4. STUDIES ON THE UPTAKE OF CINCHONA ALKALOID BASES BY SULFONIC ACID CATION EXCHANGE RESINS FROM AQUEOUS ALIPHATIC ALCOHOLS :

4.1

Introduction :

This chapter deals with the study of the equilibrium uptake of cinchona alkaloid bases (quinine and quinidine) from aqueous methanols and aqueous ethanols by four sulfonic acid cation exchange resins in hydrogen form at room temperature (∽ 30°C).

4.2

Experimental :

The resins were of the same type as used earlier, except that for X2, mesh size used was 50/100 and for X4 and X8, it was 30/40. The chemicals were from samples used earlier. The solutions were prepared by dissolving the known amounts of the alkaloid base in each aqueous alcohol studied. The concentration was rechecked by ultraviolet absorption.

Procedure :

To study the equilibrium uptake of the alkaloid bases by the sulfonic acid resins, weighed amounts of airdry resins were placed in contact with suitable volumes of the alkaloid base solution of known concentration, in well stoppered flasks with frequent shaking at room temperature (∽ 30°C).

Preliminary work was carried out to find out the time after which further uptake did not take place. After sufficiently more time than this (30 to 40 days), the solutions were analysed for alkaloid concentration in the equilibrium mixture by taking out known volume from each flask, diluting suitably with the same aqueous alcohol in which the solution was prepared and measuring the optical density for U.V.absorption.

The results were not measurably different when either the amount of alkaloid base solution was held constant and the amount of added resin varied or when the amount of added resin was held constant and the amount of alkaloid base solution varied, provided the ratio of the initial concentration (in meq./litre) of the resin to the initial concentration of the alkaloid base, was the same. Preliminary work also indicated that for small changes in temperature, the value of P_R was not significantly affected.

4.3

Nomenclature :

$\left[A \right]_i$ = initial concentration of alkaloid base solution in meq./litre,

W = weight of airdry resin taken in grams,

v = volume of alkaloid base solution added in cc.,

C = capacity of the resin in meq./gram of airdry resin,

D_i = optical density of the initial concentration of alkaloid base solution after suitable dilution,

D_o = optical density, at the same wavelength, of the solution at equilibrium after the same extent of dilution as in above,

$\left[\bar{A}\right]_e$ = $\left[A\right]_i \cdot (D_i - D_o) / D_i$ = the meq.of alkaloid in the resin phase per litre of solution, at equilibrium,

$\left[\bar{H}\right]_i$ = $W.C.10^3 / v$ = the meq. of resin per litre of the solution in the hydrogen form, initially,

P_A = $100. \left[\bar{A}\right]_e / \left[A\right]_i$ = the % exchange of alkaloid base at equilibrium,

P_R = $100. \left[\bar{A}\right]_e / \left[\bar{H}\right]_i$ = the % resin capacity exchanged at equilibrium.

4.4

Results :

Table 4.1

Capacity of resins

Resin	Mesh	Capacity in meq./gm of	
		Airdry resin	Ovendry resin
X2	50/100	3.69	4.87
X4	30/40	3.74	5.04
X8	30/40	3.57	4.92
IR-200	20/60	3.56	4.78

Table 4.2

Uptake of quinine from 10 % aqueous methanol by resins in hydrogen form.

Resin	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
X4	1.00	1.59	0.55	34.6	55.0
	1.38	1.59	0.75	47.2	54.4
	1.78	1.59	0.98	61.6	55.1
	2.12	1.59	1.13	71.1	53.3
X8	1.25	1.75	0.55	31.4	44.0
	1.78	1.75	0.81	46.3	45.5
	2.26	1.75	1.04	59.4	46.0
	2.71	1.75	1.23	70.3	45.4
	3.15	1.75	1.42	81.2	45.1
	3.46	1.75	1.56	89.2	45.1
IR-200	1.08	1.75	0.46	26.3	42.6
	1.67	1.75	0.70	34.0	41.9
	2.62	1.75	1.10	62.9	42.0
	3.06	1.75	1.27	72.6	41.5
	3.28	1.75	1.35	77.1	41.2

Table 4.3

Uptake of quinine from 20 % aqueous methanol by resins in hydrogen form.

