3. SORPTION OF STRONG ELECTROLYTES

3.1. Introduction :

Suppose that a cation exchanger (containing no sorbed electrolyte) is placed in a dilute solution of a strong electrolyte. There are considerable concentration differences between the two phases ; the cation concentration is larger in the ion exchanger, whereas the (mobile) anion concentration is larger in the solution. If the ions carried no electric charges, these concentration differences would be levelled out by diffusion. However, such a process would disturb electroneutrality since, actually, the ions are charged. Migration, both of cations into the solution and of anions into the ion exchanger results in an accumulation of positive charge in the solution and of negative charge in the ion exchanger. The first few ions which diffuse thus build up an electric potential difference between the two phases. This so-called Donnan potential pulls cations back into the (negatively charged) ion exchanger and anions back into the (positively charged) solution. An equilibrium is established in which the tendency of ions to level out the existing concentration differences is balanced by the action of the electric field. In the ion exchanger, the counter ion concentration thus remains much higher and the co-ion concentration much lower than that in the external solution.

The situation with anion exchangers is analogeus. Here, of course, the Donnan potential has the opposite sign.

The electric potential difference between ion exchangers and dilute solutions can attain very high values. Yet, this does not mean that in either the ion exchanger or the solution deviations from electroneutrality detectable by chemical analysis can occur. Migration of just a few ions is sufficient to build up so strong an electric field counteracting any further migration that deviations from electroneutrality remain far below the limit of accuracy of any method, except for the measurement of the electric field itself. Thus, for all practical purposes, the condition of electroneutrality must be considered as still valid.

The Donnan potential has one immediate consequence for electrolyte sorption ; it repels co-ions from the ion exchanger and thus prevents the internal co-ion concentration from rising beyond an equilibrium value which is usually much smaller than the concentration in the external solution. Co-ion uptake and electrolyte sorption are equivalent because of the electroneutrality requirement. Hence, the electrolyte is, at least partially, excluded by the ion exchanger. This Donnan exclusion is a unique feature of electrolyte sorption by ionic sorbents.

Electrolyte-sorption equilibria have a formal resemblance to equilibria in system such as

$$A^+, \; Y^-, \; H_2O \; \left| \begin{array}{c} \text{membrane} \\ \text{impermeable for} \\ R^- \end{array} \right| \; A^+, \; Y^-, \; R^-, \; H_2O \qquad (3.1)$$

in which a membrance permeable for all species except for R^- is between two solutions, AY and AY + AR. In both systems one ionic species (. the fixed ionic groups, or the R$^-$ ions) is restricted to one of the two phases. The resulting equations for the distribution of the mobile species and the electric potential difference in both systems are formally identical. The behaviour of membrane systems such as above was first elucidated by F.G.Donnan (1) in 1911. In his honour, such membrane equilibria are called Donnan equilibria and the electric potential differences between the two solutions Donnan potentials. Because of the formal analogies, the term Donnan equilibrium and Donnan potential are now also applied to sorption equilibria of strong electrolytes and phase boundary potentials between ion exchanger and solution.

The process of sorption of strong electrolytes, can be quantitatively described by the equation

$$\left(\frac{\bar{m}_Y}{m_Y}\right)^{\nu_Y} = \left(\frac{|z_Y|\, m_Y}{|z_Y|\,\bar{m}_Y+\bar{m}_R}\right)^{\nu_A} \left(\frac{\gamma_\pm}{\bar{\gamma}_\pm}\right)^{\nu} \left(\frac{\bar{a}_w}{a_w}\right)^{v_{AY}/v_w} \qquad (3.2)$$

where

v_{AY} , v_w = partial molar volume of electrolyte AY and the solvent,

ν_A , ν_Y = moles of ions A and Y per mole of electrolyte AY respectively,

ν = number of ions produced by the ionisation of electrolyte,

$\bar{m}_R, \bar{m}_Y, m_Y$ = molality of the (univalent) fixed ionic groups and co-ion Y in the resin phase and of co-ion Y in external solution,

z_Y = electrochemical valence of species Y,

$\bar{\gamma}_\pm , \gamma_\pm$ = the mean molal activity coefficient of the electrolyte in the resin phase and in the external solution respectively,

$\bar{a}_w , a_w$ = solvent activity in the resin phase and in the external solution respectively.

The general rules of electrolyte sorption can be summarized as follows : Strong electrolytes, in contrast to nonelectrolytes, are excluded, to the varying degrees, by ion exchangers. This electrolyte exclusion is favoured by low concentration of the solution, high capacity and crosslinking of the ion exchanger, low valence of the counter ion, high valence of the co-ion and large molar volume of the electrolyte. Electrolyte exclusion can be partially or completely offset by association, complex formation, or similar interactions between the ions of the electrolyte and the fixed ionic groups or the matrix, and by association of mobile ions with one another.

3.2. The ultraviolet absorption spectra of naphthalene-2-sulfonic (NF) acid

3.2.a Introduction :

Littoiff (2) studied the calcium salts of naphthalene-1-sulfonic acid and naphthalene-2-sulfonic acid and observed that both showed fine bands at λ = 321, 307, 275, 252 and 230 mμ . The two spectra were very similar to each other and to that of naphthalene. The absorption is slightly higher for 1-isomer than for the 2-isomer. In both, it is higher at pH 2.75 than at pH 9.1. The fluorescence is stronger in the 2-isomer than in the 1-isomer salt (Ca).

Daglish (3) has studied a number of hydroxy and sulfonic acid derivatives of naphthalene. His data for ultraviolet absorption maxima and log ϵ are given in table (3.2.3) for naphthalene (in 95% ethanol), naphthalene-1-sulfonic acid (in 95 % ethanol), and naphthalene-2-sulfonic acid (in 95 % ethanol, without and with 5 % HCl).

Naphthalene in 95 % ethanol shows three well-difined regions of absorption with the values

λmax	220	250-290	295-320
log ϵ	5	3.2 - 3.7	2.3 - 2.5

similar results were also reported priviously for hexane solution (4).

The three absorption regions are ascribed to separate states of electronic excitation of the molecule.

The presence of these regions in the curves of most of the simple derivatives examined by him suggested that absorption was due to the naphthalene molecule as a whole. However, the curve was affected both by the nature and the position of the substituent in the molecule.

Lewis and Culvin (5) suggested that light was absorbed by the polarised forms which contributed to the general resonance structure of the molecule.

Hirshberg and Jones (6) interpreted the results of simple substitution as the effect of polarised structures by vectorised electric moments of light. They ascribed the second naphthalene band with vector along the axis parallel to the linkage common to the two rings. The low intensity third band of absorption was associated with the electric vector normal to the first.

The above studies give the ultraviolet absorption spectra of calcium and sodium salts of naphthalene sulfonic acids and a number of hydroxy and sulfonic acid derivatives of naphthalene. In this section ultraviolet absorption spectrum of naphthalene-2-sulfonic acid in aqueous solution was studied with a view to assess the applicability of this method in the estimation of naphthalene-2-sulfonic acid in presence of sulfuric acid or hydrochloric acid.

This study inclues the effect of (a) acid (sulfuric or hydrochloric acid) (b) alkali (sodium hydroxide) and (c) salt (sodium sulfate) on ultraviolet absorption of naphthalene-2-sulfonic acid in aqueous solution.

3.2b Experimental :

Chemicals : Naphthalene-2-sulfonic acid (7,8) was prepared by sulfonation of naphthalene with concentrated sulfuric acid at $160^{\circ} \pm 5^{\circ}$C and was recrystallised as under. 100 gms. of naphthalene-2-sulfonic acid were dessolved in 50 cc. of hot (70-75°C) water and were allowed to cool after addition of 15 cc. HCl (D. 1.19) first slowly and then in ice cold water (refrigeration), filtered and dried in vacuum desiccator and the melting point was noted (83-84°C). Sulfuric acid, sodium hydroxide and sodium sulfate were of A.R.quality. Ammonia was of C.P.grade. Distilled water was used.

Solutions and procedure :

The stock solution of naphthalene-2-sulfonic acid was first prepared in distilled water and the concentration in gm. equivalents per liter was evaluated by titration with standard sodium hydroxide. For the solutions of sodium salt and ammonium salt of naphthalene-2-sulfonic acid, equivalent amounts of naphthalene-2-sulfonic acid and corresponding base were mixed. Measured portion of the stock solution was then suitably diluted with distilled water for ultraviolet absorption spectrum. The ultraviolet absorption was studied with Beckman Model DU spectrophotometer using 10 mm. quartz cells in the range 250-325 mu. The values of extinction coefficients, ϵ , were calculated by dividing the observed optical density D, by the concentration of NF acid or its salts, in gm. equivalents per liter.

3.2c Results :

Table (3.2.1) and figure (3.2.1) give the ultraviolet absorption spectra of NF acid and its salts.

Table (3.2.2) and figure (3.2.2) give the varification of Beer's law and extinction coefficients obtained from the figure (3.2.2).

Table (3.2.3) gives the data for ultraviolet absorption of naphthalene (95 % ethanol), naphthalene-1-sulfonic acid (in 95 % ethanol), NF acid (in 95 % ethanol and in 5 % HCl in 95 % ethanol) from the literature (3) and NF acid and its salts (sodium and ammonium) in aqueous solution from the present work.

Table 3.2.1

Ultraviolet absorption spectra of NF acid.

