4.

EQUILIBRIA WITH CINCHONA ALKALOID SULPHATES :

4.1 Equilibrium studies of organic cations with ion exchange resins :

Kressman and Kitchener (1) found that the affinity of some large organic cations viz. quaternary ammonium salts and the quininium ion, for a phenol sulphonate resin increased with increasing size of the ion. This suggested that van der Waals forces contributed largely to the affinity and the coulomb forces were less important. This was supported by the greater affinity for the resin of the trimethyl-n-amylammonium ion than of the isomeric tetra - ethyl ammonium ion. The rates of exchange, on the other hand, decreased with increasing ionic size. The saturation capacity was the same for the largest of the quaternary ions studied, viz. phenyl-benzyl-dimethyl ammonium ion, as per inorganic ions. This indicated that all the molecular pores within the resin were larger than the effective diameter of this ion.

Richardson (2) described the purification of direct cotton dyes based on the observation that selective diffusion of ionic species into the bulk of the resin structure depended on the molecular dimensions of the ion. By this means, the large organic anions of the dye could be effectively separated from those of the much smaller diluent salts.

Kressmen (3) studied the sorption of acids on De-Acidite E and on the highly porous Decolorite for the separations based upon ionic size. Inorganic acids,

H_2SO_4 , HCl were taken up rapidly by both resins from 0.01 N solutions at 22 °C. Some dye acids were also taken up rapidly by Decolorite and more slowly and to limited extent by De Acidite E. The form of the kinetics and the interruption tests indicated that the rate determing step was diffusion in the solid particle. Separation of inorganic salts from dye solutions and the feasibility of separating dye acids have been suggested.

Hale and others (4) studied the sorption of quaternary ammonium ions by sulphonated polystyrene resins of different crosslinking. In column experiments using neutral solutions of the quaternary chlorides, the amount sorbed was found to decrease with increase in the degree of cross-linking of the resin and in general with increase in the size of the organic cation. In equilibrium studies with a 15 % DVB resin the amount of tetramethyl ammonium ion, taken up from alkaline solution was equal to the theoretical exchange capacity of the resin but at pH 5 the uptake was about half the full capacity. This marked dependance of the sorption on pH (which is not observed with simple inorganic cations) corresponded to a sharp decline in the affinity of the organic cation for the resin as the latter sorbed more of the quaternary ion.

Richter (5,6) studied the selectivity of ion exchangers on the basis of soap like structures. A poly soap consisting of poly vinyl pyridine which was 40 % quaternized with dodecylbromide and cross-linked with 1 % DVB has been used and its selectivity against bromide and chloride ions has been investigated.

Yakhontova (7) observed that the stryptomycine ions (str^{+++}) were sorbed at a much slower rate than that of the mineral ions. The sorption process was slow, being limited by the rate of diffusion of the organic cation into the particles and true equilibrium was not, in general, reached. It has been suggested that the streptonium ion was sorbed on the grain surfaces and penetrated into the interior only to a certain depth setting up a concentration gradient along the radius. As the particle size decreased, exchange became more complete and finally true equilibrium was reached.

Tamamushi and Tamaki (8) determined the sorption isotherms of alkylammonium chlorides (methyl, butyl, hexyl, octyl,decyl and dodecyl ammonium chlorides) on cation exchange resins (Amberlite IR-120 and Dowex 50 X 2) and of sodium dodecyl sulphate on an anion exchange resin (Dowex 1 X 1). It was observed that as the chain length of the alkyl group of the cationic detergents increased, the influence of the pore size of the resins became more evident. The sorption of the lower homologues was chiefly of the ion exchange type whereas that of dodecyl ammonium chloride or sodium dodecyl sulphate was considered to be the superposition of the ion exchange type and the van der Waals sorption type.

Miller and others (9) studied the equilibria and kinetics of exchange of H^+ for Na^+ and NEt_4^+ with a sulphonated styrene DVB copolymer of deliberately enhanced cross-linking compared with the conventional exchanger, Zeo-Karb 225, the secondary intermeshed product was markedly more selective but both ions had higher diffusion coefficients inside the latter resin.

4.2. Equilibrium studies of cinchona alkaloid sulphates with sulphonic acid resins :

4.2.a. Introduction :

Detailed study of equilibria between sulphonic acid cation exchange resins and cinchona alkaloid sulphates (Section 1.3.b.) are not available, and hence it was considered to be of interest to undertake these studies. The present study includes the effect of (1) degree of cross-linking of the resin, (2) the ratio of resin concentration to alkaloid sulphate concentration, (3) particle size, (4) added sulphuric acid and (5) molecular size, on the equilibria of sulphonic acid cation exchange resins and cinchona alkaloid sulphates.

4.2.b. Experimental :

Resins : The resins were from the same samples which have been used earlier.

Chemicals : Recrystallised sulphates of quinine, quinidine cinchonine and cinchonidine were used from the same stock.

Solutions : Preparation of the aqueous solutions of the alkaloid sulphates and the estimation of the alkaloid sulphate was carried out in the same way as described earlier.

Procedure for equilibrium studies : To study the equilibria of the alkaloid sulphates of the cinchona group, with different resins, weighed amounts of air-dry resins were placed in contact with suitable volumes of an aqueous alkaloid sulphate solution of known concentration, in well stoppered flask with frequent shaking at room temperature ($\sim 30^{\circ}C$).

To study the equilibria of quinine sulphate and quinidine sulphate with resins X 4 and X 8 , in presence of added sulphuric acid , stock solutions of these alkaloid sulphates of known concentrations containing known (different) concentrations of sulphuric acid were prepared. Then weighed amounts of air-dry resins, X 4 and X 8 , were placed in contact with suitable volumes of the prepared stock solution (alkaloid sulphate with added sulphuric acid) 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. Table (4.01) gives the time required for attaining the equilibrium for quinine sulphate and cinchonidine sulphate with different resins, with or without added sulphuric acid.

After sufficiently more time than this, the solutions were analysed for alkaloid sulphate concentration in the equilibrium mixture by taking out a known suitable volume from each flask and diluting to a suitable volume with distilled water. Optical density of this solution was measured at the invarient wave-length (296.5 mμ for quinine-sulphate and 294.5 mμ for cinchonidine sulphate).

The total sulphate in the equilibrium mixture was estimated gravimetrically for each resin (from XI to X 20). The total sulphate thus estimated showed that no change in the sulphate concentration occured when estimated before and after the equilibrium had reached. This indicated that on the whole, apparently, only exchange occured and in no case, the alkaloid sulphate molecules were sorbed as such to a measurable extent.

Preliminary work also indicated that the values of P_{Ro} at 35°C and 45°C did not differ significantly.

