Ion-Exchange Resins on Cinchona Alkaloids IV: Effect of Resin Particle Size on Equilibrium Exchange and Column Studies

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Abstract ☐ The effect of particle size of styrene divinylbenzene copolymer-based sulfonic acid cation-exchange resins on equilibrium exchange and column studies for cinchona alkaloid sulfates was studied.

Keyphrases ☐ Ion-exchange resins–cinchona alkaloids—resin particle-size effect on equilibrium exchange, column studies ☐ Cinchona alkaloids on ion-exchange resins—resin particle-size effect on equilibrium exchange, column studies ☐ Particle size, styrene divinylbenzene copolymer-based sulfonic acid cation-exchange resins—effect on equilibrium exchange, column studies

Earlier (1–3) the equilibrium exchange and rates of exchange of cinchona alkaloid sulfates with styrene divinylbenzene copolymer-based sulfonic acid cation-exchange resins were studied; this article discusses the effect of resin particle size on equilibrium exchange and column studies.

EXPERIMENTAL

Resins (4–5)—The following were used: styrene divinylbenzene copolymer-based sulfonic acid cation-exchange resins of relative degree of crosslinking, X (percent nominal divinylbenzene content), as 2 and referred to as X2[1] of 200/400 mesh; of X as 4 and referred to as X4[2] of 20/50, 50/100, 100/200, and 200/400 mesh; of X as 8 and referred to as X8[3] of 200/400 mesh; of X as 12 and referred to as X12[4] of 200/400 mesh; and the expanded structure resin (X is presumably about 20), referred to as IR-200,[5] of 20/60 mesh. The resins were conditioned and regenerated into hydrogen form, and moisture content and capacity were estimated (4–6) (Table I). The ammonium form of the resins was prepared by treating the hydrogen form of the resins with an excess of aqueous ammonia (2).
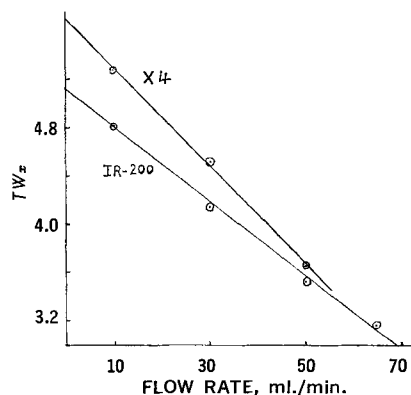

Figure 1—*Plot of* TW_x *against flow rate for resins X4 and IR-200.*

[1] Dowex 50W X2, Dow Chemical Co., Midland Mich.
[2] Dowex 50W X4, Dow Chemical Co., Midland Mich.
[3] Dowex 50W X8, Dow Chemical Co., Midland, Mich.
[4] Dowex 50W X12, Dow Chemical Co., Midland Mich.
[5] Amberlite 200, Rohm & Haas Co., Philadelphia, Pa.

Table I—Capacity of Resins

Resin	Mesh	Capacity, meq./g. Air-Dried Resin	Capacity, meq./g. Oven-Dried Resin
X2	200/400	3.58	4.97
X4	20/50	3.75	5.01
X4	50/100	3.90	5.12
X4	100/200	3.72	4.77
X4	200/400	2.90	4.83
X8	200/400	4.09	4.86
X12	200/400	3.62	4.71
IR-200	20/60	3.56	4.78

Details were given earlier (1–3, 7) regarding the chemicals used, the preparation and estimation of the solutions, the procedure, and the nomenclature.

Column Studies—The known weight of air-dried resin was taken, and the resin was slurried with distilled water and transferred to a column fitted with a sintered-glass disk. The column was backwashed with distilled water and allowed to settle under gravity; column data were then measured. After use the resin was replaced by an equal amount of resin from stock for the next run.

RESULTS AND DISCUSSION

In this study, Resins X2, X4, X8, and X12 of 200/400 mesh were studied for equilibrium exchange with quinine sulfate and cinchonine sulfate to cover a wide range of particle sizes. The results are given in Table II. These may be compared with the corresponding results for these resins of 60/80 mesh given in Tables I and II of an earlier work (1). The results indicate that the average value of P_R for resins of fine mesh (200/400) is higher than that for the same resins of larger mesh (60/80). For the resin with a low degree of crosslinking (X2), P_R increases with a decrease in P_A; for resins of a higher degree of crosslinking (X4, X8, and X12), P_R increases when P_A decreases for the smaller particle size (200/400 mesh) but

Table II—Equilibrium of Aqueous Quinine Sulfate and Cinchonine Sulfate with Cation-Exchange Resins

