# 3. EQUILIBRIUM STUDIES OF CINCHONA ALKALOID SULFATES WITH SULFONIC ACID RESINS : (A) EFFECT OF PARTICLE SIZE OF RESINS IN HYDROGEN FORM AND (B) STUDIES WITH RESINS IN AMMONIUM FORM

Page No.

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## 3.1

## Introduction :

In this section equilibrium exchange of cinchona alkaloid sulfates with styrene divinylbenzene copolymer based sulfonic acid cation exchange resins of different degree of crosslinking and (a) of different particle size in hydrogen form and (b) with resins in ammonium form have been studied at room temperature (∽ 30°C).

## 3.2

## Experimental :

Resins : Dowex 50W (Dow Chemical Co.) styrene divinylbenzene copolymer based sulfonic acid cation exchange resins of relative degree of crosslinking ( % nominal divinylbenzene content ) as 2, 4, 8 and 12 (further referred to as X2, X4, X8 and X12) ; each of 60/80 and 200/400 mesh.

Amberlite-200 (Rohm and Haas Co.) (further referred to as IR-200) of 20/60 mesh ; this is presumably styrene divinylbenzene copolymer based sulfonic acid cation exchange resin of relative degree of crosslinking about 20 but has an expanded structure.

### Moisture and capacity of the resins : (120 , 121)

The resins were washed with distilled water, cycled repeatedly between sodium chloride and hydrochloric acid, regenerated with large excess of hydrochloric acid, washed free of acid, filtered, airdried, sieved and stored in good containers.

Moisture content of each fraction of the resins was determined by heating weighed samples ( ∽ 0.5 gm ) of airdry resins in clean, dry weighing bottles, in an oven (100-103°C) to a constant weight.

For the estimation of the capacity of the resins, weighed samples ( ∽ 0.5 gm ) of airdry resins were contacted with 50 cc. of 1 N barium chloride solution in well stoppered flasks with frequent shaking. After two or three days, the liberated acid was estimated by titration with standard sodium hydroxide solution and then the capacity was calculated. Preliminary work had indicated that increase in contact time did not increase the amount of acid liberated. Table (3.1) gives the values for airdry and ovendry capacities of different resins in the hydrogen form.

The ammonium form of the resins was prepared by treating the hydrogen form of the resins with excess of aqueous ammonia through the resin bed. The resin was then washed, filtered, airdried, moisture content determined and the capacity of the airdry form of the resin calculated from the ovendry capacity in hydrogen form.

Chemicals :

Cinchona alkaloid sulfates were from samples used earlier (Chapter 2). Water of crystallisation in some of the crystallised cinchona alkaloid sulfates may not be constant. However, calculation of molecular weight of the crystallised alkaloid sulfate based on (a) gravimetric sulfate estimation and (b) moisture content determination, were in good agreement. As such gravimetric sulfate estimation can be used for the accurate determination of the concentration of the aqueous alkaloid sulfate solution irrespective of the water of crystallisation of the sample.

Hence, the gravimetric sulfate estimation was used, throughtout all this work ; for rechecking the concentration of the aqueous alkaloid sulfate solution.

## Solutions :

The stock solution of alkaloid sulfate was first prepared in distilled water and the concentration in gram equivalent per litre was evaluated by both sulfate estimation (as barium sulfate) and by determining the optical density of the solution after suitable dilution with distilled water at the invarient wavelengths (114) (296.5 mμ for quinine sulfate and quinidine sulfate ; 294.5 mμ for cinchonine sulfate and cinchonidine sulfate) with Beckman Model DU Spectrophotometer using 10 mm. matched quartz cells.

## Procedure :

To study the equilibrium exchange of the alkaloid sulfate, weighed samples of airdry resins were placed in contact with suitable volumes of an aqueous alkaloid sulfate 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 (4 to 40 days depending on the degree of crosslinking of the resin). After sufficiently more time than this, the solutions were analysed for alkaloid sulfate 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 wavelength.

