III RESULTS AND DISCUSSION

RESINIFIED LIGANDS

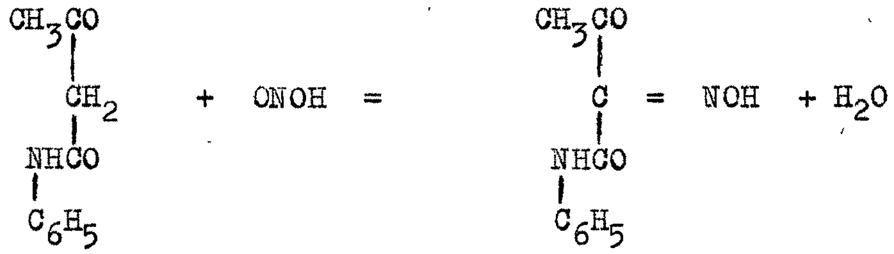
III. RESULTS AND DISCUSSION

III.1. RESINIFICATION OF LIGANDS :

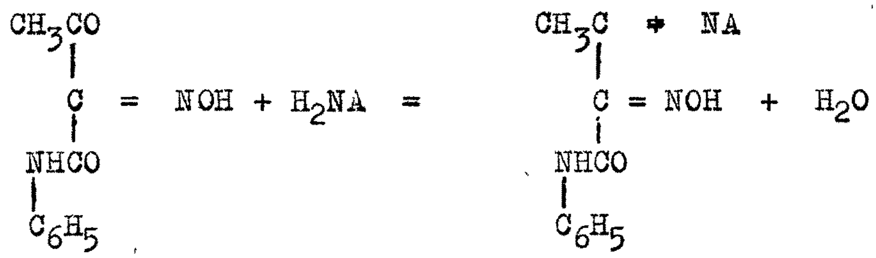
Ligands can be resinified by (i) polyaddition reaction, (ii) polycondensation reaction and (iii) insertion into polymeric matrix. We selected various polycondensation reactions for the resinification of ligands.

1(a) Resinification of vic-oxime-imine :

We began our attempts with the resinification of vic-oxime-imines. For this purpose 2,3-dioxo-butyranilide-2-oxime was prepared from acetoacetanilide and transformed into imine as shown in R.III.1. Resinification was attempted with formaldehyde under mild acidic and basic conditions and in presence of resorcinol; formation of dimers and copolymers was expected as shown in R.III.2 and R.III.3. However

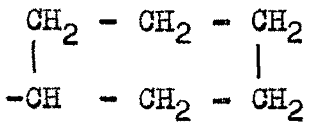


(a)



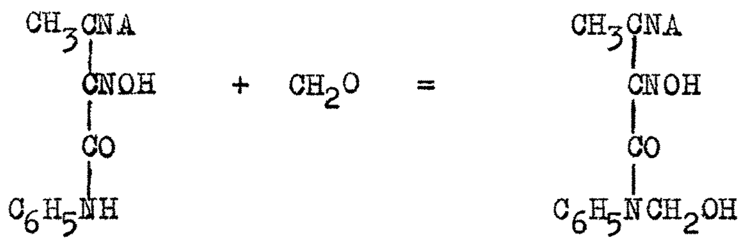
where : A = $-CH_3$, $-C_2H_5$, $-n-C_4H_9$, $-(C_6H_{12})_{1/2}$, $-(C_{10}H_{20})_{1/2}$

OR

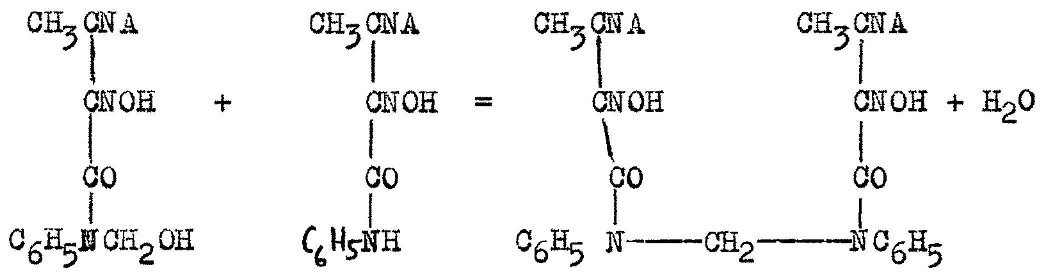


(b)

R.III 1



(a)



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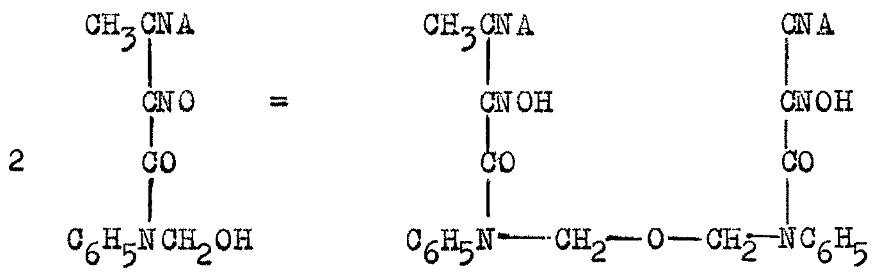
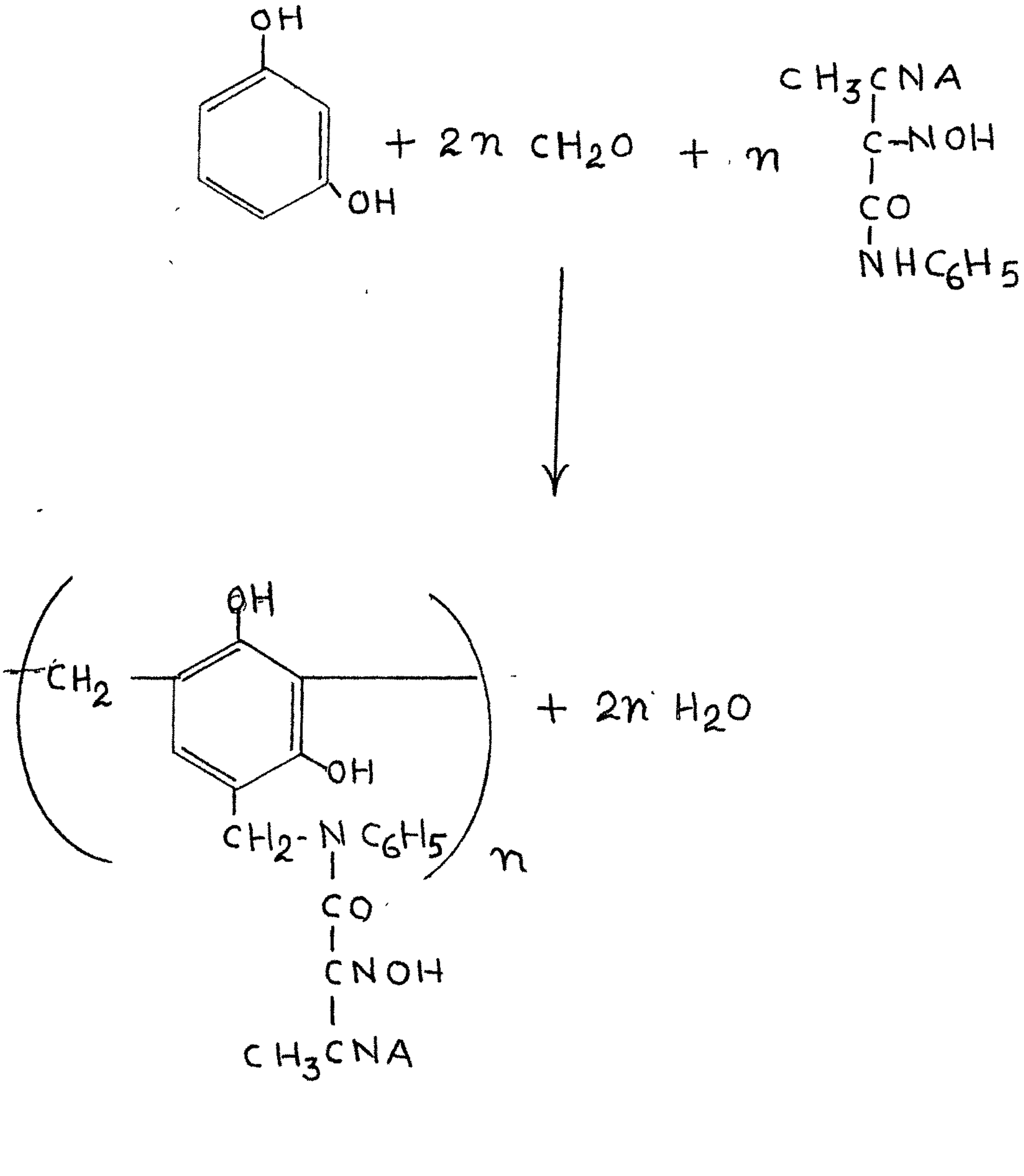


(c)

R. III 2


OH
OH
+ 2n CH2O + n
CH3CNA
C-NOH
CO
NHC6H5
OH
CH2
OH
CH2-N C6H5
CO
CNOH
CH3CNA
n
+ 2n H2O

R III 3

none of these products could be isolated. It is believed that the reactant has undergone degradation during the reaction. The work was discontinued.

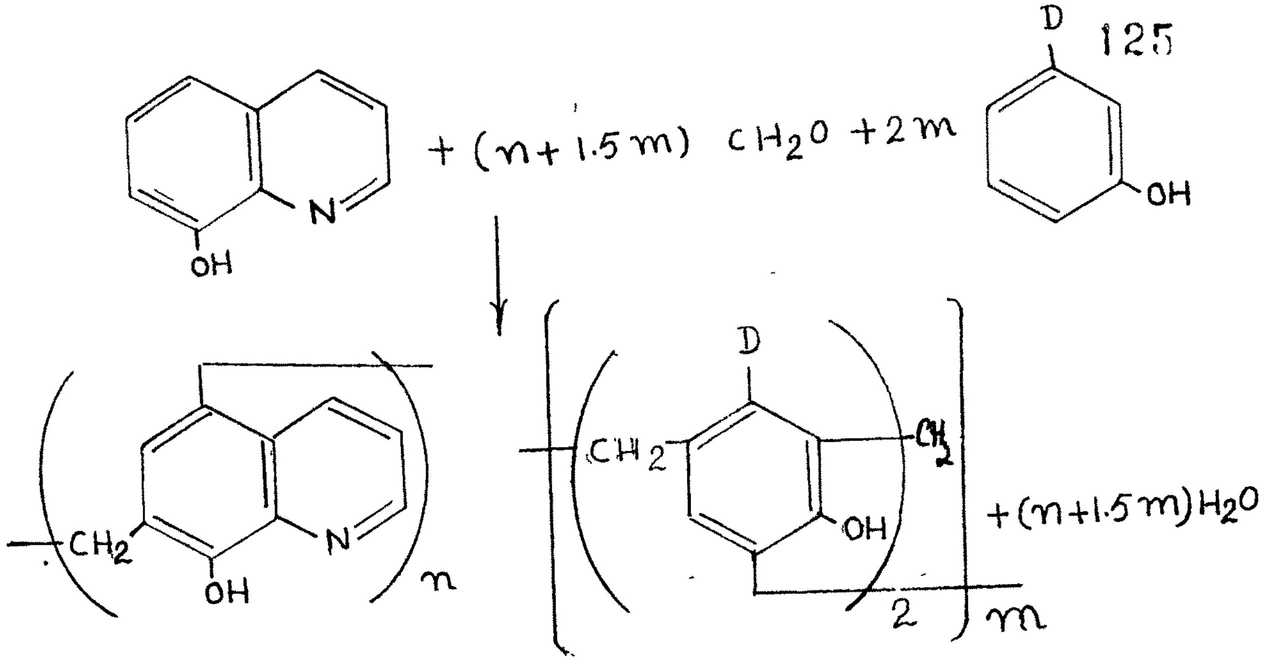
1(b) <u>Resinification of 8-hydroxy quinoline</u> :

(Copolymers of oxine and phenol).

