5.

SORPTION OF CINCHONA ALKALOID BASES :

5.1 Studies on the uptake of the alkaloid bases by resins in ethanolic and aqueous ethanolic solution .

5.1.a. Introduction :

In the previous chapter, the (molecular) sorption of the alkaloid bases by the resins was suggested. It was, therefore, considered of interest to further study the extent and relative rate of uptake of the free bases from the solution. The solutions were prepared in ethanol (sp.gr. 0.806) and aqueous ethanol (20 % by volume).

5.1.b. Experimental :

Resins : The resins were used from the samples used earlier.

Chemicals : Recrystallised sulphates of quinine, quinidine and cinchonidine, cinchonine (B.D.H.), ethanol (sp.gr. 0.806) and caustic soda (A.R.) were used.

Preparation of alkaloid bases : The bases were precipitated by slow addition of caustic soda solution, to a stirred aqueous solution of the alkaloid sulphate. A slight excess of caustic soda solution was added to ensure complete precipitation. The precipitated base was filtered at the pump and then stirred with about 300 cc. of water and again filtered at the pump. This was repeated till the washings were free from caustic soda. The base was then dried in an oven (100 - 104 ^{0}C) and its melting point checked (Table 5.1.b.).

Cinchonine (B.D.H.) was recrystallised from ethanol, dried in an oven (100 - 104°C) and the melting point was checked (Table 5.1.b.).

Solutions of the alkaloid bases : A known weight of the base was dissolved in distilled ethanol to a known volume, The ethanolic solutions, of all the four bases, quinine, quinidine, cinchonine and cinchonidine, were almost of the same concentration to facilitate the comparison of the relative rate of alkaloid uptake by the resin.

Relative rate of alkaloid (base) uptake by the resin :

The same known weight of resin X 4 was placed in well stoppered flasks and 40 cc. of the ethanolic solution of the base (prepared as above) were added to each flask. The contents were frequently shaken at room temperature ($\sim$ 30°C). After known timings the solution was decanted, a known portion suitably diluted with ethanol from the same stock and the optical density (at 296.5 mμ for quinine and quinidine; and 294.5 mμ for cinchonine and cinchonidine) also recorded. Original ethanolic solution of each base was also diluted to the same extent and the optical density recorded.

5.1.c. Nomenclature :

1. Initial concentration of the alkaloid base solution in meq. / litre = $[A]_i$

2. Weight of air-dry resin taken = W grams.

3. Volume of solution = V cc.

4. Capacity of the resin per gram of air-dry resin = C meq.

5. Optical density, of the initial (at time t = zero) solution of the alkaloid base, after suitable dilution = Di

6. Optical density, at the same wave-length (as in 5) of the solution of the alkaloid base at time t = t , after the same extent of dilution, as in 5 = Dot

7. The meq. of the alkaloid form of the resin, per litre of solution, at time t = t,

$$= \left[\bar{A}\right]t = \left[A\right]i \cdot (Di - Dot) / Di$$

8. The meq. of resin, per litre of solution, in the hydrogen form, at t = 0,

$$= \left[\bar{H}\right]i = W.C.10^{3} / V$$

9. The ratio of the initial concentration of the resin to the initial concentration of the alkaloid base,

$$= R = \left[\bar{H}\right]i / \left[A\right]i$$

10. The % exchange of alkaloid base at time t = t,

$$= P_{At} = 100. \left[\bar{A}\right]t / \left[A\right]i$$

11. The % resin capacity exchanged at time t = t,

$$= P_{Rt} = 100. \left[\bar{A}\right]t \,/\, \left[\bar{H}\right]i$$

12. The corresponding values, for 1, 10 and 11 when t = time after which equilibrium had been reached, are denoted by $\left[\bar{A}\right]e$, P_A and P_R respectively.

5.1.d. Results :

Table (5.T.a.) gives the values of $\left[\bar{H}\right]i$, $\left[A\right]i$, $\left[\bar{A}\right]t$, R, P_{At} and P_{Rt} for the uptake of quinine in 20 % ethanolic solution with resin X 4, at known time intervals. And table (5.1.b.) gives the melting points of the bases observed and the literature values.