The total sulfate in the equilibrium mixture was estimated gravimetrically for each resin and it showed no measurable difference in the initial and equilibrium values. The exchange equilibrium values were not measurably different when either the amount of alkaloid sulfate solution was held constant and the amount of added resin was varied or when the amount of added resin was held constant and the amount of alkaloid sulfate solution was varied ; provided the ratio of the initial concentration (in meq./litre) of the resin to the initial concentration of the alkaloid sulfate, was the same. Preliminary work also indicated that for small changes in temperature, the value of $P_R$ was not significantly affected.

## 3.3

## Nomenclature :

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

W = weight of airdry resin taken in grams,

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

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

$D_i$ = optical density, at the invarient wavelength, of the initial concentration of alkaloid sulfate 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,

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

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

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

## 3.4

## Results :

## Table 3.1

Capacity of resins

| Resin | Mesh | Capacity in meq./gm of | |
|---|---|---|---|
| | | Airdry resin | Ovendry resin |
| X2 | 60/80 | 4.14 | 5.2 |
| X4 | 60/80 | 3.89 | 5.12 |
| X8 | 60/80 | 3.72 | 5.09 |
| X12 | 60/80 | 3.73 | 5.04 |
| IR-200 | 20/60 | 3.53 | 4.78 |
| X2 | 200/400 | 3.58 | 4.97 |
| X4 | 200/400 | 2.90 | 4.83 |
| X8 | 200/400 | 4.09 | 4.86 |
| X12 | 200/400 | 3.62 | 4.71 |

## Table 3.2

Equilibrium exchange of aqueous quinine sulfate with resins in ammonium (M) form.

| Resin | $[\bar{M}]_i$ | $[A]_i$ | $[\bar{A}]_e$ | $P_A$ | $P_R$ |
|---|---|---|---|---|---|
| X2 | 0.77 | 2.20 | 0.50 | 22.5 | 64.0 |
| | 1.30 | 2.20 | 0.84 | 38.0 | 64.3 |
| | 1.70 | 2.20 | 1.10 | 50.0 | 64.8 |
| | 2.36 | 2.20 | 1.54 | 70.0 | 65.2 |
| X4 | 0.99 | 2.37 | 0.49 | 20.5 | 49.0 |
| | 1.58 | 2.37 | 0.79 | 33.5 | 50.1 |
| | 2.53 | 2.37 | 1.30 | 55.0 | 51.4 |
| | 3.34 | 2.37 | 1.74 | 73.5 | 52.1 |
| X8 | 1.25 | 2.08 | 0.42 | 20.0 | 33.2 |
| | 2.33 | 2.08 | 0.78 | 37.5 | 33.4 |
| | 3.65 | 2.08 | 1.23 | 59.0 | 33.6 |
| | 4.63 | 2.08 | 1.56 | 75.0 | 33.7 |
| IR-200 | 2.38 | 2.20 | 0.63 | 28.5 | 26.3 |
| | 3.52 | 2.20 | 0.89 | 40.5 | 25.3 |
| | 5.38 | 2.20 | 1.29 | 58.5 | 23.9 |
| | 7.77 | 2.20 | 1.76 | 80.0 | 22.6 |

Table 3.3

Equilibrium exchange of aqueous cinchonine sulfate with resins in ammonium (M) form.

| Resin | $\left[\bar{M}\right]_i$ | $\left[A\right]_i$ | $\left[\bar{A}\right]_e$ | $P_A$ | $P_R$ |
|---|---|---|---|---|---|
| X2 | 0.52 | 1.96 | 0.40 | 20.5 | 77.1 |
| | 1.00 | 1.96 | 0.76 | 39.0 | 76.6 |
| | 1.49 | 1.96 | 1.13 | 57.5 | 75.9 |
| | 2.04 | 1.96 | 1.54 | 78.5 | 75.4 |
| X4 | 0.76 | 2.06 | 0.52 | 25.0 | 67.5 |
| | 1.19 | 2.06 | 0.80 | 39.0 | 67.5 |
| | 1.77 | 2.06 | 1.17 | 57.0 | 66.5 |
| | 2.19 | 2.06 | 1.44 | 70.0 | 65.8 |
| X8 | 0.87 | 2.21 | 0.42 | 19.0 | 48.5 |
| | 1.79 | 2.21 | 0.86 | 39.0 | 48.2 |
| | 2.65 | 2.21 | 1.27 | 57.5 | 47.9 |
| | 3.72 | 2.21 | 1.77 | 80.0 | 47.5 |
| IR-200 | 1.91 | 2.00 | 0.50 | 25.0 | 26.2 |
| | 3.34 | 2.00 | 0.82 | 41.0 | 24.6 |
| | 5.13 | 2.00 | 1.17 | 58.5 | 22.8 |
| | 6.77 | 2.00 | 1.45 | 72.5 | 21.4 |