The resinification of 8-hydroxy quinoline (8Q) was carried out with formaldehyde. Since the functionality of 8Q is 2, soluble linear polymeric chains could be obtained. As we desired to prepare insoluble resinous mass, copolymerization of 8Q with phenols having a functionality of 3 or 4 was carried out as shown in R.III.4. Although the two reactants were used in the molar proportion of 1:1 (Table II 1(a)), the relative molar proportions of the two reactants in the product may be different depending on the functionality and relative reactivity of the reactants.

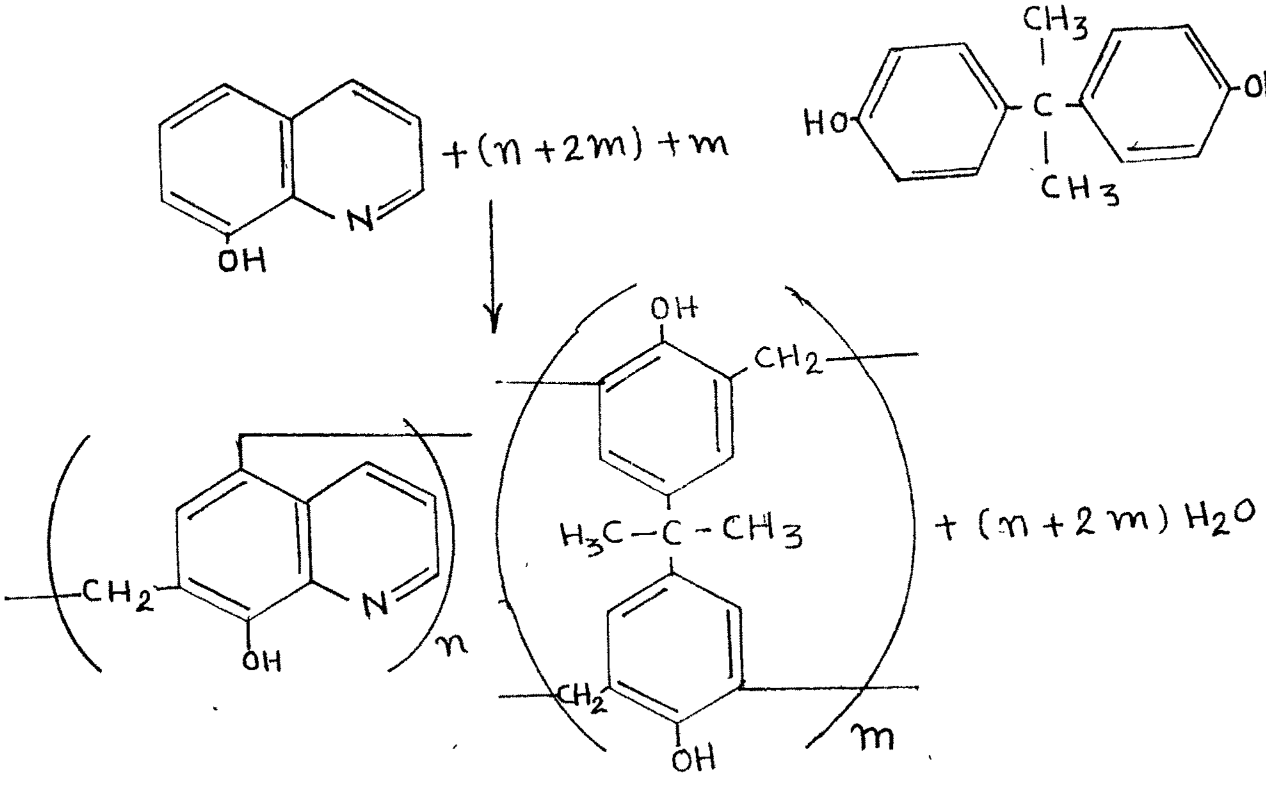
Gel period for the formation of these products (Table II 1(a)) increases in order

$$8QR < 8QM < 8QC \lesssim 8QB$$



Where D = CH_3, OH, NH_2

(a)



(b)

R III 4

In earlier investigations on the preparation of ion exchange resins, Sheth(161) observed that the gel period for various series of products increases with reference to phenolic compound in order

$$R < M \sim C < B$$

Same cure period was used for curing the products.

1(c) Resinification of salicylaldehyde :

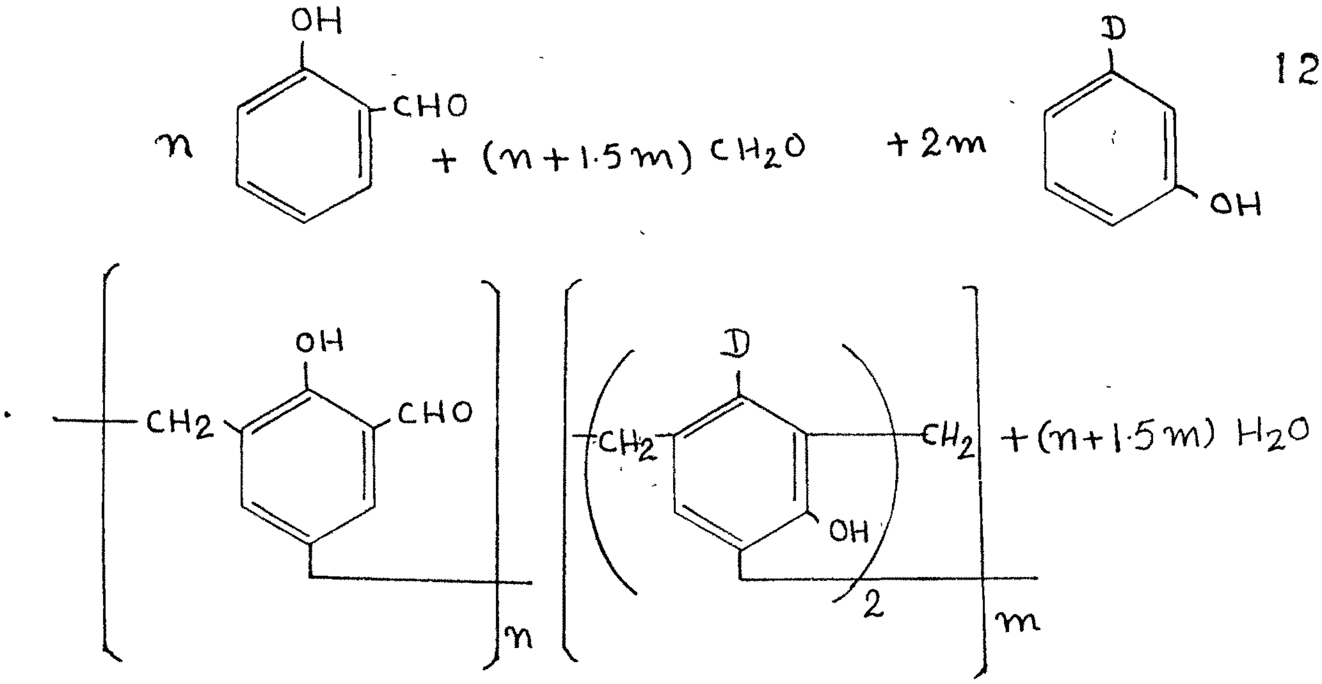
(Copolymers of salicylaldehyde and phenol)

Salicylaldehyde was copolymerized with phenols having functionality of 3 or 4 using formaldehyde for polycondensation as shown in R.III.5. Molar proportions of salicylaldehyde and phenol in the product (Table II 1(b)) depends on the functionality and reactivity of the reactants.

Gel period for the formation of these products (Table II 1(b)) increases in order