Tables (5.2 and 5.3) give the values of $\left[\bar{H}\right]i$, $\left[A\right]i$, $\left[\bar{A}\right]t$, R, P_{At} and P_{Rt} for the uptake of quinine, quinidine, cinchonine and cinchonidine in ethanolic solution with resin X 4, at known time intervals.

Table (5.4) gives the values of $\left[\bar{H}\right]i$, $\left[A\right]i$, $\left[\bar{A}\right]e$, R, P_A and P_R for the uptake of quinine in 20 % ethanolic (by volume) solution with resins X 4 and X 8 (after equilibrium had been reached).

Table 5.1.a .

The uptake of quinine base in 20 % ethanolic solution - by resin X 4.

Time (t)	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_t$	R	P_{At}	P_{Rt}
6 Hours	2.332	2.456	6.333	0.9493	25.78	27.16
16 Hours	2.332	2.456	10.40	0.9493	42.35	44.61
40 Hours	2.332	2.456	13.01	0.9495	52.97	55.78
4 Days	2.336	2.456	15.01	0.9510	61.09	64.24
7 Days	2.334	2.456	16.43	0.9504	66.86	70.36
10 Days	2.340	2.456	17.39	0.9523	70.78	74.32
17 Days	2.334	2.456	18.31	0.9779	74.52	78.41
26 Days	2.334	2.456	18.42	0.9778	74.99	78.93
40 Days	2.334	2.456	18.42	0.9778	74.99	78.93

Table 5.1.b.

The melting points of the anhydrous bases :

Alkaloid base	Melting point observed	Melting point literature value (1.4.d.)
Quinine	174 - 5°C	173.5°C
Quinidine	174 - 5°C	174.5°C
Cinchonine	256 - 7°C	254 - 268.8°C
Cinchonidine	203 - 4°C	202 - 210.5°C

Table 5.2

The uptake of free alkaloid bases in alcoholic solution by resin X 4.

Alkaloid base	Time (t)	$[\bar{H}]i$	$[A]i$	$[\bar{A}]t$	R	P_{At}	P_{Rt}
Quinine	8 Hours	11.16	33.35	0.2925	0.3347	8.772	25.07
	17 Hours	11.16	33.35	0.3844	0.3347	11.53	33.01
	41 Hours	11.16	33.35	0.4428	0.3347	13.28	37.96
	4 Days	11.16	33.35	0.4930	0.3347	14.79	42.27
Quinidine	8 Hours	11.16	33.34	0.2758	0.3347	8.275	23.67
	17 Hours	11.16	33.34	0.3799	0.3347	11.40	34.05
	41 Hours	11.16	33.34	0.4432	0.3347	13.29	38.00
	4 Days	11.16	33.34	0.4749	0.3347	14.24	42.56

Table 5.3

The uptake of free alkaloid bases in alcoholic solution by resin X 4.