Wave length	NF acid	NF acid (Na-salt)	NF acid (NH_4-salt)
(mμ)	ϵ	ϵ	ϵ
250	2308	2284	2292
252	2545	2529	2529
254	2805	2798	2798
256	3089	3066	3073
258	3311	3296	3357
260	3511	3495	3495
262	3810	3756	3794
264	4062	4062	4032
266	4231	4246	4216
268	4262	4292	4240
270	4330	4330	4307
272	4445	4438	4464
274	4591	4521	4537
276	4445	4443	4415
278	4062	4102	4078
280	3684	3686	3679
282	3472	3449	3449
284	3304	3280	3265
286	3066	3073	3059
288	2598	2629	2590
290	2016	2144	2031

Table 3.2.1 (Continued)

Wave length (mμ)	NF acid ε	NF acid (Na-salt) ε	NF acid (NH_4-salt) ε
292	1560	1573	1548
295	996.1	996.3	971.2
296	771.1	778.1	761.5
298	622.6	622.6	622.6
300	538.8	544.8	538.8
301	500.5	506.4	496.8
302	471.8	473.0	469.3
303	475.3	476.5	471.8
304	510.0	514.8	511.2
305	562.7	569.9	567.5
306	601.0	603.4	602.3
307	580.6	580.6	580.6
308	526.9	526.9	523.2
309	473.0	473.0	470.6
310	457.4	458.5	452.6
311	475.2	467.0	455.0
312	504.1	502.8	496.8
313	514.8	513.7	508.9
314	481.2	483.8	478.9
315	413.0	419.1	413.0
316	359.2	361.6	355.6

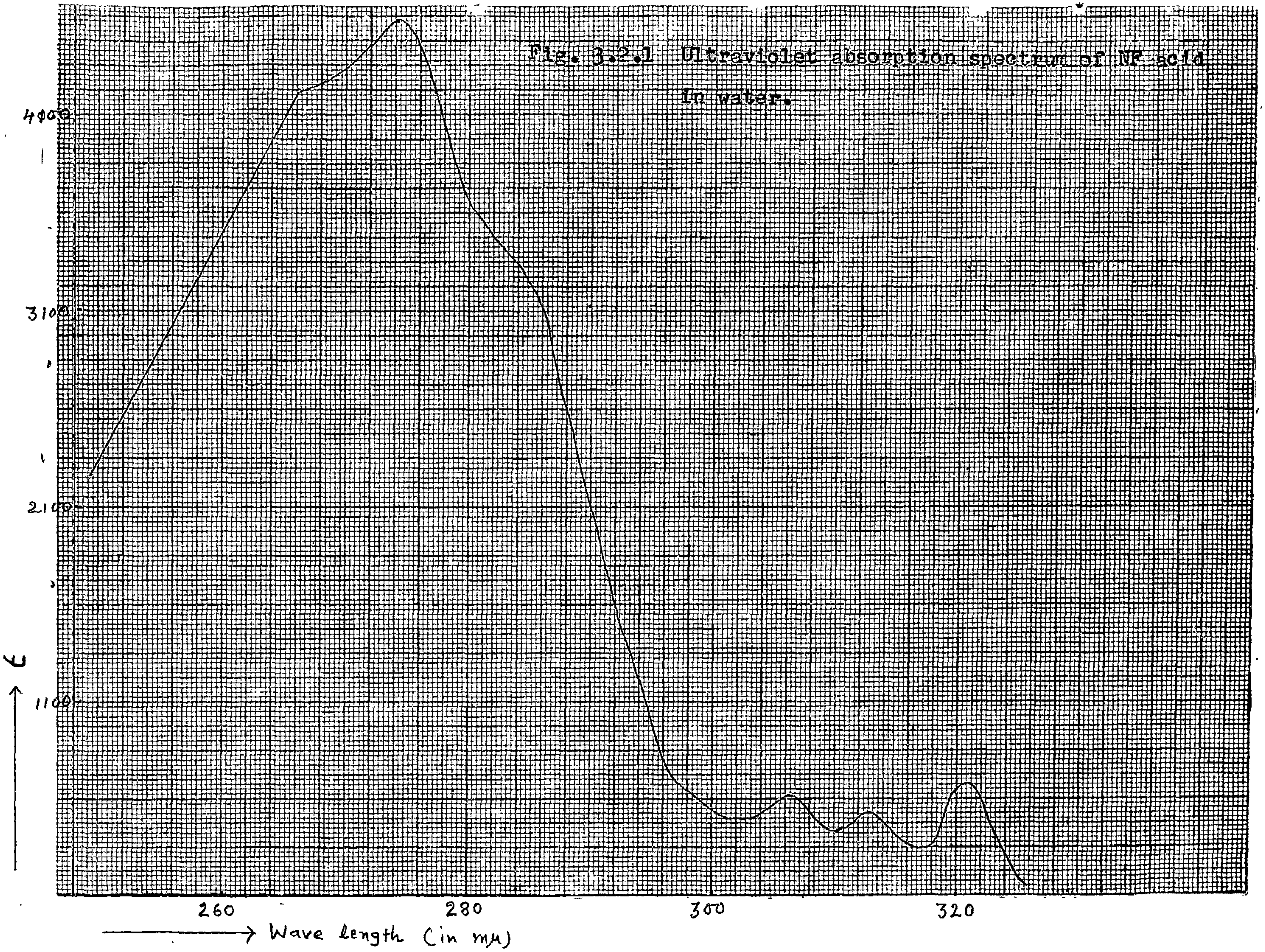

Fig. 3.2.1 Ultraviolet absorption spectrum of NF acid in water.

Table 3.2.1 (Continued)

Wave length (mμ)	NF acid	NF acid (Na-salt)	NF acid (NH_4-salt)
	ε	ε	ε
317	348.4	347.2	341.2
318	402.3	396.3	391.4
319	530.4	512.4	508.9
320	650.1	639.5	631.0
321	663.3	663.3	658.6
322	559.1	568.7	558.0
323	416.7	425.0	409.5
324	276.6	280.2	277.7
325	176.0	178.4	161.6

Fig. 3.2.2 Varification of Beer's law for NF acid in water ; (a) λ = 274 mμ , (b) λ = 306 mμ , (c) λ = 313 mμ and (d) λ = 321 mμ .

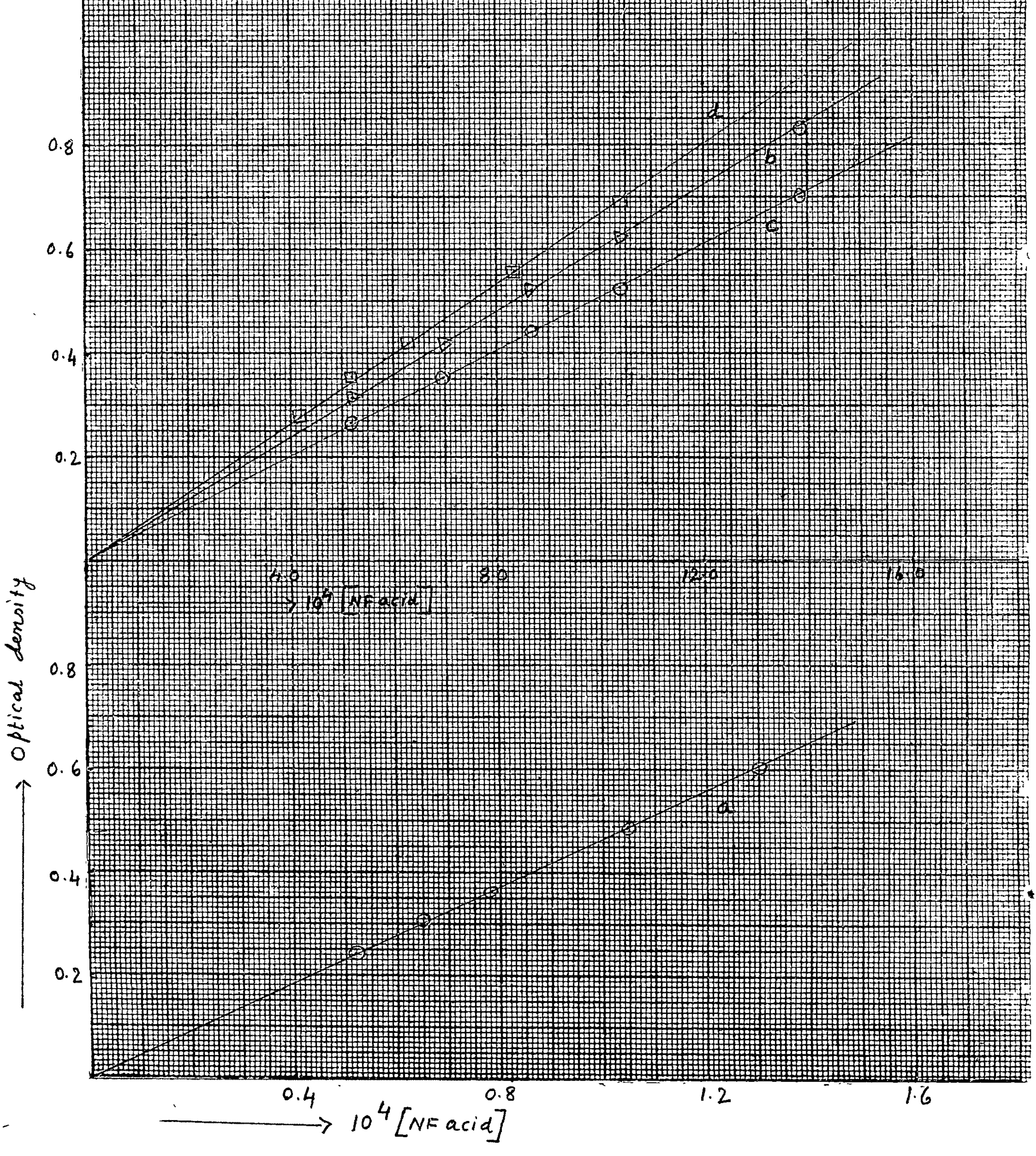

Table 3.2.2

Varification of Beer's law

10^4 [NF acid]	Optical density at 274 mμ	10^4 [NF acid]	Optical density at 306 mμ	Optical density at 313 mμ	10^4 [NF acid]	Optical density at 321 mμ
1.305	0.600	13.92	0.825	0.698	10.44	0.690
1.044	0.485	10.44	0.618	0.521	8.352	0.560
0.783	0.360	8.70	0.525	0.440	6.264	0.420
0.6525	0.310	6.96	0.420	0.354	5.22	0.355
0.522	0.245	5.22	0.317	0.272	4.176	0.283

