5. RATES OF EXCHANGE WITH CINCHONA ALKALOID SULFATES

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5.1

Ion exchange rates : (132 - 163)

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 crosslinking 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 Nernst 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 crosslinked 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 ion. (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 average 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.

5.2

Exchange rates of cinchona alkaloid sulfates with resins :

5.2.1

Introduction :

This section deals with the study of the rates of exchange from the aqueous solution of quinine sulfate by the resin. The study includes the effect of (a) the concentration of the external solution, (b) temperature and (c) the particle size of the resin.

5.2.2

Experimental :

Resin X4 of different mesh size in hydrogen form was used. Randomly taken particles (∽ 50 to 60) were measured for the particle diameter of each fraction of the airdry resin using a microscope with a mechanical stage, at room temperature (∽ 30°C) and the values for the average particle diameter, a, thus obtained were ; X4, 0.88 mm., 0.66 mm., 0.43 mm., and 0.215 mm. .

The procedure for the preparation and estimation of the aqueous solution of quinine sulfate was the same as described earlier.

Procedure for rate studies :

A known weight of the airdry resin (concentration of resin in meq./litre, on the basis of effective capacity = the concentration of the aqueous quinine sulfate solution in meq./litre) was kept in a clean,dry, three necked pyrex flask (capacity 500 cc.) clamped in a Townson and Mercer thermostat (± 0.02°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 quinine sulfate 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 10 to 15 seconds (depending upon the particle size of the 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.

In a run, not more than six samples of 5 cc. each or three samples of 10 cc. each were pipetted out depending on the initial quinine sulfate concentration from an initial total volume of 450 cc. of the solution. To obtain more points, the run was repeated as many time as required.

The contents of the test tubes were suitably diluted by adding known volume of distilled water with a pipette and the optical density, D_o , was noted at the invarient wavelength (296.5 mμ. for quinine sulfate) (114). The original aqueous solution of quinine sulfate was diluted to the same extent and the optical density, D_i , measured at the same wavelength.

Then, $(D_i - D_o) / D_o$ represents the values of $x / (b - x)$, where b = the concentration of quinine sulfate at time t = zero, and $(b - x)$ = the concentration of quinine sulfate 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 stirring rate. Hence throughout this work, the speed of the stirrer was kept at $\sim$ 800 - 900 r.p.m. It was also observed that when the stirrer was switched off, 10 to 15 seconds were quite sufficient for settling down of the resin particles.

Runs were carried out with different concentrations of quinine sulfate 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 quinine sulfate solution with different particle sizes of the resin at 35°C and 45°C are given in the following tables.

5.3

Results :

