Part III : STUDIES WITH CINCHONA ALKALOIDS

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CINCHONA ALKALOIDS : (1)

Introduction :

The most important alkaloid of cinchona is quinine. In addition about 20 other alkaloids have been isolated from cinchona (Table 9.1) of which cinchonidine, quinidine and cinchonine are important. The alkaloids chiefly exist as salts of quinic and cinchotannic acids and their relative concentrations vary in different species. The bark which is known to the trade as druggist's bark has a quinine content of 1.8 to 2.0 %.

In the early years of planting, the total alkaloids were used for medicinal purposes under the name of quinetum. In India quinetum was gradually replaced by cinchona febrifuge consisting of the residual alkaloids left after the removal of quinine. The Malaria Commission of the league of Nations redefined quinetum as a mixture of equal parts of quinine, cinchonidine and cinchonine and introduced a new product called totaquine or totaquina which is defined in the B.P. as containing not less than 70 % of crystallisable cinchona alkaloids-quinine, cinchonidine, cinchonine and quinidine of which not less than one fifth is quinine. Cinchonafebrifuge varies greatly in physical character and composition, for use as an antimalarial drug. It should be of the same standard as totaquine.

Extraction :

The greater part of the world's production of cinchona barks is employed in the manufacture of quinine.

Table 9.1

Cinchona Alkaloids

Name of the alkaloid.	Formula	m.p. °C	Dextro(D) or Laevo(L) Rotatory.
Quinine	$C_{20}H_{24}O_2N_2$	175	L
Quinidine	$C_{20}H_{24}O_2N_2$	173.5	D
Cinchonine	$C_{19}H_{22}ON_2$	264	D
Cinchonidine	$C_{19}H_{22}ON_2$	204.5	L
Quinicine	$C_{20}H_{24}O_2N_2$	Viscous Liquid	D
epiQuinine	$C_{20}H_{24}O_2N_2$	011	D
epiQuinidine	$C_{20}H_{24}O_2N_2$	113	D
Cinchotine	$C_{19}H_{24}ON_2$	267	D
Hydrocinchonidine	$C_{19}H_{24}ON_2$	232	L
Hydroquinine	$C_{20}H_{26}O_2N_2.2H_2O$	173.5	L
Hydroquinidine	$C_{20}H_{26}O_2N_2.2\frac{1}{2}H_2O$	169.5	D
Quinamine	$C_{19}H_{24}O_2N_2$	185.6	D
Conquinamine	$C_{19}H_{24}O_2N_2$	121	D
Paricine	$C_{16}H_{18}ON_2.\ \frac{1}{2}H_2O$	136	-
Dicinchonine	$C_{38}H_{44}O_2N_4$	40	D
Diconquinine	$C_{40}H_{46}O_3N_4$	-	D
Javanine	-	-	-
Aricine	$C_{23}H_{26}O_4N_2$	188	L
Cusconine	$C_{23}H_{26}O_4N_2.2H_2O$	110	L
Cusconidine	-	-	-
Cuscamine	-	218	-
Cuscamidine	-	-	-

For this purpose finely powdered bark is mixed with about one third of its weight of sifted slaked lime and a 5 % aqueous solution of caustic soda. The mixture is extracted under stirring in steam jacketed vessels, with high boiling kerosene. Three successive extractions are made. The mixed extracts are shaken with sufficient hot,dilute sulphuric acid to convert the alkaloids into sulphates. The oil is separated while hot and then neutral aqueous solution cooled when quinine sulphate separates out and is subsequently purified by recrystallisation from aqueous solutions after decolourising with animal charcoal. The mother liquor containing the other alkaloids is treated with caustic soda and the precipitate of quinidine, cinchonidine and cinchonine extracted with dilute alcohol which dissolves the first two,leaving cinchomine behind ; the former two can then be separated by means of their neutral tartarates, that of quinidine being considerably more soluble.

The method adopted by the Bureau of Science, Philippines, is to percolate to exhaustion with alcohol, a mixture of finely powdered bark, lime and water. The percolate is distilled to recover the alcohol, and the gummy residue treated with sulphuric acid to dissolve the alkaloids. The solution is decolourised with charcoal, filtered and the mixed alkaloids precipitated by the addition of sodium hydroxide.

An ion exchange process for the separation of alkaloids from cinchona barks poor in alkaloids has been developed and was successfully employed in the U.S.A.

during the war period. This sorption procedure has been recommended for adoption in India for the recovery of alkaloids from the waste material left after the separation of barks. On the basis of figures for quinine manufactured in 1944-45, it is computed that the wastage of cinchona alkaloids from Indian plantations is about 69,679 lbs. a good part of which is recoverable by the application of the sorption process.

The estimation of individual alkaloids in mixtures has assumed importance since the therapeutical recognition of totaquina. A number of methods based on differences in the solubilities of salts and polarimetric, colorimetric, turbidimetric,fluorometric and chromatographic methods have been developed.

Uses :

The oldest and the most important use of quinine is for the treatment of malarial fevers. Quinine continues to be effective inspite of its prolonged used. Quinine possesses marked bactericidal action and until the advent of sulphanilamide derivatives,quinine and certain of its derivatives were being employed in the treatment of baterial infections. Thus β-hydroxy-ethyl apoquinine and sulphapyridine give equal protection to mice against virulent pneumococci and the drug has been successfully used in large number of cases of human pneumonia. Quinine has been used as a sclerosing agent in the treatment of internal haemorrhoids and vericose veins.

Quinine added to aquaphor,protects the skin against sun burn.

Quinine sulphate is the most important salt of quinine used in therapy. Other salts of quinine such as acetyl salicylate, arsenate, benzoate, citrate, dihydrobromide, dihydrochloride, disalicylo-salicylate, ethyl carbonate, glycerophosphate, lactate, phosphate, salicylate, tannate and valerianate are recognised by the B.P.C. Quinine ethyl carbonate and tannate are almost tasteless and are specially useful for children. Quinine with urea hydrochloride is used as a local anaesthetic. Practically tasteless compounds are obtained by combining quinine with an acid mixture derived from camphoric acid and an aromatic alcohol or a terpene alcohol or a phenol.

In addition to their use in pharmacy, quinine and quinidine and their derivatives are utilised in insecticide compositions for the preservation of fur, feathers, wool felts and textiles. They are also ingredients of moth repelling preparations. Quinine sterate is used in hair lotions and pomades. The residual bark of quinine factories after the extraction of the alkaloids is a tanning material. Debarked cinchona poles are durable and resistant to termites.

New and effective antimalarial drugs, specially, paludrine have certain advantages over quinine in the treatment of malaria. These new developments have no doubt affected cinchona expansion schemes in India. However, from a strategic point of view, cinchona alkaloids are still of importance as indigenous materials particularly in war time, when imports may not be feasible.

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(1) The wealth of India, Raw Materials, Vol. II, P. 163-173, Council of Scientific and Industrial Research, Delhi. (1951).

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ION EXCHANGE STUDIES WITH CINCHONA ALKALOIDS

Ungerer (1) first examined the uptake of salts of quinine, cinchonine and strychnine on the calcium form of synthetic zeolites. Fink (2) took a patent for isolating cinchonine, strychnine and adrenaline from their aqueous extracts by a filtering material having adsorptive properties, such as asbestos and kaolin, cotton and asbestos or asbestos and kieselguhr. The pH of the solution was suitably adjusted to facilitate the separation. Applezweig (3) studied the removal of cinchona alkaloids by a cation exchanger of sulphonic acid type. Three possibilities were explored : (a) recovery of alkaloids from the mother liquor of the acid extracts of the bark after the major portion had been removed by alkaline precipitation, (b) purification of the crude totaquine obtained from alkaline precipitation and (c) application of ion exchange directly to the acid extracts of the bark in a cyclic system. Capacity determinations were carried out on a 200 cc. Zeo-karb column using quinine concentrations of 0.033 and 0.0033 M and flow rates of approximately 5 and 50 cc./min. The capacity of a 200 cc. bed of Zeo-karb for quinine, from acid solution (1 % H_2SO_4) was found to be between 7 and 8 grams, before break through (Mayer's Reagent). To liberate the alkaloids from the column ammonical alcohol was used. Purification of totaquine prepared by alkaline precipitation of acid extracts of the bark was attempted by ion exchange. From 20 grams of totaquine precipitate, 2.5 grams of white crystalline material was obtained. This technique was also successfully employed in the isolation of atropine, morphine and scopolamine. Recoveries of totaquine from cinchona bark and scopolamine from datura plants were also effected by Sussman and others (4). The extract containing the alkaloids was brought into contact with a cation exchanger and then the cation exchanger was treated with aqueous alkali and a solvent. In a subsequent paper, Applezweig and Ronzone (5) described a portable unit for extracting usable antimalerial from freshly stripped cinchona bark in the field. Commercially dried cinchona bark was macerated with 0.1 N H_2SO_4. The acid was repeatedly cycled through a sulphonated coal cation exchanger and back into the maceration tank. The exchanger was regenerated with 0.5 N NaOH and stripped with alcohol, the crude alkaloid being recovered by evaporation. Rectified totaquine was obtained by precipitation from aqueous solution. An overall yield of 81.2 % within 82 hours was obtained. Mukherjee and Gupta (6) investigated the extraction of alkaloids from cinchona bark with hydrochloric acid and sulphuric acid over a range of acid concentrations and temperatures in the presence and absence of sodium chloride with Amberlite IR-100 and Ionac C-284. For elution, alkali was used and after an interval, alcohol was percolated. Ionac C-284 proved to be the best sorbent and showed highest elution effeciency but tended to soften and form a jelly in contact with alkali. Hence Zeo-karb, the next best and free from this defect was used. Applezweig (7) took a patent for the removal of quinine from a dilute solution in acid with Zeo-karb cation exchanger. The juice of the fresh material was passed through a column of Zeo-karb or Amberlite IR-100 or Ionac C-284. The sorbed alkaloids were eluted with ammonical ethanol. This method was used for the extraction of atropine, scopolamine and quinine alkaloids. Mukherjee and others (8) examined three cation exchange resins (Zeo-karb, Amberlite IR-100 and Ionac C-284) and two anion exchange resins (Deacidite and Ionac A-293) for the sorption of quinine sulphate, strychnine hydrochloride and other organic bases. The results showed that a resin having high sorption power for one alkaloid may not behave similarly with another alkaloid. The relative sorptive powers of the different resins, for each of the alkaloids studied were given.

Jindra (9) used an anion exchange resin of weakly basic type for the determination of several alkaloids. 0.1 to 0.2 grams of alkaloid salt was dissolved in 20 cc. of alcohol and passed through a prepared column of Amberlite IR-4B. The flask and the column were washed with 50 cc. of alcohol at 50°C and the alkaloidal solution in alcohol was titrated with 0.1 N hydrochloric acid using a mixture of 10 drops of methyl red and 2 drops of methylene blue as indicator. The method was applied to quinine and cinchonine hydrochlorides and to a number of other alkaloids. Jindra and Pohorsky (10) have given detailed descriptions of the apparatus, reagents, preparations of the ion exchange column and general micro and semi-micro methods of assay, applied to cinchona bark and other alkaloids. Bucke and Furrer (11) have described in detail, the determination of quinine and total alkaloids in the cinchona bark extracts by the use of ion exchange resins. In a subsequent paper they (12) found that sorption from cinchona bark was best with sulphuric acid extracts and the elution was best done with ethanol with or without addition of sodium hydroxide. A quantitative sorption occured within 14 hours by shaking the powdered cinchona bark and Duolite in dilute sulphuric acid but the subsequent separation of alkaloids from the resin was found to be difficult. Sanders and others (13) described an assay process using strongly basic anion exchange columns to separate quinine salts and ephedrine hydrochloride which was capable of giving results within 0.5 %. One and two column procedures are described. Yoshino and Sugihara (14) separated quinine and strychnine chromatographically by sorption on weakly acidic cation exchange (NH_4-R) resins such as Duolite CS-101 or Amberlite IRC-50 and the subsequent elution with 0.1 - 0.3 M ammonium chloride respectively. H-R exchanger could also be used but then a large amount of eluting solution was required to separate strychnine. Toshino and others (15) classified some organic bases (a) quinine, cinchonine, ephedrine and berberine (b) nicotine and yohimbine (c) amino pyridine (d) antipyrine (e) acetanilide, caffeine, theobromine and theophylline, according to the facilities of being eluted with water from the cation exchange columns (sulphonic acid type and carboxylic acid type in the H and NH_4 form), on to which they had been sorbed. Street and Niyogi (16) separated a mixture of acetophenetidine, sulphacetamide, promacyine and quinine by a combination of chromatography and ionophoresis on cellulosic ionexchange sheets. Detection was accomplished by examination in ultraviolet light. Similarly (17) separation of a mixture of tablet fragments containing amobarbital, acetylsalicyclic acid, acetophenetidine, caffine, codeine and quinine into its constituent parts was accomplished by chromatography on modified cellulose ion exchange papers using both horizontal circular and ascending cylindrical paper chromatography. Street (18) has described a rapid method using ionexchange paper for the preliminary separation and detection of a mixture of quinine, strychnine and nicotine in whole blood. Proteins were precipitated and the acid filtrate was extracted with ether. The aqueous phase was made alkaline with ammonium hydroxide and shaken with ether to extract basic compounds. The ether extract was evaporated to dryness and the residue was taken up in the chloroform. This solution was spotted on a cellulose cation exchange paper and subjected to chromatography in an aqueous solvent at pH 4.5. The separated compounds were detected by their fluorescence or absorbance in ultraviolet light at 254 mμ. Quinine showed a bright blue fluorescent spot and strychnine and nicotine as dark purple absorbing areas.

Saunders and Srivastava (19) studied the rates of sorption on, and elution from a carboxylic acid cation exchange resin for quinine. The factors which influenced the rate of sorption of quinine on Amberlite IRC-50 were found to be

(a) the initial concentration of the solute ('a' milimoles /100 cc.) (b) the nature of solvent, sorption from 50 % ethanol solution being more rapid than that from pure ethanol for a given value of 'a' (c) the method by which the resin was converted to the hydrogen form, aqueous 2 N acid producing a less effective absorbent than alcoholic 2 N acid (d) the amount of base already sorbed on the resin (x milimoles) (e) the stirring condition (f) the particle size of the resin and (g) the initial pH of the solution. An empirical relation $dx / dt = Ka (a - x) / x^2$ (where K = constant ; a = initial solution concentration in milimoles / 100 cc. ; x = milimoles sorbed by 5 grams of resin and t = time in hours), represented the rate of sorption quite closely for values upto 24 hours. The interaction of quinine with the resin was considered to be mainly a molecular sorption process. The sorption process has been visualised as a diffusion of base into the resin particle under chemical potential difference enhanced by the acid-base interaction with the resin and by the van der Waal's forces between the base molecule and gel structure of the resin ; the effect of viscous flow into spherical particles and the swelling of the resin caused the rate of sorption to fall off rapidly as the resin became saturated with base. Saunders and Srivastava(20) also examined the sorption of a number of organic bases from aqueous, water ethanol or ethanolic solutions by various carboxylic acid ion exchange resins and described the results of studies of the equilibrium distributions of some bases between the solutions and the resins. This, in the case of quinine has been demonstrated by showing that the distribution was independent of resin particle size and also that it was reversible. The systems studied have been classified into two groups. The first consisted of very weak bases which followed a simple distribution law, concentration of base in resin /concentration in equilibrium solution = constant. The second group, consisted of strong bases, the distributions mostly followed a logarithmic law $Y = A \log C + B$ where C = concentration of base in the equilibrium solution in moles per litre of total phase volume and Y = corresponding base concentration in the resin phase in moles of base per litre of total resin phase volume. Observations have also been made of the swelling of the resins caused by saturating them with the different bases and it was found that swelling was a function of base sorbed.

Segal, Miller and Morton (21) have described the quinine form of a weak cation exchanger as an indicator for the determination of the presence of free hydrochloric acid in gastric juice without intubation. If a special cation (quinine) is combined with a cation exchange resin (Amberlite IRC-50 or XE-96) and the cation is displaceable only or mainly by hydrogen ion, is readily sorbed from the stomach and detectable in the urine or blood, the presence of free hydrochloric acid in gastric juice can be detected if quinine appears in the urine within 2 hours, after introduction of the complex, without subjecting the patient to intubation. Shay and others (22) found that the results of studies in patients after subtotal gastric resection indicated that the tubeless method for detection of the presence of free hydrochloric acid in the remaining gastric pouch was not suitable in these patients because of the rapid emptying of the quininium resin from the pouch. In such patients the determination of pH of gastric contents during fractional gastric analysis was the best method for studying gastric acidity. Kamp (23) determined quinine together with caffeine and strychnine in cola sirup by ion exchange resin.

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11.

ESTIMATION OF CINCHONA ALKALOIDS : GRAVIMETRIC STUDIES

The illustrative data given below indicate that the gravimetric sulphate estimation can be used for the determination of the concentration of the aqueous alkaloid sulphate solution and this has been used in this work for rechecking the concentration.

Gravimetric sulphate estimation of crystallised quinidine sulphate :

A known weight of crystallised quinidine sulphate was dissolved in about 500 cc. of distilled water, five drops of hydrochloric acid (1 N) were added and precipitation was carried out with 1 % aqeuous barium chloride solution. From the weight of barium sulphate obtained the molecular weight of the crystallised quinidine sulphate was calculated

Crystallised quinidine sulphate taken = 0.8353 gms.
barium sulphate obtained = 0.2488 gms.

Hence molecular weight of crystallised quinidine sulphate = 782.3

Gravimetric total sulphate estimation of a mixture of sulphuric acid and sulphate :

A known volume of standard sulphuric acid was added to an aqueous solution of quinidine sulphate (from the sample used above) and the total sulphate was estimated gravimetrically.

crystallised quinidine sulphate taken	= 0.6101 gms.
sulphuric acid (0.04819 N) added	= 30.0 cc.
barium sulphate obtained	= 0.3509 gms.
weight of barium sulphate required	= 0.3503 gms.

ESTIMATION OF CINCHONA ALKALOIDS : ULTRAVIOLET ABSORPTION STUDIES : (1)

Introduction :

Dobbie and Fox (2) studied the absorption spectra of quinine and reported three maxima at 1 /λ 3050, 1 /λ 3500 and 1 /λ 3750. The hydrochlorides of quinine and 6-methoxyquinoline exhibited identical bands and those given by 0.01 N solution of the sulphate of these two differed only in the greater absorption of the former.

Manta (3) obtained the extinction curves of the following alkaloids in 0.001 N and 0.005 N alcoholic solutions : quinoline and p-methoxylepidine, quinidine and quinine ; cinchonine and cinchonidine ; ethyliodoquinine and diiodoethylquinine. The pair of compounds showed nearly the same form of curve.

Heidt and Forbes (4) studied the absorption spectra from 20,000 to 45000 cm^{-1}. and the fluorescence spectra of the bisulphates of cinchonine, cinchonidine, quinine, quinidine etc. in 0.09 M sulphuric acid solution. The curves were shifted about 200 cm^{-1}. to the ultraviolet when water was used as a solvent.

Fuchs and Kampitsch (5) determined the ultraviolet absorption spectra of pure quinine, cinchonine, quinidine and cinchonidine under different conditions and noted two absorption types. The aqueous and alcoholic solutions of the neutral salts corresponded to the type of the absorption spectra of their bases. The influence of the pH only appeared in the solutions of acid salts or in excess acid. The latter formed the second type of absorption spectra. In between were found the aqueous solutions of acid salts, which in alcoholic solution, corresponding to the lower pH concentration, showed a very similar spectrum to the base. In all the solvents examined, a distinct difference between the quinine and cinchonine spectra was noted.

Carol (6) studied the ultraviolet absorption curve of quinine in dilute hydrochloric acid. The location and magnitude of the 3 regions of maximum absorption were found to be : 250.5 mμ $E^{1\%}_{1\,\text{cm.}}$ 901 ; 318.0 mμ $E^{1\%}_{1\,\text{cm.}}$ 142; 347.5 mμ $E^{1\%}_{1\,\text{cm.}}$ 168. The Beer-Lambert law was followed at each maxima. It was suggested that quinine could be determined directly at 347.5 mμ without separation since practically all alkaloids and synthetics exhibit negligible absorption in this region.

Beguiristain (7) found maximum absorption in the ultraviolet for solutions of quinine hydrochloride and progressively weaker absorptions for strychnine sulphate, morphine hydrochloride, aconitine nitrate and atropine sulphate.

Stimson and Reuter (8) measured the ultraviolet spectra of the 4 common naturally occuring alkaloids in alcoholic solutions or alcoholic / hydrochloric acid solutions and some related compounds over a pH range 1-10 to facilitate the estimation of methoxy cinchona alkaloids.

The melting points and crystal habits are also given for quinine, quinidine, cinchonidine, cinchonine and their dihydro derivatives. Other compounds studied were epiquinine, epiquinidine and totaquine.

The above indicates that the ultraviolet absorption spectra of cinchona alkaloids are significantly affected by the pH of the solution ; however, detailed data, of interest in the estimation of cinchona alkaloid sulphates in dilute aqueous or aqueous sulphuric acid solutions of different pH , are not available.

This chapter gives the study of the ultraviolet absorption spectra of the sulphates of four cinchona alkaloids (as $Q_2H_2SO_4.nH_2O$, where Q denotes the alkaloid) quinine, quinidine, cinchonine and cinchonidine, in aqueous solution of pH about 1 to 7, adjusted by the addition of sulphuric acid or sodium hydroxide at room temperature ($\sim 30^{\circ}C$).

Experimental :

Chemicals :

Quinidine sulphate (P.B.; Howard, London) was crystallised three times from hot water. Cinchonine sulphate was prepared by dissolving cinchonine (pure crystals ; Riedel, Germany) in aqueous sulphuric acid and crystallising out the sulphate ; this was then crystallised twice from hot water. Sulphuric acid and sodium hydroxide used were A.R. quality. Distilled water was used.

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Solutions and procedure :

The stock solution of alkaloid sulphate was first prepared in distilled water and the concentration in gram equivalents per litre was evaluated by sulphate estimation (as barium sulphate). Measured portion of the stock solution was then suitably diluted with distilled water or aqueous sulphuric acid or aqueous sodium hydroxide and the pH of the solution measured with Beckman Model H2 pH meter. The ultraviolet absorption was studied with Beckman Model DU spectrophotometer using 10 mm. matched quartz cells in the range 250-350 mμ. The values of the extinction coefficients, ϵ , were calculated by dividing the observed optical density by the concentration of the alkaloid sulphate in gram-equivalents per litre.

Results :

Table 12.01

Ultraviolet absorption of quinidine sulphate solution.

pH = 7.0 Concentration = 0.1139 meq. / litre.

Wavelength in $m\mu$	ϵ	Wavelength in $m\mu$	ϵ	Wavelength in $m\mu$	ϵ
250	4557	280	3538	310	2959
252	3275	281	3547	315	3705
254	2705	282	3530	317	4013
256	2520	284	3485	318	4144
258	2494	286	3398	320	4390
260	2528	288	3310	322	4565
262	2634	290	3222	325	4742
264	2739	292	3099	330	4986
266	2880	294	2923	335	4635
268	3002	295	2836	340	3275
270	3125	296	2739	345	1827
272	3230	297	2660	350	913.1
274	3328	298	2581	360	272.2
276	3415	300	2476	-	-
278	3503	305	2528	-	-

Table 12.02

Ultraviolet absorption of quinidine sulphate solution.

pH = 6.8 Concentration = 0.1139 meq. / litre.

Wavelength in mμ	ε	Wavelength in mμ	ε	Wavelength in mμ	ε
250	4513	276	3389	305	2528
252	3275	278	3485	310	2932
254	2696	280	3538	315	3697
256	2511	282	3513	320	4381
258	2476	284	3434	325	4758
260	2528	286	3371	330	4952
262	2608	288	3284	335	4627
264	2722	290	3214	340	3319
266	2855	292	3073	345	1818
268	2985	294	2906	350	9042
270	3099	296	2739	360	2634
272	3214	298	2572	-	-
274	3310	300	2467	-	-

Table 12.03

Ultraviolet absorption of quinidine sulphate solution.

pH = 5.4 Concentration = 0.1139 meq. / litre.

Wavelength in $m\mu$	ϵ	Wavelength in $m\mu$	ϵ	Wavelength in $m\mu$	ϵ
250	5777	278	3355	310	3002
252	4601	280	3389	315	3723
254	3872	281	3398	320	4408
256	3406	282	3389	325	4773
258	3047	284	3336	328	4882
260	2792	286	3266	330	4961
262	2669	288	3187	332	4969
264	2678	290	3125	335	4654
266	2757	292	3011	340	3426
268	2871	294	2871	345	1993
270	2968	296	2696	350	1115
272	3082	298	2564	360	491.7
274	3161	300	2476	-	-
276	3258	305	2564	-	-

Table 12.04

Ultraviolet absorption of quinidine sulphate solution.

pH = 4.4 Concentration = 0.1139 meq. / litre.

Wavelength in mμ	ε	Wavelength in mμ	ε	Wavelength in mμ	ε
260	4417	282	2713	310	3398
262	3222	284	2739	315	3987
264	2528	2286	2739	320	4408
266	2283	288	2757	325	4565
268	2230	290	2766	330	4785
270	2274	292	2748	335	4758
272	2344	294	2731	340	3997
274	2423	296	2696	345	3248
276	2520	298	2686	350	2634
278	2608	300	2705	360	1818
280	2669	305	2941	-	-

Table 12.05

Ultraviolet absorption of quinidine sulphate solution.

pH = 3.9 Concentration = 0.1139 meq./ litre.

Wavelength in $m\mu$	ϵ	Wavelength in $m\mu$	ϵ	Wavelength in in $m\mu$	ϵ
260	5549	286	2353	317	4293
262	4327	288	2414	318	4364
264	2390	290	2485	320	4417
266	1914	292	2537	322	4434
268	1791	294	2608	325	4462
270	1791	295	2634	330	4679
272	1852	296	2664	332	4767
274	1940	297	2705	335	4794
276	1993	298	2739	337	4707
278	2098	300	2836	340	4478
280	2178	305	3178	345	3950
282	2248	310	3746	350	3574
284	2310	315	4154	360	2686

Table 12.06

Ultraviolet absorption of quinidine sulphate solution.

pH = 3.7 Concentration = 0.1139 meq./ litre.

Wavelength in $m\mu$	ϵ	Wavelength in $m\mu$	ϵ	Wavelength in $m\mu$	ϵ
262	3714	284	2124	315	4240
264	2397	286	2204	320	4425
266	1818	288	2292	325	4434
268	1615	290	2380	330	4618
270	1598	292	2468	335	4846
272	1642	294	2564	340	4724
274	1703	296	2661	345	4398
276	1782	298	2757	350	4065
278	1870	300	2915	360	3152
280	1958	305	3310	-	-
282	2037	310	3802	-	-

Table 12.07

Ultraviolet absorption of quinidine sulphate solution.

pH = 1.8 Concentration = 0.1139 meq./litre.

Wavelength in mμ	ε	Wavelength in mμ	ε	Wavelength in mμ	ε
262	4127	284	1554	315	4513
264	2310	286	1703	320	4478
266	1388	288	1852	325	4311
268	1036	290	2037	330	4478
270	948.2	292	2230	335	4909
272	965.8	294	2432	340	5277
274	1028	296	2652	345	5479
276	1106	298	2889	350	5400
278	1203	300	3125	355	5040
280	1299	305	3679	360	4364
282	1431	310	4179	370	2599

Table 12.08

Ultraviolet absorption of quinidine sulphate solution.

pH = 1.2 Concentration = 0.1139 meq./litre.

Wavelength in mμ	ε	Wavelength in mμ	ε	Wavelength in mμ	ε
262	4240	284	1590	315	4522
264	2324	286	1721	320	4478
266	1405	288	1870	325	4302
268	1063	290	2046	330	4461
270	965.8	292	2230	335	4864
272	961.0	294	2441	340	5250
274	1036	296	2669	345	5445
276	1115	298	2906	350	5374
278	1212	300	3125	355	5023
280	1308	305	3697	360	4364
282	1440	310	4188	370	2616

Table 12.09

Ultraviolet absorption of cinchonine sulphate solution

pH = 6.6 Concentration = 0.1387 meq./ litre.

Wavelength in mμ	ε	Wavelength in mμ	ε	Wavelength in mμ	ε
250	1543	284	4657	307	3215
252	1708	286	4686	308	3057
254	1881	288	4708	309	2833
256	2076	289	4722	310	2646
258	2278	290	4708	311	2537
260	2509	291	4650	312	2530
262	2762	292	4528	313	2762
264	2978	294	4333	314	3114
266	3222	296	4110	315	3367
268	3418	298	3872	316	3252
270	3663	300	3893	317	2804
272	3893	301	3973	318	2213
274	4110	302	4023	319	1608
276	4276	303	3944	320	1153
278	4427	304	3763	325	237.9
280	4521	305	3594	-	-
282	4592	306	3338	-	-

Table 12.10

Ultraviolet absorption cinchonine sulphate solution,

pH = 6.1 Concentration = 0.1387 meq./litre.

Wavelength in mμ	ε	Wavelength in mμ	ε	Wavelength in mμ	ε
250	1528	284	4628	307	3244
252	1665	286	4646	308	3078
254	1845	288	4696	309	2869
256	2032	289	4715	310	2653
258	2256	290	4678	311	2537
260	2473	291	4614	312	2545
262	2711	292	4506	313	2754
264	2942	294	4340	314	3093
266	3187	296	4110	315	3360
268	3402	298	3872	316	3258
270	3634	300	3872	317	2797
272	3865	301	3959	318	2250
274	4081	302	3999	319	1622
276	4246	303	3937	320	1204
278	4404	304	3756	325	245.1
280	4506	305	3584	330	122.6
282	4578	306	3388	-	-

Table 12.11

Ultraviolet absorption of cinchonine sulphate solution.

pH = 4.4 Concentration = 0.1387 meq./litre.

Wavelength in mμ	ε	Wavelength in mμ	ε	Wavelength in mμ	ε
250	1514	284	4643	307	3324
252	1658	286	4693	308	3158
254	1824	288	4722	309	2942
256	2004	289	4743	310	2726
258	2213	290	4715	311	2581
260	2403	291	4643	312	2574
262	2668	292	4578	313	2797
264	2913	294	4397	314	3158
266	3129	296	4196	315	3410
268	3360	298	3942	316	2623
270	3604	300	3951	317	2869
272	3828	301	4052	318	2300
274	4037	302	4088	319	1687
276	4232	303	4023	320	1204
278	4383	304	3858	325	252.3
280	4513	305	3669	330	129.8
282	4592	306	3489	340	86.52

Table 12.12

Ultraviolet absorption of cinchonine sulphate solution.

pH = 4.0 Concentration = 0.1387 meq./litre.