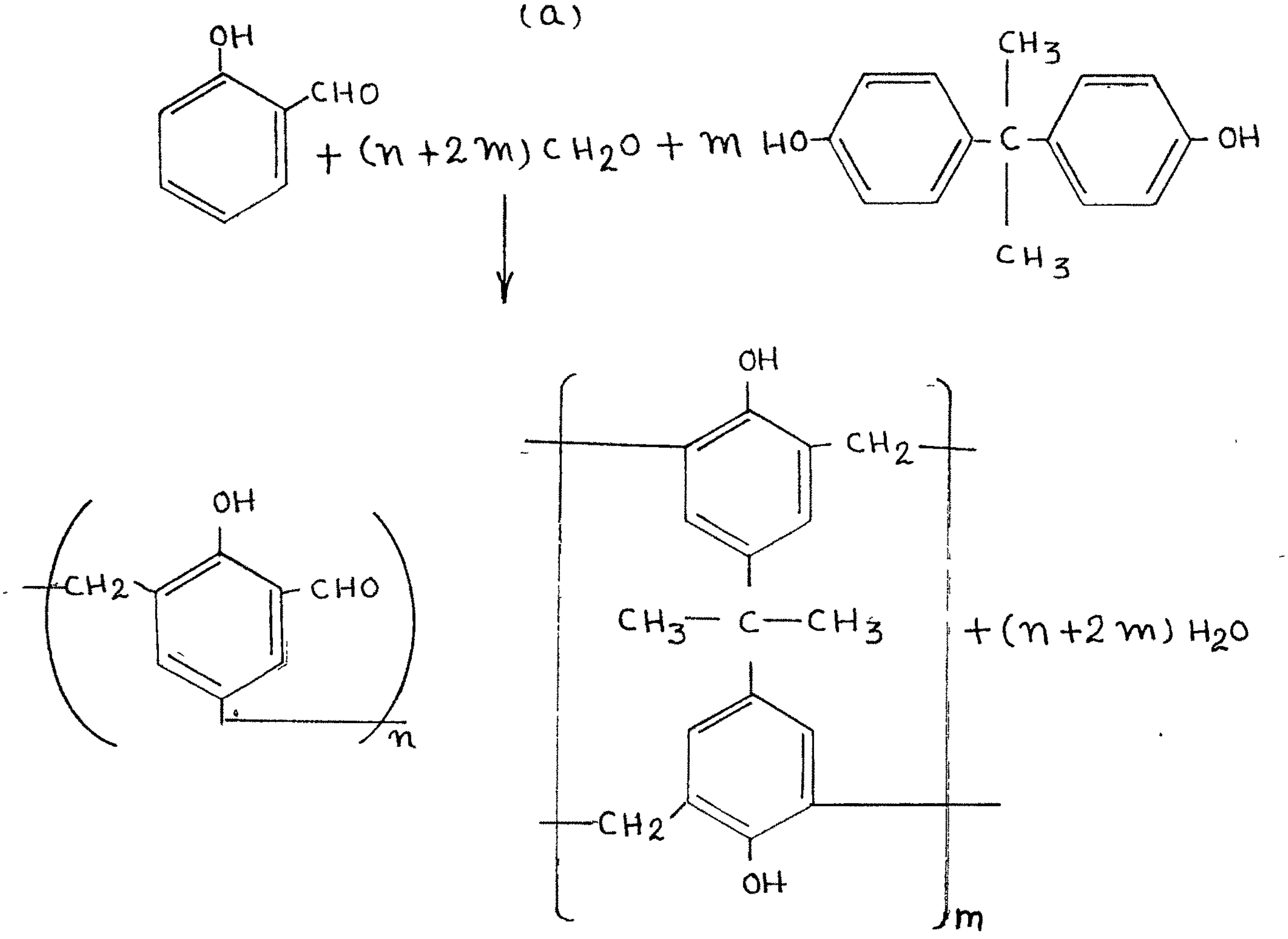
$$SR < SM < SB$$

It is in the same order as observed above for 8Q series. Same cure period was used for curing the products.



Where D = CH_3, OH, NH_2

(a)



(b)

R III 5

1(d) Resinification of salicylaldehyde :

(Copolymers of salicylaldehyde and melamine)

Salicylaldehyde was copolymerized with melamine using different condensing agents such as formaldehyde, n-butyraldehyde and glyoxal. Gel period increases with reference to condensing agents as

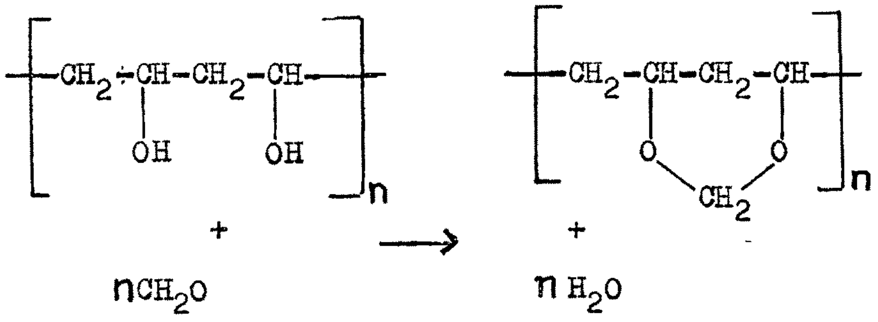
$$F < G < B$$

If we compare S and A series we find that gel period is same for melamine and resorcinol products.

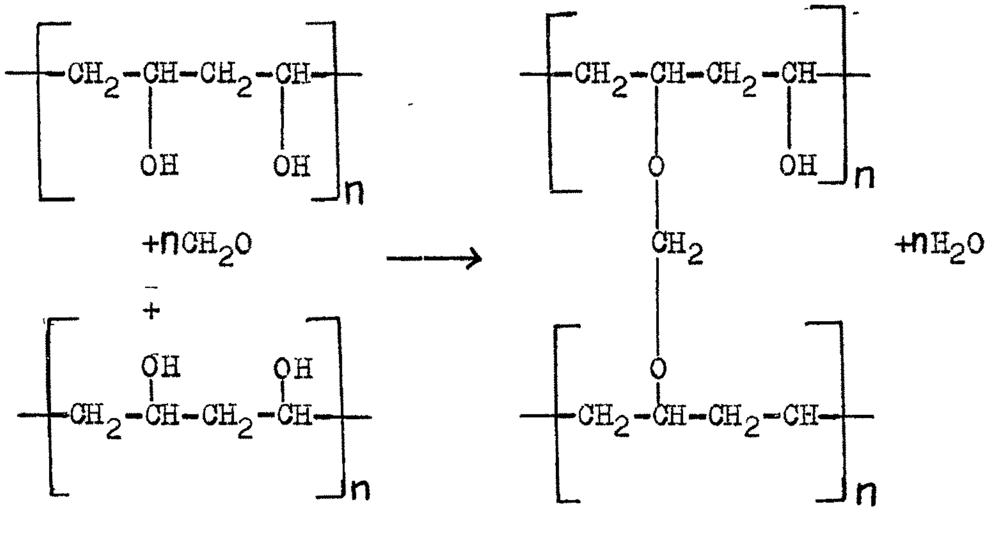
1(e) Resinification of (i) oxine and (ii) salicylaldehyde :

(Copolymers of (i) oxine and (ii) salicylaldehyde with polyvinyl alcohol)

Polyvinyl alcohol reacts with aldehyde forming acetals resulting in intra-chain rings or interchain cross-links (R.III.6). This cross-linking can be taken advantage of in forming ligand resins. Thus oxine will be linked to polyvinyl chain through acetal



(a)



(b)

R III 6

links. Similarly, salicylaldehyde will form acetal links with polyvinyl alcohol but at a much slower rate. Addition of starch in the process was with the view of modifying the porosity of the products.

1(f) Resinification of phenols :

Condensation products of m-aminophenol with formaldehyde or furfuraldehyde and copolymers of resorcinol with m-cresol and of bisphenol A with (i) thiourea and (ii) H-acid using formaldehyde were prepared for comparative studies.

III.2 RESINS IN DIFFERENT FORMS :

Since the resinified ligands contain phenolic and amino functions depending on the ligands and phenols used, they can exhibit acidic (and basic) characteristics. For this reason, they were converted into (i) acid form by treatment with excess acid and washing it free from soluble acid, (ii) basic form by treatment with excess alkali and washing it free from soluble base and (iii) NH_4- form by treatment with excess NH_4OH and washing it free from soluble base.

In case of 8-hydroxyquinoline, it can exist in (i) protonated form, (ii) unionized or neutral form and (iii) anionic form. Unionized or neutral form will be in equilibrium with zwitter ion form. Acid form refers to the neutral (unionized) or zwitter ion form and base form refers to the anionic form of 8-hydroxyquinoline. Similarly, in case of salicylaldehyde, acid form refers to its unionized or neutral form and base form to its anionic form. These products were used as required.

III.3 ANALYSIS OF RESINS :

Acid form resins of 8Q series and NH_4 form resins of 8Q and S series were analysed for N. On the basis of this analysis, formulae of repeat units of these resins were suggested in Table II.2. It is assumed that NH_4 form is mainly of 8-hydroxy quinoline or salicylaldehyde. Using these formulae, we suggest the structures as shown in S III 1 and S III 2 and present the mole fractions of the reactants in the resins in Table III 1 and % wt of repeat units in the resins in Table III 2.

Copolymer composition can be calculate from N-analysis of the samples as only one reactant (or monomer) contained N in 8Q series. If A_1, B_1, B_2 and B_3 are as shown in S III 3, total number of moles (M_A) of repeating unit A in 100 g of copolymers is

$$M_A = \frac{\%N}{14}$$

and % wt of A repeat unit in copolymer

$$= M_A \text{ x Mol. wt. of A.}$$

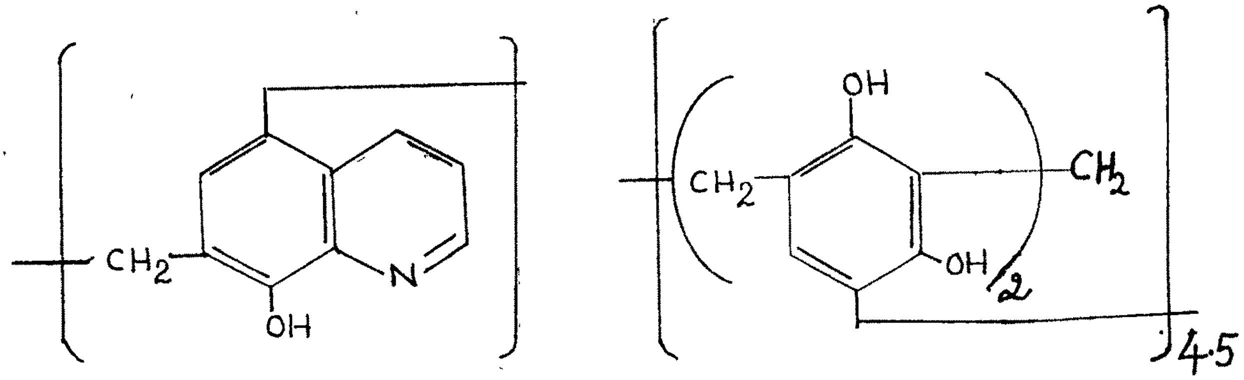
Hence, % wt of B repeat unit in copolymer

$$= 100(M_A \text{ x Mol wt of A})$$

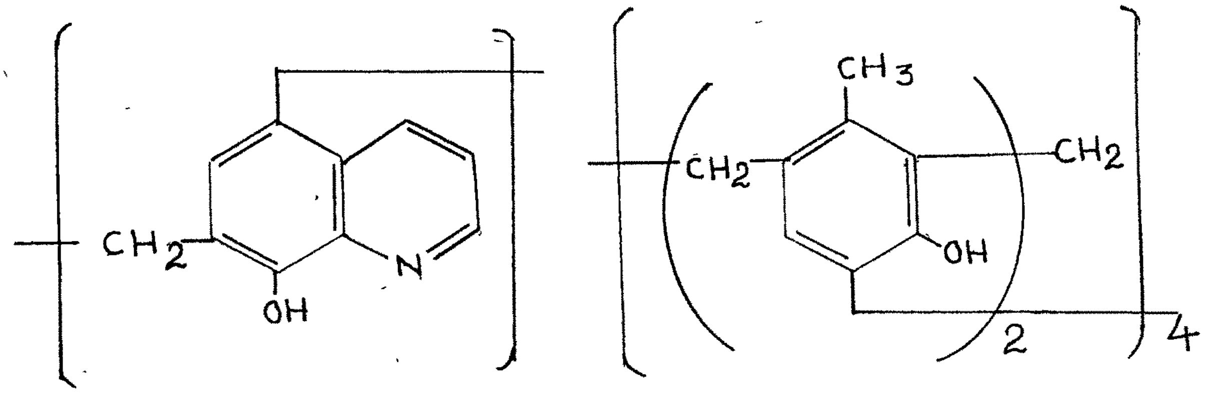
and number of moles of B repeat unit in copolymer

