleast 50 to 70 % of exchange after which there is a

Table 6.31

Slope from the plot of x / (b - x) against t (the intercept, in all cases = zero) and values of K at different concentrations (b), for quinine sulphate with different resins.

Resin	a (mm.)	35°C b	35°C Slope.10^{+1}	35°C K	45°C b	45°C Slope.10^{+1}	45°C K
X 1	0.215	1.047	1.875	179.1	1.046/2	1.225	234.2
		1.047×2/3	1.300	186.33	1.046/4	0.595	227.5
		1.047/2	0.940	179.6	-	-	-
X 2	0.215	1.047	1.515	144.6	1.046/2	0.815	155.8
		1.047×2/3	1.040	148.3	1.046/4	0.395	151.0
		1.047/2	0.750	143.2	-	-	-
X 4	0.215	1.047	0.890	85.0	1.046	0.975	93.1
		1.047×2/3	0.610	87.38	1.046/2	0.485	92.7
		1.047/2	0.460	87.46	-	-	-
IR-200	0.37	1.046/2	0.365	69.77	1.046/2	0.480	91.7
		1.046/4	0.195	74.56	1.046/4	0.235	89.8
	0.58	1.046/2	0.235	44.92	1.046/2	0.315	60.2
		1.046/4	0.125	47.79	1.046/4	0.165	63.0
	0.84	1.046/2	0.155	29.63	1.046/2	0.210	40.1
		1.046/4	0.085	32.49	1.046/4	0.105	40.1
Amb-15	0.37	1.052/2	0.385	73.19	1.052/2	0.445	84.6
	0.58	1.052/2	0.240	45.62	1.052/2	0.290	55.1
	0.84	1.052/2	0.170	32.32	1.052/2	0.210	39.9

Table 6.32

Slope from the plot of x/(b-x) against t (the intercept, in all cases = zero) and values of K at different concentrations (b) for quinidine sulphate with different resins.

		35°C			45°C		
Resin	(mm.)	b	Slope. 10^{+1}	K	b	Slope. 10^{+1}	K
X 1	0.215	1.000	1.880	188.0	1.005x⅔	1.430	213.4
		1.000/2	0.925	185.0	1.005/2	1.040	207.0
X 2	0.215	1.000	1.285	128.5	1.005x⅔	1.040	155.2
		1.000/2	0.605	121.0	1.005/2	0.79	157.2
X 4	0.215	1.000	0.805	80.5	1.005	0.975	97.5
		1.000/2	0.375	75.0	1.005/2	0.455	91.0
IR-200	0.37	1.000/2	0.360	72.0	1.005/2	0.490	97.5
		1.000/4	0.185	74.0	1.005/4	0.250	99.5
	0.58	1.004/2	0.230	45.82	1.004/2	0.320	63.7
		1.004/4	0.130	51.79	1.004/4	0.160	63.7
	0.84	1.004/2	0.160	31.87	1.004/2	0.210	41.8
		1.004/4	0.090	35.86	1.004/4	0.115	45.8
Amb-15	0.37	1.004/2	0.340	67.74	1.004/2	0.455	90.6
	0.58	1.004/2	0.230	45.82	1.004/2	0.290	57.7
	0.84	1.004/2	0.165	32.87	1.004/2	0.230	45.8

Table 6.33

Slope from the plot of x/(b-x) against t (the intercept, in all cases = zero) and values of K at different concentrations (b), for cinchonine sulphate with different resins.

Resin	a (mm.)	b	35°C		45°C	
			Slope. 10^{+1}	K	Slope. 10^{+1}	K
X 1	0.215	0.957 x 2/3	1.245	195.1	1.480	232.0
		0.957/2	0.965	201.7	1.105	231.0
X 2	0.215	0.957 x 2/3	0.940	147.3	1.115	174.8
		0.957/2	0.665	139.0	0.825	172.4
X 4	0.215	0.957 x 2/3	0.540	84.63	0.700	109.7
		0.957/2	0.395	82.54	0.485	101.4
IR-200	0.37	0.957/2	0.345	72.09	0.460	96.14
		0.957/4	0.175	73.16	0.210	87.78
	0.58	0.957/2	0.230	48.07	0.310	64.79
		0.957/4	0.110	45.98	0.145	60.60
	0.84	0.957/2	0.145	30.31	0.195	40.76
		0.957/4	0.065	27.17	0.110	45.98
Amb-15	0.37	0.957/2	0.360	75.23	0.450	94.04
	0.58	0.957/2	0.220	45.98	0.275	57.48
	0.84	0.957/2	0.160	33.44	0.205	42.85

Table 6.34

Slope from the plot of x / (b-x) against t (the intercept, in all cases = zero) and values of K at different concentrations (b), for cinchonidine sulphate with different resins.

Resin	(mm.)	35°C b	35°C Slope.10^{+1}	35°C K	45°C b	45°C Slope.10^{+1}	45°C K
X 1	0.215	1.091	1.950	179.2	1.077	2.425	225.2
		1.091×⅔	1.365	187.7	1.077×⅔	1.630	227.0
		1.091/2	0.990	181.5	1.077/2	1.230	228.4
X 2	0.215	1.091	1.410	129.2	1.077	1.880	174.6
		1.091×⅔	1.000	137.5	1.077×⅔	1.215	169.2
		1.091/2	0.675	123.7	1.077/2	0.915	169.9
X 4	0.215	1.091	0.865	79.29	1.077	1.065	98.9
		1.091×⅔	0.570	78.36	1.077×⅔	0.685	95.39
		1.091/2	0.420	77.00	1.077/2	0.545	101.2
IR-200	0.37	1.077/2	0.360	66.85	1.077/2	0.500	92.85
		1.077/4	0.180	66.85	1.077/4	0.245	90.99
	0.58	1.077/2	0.260	48.27	1.077/2	0.325	60.36
		1.077/4	0.120	45.57	1.077/4	0.165	61.28
	0.84	1.077/2	0.170	31.57	1.077/2	0.250	46.43
		1.077/4	0.080	29.71	1.077/4	0.120	44.57
Amb-15	0.37	1.077/2	0.400	74.29	1.077/2	0.470	87.28
	0.58	1.077/2	0.255	47.36	1.077/2	0.305	56.63
	0.84	1.077/2	0.180	33.43	1.077/2	0.210	38.99

Table 6.35

Slope and intercept from the plot of $x/(b-x)$ against t, at different concentrations (b) for quinine sulphate with different resins.

Resin	a (mm.)	b	35°C Slope. 10^{+1}	35°C inter-cept.	b	45°C Slope. 10^{+1}	45°C inter-cept.
X 8	0.215	1.047x2	0.225	0.270	1.046	0.300	0.360
		1.047	0.225	0.270	1.046/4	0.300	zero
		1.047/2	0.220	0.200	-	-	-
		1.047/4	0.225	zero	-	-	-
X 12	0.215	1.047	0.062	0.240	1.046/2	0.105	0.250
		1.047/2	0.062	0.240	1.046/4	0.105	0.250
		1.047/4	0.062	0.240	-	-	-
X 16	0.215	1.047/2	0.030	0.240	1.046/2	0.052	0.290
		1.047/4	0.030	0.240	1.046/4	0.052	0.290
		1.047/8	0.030	0.240	-	-	-
X 20	0.215	1.047/4	0.0055	0.050	1.046/4	0.0125	0.044
		1.047/8	0.0055	0.050	1.046/8	0.0125	0.033
IR-120	0.23	1.052/2	0.145	0.120	1.052/2	0.205	0.160
	0.37	1.047x2	0.115	0.120	1.046x2	0.153	0.230
		1.047	0.115	0.120	1.046	0.153	0.200
	0.58	1.047x2	0.095	0.060	1.046x2	0.120	0.120
		1.047	0.095	0.060	1.046	0.120	0.110
	0.84	1.047x2	0.085	0.040	1.046x2	0.110	0.100
		1.047	0.085	0.040	1.046	0.110	0.100

Table 6.36

Slope and intercept from the plot of x/(b-x) against t, at different concentrations (b) for quinidine sulphate with different resins.

Resin	a (mm.)	B	35°C Slope. 10^{+1}	35°C inter-cept.	b	45°C Slope. 10^{+1}	45°C inter-cept.
X 8	0.215	1.000	0.225	0.180	1.000	0.285	0.270
		1.000/4	0.220	zero	1.000/4	0.265	zero
X 12	0.215	1.005	0.060	0.190	1.005	0.080	0.310
		1.005/2	0.060	0.190	1.005/2	0.080	0.260
X 16	0.215	1.005/2	0.025	0.260	1.005/2	0.035	0.330
		1.005/4	0.025	0.260	1.005/4	0.035	0.310
X 20	0.215	1.000/4	0.009	0.074	1.000/4	0.017	0.070
		1.000/8	0.0055	0.063	1.000/8	0.012	0.050
IR-120	0.23	1.004/2	0.130	0.150	1.004/2	0.205	0.180
	0.37	1.005	0.0966	0.160	1.005	0.155	0.170
		1.005/2	0.0966	0.110	1.005/2	0.155	0.140
	0.58	1.004	0.080	0.080	1.004	0.125	0.120
		1.004/2	0.080	0.050	1.004/2	0.125	0.070

Table 6.37

Slope and intercept from the plot of $x/(b-x)$ against t, at different concentrations (b) for cinchonine sulphate with different resins.

Resin	a (mm.)	b	35°C Slope. 10^{+1}	35°C inter-cept.	b	45°C Slope. 10^{+1}	45°C inter-cept.
X 8	0.215	0.957	0.400	0.280	0.957	0.490	0.590
		0.957/2	0.405	zero	0.957/2	0.490	zero
X 12	0.215	0.957	0.115	0.380	0.957	0.270	0.280
		0.957/2	0.115	0.290	0.957/2	0.265	0.250
X 16	0.215	0.957/4	0.030	0.380	0.957/4	0.075	0.350
		0.957/8	0.030	0.360	0.957/8	0.075	0.280
X 20	0.215	0.957/4	0.010	0.025	0.957/4	0.0214	0.035
		0.957/8	0.010	0.025	0.957/8	0.0214	0.035
IR-120	0.23	0.957/2	0.265	zero	0.957/2	0.350	zero
	0.37	0.957	0.185	0.100	0.957	0.245	0.190
		0.957/2	0.190	zero	0.957/2	0.250	zero
	0.58	0.957	0.120	0.090	0.957	0.190	0.110
		0.957/2	0.130	zero	0.957/2	0.190	zero

Table 6.38

Slope and intercept from the plot of $x/(b-x)$ against t, at different concentrations (b) for cinchonidine sulphate with different resins.