Wavelength in mμ	ϵ	Wavelength in mμ	ϵ	Wavelength in mμ	ϵ
250	1342	286	3604	310	4801
252	1312	288	3815	311	4743
254	1326	290	4009	312	4794
256	1362	292	4146	313	4974
258	1420	294	4261	314	5241
260	1492	295	4318	315	5408
262	1601	296	4354	316	5393
264	1716	298	4390	317	5104
266	1875	300	4672	318	4672
268	2032	301	4860	319	4167
270	2206	302	4996	320	3719
272	2308	303	5083	325	2192
274	2560	304	5078	330	1507
276	2732	305	5076	335	1067
278	2920	306	5047	340	706.5
280	3100	307	5032	350	216.3
282	3252	308	4974	360	79.3
284	3439	309	4881	-	-

Table 12.13

Ultraviolet absorption of cinchonine sulphate solution.

pH = 3.7 Concentration = 0.1387 meq./litre.

Wavelength in mμ	ε	Wavelength in mμ	ε	Wavelength in mμ	ε
250	1298	286	3388	310	5241
252	1254	288	3619	311	5205
254	1212	290	3872	312	5234
256	1204	292	4052	313	5429
258	1254	294	4225	314	5659
260	1305	295	4340	315	5784
262	1385	296	4420	316	5768
264	1486	298	4571	317	5565
266	1622	300	4845	318	5176
268	1745	301	5032	319	4768
270	1932	302	5212	320	4276
272	2076	303	5284	325	2610
274	2250	304	5314	330	1817
276	2430	305	5371	335	1283
278	2617	306	5386	340	879.6
280	2804	307	5364	350	302.8
282	2991	308	5350	360	93.7
284	3186	309	5314	-	-

Table 12.14

Ultraviolet absorption of cinchonine sulphate solution.

pH = 3.6 Concentration = 0.1387 meq./litre.

Wavelength in mμ	ε	Wavelength in mμ	ε	Wavelength in mμ	ε
250	1312	286	3208	310	5696
252	1204	288	3474	311	5675
254	1148	290	3749	312	5718
256	1096	292	4017	313	5883
258	1118	294	4246	314	6099
260	1147	295	4354	315	6272
262	1190	296	4484	316	6258
264	1283	298	4700	317	6027
266	1377	300	5047	318	5708
268	1500	301	5248	319	5314
270	1644	302	5500	320	4845
272	1802	303	5538	325	3064
274	1975	304	5645	330	2113
276	2148	305	5696	335	1529
278	2343	306	5732	340	1023
280	2537	307	5746	350	317.3
282	2762	308	5746	360	108.1
284	2913	309	5732	-	-

Table 12.15

Ultraviolet absorption of cinchonine sulphate solution.

pH = 3.4 Concentration = 0.1387 meq./litre.

Wavelength in mμ	ε	Wavelength in mμ	ε	Wavelength in mμ	ε
250	1262	286	2985	311	6099
252	1125	288	3273	312	6142
254	1023	290	3604	313	6287
256	980.4	292	3914	314	6503
258	944.5	294	4218	315	6704
260	951.7	296	4499	316	6604
262	966.1	298	4787	317	6503
264	1023	300	5154	318	6229
266	1110	301	5443	319	5746
268	1218	302	5580	320	5334
270	1348	303	5732	325	3453
272	1486	304	5825	330	2436
274	1658	305	5912	335	1716
276	1831	306	5970	340	1132
278	2032	307	6013	350	396.5
280	2250	308	6113	360	122.6
282	2465	309	6027	-	-
284	2739	310	6070	-	-

Table 12.16

Ultraviolet absorption of cinchonine sulphate solution.

pH = 3.2   Concentration = 0.1387 meq./litre.

Wavelength in mμ	ϵ	Wavelength in mμ	ϵ	Wavelength in mμ	ϵ
250	1262	284	2610	309	6374
252	1104	286	2869	310	6380
254	1002	288	3186	311	6387
256	922.8	290	3511	312	6445
258	865.2	292	3879	313	6618
260	850.7	294	4196	314	6834
262	879.6	296	4513	315	6893
264	908.4	298	4886	316	6950
266	993.1	300	5321	317	6792
268	1088	301	5522	318	6518
270	1197	302	5732	319	6142
272	1326	303	5898	320	5732
274	1507	304	6070	325	3735
276	1694	305	6130	330	2646
278	1896	306	6272	335	1867
280	2098	307	6308	340	1254
282	2335	308	6330	350	403.7

Table 12.17

Ultraviolet absorption of cinchonine sulphate solution.

pH = 1.8   Concentration = 0.1387 meq./litre.

Wavelength in mμ	ϵ	Wavelength in mμ	ϵ	Wavelength in mμ	ϵ
250	1212	284	2271	309	6877
252	1009	286	2560	310	6921
254	865.2	288	2927	311	6993
256	757.0	290	3302	312	7065
258	663.0	292	3735	313	7181
260	605.6	294	4160	314	7353
262	591.2	296	4563	315	7461
264	612.8	298	5011	316	7498
266	663.3	300	5479	317	7353
268	735.3	301	5732	318	6974
270	836.4	302	5884	319	6776
272	959.0	303	6128	320	6345
274	1104	304	6330	325	4276
276	1277	305	6460	330	3028
278	1471	306	6633	335	2148
280	1701	307	6733	340	1414
282	1968	308	6848	360	461.4

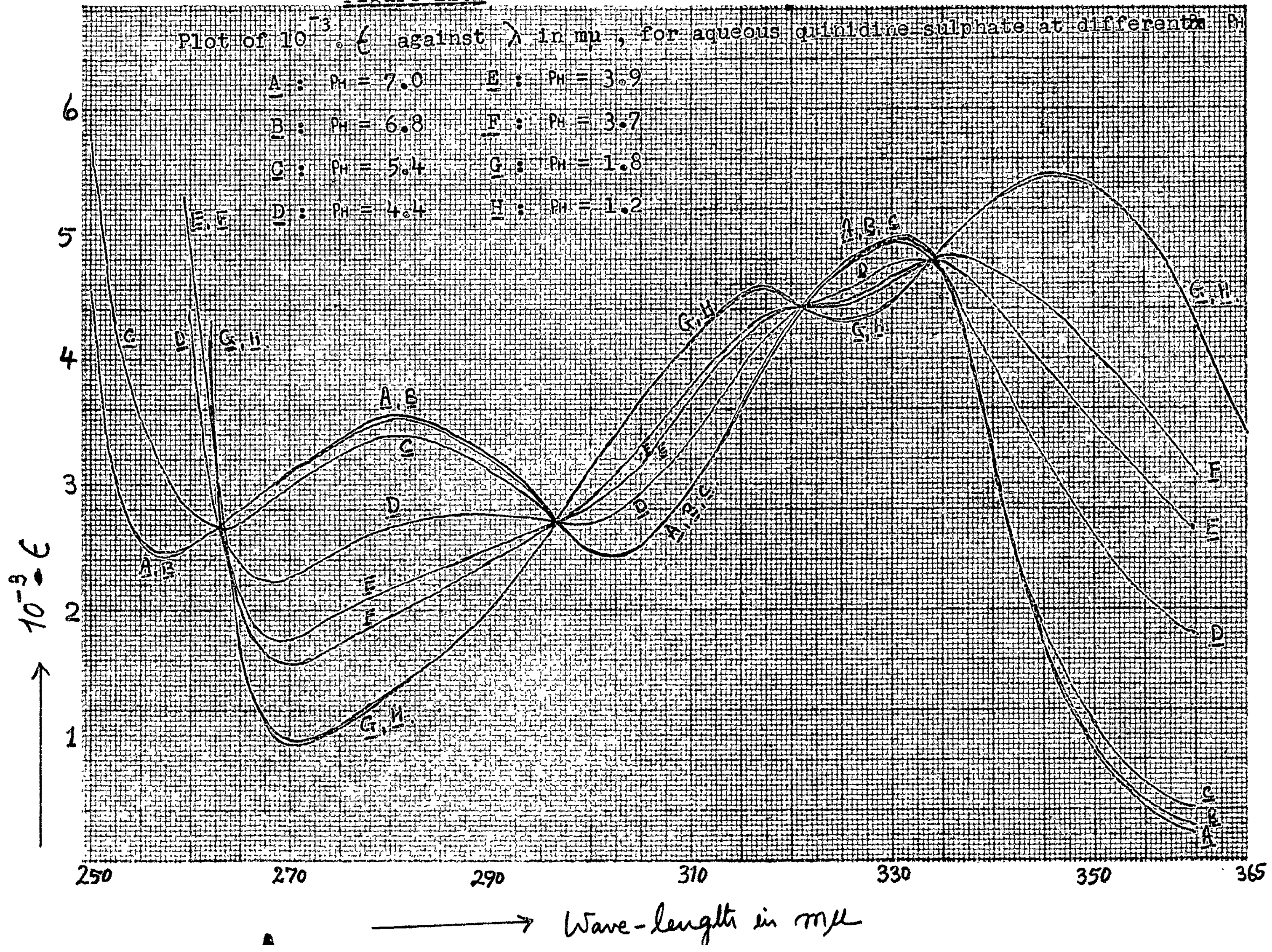
Table 12.18

Ultraviolet absorption of cinchonine sulphate solution.

pH = 1.2 Concentration = 0.1387 meq.Litre.

Wavelength in mμ	ϵ	Wavelength in mμ	ϵ	Wavelength in mμ	ϵ
250	1254	286	2574	311	6971
252	1023	288	2942	312	7065
254	876.6	290	3316	313	7209
256	764.2	292	3749	314	7353
258	670.5	294	4167	315	7461
260	620.0	296	4592	316	7534
262	598.4	298	5024	317	7389
264	605.6	300	5516	318	7152
266	656.0	301	5724	319	6776
268	735.3	302	5956	320	6345
270	836.4	303	6142	325	4340
272	951.7	304	6330	330	3071
274	1102	305	6488	335	2177
276	1283	306	6618	340	1463
278	1478	307	6733	350	475.7
280	1723	308	6807	360	144.2
282	1975	309	6848	-	-
284	2263	310	6907	-	-

Figure 12.1



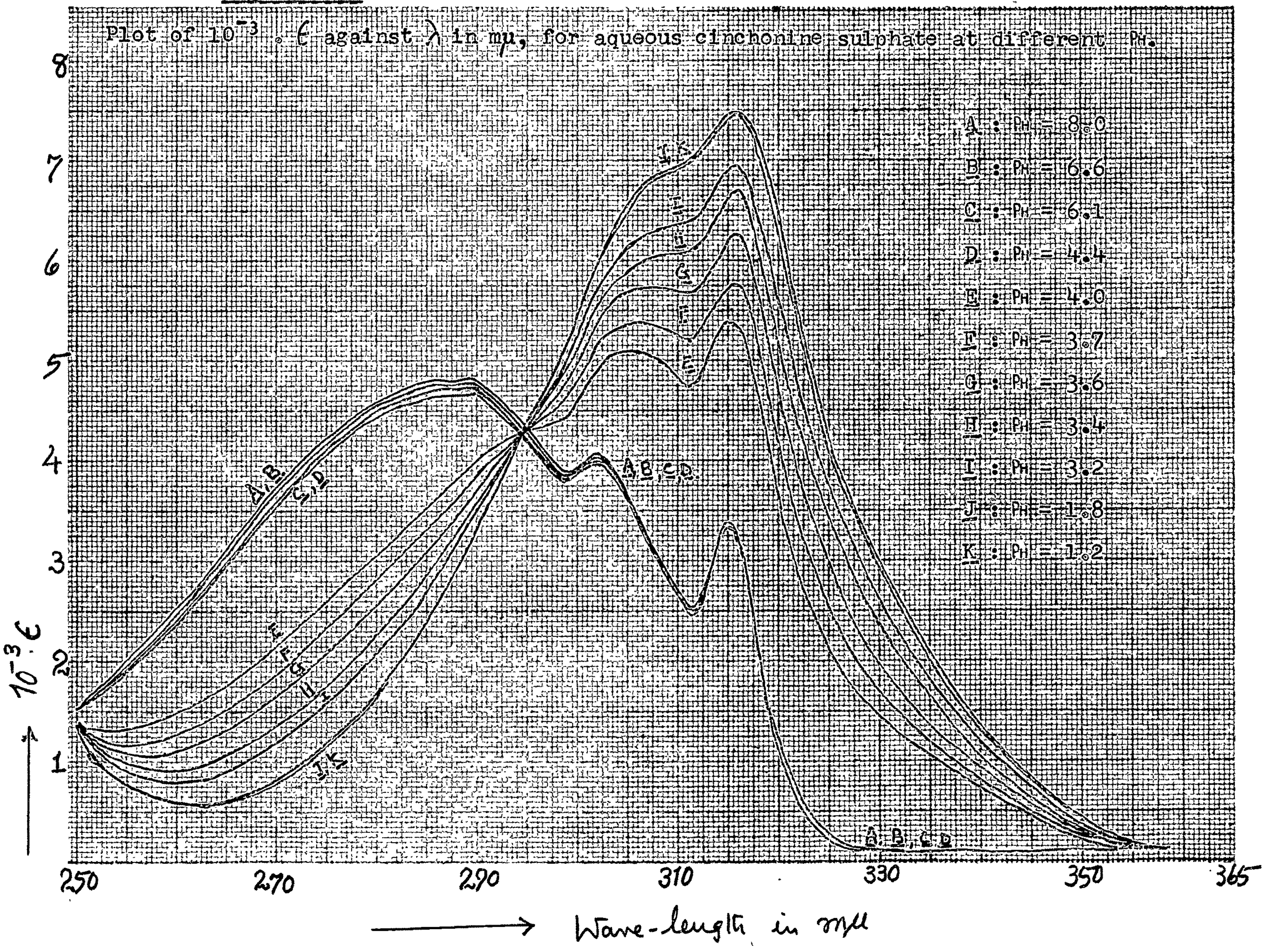
Plot of $10^{-3}.\epsilon$ against λ in mμ, for aqueous quinidine sulphate at different PH

Table 12.19

Values of λ (in $m\mu$) and ϵ for the minima and maxima of ultraviolet absorption spectra (figure 12.1) of quinidine sulphate in aqueous solution of pH about 1 to 7, adjusted by the addition of sulphuric acid or sodium hydroxide, at room temperature ($\sim 30^{\circ}C$). (λN and λX stand for the wavelengths in $m\mu$ for minima and maxima respectively).

pH	λN	$\epsilon/10$	λX	$\epsilon/10$	λN	$\epsilon/10$	λX	$\epsilon/10$	λN	$\epsilon/10$	λX	$\epsilon/10$
7.0	258	248	280.5	356	302.5	244	-	-	-	-	331	500
6.8	258	248	280.5	354	302.5	244	-	-	-	-	331	498
5.4	263	266	281	340	302.5	244	-	-	-	-	331	498
4.4	268	222	-	-	-	-	-	-	-	-	333	482
3.9	269	180	-	-	-	-	-	-	-	-	334	482
3.7	270	160	-	-	-	-	-	-	-	-	335.5	484
1.8	270.5	95	-	-	-	-	317	458	325	432	346	548
1.2	270.5	95	-	-	-	-	317	458	325	430	346	548

Figure 12.2



Plot of $10^{-3} . \epsilon$ against λ in mμ, for aqueous cinchonine sulphate at different PH.

Table 12.20

Values of λ (in mμ) and ε for the minima and maxima of ultraviolet absorption spectra (figure 12.2) of cinchonine sulphate in aqueous solution of pH about 1 to 7, adjusted by the addition of sulphuric acid or sodium hydroxide, at room temperature (~ 30°C). (λN and λX stand for the wavelengths in mμ for minima and maxima respectively).

pH	λN	ε/10	λX	ε/10	λN	ε/10	λX	ε/10	λN	ε/10	λX	ε/10
6.6	-	-	289	472	299	388	302	403	311.5	254	315	336
6.1	-	-	289	472	299	388	302	400	311.5	254	315	336
4.4	-	-	289	474	299	390	302	409	311.5	254	315	341
4.0	253	130	-	-	-	-	304	660	311	475	315.5	540
3.7	256	120	-	-	-	-	306	540	311	520	315.5	580
3.6	257	110	-	-	-	-	307.5	575	310.5	567.5	315.5	630
3.4	259	95	-	-	-	-	-	-	-	-	315.5	675
3.2	260	82.5	-	-	-	-	-	-	-	-	316	698
1.8	262	60	-	-	-	-	-	-	-	-	316	750
1.2	262	60	-	-	-	-	-	-	-	-	316	750

Table 12.21

Alkaloid salt : Quinidine sulphate

Evaluation of invarient point :

Table No.	pH	Optical Density at (1) λ 296 mμ	Optical Density at (2) λ 298 mμ	Difference of (1) and (2)	Calculated optical Density at λ 296.5 mμ
12.01	7.0	0.312	0.294	0.018	0.307
12.02	6.8	0.312	0.293	0.019	0.307
12.03	5.4	0.307	0.292	0.015	0.305
12.04	4.4	0.307	0.306	0.001	0.307
12.05	3.9	0.303	0.312	0.009	0.305
12.06	3.7	0.303	0.314	0.011	0.307
12.07	1.8	0.302	0.329	0.027	0.309
12.08	1.2	0.304	0.331	0.027	0.311

Average optical density at λ 296.5 mμ =0.307

Value of ϵ at λ 296.5 mμ =2698

Variation in optical density at λ 296.5 mμ =0.006

% Variation in optical density at λ 296.5 mμ = ± 1.0 %

Table 12.22

Alkaloid salt : Quinidine sulphate

Evaluation of invarient point :

Table No.	pH	Optical Densaity at (1) $\lambda 320$ mμ	(2) $\lambda 325$ mμ	Difference of (1)and (2)	Calculated Optical Density at $\lambda 320.5$ mμ
12.01	7.0	0.500	0.541	0.041	0.504
12.02	6.8	0.499	0.542	0.043	0.503
12.03	5.4	0.502	0.539	0.037	0.506
12.04	4.4	0.502	0.520	0.018	0.504
12.05	3.9	0.503	0.508	0.005	0.504
12.06	3.7	0.504	0.505	0.001	0.504
12.07	1.8	0.510	0.491	0.019	0.508
12.08	1.2	0.510	0.490	0.020	0.508

Average optical density at $\lambda 320.5$ mμ = 0.505

Value of ϵ at $\lambda 320.5$ mμ = 4434

Variation in optical density at $\lambda 320.5$ mμ = 0.005

% Variation in optical density at $\lambda 320.5$ mμ = ± 0.5 %

Table 12.23

Alkaloid salt : Quinidine sulphate

Evaluation of invarient point :

Table No.		Optical Density at (1)	(2)	Difference of (1) and (2)	Calculated Optical Density at
	pH	λ330 mμ	λ335 mμ		λ334 mμ
12.01	7.0	0.568	0.528	0.040	0.536
12.02	6.8	0.564	0.527	0.037	0.534
12.03	5.4	0.565	0.530	0.035	0.535
12.04	4.4	0.545	0.542	0.003	0.543
12.05	3.9	0.533	0.546	0.013	0.543
12.06	3.7	0.526	0.552	0.026	0.547
12.07	1.8	0.510	0.559	0.049	0.549
12.08	1.2	0.508	0.554	0.046	0.544

Average optical density at λ334 mμ = 0.539 m

Value of ϵ at λ334 mμ = 4733

Variation in optical density at λ334 mμ = 0.015

% Variation in optical density at λ334 mμ = ± 1.4 %

Table 12.24

Alkaloid salt : Cinchonine sulphate

Evaluation of invarient point :

Table No.	pH	Optical Density at (1) λ294 mμ	Optical Density at (2) λ296 mμ	Difference of (1) and (2)	Calculated Optical Density at λ294.5 mμ
12.09	6.6	0.601	0.570	0.031	0.593
12.10	6.1	0.602	0.570	0.032	0.594
12.11	4.4	0.610	0.582	0.028	0.603
12.12	4.0	0.591	0.604	0.013	0.594
12.13	3.7	0.586	0.613	0.027	0.593
12.14	3.6	0.589	0.622	0.033	0.597
12.15	3.4	0.585	0.624	0.039	0.595
12.16	3.2	0.582	0.626	0.044	0.593
12.17	1.8	0.577	0.633	0.056	0.591
12.18	1.2	0.578	0.637	0.059	0.593

Average optical density at λ294.5 mμ = 0.595

Value of ϵ at λ294.5 mμ = 4289

Variation in optical density at λ294.5 mμ = 0.012

% Variation in optical density at λ294.5 mμ = ±1.0 %

Table 12.25

Values of λ and ϵ for the invarient points of ultraviolet absorption spectra (figures 12.1 and 12.2) of cinchona alkaloid sulphates in aqueous solutions of pH about 1 to 7, adjusted by the addition of sulphuric acid or sodium hydroxide, at room temperature ($\sim$ 30°C).

Alkaloid salt	Wavelength in mμ	ϵ	
Quinine sulphate*	296.5	2452	± 1.1 %
	321.0	3974	± 1.3 %
	334.0	4235	± 1.4 %
Quinidine sulphate	296.5	2698	± 1.0 %
	320.5	4434	± 0.5 %
	334.0	4733	± 1.4 %
Cinchonine sulphate	294.5	4289	± 1.0 %
Cinchonidine sulphate*	294.5	4128	± 0.8 %

* Data for quinine sulphate and cinchonidine sulphate are from Shri.S.S.Kanhere of this laboratory.

Discussion :

The data (tables 12.19 and 12.20) together with the data of Shri S.S.Kanhere of this laboratory, indicate that the ultraviolet absorption spectra of each of the alkaloid sulphates can be, broadly divided into three groups : (a) pH 7-4.5, (b) pH 4.5-3.5 and (c) pH 3.5-1.0. The spectra of quinine and quinidine sulphates are similar but not the same ; the same applies to those of cinchonine and cinchonidine sulphates. The spectra of quinine and quinidine sulphates are distinctly different from those of cinchonine and cinchonidine sulphates.

For quinine and quinidine sulphates there are three invarient points, (tables 12.21 to 12.23 and 12.25) and for cinchonine and cinchonidine sulphates, there is one invarient point, (tables 12.24 and 12.25) where the extinction coefficient, ϵ , is independent of pH within ± 1.0 to 1.5 %.

These data (tables 12.19, 12.20 and 12.25) can permit the estimation of one alkaloid sulphate in dilute aqueous solution, in presence of sulphuric acid or in the absence of presence of other alkaloid sulphates studied, by suitable choice of experimental conditions.

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13.

THE SELECTIVITY COEFFICIENTS OF SULPHONIC ACID CATION EXCHANGE RESIN AMBERLYST-15 IN SULPHATE AND CHLORIDE SOLUTIONS : (1)

Introduction :

The cation exchange equilibria of univalent cations with sulphonic acid cation exchange resins in aqueous solution have been the subject of investigation of several workers. (2-29). In most of these studies chloride solutions have been used and the postulated theories have been applied with varying success. Since, there is no satisfactory method yet available for accurately predicting the selectivity coefficients, it was considered to be of interest to study the selectivity coefficients for sulphonic acid cation exchange resins with univalent cations in aqueous sulphate solution and to compare the results with those for univalent cinchona alkaloid cations in aqueous solution of cinchona alkaloid sulphates.

This study is concerned with the exchange equilibria of the recent sulphonic acid cation exchange resins Amberlyst - 15 with the aqueous sulphate and chloride solutions (∾ 0.04 N) at room temperature (∾ 30°C).

Experimental :

Materials : Resin used was the sulphonated styrene-divinylbenzene copolymer type sulphonic acid cation exchange resin Amberlyst - 15 (Rohm and Haas Co.), (this is further referred to as resin Am-15) of different particle sizes.

The chemicals used were of either A.R. or ~~of~~ C.P.grade.Distilled water was used.

Moisture and capacity of the resins (30,31):

The resin Am-15 was first soaked in methanol and then washed with distilled water, cycled thrice between sodium chloride and hydrochloric acid, regenerated with a large excess of hydrochloric acid, washed free of acid, filtered, air-dried, sieved and stored in a good container. A number of particles ($\sim$ 50 to 60) of resin were measured for the particle diameter, with a travelling microscope and the average value was taken as the average particle diameter, 'a' .

Moisture content was determined by heating weighed samples ($\sim$ 0.5 grams) of air-dried resin in clean, dry weighing bottles, in an oven (100 - 103°C) to a constant weight. % moisture content was then calculated.

For the estimation of the capacity of the resins, weighed samples ($\sim$ 0.5 gms.) of air-dried resins were contacted with 50 cc. of 1 N barium chloride solution in well-stoppered flasks with frequent shaking. After two to 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 (13.1) gives the obtained values for % moisture content and capacity of resin of different particle sizes.

Solutions :

The solutions of salts were prepared by dissolving known weights in distilled water to known volumes. The sulphate solutions were rechecked by sulphate estimation (as barium sulphate) and chloride solutions were by Mohr's method. The solutions were then suitably diluted ($\sim$ 0.04 N) and concentrations accurately calculated.

Determination of selectivity coefficients :

Weighed quantities of air-dry resins were contacted with known volumes of salt solutions ($\sim$0.04 N) in well stoppered flasks with frequent shaking at room temperature ($\sim 30^{\circ}C$). Preliminary work was carried out to find out the time, after which further exchange did not take place. After sufficiently more time than this, the solutions were analysed for acid liberated, by titration with standard sodium hydroxide solution.

The selectivity coefficient K_{H}^{M}, for the exchange reaction

$$\overline{H^+} + M^+ \rightleftharpoons \overline{M^+} + H^+$$

is given by

$$K_{H}^{M} = \frac{\left[\overline{M^+}\right]_e \left[H^+\right]_e}{\left[\overline{H^+}\right]_e \left[M^+\right]_e}$$

Where $\left[H^+ \right]_e$ and $\left[M^+ \right]_e$ denote the concentrations of hydrogen ions and alkali metal ions in gm. equivalents / litre, in aqueous solution at equilibrium,

and $\left[\overline{H^+} \right]_e$ and $\left[\overline{M^+} \right]_e$ denote the gm. equivalents of resin in the hydrogen form and in the alkali metal form, per litre of the solution, at equilibrium.

Hence the selectivity coefficient is given by

$$K^{M}_{H} = \frac{\left[H^+ \right]_e^2}{\left\{ \left[\overline{H^+} \right]_i - \left[H^+ \right]_e \right\} \left\{ \left[M^+ \right]_i - \left[H^+ \right]_e \right\}}$$

Where $\left[\overline{H^+} \right]_i$ denotes the gm. equivalents of resin in hydrogen form added initially, per litre of solution, and $\left[M^+ \right]_i$ denotes the initial concentration of cations M in aqueous solution, in gm, equivalents per litre.

Hence, by substituting the proper values, the selectivity coefficients were calculated.