$$= \frac{100-(M_A \text{ x Mol wt of A})}{\text{Mol wt of B}} = M_B$$

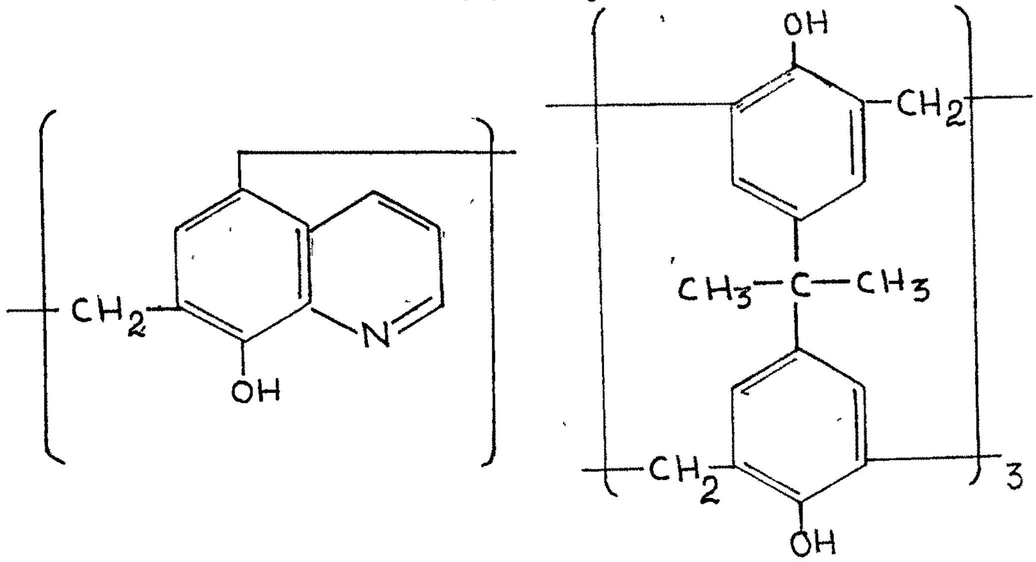
Similarly, % wt of repeat units is calculated from N-analysis of NH_4-form of resins of S series.



(a) 8QR

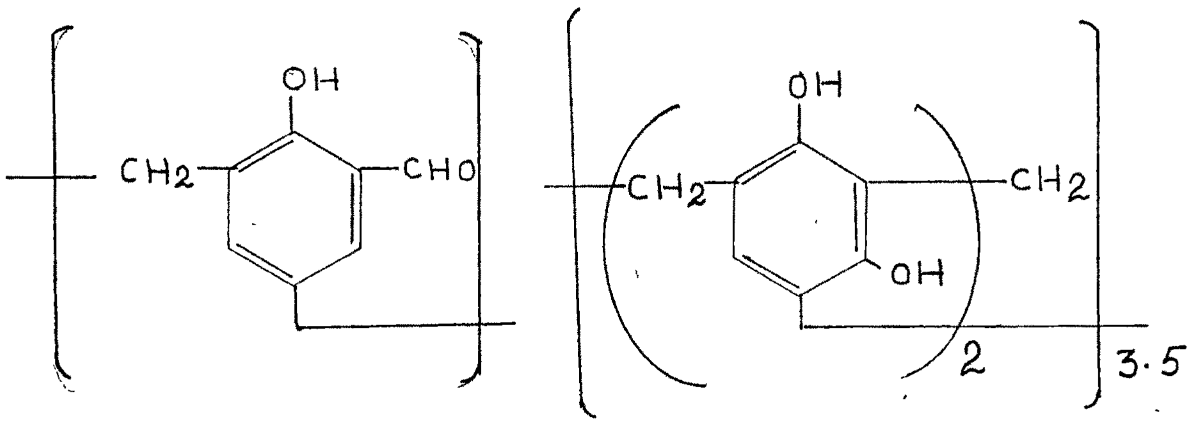


(b) 8QC

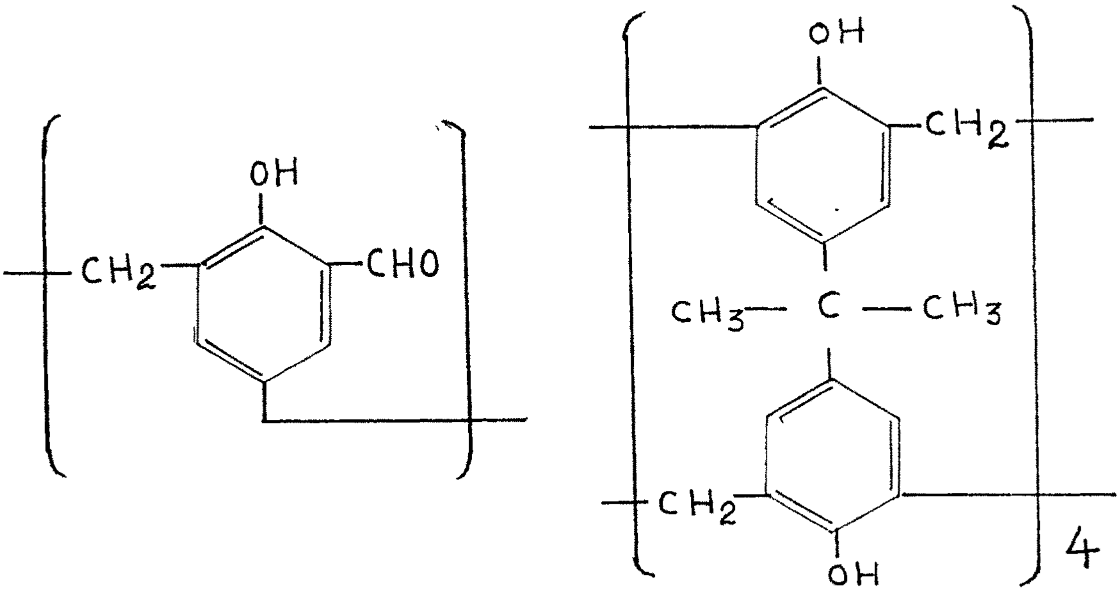


(c) 8QB

S III 1



(a) SR



(b) SB

S Ⅲ 2

Table III 1(a)

Mole fractions of reactants in resins

(8Q series)

No.	resin	mole fraction of		
		8-hydroxy quinoline	phenolic compound	formaldehyde
1	8QR	0.04	0.37	0.59
2	8QC	0.05	0.36	0.59
3	8QB	0.09	0.27	0.64

Table III 1(b)

Mole fractions of reactants in resins

(S series)

No.	resin	mole fraction of		
		salicyl aldehyde	phenolic compound	formaldehyde
1	SR	0.05	0.36	0.59
2	SB	0.07	0.29	0.64

Table III 2(a)

% wt of repeat units in resins

(on the basis of N - analysis of resins)

(8Q series)

No.	resin	% wt of repeat units of	
		8-hydroxy quinoline	phenolic compound
1	8QR	11.4	88.6
2	8QC	13.3	86.7
3	8QB	16.9	83.1

Table III 2(b)

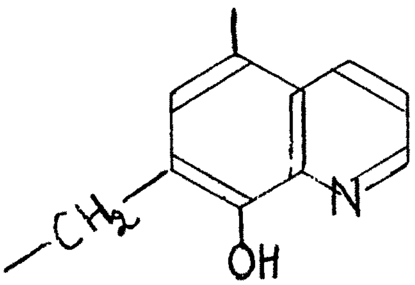
% wt of repeat units in resins

(on the basis of N-analysis of NH_4-form of resins)

(S series)

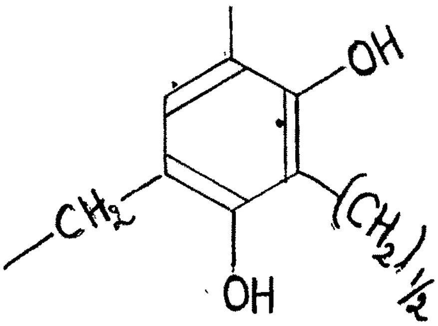
No.	resins	% wt of repeat units of	
		salicyl aldehyde	phenolic compound
1	SR	12.4	87.6
2	SB	12.3	87.7

A_1 =



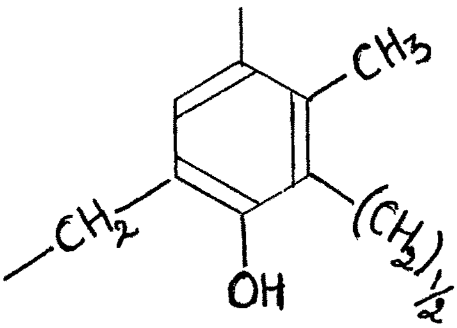
(M.wt.:157)

B_1 =



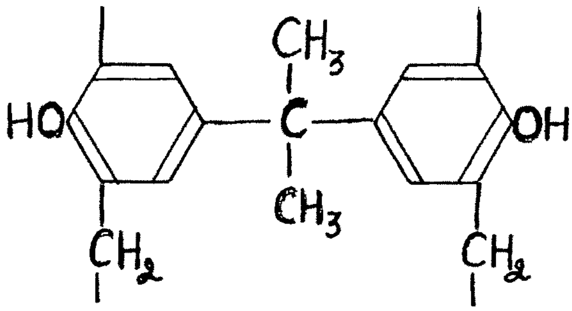
(M.wt.:128)

B_2 =



(M.wt.:126)

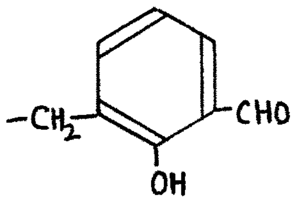
B_3 =



(M.wt.:252)

S III 3

on the basis of the consideration that

A' =  (M.wt.:134)

III.4 COPOLYCONDENSATION :

Eventhough we started with 1:1 mole proportions of reactants for condensation reaction with formaldehyde, mole proportions of these reactants in copolymers obtained are different and are dependenton the rate constants of the reactions.

If the reactants A (8-hydroxyquinoline or salicylaldehyde) and B (m- or p-substituted phenolic compound) react with C (formaldehyde),

$$A + C \xrightarrow{k}$$

$$B + C \xrightarrow{k'}$$

$$-\frac{da}{dt} = kac \qquad \text{and}$$

$$-\frac{db}{dt} = k'bc$$

where $-\frac{da}{dt}$ and $-\frac{db}{dt}$ are the rates of reactions of A and B, with rate constants k and k' and the concentrations a and b.

Hence

$$\frac{da}{db} = \frac{ka}{k'b}$$

On integration, we get the expression

$$\frac{a}{a_o} = \frac{b^{k/k'}}{b_o}$$

where a_o and b_o are the initial concentrations of A and B respectively.