4.2.c. Nomenclature :

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

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

3. Volume of alkaloid sulphate solution added = V cc.

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

5. Optical density, at the invariable wave-length, of the initial concentration of alkaloid sulphate solution after suitable dilution. = Di

6. Optical density, at the same wave-length, of the equilibrium mixture solution after the same extent of dilution as in 5. $= D_o$

7. The meq. of alkaloid sulphate in the resin phase per litre of solution at equilibrium

$$= [\bar{A}]_e = [A]_i \cdot (D_i - D_o) / D_i$$

8. The meq. of resin per litre of the solution in the hydrogen form, initially,

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

9. The ratio of the initial concentration (in meq./litre) of the resin to the inital concentration of the alkaloid sulphate

$$= R = [\bar{H}]_i / [A]_i$$

10. The % exchange of alkaloid sulphate at equilibrium

$$= P_A = 100 . [\bar{A}]_e / [A]_i$$

11. The % resin capacity exchanged at equilibrium

$$= P_R = 100 . [\bar{A}]_e / [\bar{H}]_i$$

4.2.d. RESULTS :

Table (4.01.a) gives approximate time within which equilibrium for different resins with aqueous solution of quinine sulphate or cinchonidine sulphate, is attained.

Table (4.01.b.) gives the approximate time within which equilibrium for resins X 4 or X 8 with aqueous solution of quinine sulphate or quinidine sulphate is attained in presence of different concentrations of added sulphuric acid.

Tables (4.02 and 4.03) give the data for equilibrium of aqueous quinine sulphate with resins X 1 to X 20 .

Tables (4.04 to 4.07) give the data for equilibrium of aqueous quinine sulphate with resins IR-120, IR-200 and Amb-15 of different particle diameters.

Tables (4.08 and 4.09) give the data for equilibrium of aqueous cinchonidine sulphate with resins X 1 to X 20 .

Tables (4.10 to 4.12) give the data for the equilibrium of aqueous cinchonidine sulphate with resins IR-120, IR-200 and Amb-15 of different particle diameters.

Tables (4.13 and 4.14) give the data for the equilibrium of aqueous quinine sulphate with resins X 4 and X 8 with added sulphuric acid of different concentrations.

Tables (4.15 and 4.16) give the data for the equilibrium of aqueous quinidine sulphate with resins X 4 and X 8 with added sulphuric acid of different concentrations.

Table (4.17) gives the average values of P_R for the four alkaloid sulphates with resins of different X ; and values of P_R from the plots of P_R against (100 - P_A), (figure 4.1) when extrapolated to (100 - P_A) = zero .

Table(4.18) gives the values of P_R (with added sulphuric acid) for quinine sulphate and quinidine sulphate with X 4 and X 8, from the plots of P_R against (100 - P_A), (figures 4.2 and 4.3) when extrapolated to (100 - P_A) = zero.

Table (4.19) gives the average values of P_R for the four alkaloid sulphateswwith resins IR-120, IR-200 and Amb-15 of different particle diameters.

Table 4.01.a

Approximate time within which equilibrium for different resins with aqueous solution of quinine sulphate or cinchonidine sulphate is attained.

Resin	Time required to reach equilibrium	Resin	Time required to reach equilibrium
X 1	4 days	X 16	6 days
X 2	4 days	X 20	20 days
X 4	5 days	IR- 120	23 days
X 8	5 days	IR- 200	20 days
X 12	6 days	Amb- 15	20 days

Table 4.01.b.

Approximate time within which equilibrium for resins X 4 or X 8 with aqueous solution of quinine sulphate or quinidine sulphate is attained in presence of different concentrations of added sulphuric acid.

H_2SO_4	Time
10^{-3} N	6 days
10^{-2} N	22 days
10^{-1} N	22 days
1 N	22 days

Table 4.02.

Equilibrium of aqueous quinine sulphate with resins X 1 to X 8.

Resin	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
X 1	0.8553	2.118	0.4684	0.4038	22.12	54.76
	1.6890	2.118	0.8900	0.7975	42.03	52.70
	2.5160	2.118	1.2810	1.1880	60.49	50.93
	3.3820	2.118	1.6920	1.5970	79.91	50.05
	4.2210	2.118	2.0480	1.9930	96.74	48.54
X 2	0.8375	2.118	0.4420	0.3955	20.86	52.77
	1.6790	2.118	0.8594	0.7927	40.58	51.19
	2.4940	2.118	1.2470	1.1770	58.86	49.99
	3.3470	2.118	1.6450	1.5810	77.69	49.16
	4.1770	2.118	2.0140	1.9720	95.10	48.21
X 4	0.6968	2.066	0.3417	0.3372	16.54	49.04
	1.3810	2.066	0.6895	0.6683	33.36	49.90
	2.0720	2.066	1.0210	1.0020	49.41	49.26
	2.7700	2.066	1.3770	1.3410	66.64	49.72
	3.4390	2.066	1.6890	1.6640	81.70	49.09
X 8	0.9845	2.066	0.3950	0.4764	19.12	40.13
	1.4610	2.066	0.5975	0.7071	28.92	40.91
	2.0040	2.066	0.8041	0.9696	38.92	40.12
	4.0070	2.066	1.5640	1.9390	75.68	39.02

Table 44.03

Equilibrium of aqueous quinine sulphate with resins X 12, X 16 and X 20

Resin	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
X 12	1.438	2.118	0.3666	0.6792	17.31	25.49
	2.869	2.118	0.7209	1.355	34.04	25.13
	4.298	2.118	1.100	2.030	51.93	25.59
	5.727	2.118	1.479	2.704	69.81	25.81
	7.164	2.118	1.840	3.384	86.84	25.66
X 16	2.150	2.118	0.3829	1.015	18.08	17.91
	4.304	2.118	0.7800	2.032	36.83	18.23
	6.445	2.118	1.175	3.043	55.49	18.33
	8.644	2.118	1.591	4.082	75.11	18.50
	10.760	2.118	1.951	5.085	92.12	18.22
X 20	6.101	2.018	0.3299	3.024	16.35	5.406
	8.143	2.018	0.4835	4.035	23.96	5.937
	11.190	2.018	0.7171	5.546	35.54	6.407

Table 4.04

Equilibrium of aqueous quinine sulphate with resin IR-120 of different particle diameters.

a (mm.)	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
0.84	2.666	2.018	1.086	1.321	53.81	40.74
	3.838	2.018	1.562	1.902	77.38	40.68
	5.036	2.018	1.987	2.496	98.49	39.47
0.58	2.622	2.018	1.064	1.299	52.70	40.56
	3.813	2.018	1.540	1.889	76.35	40.41
	5.003	2.018	1.975	2.479	97.88	39.48
0.23	2.695	2.018	1.104	1.336	54.73	40.99
	3.943	2.018	1.658	1.954	82.13	42.04
	5.162	2.018	2.010	2.558	99.61	38.94

Table 4.05

Equilibrium of aqueous quinine sulphate with resin IR-200 of different particle diameters.

a (mm.)	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
1.13	2.822	2.018	0.8666	1.398	42.94	30.70
	4.184	2.018	1.264	2.073	62.65	30.21
	5.584	2.018	1.651	2.767	81.83	29.57
0.84	2.754	2.018	0.8584	1.365	42.54	31.17
	4.114	2.018	1.246	2.039	61.73	30.28
	5.463	2.018	1.621	2.707	80.32	29.67
0.58	2.773	2.018	0.8626	1.374	42.75	31.11
	4.181	2.018	1.264	2.072	62.65	30.24
	5.524	2.018	1.645	2.737	81.53	29.79