Resin	a (mm.)	35°C b	35°C Slope. 10^{+1}	35°C inter-cept.	45°C b	45°C Slope. 10^{+1}	45°C inter-cept.
X 8	0.215	1.091	0.410	0.240	1.077	0.540	0.440
		1.091/2	0.390	zero	1.077/2	0.520	zero
X 12	0.215	1.091	0.120	0.260	1.077	0.230	0.290
		1.091/2	0.120	0.220	1.077/2	0.235	0.250
X 16	0.215	1.091/4	0.040	0.360	1.077/4	0.070	0.340
		1.091/8	0.035	0.340	1.077/8	0.070	0.300
X 20	0.215	1.091/4	0.0110	0.075	1.077/4	0.0237	0.070
		1.091/8	0.0108	0.035	1.077/8	0.0237	0.070
IR-120	0.23	1.077/2	0.300	zero	1.077/2	0.420	zero
	037	1.077	0.215	0.110	1.077	0.305	0.160
		1.077/2	0.215	zero	1.077/2	0.310	zero
	0.58	1.077	0.135	0.110	1.077	0.215	0.150
		1.077/2	0.130	zero	1.077/2	0.215	zero

Figure 6.26

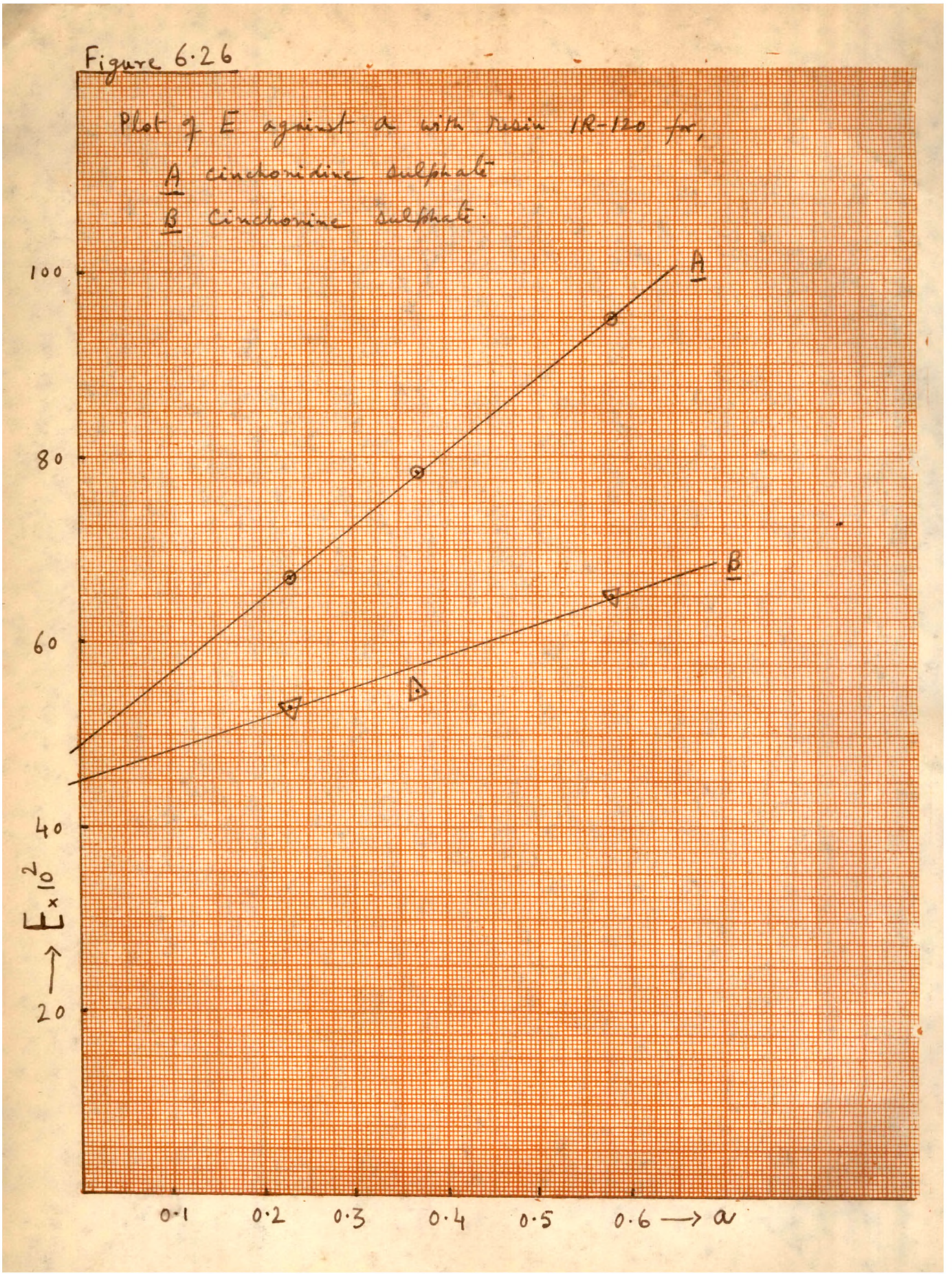
Plot of E against a with resin IR-120 for,
A cinchonidine sulphate
B Cinchonine sulphate.
100
80
60
40
20
$E \times 10^2$
A
B
0·1
0·2
0·3
0·4
0·5
0·6 → a

Figure 6.25

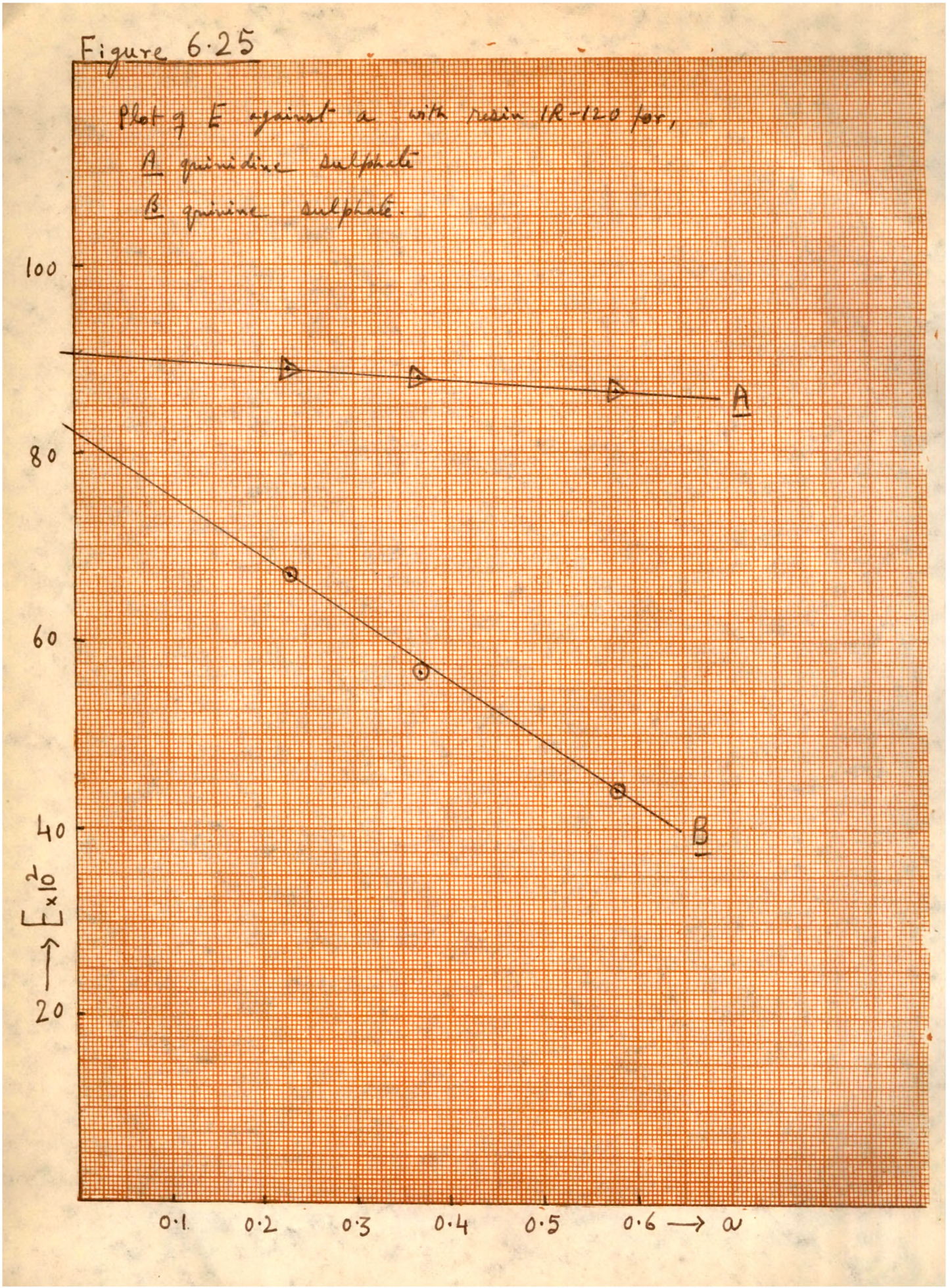
Plot of E against α with resin IR-120 for,
A quinidine sulphate
B quinine sulphate.
100
80
60
40
20
E = 1/x
0·1
0·2
0·3
0·4
0·5
0·6 → α
A
B

Figure 6.24

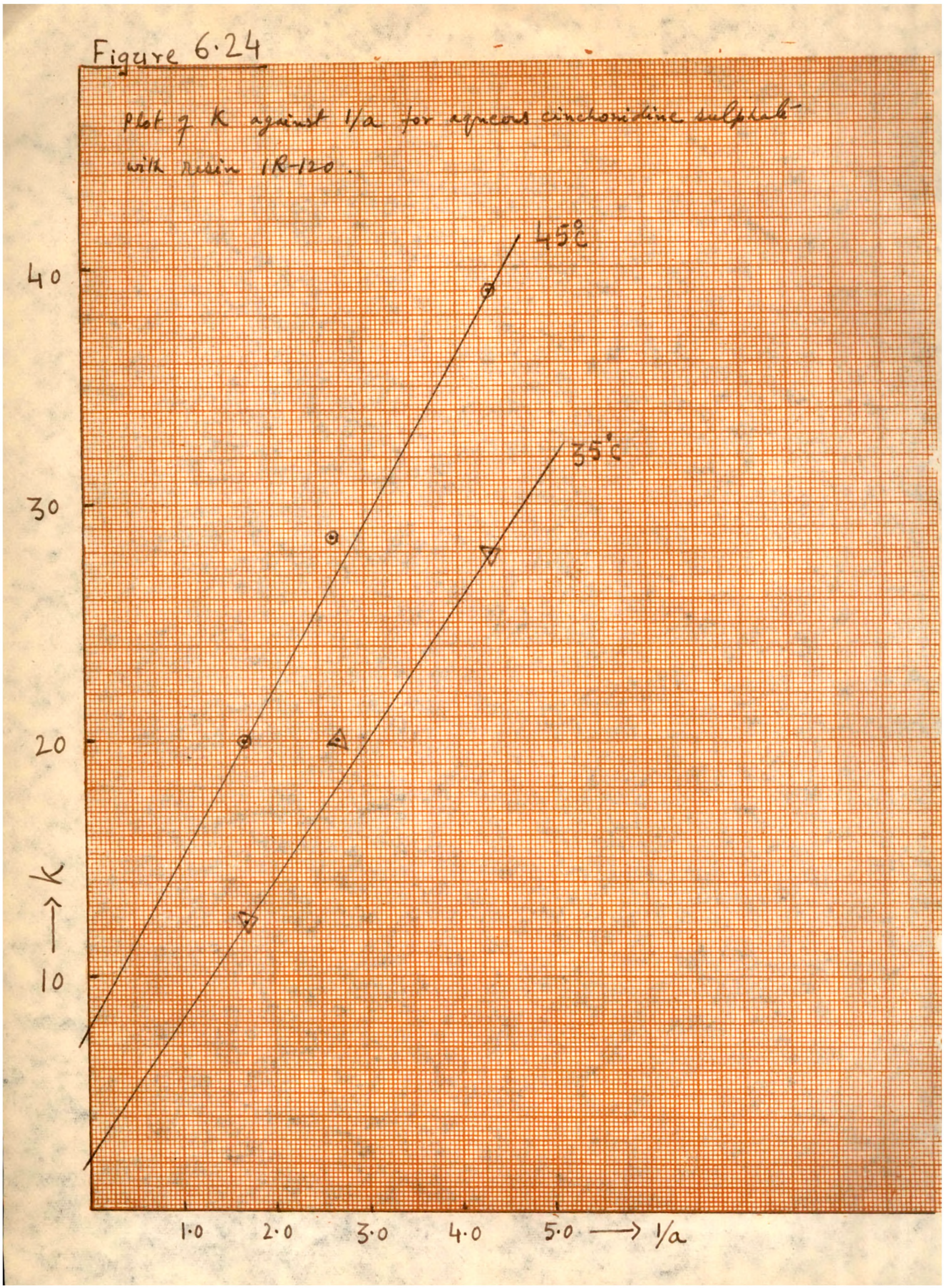
Plot of K against 1/a for aqueous cinchonidine sulphate with resin IR-120.
45°C
35°C
40
30
20
10
K
1·0
2·0
3·0
4·0
5·0
1/a