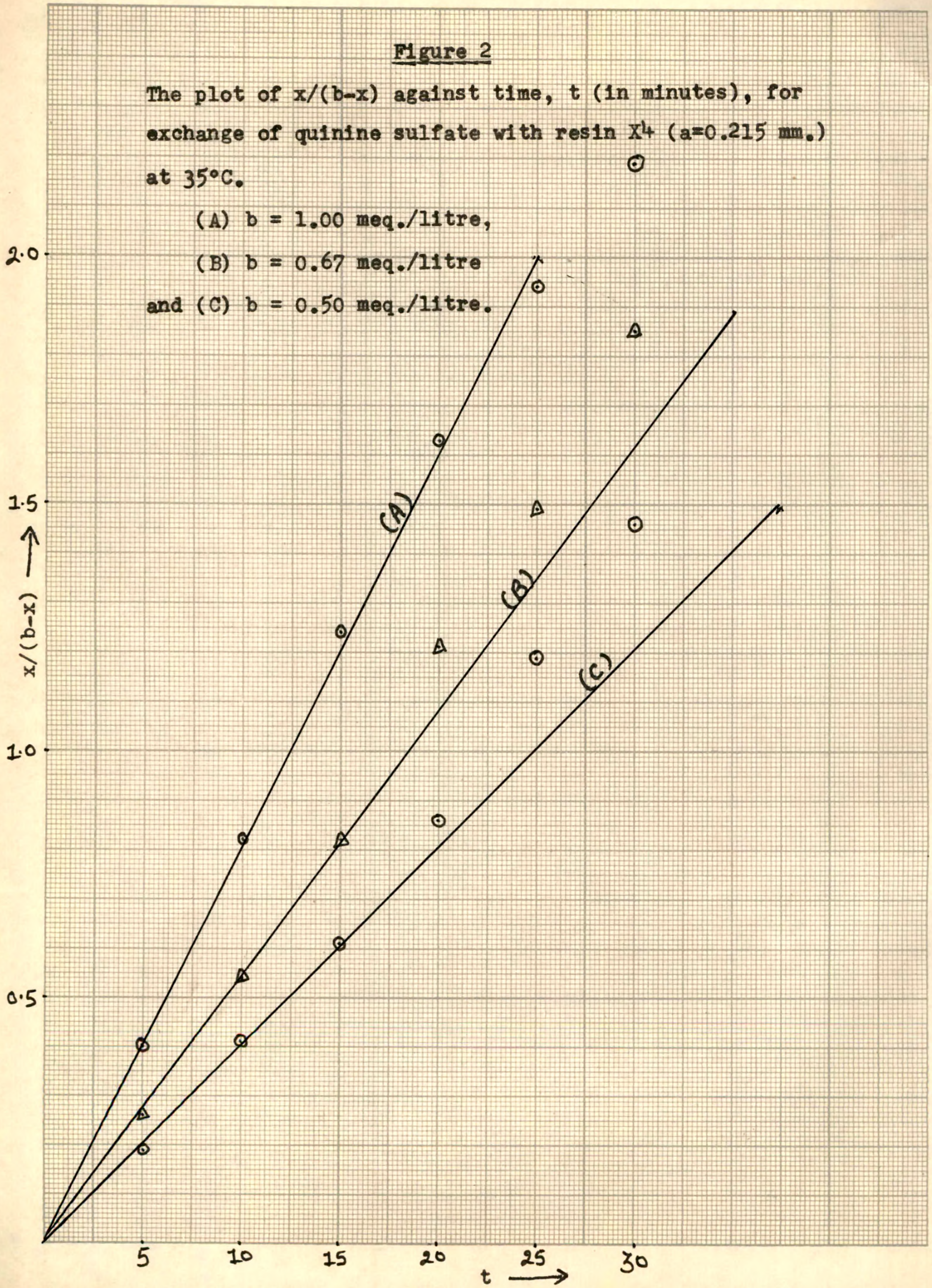


Figure 2

The plot of x/(b-x) against time, t (in minutes), for exchange of quinine sulfate with resin X4 (a=0.215 mm.) at 35°C.

(A) b = 1.00 meq./litre,

(B) b = 0.67 meq./litre

and (C) b = 0.50 meq./litre.

Figure 1

The plot of x/(b-x) against time, t (in minutes), for exchange of quinine sulfate with resin X^4 (a=0.43 mm.) at 35°C.

(A) b = 1.00 meq./litre,

(B) b = 0.50 meq./litre

and (C) b = 0.25 meq./litre.