Table 4.06

Equilibrium of aqueous quinine sulphate with resin IR-200 of different particle diameters.

a (mm.)	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
0.37	2.872	2.018	0.9035	1.423	44.77	31.47
	4.287	2.018	1.315	2.174	65.18	30.68
	5.703	2.018	1.704	2.826	84.47	29.88
0.23	2.837	2.018	0.8974	1.406	44.47	31.63
	4.256	2.018	1.315	2.109	65.18	30.90
	5.675	2.018	1.717	2.813	85.07	30.25

Table 4.07

Equilibrium of aqueous quinine sulphate with Amb-15 of different particle diameters.

a (mm.)	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
1.13	2.558	2.104	0.8390	1.215	39.88	32.81
	3.414	2.104	1.0860	1.623	51.63	31.82
	4.248	2.104	1.3460	2.019	63.96	31.67
	5.093	2.104	1.6010	2.421	76.10	31.44
0.84	2.567	2.104	0.8351	1.220	39.69	32.53
	3.434	2.104	1.0900	1.632	51.83	31.77
	4.281	2.104	1.3540	2.034	64.34	31.62
	5.166	2.104	1.6210	2.466	77.07	31.38
0.58	2.550	2.104	0.8351	1.212	39.69	32.75
	3.383	2.104	1.0820	1.608	51.43	32.00
	4.212	2.104	1.3340	2.002	63.39	31.66
	5.076	2.104	1.6050	2.413	76.30	31.62
0.37	2.649	2.104	0.8592	1.259	40.84	32.44
	3.519	2.104	1.1190	1.673	53.18	31.80
	4.401	2.104	1.3900	2.092	66.09	31.59
	5.289	2.104	1.6650	2.514	79.18	31.49

Table 4.08

Equilibrium of aqueous cinchonidine sulphate with reins X 1 to X 8.

Resin	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
X 1	1.343	2.182	0.7889	0.6153	36.15	58.75
	1.674	2.182	0.9393	0.7674	43.04	56.10
	2.306	2.182	1.2090	1.0570	55.39	52.41
	2.936	2.182	1.4930	1.3450	68.41	50.85
	3.477	2.182	1.7380	1.5930	79.64	49.97
X 2	1.263	2.182	0.7427	0.5785	34.03	58.83
	1.576	2.182	0.8884	0.7221	40.70	56.37
	2.168	2.182	1.1360	0.9935	52.05	52.38
	2.751	2.182	1.4100	1.2600	64.63	51.28
	3.271	2.182	1.6500	1.4980	75.63	50.47
X 4	1.544	2.182	0.8399	0.7074	38.49	54.41
	2.114	2.182	1.1210	0.9690	51.39	53.03
	2.706	2.182	1.3960	1.2400	63.96	51.58
	3.256	2.182	1.6550	1.4920	75.86	50.84
X 8	1.491	2.182	0.6723	0.6832	30.81	45.09
	2.060	2.182	0.9346	0.9441	42.83	45.36
	2.614	2.182	1.1870	1.1980	54.39	45.40
	3.162	2.182	1.4240	1.4490	65.28	45.05
	3.727	2.182	1.6740	1.7080	76.74	44.93

Table 4.09

Equilibrium of aqueous cinchonidine sulphate with resins X 12 to X 20.

Resin	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
X 12	3.002	2.182	0.8569	1.376	39.26	28.54
	3.753	2.182	1.0950	1.720	50.17	29.17
	4.490	2.182	1.3150	2.058	60.29	29.29
	5.277	2.182	1.5460	2.418	70.84	29.29
	5.981	2.182	1.7720	2.741	81.19	29.62
X 16	3.572	2.182	0.7839	1.637	35.92	21.95
	4.458	2.182	0.9926	2.043	45.48	22.27
	5.328	2.182	1.1940	2.442	54.73	22.42
	6.256	2.182	1.4080	2.867	64.51	22.50
	7.103	2.182	1.6020	3.255	73.40	22.55
X 20	11.10	2.182	0.7766	5.089	35.59	6.993
	13.71	2.182	1.0350	6.281	47.49	7.561
	16.66	2.182	1.3380	7.637	61.30	8.026

Table 4.10

Equilibrium of aqueous cinchonidine sulphate with resin IR-120 of different particle diameters.

a (mm.)	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
0.58	1.910	2.182	0.8058	0.8752	36.93	42.19
	2.751	2.182	1.1740	1.2610	53.83	42.70
	3.607	2.182	1.5660	1.6530	71.74	43.41
	4.488	2.182	1.9320	2.0570	88.53	43.04
0.37	1.958	2.182	0.8351	0.8974	38.26	42.64
	2.809	2.182	1.2160	1.2870	55.72	43.28
	3.683	2.182	1.5820	1.6880	72.51	42.96
	4.567	2.182	1.983	2.0930	90.86	43.41

Table 4.11

Equilibrium of aqueous cinchonidine sulphate with resin IR-200 of different particle diameters.

a (mm.)	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
0.58	2.622	2.182	0.8786	1.201	40.26	33.52
	3.449	2.182	1.1410	1.581	52.27	33.07
	4.305	2.182	1.4100	1.972	64.63	32.76
	5.249	2.182	1.6960	2.405	77.75	32.32
0.37	2.734	2.182	0.9319	1.253	42.71	34.09
	3.624	2.182	1.2130	1.661	55.62	33.49
	4.519	2.182	1.5030	2.070	68.85	33.25
	5.424	2.182	1.7720	2.485	81.19	32.67

Table 4.12

Equilibrium of aqueous cinchonidine sulphate with resin Amb-15 of different particle diameters.

a (mm.)	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
1.13	2.557	2.154	0.9128	1.187	42.38	35.71
	3.423	2.154	1.1990	1.590	55.68	35.03
	4.251	2.154	1.4630	1.973	67.95	34.43
	5.113	2.154	1.7400	2.374	80.79	34.03
0.84	2.565	2.154	0.9226	1.191	42.84	35.96
	3.427	2.154	1.2010	1.592	55.80	35.06
	4.274	2.154	1.4730	1.985	68.41	34.47
	5.141	2.154	1.7570	2.387	81.58	34.18
0.58	2.550	2.154	0.9251	1.184	42.95	36.28
	3.372	2.154	1.1970	1.566	55.56	35.49
	4.206	2.154	1.4630	1.953	67.95	34.80
	5.061	2.154	1.7330	2.351	80.44	34.23
0.37	2.636	2.154	0.9570	1.224	44.43	36.29
	3.522	2.154	1.2440	1.635	57.73	35.30
	4.395	2.154	1.5270	2.041	70.91	34.74
	5.278	2.154	1.8130	2.451	84.20	34.36

Table 4.13

Equilibrium of resin X 4 with aqueous quinine sulphate with added sulphuric acid of different concentrations.