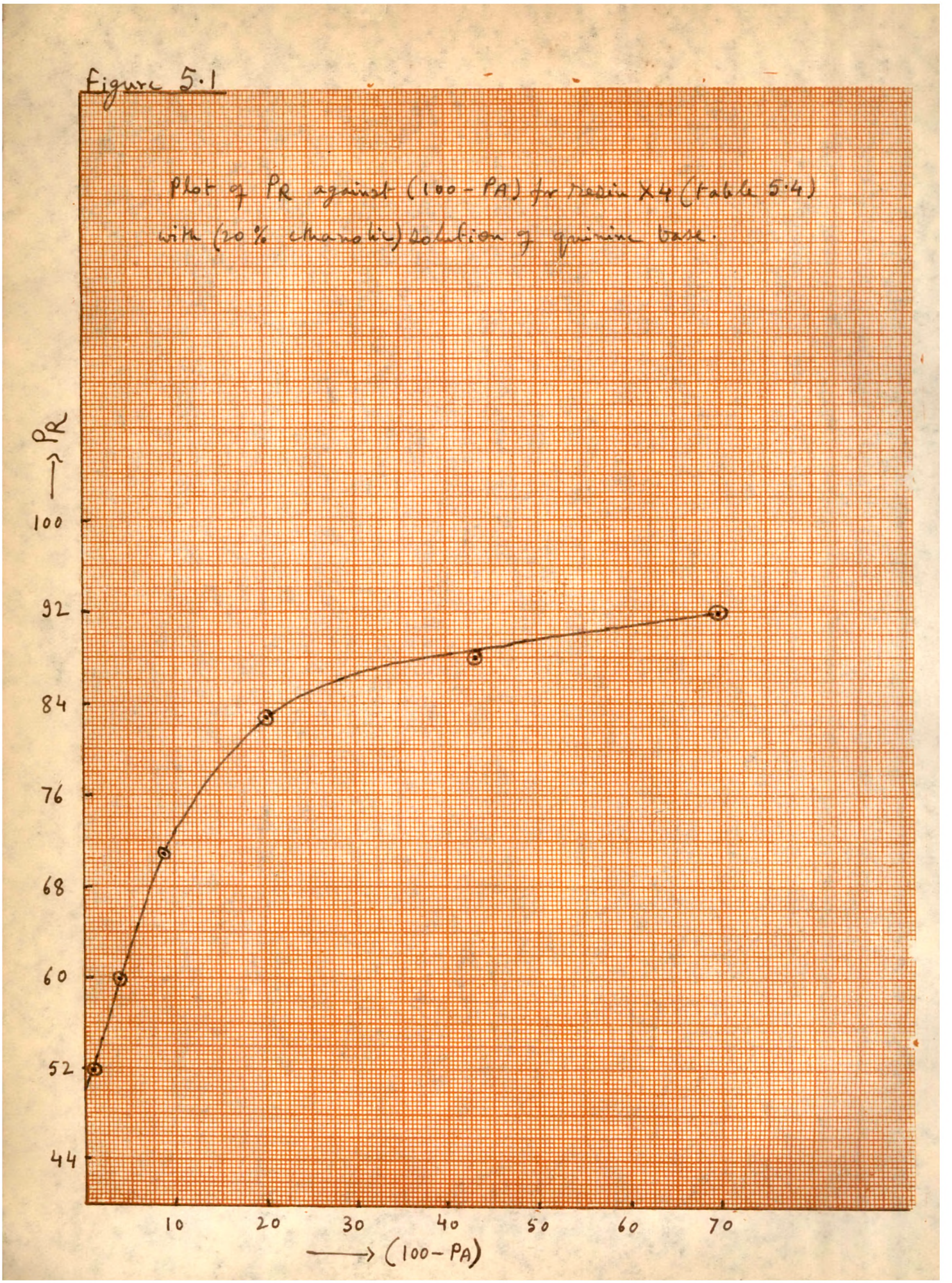
Alkaloid base	Time (t)	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_t$	R	P_{At}	P_{Rt}
Cinchonine	8 Hours	11.67	33.11	0.2746	0.3529	8.292	23.53
	17 Hours	11.68	33.11	0.4118	0.3529	12.44	35.27
	41 Hours	11.68	33.11	0.4603	0.3529	13.90	39.41
	4 Days	11.67	33.11	0.4922	0.3529	14.87	42.18
Cinchonidine	4 Hours	11.68	33.48	0.2865	0.3489	8.559	24.52
	17 Hours	11.69	33.48	0.4011	0.3489	11.98	34.31
	41 Hours	11.68	33.48	0.4585	0.3489	13.70	39.24
	4 Days	11.69	33.48	0.4819	0.3489	14.40	41.23

Table 5.4

The uptake of quinine base in 20 % ethanolic solution by resins X 4 and X 8 (after equilibrium had been reached).