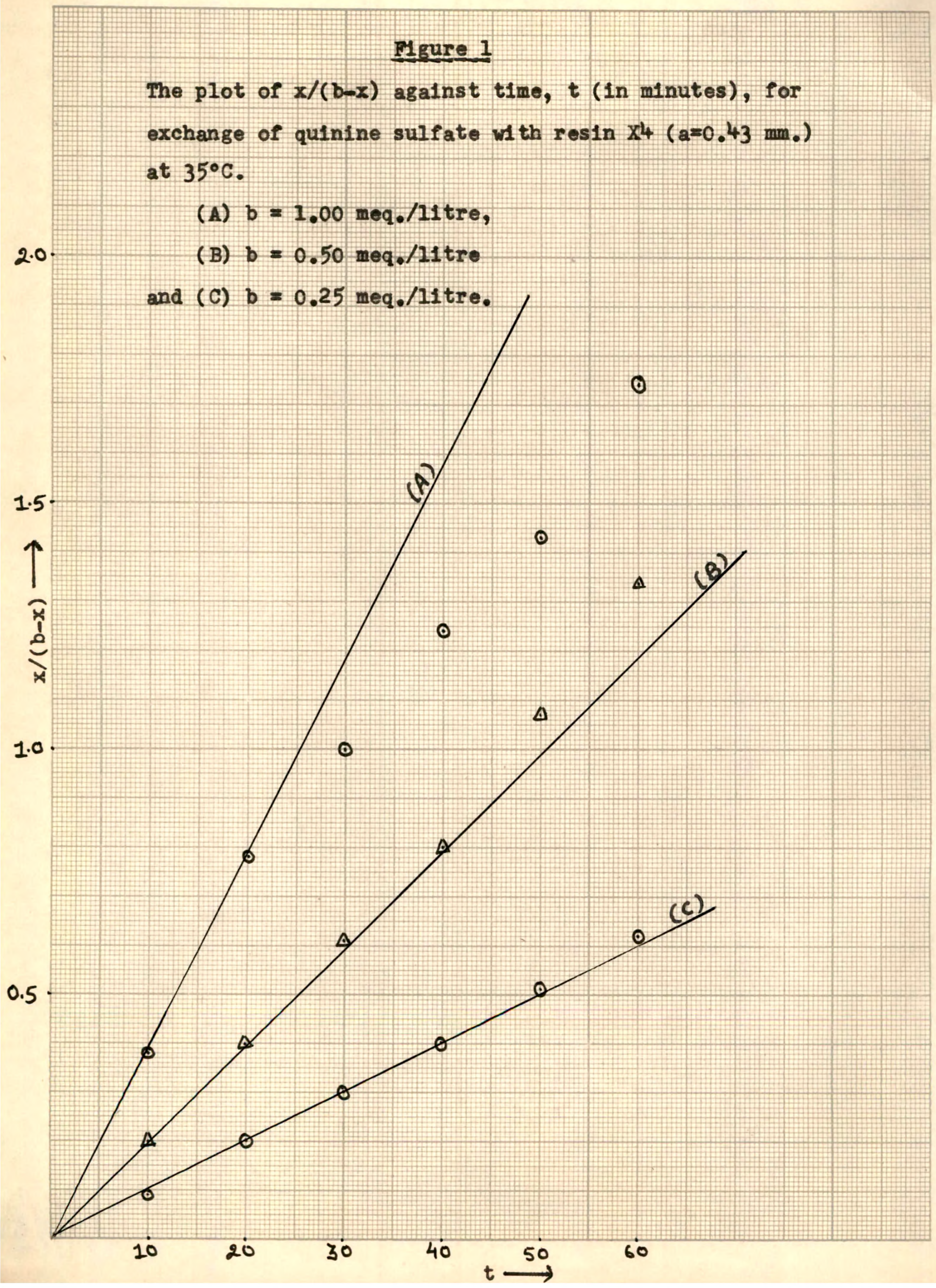


Table 5.1

Exchange rate of quinine sulfate with resin X4 at 35°C .

a	t	Values of x/(b-x) when b =				
(mm.)	(min.)	1.00	0.75	0.67	0.50	0.25
0.88	10	0.205	-	-	0.075	0.039
	20	0.400	-	-	0.195	0.094
	30	0.481	-	-	0.300	0.149
	40	0.566	-	-	0.411	0.198
	50	0.667	-	-	0.501	0.252
	60	0.748	-	-	0.605	0.313
0.66	10	0.268	0.217	-	0.128	0.068
	20	0.498	0.430	-	0.249	0.136
	30	0.683	0.598	-	0.400	0.203
	40	0.902	0.716	-	0.537	0.265
	50	1.052	0.815	-	0.661	0.330
	60	1.150	0.926	-	0.756	0.442
0.43	10	0.384	-	-	0.200	0.090
	20	0.780	-	-	0.400	0.200
	30	1.000	-	-	0.610	0.300
	40	1.237	-	-	0.804	0.400
	50	1.433	-	-	1.070	0.510
	60	1.739	-	-	1.341	0.620
0.215	5	0.400	-	0.260	0.190	-
	10	0.820	-	0.540	0.410	-
	15	1.240	-	0.820	0.610	-
	20	1.630	-	1.210	0.860	-
	25	1.940	-	1.490	1.190	-
	30	2.190	-	1.850	1.460	-