Figure 6.23

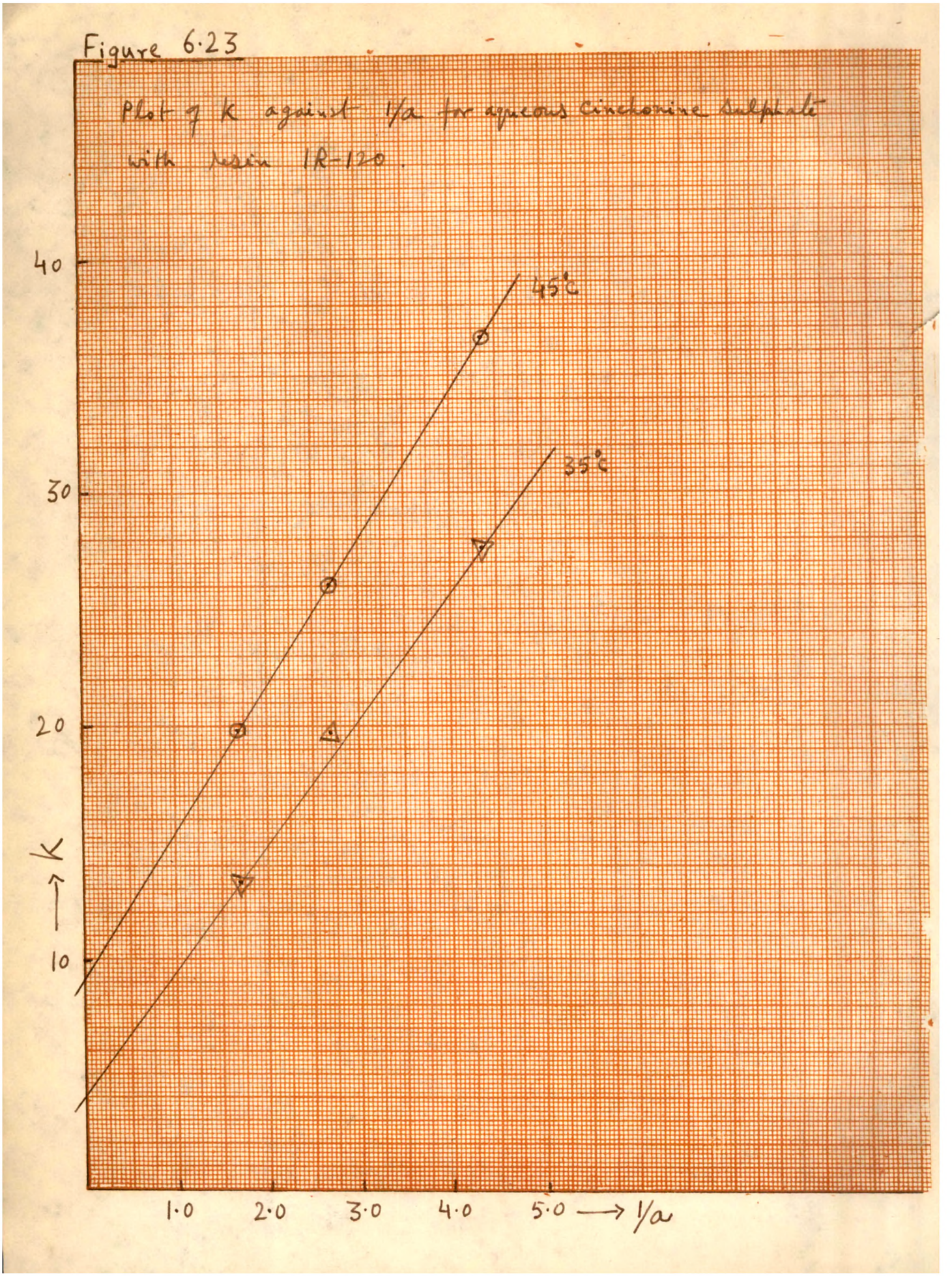
Plot of K against 1/a for aqueous cinchonine sulphate with resin IR-120.
40
30
20
10
K
45°C
35°C
1·0
2·0
3·0
4·0
5·0
1/a

Figure 6.22

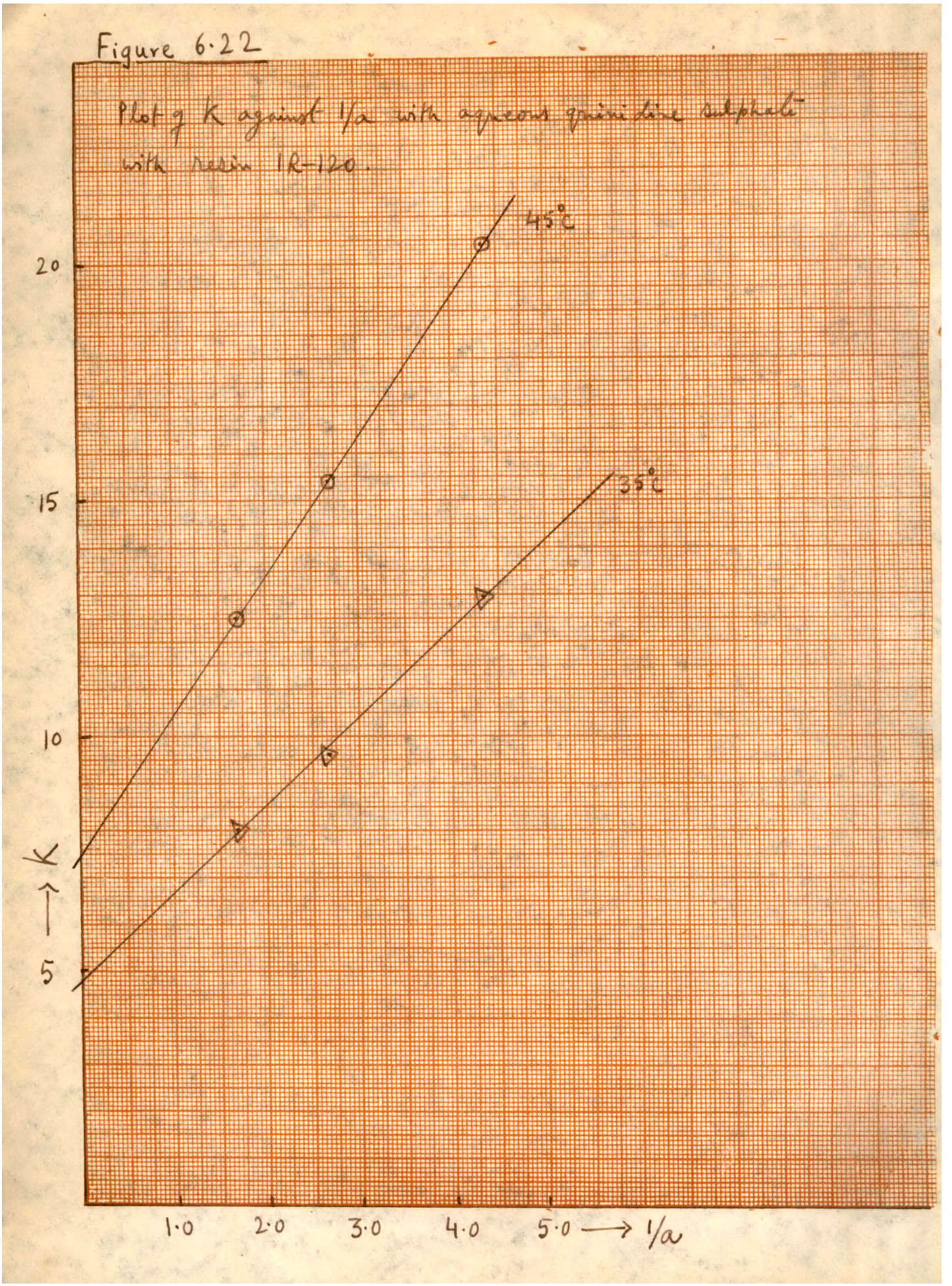
Plot of K against 1/a with aqueous quinidine sulphate with resin IR-120.
45°C
35°C
20
15
10
5
K
1·0
2·0
3·0
4·0
5·0
1/a

Figure 6.21

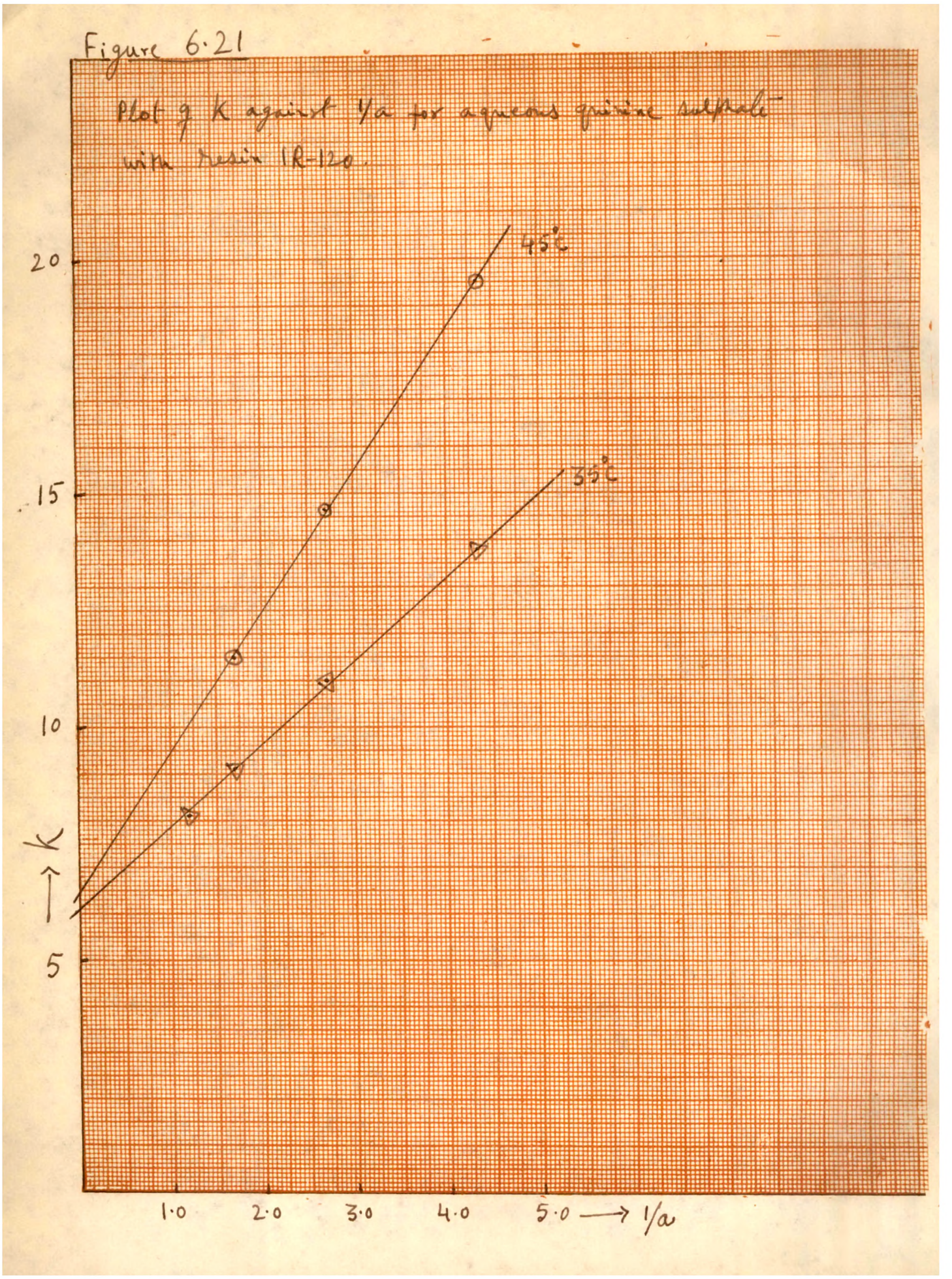
Plot of K against 1/a for aqueous guinine sulphate with resin IR-120.
45°C
35°C
20
15
10
5
K
1·0
2·0
3·0
4·0
5·0
1/a