Values of ϵ obtained from figure 3.2.2

Wave length (mμ)	ϵ	log ϵ
274	4600	3.6628
306	600	2.7782
313	510	2.7076
321	665	2.8228

3.2d Discussion :

Table (3.2.1) and figure (3.2.1) give the ultraviolet absorption spectra of NF acid and its salts (sodium and ammonium). There are maxima at λ= 266,274,306,313 and 321 mµ. The first maxima at 266 mµ is not well defined. The data for NF acid and its salts in aqueous solution and the data from literature for naphthalene (in 95 % ethanol), naphthalene-1-sulfonic acid (in 95 % ethanol) and NF acid (in 95 % ethanol and in 5 % HCl in 95 % ethanol) are given in table (3.2.3). For all the five maxima the wave length, λ is essentially same but the ϵ value is some what higher in ethanolic solution than in aqueous solution for the first two maxima (266 and 274 mµ) while ϵ value is some what higher in aqueous solution than ethanolic solution at other three maxima (306,313 and 321 mµ) for NF acid. The values of wave length for all five maxima and ϵ are essentially same for NF acid and its salts (Na or NH_4) in aqueous solution. This should be attributed to practically complete ionisation of NF acid or its salts (Na or NH_4) in dilute aqueous solution and presumably the absorbing species is naphthalene-2-sulfonate ion.

Varification of Beer's law :

The table (3.3.2) gives the different concentrations of NF acid and observed optical density at the four maxima, λ = 274,306,313 and 321 mµ and figure (3.2.2) gives plots of observed D against [NF acid] at these maxima. All the plots are straight lines passing through the origin. The

Table 3.2.3

Values of λmax. and log ϵ obtained from table 3.2.1 and figure 3.2.1

	Data from literature (3)				Data from present work		
	Naphthalene in 95 % ethanol	Naphthalene-1-sulfonic acid (Na-salt) in 95 % ethanol	NF acid (Na-salt) in 95 % ethanol	NF acid (Na-salt) in 5 % HCl in 95 % ethanol	NF acid in water	NF acid (Na-salt) in water	NF acid (NH_4-salt) in water
λmax.	220	224	227	227	-	-	-
Log ϵ	5.01	4.84	5.00	4.98	-	-	-
λmax.	266	-	266.5	266	266	266	266
Log ϵ	3.71	-	3.66	3.66	3.6264	3.6280	3.6249
λmax.	275.5	274.5	274.5	275	274	274	274
Log ϵ	3.76	3.77	3.69	3.67	3.6619	3.655	3.657
λmax.	286	283	-	-	-	-	-
Log ϵ	3.59	3.83	-	-	-	-	-
λmax.	301	-	306	306	306	306	306
Log ϵ	2.48	-	2.65	2.67	2.7789	2.7806	2.7798
λmax.	312	315	313	313	313	313	313
Log ϵ	2.24	2.63	2.53	2.57	2.7117	2.7107	2.7067
λmax.	-	-	320	320	321	321	321
Log ϵ	-	-	2.58	2.62	2.8217	2.8217	2.8186

values of ϵ obtained from the figure (3.2.2) are tabulated at the bottom of the table (3.2.2). This indicate the validity of Beer's law.

Effect of acids, alkali and salt :

In this study it was observed that the presence of acids (sulfuric or hydrochloric upto 0.05 N), alkali (sodium hydroxide upto 0.05 N) and salt (sodium sulfate upto 0.005 N) in NF acid, have practically no effect on ultraviolet absorption at the four maxima λ = 274,306, 313 and 321 mμ. Hence, in later study in binary mixtures (NF acid with sulfuric or hydrochloric acid), NF acid was estimated by absorption at 274 mμ and total acids were estimated by titration against standard sodium hydroxide. Thus the composition of binary mixtures could be estimated.

3.3 Separation of naphthalene-2-sulfonic acid from sulfuric acid and hydrochloric acid

3.3.1 Introduction :

3.3.1a Separation of naphthalene sulfonic acids and sulfuric acid

Dennis (9) separated the sulfonic acids of aromatic hydrocarbons from excess of sulfuric acid contained in the product of sulfonation by treating the mass with an organic solvent preferably above 100° which dissolved sulfonic acid but not the sulfuric acid, separating the layer of sulfonic acid solution from the sulfuric acid and then isolating the sulfonic acid as such or in the form of a salt. Toluene is a suitable solvent for naphthalene sulfonic acid. The isolation of sulfonic acid from the solution in organic solvent may be effected (I) by cooling ($\sim 250^{\circ}C$) to solidify the sulfuric acids (II) by diluting with water and separating the aqueous solution or (III) by adding a base (NaOH, Na_2CO_3 or $NaHCO_3$) in solid form or in solution, either to the solution of sulfonic acid in organic solvent or to the aqueous solution, referred to in (II) above, the sulfonate either pricipitating out or its aqueous solution is recovered and evaporated. The recovered organic solvent is reused and sulfuric acid may be drawn off, for any desired use. The process may be carried out continuously, solvent circulating through the sulfonation mass, the solution obtained being treated as above described and the recovered solvent passed again through the extraction vessel.

In the study of sulfonation of naphthalene, Othmer and co-workers (10) analysed the sulfonation mass by dissolving in water, clarifying with activited carbon , neutralising with $Ca(OH)_2$, concentrating, filtering hot, cooling and filtering again. The filteration are evaporated to dryness and calculated as calcium salts. Accuracy of about 2 % was obtained.

Ito and Hiyama (11) have reported the separation of naphthalene sulfonic acids and sulfuric acid by column chromatography on alumina column. Aqueous ammonia was used as solvent. The elution curves were obtained by measuring the electrical conductivity of the effluent. The elution curves showed peaks for mono-, di-and tri sulfonic acids and sulfuric acid in this order, irrespective of the position of the sulfonic groups.

Anderson, Bauman and Herrington (12) have developed a method by which a strong acid such as sulfuric acid could be separated from a weak acid, an organic material or certain salts by taking advantage of the sulfate-bisulfate equilibrium on an anion exchange resin. In this method, sulfuric acid is picked up from an aqueous two component solution by a column of resin such as Dowex 1-X8 in the sulfate form by means of the following reaction :

$$R_2SO_4 + H_2SO_4 \rightleftharpoons 2RHSO_4 \qquad (3.3)$$

The other component passes through the solution, thus effecting the separation. The resin is regenerated to the sulfate form only by washing with water.

$$2\ RHSO_4 \xrightarrow{H_2O} R_2SO_4 + 2H^+ + SO_4^= \qquad (3.4)$$

Glogan (13) extended the above work by substituting a more highly crosslinked anion exchange resin for Dowex 1-X8 and studied the separation of two strong acids, provided they differ in molecular size, the uptake of the larger acid being hindered. By using highly concentrated acid solutions, physical adsorption of undissociated sulfuric acid was also of importance and added in the separation. The separation of sulfuric acid from 5-sulfoiso-phthalic acid, from benzene sulfonic acid and from p-toluene sulfonic acid was studied. Most of the work was carried out with 5-sulfoisophthalic acid and Dowex 1-X16. Experiments were carried out by batch technique, in fixed bed columns and in moving bed systems. Effect of resin corsslinking indicated that X22 should be most suitable. The physical sorption of organic acid was also observed to some extent which gradually decreased the efficiency of the resin. Other variables studied included feed concentration, flow rate, rinsing the resin and regeneration. In this study, two experiments were done to show that other sulfonic acids could be separated from sulfuric acid by this method.

An aqueous solution of benzene sulfonic acid and sulfuric acid was passed through a short column of Dowex 1-X16 in the sulfate form. A maximum of 89 % of sulfuric acid was removed from the influent solution. Over 95 % of sulfonic acid was recovered by rinsing the resin with water. When an aqueous solution of sulfuric acid and p-toluene sulfonic acid was treated in a similar manner, maximum of 68 % removal of sulfuric acid was obtained and over 95 % of sulfonic acid was recovered by rinsing.

This scheme offers an interesting method for separating two strong acids, particularly sulfuric acid and sulfonic acids. Because of the large volume of sulfonic acids manufactured, this process has definite industrial potential since expensive chemical regeneration of the resin is unnecessary.

3.3.1b <u>Separation of naphthalene-2-sulfonic acid and naphthalene-1-sulfonic acid</u>

Forster and Keyworth (14) observed that 1- and 2-sulfonic acids were separated easily, but not quantitatively, forming salts with aniline, p-toluidine or m-toluidine , if only a slight excess of amine was added to neutralise 2-sulfonic acid. Its salt was precipitated leaving the 1-sulfonic acid in solution. This can then be obtained in comparatively pure state by evaporation or by addition of a further quantity of the base. Tedeschi (15) has used o-toluidine. Zinkov and co-workers (16) precipitated 2-sulfonic acid with $C_6H_5NHNH_2HCl$ from neutral solution in one hour (in ice-box) and the precipitate, after boiling in water is titrated with 0.1 N NaOH in the presence of phenolphthalein. The % of 2-sulfonic acid is : cc. of 0.1 N NaOH used time 2.08 + 0.32. The error is ± 0.22 %. 1-sulphonic acid is precipitated with 3,2 $O_2N(MeO)\ C_6H_3.NH_2HCl$ from neutral solution added at boiling temperature to dissolve the amine and after cooling in an ice-box, the precipitate is titrated as above. The % of 1-acid is : 2.08 a + 2.19 ± 0.3 %.

Muramoto and Hikao (17) analysed the mixture of 1-sulfonic acid and 2-sulfonic acid by studying the melting point curve of mixtures of their S-benzylthiourea salts. The m.p. of 1-sulfonic acid salt is 138.5° ; of 2-sulfonic acid salt is 192.5°C ; the m.p. curve of the mixture showed the eutectic point at 125° ; % 1-sulfonic acid 17.5 ; % 2-sulfonic acid 82.5 %.