Table 13.1

Capacity of cation exchange resin

Resin	a (mm)	Moisture (%)	Capacity	
			Meq. per gm. air-dry resin	Meq. per gm. oven-dry resin
Am-15	1.13	25.9	3.39	4.58
Am-15	0.84	25.4	3.42	4.58
Am-15	0.58	26.7	3.36	4.58
Am-15	0.37	23.5	3.51	4.58

Results :

Table 13.2

Exchange equilibrium between lithium chloride and resin Am-15 : $10^2 \left[M^+\right]_i$ = ~~4.00~~ 3.85

a (mm)	$10^2 \left[\bar{H}^+\right]_i$	$10^2 \left[H^+\right]_e$	$\bar{X}_M$	K^M_H
0.84	1.030	0.7868	0.764	0.83
	1.718	1.1550	0.672	0.88
	2.558	1.5050	0.588	0.92
	3.416	1.7860	0.523	0.95
	5.136	2.1990	0.428	0.99
	6.831	2.4980	0.366	1.07
	10.240	2.8730	0.280	1.15
0.58	1.011	0.7686	0.760	0.79
	1.683	1.1190	0.665	0.81
	2.521	1.4690	0.583	0.86
	3.366	1.7430	0.518	0.89
	5.039	2.1680	0.430	0.97
	6.717	2.4430	0.364	0.99
	10.100	2.8000	0.277	1.03
	13.440	3.1020	0.231	1.25

Table 13.3

Exchange equilibrium between sodium chloride and resin Am-15 : $10^2 [M^+]_i = 4.00$

a (mm)	$10^2 [\overline{H^+}]_i$	$10^2 [H^+]_e$	$\overline{X}_M$	K^M_H
0.84	1.054	0.8680	0.823	1.29
	1.752	1.3050	0.745	1.41
	2.630	1.7670	0.672	1.62
	3.496	2.1360	0.611	1.80
	5.242	2.6350	0.503	1.95
	6.997	2.9730	0.425	2.14
	10.490	3.3970	0.324	2.70
0.58	1.011	0.8373	0.828	1.28
	1.685	1.2830	0.762	1.51
	2.522	1.7300	0.686	1.66
	3.372	2.1000	0.623	1.82
	5.042	2.6680	0.517	2.01
	6.717	2.9650	0.441	2.26
	10.110	3.3500	0.331	2.55
	13.440	3.5420	0.263	2.77

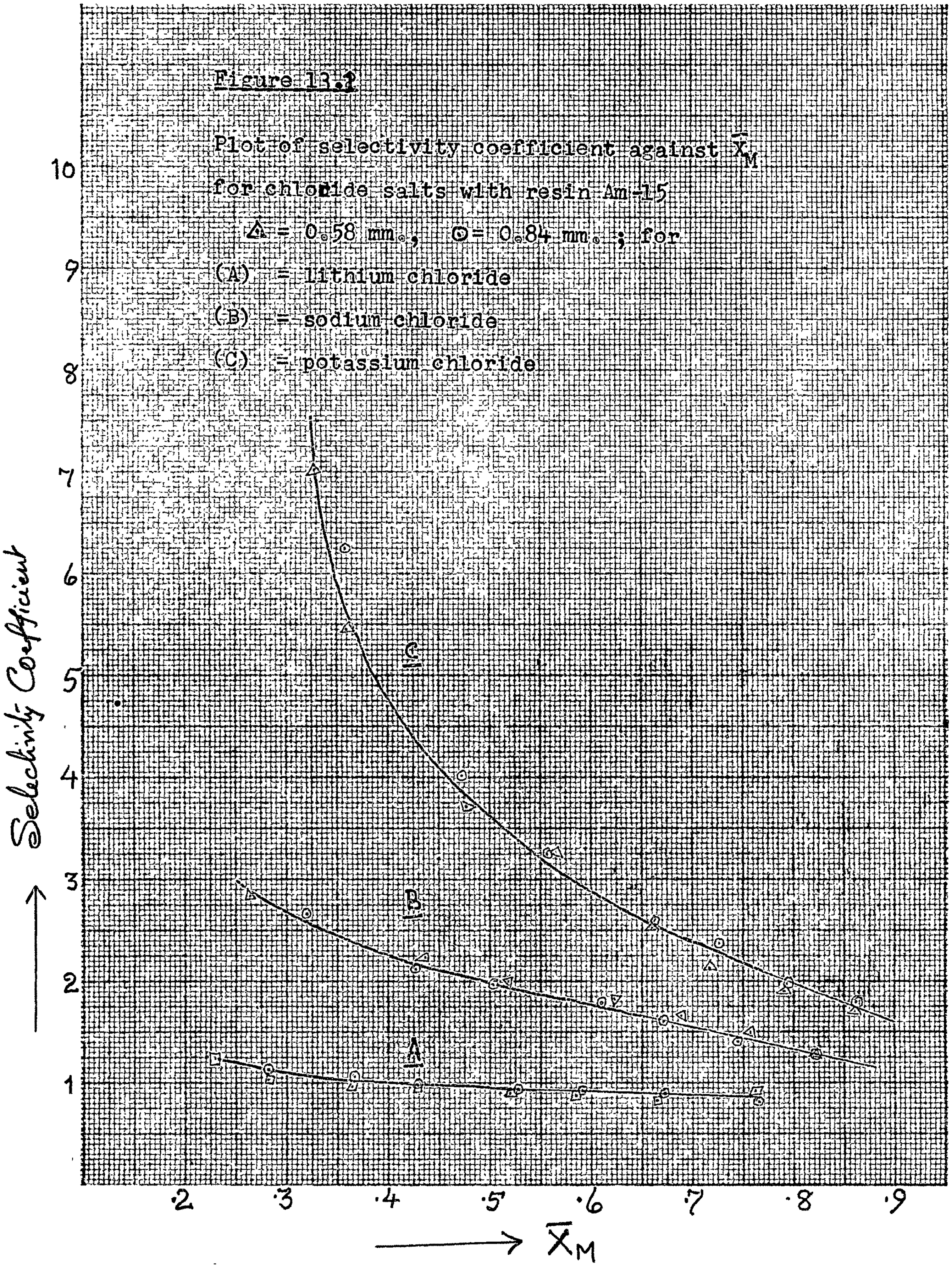

Figure 13.1

Plot of selectivity coefficient against $\bar{X}_M$ for chloride salts with resin Am-15

△ = 0.58 mm., ⊙ = 0.84 mm. ; for

(A) = lithium chloride

(B) = sodium chloride

(C) = potassium chloride

Table 13.4

Exchange equilibrium between potassium chloride and resin Am-15 : $10^2 \left[M^+\right]_i = 4.00$

a (mm)	$10^2 \left[\overline{H^+}\right]_i$	$10^2 \left[H^+\right]_e$	$\overline{X}_M$	K^M_H
0.84	1.035	0.8932	0.863	1.81
	1.708	1.3550	0.794	1.97
	2.564	1.8740	0.731	2.39
	3.430	2.2730	0.663	2.59
	5.116	2.8730	0.561	3.27
	6.885	3.2590	0.475	3.99
	10.250	3.6720	0.358	6.27
0.58	1.012	0.8718	0.862	1.73
	1.685	1.3310	0.790	1.88
	2.521	1.8190	0.721	2.07
	3.366	2.2380	0.665	2.52
	5.046	2.8550	0.566	3.25
	6.723	3.2120	0.478	3.73
	10.080	3.6240	0.359	5.42
	13.450	3.7880	0.282	7.04

Table 13.5

Exchange equilibrium between lithium sulphate and resin Am-15 : $10^2 \left[\bar{M}^+\right]_i = 4.10$

a (mm)	$10^2 \left[\bar{H}^+\right]_i$	$10^2 \left[H^+\right]_e$	$\bar{X}_M$	K^M_H
0.84	1.035	0.8494	0.821	1.19
	1.710	1.2800	0.749	1.35
	2.564	1.6920	0.660	1.36
	3.417	2.0110	0.589	1.38
	5.126	2.4850	0.485	1.45
	6.831	2.7850	0.408	1.46
	10.230	3.1730	0.310	1.54
	13.670	3.4470	0.252	1.77
0.58	1.007	0.8439	0.838	1.34
	1.680	1.2630	0.752	1.35
	2.521	1.6670	0.662	1.34
	3.359	1.9760	0.588	1.33
	5.058	2.4570	0.486	1.41
	6.717	2.7580	0.411	1.43
	10.110	3.1300	0.309	1.44
	13.450	3.3770	0.251	1.56

Table 13.6

Exchange equilibrium between sodium sulphate and resin Am-15 : $10^2 \left[M^+\right]_i = 3.99$

a (mm)	$10^2 \left[\overline{H^+}\right]_i$	$10^2 \left[H^+\right]_e$	$\overline{X}_M$	K^M_H
0.84	1.029	0.9188	0.886	2.45
	1.714	1.4050	0.820	2.46
	2.564	1.8990	0.741	2.58
	3.423	2.2980	0.671	2.76
	5.112	2.8350	0.555	2.80
	6.828	3.1850	0.466	3.43
	10.250	3.5470	0.346	4.17
	13.660	3.7220	0.273	5.07
0.58	1.006	0.8855	0.880	2.10
	1.679	1.3660	0.813	2.27
	2.518	1.8600	0.739	2.46
	3.366	2.2510	0.669	2.60
	5.038	2.8000	0.556	2.93
	6.717	3.1440	0.468	3.24
	10.080	3.4860	0.346	3.61
	13.440	3.6790	0.274	4.36

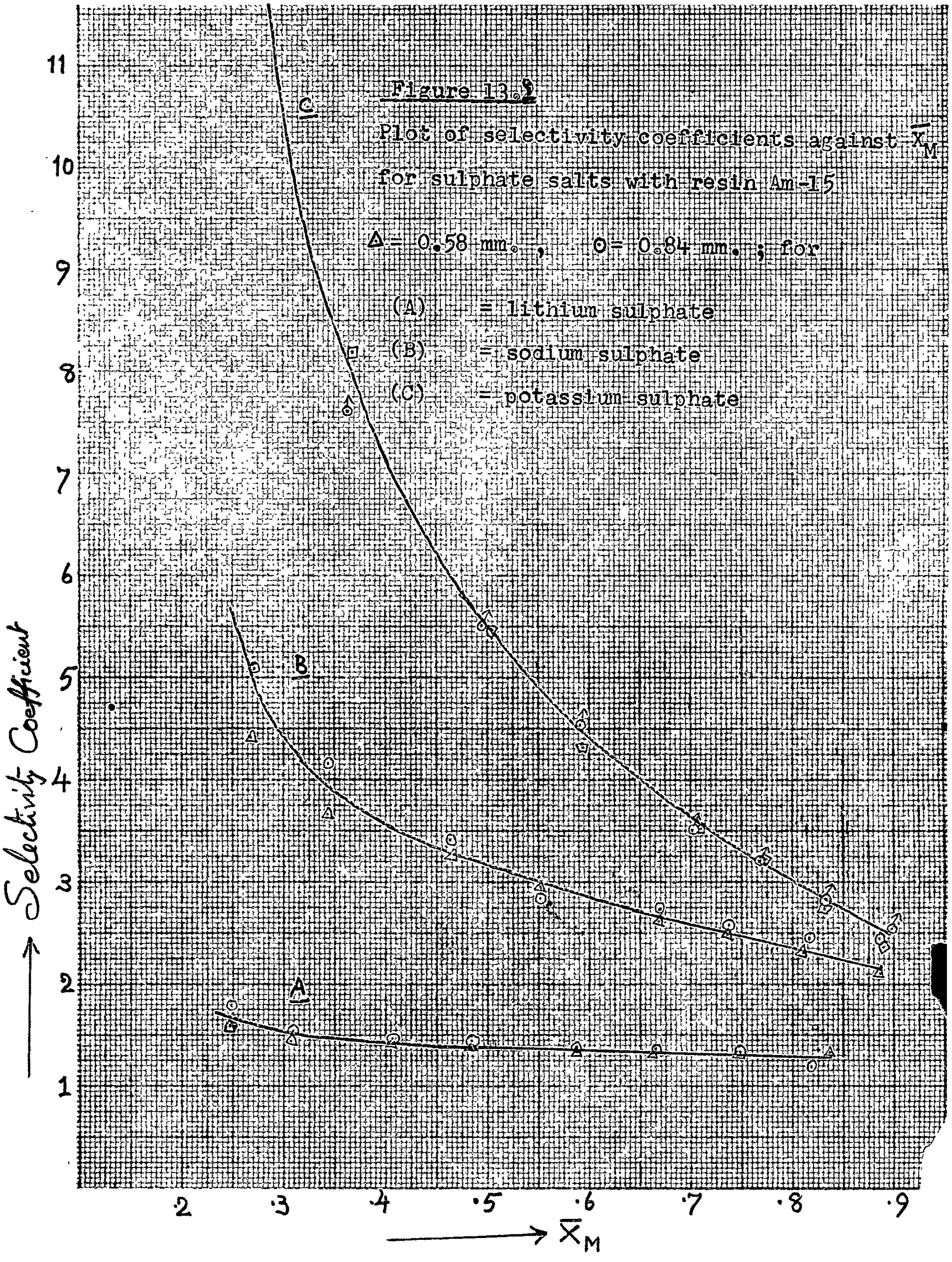

Figure 13.2

Plot of selectivity coefficients against $\overline{X}_M$ for sulphate salts with resin Am-15

△ = 0.58 mm. , ⊙ = 0.84 mm. ; for

(A) = lithium sulphate

(B) = sodium sulphate

(C) = potassium sulphate

Table 13.7

Exchange equilibrium between potassium sulphate and resin Am-15 : $10^2 \left[M^+\right]_i = 4.00$

a (mm)	$10^2 \left[\overline{H^+}\right]_i$	$10^2 \left[H^+\right]_e$	$\overline{X}_M$	K^M_H
0.84	1.023	0.9181	0.898	2.60
	1.713	1.4300	0.835	2.81
	2.563	1.9670	0.768	3.19
	3.420	2.3980	0.701	3.50
	5.130	3.0350	0.592	4.54
	6.834	3.3970	0.497	5.54
	10.230	3.7220	0.364	7.58
	13.700	3.8960	0.284	14.47
0.58	1.001	0.8923	0.891	2.35
	1.682	1.4070	0.837	2.77
	2.520	1.9490	0.774	3.24
	3.359	2.3740	0.707	3.51
	5.049	2.9920	0.593	4.30
	6.720	3.3770	0.502	5.45
	10.070	3.7340	0.370	8.18
	13.440	3.8710	0.288	11.86

Table 13.8

Values of X for resin Am-15 (1)

$\bar{X}_M$	0.40	0.50	0.60	0.70	0.80
K^{Li}_{H}	1.42	1.40	1.38	1.36	1.35
X	7.00	6.50	7.40	13.20	12.00
K^{Na}_{H}	3.40	3.12	2.85	2.57	2.30
X	-	11.00	10.00	8.80	6.50
K^{K}_{H}	7.45	5.40	4.22	3.60	3.00
X	14.50	11.40	9.90	9.00	7.00

Discussion :

According to complete Donnan theory, the selectivity coefficient, K_H^M is given by

$$\ln K_H^M = \ln (\gamma_M / \gamma_H) - \ln (\bar{\gamma}_M / \bar{\gamma}_H) - \pi (\bar{V}_H - \bar{V}_M)/RT \quad (1)$$

where γ_M , γ_H denote the activity coefficients of alkali metal ion and hydrogen ions in solution, $\bar{\gamma}_M$, $\bar{\gamma}_H$ denote the activity coefficients of alkali metal ions and hydrogen ions in the resin phase, π denotes the internal swelling pressure and $\bar{V}_M$, $\bar{V}_H$ denote the partial molar volume of alkali metal ions and hydrogen ions in the resin.

The change in the selectivity coefficient, should therefore, be considered to be due to the change in one or more of the three terms in equation (1).

Effect of nonexchanging ions :

The comparison of figures (13.1 and 13.2) indicates that the selectivity coefficients for lithium-hydrogen, sodium-hydrogen and potassium-hydrogen exchange for Am-15 are substantially higher when the nonexchanging ion is sulphate than when it is chloride. The order of the selectivity coefficient is mostly Li < H < Na < K in the chloride solution, while it is H < Li < Na < K in the sulphate solution. This is to be attributed to the changes in the first term of equation (1) and there may also be some contribution by changes in second term of equation (1), due to sorption of small quantities of electrolyte by the resin due to the Donnan membrane effect.

Effect of the mole fraction, $\overline{X}_M$, of the counter ion in the resin phase :

Figures (13.1 and 13.2) indicate that for lithium-hydrogen, sodium-hydrogen and potassium-hydrogen exchange in sulphate solution and chloride solution, the selectivity coefficient either decreases with increase in $\overline{X}_M$ or decreases with increase in $\overline{X}_M$ over some range and is practically constant over some range. This effect is to be attributed to the changes in the first two terms of equation (1). Small contribution may also be attributed to some volume changes in the resin particle as $\overline{X}_M$ increases. Another contributory reason may be that the resin, may be, to some extent, micro-heterogeneous (20). The competing counter ions M^+ , would be taken up by the different regions to different extents. For smaller values of $\overline{X}_M$, the counter ions would be mostly taken up, by regions having greater affinity for them ; for larger values of $\overline{X}_M$, the counter ions would be taken up relatively to greater extent, by regions having lower affinity for them.

Effect of 'a' and structure :

Figures (13.1 and 13.2) indicate that for resin Am-15 the selectivity coefficients are essentially independent of 'a' . It is also observed from the calculations that for some values of the selectivity coefficients (1), there are no corresponding values of the relative degree of crosslinking, X, while other values obtained for X, vary significantly with $\bar{X}_M$ (table 13.8). This means that the resin Am-15 is structurally of different type than the conventional gel type resins though this is also styrene divinylbenzene copolymer type sulphonic acid cation exchange resin (1).

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14

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 thegreater affinity for the resin of the trimethyl-n-amylammonium ion than of the isomeric tetraethylammonium 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. phenylbenzyldimethylammonium 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 determining 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 crosslinking 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 tetramethylammonium 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 polyvinylpyridine which was 40 % quaternized with dodecylbromide and crosslinked with 1 % DVB has been used and its selectivity against bromide and chloride ions has been investigated.

Yakhontova (7) observed that the streptomycine 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 sodiumdodecyl sulphate on an anion exchange resin (Dowex 1 X1). 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 sodiumdodecyl 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 crosslinking 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.

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15

EQUILIBRIUM STUDIES OF CINCHONA ALKALOID SULPHATES WITH SULPHONIC ACID RESINS :

Introduction :

Detailed study of equilibria between sulphonic acid cation exchange resins and cinchona alkaloid sulphates (Chapter 9) 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 crosslinking of the resin, (2) the ratio of resin concentration to alkaloid sulphate concentration, (3) particle size and (4) molecular size, on the equilibria of sulphonic acid cation exchange resins and two of the cinchona alkaloid sulphates - quinidine sulphate and cinchonine sulphate. ~~The~~ Similar studies with ~~the~~ quinine sulphate and cinchonidine sulphate were carried out by S.S.Kanhere (1).

Experimental :

Resins (2) : Resins used were sulphonated styrene divinylbenzene copolymer type sulphonic acid cation exchange resins of different degree of crosslinking, X. These included Dowex 50 resins (Dow Chemical Co.) of X = 1 , 2, 4, 8, 12 and 16 (these are further referred to as resins X1, X2, X4, X8, X12 and X16), sample of a similar resin (from Permutit Co., London) of X = 20 (this is further referred to as resin X20), Amberlite resins

(Rohm and Haas Co.) Amberlite IR-120, Amberlite IR-200 and Amberlyst-15 (these are further referred to as resins IR-120, IR-200 and Am-15).

Moisture and capacity of the resins : (Chapter 13)

Table 15.01 gives the values.

Chemicals (3) : (Chapter 12) Quinine sulphate (Government Quinine Factory, Madras, India) was crystallized eight times and cinchonidine sulphate (Fluka, AG, Switzerland) was crystallized four times from hot water.

Solutions and procedure : The stock solution of the alkaloid sulphate (as $Q_2H_2SO_4.nH_2O$, where Q denotes the alkaloid base) was first prepared in distilled water and its concentration in gram equivalents (half the molecular weight of the alkaloid sulphate) per litre was evaluated by sulphate estimation (as barium sulphate).

To study the exchange equilibria of the alkaloid sulphates with the resins, weighed amounts of air-dry resins were placed in contact with suitable volumes of the aqueous alkaloid sulphate solution of known concentration, in well stoppered flasks, with frequent shaking at room temperature ($\sim 30^{o}C$). Preliminary work was carried out to find out the approximate time within which equilibrium for different resins with aqueous solution of alkaloid sulphate was attained. After sufficiently more time than this (about 4 days to 25 days, depending on X), the solutions were analysed for alkaloid sulphate concentration in the equilibrium mixture by taking out a known volume from each flask and diluting suitably with distilled water. Optical density of this solution was measured at the invarient wavelength (3). The total sulphate in the equilibrium mixture was estimated gravimetrically for each resin (from X1 to X20). The total sulphate thus estimated showed that no measurable change in the sulphate concentration occured when estimated initially and after the equilibrium. This indicated that, on the whole, the alkaloid sulphate molecules were not sorbed as such to a measurable extent. Preliminary work also indicated that the values of P_{Ro} at room temperature, 35°C and 45°C did not differ significantly.

Nomenclature :

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

W = weight of air-dry resin taken in grams,

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

C = capacity of the resin in meq.per gram of air-dry resin,

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

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

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

R = $[\overline{H}]_i / [A]_i$ = the ratio of the initial concentration (in meq./litre) of the resin to the initial concentration of the alkaloid sulphate,

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

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

Results :

Table 15.01

Capacity of cation exchange resins

Resin	a (mm)	Moisture (%)	Capacity	
			Meq. per gm. air-dry resin	Meq. per gm. oven-dry resin.
X1	0.215	20.3	4.18	5.24
X2	0.215	20.4	4.14	5.20
X4	0.215	24.0	3.89	5.12
X8	0.215	27.0	3.72	5.09
X12	0.215	26.0	3.73	5.04
X16	0.215	24.7	3.54	4.70
X20	0.215	16.8	3.69	4.43
IR-120	0.84	30.0	3.47	4.96
IR-120	0.58	30.8	3.43	4.96
IR-120	0.37	29.9	3.48	4.96
IR-120	0.23	28.5	3.55	4.96
IR-200	1.13	27.2	3.48	4.78
IR-200	0.84	28.8	3.40	4.78
IR-200	0.58	28.1	3.44	4.78
IR-200	0.37	25.5	3.56	4.78
Am-15	1.13	25.9	3.39	4.58
Am-15	0.84	25.4	3.42	4.58
Am-15	0.58	26.7	3.36	4.58
Am-15	0.37	23.5	3.51	4.58

Table 15.02

Equilibrium of aqueous quinidine sulphate with resins X1 to X4.

Resin	$[\overline{H}]_i$	$[A]_i$	$[\overline{A}]_e$	R	P_A	P_R
X1	0.8531	2.000	0.4854	0.4263	24.27	56.93
	1.6980	2.000	0.8728	0.8487	43.64	51.41
	2.1330	2.000	1.0530	1.0660	52.65	49.40
	2.9220	2.000	1.3738	1.4610	68.69	47.03
	3.6150	2.000	1.6438	1.8070	82.19	45.50
X2	1.6830	2.000	0.9018	0.8415	45.09	53.58
	2.1420	2.000	1.0802	1.0710	54.01	50.42
	3.3340	2.000	1.6178	1.6670	80.89	48.53
	4.1780	2.000	1.9310	2.0890	96.55	46.22
X4	1.2801	2.000	0.6066	0.6400	30.33	47.35
	1.9780	2.000	0.9506	0.9890	47.53	48.05
	2.5370	2.000	1.2185	1.2680	60.92	48.01
	3.8330	2.000	1.8020	1.9160	90.09	46.98

Table 15.03

Equilibrium of aqueous quinidine sulphate with resins X8 to X20

Resin	$\left[\overline{H}\right]_i$	$\left[A\right]_i$	$\left[\overline{A}\right]_e$	R	P_A	P_R
X8	0.9111	2.000	0.3766	0.4555	18.83	41.33
	1.3850	2.000	0.5580	0.6925	27.90	40.31
	1.8260	2.000	0.7004	0.9130	35.03	38.38
	2.7650	2.000	1.0550	1.3825	52.73	38.14
	3.6410	2.000	1.4370	1.8205	71.87	39.49
X12	2.8650	2.000	0.7062	1.4320	35.31	24.64
	4.1260	2.000	1.0250	2.0630	51.26	24.85
	5.7240	2.000	1.3950	2.8620	69.77	24.37
	7.2160	2.000	1.7920	3.6080	89.59	24.82
X16	4.2600	2.000	0.7292	2.1300	36.46	17.12
	6.3900	2.000	1.1210	3.1950	56.05	17.54
	7.7560	2.000	1.5450	3.8780	77.23	18.10
	10.6500	2.000	1.7842	5.3250	89.21	16.74
X20	2.7730	2.000	0.1258	1.3865	6.29	4.537
	5.5340	2.000	0.2722	2.7670	113.61	4.918
	8.1160	2.000	0.4712	4.0580	23.56	5.806
	11.0900	2.000	0.7050	5.5450	35.25	6.354

Table 15.04

Equilibrium of aqueous quinidine sulphate with resins IR-120 and IR-200 of different particle diameters.

a (mm)	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
0.37	2.662	2.000	0.9510	1.311	47.55	36.26
(IR-120)	3.841	2.000	1.3990	1.920	69.93	36.41
	5.053	2.000	1.8750	2.526	93.73	37.10
	5.248	2.000	1.9840	2.624	99.81	37.80
0.58	2.765	2.000	0.8286	1.3820	41.43	30.03
(IR-200)	4.136	2.000	1.2270	2.0680	61.33	29.66
	5.487	2.000	1.5940	2.7430	79.68	29.04
	6.898	2.000	1.9230	3.4490	96.17	28.05
0.37	2.895	2.000	0.8824	1.4470	44.12	30.48
(IR-200)	4.331	2.000	1.3100	2.1650	65.48	30.24
	5.744	2.000	1.6760	2.8720	83.82	29.18
	7.186	2.000	1.9690	3.5930	98.47	27.40

Table 15.05

Equilibrium of aqueous quinidine sulphate with Am-15 of different particle diameters.

a (mm.)	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
1.13	2.045	1.998	0.5853	1.023	29.29	28.63
	2.548	1.998	0.7478	1.276	37.43	29.36
	3.407	1.998	0.9819	1.705	49.15	28.82
	4.244	1.998	1.2240	2.124	61.24	28.82
	5.090	1.998	1.4650	2.548	73.33	28.78
0.84	2.060	1.998	0.6080	1.031	30.43	29.51
	2.576	1.998	0.7630	1.289	38.19	29.61
	3.431	1.998	0.9856	1.717	49.33	28.74
	4.294	1.998	1.2350	2.149	61.80	28.76
	5.132	1.998	1.4650	2.568	73.33	28.55
0.58	2.021	1.998	0.6501	1.012	32.54	32.17
	2.533	1.998	0.8097	1.268	40.52	31.96
	3.372	1.998	1.0650	1.688	53.30	31.58
	4.212	1.998	1.320	2.108	66.07	31.34
	5.024	1.998	1.575	2.514	78.84	31.35
0.37	2.109	1.998	0.6661	1.055	33.34	31.59
	2.638	1.998	0.8296	1.320	41.53	31.45
	3.522	1.998	1.092	1.762	54.70	31.03
	4.398	1.998	1.368	2.202	68.47	31.11
	5.247	1.998	1.615	2.626	80.85	30.79

Table 15.06

Equilibrium of aqueous cinchonine sulphate with resins X1 to X8

Resin	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
X1	1.347	1.998	0.7702	0.6737	38.55	57.18
	1.692	1.998	0.9147	0.8470	45.78	54.04
	2.095	1.998	1.078	1.0477	53.98	51.46
	3.388	1.998	1.683	1.6960	84.22	49.66
	3.997	1.998	1.943	1.999	97.23	48.60
X2	1.275	1.998	0.7197	0.6381	36.02	56.49
	1.592	1.998	0.8666	0.7969	43.37	54.44
	1.968	1.998	1.0280	0.9849	51.44	52.23
	3.181	1.998	1.593	1.5920	79.77	50.10
	3.959	1.998	1.943	1.982	97.25	49.04
X4	1.427	1.998	0.7752	0.7144	38.80	54.34
	2.207	1.998	1.141	1.1050	57.11	51.71
	2.831	1.998	1.434	1.4170	71.80	50.67
	4.266	1.998	1.962	2.1350	98.19	45.99
X8	1.421	1.998	0.6234	0.7106	31.20	43.86
	2.225	1.998	0.9988	1.1130	50.00	44.88
	2.828	1.998	1.2740	1.4160	63.74	45.03
	3.719	1.998	1.6590	1.860	83.03	44.60
	5.562	1.998	1.9720	2.783	98.68	35.45

Table 15.07

Equilibrium of aqueous cinchonine sulphate with resins X12 to X20

Resin	$[\overline{H}]_i$	$[A]_i$	$[\overline{A}]_e$	R	P_A	P_R
X12	3.003	1.998	0.8085	1.5030	40.48	26.93
	4.307	1.998	1.1840	2.1550	59.29	27.50
	5.992	1.998	1.6810	2.9980	84.10	28.04
	7.536	1.998	1.9660	3.7690	98.42	26.10
	9.306	1.998	1.9760	4.6060	98.91	21.22
X16	4.267	1.998	0.9074	2.1340	45.41	21.26
	6.374	1.998	1.3890	3.1890	69.52	21.79
	8.521	1.998	1.8490	4.2670	92.53	21.70
X20	2.776	1.998	0.1348	1.3890	6.747	4.859
	5.534	1.998	0.3611	2.7690	18.07	6.52
	8.137	1.998	0.6186	4.0720	30.96	7.60
	11.06	1.998	1.0030	5.5400	50.23	9.07

Table 15.08

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

a (mm.)	$[\overline{H}]_i$	$[A]_i$	$[\overline{A}]_e$	R	P_A	P_R
0.58	1.918	1.914	0.8648	1.002	45.19	45.09
	2.849	1.914	1.2960	1.489	67.72	45.48
	3.691	1.914	1.6770	1.929	87.62	45.43
0.37	1.893	1.914	0.8288	0.9893	43.31	43.77
	2.757	1.914	1.2700	1.4400	66.34	46.06
	3.620	1.914	1.6890	1.8910	88.24	46.66

Table 15.09

Equilibrium of aqueous cinchonine sulphate with resin IR-200 of different particle daimeters.

a (mm)	$[\overline{H}]_i$	$[A]_i$	$[\overline{A}]_e$	R	P_A	P_R
0.58	2.153	1.998	0.7632	1.077	38.19	35.45
	2.885	1.998	1.003	1.443	50.23	34.78
	4.321	1.998	1.446	2.163	72.41	33.48
	5.732	1.998	1.825	2.868	91.33	31.84
0.37	2.059	1.998	0.6981	1.032	34.93	33.90
	2.751	1.998	0.9196	1.377	46.03	33.44
	4.138	1.998	1.3530	2.071	67.70	32.69
	5.492	1.998	1.7450	2.748	87.34	31.78

Table 15.10

Equilibrium of aqueous cinchonine sulphate with resin Am-15 of different particle diameters.

a (mm.)	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_e$	R	P_A	P_R
1.13	2.554	1.914	0.9031	1.335	47.19	35.36
	3.423	1.914	1.1790	1.788	61.59	34.43
	4.279	1.914	1.4520	2.236	75.86	33.93
	5.073	1.914	1.6890	2.651	88.24	33.29
0.84	2.604	1.914	0.9078	1.361	47.43	34.86
	3.447	1.914	1.1790	1.801	61.59	34.19
	4.257	1.914	1.4320	2.224	74.85	33.65
	5.148	1.914	1.7180	2.690	89.74	33.36
0.58	2.519	1.914	0.8839	1.316	46.18	35.11
	3.399	1.914	1.1600	1.776	60.57	34.10
	4.199	1.914	1.4160	2.194	73.98	33.72
	5.035	1.914	1.685	2.631	88.00	33.45
0.37	2.644	1.914	0.9294	1.381	48.56	35.14
	3.522	1.914	1.214	1.840	63.46	34.48
	4.417	1.914	1.497	2.308	78.23	33.90
	5.300	1.914	1.763	2.770	92.12	33.27

Figure 15.1

Plot of P_R against $(100-P_A)$ for :(Tables 15.02 and 15.06)

A = quinidine sulphate with X2

B = cinchonine sulphate with X1

C = cinchonine sulphate with X2

D = cinchonine sulphate with X4

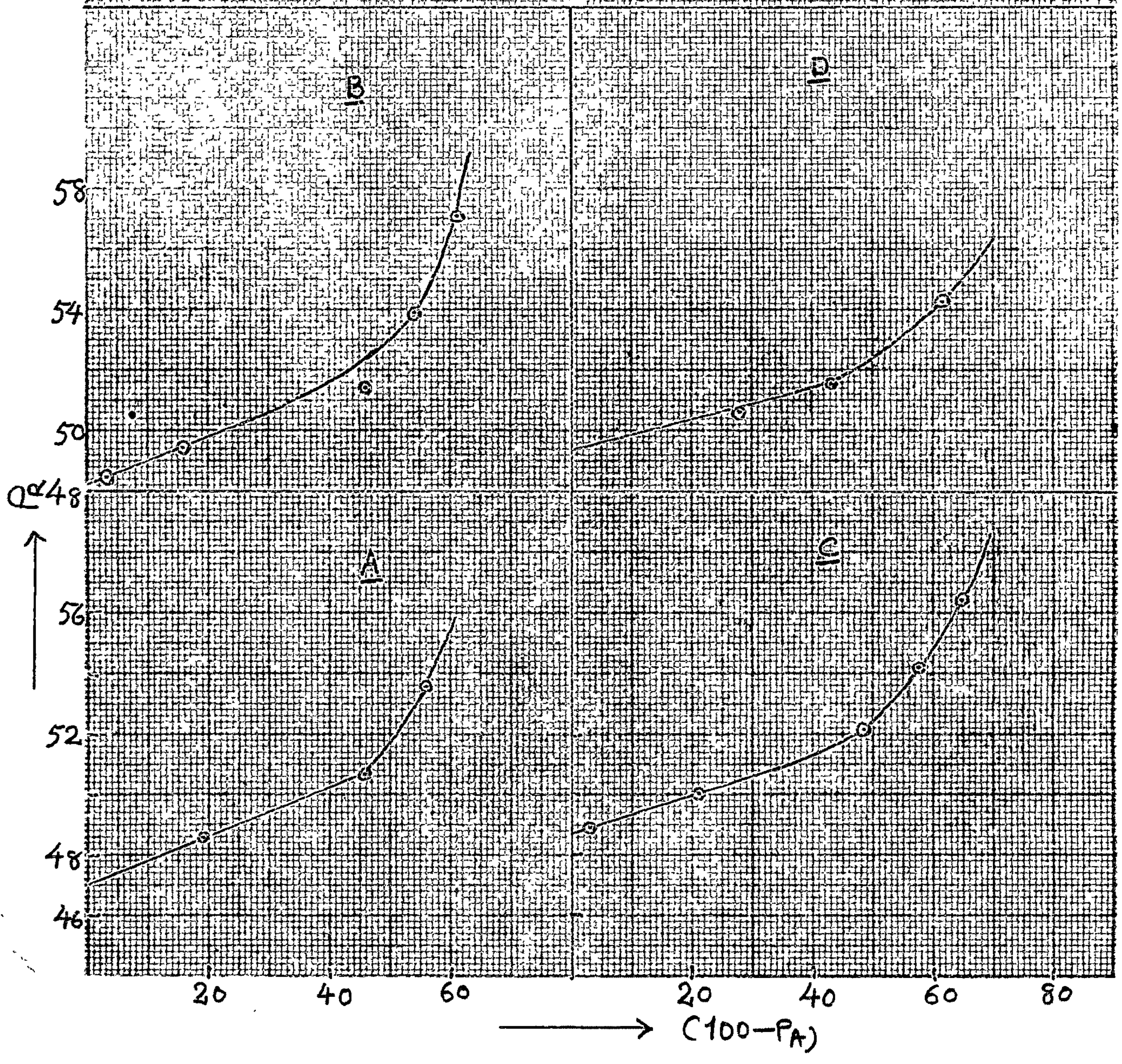

Table 15.11

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 (15.1), when extrapolated to (100-P_A) = zero, marked with dots.