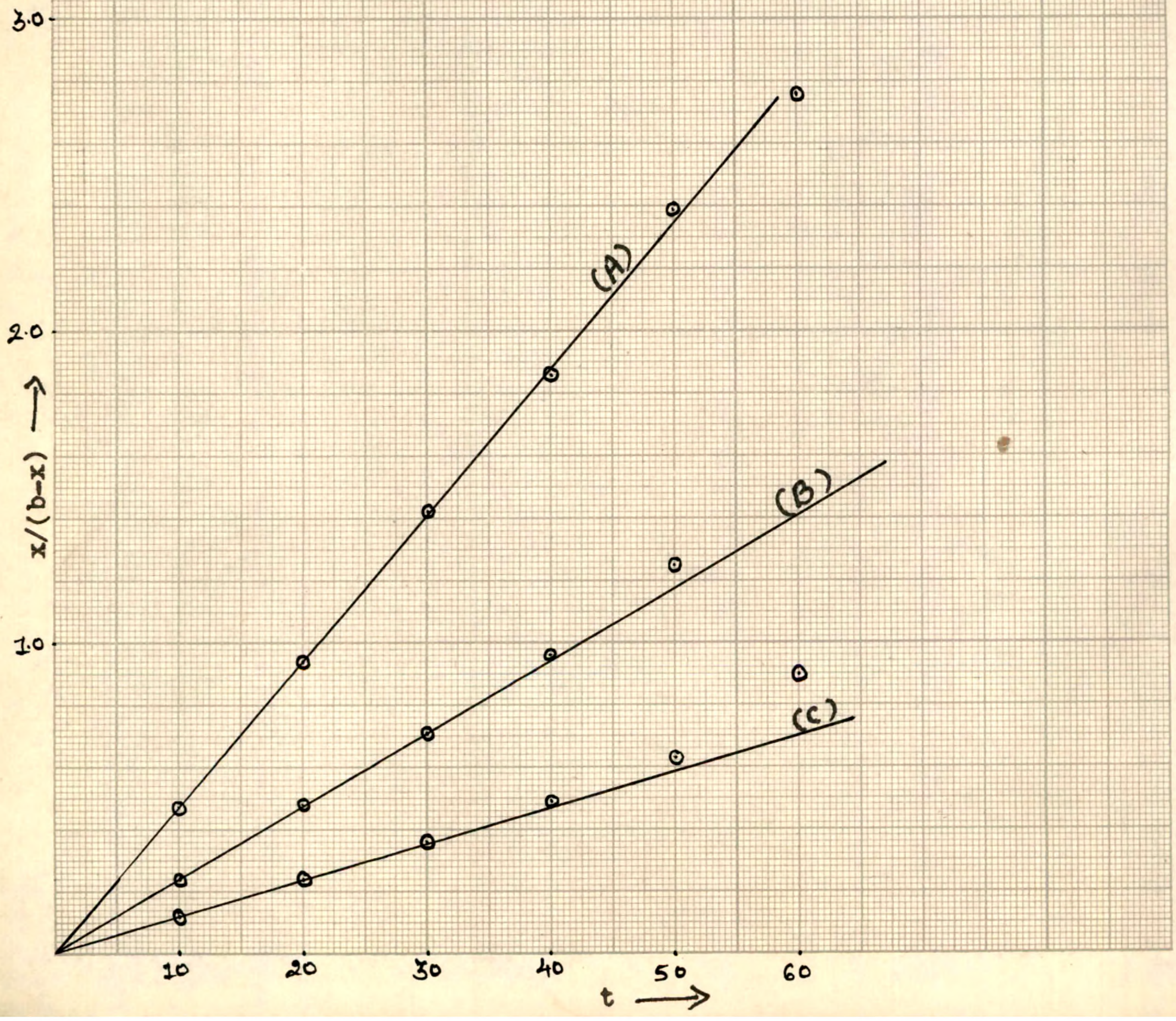
Figure 3

The plot of x/(b-x) against time, t (in minutes), for exchange of quinine sulfate with resin X^4 (a=0.43 mm.) at 45°C.

(A) b = 1.00 meq./litre,

(B) b = 0.50 meq./litre

and (C) b = 0.25 meq./litre.