A general method (18 p.92) for the estimation of 1-and 2-sulfonic acids depends on the greater case of elimination of 1-sulfonic group by electrolysis, acid hydrolysis, or bromination. Bromine replaces the 1- but not the 2-sulfonic group and in the absence of any other solubilising group, the bromo-compound is precipitated. Preferential and quantitative elimination of sulfonic acid group also occurs on the treatment of the sulfonic acid with sodium analgan, a method often used in synthetic operation to remove such a group.

Naphthalene-1-sulfonic acid (18, p.102) may be purified by the precipitation of the 2-sulfonic acid ~~by~~ as the sparingly soluble ferrous salt or by adding magnesium sulfate solution (10 % excess) to the mixture at 80-90° in the presence of 16-20 % sulfuric acid and filtering off the Mg salt of 2-sulfonic acid at 15-20°.

The following method (18,p.104) is based on the insolubility of 2-sulfonic acid salt and solubility of 1-sulfonic acid salt (Mg) in magnesium sulfate solution and on the fact that magnesium sulfate forms a stable mono-hydrate at 135^{0}.

Sulfonation mass (7.5 g.) is dissolved in water (100 cc.) and filtered. The residue is washed and weighed. The filtrate and the washings are diluted to 500 cc. and to a 50 cc. sample, hot saturated magnesium sulfate solution (40 g. of $MgSO_4.7H_2O$ in 10 cc. of water) is added. The whole is digested at $100^{0}C$ and then allowed to stand overnight. The filtrate is collected, the residue is dried at 135^{0} and weighed. The sulfate content is determined as $MgSO_4.H_2O$ by precipitation with $BaCl_2$ and the amount of magnesium 1-sulfonate by difference.

Another method (18,p.104) suitable for the total analysis of the sulfonation mass depends on (a) the practical insolubility of sodium-2-sulfonate in 27 % NaCl solution (0.0280 g.) in 100 cc. while the 1-salt is relatively soluble, (b) the practical insolubility of benzidine salt in water of 2-sulfonic acid and sulfuric acid while 1-sulfonic acid salt is relatively soluble.

Funasaka and co-workers (19) found that naphthalene sulfonic acid, in pH > 4.0 NaCl was strongly absorbed by weakly acidic cation exchange resins. The distribution coefficient was increased by increasing concentration of NaCl and lowering the pH. For example, the distribution coefficient of 2-sulfonic acid was > 70 and that of 1-sulfonic acid was 30 in 4 N NaCl at pH 3.5. They were separated by passage at 40° through an Amberlite IR C-50 (200-400 mesh) column (11 mm x 225 mm) with pH 3.3, 4 N NaCl as a developer. However, it was difficult to obtain quantitative seperation.

Literature survey indicates that there is no study available on separation of NF acid from hydrochloric acid. The object of the further studies described was to attempt the separation of NF acid from sulfuric acid and hydrochloric acid in dilute aqueous solution at room temperature using solubility and ion exchange resins.

3.3.2 Separation of naphthalene-2-sulfonic (NF) acid from sulfuric acid based on solubility

The barium salt of NF acid is soluble in hot water while the barium salt of sulfuric acid is practically insoluble ; with this in view, the separation of NF acid from sulfuric acid was tried.

Measured volumes of the solution of known strength of NF acid, sulfuric acid and mixture of NF acid and sulfuric acid were acidified with a few drops of dilute hydrochloric acid and then precipitated by slow addition (in about 20 to 25 minutes) of 1 % hot barium chloride solution ($\sim$ 2 cc. excess) with constant stirring (7). The precipitates were then digested for two hours, filtered hot, washed with hot distilled water (with same volume in each case) till free of chloride, dried in an oven at 120° and weighed. The results obtained are illustrated by the following :

	Weight of the precipitate in gms. obtained on the basis of $SO_4^{=}$	
	Calculated	Experimental
Sulfuric acid (25 cc.0.08529N)	0.2488	0.2489
NF acid (50 cc.0.04159N)	0.000	0.0220
Sulfuric acid (25 cc.0.08529N) + NF acid (25 cc.0.04159N)	0.2488	0.2514

Such results indicated that the weight of the barium salt of sulfuric acid obtained experimentally was in good agreement with the calculated value. For NF acid, the weight obtained experimentally was not negligible though it should have been so. In the mixture of NF acid and sulfuric acid the weight is much less than the calculated weight of barium salts of sulfuric acid and NF acid, and little higher than the calculated value of the barium salt of sulfuric acid alone. Repeations indicated that this excess was not reproducible for mixtures of NF acid and sulfuric acid. This could be because the barium salt of NF acid is not completely soluble in hot water.

From such studies, it was concluded thattthe separation of NF acid from sulfuric acid, is not ~~be~~ quantitative by this method.

3.3.3 Sorption of strong acids on ion exchange resins

3.3.3.1 The sorption of strong acids on a strongly basic anion exchange resin

3.3.3.1a Introduction :

Sorption of strong electrolytes by ion exchange resins due to Donnan membrane effect has been studied by several workers (20-29). If the sorption is significantly different, due to the differences in activity coefficients, it may be fesible to separate two strong electrolytes in a binary mixtures. With this in view, a study was undertaken to attempt the separation of naphthalene-2-sulfonic(NF) acid from sulfuric acid and from hydrochloric acid.

In this section the sorption of NF acid, hydrochloric acid, sulfuric acid and the mixture of NF acid and sulfuric acid on a strongly basic anion exchange resin was studied, with a view to obtain the separation of NF acid from other two.

3.3.3.1b Experimental :

Resin : Resin used was the styrene-divinylbenzene copolymer based strongly basic anion exchange resin (containing quaternary ammonium groups) Amberlite IRA-400 (Rohm and Haas Co.) of crosslinking about 8 (this is further referred to as resin IRA-400).

Moisture and capacity of the resin :

The resin was washed with distilled water, cycled thrice between sodium chloride and sodium hydroxide, regenerated with large excess of sodium hydroxide, washed free of alkali, air dried, sieved (-20, + 50 mesh) and stored in a good container.

Moisture content was determined by heating weighed samples (∽ 0.5 gms.) of air dry resin in clean, dry weighing bottles, in an oven (∽ 100°C) to a constant weight and % moisture content was then calculated.

For the estimation of the capacity of the resin, weighed samples (∽ 0.5 gms.) of air dry resin were contacted with 50 cc. of solution of acids (hydrochloric (0.04366 N), sulfuric (0.04654 N) and NF acid (0.04052 N) in well stoppered flasks with frequent shaking. Next day, the remaining acids were estimated by titration with standard sodium hydroxide solution and then the capacity was calculated.

Chemicals : NF acid was prepared as given in previous section . Sulfuric acid, hydrochloric acid and sodium hydroxide were of A.R.quality. Distilled water was used.

Solutions : The solution of NF acid was prepared by dissolving a known weight in distilled water to known volume and of hydrochloric acid and sulfuric acid were prepared by mixfng known volumes in distilled water and were estimated by titration with standard sodium hydroxide solution.

Estimation of acids : In one component solution, the acids were estimated by direct titration with standard sodium hydroxide solution. In binary mixture, NF acid was estimated by ultraviolet absorption at 274 mμ with a Beckman Model DU spectrophotometer using 10 mm. quartz cells, and total acids were estimated by titration against standard sodium hydroxide solution.

Procedure for column studies :

A series of columns were set up. For each column a known quantity of resin was first converted to a perticular anion form. This was then transferred to the column as slurry in water and washed free of acid with distilled water. Other column data are given in their respective tables.

3.3.3.1c Results :

Table(3.3.3.1.1) gives the moisture content and capacity of the resin IRA-400 in hydrochloric,sulfuric and NF acid.

Table(3.3.3.1.2) gives the column sorption of hydrochloric acid on the resin IRA-400 in chloride form and column sorption of NF acid on the resin IRA-400 in naphthalene-2-sulfonate form.

Table(3.3.3.1.3) gives elution study of NF acid and the mixture of NF acid and sulfuric acid on the resin IRA-400 in naphthalene-2-sulfonate form.

Table 3.3.3.1.1

Moisture and capacity of the resin IRA-400 in different acids

Moisture content 27.0 %

Acid	Capacity, meq. / gm.	
	air-dry resin	oven-dry resin
Hydrochloric acid	2.03	2.78
Sulfuric acid	2.54	3.48
NF acid	2.03	2.78

Table 3.3.3.1.2

Column sorption of hydrochloric acid and NF acid on strongly basic anion exchange resin

	Hydrochloric acid	NF acid
Resin	IRA-400 in chloride form	IRA-400 in naphthalene-2-sulfonate form
Bed length	25.0 cms.	25.0 cms.
Bed volume	13.2 cc.	13.2 cc.
Void volume	7.0 cc.	4.7 cc.
Column capacity	10.14 meq.	10.14 meq.
Flow rate	1 cc/min.	1 cc./min.
Sample No. each = 10 cc.	Meq.sorbed in sample	Meq.sorbed in sample
1	0.1565	0.2729
2	0.4554	0.2729
3	0.0593	0.0515
4	-	0.0206
5	-	0.0051
6	-	-
Total acid sorbed in meq.	0.6712	0.6230

Table 3.3.3.1.3

Column elution of NF acid and mixture of NF acid and sulfuric acid with the resin IRA-400

Resin = IRA-400 in naphthalene-2-sulfonate form ;
Bed length = 25.0 cms. ; Column capacity = 10.14 meq. ;
Bed volume = 13.2 cc. ; Flow rate = 1 cc./min. ;
Void volume = 4.7 cc.