Figure 6·20

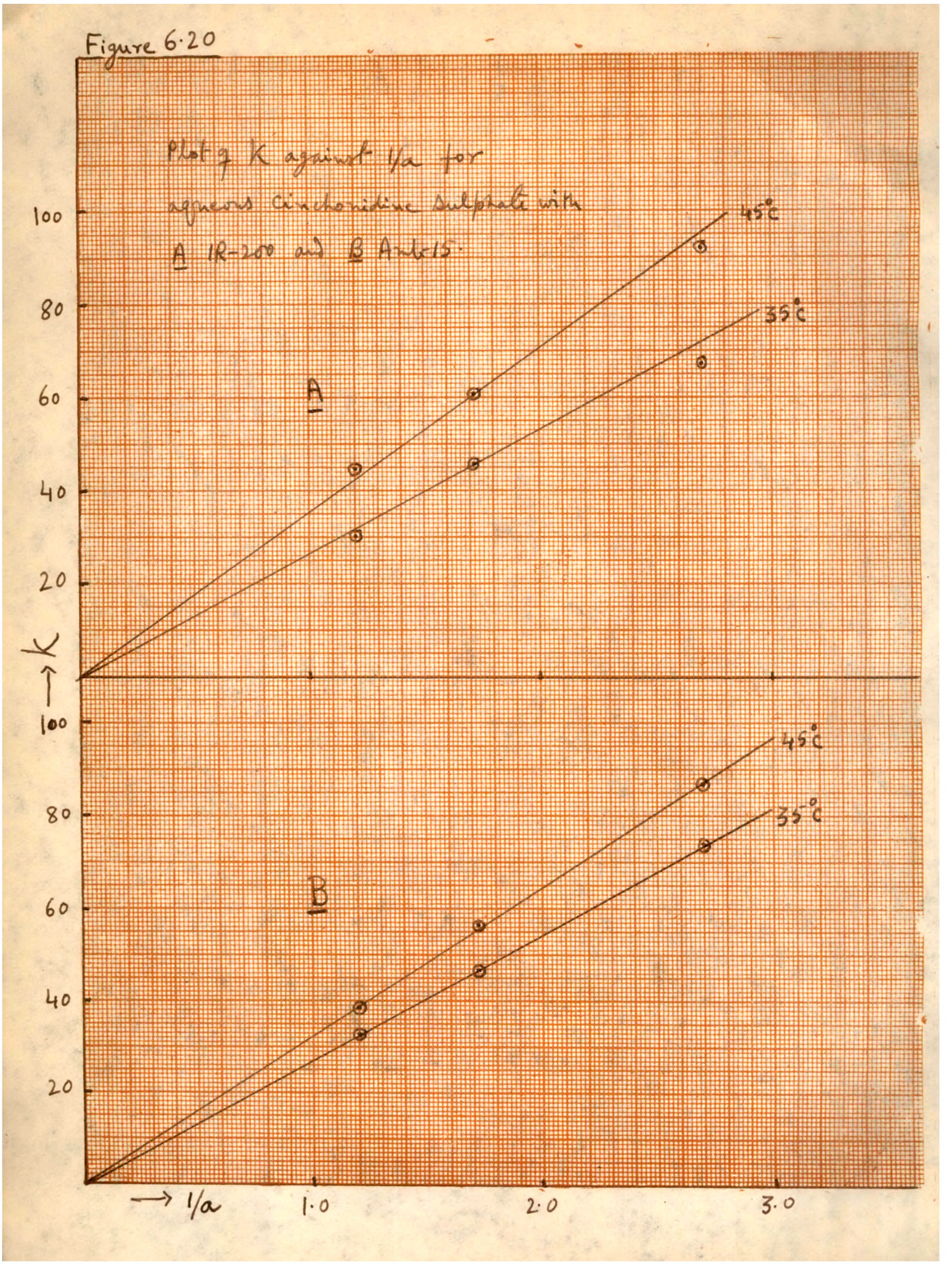
Plot of K against 1/a for aqueous cinchonidine sulphate with A IR-200 and B Amb 15.
100
80
60
40
20
K
100
80
60
40
20
A
B
45°C
35°C
45°C
35°C
1/a
1·0
2·0
3·0

Figure 6·19

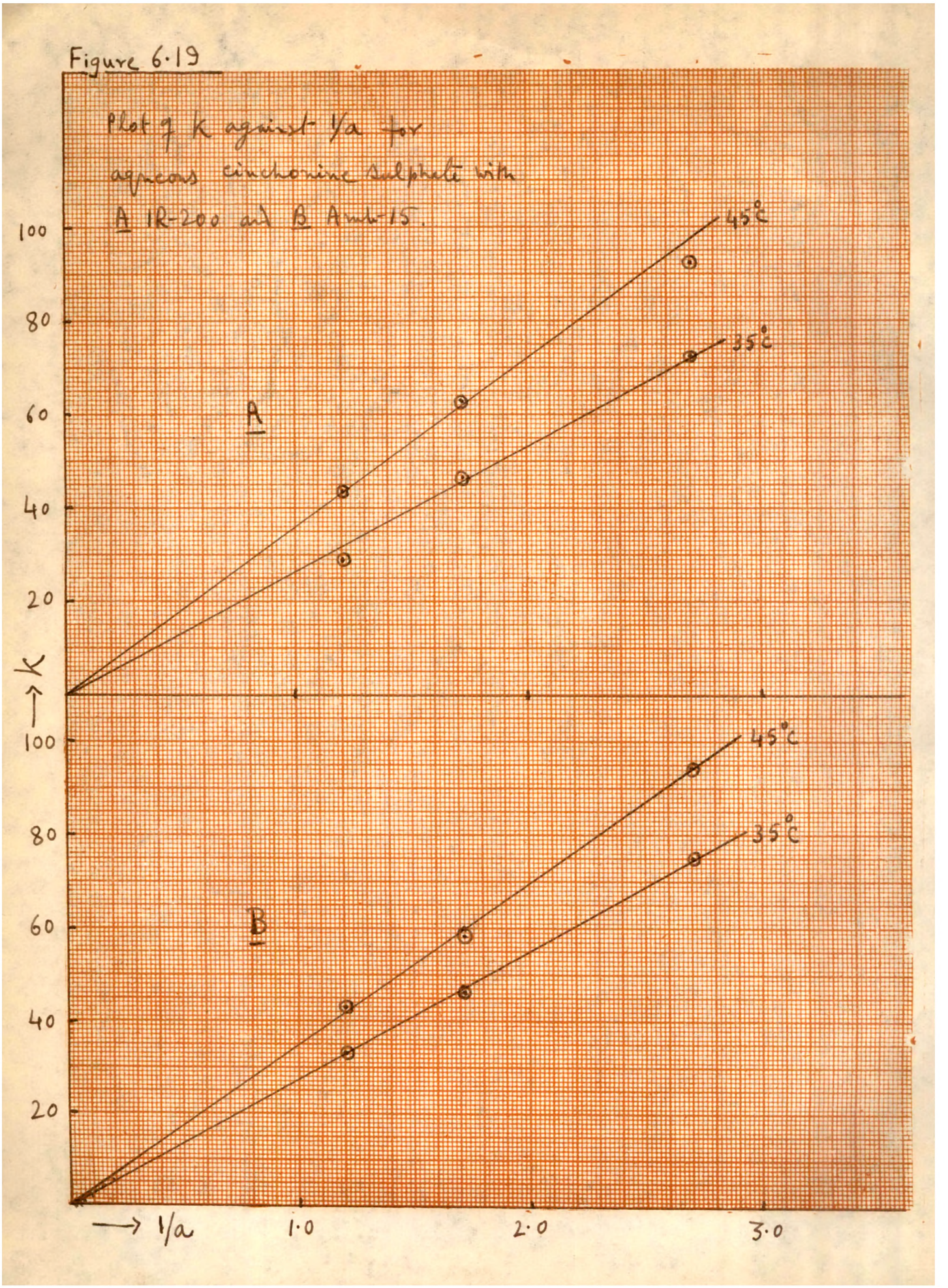
Plot of K against 1/a for aqueous cinchonine sulphate with A IR-200 and B Amb-15.
100
80
60
40
20
K
100
80
60
40
20
A
B
45°C
35°C
45°C
35°C
1/a
1·0
2·0
3·0