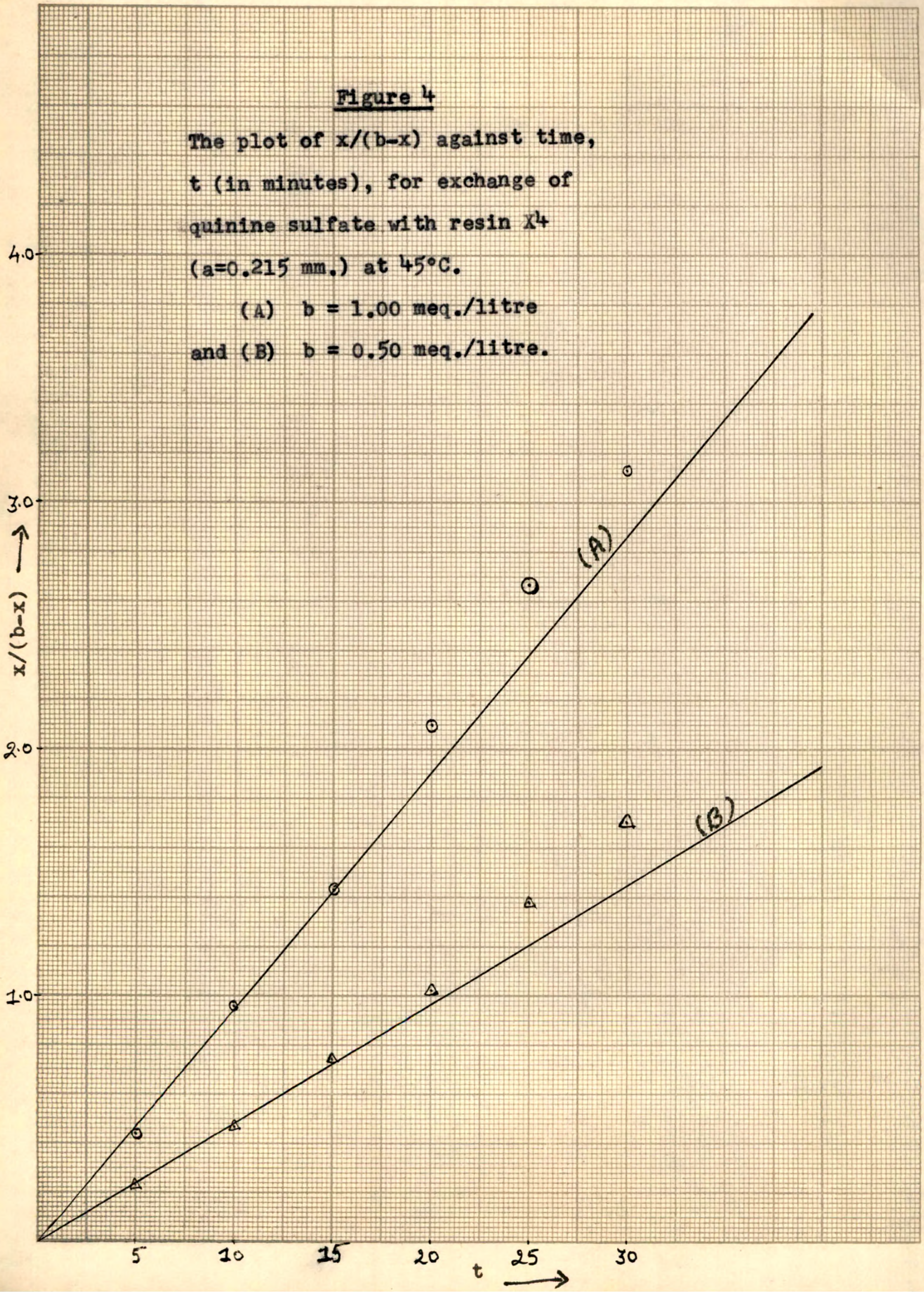


Figure 4

The plot of x/(b-x) against time, t (in minutes), for exchange of quinine sulfate with resin X4 (a=0.215 mm.) at 45°C.

(A) b = 1.00 meq./litre and (B) b = 0.50 meq./litre.