	Acid =	NF acid	NF acid	+ sulfuric acid
	In put =	0.5152 meq. in 10 cc.	(0.2576 meq. + 0.2576 meq.) in 10 cc.	
Sample No.	Sample volume	Meq.eluted in sample	Meq.eluted in sample	Meq.eluted in sample
1	30 cc.	0.4284	0.2688	0.1084
2	100 cc.	0.0712	0.0762	-
3	100 cc.	0.0169	0.0252	-
4	100 cc.	-	-	-
Total meq. eluted		0.5155	0.3682	0.1084

3.3.3.1d Discussion :

Table (3.3.3.1.1) indicates that the capacity of the resin in hydrochloric acid and NF acid is essentially same but in sulfuric acid, the capacity is definately higher. This should be attributed to the exchange by both $SO_4^{=}$ and HSO_4^{-} ions.

Table (3.3.3.1.2) indicates that the sorption of hydrochloric acid on the resin IRA-400 in chloride form and NF acid in naphthalene-2-sulfonate form is not sufficiently different. Hence, it was considered that the separation of NF acid and hydrochloric acid by this method could not be probable. Next, NF acid and the mixture of NF acid and sulfuric acid were sorbed on columns of resin IRA-400 in naphthalene-2-sulfonate form and then eluted with distilled water. Table (3.3.3.1.3) indicates that no complete separation is obtained. Part of the sulfuric acid is exchanged for NF acid, but not completely. Hence, in the total effluent, the sulfuric acid content is less than that in the influent while the NF acid content is more in the effluent than that in the influent. However the decrease in the sulfuric acid content is more than the increase in the NF acid content. This is so because both sulfate and bisulfate are the exchanging species.

From the above study, it is felt that strongly basic anion exchange resins of the type used are not suitable for the separation of NF acid from sulfuric or hydrochloric acid by this technique.

3.3.3.2 The sorption of strong acids on a weakly basic anion exchange resin

3.3.3.2a Introduction :

In the previous section the separation of NF acid from sulfuric or hydrochloric acid was tried on a strongly basic anion exchange resin. In this section, the sorption of NF acid, hydrochloric acid and the mixture of sulfuric acid and NF acid on a weakly basic anion exchange resin was studied with a view to obtain the separation of NF acid from the other two.

3.3.3.2b Experimental :

Resin : Resin used was a weakly basic anion exchange resin, Amberlite IR-4B (-20, + 50 mesh), (Rohm and Hass Co.). This is a condensation product of an aliphatic polyamine, phenol and formaldehyde and contains weakly basic amino groups. (This is further referred to as resin IR-4B).

Moisture and capacity of the resin :

The resin was washed with distilled water, cycled thriee between hydrochloric acid and sodium carbonate, regenerated with large excess of sodium carbonate, washed free of sodium carbonate, air dried, sieved (-20,+50 mesh) and stored in a good container.

Moisture content was determined as in previous section.

For the estimation of capacity of the resin, different weights (from 0.1 to 0.5 gms) of air dry resin were contacted with 100 cc. of acid(hydrochloric, sulfuric and NF acid of strength $\sim$ 0.05 N) solution in well stoppered flasks with frequent shakings The remaining acids, (hydrochloric and sulfuric after 2 days and NF acid after 10 days) were estimated by titration with standard sodium hydroxide solution and then the capacity was calculated.

Chemicals : The chemicals used were same as in previous section.

Solutions : The solutions were prepared in the same way as in previous section.

Estimation of acids : The acids were estimated as in previous section.

Procedure for column studies :

A column with the resin IR-4B in the hydroxyl form was set up. Then the mixture of sulfuric acid and NF acid was passed at the rate 5 cc. / minute, collected 50 cc. samples and analysed. Other details are given in the table 3.3.3.2.2.

3.3.3.2c Results :

Table (3.3.3.2.1) gives the moisture content and the variation of the capacity of the resin IR-4B with weight of the resin per 100 cc. of hydrochloric acid, sulfuric acid and NF acid solution.

Table(3.3.3.2.2) gives the column sorption of sulfuric acid and NF acid from the binary mixture of two on the resin IR-4B in hydroxyl form.

Fig. 3.3.3.2.1 Variation of capacity for the resin IR-4B with weight of resin per 100 cc. of acid solution ; (a) hydrochloric acid, (b) NF acid and (c) sulfuric acid.

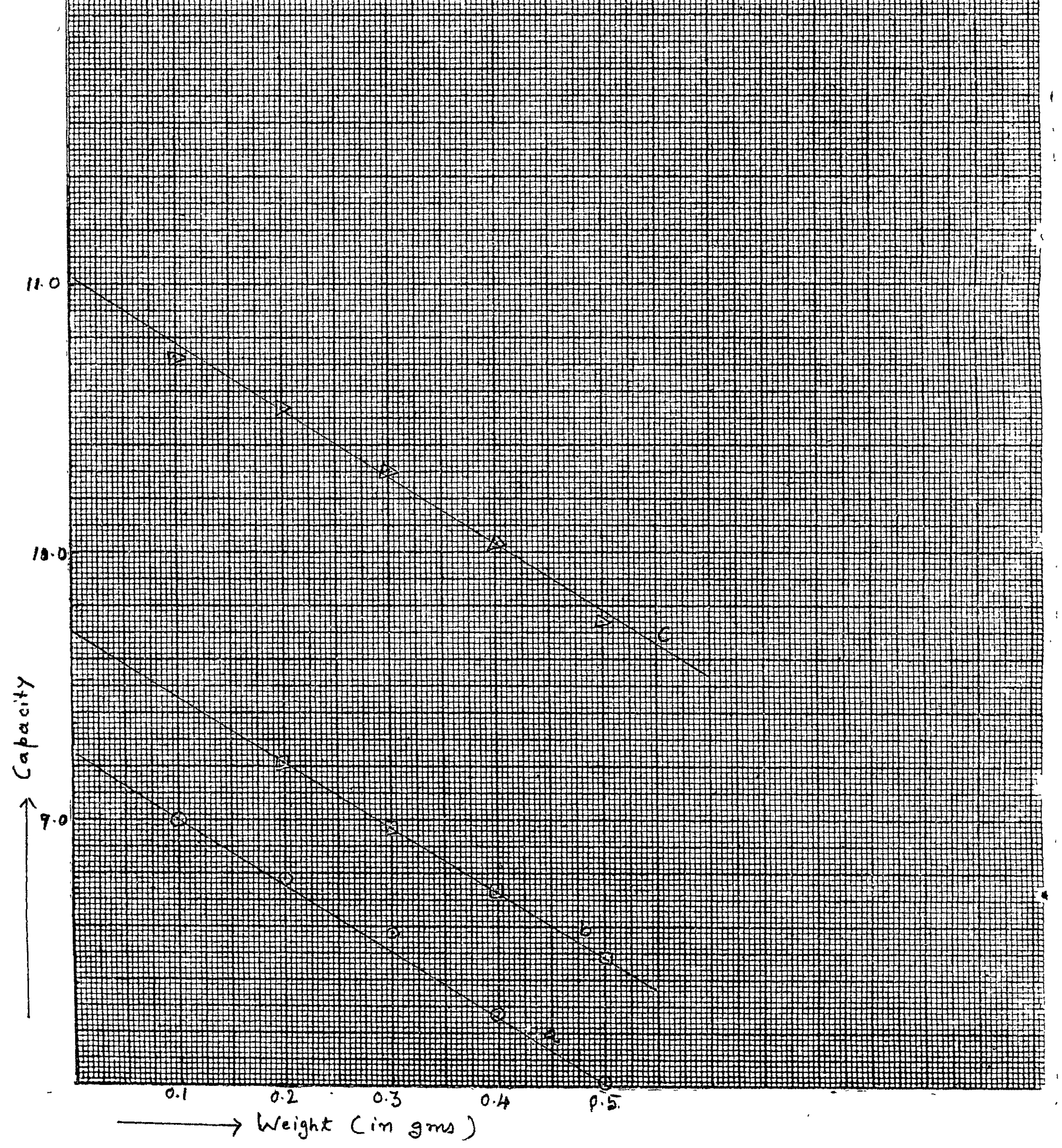

Table 3.3.3.2.1

Moisture and capacity of weakly basic anion exchange resin IR-4B in different strong acids

Moisture content : 9.91 %

Acid	Hydrochloric acid (0.05061 N)		Sulfuric acid (0.05136 N)		NF acid (0.05146 N)	
Volume contacted in cc.	Resin taken in gms.	Capacity meq./gm. oven-dry resin	Resin taken in gms.	Capacity meq./gm. oven-dry resin	Resin taken in gms.	Capacity meq./gm. oven-dry resin
100	0.1009	9.00	0.1033	10.72	-	-
100	0.2022	8.78	0.2003	10.54	0.2000	9.21
100	0.3012	8.58	0.3007	10.30	0.3008	8.97
100	0.4023	8.27	0.4035	10.03	0.4000	8.74
100	0.5008	8.02	0.5015	9.74	0.5008	8.48

Table 3.3.3.2.2

Column sorption of NF acid and sulfuric acid on weakly basic anion exchange resin in binary mixture

Resin = IR-4B in hydroxyl form. ;

Bed length = 22.0 cms. ; Column capacity = 26.21 meq. ;

Bed volume = 11.5 cc. ; Flow rate = 5 cc./min.;

Void volume = 6.2 cc.