Figure 6·18

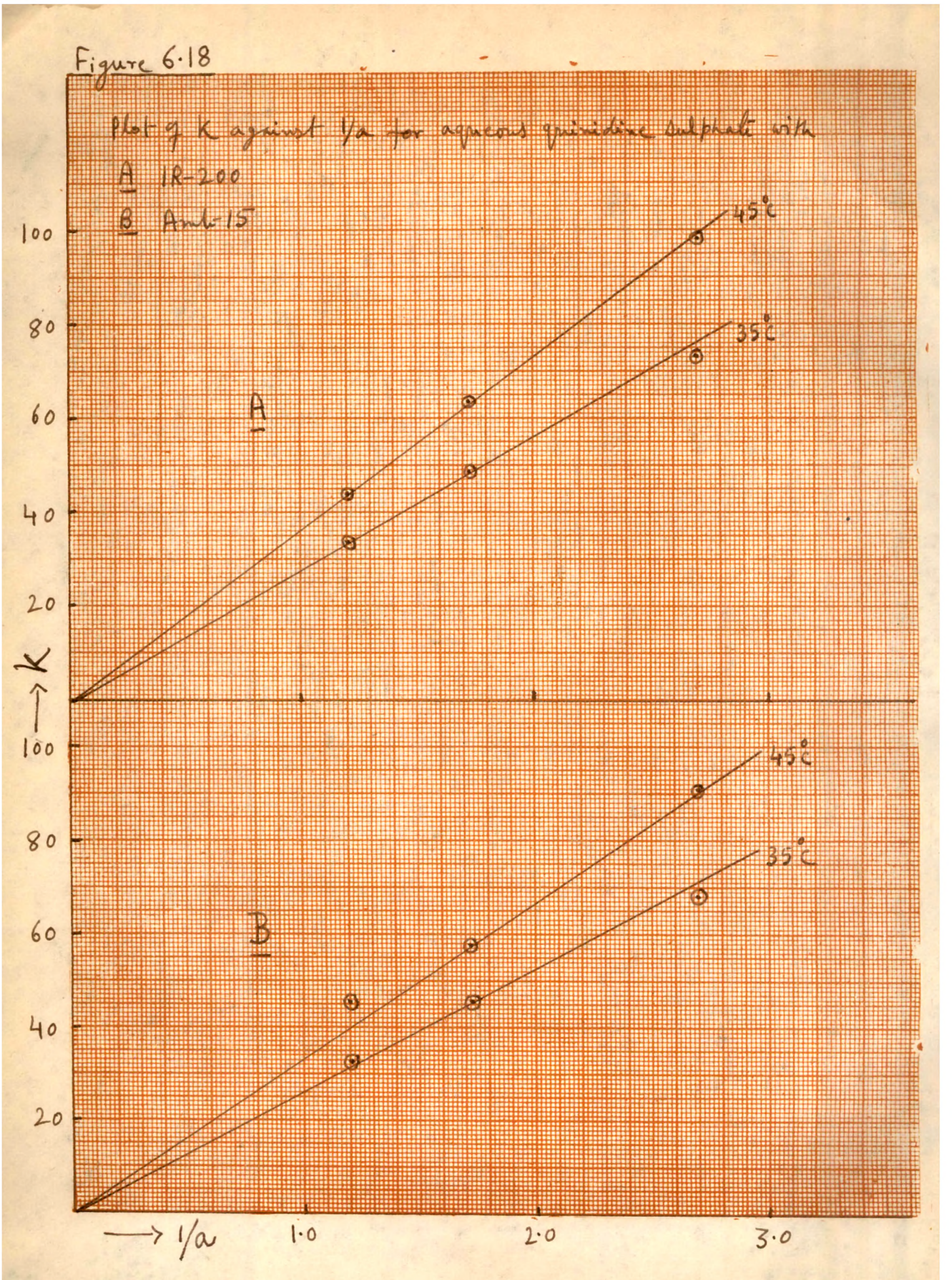
Plot of K against 1/a for aqueous pyridine sulphate with
A IR-200
B Amb-15
45°C
35°C
A
B
K
100
80
60
40
20
100
80
60
40
20
1/a
1·0
2·0
3·0

Figure 6·17

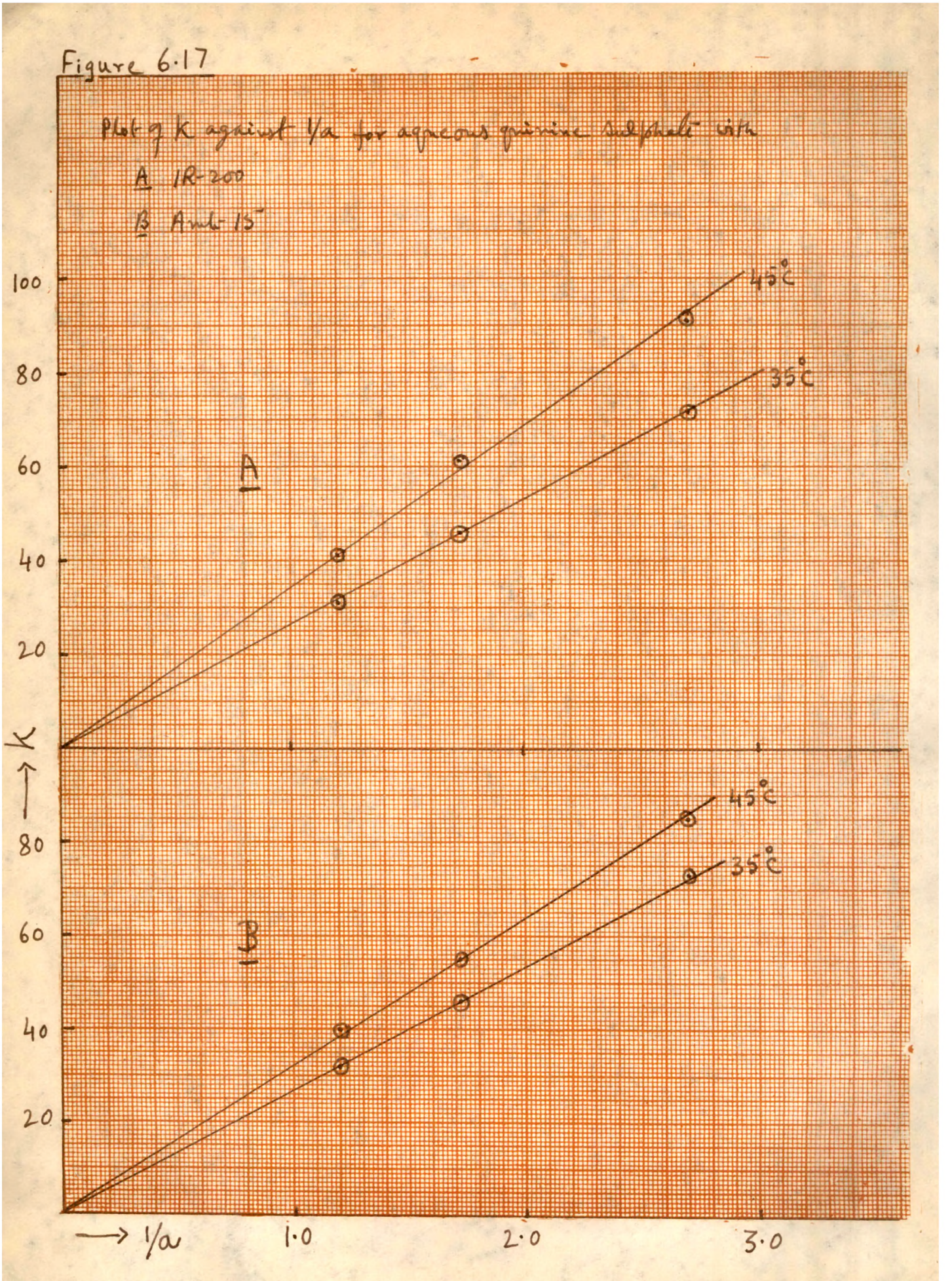
Plot of K against 1/a for aqueous quinine sulphate with
A IR-200
B Amb-15
100
80
60
40
20
K
80
60
40
20
A
B
45°C
35°C
45°C
35°C
1/a
1·0
2·0
3·0

Figure 6·16

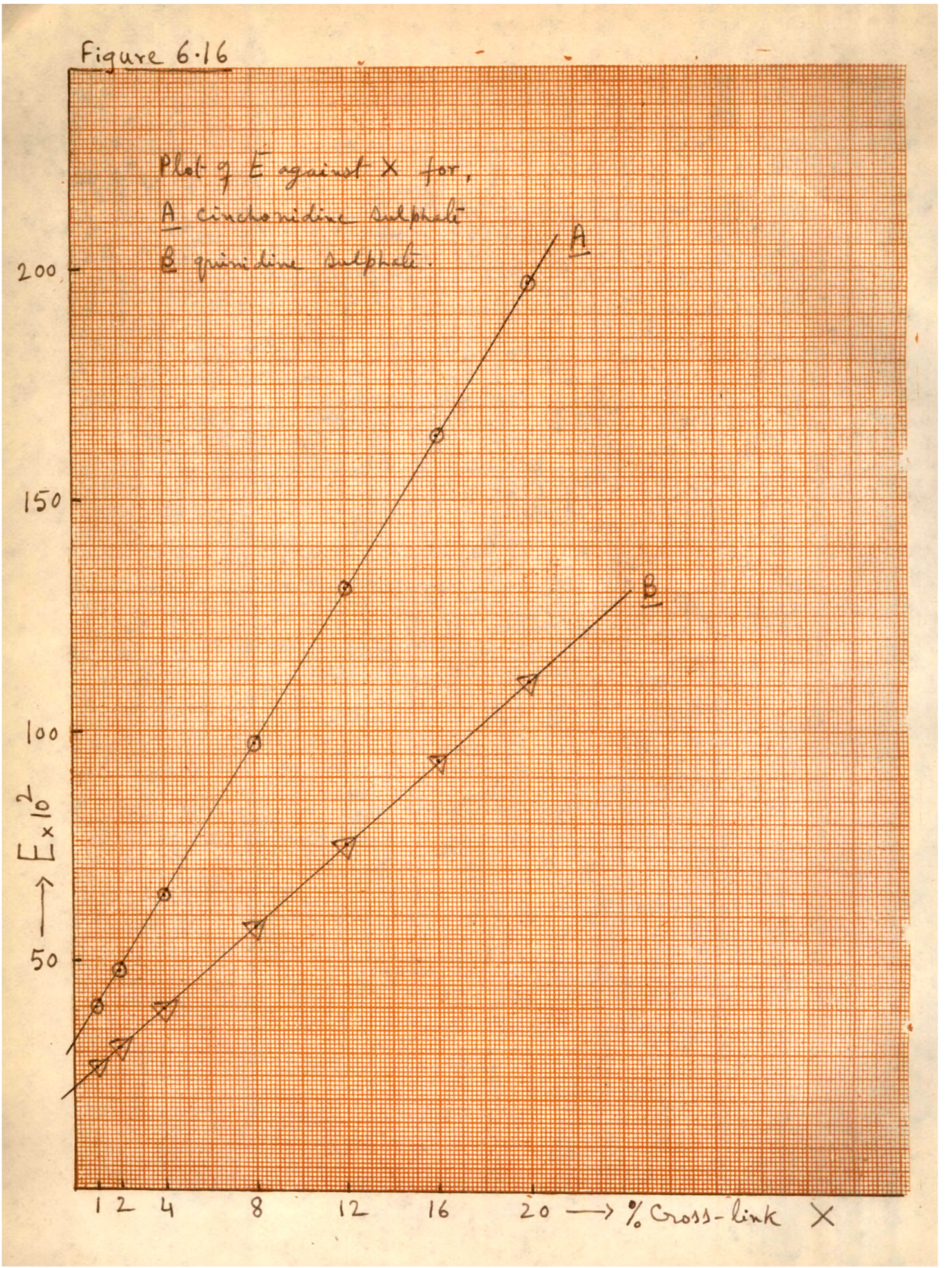
Plot of E against X for,
A cinchonidine sulphate
B quinidine sulphate.
200
150
100
50
$E_{\times 10^2}$
A
B
1 2 4 8 12 16 20 → % Cross-link X