Table 5.2

Exchange rate of quinine sulfate with resin X4 at 45°C .

a	t	Values of $x/(b-x)$ when b =			
(mm.)	(min.)	1.00	0.75	0.50	0.25
0.88	10	0.235	-	0.100	0.050
	20	0.463	-	0.241	0.120
	30	0.670	-	0.342	0.171
	40	0.840	-	0.464	0.230
	50	0.992	-	0.600	0.350
0.66	10	0.307	0.250	0.146	0.068
	20	0.617	0.471	0.303	0.155
	30	0.849	0.700	0.461	0.223
	40	1.012	0.926	0.610	0.301
	50	1.179	1.109	0.804	0.380
	60	1.374	1.258	-	0.471
0.43	10	0.470	-	0.245	0.115
	20	0.940	-	0.484	0.242
	30	1.421	-	0.714	0.363
	40	1.863	-	0.960	0.488
	50	2.390	-	1.250	0.631
	60	2.764	-	-	0.897
0.215	5	0.440	-	0.230	-
	10	0.960	-	0.470	-
	15	1.430	-	0.740	-
	20	2.100	-	1.020	-
	25	2.670	-	1.380	-
	30	3.130	-	1.700	-

Table 5.3

Values of k (minute^{-1} . gram-equivalent^{-1} litre) at 35°C and 45°C for quinine sulfate with resin X4 of different particle sizes.

a	Values of k at 35°, when b =					Values of k at 45°, when b =			
(mm.)	1.00	0.75	0.67	0.50	0.25	1.00	0.75	0.50	0.25
0.88	19.8	-	-	20.0	20.0	23.3	-	23.2	22.7
0.66	26.6	26.7	-	26.6	26.6	31.3	31.1	31.0	30.6
0.43	39.7	-	-	40.0	40.0	46.6	-	47.2	47.2
0.215	81.5	-	83.0	81.0	-	95.0	-	96.0	-

Table 5.4

Values of the product of the average rate constant, k and particle diameter, a .

a	average k		k . a	
(mm.)	35°	45°	35°	45°
0.88	19.9	23.1	17.5	20.8
0.66	26.6	31.0	17.6	20.5
0.43	39.8	47.0	17.1	20.2
0.215	81.8	95.5	17.5	20.5

5.4

Discussion :

The equilibrium exchange of quinine sulfate from dilute aqueous solution has been considered earlier (Chapter 3), and the average value of P_R has been used in further calculations.

If C denotes the capacity of the resin in meq. per gram of airdry resin, $C . P_R / 100$ is termed as the effective exchange capacity of the resin and is denoted by C_{ef} . If b denotes the concentration of the quinine sulfate in meq. per litre, and g the weight of the airdry 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 quinine sulfate 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 airdry 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 (149) 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 airdry capacity, the second order rate constant k is given by

$$k = \frac{10^3}{b \, . \, t} \; . \; \frac{x}{(b - x)}$$

where (b-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 (minute^{-1} . $\text{gram-equivalent}^{-1}$ litre).

When the data for resin X4 of different particle sizes are considered, it is observed that the above conditions are applicable to the initial part of exchange after which there is a gradual deviation from linearity. The values of k were obtained according to the above procedure for resin X4 of different particle sizes with quinine sulfate at 35° and 45°C .

The applicability of the second order law in the above cases appears to support the two assumptions : firstly, the heterogeneous system behaves apparently as a homogeneous 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 later part of the exchange may be attributed to the variation in the diffusion inside the resin particle.

The values of the rate constant, k , were calculated using the procedure given above over a range of values of b from 1.0 to 0.25 meq./litre. It was observed that the value of k obtained was practically independent of the value of b. The values of k thus obtained are given, for different particle sizes of X4, in Table 5.3. The value of k is inversely proportional to the average particle diameter, a, as indicated by the values of k.a (Table 5.4). The value of the apparent energy of activation was evaluated according to the Arrhenius equation (156) and the value is 3.06 K.cals.

The results of this study together with the results of earlier work (118), indicate that rates of exchange of four cinchona alkaloid (quinine, quinidine, cinchonine and cinchonidine) sulfates are almost same within about 5 % for resin X4. Also the value of apparent energy of activation is almost same for resins of degree of crosslinking 1 to 4.

It is realised that ion exchange is largely accepted as diffusion phenomenon requiring the use of appropriate diffusion equations. The present approach, rather empirical, is based on the feeling that since the exchange, here, is essentially complete (i.e.upto the effective capacity), one may as well look upon it as a second order reaction ; this permits a relatively simple treatment to reflect the relative rates.