## Table 3.4

Equilibrium exchange of aqueous quinidine sulfate with resins in ammonium (M) form.

| Resin | $[\bar{M}]_i$ | $[A]_i$ | $[\bar{A}]_e$ | $P_A$ | $P_R$ |
|---|---|---|---|---|---|
| X2 | 0.69 | 1.91 | 0.39 | 20.5 | 56.7 |
| | 1.60 | 1.91 | 0.90 | 47.0 | 56.0 |
| | 2.12 | 1.91 | 1.18 | 62.0 | 55.8 |
| | 2.75 | 1.91 | 1.53 | 80.0 | 55.5 |
| X4 | 0.72 | 1.91 | 0.35 | 18.5 | 48.9 |
| | 1.45 | 1.91 | 0.70 | 36.5 | 48.2 |
| | 2.44 | 1.91 | 1.16 | 61.0 | 47.8 |
| | 3.32 | 1.91 | 1.58 | 82.5 | 47.5 |
| X8 | 1.04 | 1.89 | 0.37 | 19.5 | 35.4 |
| | 1.87 | 1.89 | 0.65 | 34.5 | 34.8 |
| | 2.77 | 1.89 | 0.96 | 50.5 | 34.4 |
| | 4.31 | 1.89 | 1.46 | 77.0 | 33.8 |
| IR-200 | 1.58 | 1.91 | 0.43 | 22.5 | 27.2 |
| | 3.56 | 1.91 | 0.84 | 44.0 | 23.6 |
| | 5.17 | 1.91 | 1.13 | 59.0 | 21.8 |
| | 7.69 | 1.91 | 1.50 | 78.5 | 19.5 |

Table 3.5

Equilibrium exchange of aqueous cinchonidine sulfate with resins in ammonium (M) form.

| Resin | $[\bar{M}]_i$ | $[A]_i$ | $[\bar{A}]_e$ | $P_A$ | $P_R$ |
|---|---|---|---|---|---|
| X2 | 0.59 | 2.06 | 0.49 | 24.0 | 83.5 |
| | 1.04 | 2.06 | 0.88 | 42.5 | 83.9 |
| | 1.35 | 2.06 | 1.13 | 55.0 | 84.1 |
| | 1.86 | 2.06 | 1.57 | 76.0 | 84.3 |
| X4 | 0.66 | 2.13 | 0.45 | 21.0 | 68.1 |
| | 1.16 | 2.13 | 0.80 | 37.5 | 68.8 |
| | 1.81 | 2.13 | 1.26 | 59.0 | 69.3 |
| | 2.33 | 2.13 | 1.62 | 76.0 | 69.6 |
| X8 | 1.02 | 2.06 | 0.49 | 24.0 | 48.8 |
| | 1.67 | 2.06 | 0.80 | 39.0 | 48.0 |
| | 2.48 | 2.06 | 1.17 | 57.0 | 47.3 |
| | 3.56 | 2.06 | 1.67 | 81.0 | 46.9 |
| IR-200 | 1.78 | 2.06 | 0.52 | 25.0 | 29.0 |
| | 2.78 | 2.06 | 0.76 | 37.0 | 27.4 |
| | 4.39 | 2.06 | 1.10 | 53.5 | 25.1 |
| | 7.02 | 2.06 | 7.02 | 76.0 | 22.3 |

Table 3.6

Equilibrium exchange of aqueous quinine sulfate with cation exchange resins.