Figure 6·15

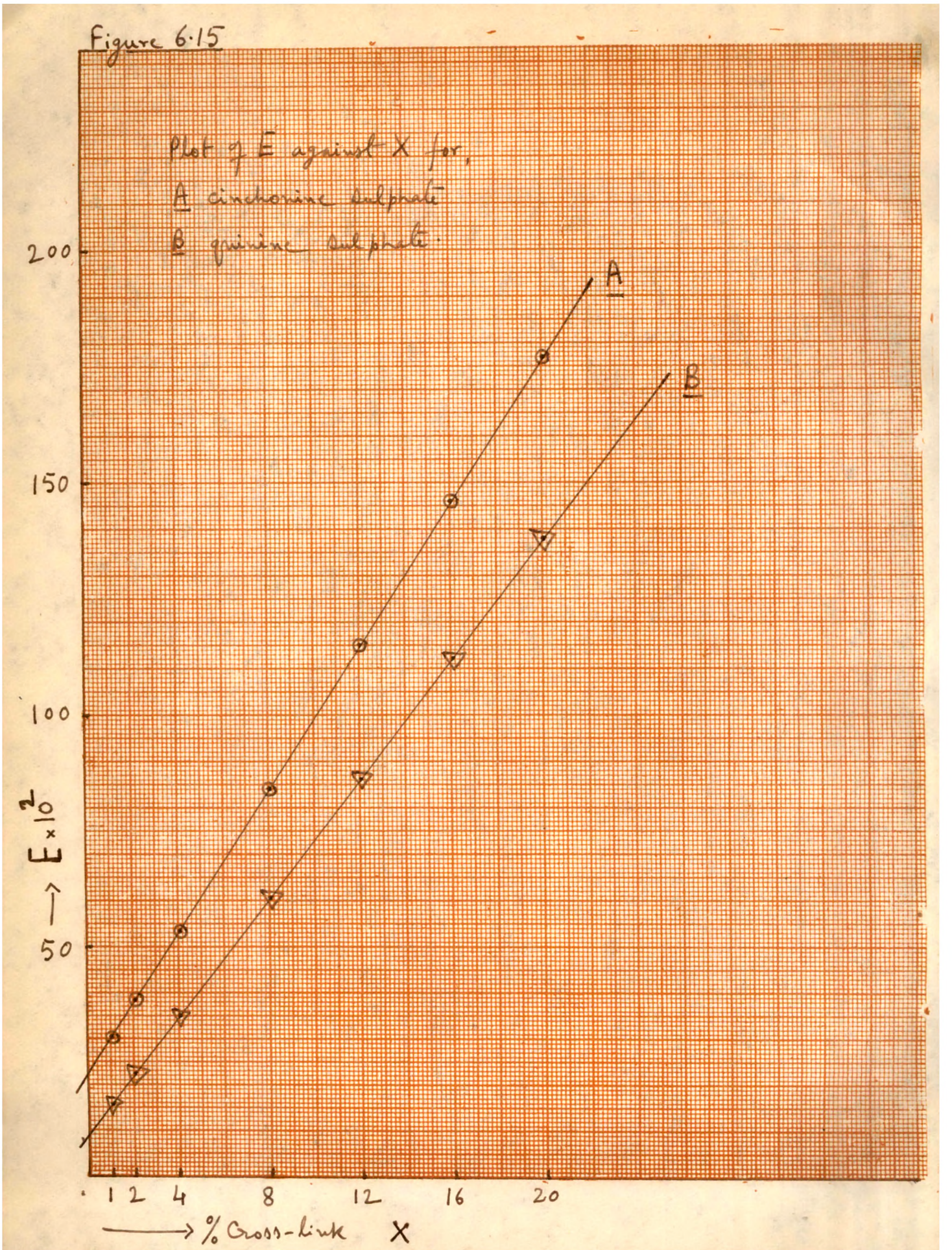
Plot of E against X for,
A cinchonine sulphate
B quinine sulphate
200
150
100
50
$E_{\times 10}^{2}$
A
B
1 2 4 8 12 16 20
% Cross-link X

Figure 6.14

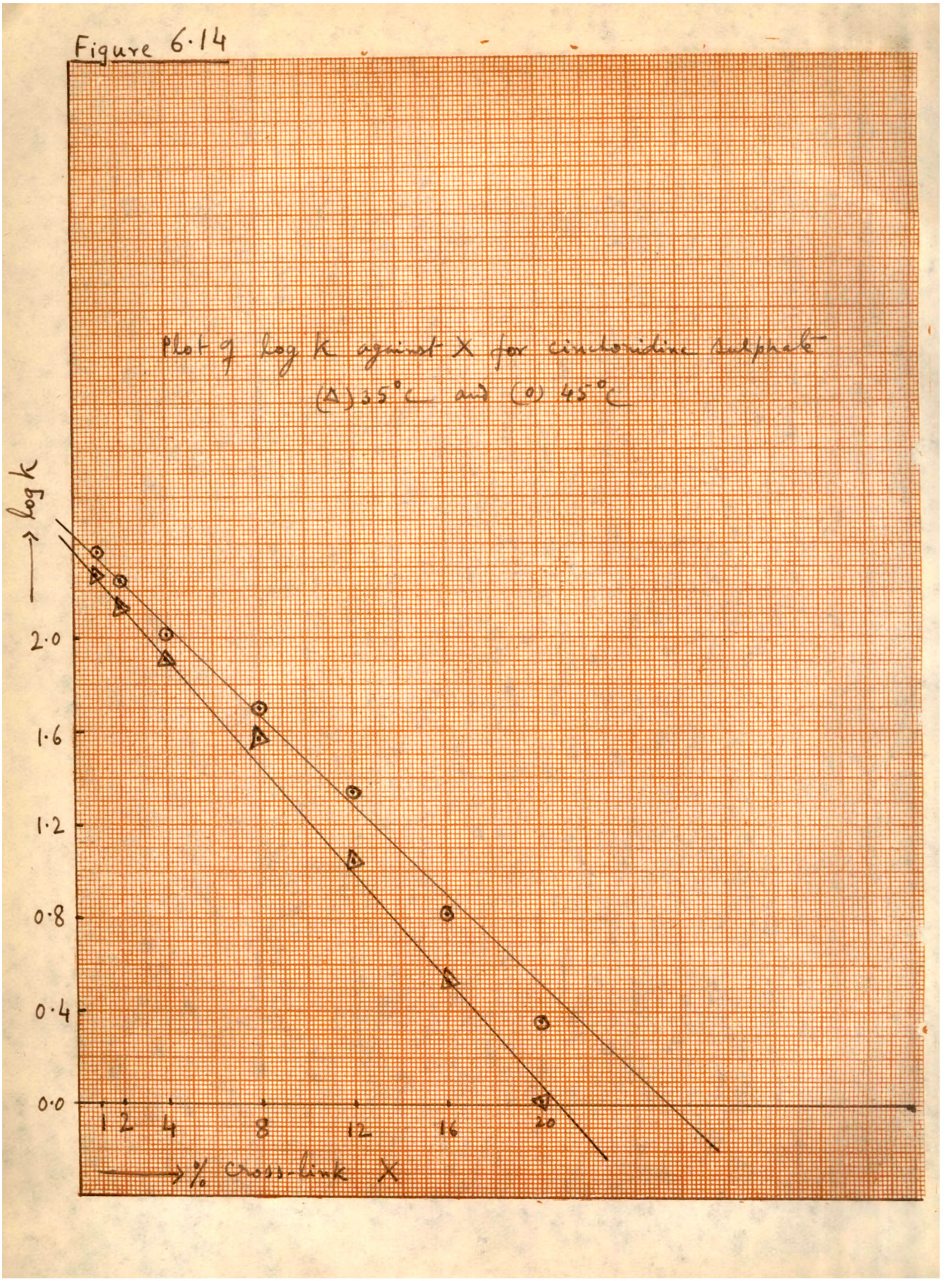
Plot of log k against X for cinchonidine sulphate
(Δ) 35°C and (o) 45°C
log k
2·0
1·6
1·2
0·8
0·4
0·0
1
2
4
8
12
16
20
% cross-link X

Figure 6·13

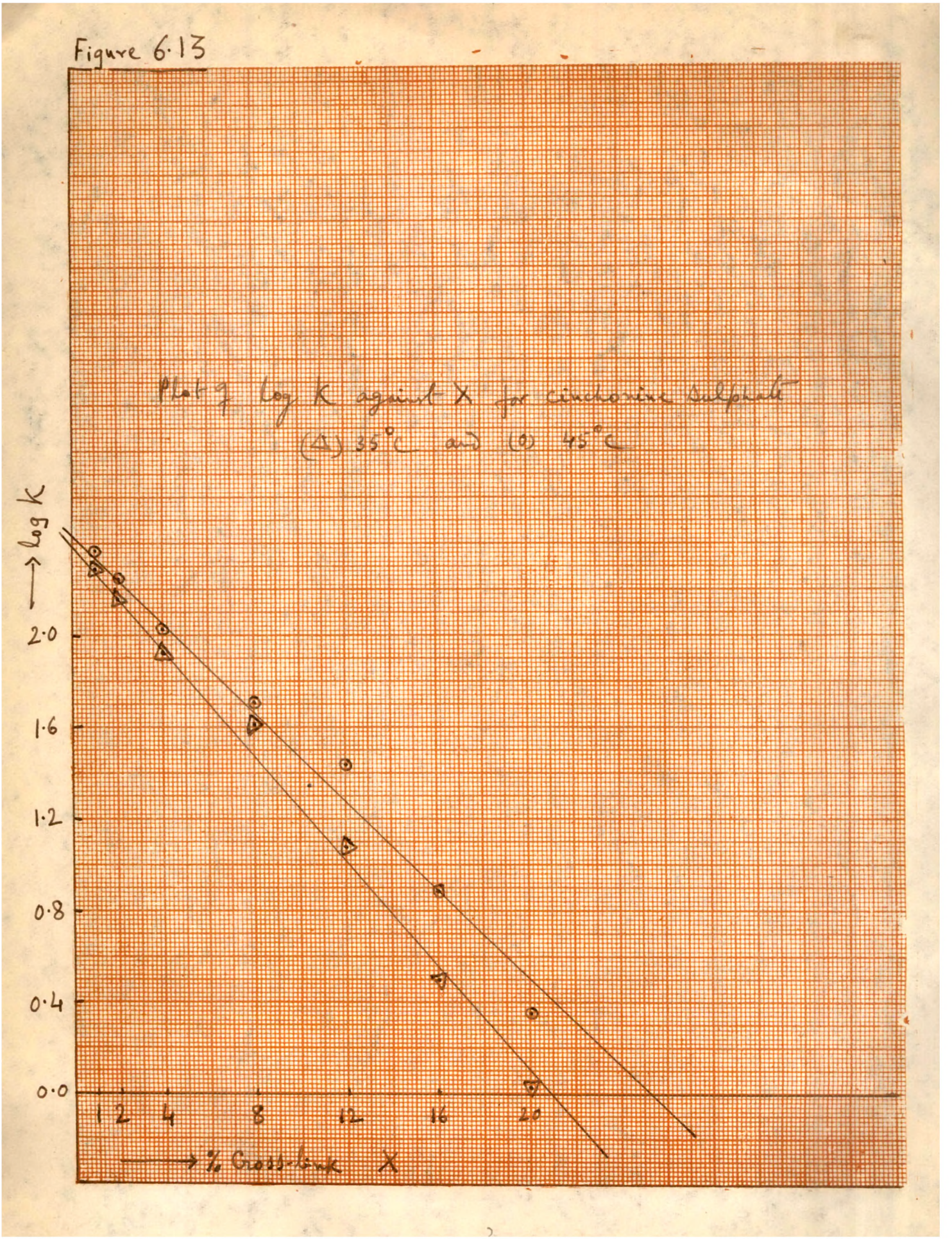
Plot of log K against X for cinchonine sulphate
(Δ) 35°C and (○) 45°C
log K
2·0
1·6
1·2
0·8
0·4
0·0
1
2
4
8
12
16
20
% Crosslink X