Concentration of added H_2SO_4	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
$1.041\ N.10^{-3}$	0.7893	1.041	0.3907	0.7582	37.53	49.50
	1.1730	1.041	0.5762	1.1270	55.35	49.10
	1.5680	1.041	0.7649	1.5060	73.47	48.78
$9.774\ N.10^{-3}$	0.7865	1.041	0.3796	0.7554	36.47	48.27
	1.1780	1.041	0.5674	1.1310	54.50	48.18
	1.5640	1.041	0.7553	1.5030	72.54	48.28
	1.9510	1.041	0.9350	1.8740	89.80	47.92
$9.774\ N.10^{-2}$	1.1760	1.041	0.5327	1.1300	51.17	45.29
	1.5580	1.041	0.6900	1.4960	66.27	44.28
	1.9470	1.041	0.8450	1.8710	81.17	43.39
$9.774\ N.10^{-1}$	0.7896	1.041	0.2347	0.7584	22.55	29.73
	1.1740	1.041	0.3388	1.1280	32.55	28.85
	1.5710	1.041	0.4368	1.5100	41.96	27.80
	1.9420	1.041	0.5225	1.8650	50.19	26.90

Table 4.14

Equilibrium of resin X 8 with aqueous quinine sulphate with added sulphuric acid of different concentrations.

Concentration of added H_2SO_4	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
1.083 N.10^{-1}	0.3779	1.052	0.1515	0.3592	14.10	40.07
	0.7668	1.052	0.3049	0.7290	28.98	39.76
	1.1360	1.052	0.4483	1.0790	42.62	39.49
	1.5040	1.052	0.5878	1.4300	55.88	39.06
	1.8770	1.052	0.7213	1.7840	68.57	38.42
1.083 N.	0.3727	1.052	0.1093	0.3543	10.40	29.35
	1.1150	1.052	0.3142	1.0600	29.86	28.17
	1.4980	1.052	0.4136	1.4240	39.31	27.60
	1.8460	1.052	0.4991	1.7550	47.44	27.04
	2.2500	1.052	0.5946	2.1390	56.52	26.42

Table 4.15

Equilibrium of resin X 4 with aqueous quinidine sulphate with added sulphuric acid of different concentrations.

Concentration of added H_2SO_4	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
$1.0\ N.10^{-3}$	0.3937	1.000	0.1898	0.3937	18.98	48.21
	0.7874	1.000	0.3773	0.7874	37.73	47.92
	1.1680	1.000	0.5555	1.1680	55.55	47.55
$9.774\ N.10^{-3}$	0.7877	1.000	0.3773	0.7877	37.73	47.89
	1.1760	1.000	0.5589	1.1760	55.89	47.54
	1.5640	1.000	0.7381	1.5640	73.81	47.20
	1.9540	1.000	0.9126	1.9540	91.26	46.71
$9.774\ N.10^{-2}$	0.3916	1.000	0.1816	0.3916	18.16	46.36
	0.7896	1.000	0.3584	0.7896	35.84	45.39
	1.1790	1.000	0.5330	1.1790	53.30	45.23
	1.5640	1.000	0.6863	1.5640	68.63	43.87
	1.9440	1.000	0.8326	1.9440	83.26	42.83
$9.774\ N.10^{-1}$	1.1630	1.000	0.3466	1.1630	34.66	29.79
	1.5560	1.000	0.4410	1.5560	44.10	28.34
	1.9420	1.000	0.5236	1.9420	52.36	26.96
	2.3460	1.000	0.6060	2.3460	60.60	25.83

Table 4.16

Equilibrium of resin X 8 with aqueous quinidine sulphate with added sulphuric acid of different concentrations.

Concentration of added H_2SO_4	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
1.083 N.10^{-1}	0.7602	1.000	0.2914	0.7602	29.14	38.32
	1.1370	1.000	0.4358	1.1370	43.58	38.33
	1.5130	1.000	0.5757	1.5130	57.57	38.06
	1.8830	1.000	0.7109	1.8830	71.09	37.75
1.083 N.	0.3757	1.000	0.1092	0.3757	10.92	29.09
	0.7578	1.000	0.2163	0.7578	21.63	28.54
	1.1080	1.000	0.3093	1.1080	30.93	27.92
	1.4960	1.000	0.4139	1.4960	41.39	27.68
	1.8730	1.000	0.5070	1.8730	50.70	27.08
	2.2340	1.000	0.5837	2.2340	58.37	26.13

4.2.e. Discussion :

Effect of P_A and X on P_R

The synthetic ion exchange resins consist of a hydrocarbon network to which ionogenic groups are attached and the surplus electric charge is balanced by mobile counter ions. The hydrocarbon network is hydrophobic but the ionogenic groups are hydrophilic. Hence, when the resin particle is placed in water, it sorbs water and swells to a limited extent. The amount of water sorbed and the extent of swelling decrease with increase in X.

When the ion exchange particle is placed in the solution of an electrolyte, ion exchange occurs in equivalent amounts and a state of equilibrium is reached. The selectivity coefficient calculated according to law of Mass Action is either fairly constant or varies within narrow limits for simple monovalent cations. The selectivity coefficients for sodium and potassium ions with resins in hydrogen form in sulphate solutions have been given earlier.

When similar calculations are carried out for exchange in solutions of two typical major cinchona alkaloid sulphates, quinine sulphate and cinchonidine sulphate (as $Q_2.H_2SO_4, nH_2O$, where Q is the alkaloid base) with resins in the hydrogen form, the selectivity coefficients were found to vary widely. However the calculated values of P_R were either fairly constant or varied within narrow limits when R or P_A was varied.

This is a significant difference in the exchange behaviour of simple alkali cations and these organic cations.

To explain the results, the plausible assumption is made that the uptake of such organic cations or base from solution by the resin takes place by two mechanisms : exchange mechanism and (molecular) sorption mechanism.(10-29)

Quinine or cinchonidine is a weak diacidic organic base with second acid dissociation constant smaller than the first. The exchange for the cation QH^+ where Q is the organic diacidic base, is postulated as :

$$(1) \quad H_2R + QH^+ \dashrightarrow RQH_2 + H^+$$

where H_2R represents the cation exchange resin in the hydrogen form. (it does not imply that R is divalent but is written as such only for clarity and convenience). The reverse reaction