Resin	Quinine* sulphate	Quinidine sulphate	Cinchonine sulphate	Cinchonidine* sulphate
X1	48.3	47.2	48.3	48.7
X2	48.2	47.0	48.8	48.4
X4	49.4	47.8	49.5	49.5
X8	40.0	39.5	44.6	45.2
X12	25.5	24.8	27.4	29.2
X16	18.2	17.4	21.6	22.3
X20	5.9	5.7	7.7	7.5

* Data taken from the Ph. D. Thesis of Shri S. S. Kanhere .

Table 15.12

Average values of P_R for the four alkaloid sulphates with resins IR-120, IR-200 and Am-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
Am-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 Ph. D. Thesis of Shri S. S. Kanbare.

Discussion :

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 resin particle is placed in the solution of an electrolyte, ion exchange occurs in equivalent amounts and after some time a state of equilibrium is reached. The calculated selectivity coefficient is either fairly constant or varies within relatively narrow limits for simple monovalent cations. The selectivity coefficients for alkali metal ions with resins in hydrogen form in sulphate solutions were described earlier (2). When similar calculations are carried out for exchange in solutions of the two cinchona alkaloid sulphates, quinidine sulphate and cinchonine sulphate studied, with resins in the hydrogen form, the selectivity coefficients were found to vary rather widely. However, the calculated values of P_R (Tables15.02 to 15.10) were either fairly constant or varied within relatively narrow limits when R or P_A was varied. This is a significant difference in the exchange behaviour of the simple alkali metal cations and these organic cations. The plausible assumption may be made that the uptake of such organic cations or bases from solution by the resin takes place by two mechanisms : exchange mechanism and (molecular) sorption mechanism (4,5). The exchange for the cation $\overset{+}{QH}$ where Q is the organic alkaloid base, is postulated as

$$HR + QH^{+} \longrightarrow RQH + H^{+}$$

However even for the most swollen or porous resin, all the replacable hydrogen ions in the resin phase are not exchanged due to relatively large molecular size of the exchanging species as compared to the overall spacing between the ionogenic groups in the swollen resin ; hence the percent of the replacable hydrogen ions actually exchanged is considerably below 100. The reverse reaction

$$RQH + H^{+} \longrightarrow HR + QH^{+}$$

is considered to be negligible in the absence of added hydrogen ions due to the operation of nonexchange interactions. The sorption mechanism is postulated as

$$QH^{+} + H_2O \rightleftharpoons Q + H_3O^{+}$$

$$Resin + Q \longrightarrow Resin.\ Q.$$

The uptake of $\overset{+}{QH}$ by sorption mechanism by the resin is not considered because of the observation that the sulphate ion concentration in the solution, initially and after equilibrium, was practically unchanged as studied in the 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 with one another and with the polar groups of the solute. The sorption of the solute for sulphonic acid resins decreases with decrease in the equilibrium concentration of the solute in the solution and increase in X of the resin.

From the observed values of P_R, the contribution due to exchange mechanism was calculated by plotting P_R against (100 - P_A) and obtaining the value of P_R at (100 -P_A) equal to zero, by extrapolating the plot (Figure 15.1) ; this value of P_R is denoted hereafter by P_{Ro} (Tables 15.11 and 15.12). It should be reasonable to assume that at, (100 - P_A) equal to zero, the contribution due to sorption mechanism is zero, since then the concentration of the solute in the external solution at equilibrium is zero. The value of (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 results (Tables 15.02 to 15.07) may be considered. For resin X1 which, in the swollen state is highly porous, as the degree of crosslinking is low, the values of P_{Ro} for the four alkaloid sulphates are given in Tables (15.11. and 15.12). The difference (P_R - P_{Ro}) is the contribution due to the sorption mechanism and this increases with increase in the equilibrium concentration of organic cations (and hence the base) in the external solution or with decrease in P_A. For the resin X2, similar remarks hold. The difference (P_R - P_{Ro}) is the contribution due to sorption mechanism and is less than that for resin X1, this decrease being due to the increase in X.

For the resin X4, the contribution due to the sorption mechanism is negligible for quinidine sulphate and is to a lesser extent than that for resin X2 for cinchonine sulphate. For quinidine 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 (X1, X2 and X4), since the swelling is relatively large, the pore diameter could not be considered to be responsible for the decrease in the value of P_{Ro} from 100.

For the resin X8 the values of P_R for both quinidine sulphate and cinchonine sulphate solutions are practically independent of P_A or R. The average 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 relatively less than that given for the resins X1, X2 and X4. The decrease is more for quinidine sulphate than that for cinchonine sulphate. This decrease is to be attributed to the reduced pore size because of higher X. The higher value of P_{Ro} for cinchonine sulphate than that for quinidine sulphate is possibly due to the smaller molecular size of cinchonine than that of quinidine . For resins of higher degree of crosslinking (X12, X16, and X20) similar remarks 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 cinchonine sulphate than that for quinidine sulphate for each resin. The value of P_{Ro} decreases as X increases. It is observed that the decrease in the value of P_{Ro} when X increase from 8 to 12 and again from 16 to 20 is relatively more than the decrease in P_{Ro} for other increases in the value of X. This may be related to the shape and size of the exchanging species affecting their ability to diffuse into the resin as the pore diameter decreases with increasing X.

Similar studies were carried out with resins IR-120, IR-200 and Am-15 of different particle size (IR-120 : a = 0.58, 0.37 ; IR-200 : a = 0.84, 0.58, 0.37, 0.23 ; Am-15 : a = 1.13, 0.84, 0.58, 0.37). It was observed that the values of P_R were practically independent of 'a' and P_A . Tables (15.08 to 15.10) give the data for different values of 'a' for each of the three resins. The values of P_{Ro} are given in table 15.12. The resins X8, IR-120, IR-200 and Am-15 presumably have almost same value of X but IR-200 and Am-15 are considerably more porous than X8 and IR-120 ; hence the pore diameters for IR-200 and Am-15 are larger than those for IR-120 and X8. However the values of P_{Ro} for IR-200 and Am-15 are substantially less than those for IR-120 and X8. It may be that the overall spacing of the ionogenic groups is less for IR-200 and Am-15 than that for IR-120 and X8.

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16

EFFECT OF ADDED SULPHURIC ACID ON EQUILIBRIUM EXCHANGE OF CINCHONA ALKALOID SULPHATES WITH SULPHONIC ACID RESINS :

Introduction :

This chapter is concerned with the study of the effect of added sulphuric acid on equilibrium exchange of four cinchona alkaloid sulphates with sulphonic acid cation exchange resins.

Experimental : (Chapter 15)

To study the equilibria of cinchona alkaloid sulphates with different resins 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 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 ($\sim 30^{\circ}C$).

Nomenclature : (Chapter 15)

Results : (Tables 16.01 to 16.17)

Results :

Table 16.01

Equilibrium of resin X4 with aqueous cinchonine 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
$1.010\ N.10^{-3}$	0.3886	0.9819	0.2018	0.3958	20.54	51.91
	0.7865	0.9819	0.3954	0.8009	40.26	50.26
	1.1820	0.9819	0.5832	1.2040	59.39	49.32
$1.010\ N.10^{-2}$	0.3838	0.9601	0.2096	0.3997	21.83	54.62
	0.7637	0.9601	0.3922	0.7954	40.85	51.36
	1.1490	0.9601	0.5611	1.1980	58.45	48.82
	1.9450	0.9601	0.8734	2.0270	90.97	44.88
$1.010\ N.10^{-1}$	0.7879	0.9601	0.3674	0.8208	38.26	46.62
	1.5570	0.9601	0.6558	1.6220	68.31	42.12
	1.9600	0.9601	0.7989	2.0410	83.22	40.77
1.010 N	1.1600	0.9601	0.2930	1.2090	30.52	25.25
	1.5380	0.9601	0.3640	1.6020	37.91	23.67
	1.9380	0.9601	0.4215	2.0180	43.90	21.75

Table 16.02

Equilibrium of resin X8 with aqueous cinchonine 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
$1.010\ N.10^{-1}$	0.7243	0.9601	0.3098	0.7544	32.28	42.79
	1.1230	0.9601	0.4643	1.1690	48.37	41.35
	1.4980	0.9601	0.5962	1.5610	62.10	39.79
	1.8660	0.9601	0.7089	1.9440	73.84	37.98
1.010 N.	0.7411	0.9601	0.2220	0.7720	23.13	29.95
	1.4830	0.9601	0.3978	1.5440	41.44	26.83
	1.8630	0.9601	0.4744	1.9410	49.42	25.46

Table 16.03

Equilibrium of resin X4 with aqueous cinchonidine sulphate with added sulphuric acid of different concentrations.

Concentration of added H_2SO_4	$[\overline{H}]_i$	$[A]_i$	$[\overline{A}]_e$	R	p_A	p_R
$1.010\ N.10^{-3}$	0.7886	1.028	0.4172	0.7672	40.58	52.89
	1.1660	1.028	0.5948	1.1340	57.86	50.99
	1.5570	1.028	0.7750	1.5150	75.39	49.76
$1.010\ N.10^{-2}$	0.3909	1.028	0.1963	0.3803	19.10	49.99
	1.1840	1.028	0.5798	1.1520	56.40	48.99
	1.5550	1.028	0.7560	1.5130	73.53	48.61
	1.9440	1.028	0.9285	1.8910	90.33	47.77
$1.010\ N.10^{-1}$	0.7416	1.028	0.3307	0.7214	32.17	44.59
	1.1510	1.028	0.5104	1.1190	49.65	44.35
	1.5530	1.028	0.6722	1.5110	65.39	43.27
	1.9450	1.028	0.8172	1.8920	79.49	42.02
1.010 N.	0.8137	1.028	0.2036	0.7916	19.81	25.02
	1.1550	1.028	0.2744	1.1240	26.69	23.74
	1.5480	1.028	0.3486	1.5060	33.91	22.51
	1.9320	1.028	0.4194	1.8790	40.80	21.71

Table 16.04

Equilibrium of resin X8 with aqueous cinchonidine sulphate with added sulphuric acid of different concentrations

Concentration of added H_2SO_4	$\left[\overline{H}\right]_i$	$\left[A\right]_i$	$\left[\overline{A}\right]_e$	R	P_A	P_R
$1.010\ N.10^{-1}$	0.3951	1.028	0.1701	0.3843	16.55	43.06
	1.1510	1.028	0.4673	1.1190	45.45	40.61
	1.5380	1.028	0.6087	1.4960	59.21	39.58
	1.9360	1.028	0.7513	1.8840	73.08	38.79
1.010 N.	0.7973	1.028	0.2169	0.7756	21.10	27.20
	1.1600	1.028	0.3116	1.1280	30.31	26.86
	1.5450	1.028	0.3942	1.5030	38.34	25.52
	1.9340	1.028	0.4841	1.8810	47.09	25.03

Table 16.05

Equilibrium of resin IR-200 (a = 0.58 mm.) 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
$1.048\ N.10^{-3}$	0.6197	0.9391	0.1984	0.6600	21.12	32.00
	1.2380	0.9391	0.3870	1.3180	41.21	31.27
	1.7200	0.9391	0.5347	1.8310	56.94	31.10
	2.2020	0.9391	0.6747	2.3440	71.85	30.65
	2.7300	0.9391	0.8224	2.9070	87.58	30.13
$1.048\ N.10^{-2}$	0.6163	0.9391	0.1808	0.6563	19.26	29.34
	1.7220	0.9391	0.4997	1.8330	53.21	29.02
	2.1910	0.9391	0.6241	2.3320	66.46	28.49
	2.7350	0.9391	0.7759	2.9130	82.62	28.36
$1.048\ N.10^{-1}$	1.2380	0.9391	0.3130	1.3180	33.34	25.28
	1.7360	0.9391	0.4375	1.8480	46.59	25.21
	2.2020	0.9391	0.5405	2.3440	57.55	24.56
	2.6010	0.9391	0.6339	2.7700	67.50	24.37
1.048 N.	1.5220	0.9391	0.2566	1.6210	27.33	16.87
	2.0680	0.9391	0.3423	2.2030	36.44	16.55
	3.8920	0.9391	0.5950	4.1450	63.36	15.29

Table 16.06

Equilibrium of resin Am-15 (a = 0.58 mm.) 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
1.048 N.10^{-1}	1.2150	0.9391	0.4375	1.2940	46.59	25.92
	1.6890	0.9391	0.5483	1.7980	58.38	25.90
	2.7040	0.9391	0.6747	2.8780	71.85	24.96
1.048 N.	1.4890	0.9391	0.2644	1.5860	28.16	17.75
	2.7130	0.9391	0.4433	2.8890	47.21	16.34
	3.3720	0.9391	0.5347	3.5910	56.94	15.86

Table 16.07

Equilibrium of resin IR-200 (a = 0.58 mm.) 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
$1.048\ N.10^{-3}$	1.2310	0.9596	0.3704	1.2830	38.60	30.09
	1.7090	0.9596	0.5064	1.7800	52.79	29.65
	2.2020	0.9596	0.6525	2.2920	68.00	29.64
	2.7380	0.9596	0.7945	2.8540	82.79	29.01
$1.048\ N.10^{-2}$	1.2310	0.9596	0.3454	1.2820	36.00	28.08
	2.1930	0.9596	0.6084	2.2840	63.40	27.75
	2.7520	0.9596	0.7504	2.8680	78.20	27.27
$1.048\ N.10^{-1}$	0.6183	0.9596	0.1497	0.6443	15.60	24.21
	1.2530	0.9596	0.3052	1.3060	31.80	24.35
	1.7130	0.9596	0.4222	1.7850	43.99	24.64
	2.1960	0.9596	0.5316	2.2880	55.40	24.22
1.048 N.	0.7670	0.9596	0.1362	0.7993	14.20	17.76
	1.5280	0.9596	0.2629	1.5920	27.39	17.21
	2.0630	0.9596	0.3436	2.1490	35.80	16.65
	2.7480	0.9596	0.4529	2.8630	47.20	16.48
	3.4270	0.9596	0.5456	3.5720	56.79	15.91

Table 16.08

Equilibrium of resin Am-15 (a = 0.58 mm.) 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
$1.048\ N.10^{-1}$	0.6059	0.9596	0.1516	0.6314	15.80	25.02
	1.2230	0.9596	0.2993	1.2750	31.20	24.47
	2.1700	0.9596	0.5201	2.2610	54.20	23.97
	2.7040	0.9596	0.6352	2.8170	66.19	23.50
1.048 N.	1.4930	0.9596	0.2571	1.5560	26.80	17.22
	2.0200	0.9596	0.3473	2.1050	36.20	17.20
	2.6850	0.9596	0.4472	2.7990	46.60	16.65
	3.3720	0.9596	0.5431	3.5140	56.59	16.11

Table 16.09

Equilibrium of resin IR-200 (a = 0.58 mm.) with aqueous cinchonine sulphate with added sulphuric acid of different concentrations.

Concentration of added H_2SO_4	$[\overline{H}]_i$	$[A]_i$	$[\overline{A}]_e$	R	P_A	P_R
1.048 N. 10^{-3}	1.2350	0.9819	0.4129	1.2570	42.05	33.44
	1.7170	0.9819	0.5692	1.7480	57.95	33.15
	2.1940	0.9819	0.7161	2.2350	72.93	32.64
	2.7330	0.9819	0.8712	2.7840	88.72	31.87
1.048 N. 10^{-2}	1.2370	0.9819	0.3906	1.2600	39.78	31.59
	1.7110	0.9819	0.5319	1.7430	54.17	31.09
	2.1890	0.9819	0.6648	2.2290	67.70	30.38
	2.7370	0.9819	0.8106	2.7870	82.54	29.61
1.048 N. 10^{-1}	0.6203	0.9819	0.1750	0.6317	17.81	28.20
	1.2410	0.9819	0.3406	1.2640	34.68	27.45
	1.7260	0.9819	0.4630	1.7580	47.15	26.82
	2.2040	0.9819	0.5749	2.2450	58.55	26.08
1.048 N.	1.5120	0.9819	0.2729	1.5390	27.79	18.05
	2.0610	0.9819	0.3580	2.0990	36.46	17.37
	2.7270	0.9819	0.4548	2.7760	46.33	16.68
	3.4340	0.9819	0.5470	3.4960	55.71	15.93

Table 16.10

Equilibrium of resin Am-15 (a = 0.58 mm.) with aqueous cinchonine sulphate with added sulphuric acid of different concentrations.

Concentration of added H_2SO_4	$\left[\overline{H}\right]_i$	$\left[A\right]_i$	$\left[\overline{A}\right]_e$	R	P_A	P_R
1.048 N. 10^{-1}	1.2170	0.9819	0.3242	1.2400	33.01	26.63
	1.6820	0.9819	0.4432	1.7130	45.13	26.35
	2.1450	0.9819	0.5551	2.1850	56.53	25.87
1.048 N.	0.7501	0.9819	0.1457	0.7638	14.85	19.44
	1.4830	0.9819	0.2682	1.5100	27.32	18.09
	2.6940	0.9819	0.4490	2.7430	45.73	16.67
	3.3720	0.9819	0.5365	3.4340	54.64	15.92

Table 16.11

Equilibrium of resin IR-200 (a = 0.58 mm.) with aqueous cinchonidine 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
$1.048\ N.10^{-3}$	1.2360	1.028	0.4229	1.2020	41.13	34.22
	1.7180	1.028	0.5794	1.6710	56.36	33.73
	2.1960	1.028	0.7243	2.1350	70.46	32.99
	2.7400	1.028	0.8865	2.6660	86.24	32.35
$1.048\ N.10^{-2}$	1.7180	1.028	0.5361	1.6710	52.15	31.21
	2.2010	1.028	0.6751	2.1400	65.67	30.68
	2.7340	1.028	0.8213	2.6600	79.89	30.04
$1.048\ N.10^{-1}$	1.2310	1.028	0.3317	1.1980	32.27	26.95
	1.7080	1.028	0.4591	1.6620	44.66	26.87
	2.1880	1.028	0.5748	2.1280	55.91	26.27
	2.7440	1.028	0.7044	2.6690	68.52	25.67
1.048 N.	1.5130	1.028	0.2781	1.4720	27.05	18.38
	2.0630	1.028	0.3645	2.0060	35.46	17.67
	2.7440	1.028	0.4603	2.6690	44.77	16.78
	3.4310	1.028	0.5585	3.3370	54.20	16.25

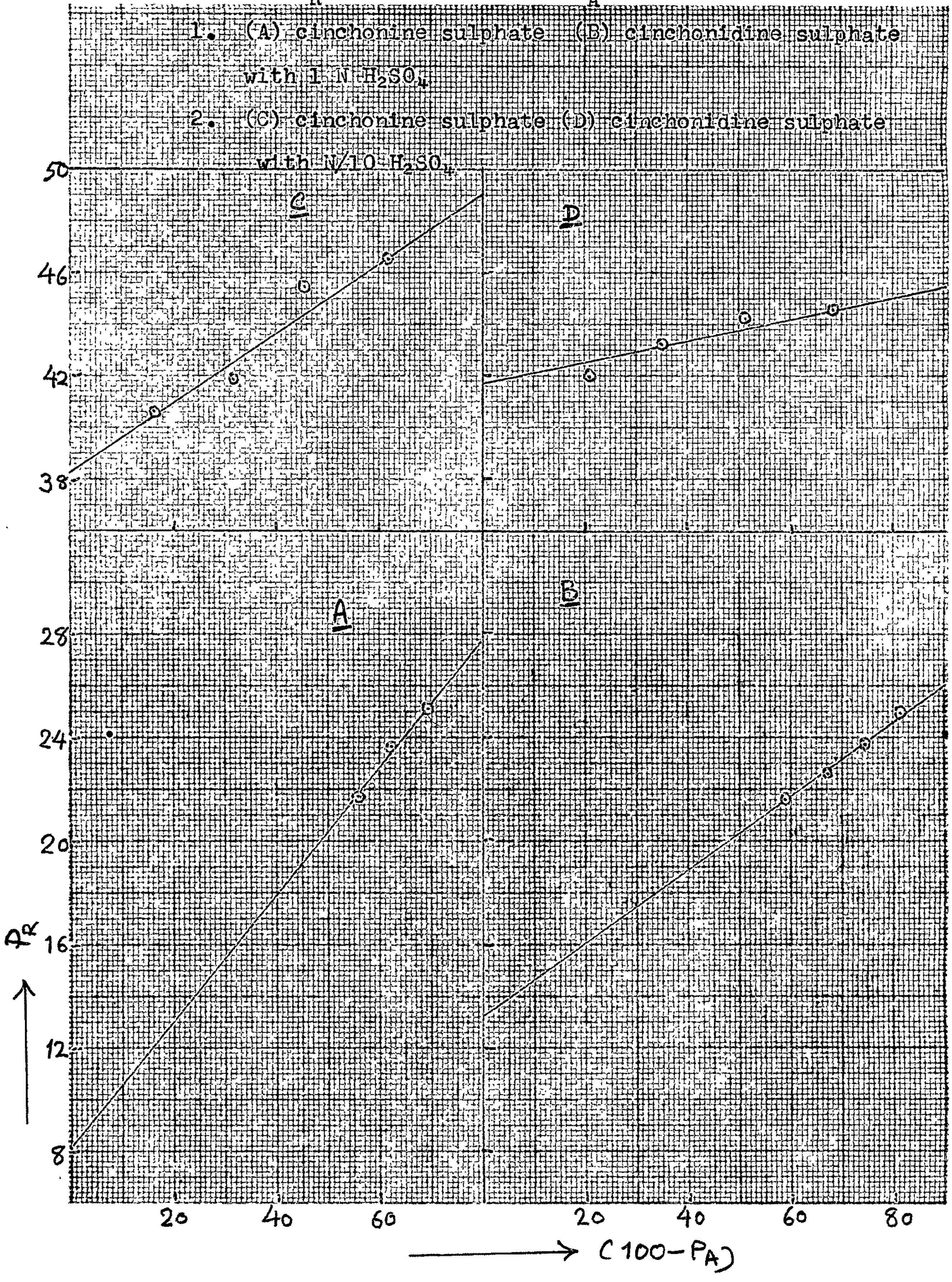
Table 16.12

Equilibrium of resin Am-15 (a = 0.58 mm.) with aqueouss cinchonidine sulphate with added sulphuric acid of different concentrations.

Concentration of added H_2SO_4	$[\overline{H}]_i$	$[A]_i$	$[\overline{A}]_e$	R	P_A	P_R
$1.048\ N.10^{-1}$	1.2150	1.028	0.3353	1.1820	32.61	27.58
	1.6940	1.028	0.4603	1.6480	44.77	27.16
	2.1600	1.028	0.5758	2.1010	56.02	26.66
	2.6880	1.028	0.6915	2.6150	67.26	25.72
1.048 N.	1.4810	1.028	0.2628	1.4410	25.57	17.75
	2.0210	1.028	0.3470	1.9660	33.76	17.16
	2.6980	1.028	0.4450	2.6230	43.29	16.50
	3.3660	1.028	0.5396	3.2740	52.49	16.03

Figure 16.01

Plot of P_R against (100 - P_A) for resin X4



1. (A) cinchonine sulphate (B) cinchonidine sulphate with 1 N H_2SO_4

2. (C) cinchonine sulphate (D) cinchonidine sulphate with N/10 H_2SO_4

Figure 16.02

Plot of P_R against (100 - P_A) for resin X4

1. (A) cinchonine sulphate (B) cinchonidine sulphate with N/100 H_2SO_4

2. (C) cinchonine sulphate (D) cinchonidine sulphate with N/1000 H_2SO_4

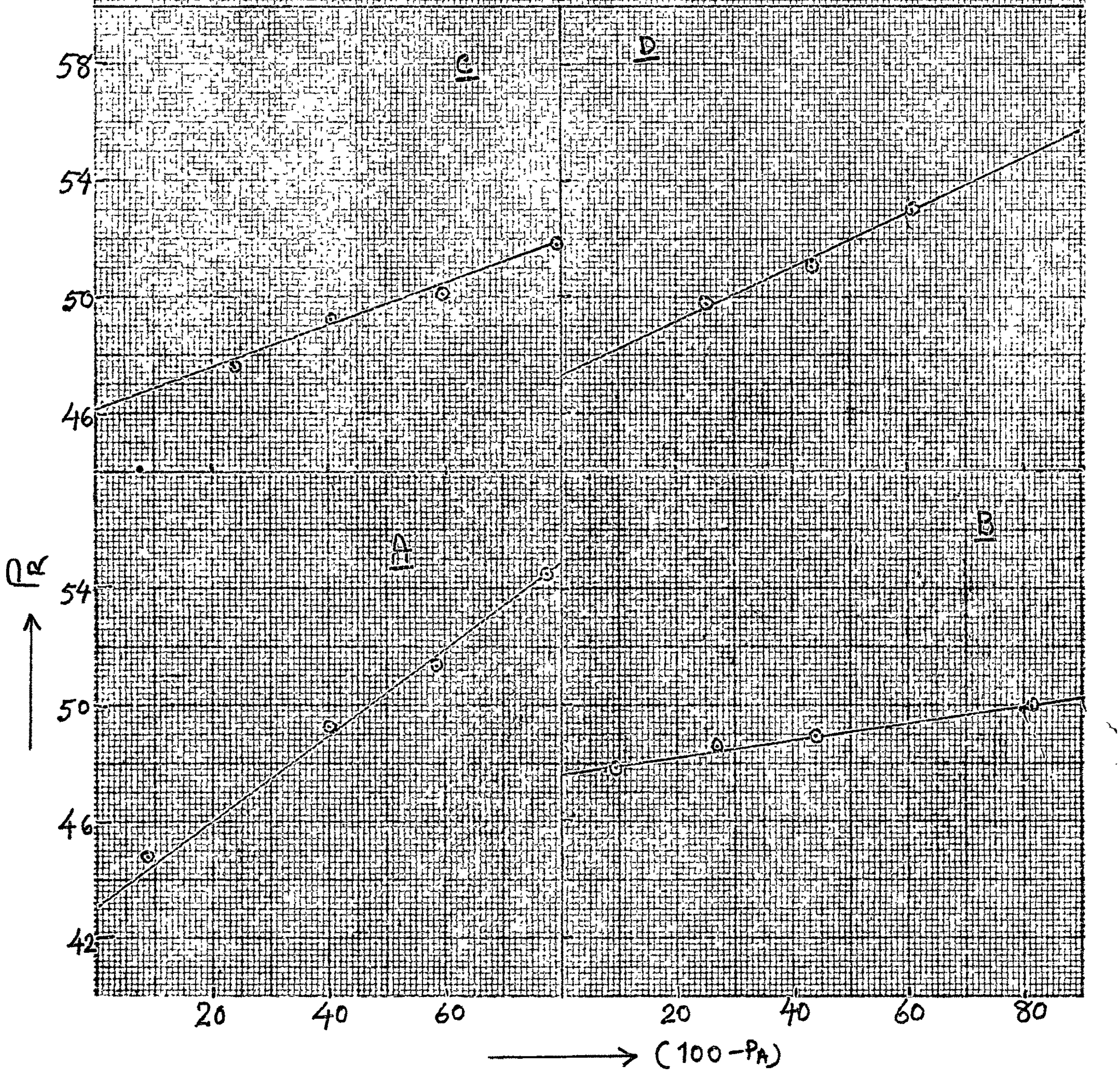


Table 16.13

Values of P_R (with added sulphuric acid) for the four alkaloid sulphates with resin X4 from the plots of P_R against (100 - P_A), figures (16.01 to 16.02) , when extrapolated to (100 - P_A = zero)

$[H_2SO_4]$	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 cinchonine sulphate	Values of P_R for cinchonidine sulphate
9.774 N. 10^{-1}	22.0	9.774 N. 10^{-1}	20.0	1.010 N.	10.2	13.2
9.774 N. 10^{-2}	42.2	9.774 N. 10^{-2}	42.4	1.010 N. 10^{-1}	38.4	41.8
9.774 N. 10^{-3}	48.2	9.774 N. 10^{-3}	47.3	1.010 N. 10^{-2}	43.0	47.6
1.041 N. 10^{-3}	49.1	1.000 N. 10^{-3}	47.6	1.010 N. 10^{-3}	46.2	47.4
Zero	49.4	Zero	47.8	Zero	49.5	49.5

* Data of these columns are taken from the Ph. D. Thesis of Shri S. S. Kanhere.