| Resin | Mesh | $[\bar{H}]_i$ | $[A]_i$ | $[\bar{A}]_e$ | $P_A$ | $P_R$ |
|---|---|---|---|---|---|---|
| X2 | 60/80 | 0.84 | 2.12 | 0.44 | 20.8 | 52.7 |
| | | 1.68 | 2.12 | 0.86 | 40.5 | 51.1 |
| | | 2.49 | 2.12 | 1.25 | 59.0 | 50.2 |
| | | 3.35 | 2.12 | 1.64 | 77.4 | 49.0 |
| | | 4.18 | 2.12 | 2.01 | 94.8 | 48.1 |
| X2 | 200/400 | 0.79 | 1.92 | 0.50 | 26.2 | 63.5 |
| | | 1.61 | 1.92 | 0.92 | 48.1 | 57.2 |
| | | 2.03 | 1.92 | 1.10 | 57.5 | 54.2 |
| | | 2.61 | 1.92 | 1.37 | 71.3 | 52.4 |
| X4 | 60/80 | 0.70 | 2.07 | 0.34 | 16.5 | 49.1 |
| | | 1.38 | 2.07 | 0.69 | 33.3 | 49.9 |
| | | 2.77 | 2.07 | 1.38 | 66.7 | 49.8 |
| | | 3.44 | 2.07 | 1.69 | 81.6 | 49.1 |
| X4 | 200/400 | 1.66 | 1.95 | 0.93 | 47.9 | 56.0 |
| | | 2.00 | 1.95 | 1.11 | 57.2 | 55.5 |
| | | 2.68 | 1.95 | 1.44 | 74.2 | 53.7 |
| | | 3.46 | 1.95 | 1.80 | 92.0 | 52.0 |

Table 3.6 (Contd.)

| Resin | Mesh | $\left[\bar{H}\right]_i$ | $\left[A\right]_i$ | $\left[\bar{A}\right]_e$ | $P_A$ | $P_R$ |
|---|---|---|---|---|---|---|
| X8 | 60/80 | 0.98 | 2.07 | 0.39 | 19.1 | 40.1 |
| | | 1.46 | 2.07 | 0.60 | 28.8 | 40.9 |
| | | 2.00 | 2.07 | 0.80 | 38.8 | 40.2 |
| | | 4.01 | 2.07 | 1.56 | 75.4 | 39.0 |
| X8 | 200/400 | 1.37 | 1.92 | 0.73 | 37.8 | 53.3 |
| | | 2.03 | 1.92 | 1.02 | 52.8 | 50.2 |
| | | 2.76 | 1.92 | 1.33 | 68.9 | 48.2 |
| | | 3.38 | 1.92 | 1.62 | 83.9 | 48.0 |
| X12 | 60/80 | 1.44 | 2.12 | 0.37 | 17.3 | 25.5 |
| | | 2.87 | 2.12 | 0.72 | 34.0 | 25.1 |
| | | 5.73 | 2.12 | 1.48 | 69.8 | 25.8 |
| | | 7.16 | 2.12 | 1.84 | 86.8 | 25.7 |
| X12 | 200/400 | 0.99 | 1.92 | 0.37 | 19.3 | 37.4 |
| | | 1.56 | 1.92 | 0.58 | 30.2 | 37.2 |
| | | 2.04 | 1.92 | 0.74 | 38.5 | 36.3 |
| | | 3.19 | 1.92 | 1.14 | 58.6 | 35.7 |

## Table 3.7

Equilibrium exchange of aqueous cinchonine sulfate with cation exchange resins.