If $k \neq k'$, the composition of the copolymer differs from that of the initial reaction mixture.

Assuming 90% conversion of comonomer (R, C or B) and the conversion of the ligand (8Q or S) evaluated on the basis of the mole composition as derived from analysis, values of the ratio k/k' are calculated and presented in Table III.3.

The results indicate that with the ligand 8Q or S, the reactivity of R, C or B increases in order

$$B < R < C$$

and with R or B, the reactivity of the ligand (8Q or S) increases in order

$$S < B .$$

III.5 SOLUBILITY OF RESINS :

Solubility of these resins in different solvents was studied. It was observed that these resins are insoluble in water and organic solvents (8QC and SB are very slightly soluble in DMF). They are also insoluble in 3N acid except resins of V series which were slightly soluble. Similarly these resins are

Table III 3

Evaluation of k/k'

No.	resin	k/k'
1	8QR	0.315
2	8QC	0.043
3	8QB	0.500
4	SR	0.119
5	SB	0.359

resins of different series increases in order :

A-series $\angle$ P-series $\angle$ 8Q-series $\angle$ S-series.

Water content of the resins can be related to (i) degree of cross-linking, (ii) concentration and solvation tendency of fixed ionogenic groups (iii) concentration, valency and solvation tendency of counter ions and (iv) electrostatic interactions of ions in the resins. Since we are comparing acid form of the resins, the counter ions are the same. Fixed ionogenic groups are also the same with difference in their chelation characteristics. Hence electrostatic interactions will be comparable. The major factor affecting the variation in water content in each series will then be relative degree of cross-linking. We can suggest that the degree of cross-linking in a series increases in order :

(i)	8QR $\angle$ 8QB $\angle$ 8QM $\angle$ 8QC	for 8Q series,
(ii)	SM $\angle$ SR $\angle$ SB	for S series,
(iii)	MSG $\sim$ MSB $\angle$ MSF	for A series and
(iv)	FTB $\angle$ FuA $\angle$ FCR $\angle$ FA $\angle$ FBHa	for P series.

resins of P series. The range of values of D_W is comparable for resins of 8Q and S series. However, the range of values of D_C expands in order

8Q series < S series < P series

The wide range of values of D_C for resins of P series may be related to the differences in monomers and condensing agents used in copolycondensation.

III.8 PORE VOLUME AND POROSITY OF RESINS :

Pore volume (PV) of the resins is calculated by the expression :

$$PV = \frac{1}{D_C} - \frac{1}{D_W}$$

and porosity (%P) of the resins is calculated by the expression :

$$\% P = (1-D_C/D_W) \times 100.$$

Calculated values of PV and %P are presented in Table III.4. The values of pore volume lie in the range (i) 1.00 - 1.61 for resins of 8Q series (ii) 0.80 - 1.83 for resins of S series and (iii) 0.59 - 2.23 for resins of P series. Similarly the values of porosity lie in the range (i) 60.5 - 64.3 for the resins of 8Q series (ii) 52.9 - 67.5 for resins of S series and (iii) 50.6 - 75.7 for resins of P series.

Porosity is necessary for the diffusion process. A rate theory was derived for the rate control by " pore diffusion " i.e. interdiffusion in pores of the solid which are freely accessible to the bulk fluid outside and in which the composition of the fluid does not differ from that outside when equilibrium is established(166).

Table III 4(a)

Pore volume (PV) and porosity (%P) of resins (acid form)

(8Q series)

No.	resin	Pore volume (PV) (ml/g)	Porosity (%P) (%)
1	8QR	1.01	60.5
2	8QM	1.33	62.1
3	8QC	1.12	61.5
4	8QB	1.61	64.3

Table III 4(b)

Pore volume (PV) and porosity (%P) of resins (acid form)

(S series)

No.	resin	Pore volume (PV) (ml/g)	Porosity (%P) (%)
1	SR	0.80	52.9
2	SB	0.95	59.9
3	SM	1.83	67.5

Table III 4(c)

Pore volume (PV) and porosity (%P) of resins (acid form)

(P series)

No.	resin	Pore volume (PV) (ml/g)	Porosity (%P) (%)
1	FCR	1.23	67.5
2	FA	2.23	75.7
3	FBHa	1.07	57.8
4	FTB	0.60	50.6
5	FuA	0.90	53.8

III.9 pH TITRATION OF RESINS :

Results of pH titration of resins are presented graphically in figures III.1. The curves indicate the weak acid, (and weak base) nature of the resins. Titrations have been carried out over a wide range of alkali concentrations. Even then constancy of ion uptake could not be obtained. Hence maximum ion uptake (i.e. cation exchange capacity - CEC) possible for the monomers used was calculated and is presented in Table III.5. Calculations were also made for the theoretical CEC for (i) the resins which can be obtained by condensing the monomers with formaldehyde and (ii) the resins prepared in this work and having the structures as suggested. It is seen that for the resins 8QC, 8QB and SB, CEC value is not more than 8. Hence values of ion uptake above 8 for these resins should indicate alkali sorption by them. Thus ion uptake in pH titration curve is indicative not only of ion exchange but also of solute sorption.