Figure 16.03

Plot of P_R against (100 - P_A) for resin X8

(A) cinchonine sulphate with 1 N H_2SO_4

(B) cinchonidine sulphate with 1 N H_2SO_4

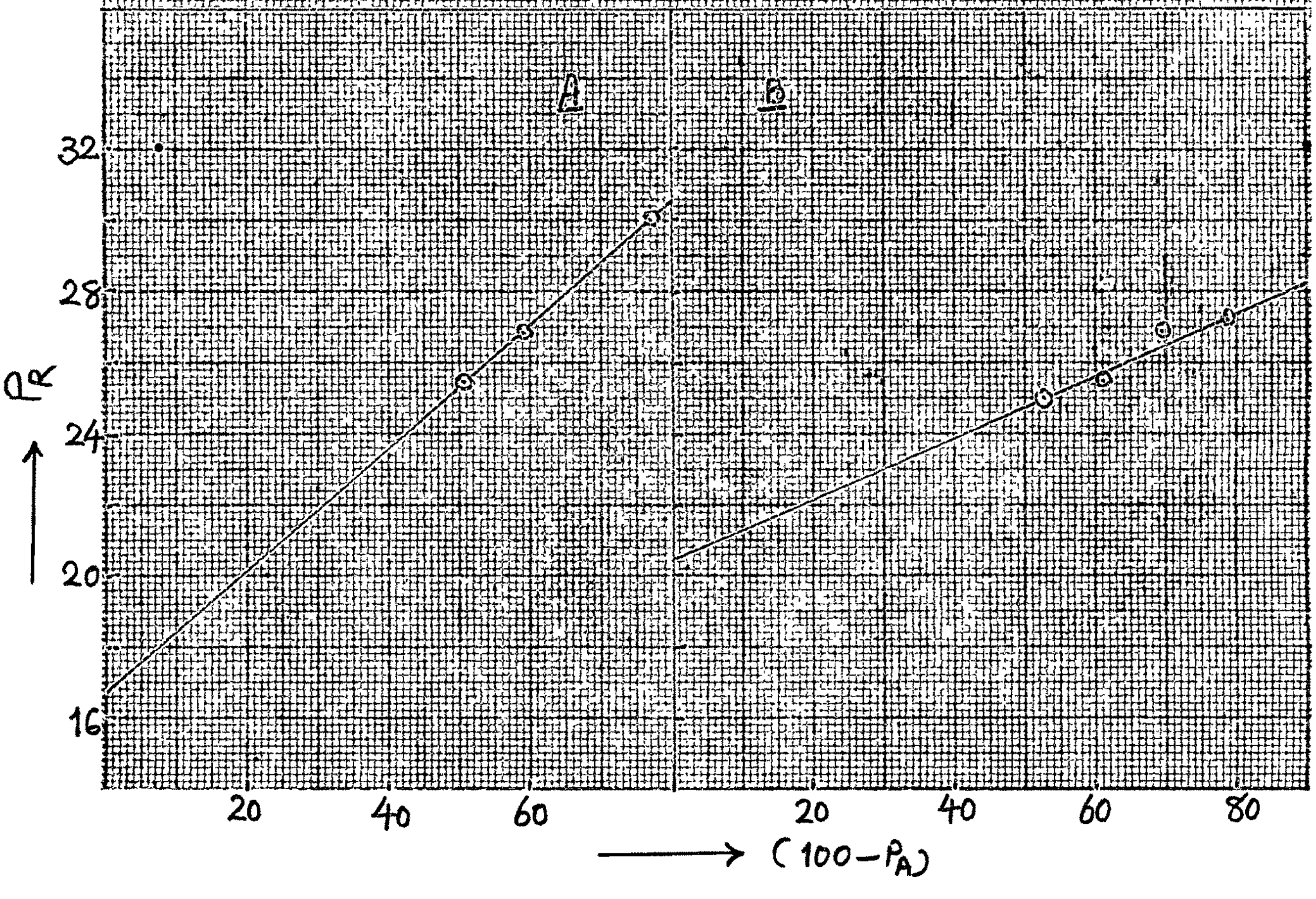


Figure 16.04

Plot of P_R against (100 - P_A) for resin X8

(A) cinchonine sulphate with N/10 H_2SO_4

(B) cinchonidine sulphate with N/10 H_2SO_4

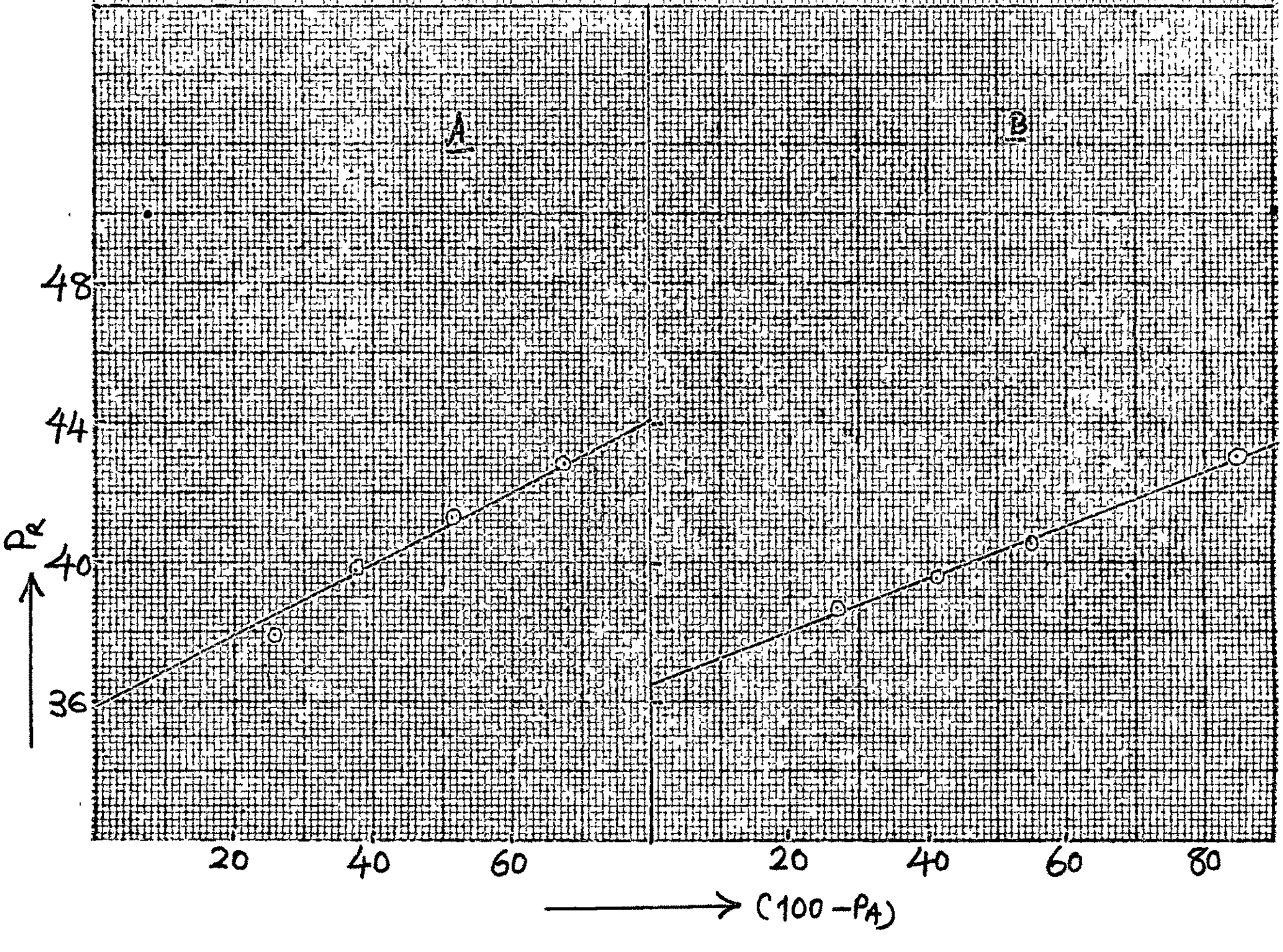


Table 16.14

Values of P_R (with added sulphuric acid) for the four alkaloid sulphates with resin X8 from the plots of P_R against (100 - P_A) , figures (16·03 to 16·04) when extrapolated to (100 - P_A = zero)

$[H_2SO_4]$	Values of P_R* for quinine sulphate	Values of P_R* for quinidine sulphate	$[H_2SO_4]$	Values of P_R for cinchonine sulphate	Values of P_R for cinchonidine sulphate
1.083 N.	23.8	24.0	1.010 N.	16.7	20.5
1.083 N.10^{-1}	37.9	37.5	1.010 N.10^{-1}	35.8	36.6
Zero	40.0	39.5	Zero	44.6	45.2

* Date of these columns are taken from the Ph. D. Thesis of Shri S. S. Kanhere.

Figure 16.05

Plot of P_R against $(100-P_A)$ for resin IR-200

1. (A) quinine sulphate (B) quinidine sulphate with 1 N H_2SO_4
2. (C) quinine sulphate (D) quinidine sulphate with N/10 H_2SO_4
3. (E) aqueous quinine sulphate

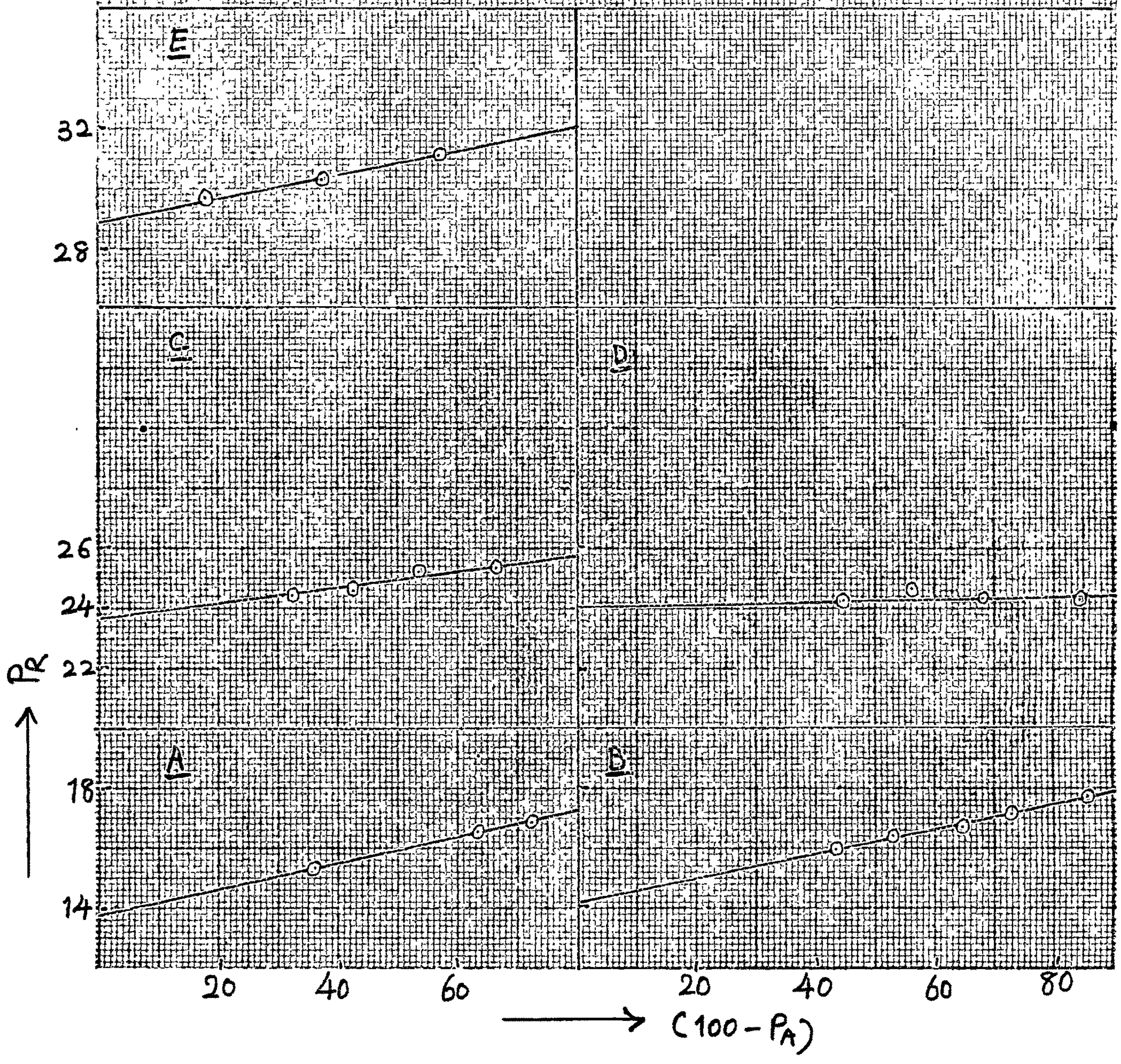


Figure 16.07

Plot of P_R against (100 - P_A) for resin IR-200

1. (A) cinchonine sulphate (B) cinchonidine sulphate with 1 N H_2SO_4
2. (C) cinchonine sulphate (D) cinchonidine sulphate with N/10 H_2SO_4
3. (E) aqueous cinchonine sulphate

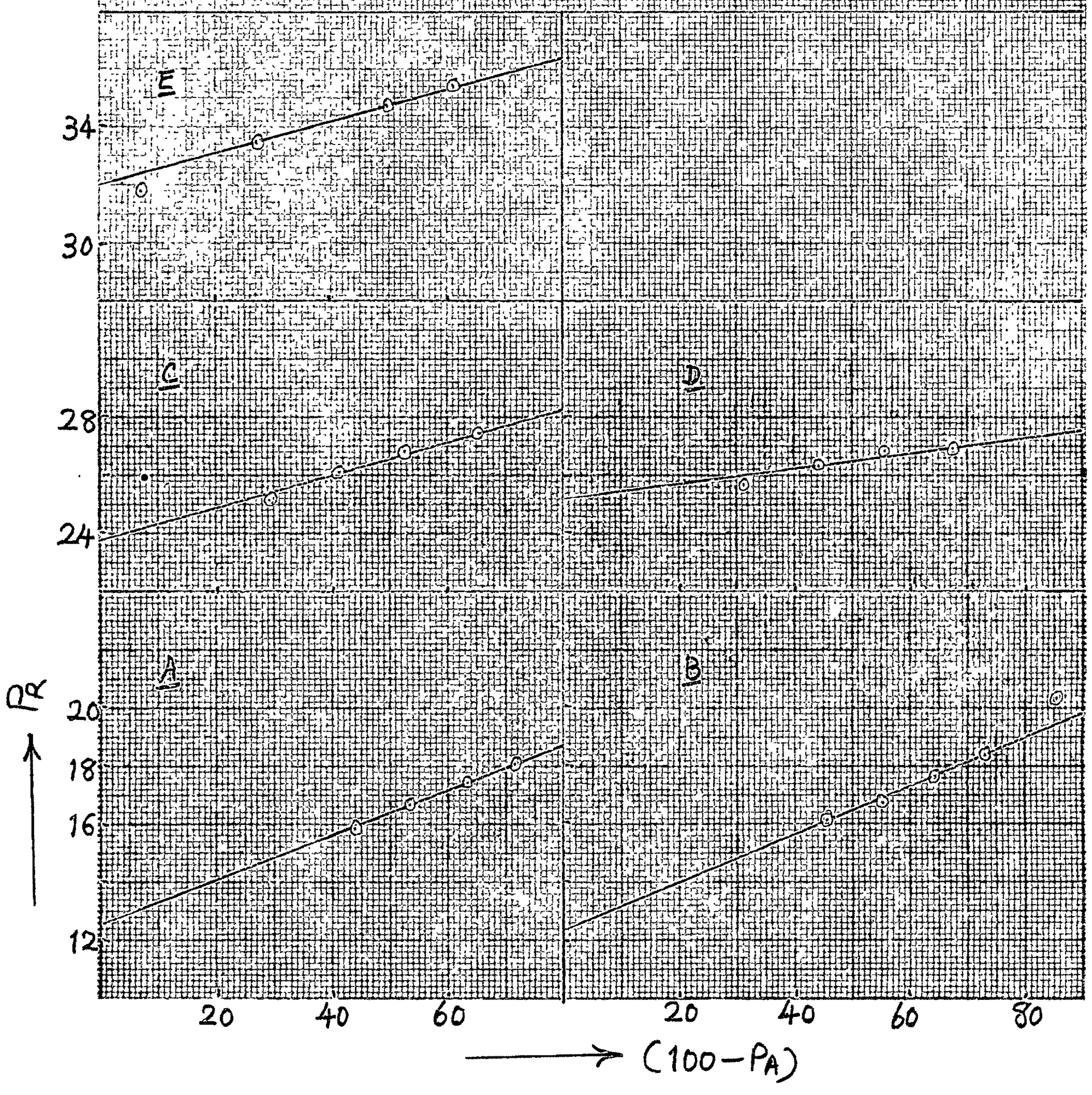


Figure 16.06

Plot of P_R against ($100 - P_A$) for resin IR-200

1. (A) quinine sulphate (B) quinidine sulphate with
   N / 100 H_2SO_4
2. (C) quinine sulphate (D) quinidine sulphate with
   N / 1000 H_2SO_4
3. (E) aqueous quinidine sulphate

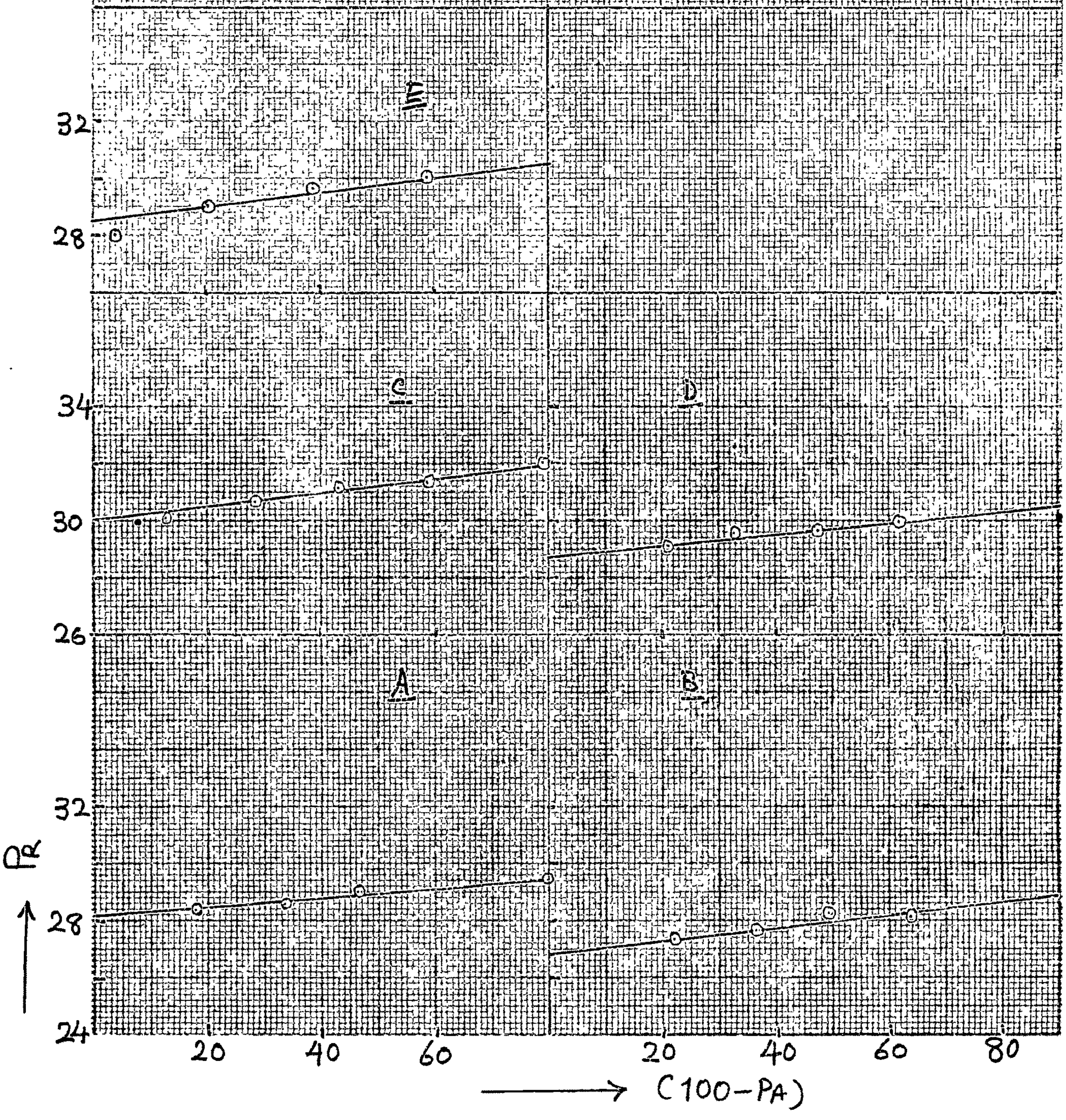


Figure 16.08

Plot of P_R against ($100-P_A$) for resin IR-200

1. (A) cinchonine sulphate (B) cinchonidine sulphate with N/100 H_2SO_4

2. (C) cinchonine sulphate (D) cinchonidine sulphate with N/1000 H_2SO_4

3. (E) aquaous cinchonidine sulphate

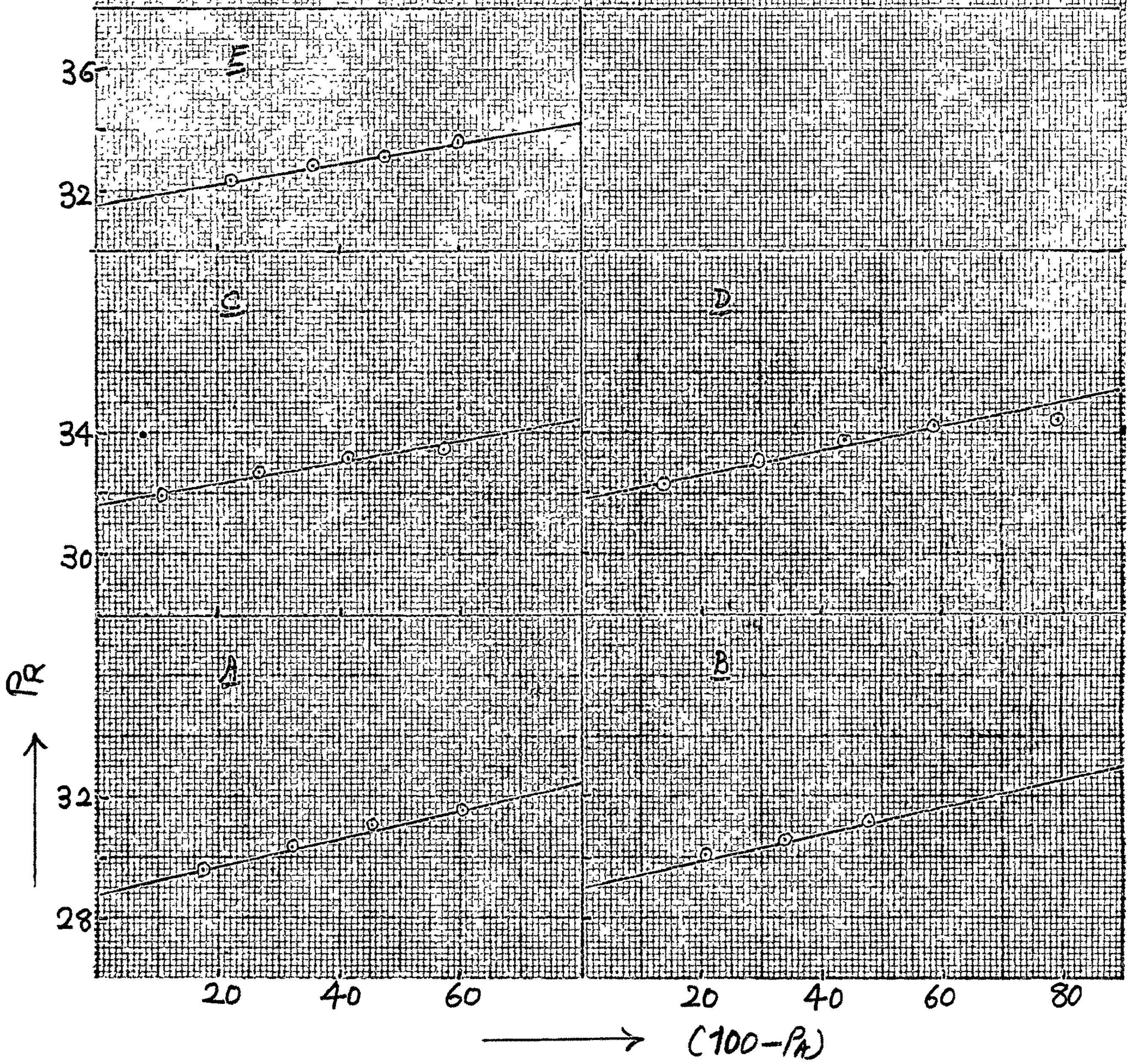


Table 16.15

Values of P_R (with added sulphuric acid) for the four alkaloid sulphates with resin IR-200 (a = 0.58 mm.) from the plots of P_R against (100 - P_A), figures (16·05 to 16·08), when extrapolated to (100 - P_A = zero).

$[H_2SO_4]$	Values of P_R for quinine sulphate	Values of P_R for quinidine sulphate	Values of P_R for cinchonine sulphate	Values of P_R for cinchonidine sulphate
1.048 N.	13.8	14.2	12.6	12.4
1.048 N.10^{-1}	23.7	24.0	23.8	25.2
1.048 N.10^{-2}	28.1	26.8	28.8	29.0
1.048 N.10^{-3}	30.0	28.6	31.6	31.8
Zero	30.4	29.8	32.9	32.9