Influent conc. of influent.	NF acid (a) (0.02085 N	+ Sulfuric acid (b) + 0.04264 N) in binary mixture	a/b = 0.4891
Sample No. each = 50 cc.	10^2 [NF acid] (a′)	10^2 [Sulfuric acid] (b′)	a′ / b′
1	0.0869	0.0654	1.326
2	0.7956	0.2794	2.851
3	0.8648	0.1872	4.641
4	1.376	0.6690	2.059
5	1.464	1.036	1.415
6	1.499	1.176	1.277
7	1.644	1.192	1.406
8	1.646	1.403	1.175
9	1.706	1.612	1.058
10	1.716	1.905	0.901

Table 3.3.3.2.2 (Continued)

Sample No. each = 50 cc.	10^2 [NF acid] (a′)	10^2 [Sulfuric acid] (b′)	a′ / b′
11	1.776	2.248	0.794
12	1.818	2.528	0.706
13	1.882	2.395	0.787
14	1.882	3.095	0.611
15	1.914	3.367	0.574
16	1.932	3.653	0.529
17	1.970	3.908	0.506
18	1.984	4.033	0.493
19	2.006	4.128	0.4897
20	2.052	4.186	0.4902

3.3.3.2d Discussion :

Table (3.3.3.2.1) and figure (3.3.3.2.1) indicate that the capacity of the resin, in hydrochloric, sulfuric and NF acid decreases as concentration of the resin IR-4B in acid solution increases. This should be attributed to the change in pH of equilibrium solution ; as the concentration of the resin in acid solution increases, pH in solution at equilibrium increases. Hence, ionisation of exchangable groups in resin would decrease and the capacity of the resin will decrease. Plots of resin capacity against resin concentration in gms./ 100 cc. acid solution are parallel straight lines and have negative slope. The plots are extrapolated and the capacity at zero concentration of resin in acid solution were read from figure (3.3.3.2.1). They are considered as maximum capacity of the resin (in acid concentration $\backsim$ 0.05 N). The values for maximum capacity are 9.24, 9.7 and 11.02 meq.per gram in hydrochloric acid, NF acid and sulfuric acid respectively. The maximum capacity in NF acid is somewhat higher and in sulfuric acid relatively higher than in hydrochloric acid. This should be due to some sorption of NF acid on the resin and in sulfuric acid due to both $SO_4^=$ and HSO_4^- being the exchanging ions.

Table (3.3.3.2.2) gives the sorption of sulfuric acid and NF acid in binary mixture on the resin IR-4B in hydroxyl form. The ratio a' / b' of the concentration in gm. equivalents per liter of NF acid to that of sulfuric acid first increases and then decreases as effluent volume increases. However the ratio is not sufficiently different from the ratio, a/b (0.4891) of the concentration of NF acid to that of sulfuric acid in the influent.

From the above preliminary study, it is felt that the weakly basic anion exchange resins of the type used are not suitable for the separation of NF acid from sulfuric or hydrochloric acid by this technique.

3.3.3.3 The sorption of strong acids on strongly acidic cation exchange resins

3.3.3.3a Introduction :

In the previous sections the separation of NF acid from sulfuric or hydrochloric acid was tried on strongly basic and weakly basic anion exchange resins. In this section the sorption of hydrochloric, sulfuric and NF acid on strongly acidic cation exchange resins has been studied with a view to obtain the separation of NF acid from other two.

3.3.3.3b Experimental :

Resins : Resins used were sulfonated styrene divinylbenzene copolymer type sulfonic acid cation exchange resins of different crosslinking. These included Dowex 50 W and Dowex 50 resins (Dow Chemical Co.) of X = 4 and 8 (these are further referred to as resins X4 and X8), and prepared samples of similar resins (from Permutit Co., London) of X = 5 and 30 (these are further referred to as resins X5 and X30)

Moisture and capacity of the resins :

The resins were washed, cycled between sodium chloride and hydrochloric acid, regenerated with large excess of hydrochloric acid, washed free of acid, filtered, air-dried and stored in well stoppered containers and moisture content and capacity were determined (30).

Chemicals : The chemicals used were the same as in previous section.

Solutions : The solutions were prepared in the same way as in previous section.

Estimation of acids :

The acids were estimated by direct titration against standard sodium hydroxide solution.

Procedure for column studies :

Columns were set up for each resin. The column data for each column are given in their respective tables. Solution of hydrochloric acid was passed through the column, and samples were collected and estimated for acid sorbed by titration in each sample with standard sodium hydroxide solution. The run was continued till there was no further sorption.The column was then washed free of acid with distilled water and the run was repeated with sulfuric acid and then with NF acid.

3.3.3.3c Results :

Table (3.3.3.3.1) gives the moisture content and capacity of the strongly acidic cation exchange resins.

Table (3.3.3.3.2) gives the column sorption of hydrochloric acid,sulfuric acid and NF acid on the resin X4.

Table (3.3.3.3.3) gives the column sorption of hydrochloric acid,sulfuric acid and NF acid on the resin X5.

Table (3.3.3.3.4) gives the column sorption of hydrochloric acid,sulfuric acid and NF acid on the resin X8.

Table (3.3.3.3.5) gives the column sorption of hydrochloric acid,sulfuric acid and NF acid on the resin X30.

Table (3.3.3.3.6) gives the values for the sorption of hydrochloric acid,sulfuric acid and NF acid on strongly acidic cation exchange resins obtained from tables (3.3.3.3.2 to 3.3.3.3.5).

Table 3.3.3.3.1

Moisture and capacity of strongly acidic cation exchange resins

Resin	Moisture (%)	Capacity, meq. / gm.	
		air-dry resin	oven-dry resin
X4	29.9	3.55	5.064
X5	27.8	3.497	4.848
X8	26.97	3.715	5.088
X30	12.89	2.828	3.017

Table 3.3.3.3.2

Column sorption of strong acids on strongly acidic cation exchange resin

Resin = X4 (-100, + 200 mesh) ;
Bed length = 50.0 cms. ; Column capacity = 32.94 meq. ;
Bed volume = 26.0 cc. ; Flow rate = 1 cc./ min. ;
Void volume = 8.2 cc.

Influent Conc.of influent	Hydrochloric acid (0.04896 N)	Sulfuric acid (0.05216 N)	NF acid (0.05146 N)
Sample No. each =25 cc.	Meq. sorbed in sample	Meq. sorbed in sample	Meq. sorbed in sample
1	0.2427	0.2415	0.3539
2	-	-	-
3	-	-	-
4	-	-	-

Table 3.3.3.3.3

Column sorption of strong acids on strongly acidic cation exchange resin

Resin = X5 (-80, + 200 mesh) ;
Bed length = 66.0 cms. ; Column capacity = 34.97 meq. ;
Bed volume = 35.0 cc. ; Flow rate = 1 cc./min. ;
Void volume = 9.0 cc.

Influent Conc.of influent	Hydrochloric acid (0.05093 N)	Sulfuric acid (0.05216 N)	NF acid (0.05216 N)
Sample No. each = 25 cc.	Meq. sorbed in sample	Meq. sorbed in sample	Meq.sorbed in sample
1	0.3641	0.3542	0.4526
2	-	0.0090	-
3	-	-	-
4	-	-	-

Table 3.3.3.3.4

Column sorption of strong acids on strongly acidic cation exchange resin

Resin = X8 (- 60, + 100 mesh) ;
Bed length = 51.0 cms. ; Column capacity = 47.56 meq. ;
Bed volume = 26.7 cc. ; Flow rate = 1 cc./min. ;
Void volume = 10.8 cc.

Influent Conc.of influent	Hydrochloric acid (0.05246 N)	Sulfuric acid (0.05219 N)	NF acid (0.05167 N)
Sample No. each = 10 cc.	Meq. sorbed in sample	Meq. sorbed in sample	Meq. sorbed in sample
1	-	-	-
2	0.1866	0.1800	0.1738
3	0.0077	0.0130	0.0129
4	-	-	0.0077
5	-	-	-

Table 3.3.3.3.5

Column sorption of strong acids on strongly acidic cation exchange resin

Resin = X30 (-60, + 100 mesh);
Bed length = 47.0 cms. ; Column capacity = 44.41 meq. ;
Bed volume = 25.0 cc. ; Flow rate = 1 cc./min. ;
Void volume = 10.8 cc.

Influent	Hydrochloric acid	Sulfuric acid	NF acid
Conc. of influent	(0.05040 N)	(0.05206 N)	(0.05167 N)
Sample No. each = 10 cc.	Meq. sorbed in sample	Meq. sorbed in sample	Meq. sorbed in sample
1	-	-	-
2	0.0926	0.1362	0.1029
3	0.0310	0.0128	0.0154
4	0.0232	0.0052	-
5	0.0077	-	-
6	-	-	-

3.3.3.3d <u>Discussion</u>:

Table (3.3.3.3.6) indicates that the amount of sulfuric acid and hydrochloric acid sorbed were essentially same, the quantity of acid sorbed per equivalent of resin first increases and then decreases as X increases and the ratio, r, given by NF acid sorbed per equivalent of the resin divided by sulfuric acid or hydrochloric acid sorbed per equivalent of resin, decreases when X increases. The sorption of NF acid on resin X30 is relatively low, but not nil ; this should be attributed, in part, to the steric hindrance due to high crosslinking of the resin.

The amount of acids sorbed here are small and the ratio, r, is also not sufficiently different from unity. Hence, it is felt that strongly acidic cation exchange resins of the type used are not suitable for the separation of NF acid from sulfuric acid and hydrochloric acid by this technique.

Table 3.3.3.3.6

Values for the column sorption of strong acids on strongly acidic cation exchange resins, obtained from tables 3.3.3.3.2 to 3.3.3.3.5

Resin	X	Acid sorbed in meq./eq. of resin NF acid (a)	 Sulfuric acid (b)	 Hydrochloric acid (c)	Ratio, r given by a / b	 a / c
X4	4	10.74	7.331	7.367	1.466	1.458
X5	5	12.94	10.39	10.41	1.247	1.243
X8	8	4.088	4.059	4.086	1.007	1.000
X30	30	2.664	3.472	3.479	0.7672	0.7658

3.3.3.4 The sorption of strong acids on weakly acidic cation exchange resins

3.3.3.4a Introduction :

In previous sections the separation of NF acid from hydrochloric acid or sulfuric acid was tried on strongly basic and weakly basic anion exchange resins and on strongly acidic cation exchange resins. In this section the sorption of NF acid,hydrochloric acid and sulfuric acid in dilute aqueous solution, on monofunctional carboxylic acid cation exchange resins, has been applied for the separation of binary mixtures of NF acid with other two.

