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

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

Introduction :

This chapter deals with the study of the equilibrium uptake of quinidine and cinchonine from aliphatic alcohols by four sulfonic acid cation exchange resins in hydrogen form at room temperature. The literature survey indicates that such studies are not available.

Experimental :

Resins and Chemicals : The resins and chemicals were from samples used earlier.

Solutions : The solutions were prepared by dissolving the known amounts of the alkaloid bases in each of the alcohols 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 ($\sim 30^{\circ}C$).

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 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./liter) 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.

Nomenclature :

$[A]_i$ = initial concentration of alkaloid base solution in meq./liter,

W = weight of airdry resin taken in grams,

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

C = capacity of the resin in meq. per 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,

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

$[H]_i$ = $W.C.10^3 / v$ = the meq.of resin per liter of the solution in the hydrogen form, initially,

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

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

Results :

Table 4.1

Uptake of quinidine from alcohols by resin X2 in hydrogen form.

alcohol	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
methyl	8.26	16.5	3.11	18.8	37.5
alcohol	14.9	16.5	5.83	35.3	39.1
	20.7	16.5	8.45	51.3	40.8
	27.5	16.5	11.6	70.3	42.2
	31.8	16.5	13.5	81.8	42.5
ethyl	8.8	16.8	2.62	15.6	29.8
alcohol	14.9	16.8	4.72	28.1	31.7
(absolute)	19.1	16.8	6.26	37.3	32.8
	23.0	16.8	7.87	46.9	34.2
	25.0	16.8	8.68	51.7	34.7
	27.8	16.8	9.59	57.1	34.5
n-propyl	12.1	15.1	2.88	19.1	23.8
alcohol	24.5	15.1	5.65	37.4	23.1
	31.7	15.1	7.47	49.5	23.6
	37.1	15.1	8.91	59.0	24.0
	40.1	15.1	9.87	65.4	24.6
	45.5	15.1	11.3	74.8	24.8

Table 4.1 (Contd.)

alcohol	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
n-butyl	13.8	16.1	3.30	20.5	23.9
alcohol	23.3	16.1	5.17	32.1	23.2
	30.2	16.1	7.03	43.7	23.3
	31.9	16.1	7.65	47.5	24.0
	37.8	16.1	9.31	57.8	24.6
	44.4	16.1	10.9	67.7	24.6
tert-amyl	25.5	15.9	3.76	23.6	14.7
alcohol	27.5	15.9	3.87	24.3	14.1
	30.7	15.9	4.60	28.9	15.0
	36.9	15.9	6.90	43.4	18.7
	45.3	15.9	8.99	56.5	19.9
n-hexyl	14.4	16.3	5.35	32.8	37.2
alcohol	19.6	16.3	6.63	40.7	33.8
	23.7	16.3	7.70	47.2	32.5
	26.5	16.3	9.80	60.1	37.0
	30.0	16.3	11.6	71.2	38.7

Table 4.2

Uptake of quinidine from alcohols by resin X4 in hydrogen form.

alcohol	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
methyl	4.23	16.5	1.36	8.24	32.2
alcohol	13.6	16.5	4.00	24.2	29.4
	19.3	16.5	6.31	38.2	32.7
	25.5	16.5	8.45	51.2	33.1
	29.1	16.5	9.71	58.8	33.4
ethyl	14.1	16.8	3.03	18.0	21.5
alcohol	16.0	16.8	4.04	24.1	25.3
(absolute)	20.6	16.8	5.05	30.1	25.2
	28.2	16.8	7.67	45.9	27.2
	32.6	16.8	8.68	51.7	26.6
n-propyl	22.8	15.1	3.64	24.1	16.0
alcohol	32.5	15.1	5.27	34.9	16.2
	41.7	15.1	6.9	45.7	16.6
	47.3	15.1	8.05	53.3	17.0
	57.5	15.1	10.0	66.1	17.4
	63.0	15.1	11.5	76.2	18.2

Table 4.2 (Contd.)

alcohol	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
n-butyl	23.4	16.1	3.31	20.6	14.2
alcohol	33.9	16.1	4.96	30.8	14.6
	39.9	16.1	6.00	37.3	15.0
	46.0	16.1	7.03	43.7	15.3
	53.6	16.1	8.17	50.8	15.2
	59.7	16.1	9.31	57.8	15.6
tert-amyl	30.8	15.9	3.35	20.9	10.9
alcohol	45.2	15.9	5.02	31.6	11.1
	46.6	15.9	6.06	38.1	13.0
	53.9	15.9	8.26	51.9	15.3
	60.8	15.9	10.5	66.0	17.3
n-hexyl	15.2	16.3	2.14	13.1	14.1
alcohol	28.0	16.3	4.06	24.9	14.5
	43.5	16.3	5.56	34.0	12.8
	58.6	16.3	8.02	49.2	13.7