When ion exchange is coupled with sorption of

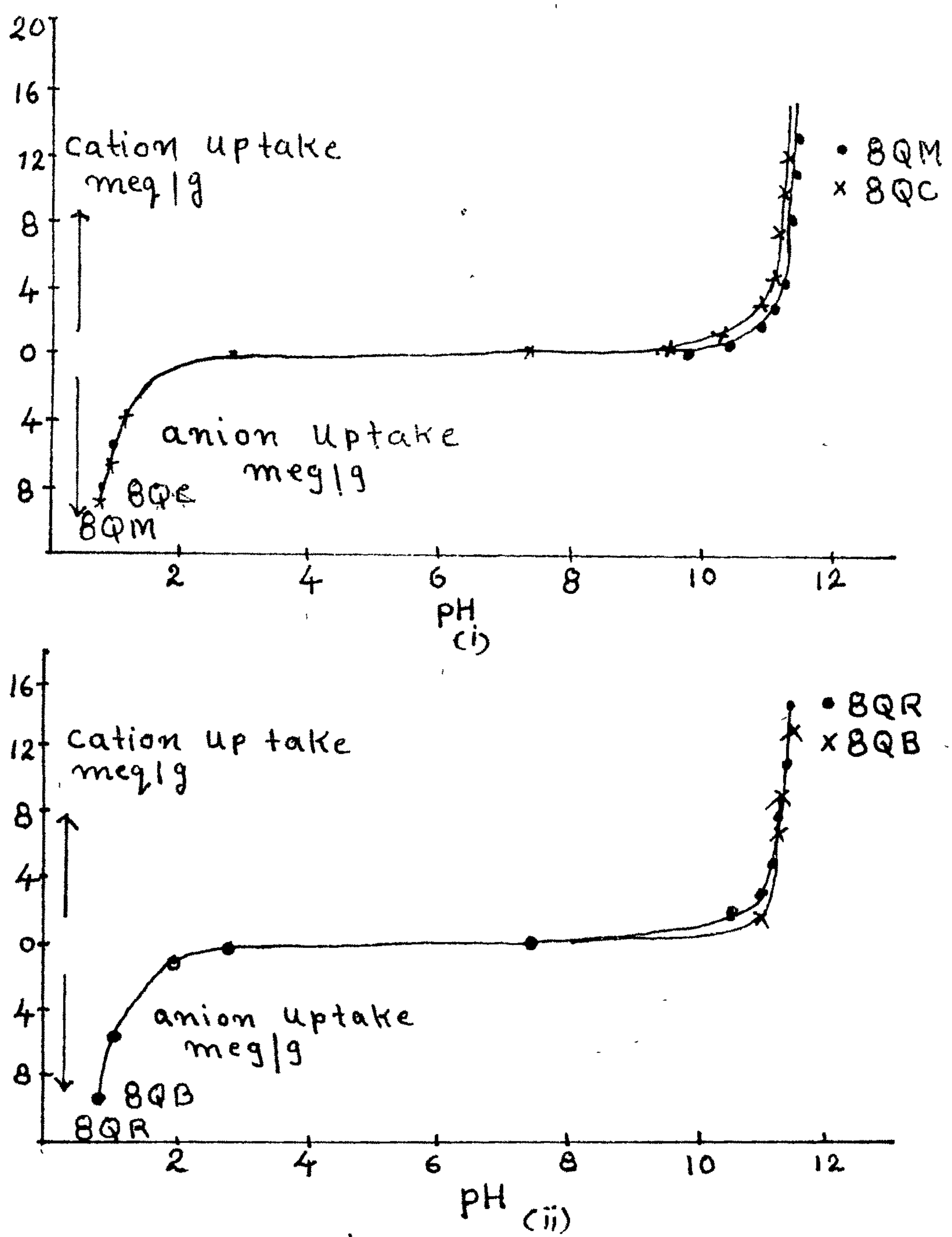


Fig III 1 (a) ion-uptake vs pH
Plots for 8QR, 8QC, 8QM & 8QB

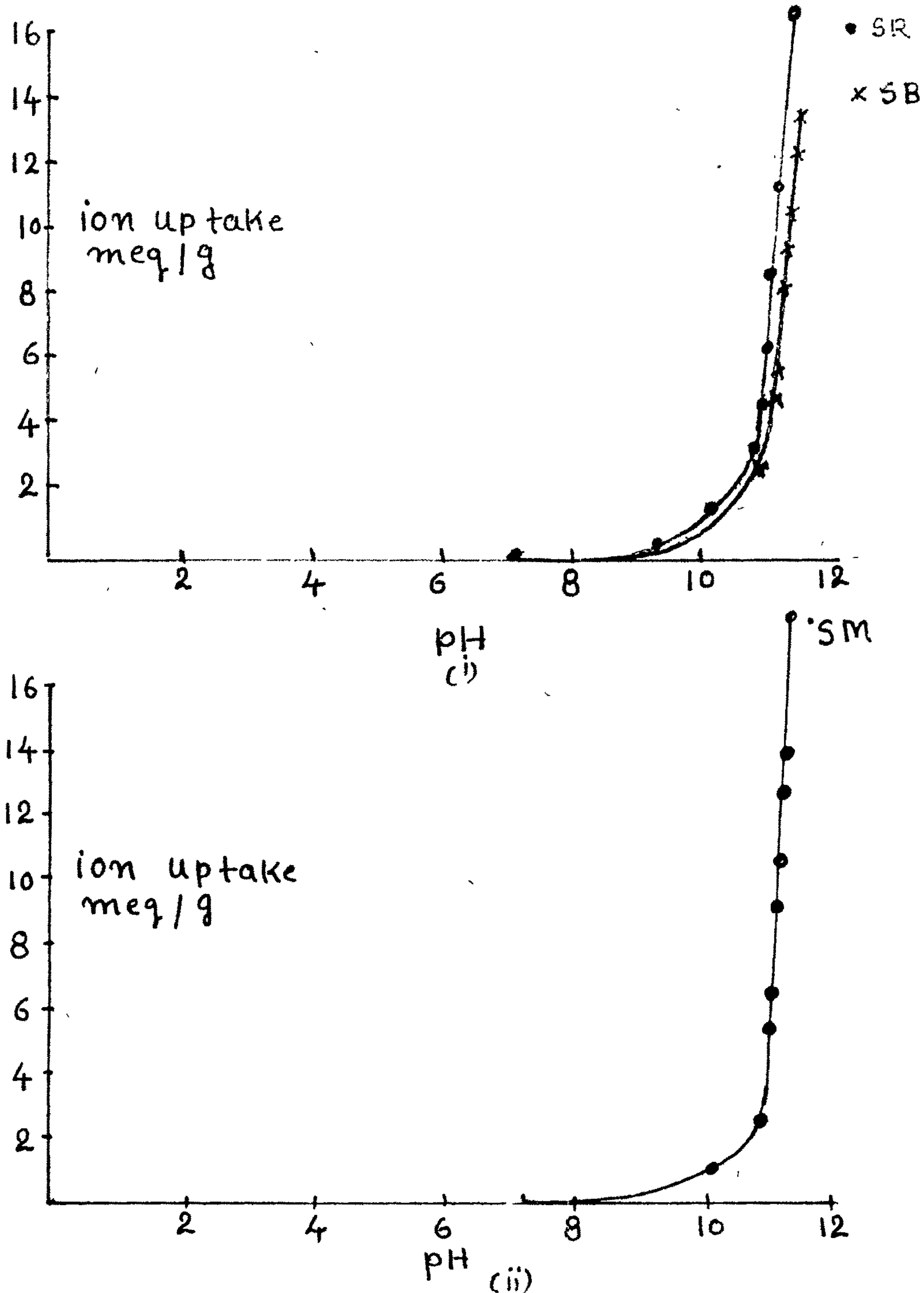


Fig III 1(b). ion uptake Vs pH plots for SR, SM & SB

Table III 5

Calculated cation exchange capacity of ligands and resins

No.	ligand	CEC calc	No.	resin	CEC calc	No.	resin	CEC calc
1	resorcinol	18.2	6	RF	15.6	11	8QR	14.2
2	m-cresol	9.3	7	CF	7.9	12	8QC	7.7
3	bis phenol A	8.8	8	BF	8.0	13	8QB	7.7
4	oxine	6.9	9	8QF	6.4	14	SR	14.6
5	salicylaldehyde	8.2	10	SF	7.0	15	SB	8.0

strong electrolytes, the equilibria are more complex. If we consider the sorption of the strong electrolyte AY by the ion exchanger in A form (or A+B form), we suggest that (i) the ion exchanger contains counter ion A prior to sorption, (ii) sorbed ions A are indistinguishable from exchanged ions A in the resin and (iii) mobile ions A and Y are subject to electrostatic forces in the system. Much lower concentration of coion in the cation exchanger than in the external solution has been explained in terms of such electrostatic forces related to Donnan potential and is termed as Donnan exclusion. The efficiency of exclusion increases with decreasing solution concentration and with increasing capacity and degree of cross-linking of the cation exchanger. Hence distribution coefficient of the coion rises with increasing concentration.

Further, ion pair formation between the counter ions and fixed ionogenic groups localizes the counter ions in the ion exchangerand reduces the efficiency of the electrolyte exclusion. Thus weak acid cation exchanger in acid form is very little ionized and hence do not exclude acids(167) and weak base anion exchanger in base form would not exclude bases. In the case of resins under investigation, it is suggested that sorption takes place before the completion of ion exchange and hence the range of ion uptake can be split into three : (i) range of ion exchange, (ii) range of ion exchange + sorption and (iii) range of sorption.

Concentration (C_s) of alkali in solution at equilibrium was calculated and plots x were obtained for ion uptake versus log C_s. These curves are similar in nature to pH titration curves. However, plots for ion uptake versus C_s are different. These are presented in Fig.III.2. Breaks have been observed and are presented in Table III 5/1. Ion uptake at these breaks do not correspond to the maxium CEC values calculated for the resins. Hence no simple generalizations can be made. However, three regions are observed in most cases and can be interpreted as suggested above. If we assume that ion uptake corresponding to the first break in each curve relates

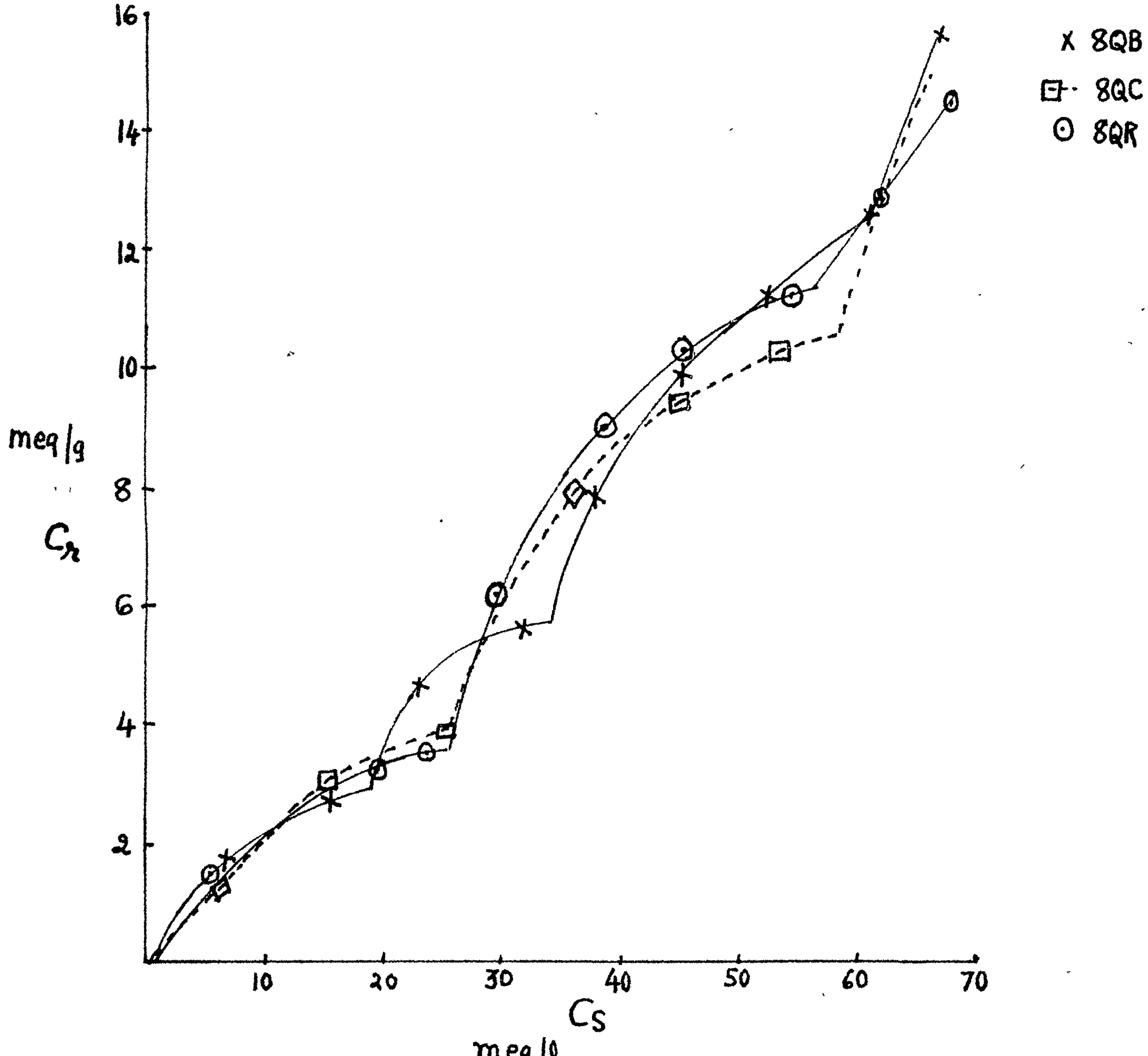


Fig. III.2(a) Plot of C_r versus C_s for 8QB 8QC and 8QR

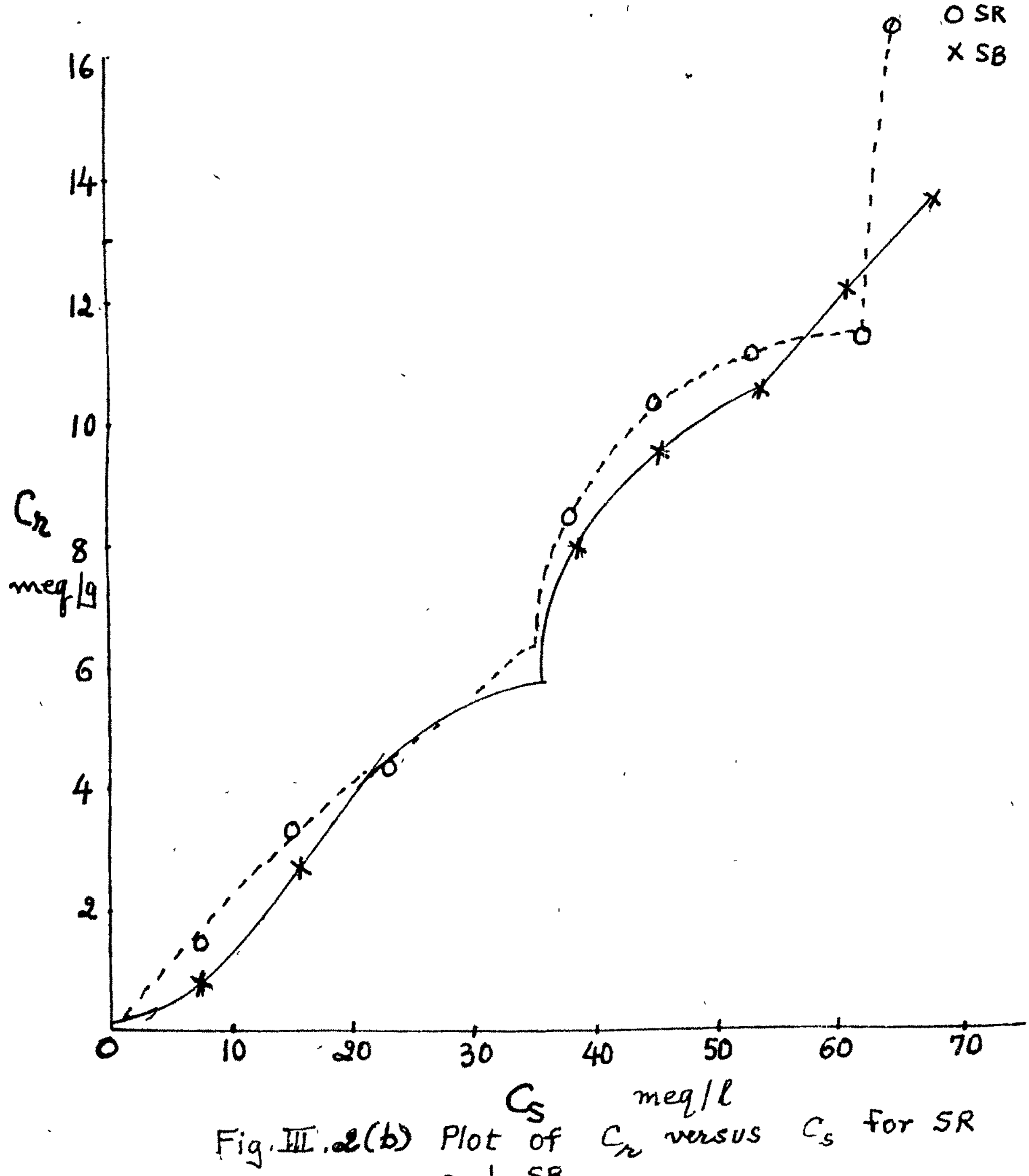


Fig. III.2(b) Plot of C_r versus C_s for SR and SB

Table III 5/1

Breaks in curves

(ref. Fig. III 2)