| Resin | Mesh | $[\bar{H}]_i$ | $[A]_i$ | $[\bar{A}]_e$ | $P_A$ | $P_R$ |
|---|---|---|---|---|---|---|
| X2 | 60/80 | 1.27 | 2.00 | 0.72 | 36.0 | 56.7 |
| | | 1.59 | 2.00 | 0.87 | 43.5 | 54.7 |
| | | 1.97 | 2.00 | 1.03 | 51.5 | 52.3 |
| | | 3.18 | 2.00 | 1.59 | 79.5 | 50.0 |
| | | 3.96 | 2.00 | 1.94 | 97.0 | 49.0 |
| X2 | 200/400 | 0.84 | 1.89 | 0.54 | 28.6 | 64.2 |
| | | 1.33 | 1.89 | 0.77 | 40.7 | 57.9 |
| | | 2.03 | 1.89 | 1.10 | 58.2 | 54.2 |
| | | 2.69 | 1.89 | 1.39 | 73.5 | 51.7 |
| X4 | 60/80 | 1.43 | 2.00 | 0.77 | 38.5 | 53.9 |
| | | 2.21 | 2.00 | 1.14 | 57.0 | 51.6 |
| | | 2.83 | 2.00 | 1.43 | 71.5 | 50.5 |
| | | 4.27 | 2.00 | 1.96 | 98.0 | 45.8 |
| X4 | 200/400 | 1.63 | 1.98 | 0.91 | 46.0 | 56.0 |
| | | 1.99 | 1.98 | 1.06 | 53.5 | 53.3 |
| | | 2.67 | 1.98 | 1.40 | 70.7 | 52.4 |
| | | 3.47 | 1.98 | 1.77 | 89.4 | 51.0 |

Table 3.7 (Contd.)

| Resin | Mesh | $[\bar{H}]_i$ | $[A]_i$ | $[\bar{A}]_e$ | $P_A$ | $P_R$ |
|---|---|---|---|---|---|---|
| X8 | 60/80 | 1.42 | 2.00 | 0.62 | 31.0 | 43.7 |
| | | 2.21 | 2.00 | 1.00 | 50.0 | 45.0 |
| | | 2.83 | 2.00 | 1.27 | 63.5 | 44.9 |
| | | 3.72 | 2.00 | 1.66 | 83.0 | 44.6 |
| X8 | 200/400 | 1.38 | 2.02 | 0.75 | 37.2 | 54.4 |
| | | 1.68 | 2.02 | 0.90 | 44.5 | 53.6 |
| | | 2.11 | 2.02 | 1.08 | 53.5 | 51.2 |
| | | 3.22 | 2.02 | 1.59 | 78.7 | 49.4 |
| X12 | 60/80 | 3.00 | 2.00 | 0.81 | 40.5 | 27.0 |
| | | 4.31 | 2.00 | 1.18 | 59.0 | 27.4 |
| | | 7.54 | 2.00 | 1.97 | 98.5 | 26.1 |
| X12 | 200/400 | 1.01 | 1.87 | 0.43 | 23.0 | 42.6 |
| | | 1.98 | 1.87 | 0.83 | 44.4 | 42.0 |
| | | 2.63 | 1.87 | 1.08 | 57.8 | 41.1 |
| | | 3.23 | 1.87 | 1.29 | 69.0 | 40.0 |

3.5

## Discussion :

The synthetic organic ion exchange resins (7,10) consist of an irregular, three dimensional network of hydrocarbon chains, 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 depends on the degree of crosslinking and the counter ions. The selectivity coefficients for alkali metal ions with resins in hydrogen form in sulfate solutions had been studied earlier (122). When calculations were carried out for exchange in solutions of the cinchona alkaloid sulfates studied, with resins in different ionic forms (hydrogen or ammonium form), the calculated values of $P_R$ were either practically constant or varied to some extent, when $P_A$ was varied. The results were not measurably different when either the amount of alkaloid sulfate solution was held constant and the amount of added resin was varied or when the amount of added resin was held constant and the amount of alkaloid sulfate solution was varied, provided the ratio of the initial concentration (in meq./litre) of the resin to the initial concentration of the alkaloid sulfate, was the same. It is suggested that the value of the equilibrium constant for the exchange (123-131) of the cation $QH^+$ is large and the equilibrium $MR + QH^{+} \rightleftharpoons RQH + M^{+}$ is shifted very much to the right ; however, all the replaceable cations in the resin phase are not accessible for exchange or the available capacity is only a fraction of the total capacity, probably due to the size of the organic counter ions. It is likely that the marked shift of the equilibrium to the right is aided by the operation of nonexchange interactions (120,130,131) and that the interactions tend to increase the extent of exchange with increase in $[\overset{-}{A}]_e$. This may be feasible to some extent by further expansion of and / or further separation between some segments in the swollen (7,10) or expanded resin network and should depend on the degree of crosslinking and the extent to which exchange has already occurred. If the further expansion and / or segment separation is sufficient to accommodate some more organic cations by exchange, $P_R$ should increase with decrease in $[\overset{-}{A}]_e$ or decrease in $P_A$. This appears to be so for the resins used, of very small particle size and also for lower crosslinked resins in hydrogen form. On the other hand, if the further expansion and / or segment separation is too small to accommodate some more organic cations by exchange, $P_R$ should remain practically constant with decrease $[\overset{-}{A}]_e$ or decrease in $P_A$. This appears to be so for resins of higher X and relatively larger particle size in hydrogen form.