Table 4.3

Uptake of quinidine from alcohols by resin X8 in hydrogen form.

alcohol	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
methyl	17.2	16.5	4.27	25.9	24.8
alcohol	27.1	16.5	6.41	38.9	23.7
	33.9	16.5	7.77	47.1	22.9
	38.5	16.5	8.84	53.6	23.0
ethyl	9.33	16.8	1.62	9.64	17.4
alcohol	18.4	16.8	2.62	15.6	14.2
(absolute)	28.5	16.8	4.04	24.1	14.2
	35.5	16.8	5.37	32.0	15.1
	39.4	16.8	6.26	37.3	15.9
n-propyl	32.6	15.1	2.49	16.5	7.64
alcohol	46.7	15.1	3.45	22.9	7.39
	63.5	15.1	5.17	34.2	8.13
	72.0	15.1	6.13	40.6	8.51
	81.6	15.1	6.9	45.7	8.46
	91.0	15.1	8.14	53.9	8.95

Table 4.3 (Contd.)

alcohol	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
n-butyl	33.9	16.1	2.28	14.2	6.72
alcohol	45.2	16.1	3.10	19.3	6.86
	48.3	16.1	3.31	20.6	6.85
	60.8	16.1	3.93	24.4	6.46
	66.1	16.1	4.55	28.3	6.88
	87.8	16.1	6.62	41.1	7.54
tert-amyl	56.0	15.9	3.35	21.1	5.91
alcohol	68.8	15.9	5.23	32.9	7.60
	80.2	15.9	7.11	44.7	8.85
	96.9	15.9	9.82	61.7	9.98
n-hexyl	33.2	16.3	2.25	13.8	6.78
alcohol	49.1	16.3	4.15	25.5	8.45
	79.0	16.3	5.56	34.1	7.04
	96.4	16.3	8.24	50.6	8.55
	130.	16.3	10.7	65.6	8.23

Table 4.4

Uptake of quinidine from alcohols by resin IR-200 in hydrogen form.

alcohol	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
methyl	11.0	16.5	3.11	18.9	28.3
alcohol	18.2	16.5	5.24	31.8	28.8
	26.0	16.5	7.97	48.3	30.6
	33.3	16.5	10.1	61.2	30.3
	38.6	16.5	11.7	70.9	30.3
ethyl	17.0	16.8	4.85	28.9	28.5
alcohol	21.1	16.8	6.06	36.1	28.7
(absolute)	25.1	16.8	7.87	46.8	31.4
	30.7	16.8	9.08	54.0	29.6
	35.6	16.8	10.1	60.0	28.3
n-propyl	14.3	15.1	3.64	24.1	25.5
alcohol	25.3	15.1	6.80	45.7	26.9
	28.9	15.1	8.05	53.3	27.9
	32.6	15.1	8.81	58.3	27.0
	41.3	15.1	11.1	73.5	26.9

Table 4.4 (Contd.)

alcohol	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
n-butyl	8.74	16.1	2.48	15.4	28.4
alcohol	17.1	16.1	5.37	33.3	31.4
	22.5	16.1	6.62	41.1	29.4
	29.2	16.1	8.48	52.7	29.0
	36.9	16.1	10.3	63.4	27.9
	41.5	16.1	11.7	72.7	28.2
tert-amyl	27.1	15.9	8.26	51.9	30.5
alcohol	30.9	15.9	8.36	52.5	27.1
	35.7	15.9	10.1	63.5	28.5
	38.2	15.9	10.9	68.5	28.5
	43.5	15.9	12.8	80.4	29.4
n-hexyl	26.7	16.3	7.92	48.6	29.7
alcohol	30.1	16.3	9.41	57.7	31.3
	32.6	16.3	10.8	66.3	33.1
	36.7	16.3	12.0	73.6	32.7

Table 4.5

Uptake of cinchonine from alcohols by resin X2 in hydrogen form.