Resin[a]	Quinine Sulfate $[\bar{A}]_e$	Quinine Sulfate P_A	Quinine Sulfate P_R	Cinchonine Sulfate $[\bar{A}]_e$	Cinchonine Sulfate P_A	Cinchonine Sulfate P_R
X2	0.50	26.2	63.5	0.54	28.6	64.2
	0.92	48.1	57.2	0.77	40.7	57.9
	1.10	57.5	54.2	1.10	58.2	54.2
	1.37	71.3	52.4	1.39	73.5	51.7
X4	0.93	47.9	56.0	0.91	46.0	56.0
	1.11	57.2	55.5	1.06	53.5	53.3
	1.44	74.2	53.7	1.40	70.7	52.4
	1.80	92.0	52.0	1.77	89.4	51.0
X8	0.73	37.8	53.3	0.75	37.2	54.4
	1.02	52.8	50.2	0.90	44.5	53.6
	1.33	68.9	48.2	1.08	53.5	51.2
	1.62	83.9	48.0	1.59	78.7	49.4
X12	0.37	19.3	37.4	0.43	23.0	42.6
	0.58	30.2	37.2	0.83	44.4	42.0
	0.74	38.5	36.3	1.08	57.8	41.1
	1.14	58.6	35.7	1.29	69.0	40.0

[a] Mesh size of the resins = 200/400.

Table III—Total Amount of Alkaloid Exchange (TW_x) for Quinine Sulfate with Resin Column[a]

Run No.	Resin	Mesh	Ionic Form	Bed Length,[b] cm.	Bed Volume,[b] ml.	Flow Rate, ml./min.	Solvent Medium[c]	TW_x
1	IR-200	20/60	H^+	21	9	10	aq.	4.82
2						30		4.15
3						50		3.52
4						65		3.18
5			NH_4^+			50	aq.	2.45
6						50	aq. acid	2.45
7	X4	20/50	H^+	32	14	10	aq.	5.28
8						30		4.52
9						50		3.65
10	X4	50/100	H^+	30	13	10	aq.	6.66
11						30		6.01
12	X4	100/200	H^+	28	12	4	aq.	7.25
13			NH_4^+			4	aq.	7.29
14			NH_4^+			4	aq. acid	7.29

[a] Capacity of resin in column = 16.3 meq. [b] For resin in the hydrogen form. [c] aq. = aqueous; aq. acid = 0.01 N aqueous sulfuric acid.

is practically constant with the increase in P_A for the larger particle size (60/80 mesh). The results imply that for a resin of larger particle size, depending on the degree of crosslinking, P_R is practically constant when P_A is decreased; but when the particle size is sufficiently decreased, P_R increases when P_A decreases and the average value of P_R is higher.

Column Studies—Studies were carried out at different flow rates with the resins in hydrogen form for exchange with aqueous quinine sulfate. Four liters of aqueous quinine sulfate solution (concentration = 2 meq./l.) was passed through the column. The effluent was collected in eight samples, each 500 ml., and W_x (milliequivalents of alkaloid sulfate exchanged) for each sample was calculated from UV absorption. For example, the values of the sample number and 100 W_x for Run 1 of Table III were: 1, 100; 2, 100; 3, 93; 4, 76; 5, 54; 6, 28; 7, 19; and 8, 12. The values of TW_x (total amount, in milliequivalents, of alkaloid exchanged) obtained from such data are given in Table III. The data indicate that for the column used, with the flow rate at 10 ml./min., the exchange is close to the effective capacity of Resin IR-200 (1, 2) in the column. Under the same conditions, for Resin X4 in the column, TW_x is less than the effective capacity and increases with decreases in particle size. For both the resins, TW_x decreases almost linearly with an increase in flow rate (Fig. 1).

Runs were then carried out with quinine sulfate from aqueous and 0.01 N aqueous sulfuric acid medium with a column of resin in the ammonium form. The procedure was similar to that already described. After each exchange run, for the elution, the column was washed with distilled water and eluted with ammoniacal (0.1 N) ethyl alcohol. The rate was 20 ml./min. for Resin IR-200 of 20/60 mesh and 4 ml./min. for Resin X4 of 100/200 mesh. The effluent was collected in 200-ml. samples, and W_1 (milliequivalents of alkaloid base eluted) in each sample was calculated from UV absorption. Complete elution of the alkaloid was obtained. For example, the values of the sample number and 500 W_1 for the elution run after the exchange Run 5 of Table III were: 1, 1096; 2, 85; 3, 17.8;

4, 9; 5, 5.5; 6, 4.1; 7, 3.8; and 8, 3.1; the values of TW_x are given in Table III. With resin in the ammonium form, TW_x was practically the same with aqueous and 0.01 N aqueous sulfuric acid as the solvent medium.

The runs suggest that a resin of relatively lower degree of crosslinking such as X4 or of expanded structure such as IR-200 in ammonium form could be suitable for recovery of cinchona alkaloids with aqueous sulfuric acid as solvent for the exchange runs and ammoniacal alcohol as solvent for the elution run.

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