Resin	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
X 4	0.8002	2.456	0.7369	0.3258	30.00	92.08
	1.577	2.456	1.390	0.6422	56.56	88.08
	2.351	2.456	1.950	0.9568	79.38	82.96
	3.131	2.456	2.242	1.275	91.24	71.58
	3.929	2.456	2.360	1.600	96.10	60.08
	4.693	2.456	2.430	1.911	98.91	51.76
X 8	1.505	2.456	0.5977	0.6127	24.33	39.72
	2.233	2.456	0.9080	0.9090	36.97	40.66
	2.987	2.456	1.253	1.216	51.00	41.94
	3.738	2.456	1.560	1.522	63.49	41.73
	4.499	2.456	1.881	1.831	76.60	41.82

Figure 5.1


Plot of P_R against (100 - PA) for resin X4 (Table 5.4) with (20% ethanolic) solution of quinine base.
P_R →
100
92
84
76
68
60
52
44
10
20
30
40
50
60
70
→ (100 - PA)

5.1.e. DISCUSSION :

The cinchona alkaloids, quinine, quinidine, cinchonine and cinchonidine are weak, diacidic organic bases with the second acid dissociation constant lower than the first one. The uptake of the base quinine, from alcoholic and 20 % aqueous alcoholic (by volume) solution is a slow process ; tables (5.1.a. and 5.2) indicate that the rate is slower in alcoholic solution than that in 20 % aqueous alcoholic solution. In alcoholic solution the uptake of the four bases, quinine, quinidine, cinchonine and cinchonidine is practically at the same rate, by resin X 4 , tables (5.2 and 5.3). This indicates that X 4 is sufficiently porous and the difference in molecular size does not matter under these conditions.

The total uptake, at equilibrium, should be determined, as suggested earlier, by two mechanisms: (a) the exchange mechanism and (b) the (molecular) sorption mechanism. According to the first , when it is fully operative, the value of P_R should be 50. With resin X 4 in 20 % alcoholic solution of quinine, the values of P_R (table 5.4) are considerably above 50 and the value of P_R increases with increase in (100 - P_A) . The plot of P_R against (100 - P_A) was extrapolated to zero-value of (100 - P_A) and the value of P_{Ro} (figure 5.1) obtained is 49.5 , which is in good agreement with the value of P_{Ro} for quinine sulphate in aqueous solution with resin X 4 (given earlier).

This is the contribution of exchange mechanism to the observed value of P_R . The small reduction from 50 is to be attributed to the steric non-accessibility of a few exchange sites.

The difference $P_R - P_{Ro}$ is the contribution of the sorption mechanism to the observed value of P_R . This contribution is considerably greater in this case than in the case of quinine sulphate in aqueous solution and provides support to the postulation of two mechanisms.

As the degree of cross-linking of the resin is increased, the contribution of the sorption mechanism is reduced due to lesser extent of swelling of the resin (1) With resin X 8 (table 5.4) the uptake of quinine from 20 % aqueous alcoholic solution was studied and the values of P_R are given. It is observed that the value of P_R is practically independent of P_A and the average value, taken as value of P_{Ro} , is 41 . This value is in agreement with the value of P_{Ro} for quinine sulphate in aqueous solution with resin X 8 (given earlier). The contribution of sorption mechanism is, here also, practically negligible. The decrease in the value of P_{Ro} from 50 is to be attributed to (a) the reduced pore diameter and (b) the steric non-accessibility of some exchange sites.

The observation that the contribution of exchange mechanism to the observed value of P_R , i.e. P_{Ro} , is the same for uptake from aqueous alcoholic solution of quinine and

aqueous solution of quinine-
sulphate indicates, as should be expected, that exchange mechanism provides the same value of P_{Ro} for a given resin and alkaloid ; it is independent of the nature of the solvent and whether the exchanging species is QH^+ or Q . However, the contribution of sorption mechanism to the observed value of P_R appears to be dependent on the solvent medium and concentration and is a rather specific effect.

Reference :

(1). D.J.Patel and S.L.Bafna, Ind.Eng.Chem. accepted.