3.3.3.4b Experimental :

Resins : The resins used were from sample of Zeo-Carb-226 type (Permutit Co., London) monofunctional carboxylic acid cation exchange resins of relative degree of crosslinking (% nominal divinylbenzene content), X = 2.5, 6,11 and 16 (hereafter referred to as resins Cx-2.5, Cx-6, Cx-11 and Cx-16 and Amberlite IRC-50 (Rohm and Haas Co) (hereafter referred to as resin Cx-8 (as its X is considered to be close to 8). The resins were washed, conditioned, regenerated and moisture content was determined by heating weighed samples (∽ 0.5 gms.) of air-dry resin in clean,dry weighing bottles, in an oven (100-102°C) to a constant weight and % moisture content was then calculated.

For the estimation of the capacity of the resins, weighed samples (∽ 0.5 gms.) of air-dry resins were contacted with 50 cc. of 0.25 N sodium hydroxide solution in well-stoppered flasks with frequent shaking. After two to three days, the remaining sodium hydroxide was estimated by titration with standard hydrochloric acid solution and then the capacity was calculated.

Chemicals : The chemicals were same as in previous sections.

Solutions : The solutions were prepared in the same way as given in previous sections.

Estimation of acids : The acids were estimated as given in the previous sections.

Procedure for column studies : Columns were set up for each resin in hydrogen form. Solution of NF acid (∽ 0.05 N) was passed through the column and samples were collected and estimated for acid sorbed. The run was continued till there was no further sorption. The column was then washed free of acid with distilled water and then the run was repeated with sulfuric acid (∽ 0.05 N) and then with hydrochloric acid (∽ 0.05 N).

Next, a column of resin Cx-6 was set up. The column data were as follows : column capacity, 310.1 meq.; bed volume, 102.4 cc. ; bed length, 43 cm. ; flow rate, 1 cc/min. ; 20 cc. of NF acid (0.0525 N) were sorbed on the resin column and then eluted with distilled water till free of acid. The run was then repeated with sulfuric acid (0.0520 N) and hydrochloric acid (0.05093 N). Next, different binary mixtures of NF acid with hydrochloric acid and sulfuric acid were sorbed and eluted similarly.

3.3.3.4c <u>Results</u> :

Table (3.3.3.4.1) gives the moisture content and capacity of the weakly acidic cation exchange resins.
Table (3.3.3.4.2) gives the column sorption of hydrochloric acid, sulfuric acid and NF acid with the resin Cx-2.5.
Table (3.3.3.4.3) gives the column sorption of hydrochloric acid,sulfuric acid and NF acid with the resin Cx-6.
Table (3.3.3.4.4) gives the column sorption of hydrochloric acid,sulfuric acid and NF acid with the resin Cx-8.
Table (3.3.3.4.5) gives the column sorption of hydrochloric acid, sulfuric acid and NF acid with the resin Cx-11.
Table (3.3.3.4.6) gives the column sorption of hydrochloric acid,sulfuric acid and NF acid with the resin Cx-16.
Table (3.3.3.4.7) gives the values for the sorption of hydrochloric acid,sulfuric acid and NF acid on weakly acidic cation exchange resins, obtained from tables (3.3.3.4.2 to 3.3.3.4.6).
Table (3.3.3.4.8) and figure (3.3.3.4.1) give the separate column elution of hydrochloric acid,sulfuric acid and NF acid with the resin Cx-6.
Table (3.3.3.4.9) and figure (3.3.3.4.2) give the column separation of NF acid from hydrochloric acid and sulfuric acid with the resin Cx-6.

Table 3.3.3.4.1

Moisture and capacity of weakly acidic cation exchange resins

Resin	Moisture (%)	capacity, meq./1 gm.	
		Air-dry resin	Oven-dry resin
Cx - 2.5	23.4	8.095	10.60
Cx - 6	20.9	7.730	9.77
Cx - 8	15.6	8.745	10.40
Cx -11	17.0	7.223	8.70
Cx -16	12.0	6.088	6.84

Table 3.3.3.4.2

Column sorption of strong acids on weakly acidic cation exchange resin

Resin = Cx - 2.5 (- 20, + 30 mesh) ;
Bed length = 60.0 cms. ; Column capacity = 67.95 meq. ;
Bed volume = 31.5 cc. ; Flow rate = 1 cc/min. ;
Void volume = 16.0 cc.

Influent	Hydrochloric acid	Sulfuric acid	NF acid
Conc. of influent	(0.0501 N)	(0.05142 N)	(0.05107 N)
Sample No. each = 25 cc.	Meq. sorbed in sample	Meq. sorbed in sample	Meq. sorbed in sample
1	0.4288	0.4048	0.4529
2	0.2963	0.3305	0.6263
3	0.0120	-	0.0241
4	-	-	-
5	-	-	-

Table 3.3.3.4.3

Column sorption of strong acids on weakly acidic cation exchange resin

Resin = Cx - 6 (- 60, + 100 mesh) ;
Bed length = 54.5 cms ; Column capacity = 95.66 meq. ;
Bed volume = 29.3 cc. ; Flow rate = 1 cc./min. ;
Void volume = 11.4 cc.

Influent	Hydrochloric acid	Sulfuric acid	NF acid
Conc. of influent	(0.05067 N)	(0.05169 N)	(0.05195 N)
Sample No. each = 25 cc.	Meq. sorbed in sample	Meq. sorbed in sample	Meq. sorbed in sample
1	0.5394	0.5244	0.6792
2	0.0250	0.0397	0.3871
3	-	-	0.0200
4	-	-	0.0074
5	-	-	-

Table 3.3.3.4.4

Column sorption of strong acids on weakly acidic cation exchange resin

Resin = Cx - 8 (- 40, + 60 mesh) ;

Bed length = 44. 0 cms ; Column capacity = 87.75 meq. ;

Bed volume = 23.5 cc. ; Flow rate = 1 cc./ min.;

Void volume = 9.6 cc.

Influent Conc. of influents	Hydrochloric acid (0.05143 N)	Sulfuric acid (0.05143 N)	NF acid (0.05066 N)
Sample No. each = 10 cc.	Meq. sorbed in sample	Meq. sorbed in sample	Meq. sorbed in sample
1	0.0077	0.0330	0.0129
2	0.3472	0.3087	0.4861
3	0.0129	0.0283	0.2058
4	-	-	0.0283
5	-	-	0.0077
6	-	-	-

Table 3.3.3.4.5

Column sorption of strong acids on weakly acidic cation exchange resin

Resin = Cx - 11 (-60, + 100 mesh) ;

Bed length = 50.8 cms. ; Column capacity = 115.3 meq.;

Bed volume = 27,0 cc, ; Flow rate = 1 cc./min.;

Void volume = 11.0 cc.

Influent Conc. of influent	Hydrochloric acid (0.05094 N)	Sulfuric acid (0.05219 N)	NF acid (0.05066 N)
Sample No. each = 25 cc.	Meq. sorbed in sample	Meq. sorbed in sample	Meq. sorbed in sample
1	0.3546	0.3473	0.4844
2	0.0050	0.0127	0.1174
3	-	-	0.0175
4	-	-	0.0175
5	-	-	0.0125
6	-	-	-

Table 3.3.3.4.6

Column sorption of strong acids on weakly acidic cation exchange resin

Resin = Cx-16 (-60, + 100 mesh);
Bed length = 53.0 cms. ; Column capacity = 112.0 meq. ;
Bed volume = 27.9 cc. ; Flow rate = 1 cc./min.;
Void volume = 10.8 cc.

Influent	Hydrochloric acid	Sulfuric acid	NF acid
Conc.of influent	(0.05140 N)	(0.05236 N)	(0.05236 N)
Sample No. each 25 cc.	Meq.sorbed in sample	Meq.sorbed in sample	Meq.sorbed in sample
1	0.3181	0.3200	0.3100
2	0.0294	0.0249	0.0290
3	-	-	0.0084
4	-	-	-

Table 3.3.3.4.7

Values for the column sorption of strong acids on weakly acidic cation exchange resins, obtained from tables 3.3.3.4.2 to 3.3.3.4.6

Resin	X	Acid sorbed in meq./eq. of resin			Ratio, r given by	
		NF acid (a)	Sulfuric acid (b)	Hydrochloric acid (c)	a / b	a / c
Cx-2.5	2.5	16.25	10.82	10.85	1.502	1.496
Cx-6	6	11.43	5.896	5.899	1.939	1.937
Cx-8	8	8.439	4.21	4.19	2.004	2.014
Cx-11	11	5.631	3.122	3.119	1.803	1.805
Cx-16	16	3.101	3.08	3.102	1.007	1.000

Fig. 5.3.3.4.1 Elution curves of (A) NF acid, (B) hydrochloric acid and (C) sulfuric acid with the resin Cx-6.