alcohol	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
methyl	3.74	15.3	2.28	14.9	61.0
alcohol	10.0	15.3	6.62	43.3	66.2
	12.1	15.3	7.71	50.4	63.7
	14.6	15.3	8.90	58.2	61.0
n-propyl	12.0	14.5	2.84	19.6	23.7
alcohol	19.6	14.5	4.71	32.5	24.0
	28.2	14.5	6.58	45.4	23.3
	28.8	14.5	6.91	47.7	24.0
	36.6	14.5	9.32	64.3	25.5
	42.5	14.5	10.8	74.5	25.4
tert-amyl	19.0	15.8	4.77	30.2	25.1
alcohol	25.1	15.8	5.97	37.8	23.8
	29.1	15.8	7.04	44.5	24.2
	35.4	15.8	9.31	58.9	26.3
	45.4	15.8	11.9	75.3	26.2

Table 4.6

Uptake of cinchonine from alcohols by resin X4 in hydrogen form.

alcohol	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
methyl	14.2	16.3	5.41	34.0	38.1
alcohol	17.9	16.3	7.07	43.4	39.5
	23.8	16.3	9.41	57.7	39.5
	33.3	16.3	13.4	82.2	40.2
n-propyl	28.7	14.5	5.00	34.5	17.5
alcohol	38.5	14.5	6.80	46.9	17.7
	43.5	14.5	7.89	54.4	18.1
	50.3	14.5	9.21	63.5	18.3
	53.5	14.5	10.0	69.0	18.7
n-butyl	20.3	16.1	4.64	28.8	22.9
alcohol	28.5	16.1	6.56	40.8	23.0
	37.0	16.1	8.60	53.4	23.3
	45.2	16.1	10.9	67.7	24.1
	53.5	16.1	13.0	80.7	24.3
tert-amyl	35.0	15.8	8.00	50.6	22.9
alcohol	44.9	15.8	9.79	62.0	21.9
	52.0	15.8	12.5	79.1	22.6
	61.0	15.8	14.2	89.9	23.3

Table 4.7

Uptake of cinchonine from alcohols by resin X8 in hydrogen form.

alcohol	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
ethyl	19.7	15.8	3.01	19.5	15.3
alcohol	23.5	15.8	3.71	23.5	15.8
(absolute)	29.1	15.8	4.18	26.5	14.4
	34.7	15.8	5.57	35.3	16.1
	39.1	15.8	6.26	39.6	16.0
n-propyl	34.0	14.5	2.41	16.6	7.09
alcohol	37.2	14.5	2.85	19.7	7.66
	50.4	14.5	4.28	29.5	8.49
	58.1	14.5	5.04	34.8	8.67
	62.1	14.5	5.70	39.3	9.18
	71.9	14.5	6.80	46.9	9.46
tert-amyl	42.8	15.8	4.30	27.2	10.5
alcohol	50.1	15.8	5.37	34.0	10.7
	60.1	15.8	7.64	48.3	12.7
	69.3	15.8	9.79	63.4	14.1
	80.8	15.8	11.0	69.6	13.6
n-hexyl	34.4	15.6	3.40	21.8	9.88
alcohol	48.6	15.6	6.45	41.4	12.4
	83.5	15.6	8.68	55.6	10.4
	95.9	15.6	10.3	66.0	10.7

Table 4.8

Uptake of cinchonine from alcohols by resin IR-200 in hydrogen form.

alcohol	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
methyl	6.00	16.3	2.12	13.0	35.3
alcohol	14.6	16.3	5.32	32.6	36.4
	23.2	16.3	8.44	51.8	36.4
	29.4	16.3	10.5	64.4	36.2
ethyl	21.8	15.8	6.49	41.1	29.8
alcohol	27.8	15.8	8.47	53.6	30.5
(absolute)	33.2	15.8	10.3	65.2	31.0
	39.2	15.8	12.4	78.5	31.6
n-propyl	12.4	14.5	3.73	25.7	30.1
alcohol	23.8	14.5	6.91	47.6	29.0
	27.7	14.5	8.11	55.9	29.3
	32.4	14.5	9.54	65.6	29.4
	36.1	14.5	10.6	73.1	29.4
	45.5	14.5	13.1	91.0	28.9

Table 4.8 (Contd.)