Figure 6·12

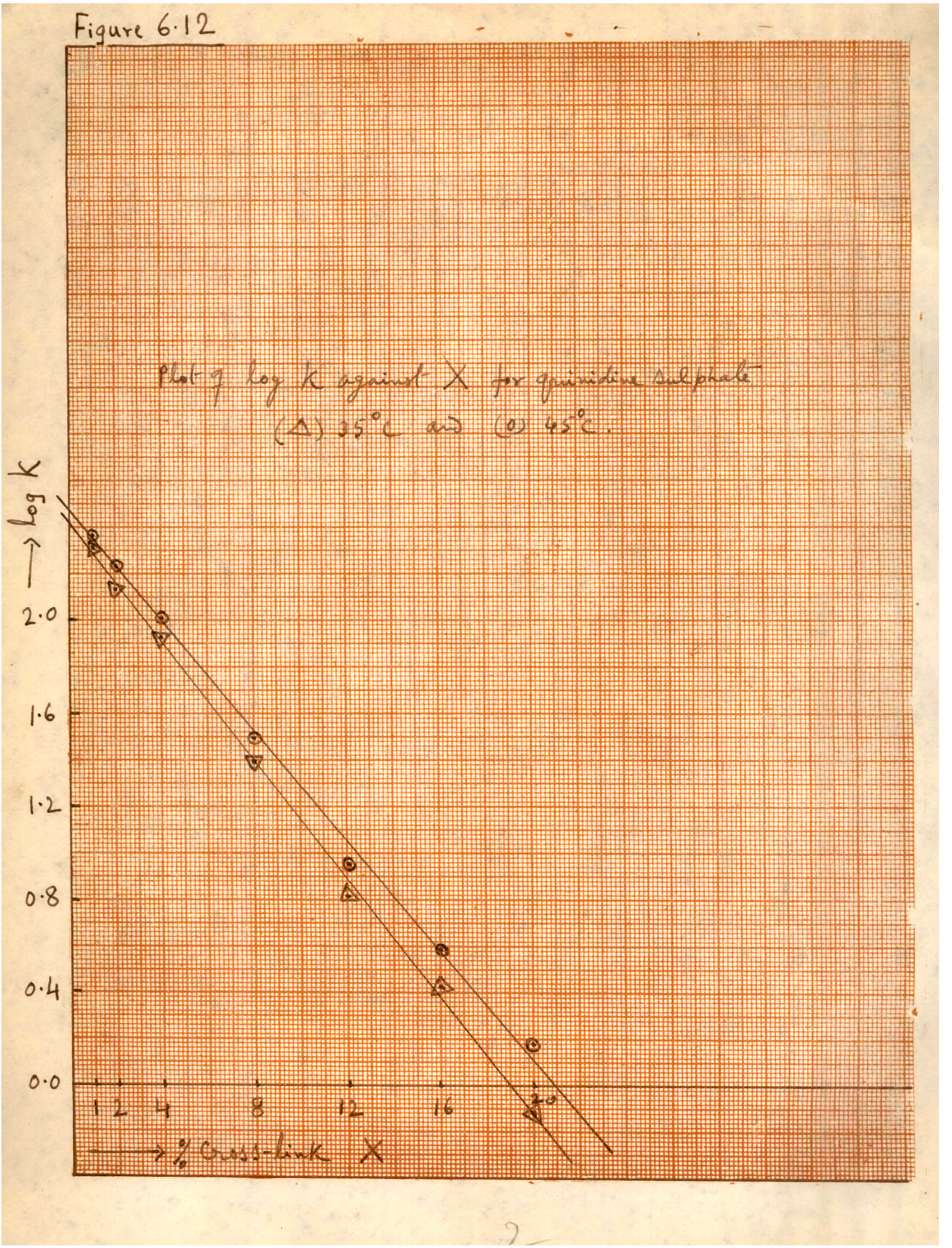
Plot of log k against X for quinidine sulphate
(△) 35°C and (○) 45°C.
log k
2·0
1·6
1·2
0·8
0·4
0·0
1
2
4
8
12
16
20
% Cross-link X

Figure 6·11

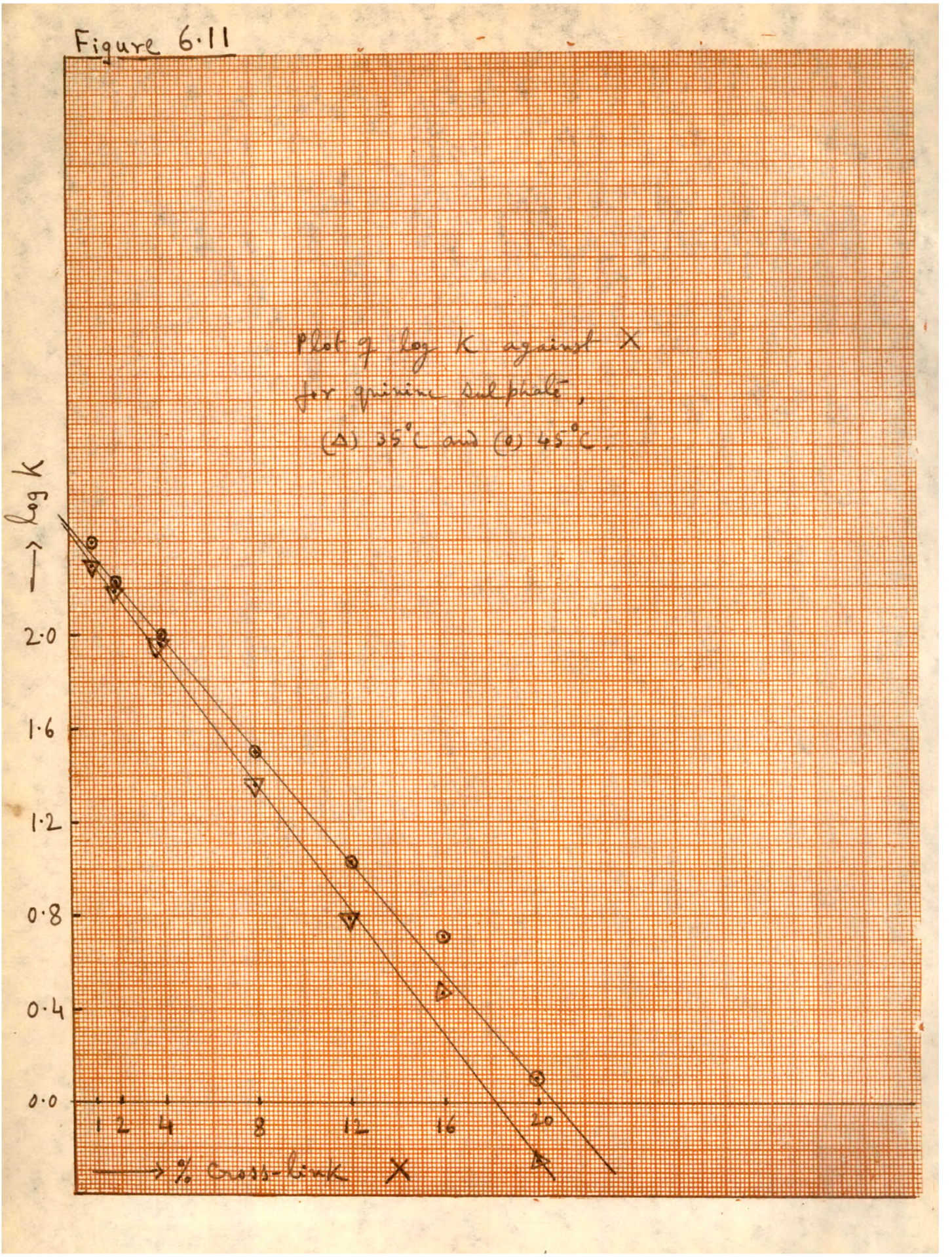
Plot of log K against X
for quinine sulphate,
(Δ) 25°C and (o) 45°C.
log K
2·0
1·6
1·2
0·8
0·4
0·0
1
2
4
8
12
16
20
% Cross-link X

Table 6.39

Values of K in $(\text{minute})^{-1} \cdot (\text{gram-equivalent per litre})^{-1}$ at $35^{\circ}C$ and $45^{\circ}C$ for the four alkaloid sulphates with resins from X 1 to X 20 .

Resin	a (mm.)	Quinine sulphate		Quinidine sulphate		Cinchonine sulphate		Cinchonidine sulphate	
		K35	K 45	K 35	K 45	K 35	K 45	K 35	K 45
X 1	0.215	181.7	230.8	186.5	210.2	198.4	231.5	182.8	226.8
X 2	0.215	145.4	153.4	124.7	156.2	143.1	173.6	130.1	171.2
X 4	0.215	86.61	92.95	77.75	94.25	83.58	105.5	78.22	98.49
X 8	0.215	21.27	28.67	22.25	27.50	42.15	51.2	36.36	48.90
X 12	0.215	5.893	10.00	5.971	7.962	12.01	27.86	11.00	21.66
X 16	0.215	2.852	4.97	2.488	3.483	3.135	7.835	3.36	6.50
X 20	0.215	0.5229	1.195	0.6665	1.366	1.045	2.237	0.9990	2.201

Table 6.40

Values of K in (minute)$^{-1}$. (gram-equivalent per litre)$^{-1}$ at 35°C and 45°C for the four alkaloid sulphates with resins IR-200, Amb-15 and IR-120 (of different particle diameters.).

Resin	a (mm.)	Quinine sulphate		Quinidine sulphate		Cinchonine sulphate		Cinchonidine sulphate	
		K 35	K 45	K 35	K 45	K 35	K 45	K 35	K 45
IR-200	0.84	31.06	40.15	33.86	43.82	28.74	43.37	30.64	45.50
	0.58	46.34	61.64	48.80	63.75	47.02	62.64	46.42	60.82
	0.37	72.16	90.80	73.00	98.50	72.62	91.96	66.84	91.92
Amb-15	0.84	32.32	39.92	32.87	45.82	33.44	42.85	33.43	38.99
	0.58	45.62	55.13	45.82	57.77	45.98	57.48	47.36	56.63
	0.37	73.19	84.61	67.74	90.63	75.23	94.04	74.29	87.28
IR-120	0.84	8.117	10.51	-	-	-	-	-	-
	0.58	9.074	11.47	7.969	12.46	13.24	19.85	12.29	19.96
	0.37	10.98	14.66	9.620	15.43	19.68	25.95	19.96	28.63
	0.23	13.78	19.48	12.95	20.42	27.69	36.57	27.86	39.00

Table 6.41

Slopes and intercepts of the plot of log K against X from , figures (6.11 to 6.14).

Alkaloid sulphate	35°C		45°C	
	Slope	Inter-cept.	Slope	Inter-cept.
Quinine sulphate	- 0.1324	2.41	- 0.1180	2.43
Quinidine sulphate	- 0.1279	2.38	- 0.1180	2.43
Cinchonine sulphate	- 0.1133	2.38	- 0.09605	2.43
Cinchonidine sulphate	- 0.1141	2.35	- 0.09566	2.42

Table 6.42

Slopes and intercepts of the plot of E against X from, figures (6.15 and 6.16).

Alkaloid sulphate	Slope	Intercept.
Quinine sulphate	645	900
Quinidine sulphate	445	2250
Cinchonine sulphate	775	2200
Cinchonidine sulphate	827.5	3150

Table 6.43

Slopes and intercepts of the plot of K against 1/a of resin IR-200 from, figures (6.17.A to 6.20.A) and values of γ and E.

Alkaloid sulphate	Slope 35°C	Slope 45°C	γ	E
Quinine sulphate	26.75	34.00	1.272	4676
Quinidine sulphate	27.75	36.75	1.324	5474
Cinchonine sulphate	27.00	36.25	1.343	5738
Cinchonidine sulphate	25.75	35.25	1.369	6115

Table 6.44

Slopes and intercepts of the plot of K against 1 / a of resin Amb-15 from, figures (6.17.B to 6.20.B) and values of γ and E.