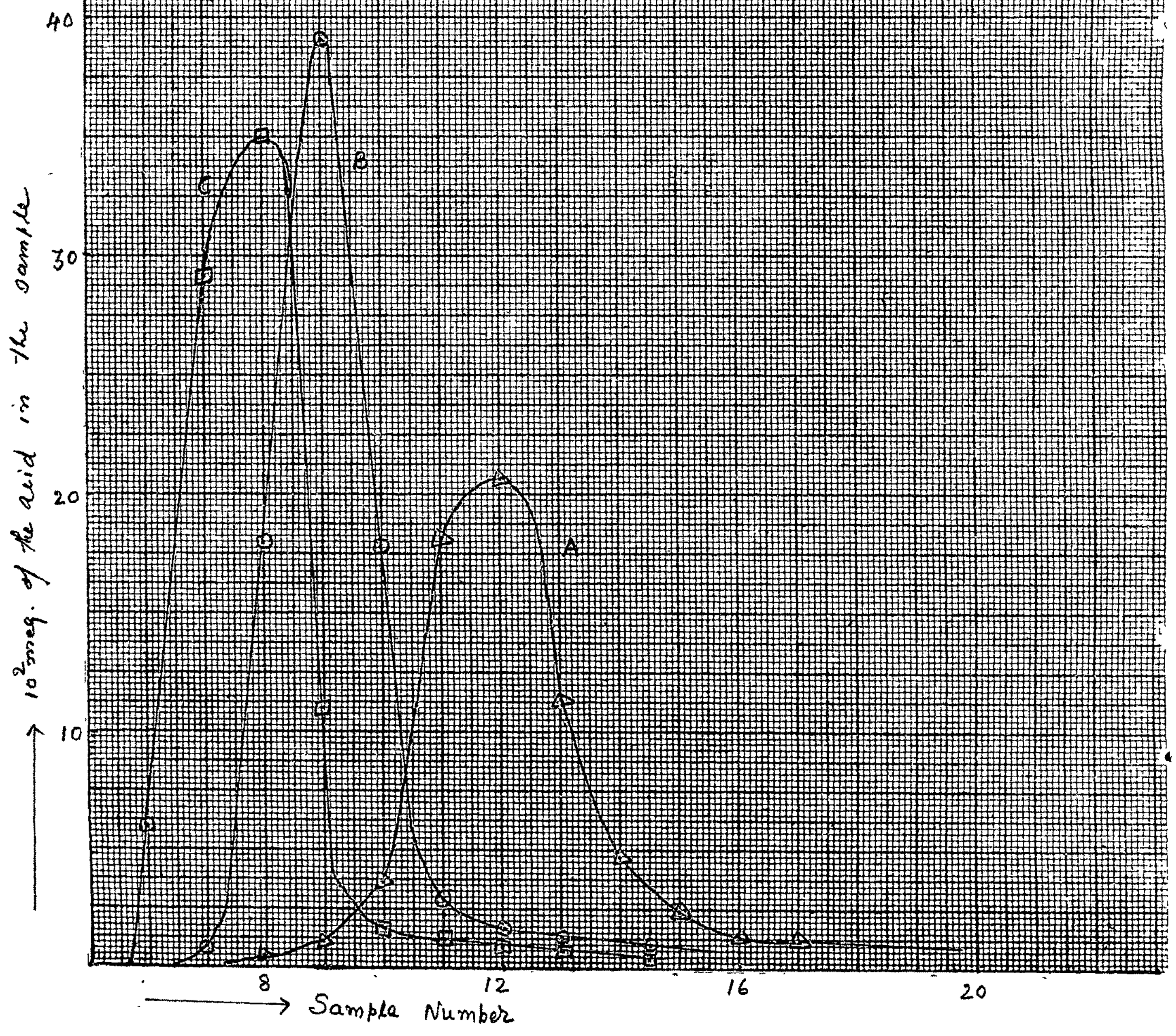

Table 3.3.3.4.8

Column elution of strong acids with resin Cx-6

Acid In put	Hydrochloric 1.0186 meq.in 20 cc.	Sulfuric 1.039 meq. in 20 cc.	NF acid 1.050 meq. in 20 cc.
Sample No. each =10 cc.	10^3 meq.eluted in sample	10^3 meq.eluted in sample	10^3 meq.eluted in sample
1	-	-	-
2	-	-	-
3	-	-	-
4	-	-	-
5	1.25	-	-
6	2.46	61.55	-
7	11.08	292.9	1.25
8	179.70	352.1	7.50
9	391.4	110.8	12.50
10	178.4	19.70	37.50
11	32.0	12.31	181.2
12	17.24	9.85	205.0
13	12.50	7.39	111.2
14	10.00	4.20	46.25
15			22.50
16			12.50
17			10.00
18			6.00

Then the runs were discontinued

Fig. 3.3.3.4.2 Separation of HF acid (A) from hydrochloric acid (B) and sulfuric acid (C) with the resin Cx-6.

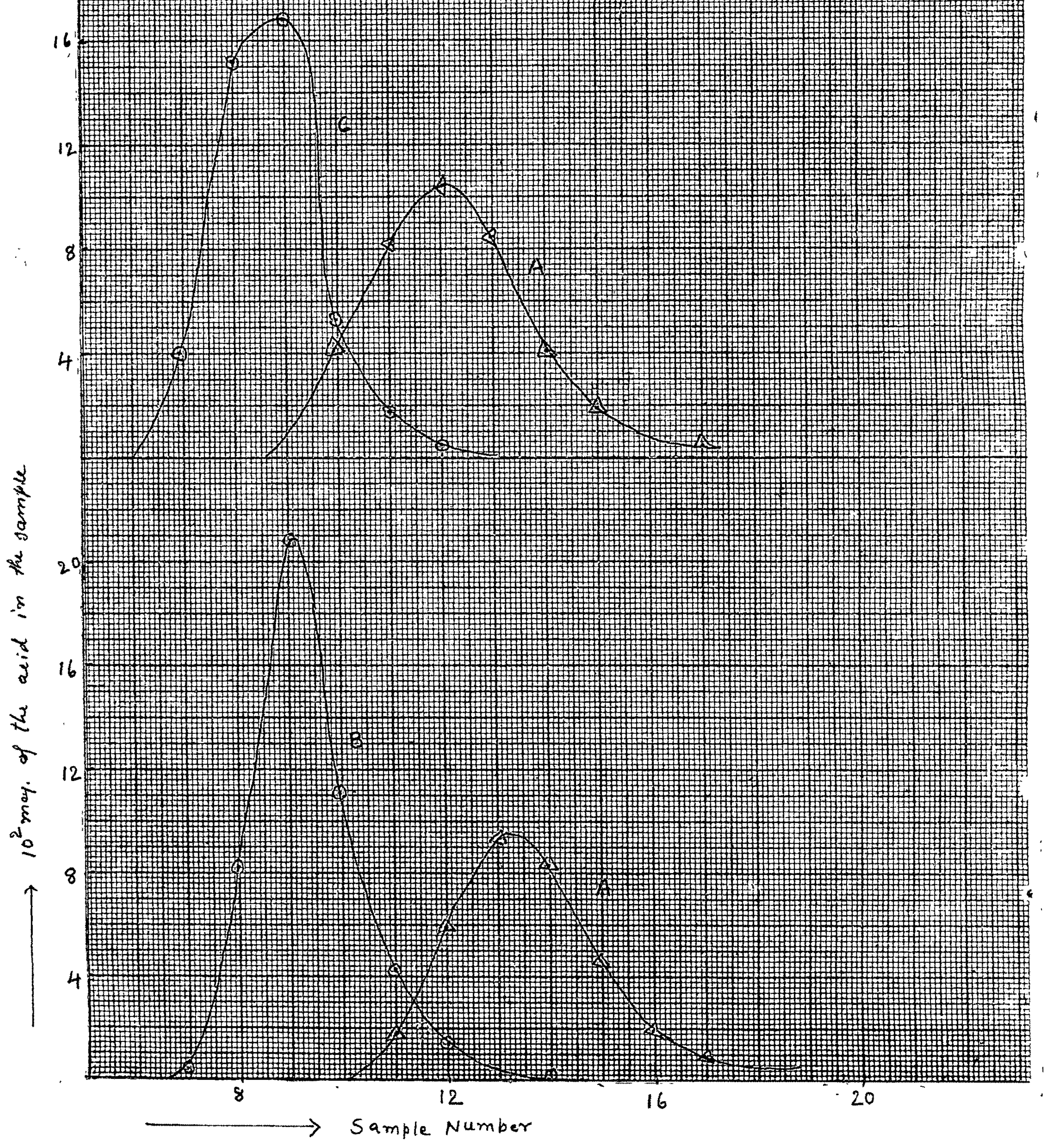

Table 3.3.3.4.9

Column separation of strong acids with the resin Cx-6

Acid Input	Sulfuric (0.525 meq.	+ NF acid + 0.525 meq.) in 20 cc.	Hydrochloric (0.5093 meq.	+ NF acid + 0.5216 meq.) in 20 cc.
Sample No. each = 10 cc.	10^3 meq. eluted in sample	10^3 meq. eluted in sample	10^3 meq. eluted in sample	10^3 meq. eluted in sample
1	-	-	-	-
2	-	-	-	-
3	-	-	-	-
4	-	-	-	-
5	-	-	-	-
6	-	-	-	-
7	40.0	-	7.27	-
8	151.9	3.15	83.41	0.28
9	166.7	3.28	209.1	0.34
10	53.4	41.56	112.7	0.27
11	18.1	81.92	45.19	18.81
12	6.26	103.7	16.38	59.94
13	2.0	86.0	2.50	93.50
14	0.94	41.56	2.20	84.44
15	0.82	19.68	1.28	45.50
16	0.85	10.65	-	20.00
18	0.75	8.0	-	7.14
21	0.25	6.0		

Then the runs were discontinued.

3.3.3.4d Discussion :

Table (3.3.3.4.7) indicates that the amount of sulfuric acid and hydrochloric acid sorbed were essentially same. It is observed that while the quantity of acid sorbed per equivalent of resin decreases as X increases, the ratio, r, given by NF acid sorbed per equivalent of resin divided by sulfuric acid or hydrochloric acid sorbed per equivalent of resin, increases, reaches a maximum and then decreases as X increases.

Table (3.3.3.4.8) and figure (3.3.3.4.1) give the separate elution curves for (A) NF acid, (B) hydrochloric acid, (C) sulfuric acid on the resin Cx-6. It is indicated that elution of the later portion is relatively slow and the later part of the elution curve trails along volume-axis ; the break through volume for NF acid is significantly different from that for other two acids. Next, different binary mixtures of NF acid with hydrochloric acid and sulfuric acid in ratio 25 : 75 to 75 : 25 were sorbed and eluted using resin Cx-6. Tables (3.3.3.4.9) and figure (3.3.3.4.2) give one illustrative example for the type of separation of NF acid from hydrochloric acid and sulfuric acid achieved by this technique.

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