Figure 16.09

Plot of P_R against (100 - P_A) for resin Am-15

(A) quinine sulphate with 1 N H_2SO_4

(B) quinidine sulphate with 1 N H_2SO_4

(C) aqueous quinine sulphate

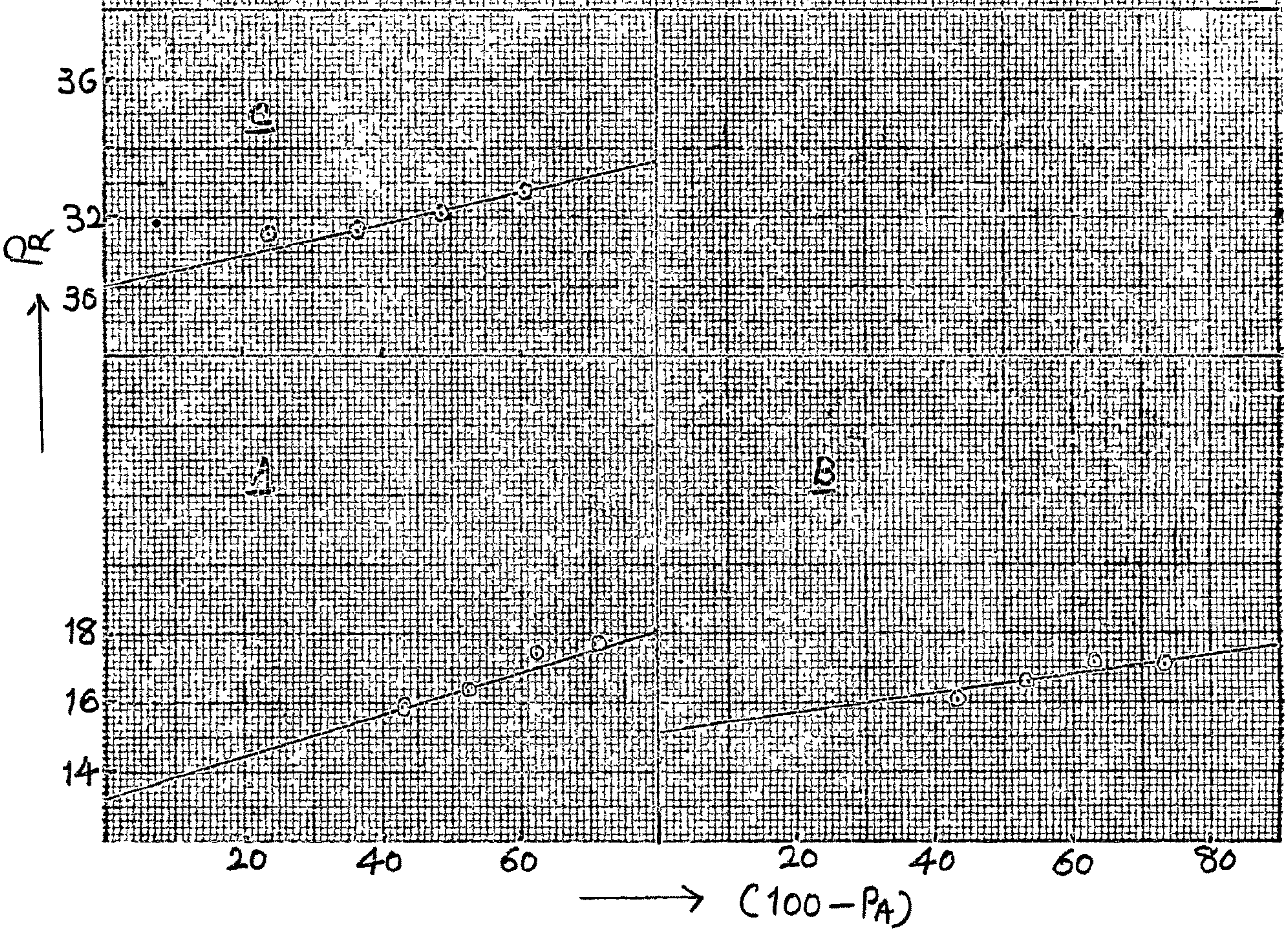


Figure 16.10

Plot of P_R against (100 - P_A) for resin Am-15

(A) quinine sulphate with N/10 H_2SO_4

(B) quinidine sulphate with N/10 H_2SO_4

(C) aqueous quinidine sulphate

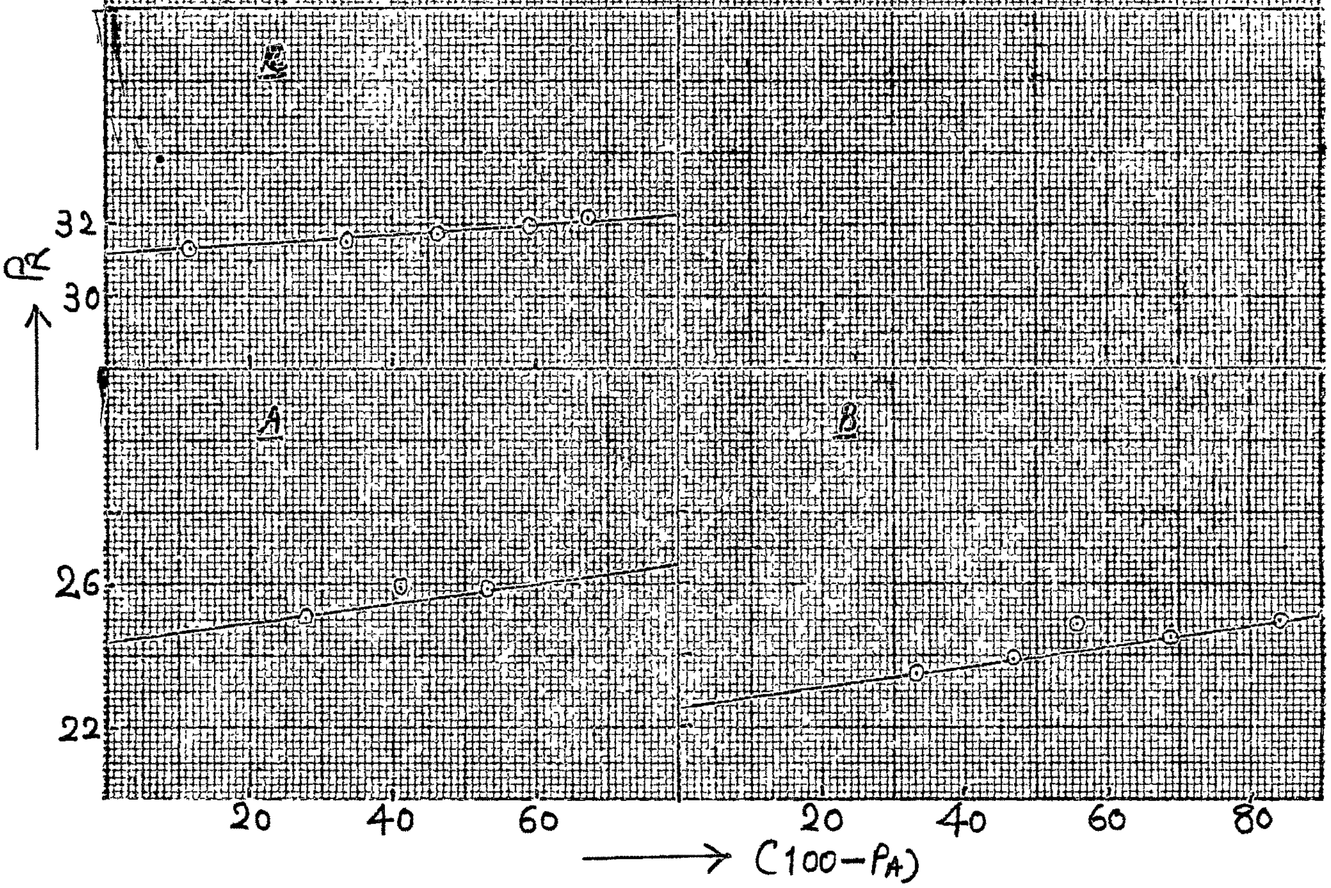


Figure 16.11

Plot of P_R against (100 - P_A) for resin Am -15

(A) cinchonine sulphate with 1 N H_2SO_4

(B) cinchonidine sulphate with 1 N H_2SO_4

(C) aqueous cinchonine sulphate

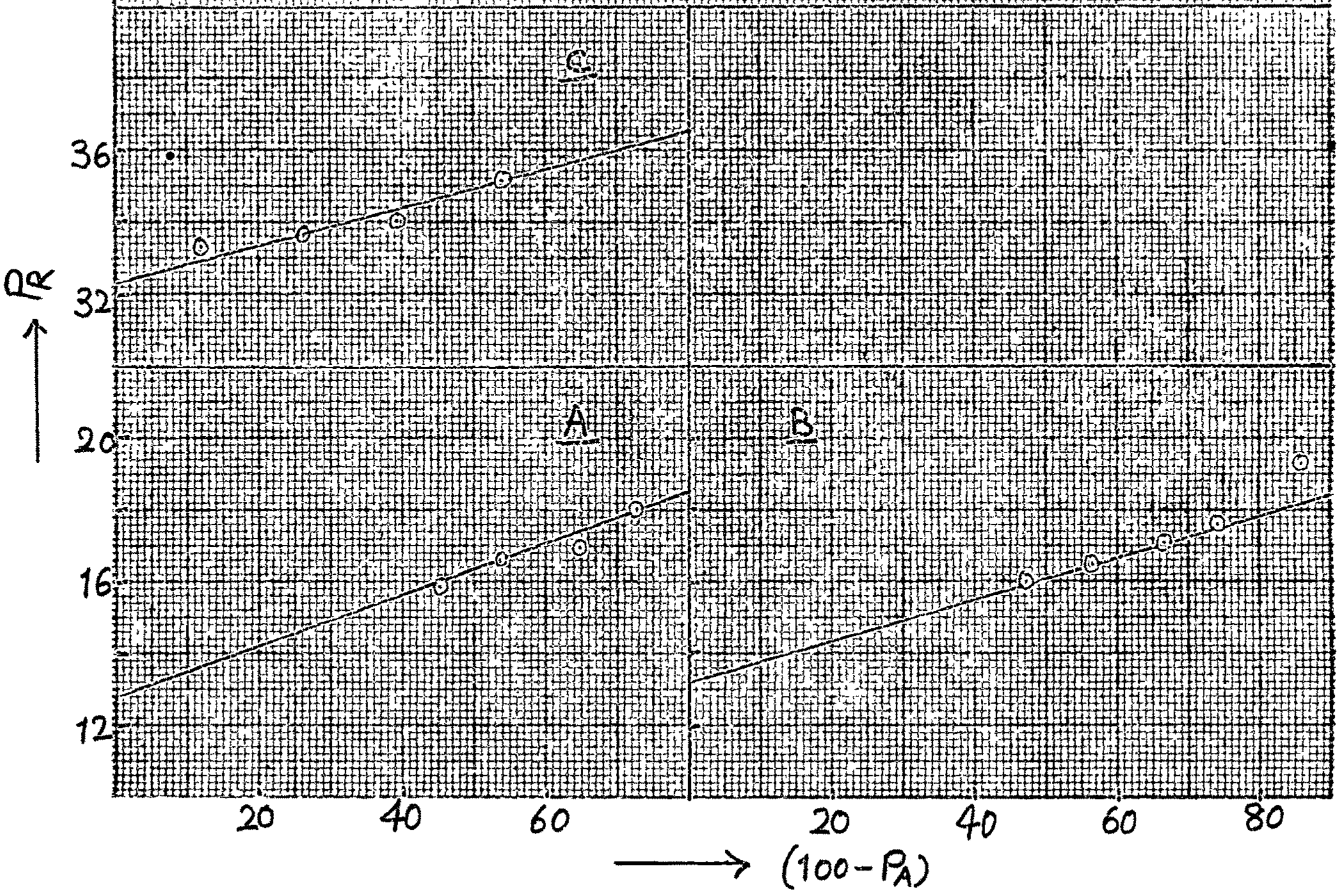


Figure 16.12

Plot of P_R against (100 - P_A) for resin Am-15

(A) cinchonine sulphate with 1 N H_2SO_4

(B) cinchonidine sulphate with 1 N H_2SO_4

(C) aqueous cinchonine sulphate

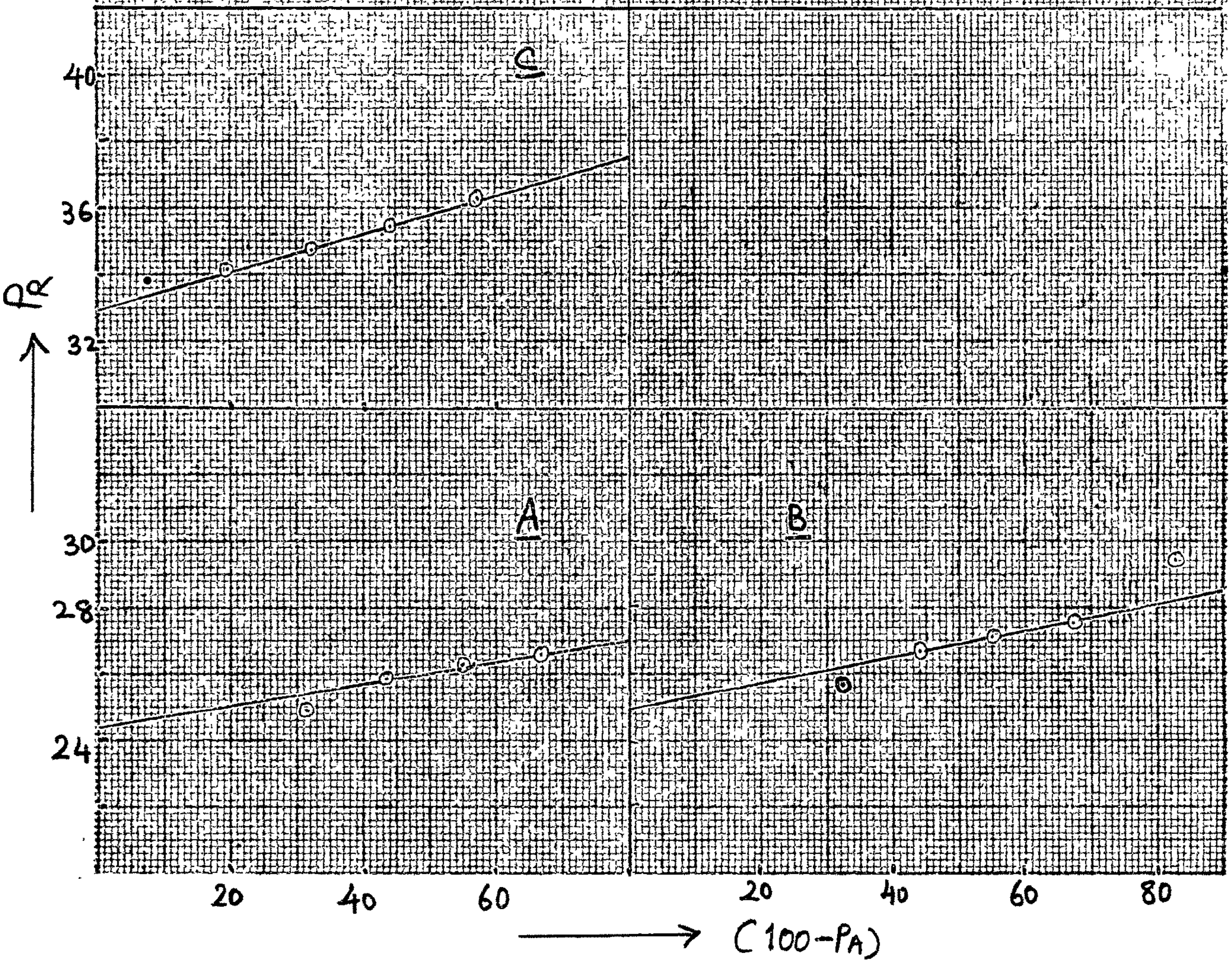


Table 16.16

Values of P_R (with added sulphuric acid) for the four alkaloid sulphates with resin IAm-15 (a = 0.58 mm.) from the plots of P_R against (100 - P_A), figures (16·09 to 16·12), when extrapolated to (100 - P_A = zero).

$[H_2SO_4]$	Values of P_R for quinine sulphate	Values of P_R for quinidine sulphate	Values of P_R for cinchonine sulphate	Values of P_R for cinchonidine sulphate
1.048 N.	13.2	15.1	12.8	13.2
1.048 N. 10^{-1}	24.4	22.5	24.4	25.0
Zero	32.0	31.5	34.1	35.2

Table 16.17

Initial slopes (S) of the plots of P_R against ($100-P_A$) for four cinchona alkaloids (Figures 16.01 to 16.12).

Resin	Quinine sulphate		Quinidine sulphate		Cinchonine sulphate		Cinchonidine sulphate	
	$[H_2SO_4\ (N)]$	S	$[H_2SO_4\ (N)]$	S	$[H_2SO_4\ (N)]$	S	$[H_2SO_4\ (N)]$	S
X4 (a = 0.215 mm.)	$9.774 \cdot 10^{-1}$	0.10	$9.774 \cdot 10^{-1}$	0.15	1.010.	0.24	1.010.	0.14
	$9.774 \cdot 10^{-2}$	0.06	$9.774 \cdot 10^{-2}$	0.05	$1.010 \cdot 10^{-1}$	0.13	$1.010 \cdot 10^{-1}$	0.04
	$9.774 \cdot 10^{-3}$	Zero	$9.774 \cdot 10^{-3}$	0.02	$1.010 \cdot 10^{-2}$	0.15	$1.010 \cdot 10^{-2}$	0.03
	$10.410 \cdot 10^{-4}$	0.02	$1.000 \cdot 10^{-3}$	0.02	$1.010 \cdot 10^{-3}$	0.07	$1.010 \cdot 10^{-3}$	0.09
	0.00	Zero	0.00	0.02	0.00	0.14	0.00	0.09
X8 (a = 0.215 mm.)	1.083	0.06	1.083	0.06	1.010	0.17	1.010	0.08
	$1.083 \cdot 10^{-1}$	0.02	$1.083 \cdot 10^{-1}$	0.01	$1.010 \cdot 10^{-1}$	0.10	$1.010 \cdot 10^{-1}$	0.07
	0.00	0.02	0.00	0.02	0.00	0.01	0.00	Zero

Table 16.17 (Continued)

Resin	Quinine sulphate		Quinidine sulphate		Cinchonine sulphate		Cinchonidine sulphate	
	[H_2SO_4 (N)]	S	[H_2SO_4 (N)]	S	[H_2SO_4 (N)]	S	[H_2SO_4 (N)]	S
IR-200 (a = 0.58 mm)	1.048	0.04	1.048	0.04	1.048	0.08	1.048	0.08
	$1.048 \cdot 10^{-1}$	0.03	$1.048 \cdot 10^{-1}$	Zero	$1.048 \cdot 10^{-1}$	0.06	$1.048 \cdot 10^{-1}$	0.03
	$1.048 \cdot 10^{-2}$	0.02	$1.048 \cdot 10^{-2}$	0.02	$1.048 \cdot 10^{-2}$	0.05	$1.048 \cdot 10^{-2}$	0.04
	$1.048 \cdot 10^{-3}$	0.02	$1.048 \cdot 10^{-3}$	0.02	$1.048 \cdot 10^{-3}$	0.03	$1.048 \cdot 10^{-3}$	0.04
	0.00	0.04	0.00	0.02	0.00	0.05	0.00	0.03
Am-15 (a = 0.58 mm)	1.048	0.06	1.048	0.02	1.048	0.07	1.048	0.06
	$1.048 \cdot 10^{-1}$	0.03	$1.048 \cdot 10^{-1}$	0.03	$1.048 \cdot 10^{-1}$	0.03	$1.048 \cdot 10^{-1}$	0.04
	0.00	0.04	0.00	0.01	0.00	0.05	0.00	0.06

Discussion :

Tables (16.01 to 16.12) give the results ~~for~~ P_R for four cinchona alkaloid sulphates with resins X4, X8, IR-200 and Am-15 at various concentrations of added sulphuric acid. 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 increased. The plots of P_R against $(100-P_A)$ are linear and by extrapolation, the values of P_{Ro} are obtained, (figures 16.01 to 16.12). When the concentration of the added acid is low, the value of P_R is relatively less dependent ~~of~~ on P_A.

Tables (16.13 to 16.16) give the values of P_{Ro} for four cinchona alkaloid sulphates with resins X4, X8, IR-200 and Am-15 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 low.

The reduction in the value of P_{Ro} in the presence of added sulphuric acid can be considered to be 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) can not be solely due to the sorption of base Q, since such effect is either negligible or relatively much less 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 (1 - 20), when present in high concentration. Since sulphuric acid is present in high concentration, some H^+ ions and sulphate ions are sorbed in accordance with Donnan membrane 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 much less the value of P_R also becomes much less dependent on P_A.

Table (16.17) indicates that for the gel type resins X4 and X8, the value of the initial slope S (figures 16.01 to 16.12) is significantally higher for cinchonine sulphate. Also the values of the slope S for the macromolecular resins IR-200 and Am-15 are relatively less than those for the gel type resins X4 and X8. This brings out another point of difference in the behaviour of the gel type resins and the macromolecular resins.

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.

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17

STUDIES ON THE UPTAKE OF THE ALKALOID BASES BY RESINS IN ETHANOLIC AND AQUEOUS ETHANOLIC SOLUTION.

Introduction :

Earlier (Chapter 15) , the (molecular) sorption of the alkaloid bases by the resins was suggested. It was, therefore, considered of interest to further study the uptake of the bases from the solution. The solutions were prepared in ethanol (sp.gr. 0.806) and aqueous ethanol (20 % by volume).

Experimental : (Chapter 15)

Ethanol (sp.gr. 0.806) and caustic soda (A.R.) were used. The bases were precipitated by slow addition of caustic soda solution, to a stirred aqueous solution of the alkaloid sulphate. A slight excess of caustic soda solution was added to ensure complete precipitation. The precipitated base was filtered at the pump and then stirred with about 300 c.c. of water and again filtered at the pump. This was repeated till the washings were free from caustic soda. The base was then dried in an oven (100- 104°C) and its melting point was checked.

The same known weight of resins X8 and IR-200 were placed in well stoppered flasks and same volume of the base was added to each flask. The contents were frequently shaken at room temperature ($\sim$30°C) . After known time interval the solution was decanted, a known portion suitably diluted with solvent from the same stock and the optical density (at 296.5 mµ for quinine and 294.5 mµ for cinchonine) recorded. Original solution of each base was also diluted to the same extent and the optical density was recorded.

Nomenclature :

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

W = weight of air-dry resin taken in grams,

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

C = capacity of the resin in meq.per gram of air-dry resin,

D_i = optical density, at the invarient wavelength, of the initial (at time t = zero) solution of the alkaloid base, after suitable dilution,

D_{ot} = optical density, at the same wave-length of the solution of the alkaloid base at time t = t , after the same extent of dilution as in above,

$[\bar{A}]_t$ = $[A]_i \cdot (D_i - D_{ot}) / D_i$ = the meq.of the alkaloid form of the resin, per litre of solution, at time t = t ,

$[\bar{H}]_i$ = $W.C.10^3 / v$ = the meq.of resin,per litre of the solution,in the hydrogen form, at t = 0,

R = $[\bar{H}]_i / [A]_i$ = the ratio of the initial concentration (in meq./litre) of the resin to the initial concentration of the alkaloid base,

P_{At} = $100 . [\bar{A}]_t / [A]_i$ = the % exchange of alkaloid base at time t = t,

P_{Rt} = $100 . [\overline{A}]_t / [\overline{H}]_i$ = the % resin capacity exchanged at time t = t,

The corresponding values, for $[\overline{A}]_t$, P_{At} and P_{Rt} when t = time after which equilibrium had been reached, are denoted by $[\overline{A}]_e$, P_A and P_R respectively.

Results :

Table 17.1

The uptake of quinine in 20 % ethanolic solution by resins X4 and IR-200

Resin	Time (t)	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_t$	R	P_{At}	P_{Rt}
X4	6 Hours	2.332	2.456	0.6333	0.9493	25.8	27.2
(a =	16 Hours	2.332	2.456	1.040	0.9493	42.3	44.6
0.215 mm.)	40 Hours	2.332	2.456	1.301	0.9495	53.0	55.8
	4 Days	2.336	2.456	1.501	0.9510	61.1	64.2
	7 Days	2.334	2.456	1.643	0.9504	66.9	70.4
	10 Days	2.340	2.456	1.739	0.9523	70.8	74.3
	17 Days	2.334	2.456	1.831	0.9779	74.5	78.4
	26 Days	2.334	2.456	1.842	0.9778	75.0	78.9
	40 Days	2.334	2.456	1.842	0.9778	75.0	78.9
IR-200	6 Hours	3.085	2.015	0.6175	1.531	30.6	20.0
	22 Hours	3.083	2.015	0.8578	1.530	42.6	27.8
	44 Hours	3.083	2.015	1.0310	1.530	51.2	33.5
	4 Days	3.098	2.015	1.0610	1.537	52.7	34.3
	7 Days	3.084	2.015	1.1910	1.531	59.1	38.6
	10 Days	3.090	2.015	1.2090	1.535	60.0	39.1
	17 Days	3.089	2.015	1.2430	1.534	61.6	40.2
	27 Days	3.085	2.015	1.2610	1.532	62.6	40.9
	40 Days	3.083	2.015	1.2610	1.531	62.6	40.9

Data for resin X4 are from (1).

Table 17.2

The uptake of quinine in alcoholic solution by resins.

Resin	Time (t) (hours)	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_t$	R	P_{At}	P_{Rt}
X4 (a = 0.215 mm.)	8	11.16	33.35	2.925	0.3347	8.8	25.1
	17	11.16	33.35	3.844	0.3347	11.5	33.0
	41	11.16	33.35	4.428	0.3347	13.3	38.0
	96	11.16	33.35	4.930	0.3347	14.8	42.3
X8 (a = 0.215 mm.)	8	11.21	33.09	3.008	0.3388	9.1	26.8
	72	11.23	33.09	4.474	0.3395	13.5	39.8
IR-200 (a = 0.58 mm.)	4	11.11	33.09	1.543	0.3359	4.7	13.9
	8	11.12	33.09	2.527	0.3360	7.6	22.7
	24	11.15	33.09	3.857	0.3371	11.6	34.6
	72	11.14	33.09	4.165	0.3364	13.0	37.4

Data for resin X4 are from (1).

Table 17.3

The uptake of cinchonine in alcoholic solution by resins.

Resin	Time(t) (hours)	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_t$	R	P_{At}	P_{Rt}
X4	8	11.67	33.11	2.746	0.3529	8.3	23.5
(a =	17	11.68	33.11	4.118	0.3529	12.4	35.3
0.215 mm.)	41	11.68	33.11	4.603	0.3529	14.0	39.4
	96	11.67	33.11	4.922	0.3529	14.9	42.2
X8	4	11.16	33.01	1.408	0.3382	4.3	12.6
(a =	8	11.20	33.01	1.848	0.3394	5.6	16.5
0.215 mm.)	18	11.19	33.01	2.201	0.3391	6.7	19.6
	120	11.21	33.01	2.376	0.3397	7.2	21.2
IR-200	4	11.14	33.01	1.408	0.3377	4.3	12.6
(a =	8	11.13	33.01	1.760	0.3373	5.3	15.8
0.58 mm.)							

Data for resin X4 are from (1).

Table 17.4

The uptake of cinchonine in alcoholic solution by resin X8 (a = 0.215 mm.)

Time	$[\bar{H}]_i$	$[A]_i$	$[\bar{A}]_t$	R	P_{At}	P_{Rt}
4	11.16	33.01	1.408	0.3382	4.3	12.6
8	11.20	33.01	1.848	0.3394	5.6	16.5
18	11.19	33.01	2.201	0.3391	6.7	19.6
120	11.21	33.01	2.376	0.3397	7.2	21.2
4	11.24	6.61	0.9187	1.699	13.1	8.2
8	11.24	6.61	1.4790	1.700	22.4	13.1
18	11.25	6.61	1.7030	1.701	25.7	15.1
120	11.19	6.61	2.3640	1.693	35.8	21.1
4	11.19	3.30	0.6855	3.392	20.8	6.1
8	11.18	3.30	1.3030	3.386	39.5	11.7

Table 17.5

The uptake of cinchonine in alcoholic solution by resin IR-200 (a = 0.58 mm.)

Time (t) (hours)	$[\overline{H}]_i$	$[A]_i$	$[\overline{A}]_t$	R	P_{At}	P_{Rt}
4	11.14	33.01	1.408	0.3377	4.3	12.6
8	11.13	33.01	1.760	0.3373	5.3	15.8
8	11.15	6.61	1.345	1.687	20.3	12.1
18	11.14	6.61	1.893	1.685	28.6	17.0
120	11.15	6.61	2.936	1.687	44.40	26.3
4	11.14	3.30	0.5035	3.375	15.2	4.5
8	11.14	3.30	0.9477	3.375	28.7	8.5
18	11.13	3.30	1.7440	3.370	52.8	15.7
120	11.12	3.30	3.0890	3.368	93.6	27.8

Table 17.6

The equilibrium uptake of quinine in 20 % ethanolic solution by resins.

Resin	$[\overline{H}]_i$	$[A]_i$	$[\overline{A}]_e$	R	P_A	P_R
X4	0.8002	2.456	0.7369	0.3258	30.0	92.1
	1.577	2.456	1.390	0.6422	56.6	88.1
	2.351	2.456	1.950	0.9568	79.4	83.0
	3.131	2.456	2.242	1.275	91.2	71.6
	3.929	2.456	2.360	1.600	96.1	60.1
	4.693	2.456	2.430	1.911	98.9	51.8
X8	1.505	2.456	0.5977	0.6127	24.3	39.7
	2.233	2.456	0.9080	0.9090	37.0	40.7
	2.987	2.456	1.2530	1.2160	51.0	41.9
	3.738	2.456	1.560	1.522	63.5	41.7
	4.499	2.456	1.881	1.831	76.6	41.8
IR-200	1.029	2.005	0.4349	0.5135	21.7	42.2
	1.984	2.005	0.8198	0.9893	40.9	41.3
	2.830	2.005	1.1730	1.4110	58.5	41.5
	3.752	2.005	1.505	1.8710	75.1	40.1

Data for resins X4 and X8 are from (1).

Table 17.7

Summary of tables 17.2 and 17.3

Resin	Time (hours)	Value of P_{Rt} for	
		quinine	cinchonine
X4	8	25.1	23.5
	17	33.0	35.3
	41	38.0	39.4
	96	42.3	42.2
X8	4	-	12.6
	8	26.8	16.5
	18	-	19.6
	72	39.8	-
	120	-	21.2
IR-200	4	13.9	12.6
	8	22.7	15.8
	24	34.6	-
	72	37.4	-

Table 17.8

Summary of tables 17.4 and 17.5

Resin	Time (hours)	Value of P_{Rt} when concentration of cinchonine (meq./litre) =		
		33.01	6.61	3.30
X8	4	12.6	8.2	6.1
	8	16.5	13.1	11.7
	18	19.6	15.1	-
	120	21.2	21.1	-
IR-200	4	12.6	-	4.5
	8	15.8	12.1	8.5
	18	-	17.0	15.7
	120	-	26.3	27.8

Discussion :

The cinchona alkaloids, quinine, quinidine, cinchonine and cinchonidine are weak bases. Their uptake, from alcoholic solution by resins in hydrogen form is a relatively slow process. Tables 17.1 and 17.2 indicate that the rate of uptake is slower in alcoholic solution than that in 20 % aqueous alcoholic (by volume) solution. Table 17.1 also indicates that the uptake of quinine in 20 % aqueous alcoholic solution is to a lesser extent by resin IR-200 than that by resin X4. Table 17.2 indicates that in alcoholic solution the initial uptake of quinine by resins X4,X8 and IR-200 is comparable. This is of interest since the resins IR-200 and X4 are more porous than the resin X8. Table 17.3 indicates that the uptake of cinchonine by resins X8 and IR-200 is comparable and is to a lesser extent than that for resin X4. Further comparision of data in table 17.3 indicates that the uptake of quinine and cinchonine by resin X4 in alcoholic solution is at comparable rates but the uptake of cinchonine by resins X8 and IR-200 is to a lesser extent than the uptake of quinine by these resins in alcoholic solution,although cinchonine is a smaller molecule than quinine. Tables 17.4 and 17.5 indicate that the rate of uptake of cinchonine by X8 and IR-200 in alcoholic solution increases with increase in the cinchonine concentration in solution. Table 17.6 gives the equilibrium uptake of quinine in 20 % aqueous ethanol by resins X4,X8 and IR-200. The total uptake, at equilibrium should be determined, as suggested earlier, by two mechanisms : (a) the exchange mechanism and (b) the molecular sorption mechanism. For resin X4 the value of P_R increases with increase in ($100 - P_A$). The plot of P_R against ($100 - P_A$) ~~was~~ extrapolated to zero value of ($100 - P_A$), gives the value of P_{Ro} as 49.5. This is in good agreement with the value of P_{Ro} for quinine sulphate in aqueous solution with resin X4 (chapter 15). This is the contribution of exchange mechanism to the observed value of P_R. The difference $P_R - P_{Ro}$ is the contribution of the sorption mechanism to the observed value of P_R. This contribution is considerably greater in this case than in the case of quinine sulphate in aqueous solution and provides support to the postulation of two mechanisms.

As the degree of crosslinking of the resin is increased, the contribution of the sorption mechanism is reduced due to lesser extent of swelling of the resin (2). With resin X8 (table 17.6) the uptake of quinine from 20 % aqueous alcoholic solution indicates that the value of P_R is practically independent of P_A and the average value of P_{Ro} is 41. This value is in agreement with the value of P_{Ro} for quinine sulphate in aqueous solution with resin X8 (chapter 15) . Hence the contribution of sorption mechanism is , here also, practically negligible. For resin IR-200 the value of P_{Ro} from the average value of P_R in table 17.6 is 41. This value is substantially higher than that given for quinine sulphate in aqueous solution for resin IR-200. Hence the difference 10.5 should be the contribution of the sorption mechanism to the total uptake of quinine by resin IR-200. However, the value of P_R in this case is practically independent of P_A . This should indicate that the sorption contribution is practically independent of P_A for resin IR-200. This is a marked difference in the behaviour of resin IR-200 and that of resins X4 and X8.

The observation that the contribution of the exchange mechanism to the observed value of P_R , i.e. P_{Ro} , is same for uptake from aqueous alcoholic solution of quinine and aqueous solution of quinine sulphate by resins X4 and X8 indicates that the exchange mechanism provides the same value of P_{Ro} for a resin of such type and a given alkaloid ; it is independent of the nature of solvent and whether the exchanging species is $\overset{+}{QH}$ or Q. However the contribution of sorption mechanism to the observed value of P_R appears to be dependent on the solvent medium and concentration and hence is a rather specific effect. However for resin IR-200 the behaviour is markedly different from that of resins X4 and X8.

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18

COLUMN STUDIES WITH CINCHONINE SULPHATE

Introduction :

Earlier, Kanhere (1) has made a preliminary study of relative column behaviour of sodium sulphate and quinine sulphate. The variables studied are (a) the degree of crosslinking, (b) the particle size and (c) the structure of the resin. Elution has been studied with N/10 sulphuric acid, 1 N sulphuric acid and ethanol, (after the base was liberated in the resin particle with sodium hydroxide).