alcohol	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
n-butyl	18.0	14.7	5.21	35.4	28.9
alcohol	23.9	14.7	7.13	48.5	29.8
	30.7	14.7	8.96	61.0	29.2
	35.5	14.7	10.4	70.6	29.3
	38.9	14.7	11.6	78.9	29.8
tert-amyl	23.8	15.8	8.59	54.4	36.1
alcohol	27.0	15.8	9.79	62.0	36.3
	30.8	15.8	11.3	71.5	36.7
	35.9	15.8	13.4	84.8	37.3
	40.2	15.8	15.1	95.6	37.6
n-hexyl	27.2	15.6	9.6	61.5	35.3
alcohol	30.9	15.6	11.0	70.5	35.6
	32.4	15.6	11.7	75.5	36.1
	36.0	15.6	12.8	82.1	35.6
	39.7	15.6	14.1	90.4	35.5

Table 4.9

Average values of P_R for the uptake of cinchona alkaloids by sulfonic acid cation exchange resins.

alkaloid =	quinine				quinidine			
resin =	X2	X4	X8	IR-200	X2	X4	X8	IR-200
alcohol		P_R =				P_R =		
methyl alcohol	42	33	23	31	41	33	23	30
ethyl alcohol(absolute)	35	27	18	32	34	26	16	30
n-propyl alcohol	-	-	-	-	23	16	09	27
n-butyl alcohol	24	-	-	27	24	15	07	28
tert-amyl alcohol	18	-	07	28	17	11	08	28
n-hexyl alcohol	38	14	07	31	37	14	08	32

Table 4.9 (Contd.)

alkaloid =	cinchonine				cinchonidine			
resin =	X2	X4	X8	IR-200	X2	X4	X8	IR-200
alcohol		P_R =				P_R =		
methyl alcohol	63	39	-	36	67	38	26	34
ethyl alcohol(absolute)	-	-	15	30	-	25	17	33
n-propyl alcohol	24	18	09	29	-	-	11	31
n-butyl alcohol	-	23	-	29	32	20	11	33
tert-amyl alcohol	25	23	13	37	25	22	13	37
n-hexyl alcohol	-	-	11	36	63	29	-	39

Discussion :

Tables(4.1 to 4.8) give the values for the equilibrium uptake of quinidine and cinchonine by sulfonic acid cation exchange resins in the hydrogen form from aliphatic alcohols. The value of P_R is not significantly changed when P_A is varied. Table (4.9) gives the average values of P_R for the uptakes of quinidine and cinchonine by the sulfonic acid resins X2, X4, X8 and IR-200. The table also includes the values for quinine and cinchonidine from the work of Shri C.V. Bhat. The factors determining the value of P_R should include the swollen volume of the resin particle in the solvent and the size of the organic counter ions.

The values of P_R for the uptake of the optical isomers are not significantly different ; the values for quinine and quinidine are significantly lower than those for cinchonine and cinchonidine in methyl alcohol. With increase in the chain length of the alcohol molecule the difference in the values of P_R for quinine and quinidine and those for cinchonine and cinchonidine becomes much less and in ethyl alcohol (absolute) and n-propyl alcohol the values of P_R for the four bases are fairly close for each resin. With further increase in the chain length the difference in the values of quinine and quinidine and those of cinchonine and cinchonidine becomes significant. For n-butyl alcohol, n-hexyl alcohol and tertiary amyl alcohol the values of P_R for quinine and quinidine are lower than those for cinchonine and cinchonidine. This pattern of behaviour should be attributed to the size of the organic counter ions relative to the swollen volume of the resin particle in the alcohol.

The effect of the degree of crosslinking of the resin is marked and the value of P_R decreases with increase in the value of X from 2 to 8 for resins X2, X4, and X8 for each solvent. The reason for this is the decrease in the swollen volume of the resin with increase in the degree of crosslinking.

With increase in the chain length of the alcohol molecule, for resin X2, the value of P_R for the four bases first decreases and then increases. With increase in the value of X, that is for resins X4 and X8 with increase in the chain length of the alcohol molecule, the value of P_R first decreases and then remains almost unchanged for the four bases studied. With resin IR-200 which has expanded structure, the value of P_R first decreases and then increases with increase in the chain length of the alcohol molecule. The variation in the value of P_R for the series of alcohols, should be dependent on the swollen volume of the resin in the alcohol.

Conclusion :

The exchange uptake of cinchona bases occurs with sulfonic acid resins in aliphatic alcohols. The value of P_R decreases with increase in X ; decreases or remains almost constant with increase in the size of the counter ions and first decreases and then again either increases or remains almost unchanged with increase in the chain length of the solvent (alcohol) molecule.