Resin	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
X2	1.34	2.91	1.13	38.8	84.3
	1.73	2.91	1.48	50.9	85.6
	2.06	2.91	1.76	60.5	85.4
	2.38	2.91	2.03	69.8	85.3
X4	2.07	3.71	1.18	31.8	57.0
	2.69	3.71	1.57	42.3	58.4
	3.24	3.71	1.86	50.1	57.4
	3.81	3.71	2.20	59.3	57.8
	4.30	3.71	2.47	66.6	57.4
X8	2.67	3.99	1.30	32.6	48.7
	3.59	3.99	1.72	43.1	47.9
	4.51	3.99	2.14	53.6	47.4
	5.57	3.99	2.63	65.9	47.2
	6.41	3.99	3.03	75.9	47.3
	7.06	3.99	3.34	83.7	47.3
IR-200	2.31	3.78	0.96	25.4	41.6
	4.47	3.78	1.96	51.9	43.9
	5.02	3.78	2.18	57.7	43.4
	5.62	3.78	2.40	63.5	42.7
	6.61	3.78	2.80	74.0	42.4

Table 4.4

Uptake of quinine from 40 % aqueous methanol by resins in hydrogen form.

Resin	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
X2	2.10	5.59	2.31	41.3	110.0
	2.77	5.59	3.00	53.7	108.2
	3.51	5.59	3.75	67.1	106.9
	4.03	5.59	4.27	76.4	105.9
	4.89	5.59	5.03	90.0	102.9
X4	2.04	4.90	1.43	29.2	70.1
	2.72	4.90	1.87	38.6	69.5
	3.45	4.90	2.30	46.9	68.7
X8	4.94	6.03	3.12	51.8	63.1
	6.35	6.03	3.88	64.3	61.1
	7.66	6.03	4.46	74.0	58.2
	8.84	6.03	4.98	82.6	56.3
	9.71	6.03	5.41	89.7	55.7
IR-200	2.62	4.90	1.07	21.8	40.8
	3.79	4.90	1.50	30.6	39.6
	4.88	4.90	2.01	41.0	41.2
	6.86	4.90	2.82	57.5	41.1
	7.70	4.90	3.15	64.3	40.9

Table 4.5

(A) Uptake of quinine from aqueous ethanols by resin X8 in hydrogen form.

% Ethanol	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
20	4.57	4.02	2.25	56.0	49.3
	5.38	4.02	2.63	65.4	48.9
	6.43	4.02	3.05	75.9	47.4
	7.03	4.02	3.37	83.8	47.9
40	5.30	6.29	3.40	54.1	64.2
	6.65	6.29	4.10	65.2	61.7
	7.93	6.29	4.67	74.2	58.9
	9.37	6.29	5.37	85.4	57.3
	10.40	6.29	5.85	93.0	56.3

(B) Uptake of quinidine from aqueous ethanol by resin X8 in hydrogen form.

% Ethanol	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
40	1.78	1.17	0.79	67.5	44.4
	2.21	1.17	0.97	82.9	43.9
	2.72	1.17	1.16	99.1	42.6

Table 4.6

Uptake of quinidine from 40 % aqueous methanol by resins in hydrogen form.

Resin	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
X2	1.31	1.66	1.24	74.7	94.6
	1.55	1.66	1.40	84.3	90.3
	1.83	1.66	1.48	89.2	80.9
	2.02	1.66	1.59	95.8	78.7
X8	1.27	1.13	0.52	46.0	41.0
	1.77	1.13	0.75	66.4	42.4
	2.24	1.13	0.93	82.3	41.5
	2.67	1.13	1.09	96.4	40.8
IR-200	1.33	1.76	0.54	30.7	40.6
	1.92	1.76	0.77	43.8	40.1
	2.00	1.76	0.84	47.7	42.0
	3.45	1.76	1.34	76.1	38.9

Table 4.7

Uptake of quinidine from 60 % aqueous methanol by resins in hydrogen form.