In this chapter, a similar preliminary study of the column behaviour of cinchonine sulphate has been made.

Experimental :

Resins and Chemicals : (Chapter 12 and 15)

Procedure for column studies :

Preparation of the column : A known weight (same as used by (1) of the air-dry resin was taken and slurried with distilled water. This slurry was transferred to a column (length ∼125 cms. and diameter ∼1 cm. ; fitted with a zero porosity disc near the bottom). The column was back-washed with distilled water and then the resin was allowed to settle down slowly under gravity and bedvolume was estimated. The weight of the resin taken was so adjusted as to give a bedlength of 18 cms. for each resin studied.

Run (a). Exchange with cinchonine sulphate solution :

Cinchonine sulphate solution (concentration = 2 meq./litre) was passed through the column and the effluent was collected in samples of suitable volumes at a flow rate of 10 cc. / minutes

The concentration of cinchonine sulphate, in each sample was estimated by measuring the optical density at 294.5 mµ with or without suitable dilution with distilled water. Knowing the optical density of the influent cinchonine sulphate solution at the same wavelength and with the same extent of dilution, the % exchange of cinchonine sulphate per sample was calculated from % exchange = (Di -Do)x 100 /Di , where Do represents the observed optical density at 294.5 mµ after suitable dilution with distilled water, and Di represents the optical density of the influent cinchonine sulphate solution at the same wavelength with the same extent of dilution. After the run was over, the column was washed with about five bedvolumes ~~quantity~~ of distilled water.

Run (b). Elution of the column :

(i) Elution with N/10 sulphuric acid : N/10 sulphuric acid was passed in the column and the effluent was collected in samples (each of 250 cc.) at a flow rate of 10 cc./minute. The concentration of cinchonine sulphate in each sample of the effluent was estimated by measuring the optical density, at 294.5 mµ of each sample with or without suitable dilution with distilled water. Knowing the optical density of the influent cinchonine sulphate solution of run (a), at the same wavelength and with the same dilution, the % elution of cinchonine sulphate per sample was calculated from, Do.100/Di. as given above. Flow of N/10 sulphuric acid was discontinued after some samples had been collected.

(ii) Elution with 1 N sulphuric acid : Then 1 N sulphuric acid was passed in the above column and the effluent was again collected in samples (each of 250 cc.) at the same flow rate. Several such samples were collected and the % elution for each sample was calculated as described above.

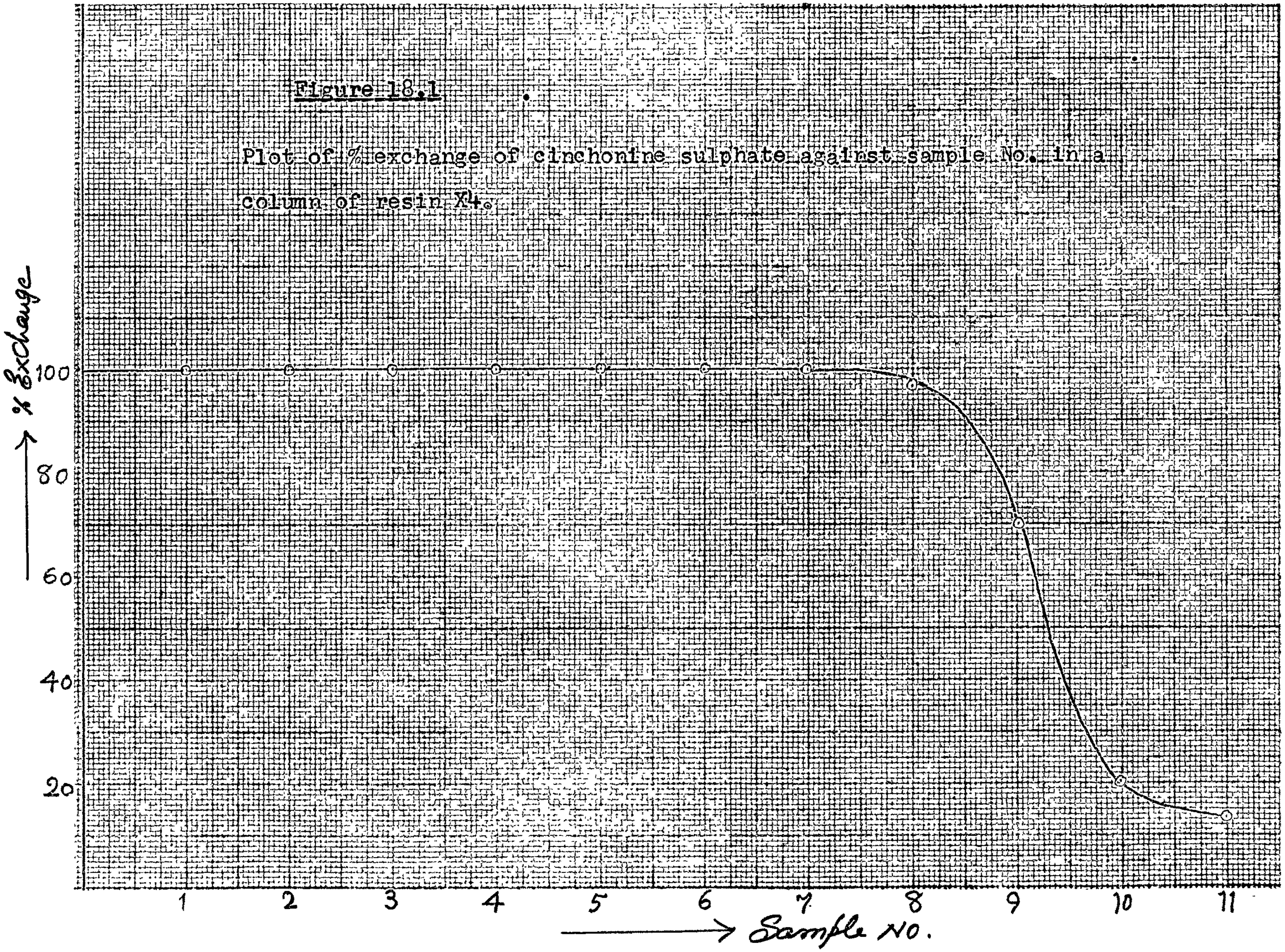
(iii) Elution with ethanol : The flow of 1 N sulphuric acid was then stopped, acid washed with water, and an excess of 1 N sodium hydroxide solution was passed through the column at a slow rate, to liberated the cinchonine in the resin phase. Ethanol was then passed in the column to elute the liberated cinchonine. The effluent was collected at a flow rate of 1 cc./minute. The optical density of the effluent was noted at 294.5 mμ after suitable dilution. Knowing the optical density of the cinchonine solution in alcohol (concentration = 2 meq./litre) at the same wavelength and with the same dilution, the % elution of cinchonine was calculated. The run was then discontinued.

The column was then emptied out and a column of the next resin was set up. The run was then repeated in the same way as above. In this way, runs were carried out with resins X4, X8, X12 and X16 and resins IR-200 and Am-15 of different particle diameters. The results are given in the following tables.

(Break-through capacity was calculated at 99 % exchange for each run.)

Figure 18.1

Plot of % exchange of cinchonine sulphate against sample No. in a column of resin X4.



Results :

Table 18.01

Exchange with cinchonine sulphate solution, in a column of resin X4.

Column capacity = 16.3 meq. each sample = 500 cc.

Sample No.	% exchange	Sample No.	% exchange	Sample No.	% exchange
1	100.0	5	100.0	9	69.6
2	100.0	6	100.0	10	20.5
3	100.0	7	99.5	11	12.5
4	100.0	8	96.5	12	-

Table 18.01 a

Elution of cinchonine sulphate / cinchonine from the above column of resin X4. each sample = 250 cc.

Eluent	Sample No.	% elution	Sample No.	% elution	Sample No.	% elution
N/10 H_2SO_4	1	157.1	4	38.2	7	24.4
(flow rate	2	59.5	5	31.4	8	-
10 cc./min.)	3	46.2	6	27.6	9	-
1 N H_2SO_4	1	288.0	4	93.8	7	52.4
(flow rate	2	170.2	5	74.8	8	45.0
10 cc./min.)	3	115.0	6	63.0	9	39.5

Ethanol (One lot of 250 cc. at 1 cc/min.)

0.7711 meq. of cinchonine was found in the effluent.

After this the run was discontinued.

Table 18.02

Exchange with cinchonine sulphate solution in a column of resin X8

Column capacity = 19.04 meq. each sample = 250 cc.

Sample No.	% exchange	Sample No.	% exchange	Sample No.	% exchange
1	100.0	7	100.0	13	91.4
2	100.0	8	100.0	14	74.3
3	100.0	9	100.0	15	50.0
4	100.0	10	100.0	16	29.5
5	100.0	11	99.5	17	23.4
6	100.0	12	98.2	18	-

Table 18.02 a

Elution of cinchonine sulphate / cinchonine from the above column of resin X8. each sample = 250 cc.

Eluent	Sample No.	% elution	Sample No.	% elution	Sample No.	% elution
N/10 H_2SO_4	1	9.8	3	8.7	5	7.4
(flow rate 10 cc./min.)	2	9.4	4	8.0	6	-
1 N H_2SO_4	1	149.1	4	58.6	7	40.6
(flow rate	2	84.7	5	52.9	8	-
10 cc/min.)	3	67.2	6	46.3	9	-

Ethanol (One lot of 250 cc. at 1 cc/min.)

3.86 meq. of cinchonine was found in the effluent.

After this the run was discontinued.

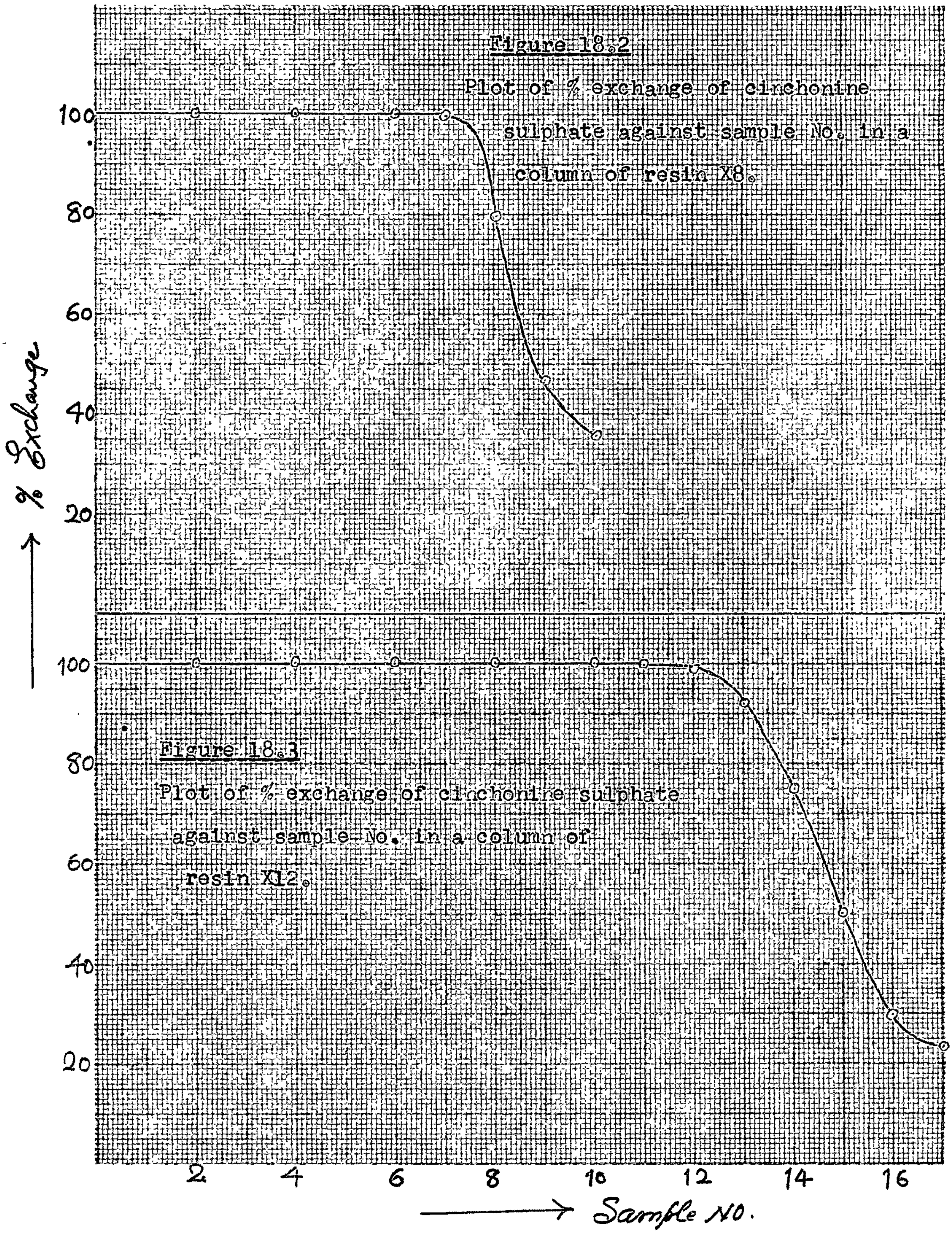


Figure 18.2

Plot of % exchange of cinchonine sulphate against sample No. in a column of resin X8.

Figure 18.3

Plot of % exchange of cinchonine sulphate against sample No. in a column of resin X12.

Table 18.03

Exchange with cinchonine sulphate solution in a column of resin X12.

Column capacity = 22.05 meq. Each sample = 250 cc.

Sample No.	% exchange	Sample No.	% exchange	Sample No.	% exchange
1	100.0	5	100.0	9	46.6
2	100.0	6	100.0	10	35.6
3	100.0	7	99.0	11	-
4	100.0	8	79.8	12	-

Table 18.03 a

Elution of cinchonine sulphate / cinchonine from the above column of resin X12. each sample = 250 cc.

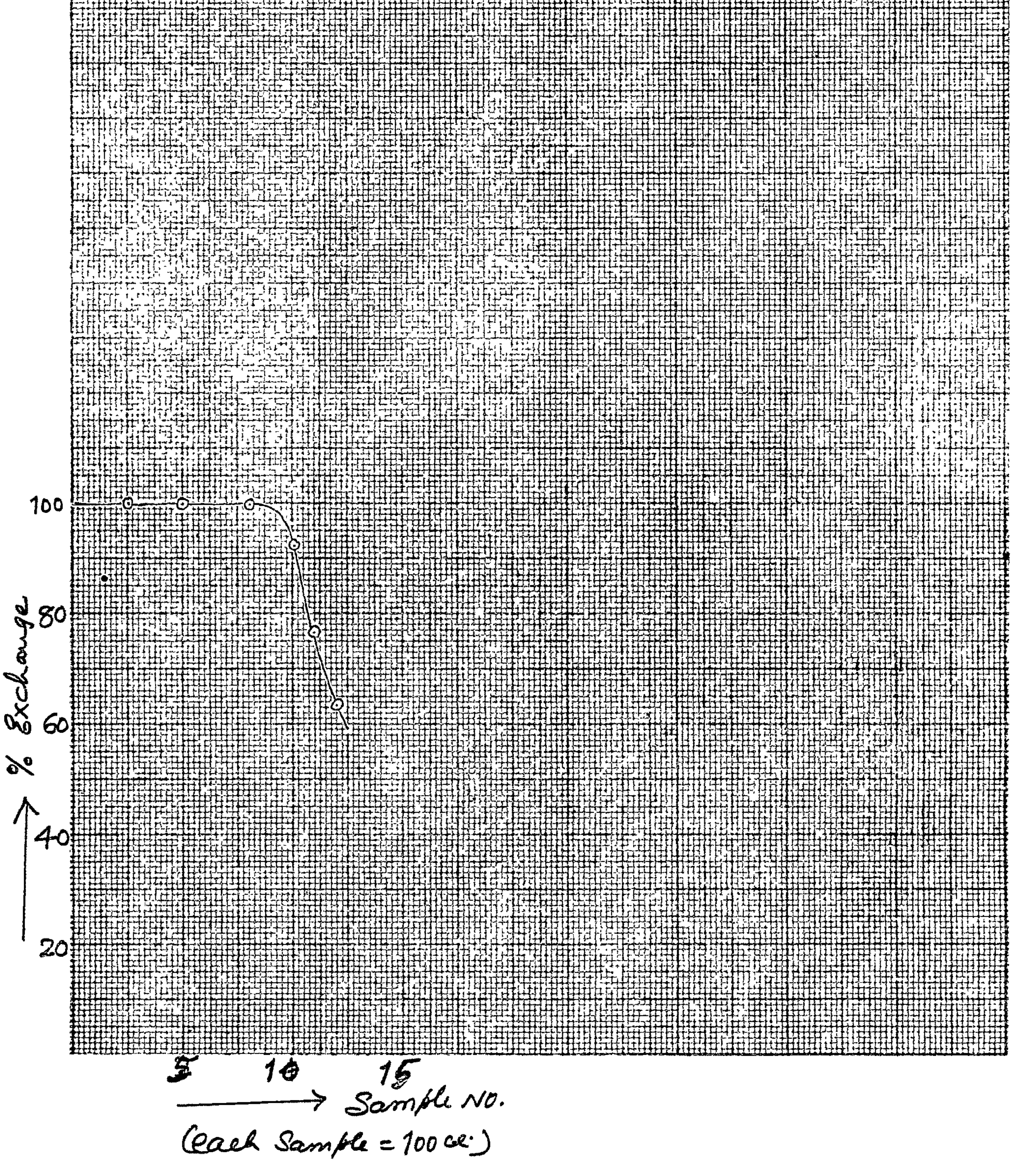
Eluent	Sample No.	% elution	Sample No.	% elution	Sample No.	% elution
N/10 H_2SO_4	1	0.13	3	0.12	5	0.10
(flow rate	2	0.12	4	0.10	6	-
10 cc./min.)						
1 N H_2SO_4	1	10.8	4	10.4	7	9.5
(flow rate	2	10.5	5	10.0	8	-
10 cc./min.)	3	10.4	6	9.7	9	-

Ethanol (One lot of 250 cc. at 1 cc./min.)

2.478 meq. of cinchonine was found in the effluent. After this the run was discontinued.

Figure 18.4

Plot of % exchange of cinchonine sulphate against sample No. in a column of resin X16.



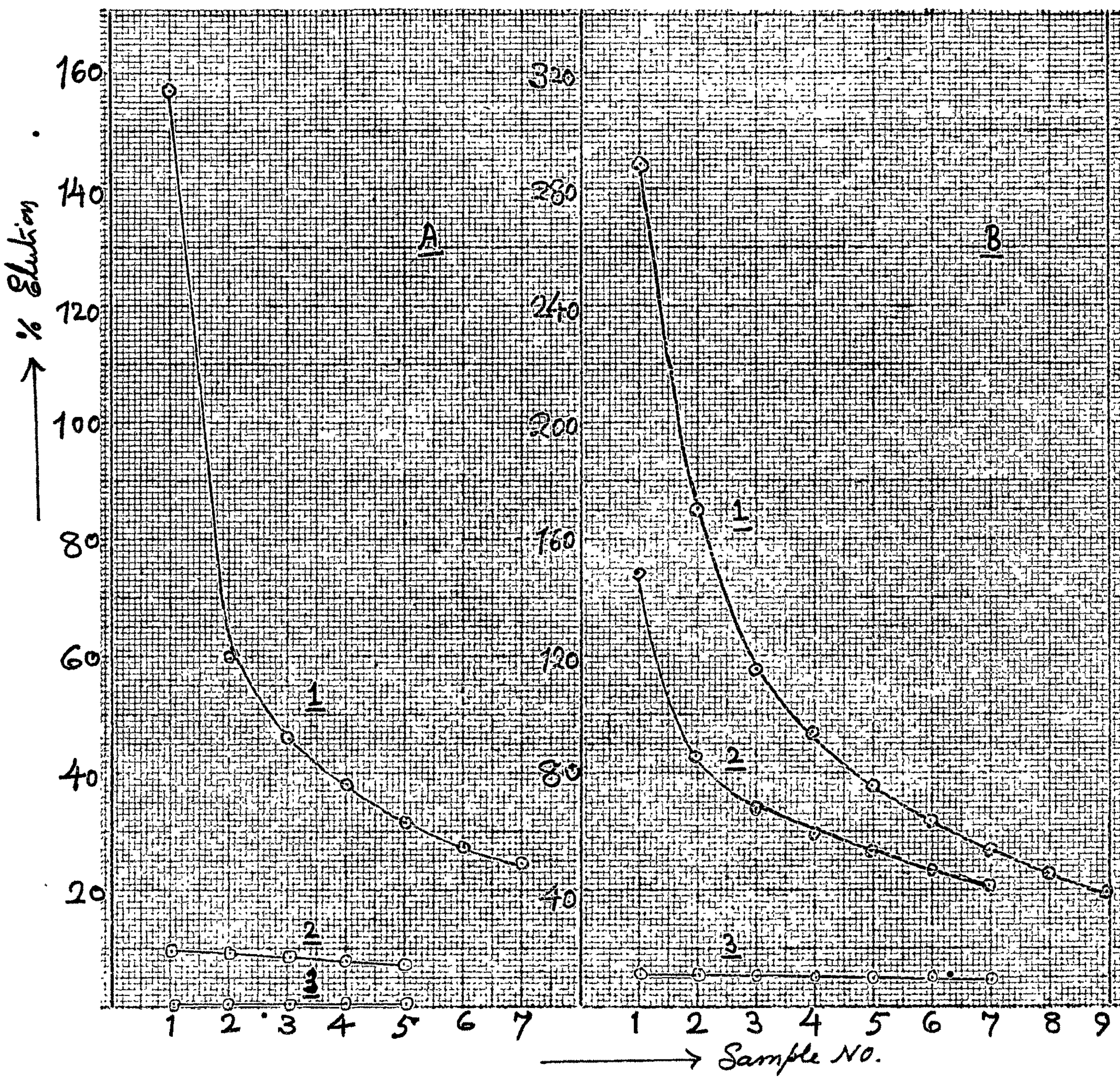


Figure 18.5

Plot of % elution of cinchonine sulphate against sample No. with

(A) N/10 H_2SO_4

(B) 1 N H_2SO_4 for

column of

1. resin X4
2. resin X8
3. resin X12

Table 18.04

Exchange with cinchonine sulphate solution in a column of resin X16.

Column capacity = 21.3 meq.   Each sample = 100 cc.

Sample No.	% exchange	Sample No.	% exchange	Sample No.	% exchange
1	100.0	5	100.0	9	98.8
2	100.0	6	100.0	10	92.5
3	100.0	7	100.0	11	77.0
4	100.0	8	100.0	12	63.5

Table 18.04 a

Elution of cinchonine from the above column of resin X16.

Eluent	
Ethanol	(One lot of 100 cc. at 1 cc./min.) 0.2851 meq. of cinchonine was found in 100 cc. of the effluent. After this the run was discontinued.

Table 18.05

Exchange with cinchonine sulphate solution in a column of resin IR-200 (a = 1.13 mm.)

Column capacity = 15.70 meq. each sample = 250 cc.

Sample No.	% exchange	Sample No.	% exchange	Sample No.	% exchange
1	94.7	6	63.6	11	36.9
2	91.6	7	56.9	12	33.5
3	88.7	8	51.0	13	31.1
4	79.9	9	45.6	14	-
5	70.3	10	42.1	15	-

Table 18.05 a

Elution of cinchonine sulphate/ cinchonine from the above column of resin IR-200. each sample = 250 cc.

Eluent	Sample No.	% elution	Sample No.	% elution	Sample No.	% elution
N/10 H_2SO_4	1	20.0	3	7.6	5	5.9
(flow rate	2	9.8	4	6.4	6	5.3
10 cc./min.)						
1 N H_2SO_4	1	67.6	4	20.1	7	12.1
(flow rate	2	35.2	5	17.4	8	-
10 cc./min.)	3	26.2	6	15.8	9	-

Ethanol (One lot of 100 cc. at 1 cc./min.)

1.887 meq. of cinchonine was found in 100 cc. of the effluent.

After this the run was discontined.

Table 18.06

Exchange with cinchonine sulphate solution in a column of resin IR-200 (a = 0.84 mm.)
Column capacity = 15.32 meq. each sample = 250 cc.

Sample No.	% exchange	Sample No.	% exchange	Sample No.	% exchange
1	99.3	5	92.4	9	65.7
2	98.4	6	86.4	10	58.7
3	97.8	7	81.6	11	50.2
4	95.0	8	74.1	12	43.0

Table 18.06 a

Elution of cinchonine sulphate / cinchonine from the above column of resin IR-200. each sample = 250 cc.

Eluent	Sample No.	% elution	Sample No.	% elution	Sample No.	% elution
N/10 H_2SO_4 (flow rate 10 cc./min.)	1	68.0	3	18.8	5	11.4
	2	26.7	4	14.2	6	10.3
1 N H_2SO_4 (flow rate 10 cc./min.)	1	104.3	4	27.5	7	13.6
	2	42.7	5	18.9	8	-
	3	32.5	6	16.9	9	-

Ethanol (One lot of 100 cc. at 1 cc./min.)

1.508 meq. of cinchonine was found in 100 cc. of the effluent.

After this the run was discontinued.

Table 18.07

Exchange with cinchonine sulphate solution in a column of resin IR-200 (a = 0.58 mm.)
Column capacity = 15.47 meq. each sample = 250 cc.

Sample No.	% exchange	Sample No.	% exchange	Sample No.	% exchange
1	99.7	6	98.5	11	50.8
2	99.7	7	95.7	12	40.1
3	99.6	8	93.9	13	30.9
4	99.5	9	84.8	14	23.9
5	99.0	10	63.9	15	-

Table 18.07 a

Elution of cinchonine sulphate / cinchonine from the above column of resin IR-200 each sample = 250 cc.

Eluent	Sample No.	% elution	Sample No.	% elution	Sample No.	% elution
N/10 H_2SO_4	1	135.0	3	26.7	5	17.8
(flow rate	2	41.0	4	22.1	6	15.3
10 cc./min.)						
1 N H_2SO_4	1	137.4	4	27.5	7	17.2
(flow rate	2	61.6	5	22.6	8	-
10 cc./min.)	3	34.1	6	19.9	9	-

Ethanol (One lot of 100 cc. at 1 cc./min.)

2.014 meq. of cinchonine was found in the effluent. After this the run was discontinued.

Table 18.08

Exchange with cinchonine sulphate solution in a column of resin IR-200 (a = 0.37 mm.)
Column capacity = 16.03 meq. each sample = 250 cc.

Sample No.	% exchange	Sample No.	% exchange	Sample No.	% exchange
1	100.0	6	100.0	11	69.4
2	100.0	7	99.7	12	46.2
3	100.0	8	99.4	13	27.6
4	100.0	9	97.2	14	16.6
5	100.0	10	88.6	15	-

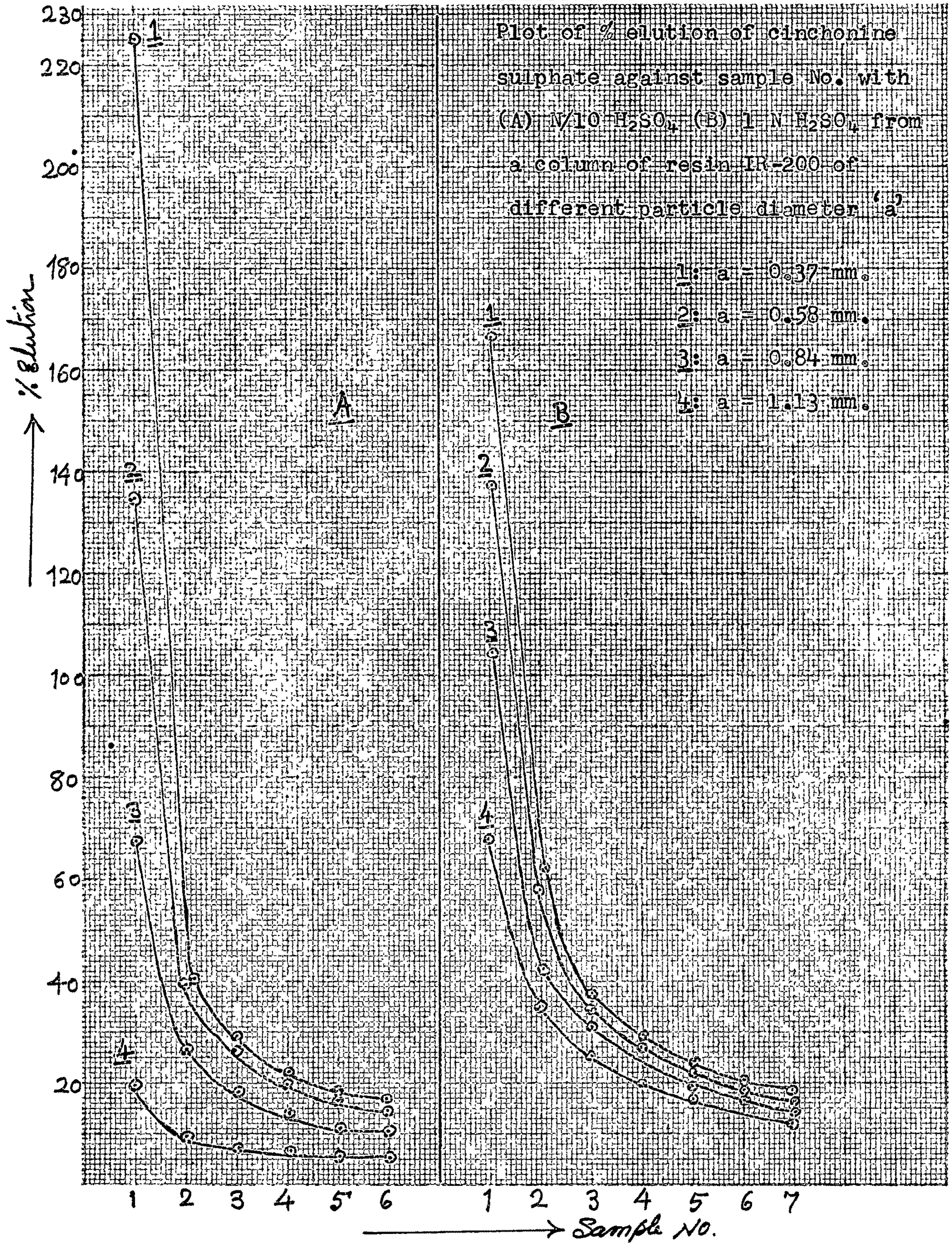
Table 18.08 a

Elution of cinchonine sulphate/ cinchonine from the above column of resin IR-200. each sample = 250 cc.