$$(2) \quad RQH_2 + H^+ \dashrightarrow H_2R + QH^+$$

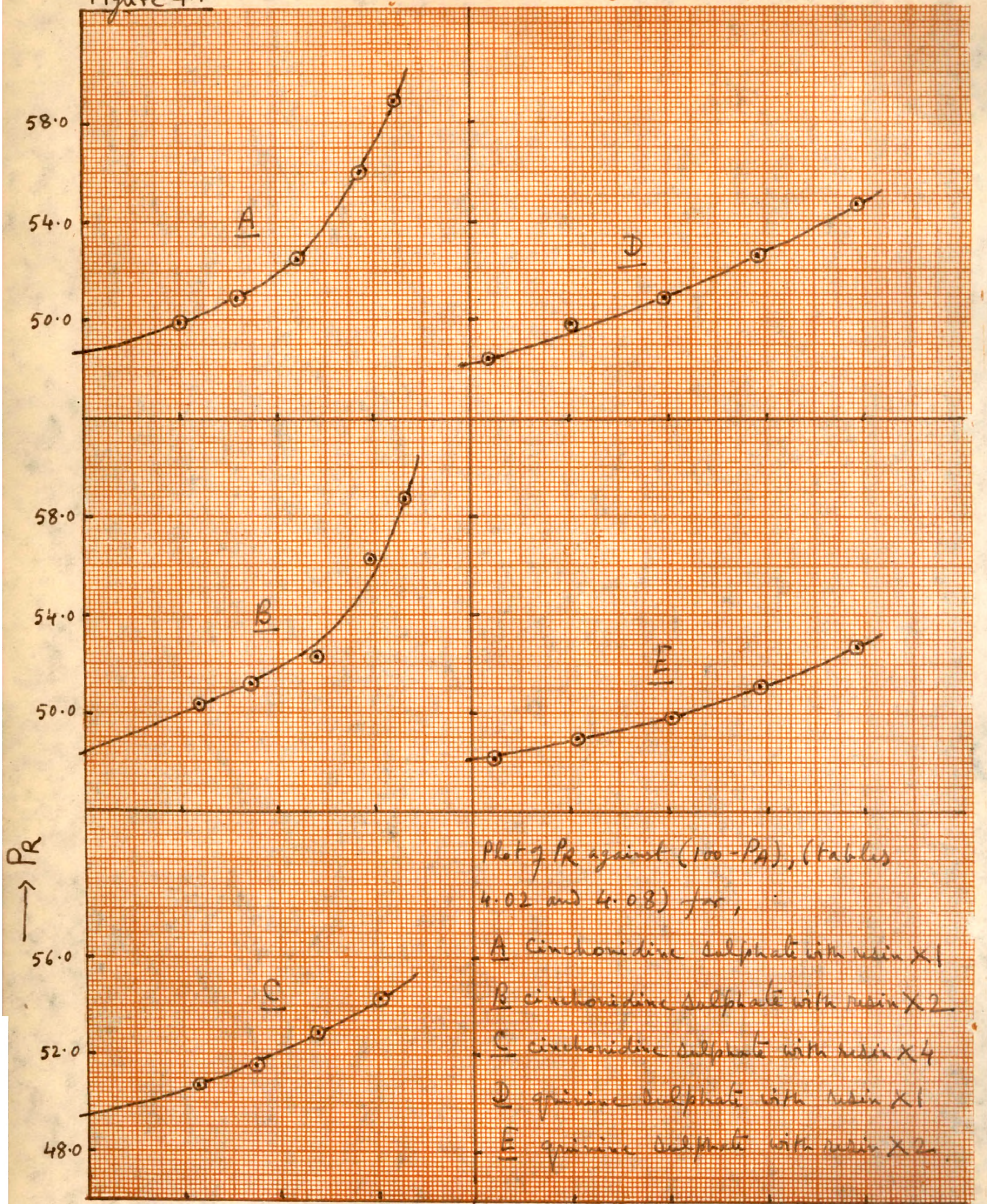
is considered to be negligible in the absence of added H^+ ions.

The sorption mechanism is postulated as

$$(3) \quad (a) \quad QH^+ + H_2O \rightleftharpoons Q + H_3O^+$$

$$(b) \quad \text{Resin} + Q \longrightarrow \text{Resin.Q.}$$

Figure 4.1



Plot of PR against (100 - PA), (tables 4·02 and 4·08) for,

A Cinchonidine sulphate with resin X 1

B cinchonidine sulphate with resin X 2

C cinchonidine sulphate with resin X 4

D quinine sulphate with resin X 1

E quinine sulphate with resin X 2

Table 4.17

Average values of P_R , (i.e. P_{Ro}) for the four alkaloid-sulphates with resins of different X and values of P_R (i.e. P_{Ro}) from the plots of P_R against (100 - P_A) , figure (4.1) , when extrapolated to (100 - P_A) = zero , marked with dots.

Resin	Quinine sulphate	Quinidine* sulphate	Cinchonine* sulphate	Cinchonidine Sulphate
X 1	48.3●	47.2●	48.3●	48.7●
X 2	48.2●	47.0●	48.8●	48.4●
X 4	49.4	47.8	49.5●	49.5●
X 8	40.0	39.5	44.6	45.2
X 12	25.5	24.8	27.4	29.2
X 16	18.2	17.4	21.6	22.3
X 20	5.9	5.7	7.7	7.5

* Data taken from the unpublished work of Shri R. S. Shah of this laboratory.

Figure 4.2

Plot of P_R against $(100-P_A)$ for resin X4 (tables 4.13 and 4.15); **A** quinine sulphate, **B** quinidine sulphate, with N/10 H_2SO_4, **C** quinine sulphate, **D** quinidine sulphate, with 1N H_2SO_4.