Resin	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
X2	1.00	2.66	1.06	39.9	106.0
	1.74	2.66	1.73	65.5	99.4
	2.11	2.66	2.04	76.7	96.7
	2.77	2.66	2.43	91.4	87.7
X8	2.57	2.53	1.11	43.9	43.2
	3.37	2.53	1.45	57.3	43.0
	4.01	2.53	1.72	68.0	42.9
	4.74	2.53	2.02	79.9	42.6
	5.29	2.53	2.26	89.3	42.7
IR-200	1.75	2.53	0.71	28.1	40.6
	2.36	2.53	0.94	37.2	39.8
	3.28	2.53	1.31	51.8	39.9
	3.89	2.53	1.53	60.5	39.3
	4.55	2.53	1.75	69.2	38.5
	5.04	2.53	1.94	76.7	38.5

Table 4.8

Values of P_R for the uptake of cinchona alkaloid bases from aliphatic alcohols by sulfonic acid cation exchange resins in hydrogen form.

Alkaloid =	. . . . Quinine or Quinidine			
Resin =	X2	X4	X8	IR-200
Alcohol				
Methyl	42	33	23	30
Ethyl(abs.)	34	26	16	30

4.5

Discussion :

Tables (4.2 to 4.7) give the values for the equilibrium uptake of quinine and quinidine by sulfonic acid cation exchange resins in the hydrogen form from aqueous methanols and aqueous ethanols. The values of P_R for quinine and quinidine in pure methanol and absolute ethanol are given in Table 4.8 from earlier work (117). The data indicate that the value of P_R either remains almost constant or decreases to some extent as the value of P_A is increased. For the gel type resins, X2, X4 and X8, the value of P_R decreases as the degree of crosslinking, X, increases. The values of P_R for resin X8 in aqueous methanols and aqueous ethanols do not appear to be much different. However, in aqueous methanols, the value of P_R is somewhat higher for quinine than that of quinidine. The values given earlier for equilibrium exchange of alkaloid sulfates in water may be considered as a measure of the value of P_R in zero percent alcohol. As the percent methanol content of the solvent medium is increased from 0 to 40 % , the equilibrium uptake of quinine increases ; but in 100 % methanol the equilibrium uptake is less than that in water.

For resin IR-200, which has got expanded structure, the value of equilibrium uptake is almost same for 0 % and 100 % methanol, but the equilibrium uptake of quinine is higher in 10 to 40 % aqueous methanols. It may be noted that the value of P_R for resin X2 in 40 % aqueous methanol

is greater than 100, implying that the equilibrium uptake of quinine is more than the replaceable hydrogen ions in the resin. For quinidine also, the values of P_R in 40 % and 60 % aqueous methanols are greater than those for 0 % methanol i.e. quinidine sulfate in water.

The factors determining the equilibrium uptake of alkaloid bases in aqueous alcohols may include (a) the swollen volume of the resin relative to the size of the organic counter ion or the organic base molecule, (b) the decrease in the size of solvation shell around the proton and the ionogenic group, (c) the increase in the extent of ion-pair formation, (d) increase in the solubility of organic base in aqueous alcoholic medium, around and within the resin particle and (e) the operations of nonexchange interactions.

Factors (b) and (c) should tend to accommodate more organic base molecules or organic counter ions on the surface and inside the resin particle and thus, increase in value of P_R as compared to that in water. This uptake should be aided by the factors (d) and (e). The difference in somewhat higher uptake of quinine as compared to that of optical isomer quinidine may be attributed to the solubility differences of the two optical isomers in aqueous methanols. The smaller value of P_R in pure alcohols, for resins X2, X4 and X8 should be due to the deswelling of resin particle as the major factor, when other contributory factors become of relatively much less

significance. For resin IR-200, the deswelling of the resin particle could not be significant because of the regid expanded structure. The behaviour of resin IR-200 is somewhat different from the gel type resins X2, X4 and X8, which may be attributed to its somewhat regid expanded structure.

The relatively high equilibrium uptake of the alkaloid bases in aqueous alcohols should be of interest and this study should provide the basis for a detail investigation of this aspect.