Alkaloid sulphate	Slope 35°C	Slope 45°C	γ	E
Quinine sulphate	26.75	32.00	1.196	3490
Quinidine sulphate	26.25	33.50	1.277	4750
Cinchonine sulphate	27.50	34.50	1.254	3257
Cinchonidine sulphate	27.50	32.50	1.182	4419

Table 6.45

Slopes and intercepts of the plot of K against 1 / a of resin IR-120 from , figures (6.21 to 6.24).

Alkaloid sulphate	35°C		45°C	
	Slope	Intercept	Slope	Intercept
Quinine sulphate	1.78	6.1	3.05	6.25
Quinidine sulphate	1.84	4.9	2.98	7.45
Cinchonine sulphate	5.40	4.1	6.32	9.00
Cinchonidine sulphate	5.86	2.3	7.12	7.90

Table 6.46

Slopes and intercepts of the plot of E against a of resin IR-120 from, figures (6.25 and 6.26).

Alkaloid sulphate	Slope	Intercept
Quinine sulphate	- 6562.5	8200
Quinidine sulphate	- 687.5	9050
Cinchonine sulphate	+ 3462.5	4500
Cinchonidine sulphate	+ 7875.0	4900

Table 6.47

Experimental and calculated (from figures 6.21 to 6.24) values of K for the four alkaloid sulphates with resin IR-120 of different particle diameters.

Alkaloid salt : Quinine sulphate.

a (mm.)	$K_{35^\circ C}$ Experimental.	$K_{35^\circ C}$ Calculated.	$K_{45^\circ C}$ Experimental.	$K_{45^\circ C}$ Calculated.	Y	E
0.84	8.117	8.217	10.51	9.879	1.202	3589
0.58	9.074	9.168	11.47	11.508	1.255	4433
0.37	10.980	10.910	14.66	14.595	1.338	5662
0.23	13.780	13.841	19.48	19.51	1.409	6685
	Alkaloid salt : Quinidine sulphate					
0.58	7.969	8.070	12.46	12.587	1.559	8654
0.37	9.620	9.874	15.43	15.506	1.570	8798
0.23	12.950	12.900	20.42	20.41	1.582	8937
	Alkaloid salt : Cinchonine sulphate					
0.58	13.24	13.41	19.85	19.89	1.484	6483
0.37	19.68	18.70	25.95	26.08	1.395	5451
0.23	27.69	27.58	36.57	36.48	1.323	5321
	Alkaloid salt : Cinchonidine sulphate					
0.58	12.29	12.40	19.96	20.17	1.627	9479
0.37	19.96	18.14	28.63	27.15	1.497	7859
0.23	27.86	27.51	39.00	38.86	1.413	6730

Table 6.48

Experimental and calculated (from figures 6.11 and 6.12) values of log K for quinine sulphate and quinidine sulphate with resin X 1 to X 20

Alkaloid salt : Quinine sulphate

Resin	Log K 35		Log K 45		Y	E
	Experimental.	Calculated.	Experimental.	Calculated.		
X 1	2.2593	2.2776	2.3632	2.312	1.082	1544
X 2	2.1626	2.1452	2.1858	2.194	1.119	2190
X 4	1.9376	1.8804	1.9682	1.958	1.196	3481
X 8	1.3277	1.3508	1.4575	1.486	1.366	6066
X 12	0.7703	0.8212	1.0013	1.014	1.559	8650
X 16	0.4551	0.2916	0.6964	0.542	1.780	11230
X 20	$\bar{1}$.7184	$\bar{1}$.7620	0.0773	0.070	2.032	13820

Alkaloid salt : Quinidine sulphate

X 1	2.2706	2.2521	2.3226	2.3120	1.148	2687
X 2	2.0959	2.1242	2.1937	2.1940	1.174	3132
X 4	1.8907	1.8684	1.9743	1.9580	1.229	4020
X 8	1.3474	1.3568	1.4393	1.4860	1.347	5797
X 12	0.7761	0.8452	0.9009	1.0140	1.475	7573
X 16	0.3959	0.3336	0.5420	0.5420	1.615	9350
X 20	$\bar{1}$.8238	$\bar{1}$.8220	0.1354	0.0700	1.770	11130

Table 6.49

Experimental and calculated (from figures 6.13 and 6.14) values of log K for cinchonine sulphate and cinchonidine sulphate with resins X 1 to X 20 .

Alkaloid salt : Cinchonine sulphate

Resin	Log K 35		Log K 45		Y	E
	Experimental.	Calculated.	Experimental.	Calculated.		
X 1	2.2975	2.2667	2.3645	2.3339	1.168	3015
X 2	2.1556	2.1534	2.2395	2.2379	1.214	3791
X 4	1.9221	1.9268	2.0232	2.0458	1.315	5338
X 8	1.6248	1.4736	1.7093	1.6616	1.542	8435
X 12	1.0795	1.0204	1.4449	1.2774	1.807	11530
X 16	0.4962	0.5672	0.8941	0.8932	2.118	14620
X 20	0.0191	0.1140	0.3495	0.5090	2.483	17720

Alkaloid salt : Cinchonidine sulphate

X 1	2.2620	2.2359	2.3556	2.3243	1.226	3967
X 2	2.1142	2.1218	2.2335	2.2287	1.279	4795
X 4	1.8933	1.8936	1.9934	2.0374	1.393	6452
X 8	1.5606	1.4372	1.6893	1.6547	1.650	9759
X 12	1.0414	0.9808	1.3357	1.2721	1.955	13070
X 16	0.5263	0.5244	0.8129	0.8894	2.317	16380
X 20	$\bar{1}$.9996	0.0680	0.3425	0.5068	2.747	19690

gradual deviation from linearity . This is illustrated by a typical run with resin X 4 (table 6.02.b. and figure 6.03) which was carried out in duplicate to obtained more points. The values of K were obtained according to the above procedure for resins X 1, X 2 and X 4 with quinine sulphate, quinidine sulphate, cinchonine sulphate and cinchonidine sulphate at $35^{\circ}C$ and $45^{\circ}C$ (tables 6.31 to 6.34).

The applicability of the second order law in the above cases supports the two assumptions : firstly, the heterogeneous system behaves apparently as a homogenous system and secondly, the values of the activity coefficients may be ignored. The gradual change of the slope of the plot of $x/(b-x)$ against t , during the latter part of the exchange may be attributed to the variation in the diffusion inside the resin particle.

With resin X 8 (tables 6.03, 6.07, 6.11 and 6.15 and figure 6.04) when $x/(b-x)$ is plotted against t , it is observed that, the plots are quite linear. At low value of b , the line passes through the origin but it does not, when the value of b is increased ; however the slope remains almost independent of b . The value of the intercept on y-axis increases as b increases and then gradually becomes practically independent of b .

This behaviour may be explained as follows : As the degree of cross-linking of the resin increases, the pore size decreases. The rate of exchange, then, may be considered to be determined by either of the two :

The first is possibly the rate of exchange with surface and near surface groups, which is relatively quite fast and of a short duration. The second rate is the rate of exchange at the less easily accessible exchange sites inside the resin particle. This is dependent on the slow diffusion of the organic cations inside the resin particle and is relatively slow and of longer duration. As the value of b is decreased, the first will presumably decrease, but the second is presumably independent of b .

At higher values of b , it may be supposed that the surface and near surface sites get quickly exchanged and then the rate of exchange is dependent on the diffusion of cation inwards. Hence, the increase of concentration in the external solution does not influence the slow rate of exchange with inner and less accessible sites.

In order to maintain a uniform method of calculation, the rate constant K was calculated for b = 1 meq./litre for X 8 from the values of the slope (tables 6.35 to 6.38) . This choice is, of course, rather arbitrary, but is useful as will be indicated further, because of simple co-relations, this permits.

For resins X 12, X 16 and X 20 (tables 6.04, 6.05, 6.08, 6.09, 6.12, 6.13, 6.16 and 6.17 and figures 6.05 to 6.07) the slopes of the plot of x/(b-x) against time t becomes practically independent of b and at higher values of b the lines do not pass through the origin. The same

remarks, as given above for X 8 , apply here also. The same method for the calculation of the values of K (i.e. at b = 1 meq. / litre) is adopted here also.

Table (6.39) gives the value of K obtained in this way for the four alkaloid sulphates studied at 35°C and 45°C.

When the values of log K are plotted against X, (figures 6.11 to 6.14) fairly linear plots are obtained for the four alkaloid sulphates studied and the slopes and intercepts of the lines are given in table (6.41).

The values of log K calculated according to the above values of slopes and intercepts are compared with the experimental values of log K in tables (6.48 and 6.49).

The data of the above tables indicate that the value of K or the exchange rate decreases as X increases. The values for quinine sulphate and quinidine sulphate, which are optical isomers differ by a small amount. Same is true with the optical isomers, cinchonine sulphate and cinchonidine sulphate. At higher values of X, the values of K for quinine sulphate and quinidine sulphate are smaller than those for cinchonine sulphate and cinchonidine sulphate. This is due to smaller molecular size of cinchonine and cinchonidine than that of quinine and quinidine.

From the calculated values of log K, based on the values of slopes and intercepts from table (6.41), the values of apparent energy of activation, E, are calculated

and are given in tables (6.48 and 6.49) . The plots of E against X (figures 6.15 and 6.16) are linear and the slopes and intercepts are given in table (6.42).

It is observed that the value of E increases with X . The value is low at low value of X , but becomes fairly high at high values of X . This increase in E with increase in X , is to be attributed to the increase in resistance to diffusion of the cations inside the resin as X increases . The values of slopes and intercepts are different for each alkaloid by small amounts, indicating that even for the optical isomers, some specific effects exist.

The resins IR-120, IR-200 and Amb-15 were studied with different particle diameters. The behaviour of IR-120 is similar to that of X 8 but of IR-200 and Amb-15, is similar to that of X 1, X 2 or X 4 .

The resins IR-120, IR-200 and Amb-15 are considered to have practically the same relative degree of cross-linking , but IR-200 and Amb-15 are considerably more porous than IR-120. This increased porocity is the reason for the difference in the behaviour of IR-120 on one hand and IR-200 and Amb-15 on the other hand.

The values of K were calculated by the same procedure as given before and are given in table (6.40). It is observed that though the value of P_{Ro} is less for

IR-200 and Amb-15 than those for IR-120, the values of K are considerably higher for the former than those for the later. It is further observed that the values of K decrease as particle diameter a increases. The plots (figures 6.17 to 6.24) of K against 1/a (tables 6.18 to 6.30) are linear and the slopes and intercepts of the lines are given in tables (6.43 to 6.45). The plots for IR-200 and Amb-15 pass through the origin, but those for IR-120 do not. The values of E calculated from the values of K , according to the plots of K against 1/a (table 6.45 ; figures 6.21 to 6.24) are given in table (6.47) . The plots of E against a (figures 6.25 and 6.26) are linear and the slopes and the intercepts are given in the table (6.46). The values for IR-200 and Amb-15 are independent of the particle diameter, but the values of E for IR-120 are not ; here the values of E decrease with increasing particle diameter for quinine sulphate and quinidine sulphate but increase with increasing particle diameter for cinchonine sulphate and cinchonidine sulphate. This difference is significant in relation to the molecular size of the alkaloids. The values of slopes and intercepts and the values of E are some-what different for each alkaloid, supporting the assumption that some specific effects are also operative, even for optical isomers.

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