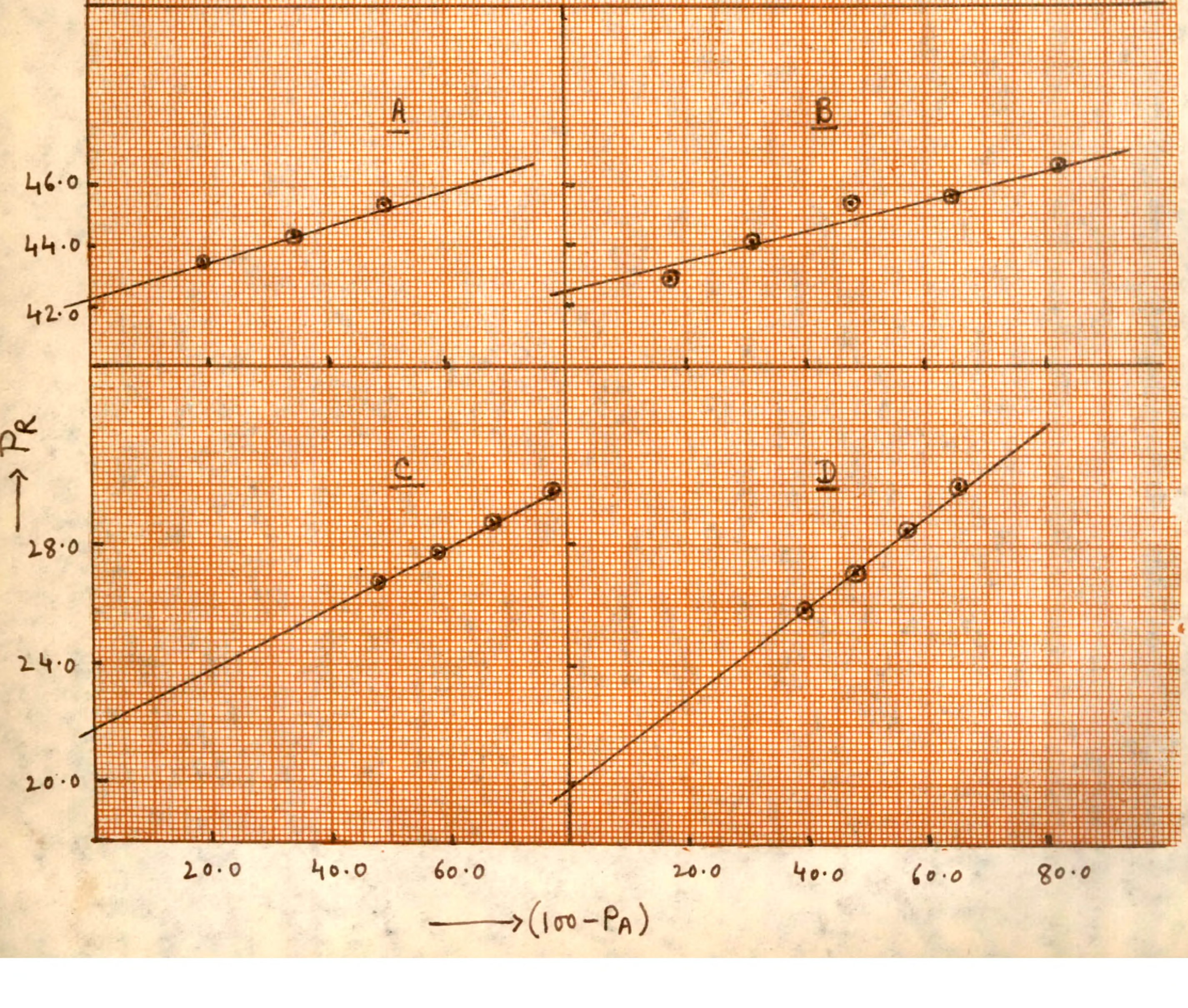


Figure 4.3

Plot of P_R against $(100 - P_A)$ for resin X8 (tables 4.14 and 4.16),
A quinine sulphate; B quinidine sulphate, with 1N H_2SO_4,
C quinine sulphate; D quinidine sulphate, with N/10 H_2SO_4.

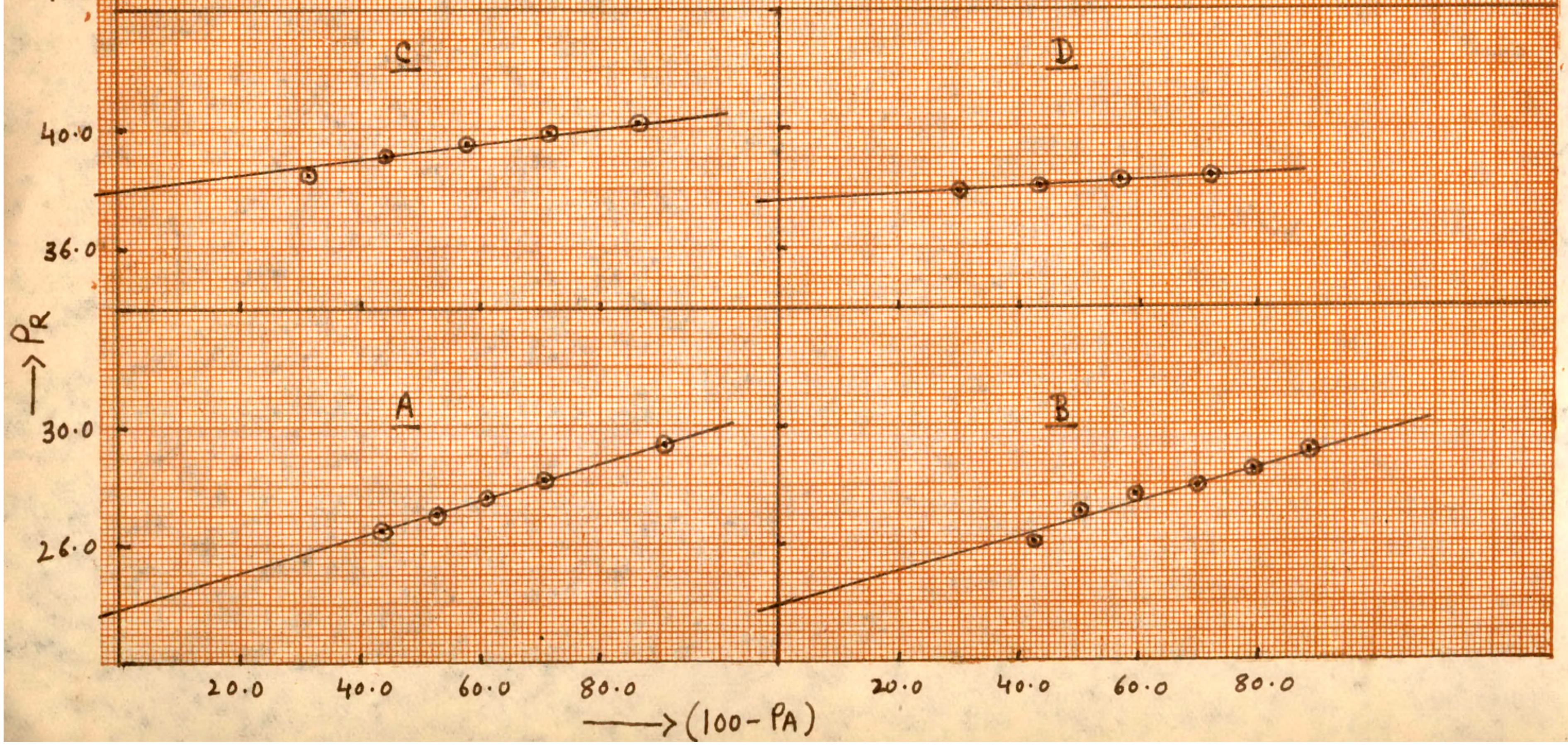


Table 4.18

Values of P_R (with added sulphuric acid) from the plots of P_R against (100 - P_A) , figures (4.2 and 4.3) , when extrapolated to (100 - P_A = zero)

Resin X 4				Resin X 8		
$[H_2SO_4]$	Values of P_R for quinine-sulphate	$[H_2SO_4]$	Values of P_R for quinidine sulphate	$[H_2SO_4]$	Values of P_R for quinine sulphate	Values of P_R for quinidine sulphate
9.774 N.10^{-1}	22.0	9.774 N.10^{-1}	20.0	1.083 N	23.8	24.0
9.774 N.10^{-2}	42.2	9.774 N.10^{-2}	42.4	1.083 N.10^{-1}	37.9	37.5
9.774 N.10^{-3}	48.2	9.774 N.10^{-3}	47.3	-	-	-
1.041 N.10^{-3}	49.1	1.000 N.10^{-3}	47.6	-	-	-
Zero	49.4	zero	47.8	zero	40.0	39.5

Table 4.19

Average values of P_R for the four alkaloid sulphates with resins IR-120, IR-200 and Amb-15 of different particle diameters.