The effect of the degree of crosslinking is significant. The value of $P_R$ for all the alkaloid sulfates decreases as X increases. This is so for each of the ionic forms of the resin. This could be attributed to the decrease in swelling of the resin as the degree of crosslinking increases ; hence the number of accessible exchange sites for the alkaloid in the interior of the resin decreases.

In general, the results indicate that the $P_R$ values with quinine sulfate and the quinidine sulfate for a resin in a particular ionic form are significantly lower than those for cinchonine sulfate and cinchonidine sulfate for the same resin in the same ionic form. This should be attributed to the difference in the size of quinine or quinidine as compared to that of cinchonine or cinchonidine. Also the values of $P_R$ for a resin for optical isomers quinine and quinidine are almost same and same is true for optical isomers cinchonine and cinchonidine. The exception seems to be lower crosslinked resin X2 in ammonium form for which the values of $P_R$ for the optical isomers are somewhat different. The value for the levo isomer being higher than that for dextro isomer.

Earlier (116), the effect of particle size of styrene divinylbezene copolymer based gel type sulfonic acid cation exchange resin, Amberlite IR-120 on equilibrium exchange was studied. The degree of crosslinking of Amberlite IR-120 is presumably about 8. The particle size, 'a' (average particle diameter in mm.) studied was 0.58,0.37. Within this narrow range ; the particle size had no significant effect on equilibrium exchange with cinchona alkaloid sulfates. 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 wider range of particle size. The results are given in Tables 3.6 and 3.7 which also include the results for resins of 60/80 mesh from Tables I and II of earlier work (116). 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). Also for resin of lower degree of crosslinking, resin X2, $P_R$ increases with decrease in $P_A$ ; for resins of higher degree of crosslinking, resins X4, X8 and X12, $P_R$ increases when $P_A$ decreases for usually small particle size (200/400 mesh), but is practically constant, when $P_A$ decreases for larger particle size (60/80 mesh). The results should 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. The values of $P_R$ for resins X2, X4 and X8 in ammonium form for equilibrium exchange of cinchona alkaloid sulfates studied,are practically constant when $P_A$ is increased. The comparison of values of $P_R$ for equilibrium exchange of quinine sulfate for resins of same particle size (60/80 mesh) and in hydrogen and ammonium form indicates that the value of $P_R$ , for X2,is higher, for X4,is almost same and for X8,is less, for resin in ammonium form than that in hydrogen form. For the equilibrium exchange of cinchonine sulfate with same resins the values of $P_R$ are higher for ammonium form than those for hydrogen form.

In general, these observations may be attributed to swollen volume of the resin in different ionic forms relative to the size of organic counter ion. For resin IR-200, which probably has X about 20, but has an expanded structure, the value of $P_R$ in hydrogen form (116) is practically constant and independent of $P_A$, but for resin in ammonium form, the value of $P_R$ decreases to some extent as $P_A$ increases. Also the value of $P_R$ for hydrogen form of the resin is somewhat higher than the average value of $P_R$ in ammonium form of the resin. It appears that for low crosslinked resins, the value of $P_R$ is higher for ammonium form than that of hydrogen form ; but when degree of crosslinking is increased, this difference decreases and then the order is reversed.