No.	resin	ion uptake (meq/g dry resin)		
		at break I	at break II	at break III
1	8QR	3.6	11.4	
2	8QC	3.9	10.6	
3	8QB	3.0	5.8	12.7
4	SR	6.3	11.4	
5	SB	5.7	10.7	

to the concentration of effective ionogenic groups in the resin (without sorption), we can calculate apparent pK_a values as follows . (Alternatively the concentration of fixed ionogenic groups can be considered to be the calculated CEC values of the resins and apparent pK_a values can be calculated).

If $\overline{H}$, $\overline{R}$ and $\overline{RH}$ indicate H^+, R^- (resin anion) and RH (resin) in resin phase, for the equilibrium

$$\overline{RH} = \overline{R} + \overline{H}$$

$$K_a = [\overline{R}][\overline{H}]/[\overline{RH}] \text{ and}$$

$$pK_a = -\log K_a \text{ and } \overline{pH} = -\log \overline{H}$$

Hence $$\overline{pH} = pK_a + \log [\overline{R}]/[\overline{RH}].$$

For the weak acid resin, when the dissociation is 50%,

$$[\overline{R}] = [\overline{RH}],\ \log[\overline{R}]/[\overline{RH}] = 0$$

and $$\overline{pH} = pK_a$$

If we assume that

$$[\overline{H}]/[\overline{Na}] = (H)/(Na)$$

where (H) and (Na) indicate concentrations of H^+ and Na^+ in solution in contact with the resin, at 50% conversion,

$$\overline{[Na]} = \frac{\overline{[R]}+\overline{[RH]}}{2} \quad \text{and}$$

$$pK_a = pH + \log\overline{[Na^+]} - \log\left\{\overline{[R]} + \overline{[RH]}\right\}/2$$

Calculated values of pK_a are presented in Table 5/2.

The values lie between 10.30 and 10.62 for these resins. Values of pK_a obtained by Sheth(161) for FCR, FA, FBHa, FTB and FuA and those obtained by Sprengling and Lewis(168) for methyl and methylol derivatives of phenol are presented in Table III 5/3. From these values one can suggest that formation of methylene bridges would increase pK_a values of the phenolic system.

III.10 ION EXCHANGE EQUILIBRIA :

Preliminary studies of ion exchange by the resins x indicated that cations like Cu(II), Ni(II), Co(II), Zn(II), etc. were taken by the acid form of these resins, under basic conditions but not under acidic conditions. Hence, ammonical conditions were

Table III 5/2

pK_a values of resins

No.	resin	I			II		
		ion uptake at break(I)	pH at 50% conversion	pK_a(I)	CEC (theor)	pH at 50% conversion	pK_a(II)
1	8QR	3.6	10.6	10.34	14.5	11.3	10.45
2	8QC	3.9	10.6	10.31	7.7	11.0	10.41
3	8QB	3.0	10.8	10.62	7.7	11.1	10.51
4	SR	6.3	10.8	10.30	14.6	11.2	10.34
5	SB	5.7	10.9	10.44	8.0	11.1	10.50

Table III 5/3

pK_a of phenol derivatives and resins

No.	resin	pK_a	No.	phenol derivative (methyl)	pK_a	No.	phemol derivative (methylol)	pK_a
1	FCR	10.85	1	2 methyl	10.19	1	2-methylol	9.83
2	FBHa	11.34	2	4 methyl	10.10	2	4-methylol	9.73
3	FTB	10.74	3	2,4 dimethyl	10.49	3	2,4-dimethylol	9.68
4	FA	11.08	4	2,4,6-trimethyl	10.80	4	2,4,6-trimethylol	9.47
5	FuA	11.92	5	phenol (unsubst)	9.85			

considered suitable for ion exchange studies of these ions.

Ion exchange equilibrium is presented graphically by an ion exchange isotherm and can be described in terms of selectivity coefficient, distribution coefficient or separation factor

If Z_A represents the molar ionic fraction of monovalent counter ion A in the resin and N_A the molar ionic fraction of A in solution in contact with resin,

$$Z_A = \frac{C_{RA}}{C_{RA}+C_{RB}} \quad \text{and}$$

$$N_A = \frac{C_{SA}}{C_{SA}+C_{SB}}$$

where C_{RA} and C_{RB} are the concentrations of monovalent ions A and B in the resin and C_{SA} and C_{SB} the concentrations of A and B in solution at equilibrium. Ion exchange isotherm can be obtained by plotting Z_A versus N_A.

A plot of C_r versus C_s is another form of exchange isotherm . The molar selectivity coefficient is presented as

$$K_{B/A} = (C_{RA}/C_{RB})(C_{SB}/C_{SA})$$

and rational selectivity coefficient is represented as

$$^{r}K_{B/A} = (Z_A/Z_B)(N_B/N_A)$$

When the valency of counter ions is the same, i.e. $n_A = n_B$,

$$K_{B/A} = {}^{r}K_{B/A}$$

If the counter ions have different valancies, say 1 for A and 2 for B

$$K_{B/A} \times (C_{SA}/C_{RA}) = {}^{r}K_{B/A} \times (N_A/Z_A)$$

The molar distribution coefficient for the monovalent ion A is

$$K_{D.A} = \frac{C_{RA}}{C_{SA}}$$

Distribution coefficient is usually used in the following form :

$$K^{*}_{D.A} = \frac{M_{RA}(\text{m mole/g})}{C_{SA}(\text{m mole/ml})}$$

Molar separation factor (SF) for the monovalent ions A and B is expressed as

$$SF_{B/A} = (C_{RA}/C_{RB})(C_{SB}/C_{SA})$$

It is usually evaluated from the ion exchange isotherm as a ratio of two rectangular areas which lie above and below the isotherm and touch the latter at a point which corresponds to the experimental conditions.

For a system in which the ion exchange shows no prefrence for A ar B, the ionic fractions of A and B in the ion exchanger would be the same as those in solution and the plot of Z vs N (i.e. ion exchange isotherm) would be linear and diagonal. Actual ion exchangers would usually prefer one ion to the other. If A is preferred throughout, the isotherm would lie above the diagonal in the plot of Z_A vs N_A and if B is preferred, the isotherm would fall below the diagonal. Selectivity thus neccssiates a non-linear isotherm.

III.11 COPPER ION EXCHANGE :

To consider the establishment of equilibrium, copper ion exchange by the resins was studied for different periods of time. Copper ion uptake versus time is plotted in Fig.III.3 The plots indicate that equilibrium is established in all cases. (Equilibrium is assumed to be established in 48 hours for 8QM and SB).

Molar distribution coefficient s have been calculated as C'_r/C'_s and are presented in Table III.6. The values are increasing in order

$8QC \leq 8QB < 8QR < 8QM$ for 8Q series
$SR < SB < SM$ for S series
$MSB < MSG < MSF$ for A series
and $FTB < FuA < FA < FBHa$ for P series.

If the distribution coefficient is expressed as M'_γ/C'_s $(=K^*_D)$, the values (presented in Table III.6) are increasing in order

$8QC < 8QR < 8QB < 8QM$ for 8Q series
$SR < SB < SM$ for S series
$MSF < MSB \leq MSG$ for A series
and $FTB < FuA < FA < FBHa$ for P series.

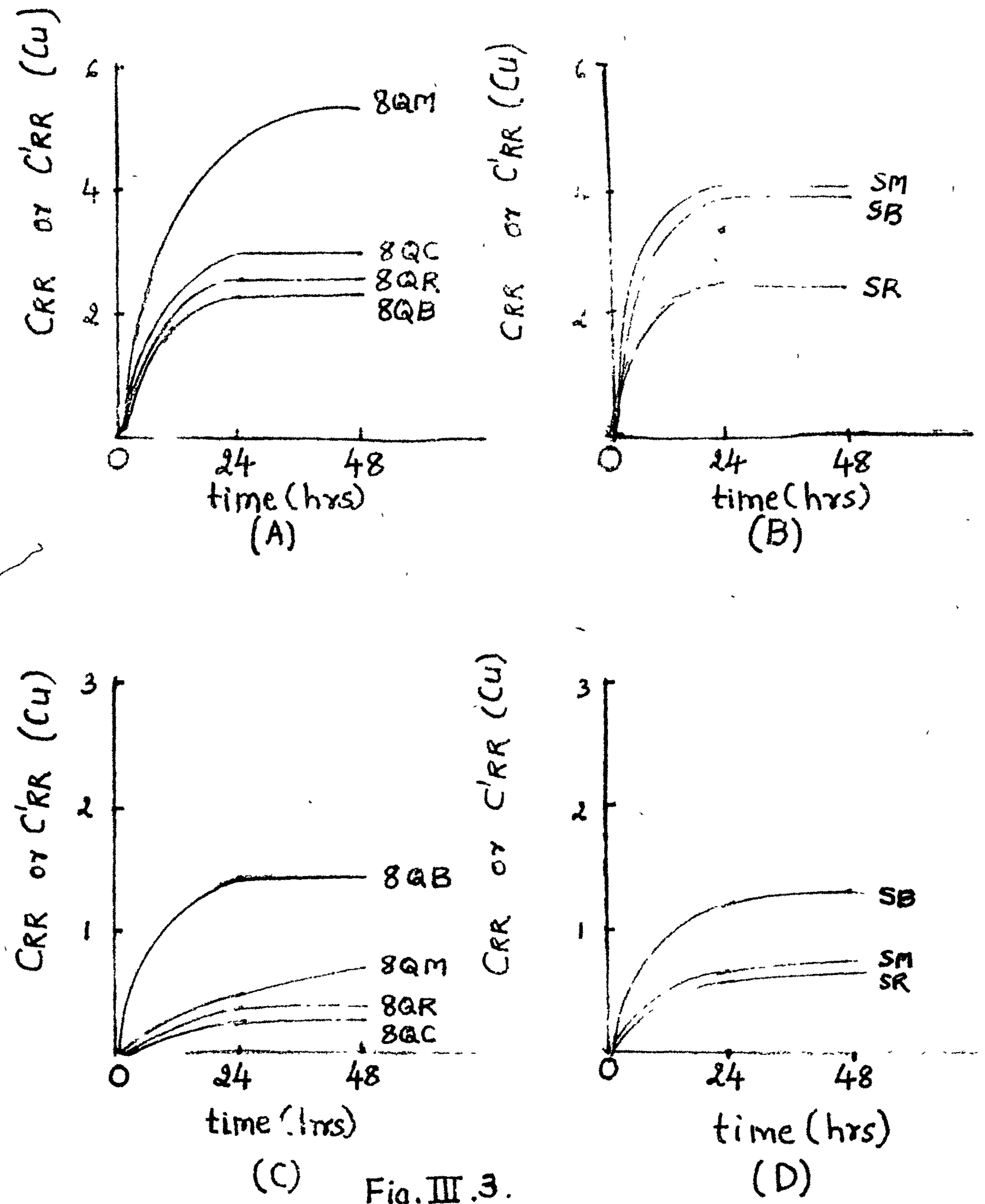


Fig. III.3.
copper ion exchange versus time

Table III 6(a)