Resin	a (mm.)	Quinine sulphate	Quinidine sulphate *	Cinchonine sulphate *	Cinchonidine sulphate
IR-120	0.23	40.5	-	-	-
	0.37	-	36.6	45.3	43.1
	0.58	40.1	-	45.5	42.8
	0.84	40.3	-	-	-
Average value of P_R		40.3	36.6	45.4	43.0
IR-200	0.23	30.9	-	-	-
	0.37	30.7	29.6	33.9	33.4
	0.58	30.4	29.8	32.9	32.9
	0.84	30.4	-	-	-
	1.13	30.2	-	-	-
Average value of P_R		30.5	29.7	33.4	33.1
Amb-15	0.37	31.8	31.1	34.2	35.2
	0.58	32.0	31.5	34.1	35.2
	0.84	31.8	-	34.0	34.9
	1.13	31.9	-	34.2	34.8
Average value of P_R		31.9	31.3	34.1	35.0

* Data of these columns are taken from the unpublished work of Shri R. S. Shah of this laboratory.

The uptake of QH^+ by sorption mechanism by the resin is ruled out because of the fact that the sulphate ion concentration, in the solution, initially and after equilibrium, was practically unchanged, as studied in preliminary work.

Sorption of solute on the resin is subject to two types of interactions, the London interactions between the solute molecules and the resin matrix, and the dipole-dipole interactions of the polar solvent molecules between one another and the polar groups of the solute.

The sorption of the solute is known to decrease with decrease in the equilibrium concentration of the solute in the solution and increase in X of the resin.

In cases where only the exchange mechanism is operating in the entrity, the value of P_R is expected to be 50 . A decrease in this value may be considered to be due to (a) steric hindrance and (b) non-accessibility of exchange sites due to reduced pore diameter.

From an observed value of P_R ,the contribution due to exchange mechanism can be calculated by plotting P_R against ($100 - P_A$) and obtaining the values of P_R at ($100 - P_A$) equal to zero, by extrapolating the plot, figures (4.1 to 4.3) and tables (4.17 to 4.19). This value of P_R , denoted hereafter by P_{Ro} , represents the contribution to the observed value of P_R by exchange mechanism. It should be justifiable to assume that at, (100 - P_A) equal to zero, the contribution to the observed value of P_R due to sorption mechanism is zero, since the concentration of the solute or cations in external solution at equilibrium is reduced to zero.

The increase in the value of P_R over P_{Ro}, that is, ($P_R - P_{Ro}$) is considered to be the contribution to the value of P_R by sorption mechanism.

On the basis of the above, the experimental values of P_R may now be discussed, table (4.17). It is observed that for resin X 1 , the values of P_{Ro} for quinine sulphate and cinchonidine sulphate, are practically same and lower by a small, but measurable amount, from 50 ; since the resin is highly swollen and hence highly porous, as the degree of cross-linking is low, this decrease from 50 , in the value of P_{Ro} is to be attributed to the steric non-accessibility of some exchange sites. The difference $P_R - P_{Ro}$ is to be attributed to the contribution of sorption mechanism and this increases with increase in the equilibrium concentration of the organic cations (and hence base) in the external solution or with decrease in P_A and R .

For resin X 2 , comments similar to those for X 1 are valid. The value of P_{Ro} is practically same as for X 1. The difference ($P_R - P_{Ro}$) is the contribution due to sorption mechanism and is less than that for resin X 1, this decrease being due to the increase in X .

For the next higher cross-linked resin, X 4, the value of P_{Ro} is again some what less than 50. Due to increased value of X, the contribution in P_R by sorption mechanism is practically negligible for quinine sulphate solution and to a measurable but lesser extent, than that for resin X 2 , for cinchonidine sulphate solution. For quinine sulphate solution, the value of P_R is practically independent of P_A and the average value is taken as the value of P_{Ro} , the contribution due to exchange mechanism.

For these resins i.e. X 1, X 2 and X 4, the swelling is quite large so that the pore diameter could not be considered to be responsible for the samll decrease in the value of P_{Ro} from 50 . This small decrease is attributed to the steric non-accessibility of a few of the exchange sites.

For the next higher cross-linked resin, X 8, the values of P_R for both quinine sulphate and cinchonidine sulphate solution, are practically independent of P_A or R . The average value of P_R , is taken as the value of P_{Ro} and represents the contribution due to the exchange mechanism. This value of P_{Ro} is less than 50 ; the difference is more for quinine sulphate than that for cinchonidine sulphate. This decrease is to be attributed to the non-accessibility of exchange sites due to both, steric effect and reduced pore size, because of higher X . The reason for the higher value of P_{Ro} for cinchonidine sulphate than that for quinine sulphate is attributed to the smaller molecular size of cinchonidine than that of quinine.

For resins of higher degree of cross-linking than X 8 i.e. X 12, X 16 and X 20, essentially similar comments hold. The values of P_R are essentially independent of P_A or R and the average value is taken as P_{Ro} . This is again higher for cinchonidine sulphate than that for quinine-sulphate for each resin. The value of P_{Ro} decreased in both cases as the degree of cross-linking X , increased, the reasons being same as given for X 8.

It is interesting to note that the decrease in the value of P_{Ro} when X increase from 8 to 12 and again from 16 to 20 is relatively, significantly more than the decrease in P_{Ro} for other increases in the value of X . This should be related to the shape and size of the exchanging cations and hence their ability to diffuse into the resin as the pore diameter decreases with increasing X .

Effect of the particle size a on P_R :

Tables (4.04 to 4.07 and 4.10 to 4.12) give the results obtained for resins IR-120, IR-200 and Amb-15. It is observed that the values of P_R are practically independent of P_A . The average values of P_R are given as P_{Ro} in table (4.19). These values are practically independent of the particle size, a,. Resin IR-120 is almost (but not exactly) same as X 8 and the discussion given for X 8 applies to IR-120 also. The resins IR-120, IR-200 and Amb-15 are considered to be prepared with same X but IR-200 and Amb-15 are considerably more porous than IR-120. This means that pore diameters for IR-200 and Amb-15 are considerably wider than those for IR-120. However the values of P_{Ro} for IR-200 and Amb-15 are substantially less than those for IR-120. This should imply that a larger number of exchange sites in IR-200 and Amb-15 are sterically non-accessicible than those in IR-120. Hence porosity alone is not enough to effect higher possible exchange ; it is also essential that steric effects should not be significantly operative.

Effect of added sulphuric acid on P_R :

Tables (4.13 to 4.16) give the results for P_R for quinine sulphate and quinidine sulphate with resins X 4 and X 8 in the presence of added sulphuric acid, the concentration of added acid being from $\sim$ 1 N to 10^{-3} N. It is observed that the value of P_R decreases as the value of P_A increases when the concentration of the added acid is relatively high. The plots of P_R against (100 - P_A) are linear and by extrapolation, the values of P_{Ro} are obtained, figure (4.2 and 4.3). When the concentration of the added acid is relatively low, the value of P_R is practically independent of P_A.

Table (4.18) gives the values of P_{Ro} for quinine-sulphate and quinidine sulphate with resin X 4 and X 8 at various concentrations of added sulphuric acid. It is observed that when the concentration of added acid is increased, the value of P_{Ro} is decreased. This decrease is small when the concentration of added acid is below N/100 for X 4 and below N/10 for X 8 . It is also observed that when the concentration of added acid is $\sim$ 1 N, the value of P_{Ro} for X 4 is some-what lower than that for X 8 ; for lower concentrations of added acid the values of P_{Ro} for X 8 are lower than those for X 4 .