Eluent	Sample No.	% elution	Sample No.	% elution	Sample No.	% elution
N/10 H_2SO_4	1	225.7	3	29.0	5	17.7
(flow rate	2	40.0	4	19.9	6	15.3
10 cc./min.)	3					
1 N H_2SO_4	1	166.8	4	29.0	7	17.4
(flow rate	2	59.1	5	23.9	8	-
10 cc./min.)	3	37.8	6	19.9	9	-

Ethanol (One lot of 100 cc. at 1 cc./min.)
2.237 meq. of cinchonine base was found in the effluent.
After this the run was discontinued.

Figure 18.7



Plot of % elution of cinchonine sulphate against sample No. with (A) N/10 H_2SO_4 (B) 1 N H_2SO_4 from a column of resin IR-200 of different particle diameter 'a'

Figure 18.6

Plot of % exchange of cinchonine sulphate against sample No. in a column of (A) IR-200 (B) Am-15 of different particle diamete 'a'

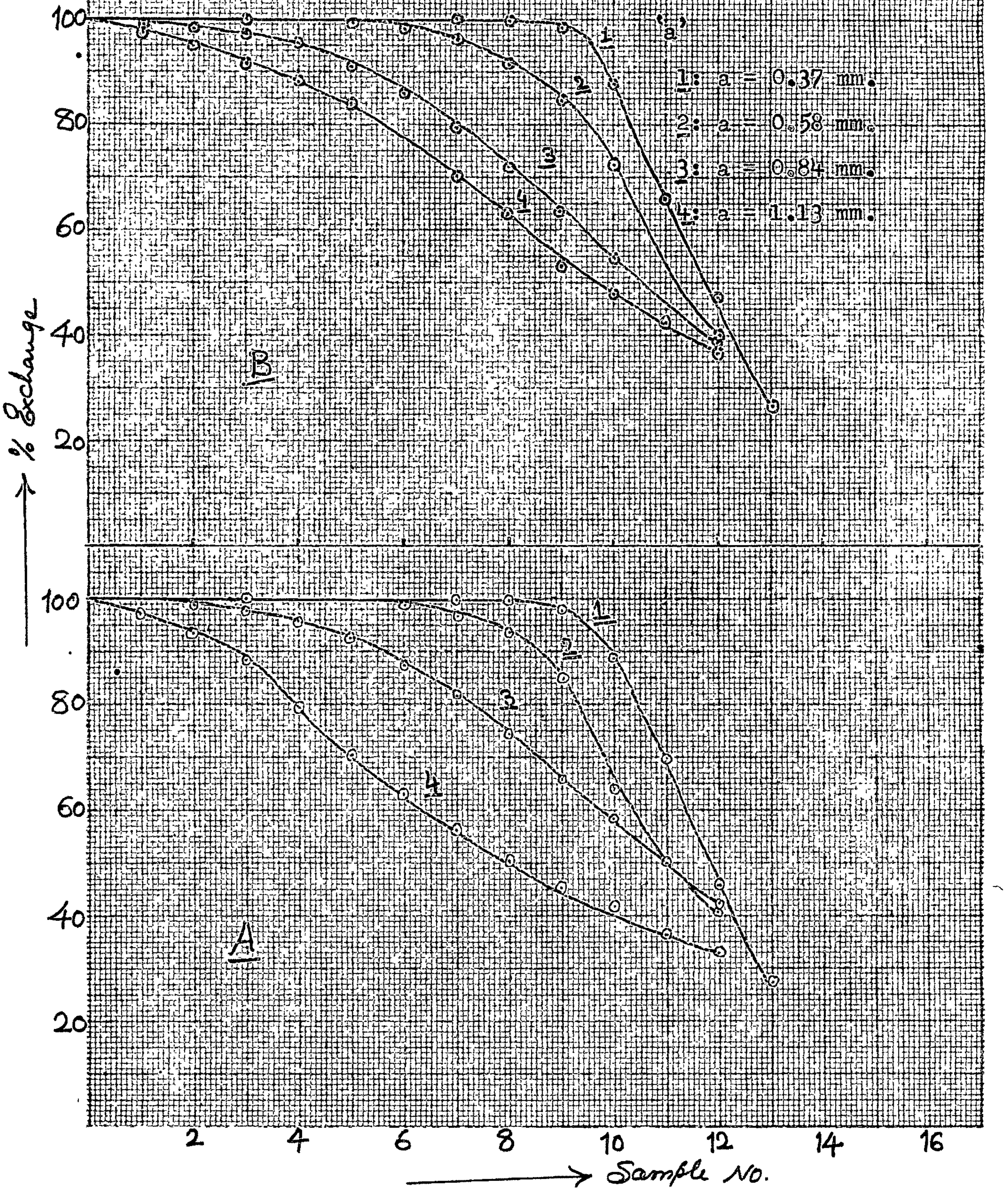


Table 18.09

Exchange with cinchonine sulphate solution in a column of resin Am-15 (a = 1.13 mm.)

Column capacity = 15.29 meq. each sample = 250 cc.

Sample No.	% exchange	Sample No.	% exchange	Sample No.	% exchange
1	97.6	6	81.5	11	42.9
2	95.0	7	69.4	12	37.2
3	91.0	8	63.4	13	34.4
4	88.8	9	52.7	14	-
5	83.9	10	47.6	15	-

Table 18.09 a

Elution of cinchonine sulphate/ cinchonine from the above column of resin Am-15. each sample = 250 cc.

Eluent	Sample No.	% elution	Sample No.	% elution	Sample No.	% elution
N/10 H_2SO_4	1	40.1	3	13.5	5	8.3
(flow rate 10 cc./min.)	2	19.3	4	9.5	6	-
1 N H_2SO_4	1	97.6	3	31.1	5	19.5
(flow rate 10 cc./min.)	2	39.6	4	25.0	6	14.6
Ethanol	(One lot of 100 cc. at 1 cc./min.) 1.796 meq. of cinchonine base was found in the effluen After this the run was discontinued.					

Table 18.10

Exchange with cinchonine sulphate solution in a column of resin Am-15 (a = 0.84 mm.)

Column capacity = 15.32 meq. each sample = 250 cc.

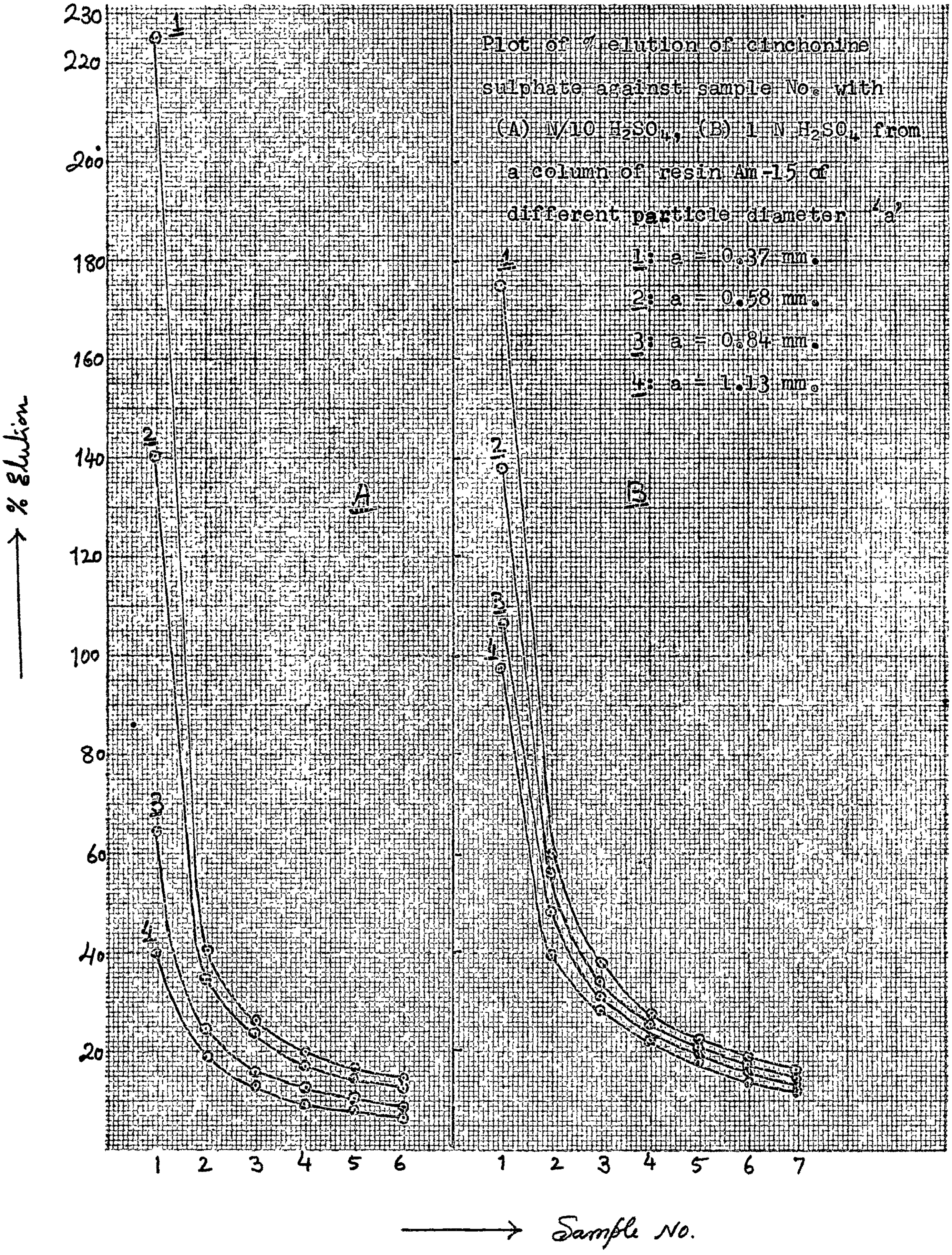
Sample No.	% exchange	Sample No.	% exchange	Sample No.	% exchange
1	98.8	6	86.3	11	47.5
2	98.1	7	79.0	12	37.9
3	96.9	8	72.3	13	32.8
4	95.6	9	63.8	14	-
5	90.6	10	54.8	15	-

Table 18.10 a

Elution of cinchonine sulphate / cinchonine from the above column of resin Am-15. each sample = 250 cc.

Eluent	Sample No.	% elution	Sample No.	% elution	Sample No.	% elution
N/10 H_2SO_4	1	64.4	3	16.0	5	10.3
(flow rate	2	24.5	4	12.8	6	8.7
10 cc./min.)						
1 N H_2SO_4	1	106.8	4	22.7	7	12.6
(flow rate	2	48.2	5	19.2	8	-
10 cc./min)	3	30.1	6	15.8	9	-
Ethanol	(One lot of 100 cc. at 1 cc./min.) 1.470 meq. of cinchonine base was found in the effluent. After this the run was discontinued.					

Figure 18.8



Plot of % elution of cinchonine sulphate against sample No. with (A) N/10 H_2SO_4, (B) 1 N H_2SO_4 from a column of resin Am-15 of different particle diameter 'a'

1: a = 0.37 mm.
2: a = 0.58 mm.
3: a = 0.84 mm.
4: a = 1.13 mm.

Table 18.11

Exchange with cinchonine sulphate solution in a column of resin Am-15 (a = 0.58 mm.)

Column capacity = 15.47 meq. each sample = 250 cc.

Sample No.	% exchange	Sample No.	% exchange	Sample No.	% exchange
1	100.0	6	97.9	11	47.8
2	100.0	7	95.9	12	38.7
3	100.0	8	91.5	13	30.5
4	99.6	9	84.5	14	26.3
5	99.0	10	72.5	15	-

Table 18.11 a

Elution of cinchonine sulphate/ cinchonine from the above column of resin Am-15. each sample = 250 cc.

Eluent	Sample No.	% elution	Sample No.	% elution	Sample No.	% elution
N/10 H_2SO_4 (flow rate 10 cc./min.)	1	140.5	3	23.9	5	15.5
	2	34.9	4	17.0	6	12.3
1 N H_2SO_4 (flow rate 10 cc./min.)	1	138.0	4	25.0	7	14.9
	2	56.0	5	20.6	8	-
	3	33.3	6	17.9	9	-
Ethanol	(One lot of 100 cc. at 1 cc./min.) 1.7890 meq. of cinchonine base was found in the effluent. After this the run was discontinued.					

Table 18.12

Exchange with cinchonine sulphate solution in a column of resin Am-15 (a = 0.37 mm.)

Column capacity = 16.03 meq. each sample = 250 cc.

Sample No.	% exchange	Sample No.	% exchange	Sample No.	% exchange
1	100.0	6	100.0	11	65.9
2	100.0	7	100.0	12	47.1
3	100.0	8	99.6	13	26.6
4	100.0	9	98.1	14	16.0
5	100.0	10	87.7	15	-

Table 18.12 a

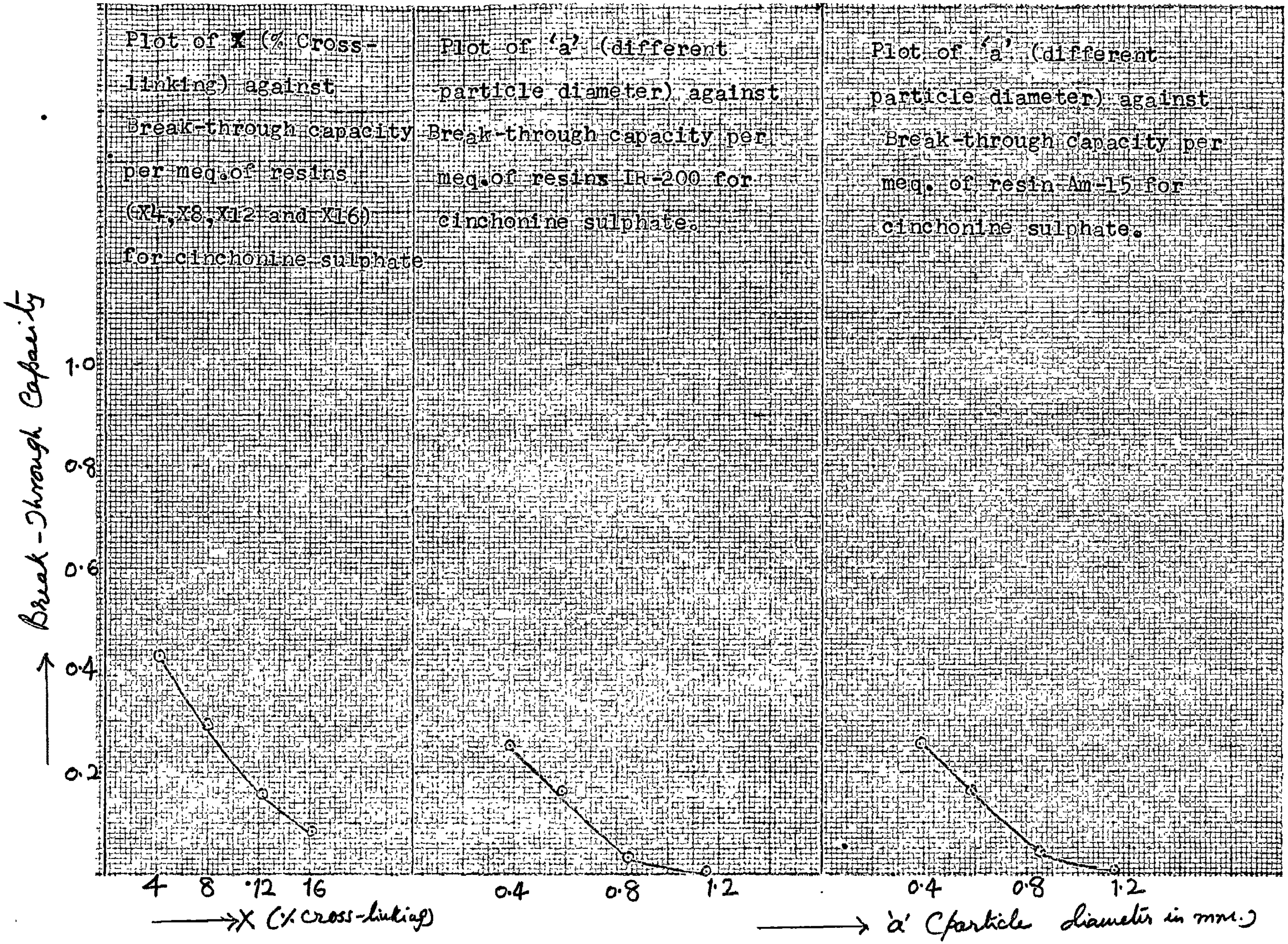
Elution of cinchonine sulphate/ cinchonine from the above column of resin Am-15 each sample = 250 cc.

Eluent	Sample No.	% elution	Sample No.	% elution	Sample No.	% elution
N/10 H_2SO_4 (flow rate 10 cc./min.)	1	225.4	3	26.6	5	16.5
	2	441.6	4	20.0	6	13.5
1 N H_2SO_4 (flow rate 10 cc./min.)	1	175.1	4	27.7	7	15.8
	2	59.8	5	21.7	8	-
	3	38.3	6	17.9	9	-

Ethanol (One lot of 100 cc. at 1 cc./min.)

1.922 meq. of cinchonine base was found in the effluent.
After this the run was discontinued.

Figure 10.9


Plot of X (% Cross-linking) against Break-through capacity per meq. of resins (X4, X8, X12 and X16) for cinchonine sulphate

Plot of 'a' (different particle diameter) against Break-through capacity per meq. of resins IR-200 for cinchonine sulphate.

Plot of 'a' (different particle diameter) against Break-through capacity per meq. of resin Am-15 for cinchonine sulphate.

Table 18.13 a.(Q)

Summary of column data for tables 7.01 a, b to 7.05 a, b.*
The numerator of the fraction in the brackets gives the number of samples and the denominator, the valume of each sample.

Resin	a (mm.)	Column capacity in meq.	P_{Ro}	C_{ef}	exchange with Na_2SO_4 solution in meq.	exchange with quinine sulphate solution in meq.	Break-through capacity in meq., per meq. of total resin capacity with		Break-through capacity in meq., per meq. of effective resin capacity with quinine-sulphate soln.	γ = (A/B)
							Na_2SO_4 (A)	Quinine sulphate (B)		
X4	0.215	16.3	49.4	8.05	16.3 (8/250)	6.97 (38/100)	0.767	0.331	0.670	2.32
X8	0.215	19.0	40.0	7.62	19.0 (9/250)	5.71 (37/100)	0.853	0.226	0.563	3.78
X12	0.215	22.0	25.5	5.62	22.0 (11/250)	2.69 (21/100)	0.907	0.070	0.276	12.9
X16	0.215	21.3	18.2	3.88	21.3 (10/250)	1.14 (18/50)	0.918	0.025	0.135	37.3
X20	0.215	21.0	5.9	1.24	21.0 (4/100+ 9/250)	0.123 (12/50)	0.905	zero	-	

*Data of the above column are taken from (I)

Table 18.13 b (Q)

Summary of column data for tables 7.06, a, b to 7.12 a, b.*
The numerator of the fraction in the brackets gives the number of samples and the denominator, the volume of each sample.

Resin	a (mm)	Column capacity in meq.	P_{Ro}	C_{ef}	exchange with Na_2SO_4 solution in meq.	exchange with quinine sulphate solution in meq.	Break-through capacity in meq., per meq. of total resin capacity with Na_2SO_4	Quinine sulphate	Break-through capacity in meq., per meq. of effective resin capacity with quinine-sulphate soln.	γ = (8/9)
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
IR-120	0.84	16.1	40.3	6.51	$\frac{16.15}{(9/250)}$	$\frac{2.86}{(24/100)}$	0.387	0.025	0.061	15.8
	0.58	15.5	40.3	6.23	$\frac{15.5}{(9/250)}$	$\frac{3.14}{(24/100)}$	0.533	0.052	0.125	10.3
	0.37	15.7	40.3	6.31	$\frac{15.7}{(8/250)}$	$\frac{3.28}{(22/100)}$	0.670	0.103	0.253	6.52

(Continued on next page)

Table 18.13 b (Q) (Continued from the previous page)*

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
IR-200	1.13	15.7	30.5	4.78	15.7 (10/250)	2.91 (26/100)	0.271	zero	-	
	0.84	15.3	30.5	4.67	15.3 (10/250)	3.55 (26/100)	0.555	0.023	0.077	23.6
	0.58	15.5	30.5	4.72	15.5 (9/250)	4.09 (25/100)	0.678	0.090	0.297	7.50
	0.37	16.0	30.5	4.88	16.0 (9/250)	4.75 (28/100)	0.796	0.182	0.594	4.37

* Data of the above column are taken from (I)

Table 18.13 c (Q)

Summary of column data for tables 7.01c to 7.12 c.*

The numerator of the fraction in the brackets gives the number of samples and the denominator, the volume of each sample.

Resin	a (mm.)	Amount in meq., eluted with Eluent			Total eluted in meq.	Total uneluted
		N/10 H_2SO_4	1 N H_2SO_4	Ethanol		
1.	2.	3.	4.	5.	6.	7.
X4	0.215	0.169 (5/250)	3.02 (9/250)	2.38 (1/100)	5.57	1.40
X8	0.215	0.007 (3/250)	0.641 (4/250)	1.88 (1/100)	2.53	3.18
X12	0.215	0.005 (4/250)	0.127 (6/250)	0.041 (5/10)	0.173	2.51
X16	0.215	-	-	0.04 (5/10)	0.040	1.10
IR-120	0.58	-	0.127 (6/250)	0.241 (1/50)	0.368	2.77
	0.37	-	0.219 (6/250)	0.329 (1/50)	0.548	2.73

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Table 18.13 c (Q)*

(Continued from the previous page).

1.	2.	3.	4.	5.	6.	7.
IR-200	1.13	$\frac{0.245}{(5/250)}$	$\frac{0.454}{(6/250)}$	$\frac{2.21}{(1/100)}$	2.909	zero
	0.84	$\frac{0.475}{(5/250)}$	$\frac{0.756}{(6/250)}$	$\frac{2.32}{(1/100)}$	3.55	zero
	0.58	$\frac{0.608}{(5/250)}$	$\frac{1.06}{(6/250)}$	$\frac{2.41}{(1/100)}$	4.09	zero
	0.37	$\frac{1.02}{(5/250)}$	$\frac{1.45}{(6/250)}$	$\frac{2.28}{(1/100)}$	4.75	zero

* Data of the above table are taken from (1)

Table 18.13 a.(C)

Summary of column data for tables 18.01 to 18.04

The numerator of the fraction in the brackets gives the number of samples and the denominator, the volume of each sample.

Resin	a (mm.)	Column capacity in meq.	P_{Ro}	C_{eff}	* exchange with Na_2SO_4 solution in meq.	exchange with cinchonine sulphate solution in meq.	Break-through capacity in meq. per meq. of total resin *capacity with		Break-through capacity in meq. per meq. of effective resin capacity with cinchonine sulphate soln.	$=\left(\frac{\gamma}{\gamma}\right)$ =(8/9)
							Na_2SO_4	Cinchonine sulphate		
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
X4	0.215	16.3	49.5	8.07	16.3 (8/250)	8.99 (11/500)	0.767	0.429	0.868	1.78
X8	0.215	19.0	44.6	8.49	19.0 (9/250)	7.33 (17/250)	0.853	0.289	0.647	2.96
X12	0.215	22.0	27.4	6.04	22.0 (11/250)	4.30 (10/250)	0.907	0.158	0.578	5.72
X16	0.215	21.30	21.6	4.60	21.3 (10/250)	2.26 (12/100)	0.918	0.084	0.391	10.8

* Data of the above columns are taken from (1)

Table 18.13 b (C).

Summary of column data for tables 18.05 to 18.12

The numerator of the fraction in the brackets gives the number of samples and the denominator, the volume of each sample.

Resin	a (mm.)	Column capacity in meq.	P_{Ro}	C_{ef}	* exchange with Na_2SO_4 solution in meq.	exchange with cinchonine sulphate solution in meq.	Break-through capacity in meq., per meq. of total resin capacity with * Na_2SO_4	Break-through capacity in meq., per meq. of total resin capacity with Cinchonine sulphate	Break-through capacity in meq., per meq. of effective resin capacity with cinchonine sulphate solution	$= (8\overset{\gamma}{/}9)$
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
IR-200	1.13	15.7	33.4	5.24	$\frac{15.7}{(10/250)}$	$\frac{3.91}{(13/250)}$	0.271	zero	-	-
	0.84	15.3	33.4	5.12	$\frac{15.3}{(10/250)}$	$\frac{4.66}{(12/250)}$	0.555	0.032	0.097	17.6
	0.58	15.5	33.4	5.17	$\frac{15.5}{(9/250)}$	$\frac{5.40}{(14/250)}$	0.678	0.160	0.480	4.24
	0.37	16.0	33.4	5.35	$\frac{16.0}{(9/250)}$	$\frac{5.72}{(14/250)}$	0.796	0.250	0.748	3.18

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Table 18.13 b (C). (Continued from the previous page)

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Am-15	1.13	15.3	34.1	5.21	-	$\frac{4.43}{(13/250)}$	-	zero	-	-
	0.84	15.3	34.1	5.22	-	$\frac{4.77}{(13/250)}$	-	0.032	0.095	-
	0.58	15.5	34.1	5.25	-	$\frac{5.42}{(14/250)}$	-	0.161	0.473	-
	0.37	16.0	34.1	5.47	-	$\frac{5.71}{(14/250)}$	-	0.250	0.732	-

* Data of the above columns are taken from (1)

Table 18.13 c (C).

Summary of column data for tables 18.01 a to 18.12 a.

The numerator of the fraction in the brackets gives the number of samples and the denominator, the volume of each sample.

Resin	a (mm.)	Amount in meq., eluted with Eluent			Total eluted in meq.	Total uneluted
		N/10 H_2SO_4	1 N H_2SO_4	Ethanol		
1.	2.	3.	4.	5.	6.	7.
X4	0.215	1.92 (7/250)	4.71 (9/250)	0.771 (1/250)	7.40	1.58
X8	0.215	0.216 (5/250)	2.50 (7/250)	3.86 (1/250)	6.57	0.76
X12	0.215	0.003 (5/250)	0.357 (7/250)	2.48 (1/250)	2.84	1.46
X16	0.215	-	-	0.285 (1/100)	0.285	1.98

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Table 18.13 c (C). (Continued from the previous page)

1.	2.	3.	4.	5.	6.	7.
IR-200	1.13	$\frac{0.278}{(6/250)}$	$\frac{0.972}{(7/250)}$	$\frac{1.89}{(1/100)}$	3.14	0.77
	0.84	$\frac{0.747}{(6/250)}$	$\frac{1.28}{(7/250)}$	$\frac{1.51}{1/100)}$	3.54	1.13
	0.58	$\frac{1.29}{(6/250)}$	$\frac{1.60}{(7/250)}$	$\frac{2.01}{(1/100)}$	4.90	0.50
	0.37	$\frac{1.71}{(6/250)}$	$\frac{1.77}{(7/250)}$	$\frac{2.24}{(1/100)}$	5.72	zero
Am-15	1.13	$\frac{0.454}{(5/250)}$	$\frac{1.14}{(6/250)}$	$\frac{1.80}{(1/100)}$	3.39	0.04
	0.84	$\frac{0.683}{(6/250)}$	$\frac{1.28}{(7/250)}$	$\frac{1.47}{(1/100)}$	3.43	1.34
	0.58	$\frac{1.22}{(6/250)}$	$\frac{1.53}{(7/250)}$	$\frac{1.79}{(1/100)}$	4.54	0.88
	0.37	$\frac{1.72}{(6/250)}$	$\frac{1.78}{(7/250)}$	$\frac{1.92}{(1/100)}$	5.42	0.28

Discussion :

The conclusions of the tables (18.01 to 18.12 a.) are summarised in tables (18.13 a, b, c), together with results obtained under similar conditions by (1).As with quinine sulphate, the break-through is relatively less sharp for cinchonine sulphate also for resin X4 and both, the sharpness and the break-through capacity decrease as X increases. The values for cinchonine sulphate are relatively higher than those for quinine sulphate. This should be attributed to the difference in the molecular size of quinine and cinchonine . The break-through capacity of cinchonine sulphate per meq. of total capacity of the resin, as well as , per meq. of effective capacity of the resin (obtained by multiplying the total capacity by P_{Ro} / 100) decreases markedly as X increases due to reduced rate of diffusion in the resin particle.

Elution of cinchonine from the column with N/100 sulphuric acid becomes less efficient as X increases. Same is true for elution with 1 N sulphuric acid. The elution in both the cases is relatively easier for cinchonine than that for quinine. Elution with 1 N sulphuric acid is better, as may be expected, than with N/10 sulphuric acid. Elution of liberated cinchonine with ethanol also becomes less efficient as X increases. The lower efficiency of elution with X increasing, is due to reduced rate of diffusion through and from the resin particles .

The conclusion from the effect of degree of crosslinking is that lower degree of crosslinking is to be preferred, as this would permit higher break-through capacity due to higher rate of exchange and higher effective capacity of the resin. However if X is reduced below 4, the volume changes during exchange would be relatively more and molecular sorption also may matter, which would be undesirable.

Resin IR-200 and Am-15 have been studied with different particle diameters. The uptake from cinchonine sulphate solution is markedly increased by decrease in particle size. This is due to increases in the exchange rate with decrease in the particle size. With resins IR-200 and Am-15 which are more porous than X8, though of X about 8, the rate of exchange is relatively higher than that for X8 and hence the uptake and elution are relatively more efficient. The elution is also better than that for X4. However, the effective capacity for IR-200 is less than that for X4 or X8. Elution of quinine is relatively easier with ethanol than that of cinchonine which may be due to better solubility of quinine in ethanol.

The above, together with the results of (1), indicates that a resin of relatively high crosslinking, such as X 20, would be suitable for removing small cations from a solution of alkaloid salt ; by passing the solution through the column, the small cations will be preferably taken up by the exchanger while most of the organic alkaloid cations will pass through. The acid in the effluent, then, may be removed with a weakly basic resin such as Amberlite IR-4B.

On the other hand for recovery of alkaloid from raw material, the choice should be between X4 and IR-200, the particle size being small ; however, the pressure-drop would increase as the particle size is decreased. Hence a compromise has to be made. Further detailed work should indicate which of the two should be preferred on the overall considerations.

Reference :

1. Kanhere, S.S., Ph.D.Thesis (Baroda 1964).