The marked reduction in the value of P_{Ro} in the presence of high concentration of added sulphuric acid is due to (a) the regenerative effect of the H^+ ions when present in considerably large excess and the (b) deswelling of the resin particles. This regenerative effect and the deswelling effect is decreased as the concentration of the added acid is reduced and hence, then the value of P_{Ro} increases .

When the added acid concentration is high but constant, the value of P_R decreases as P_A increases and the plot of P_R against (100 - P_A) is linear. The decrease in value of P_R with (100 - P_A) cannot be considered to be due to the sorption of base Q , since such effect is not observed in the absence of added acid. This reduction in the value of P_R may be considered to be due to the sorption of strong electrolytes from external solution (30-49), when present in high concentration. Since sulphuric acid is present in high concentration, some H^+ ions and sulphate ions afe sorbed in accordance with Donnan mambrane effect. As a consequence of this, some QH^+ ions are also sorbed to comply with Donnan membrane equilibrium requirement. This sorption of QH^+ ions will increase with the increase in the equilibrium concentration of QH^+ ions in the external solution . Hence the value of P_R decreases as the value of (100 - P_A) decreases. When the concentration of added acid becomes low, the electrolyte sorption due to Donnan membrane effect becomes negligible and the value of P_R becomes practically independent of P_A under such conditions.

These observations are of interest in relation to the practical aspects of the recovery of alkaloids by ion exchange process, using aqueous sulphuric acid as extraction solvent with alkaloid raw material.

References :

1. Kressman, T.R.E. and Kitchener, J.A., J.Chem.Soc., 1208 (1949).
2. Richardson, R.W., J.Chem.Soc., 910 (1951).
3. Kressman, T.R.E., J.Phys.Chem., 56, 118 (1952).
4. Hale, D.K., Packham, D.I. and Pepper, K.W., J.Chem.Soc., 844 (1953).
5. Richter, G., Z.Physik. Chem., 12, 247 (1957).
6. Richter, G. and Woermann, D., Z.Physik.Chem., 15, 454 (1958).
7. Yakhontova, L.F., Savitskaya, E.M. and Bruns, B.P., Otdel Khim. Nauk, 1959, 3-20 ; Chem.Abst., 54, 19084 h (1960).
8. Tamamushi, B. and Tamaki, K., Trans. Faraday Soc., 55, 1013 (1959).
9. Millar, J.R., Smith, D.G. and Marr, W.E., J.Chem.Soc., 1789 (1962).
10. Anderson, R.E., Hanson, R.D., Ind.Eng.Chem., 47, 71 (1955).
11. Bafna, S.L., Govindan, K.P., Ibid., 48, 310 (1956).
12. Cesarano, C., Lepscky, C., J.Inorg, and Nucl. Chem. 14, 276 (1960).
13. Cerrai, E., Godoa, F., Nature 183, 1528 (1959).
14. Chasanov, M.G., Kunin,R., Mc Gervey, F.X., Ind.Eng.Chem. 48, 305 (1956).
15. Clark, I.T., Anal. Chem. 30, 1676 (1958).
16. Govindan, K.P., Bafna, S.L., J.Sci.Ind.Rese. (India) , 16 B , 321 (1957).

17. Gregor, H.P., Collins, F.C., Pope, M., J.Colloid Sci. 6, 304 (1951).

18. Griffin, R.P., Dranoff, J.J., J.Chem.Soc., 1963, 283 .

19. Radzitzky P. de., Ind.Chem.belge, Suppl. 1, 156 (1959).

20. Reichenberg, D., Wall, W.F., J.Chem.Soc., 1956, 3364.

21. Samuelson,O., Dechema-Monograph, 26, 219 (1956).

22. Sargent, R.N., Graham, D.L., I and EC Process Design and Develop. 1, 56 (1962).

23. Simpson,D.W., Bauman,W.C., Ind.Eng.Chem., 46, 1958 (1954).

24. Tamamushi,B., Tamki,K., Trans.Faraday Soc. 55, 1013 (1959).

25. Turse,R., Gerdes,W.H., Rieman,W., Z.Physik Chem. 33, 219 (1962) .

26. Vassiliou,B., Dranoff,J., Am.Inst.Chem.Engrs. J. 8, 248 (1962).

27. Wasmer, H.B., J.Polymer Sci. 36, 461 (1959) .

28. Wheaton, R.M., Bauman,W.C., Ind.Eng.Chem. 45, 2281 (1953).

29. Wheaton, R.M., Bauman,W.C., Ann.N.Y. Acad.Sci. 57, 159 (1953).

30. Juda,W., Rosenberg, N.W., Marinsky, J.A. and Kasper, A.A., J.Am.Chem.Soc., 74, 3736 (1952).

31. Pepper,K.W., Reichenberg,D. and Hale,D.K., J.Chem.Soc., 3129 (1952) .

32. Argersinger,W.J. and Davidson, A.W., J.Phys.Chem., 56, 92 (1952).

33. Gregor, H.P. and Gottlieb, M.M., J.Am.Chem.Soc., 75, 3539 (1953).

34. Kraus,K.A. and Moore, G.E., J.Am. Chem.Soc., 75, 1457 (1953).

35. Gottlieb, M.M. and Gregor, H.P., J.Am.Chem.Soc., 76, 4639 (1954).

36. Thomos,B., Chu,P.N. and Diamond, R.M., J.Phys.Chem., 63, 2021 (1959).

37. Freeman, D.H., J.Phys.Chem., 64, 1048 (1960).

38. Tye, F.L., J.Chem.Soc., 4784 (1961).

39. Shone, M.G.T., Trans.Faraday Soc., 58, 805 (1962).

40. Dennis,L.M., Brit.Pat., 109,709 (1916) ; Swiss Pat., 75,550 (1918) ; U.S.Pat., 1,228,414 (1917) ; Can.Pat., 177,140 ; U.S.Pat., 1,332,203 (1920).

41. Othmer,D.F., Jacobs,J.J. and Buschmann, W.J., Ind.Eng.Chem., 35, 326 (1943).

42. Ito,A. and Migana,H., Chem.Abst., 55, 8179 d (1961).

43. Glogan,R.C., Halvorson,D.D. and Sloan,W.J., Ind.Eng.Chem., 53, 275 (1961).

44. Anderson,R.E., Bauman,W.C. and Harrington,D.F., Ind.Eng. Chem., 47, 1620 (1955).

45. Vogel,A.I., Practical Organic Chemistry (London), 1948, p. 531.

46. Witt,O.N., Chem.Abst., 9, 2094 (1915).

47. Bafna,S.L. and Govindan,K.P., Ind.Eng.Chem., 48, 310 (1956).

48. Litloff,D., Chem.Abst., 23, 3404 (1929).

49. Daglish,C., J.Am.Chem.Soc., 72, 4859 (1950).