Distribution of copper ions between resin and aqueous solution phases
(initial concentration of Cu(II) aqueous solution : 0.0475M; resin: 8Q series)

No.	resin	concentration of copper ion (m moles/ml) (after 48 hrs)		C'_r/C'_s	concentration of copper ion in resin (m mole/g dry resin) (after 48 hrs) (M_r)	M'_r/C'_s
		in resin phase (C'_r)	in aq.solution phase (C'_s)			
1	8QR	3.04	0.046	66.1	2.45	53.3
2	8QM	6.20	0.043	144.2	5.45	126.7
3	8QG	2.86	0.046	62.2	2.15	46.7
4	8QB	2.80	0.045	62.2	2.96	65.8

Table III 6(b)

Distribution of copper ions between resin and aqueous solution phases
(initial concentration of Cu(II) in aqueous solution : 0.0475 M, resin : S series)

No.	resin	concentration of copper ion (m moles/ml)(after 48 hrs)		C'_r/C'_s	concentration of copper in resin (m mole/g dry resin) (after 48 hrs) (M'_r)	M'_r/C'_s
		in resin phase (C'_r)	in aq.solution phase (C'_s)			
1	SR	2.80	0.046	60.9	2.37	51.5
2	SM	4.71	0.043	109.5	4.03	93.7
3	SB	3.99	0.044	90.7	3.95	89.8

Table III 6(c)

Distribution of copper ions between resin and aqueous solution phases

(initial concentration of Cu(II) in aqueous solution : 0.05M), resin : A series

No.	resin	concentration of copper ion (m mole/ml)(after 48 hours)		C'_r/C'_s	concentration of copper ion in resin(m mole/g dry resin) (after 48 hours) (M'_r)	M'_r/C'_s
		in resin phase (C'_r)	in aq.solution phase (C'_s)			
1	MSF	8.46	0.044	192.3	6.52	148.2
2	MSB	7.73	0.0435	177.7	7.14	164.1
3	MSG	8.25	0.0435	189.6	7.14	164.1

Table III 6(d)

Distribution of copper ions between resin and aqueous solution phases
(initial concentration of Cu(II) in aqueous solution : 0.05M, resin : P series)

No.	resin	concentration of copper ion (m mole/ml)(after 24 hrs)		C_r/C_s	concentration of copper ion in resin (m mole/g dry resin) (after 24 hrs) (M_r)	M_r/C_s
		in resin phase (C_r)	in aq.solution phase (C_s)			
1	FA	1.73	0.012	144.2	1.38	115.0
2	FBHa	2.93	0.011	266.2	2.54	230.9
3	FTB	0.46	0.013	35.4	0.31	23.8
4	FuA	1.06	0.013	81.5	0.93	71.5

III.12 NICKEL ION EXCHANGE :

To consider the establishment of equilibrium, nickel ion exchange by the resins was studied for different periods of time. Nickel ion uptake versus time is plotted in Fig.III.4. The plots indicate that equilibrium is established in all cases. (Equilibrium is assumed to be established in 48 hours for 8QM, 8QB and SM).

Molar distribution coefficients have been calculated as C'_r/C'_s and are presented in Table III.7. The values are increasing in order :

	8QC < 8QB < 8QR < 8QM	for 8Q series
	SR < SM < SB	for S series
and	MSF < MSB < MSG	for A series

Values of M'_r/C'_s are also calculated and presented in Table III.7. The values are increasing in order

	8QC < 8QR < 8QM < 8QB	for 8Q series
	SR < SB < SM	for S series
and	MSF < MSB < MSG	for A series.

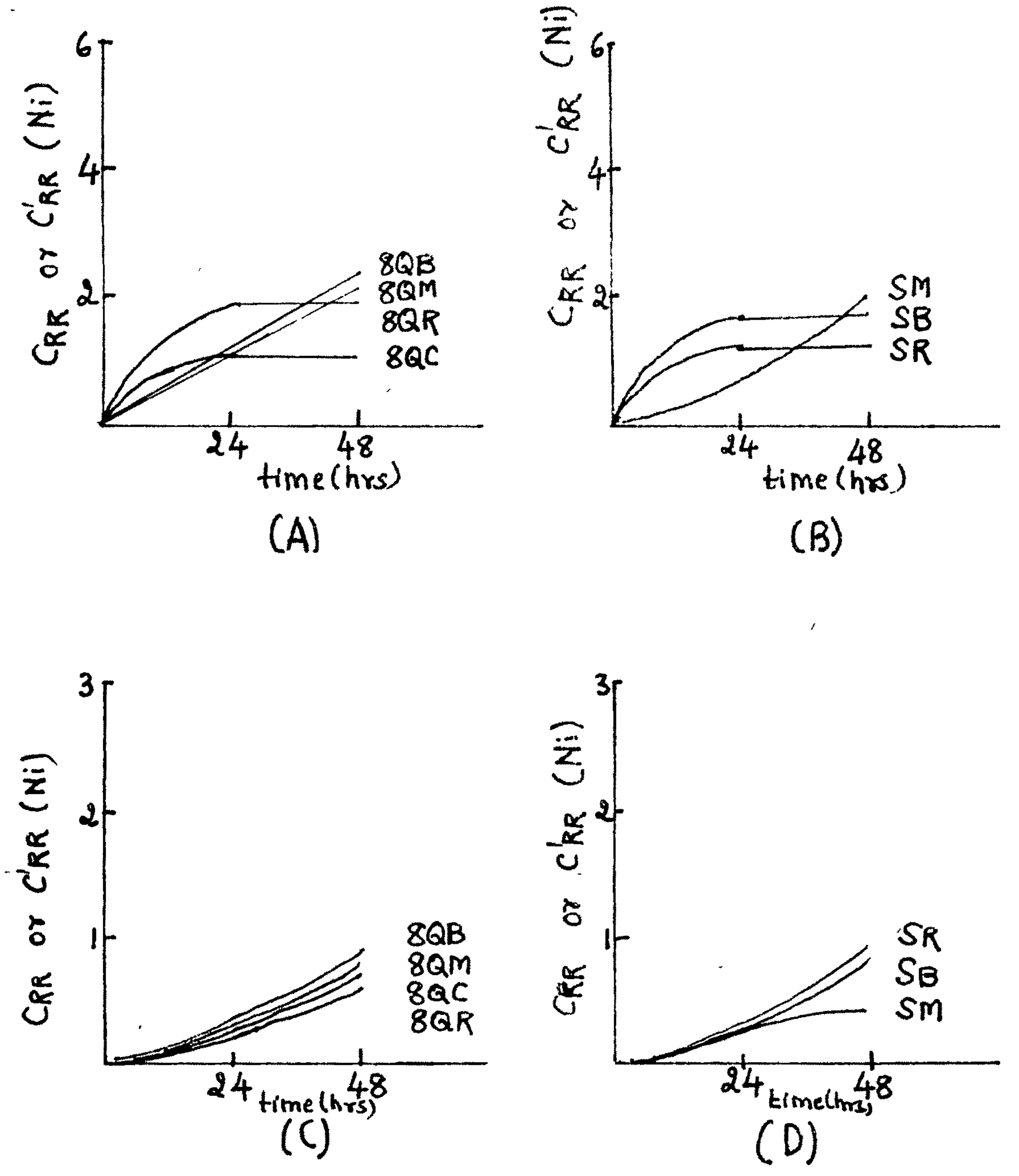


Fig III.4. Nickel ion exchange versus time

Table III 7(b)

Distribution of nickel ions between resins and aqueous solution phases
(initial concentration of Ni(II) in aqueous solution : 0.0475M, resin : S series)

No.	resin	concentration of nickel ion (m mole/ml)(after 48 hrs)		C'_r/C'_s	concentration of nickel ion in resin (m mole/g dry resin)(after 48 hrs) (M'_r)	M'_r/C'_s
		in resin (C'_r)	solution in aq.solution phase (C'_s)			
1	SR	1.39	0.047	29.6	1.18	25.1
2	SM	2.35	0.046	51.1	2.01	43.7
3	SB	1.71	0.046	37.2	1.69	36.7

Table III 7(c)

Distribution of nickel ions between resin and aqueous solution phases
(initial concentration of Ni(II) in aqueous solution : 0.052M), resin : A series

No.	resin	concentration of nickel ion (m mole/ml)(after 48 hours)		C'_r/C'_s	concentration of nickel ion in RESIN(m mole/g dry resin) (after 48 hours) (M'_r)	M'_r/C'_s
		in resin phase (C'_r)	in aq.solution phase (C'_s)			
1	MSF	4.93	0.049	100.6	3.80	77.6
2	MSB	5.35	0.048	111.4	4.94	102.9
3	MSG	5.71	0.048	119.0	4.94	102.9

III.13 ZINC ION EXCHANGE :

To consider the establishment of equilibrium, zinc ion exchange by the resins was studied for different periods of time. Zinc ion uptake versus time is plotted in Fig.III.5. The plots indicate that equlibrium is established in all cases. (Equilibrium is assumed to be established for SM in 48 hours).

Molar distribution coefficients have been calculated as C'_r/C'_s and are presented in Table III.8. The values are increasing in order :

8QB < 8QR < 8QM < 8QC for 8Q series
SR < SB < SM for S series
and MSB < MSG < MSF for A series.

Values of M'_r/C'_s are also calculated and presented in Table III.8. The values are increasing in order :

8QB < 8QR < 8QM < 8QC for 8Q series
SR < SB < SM for S series
and MSB < MSG < MSF for A series.

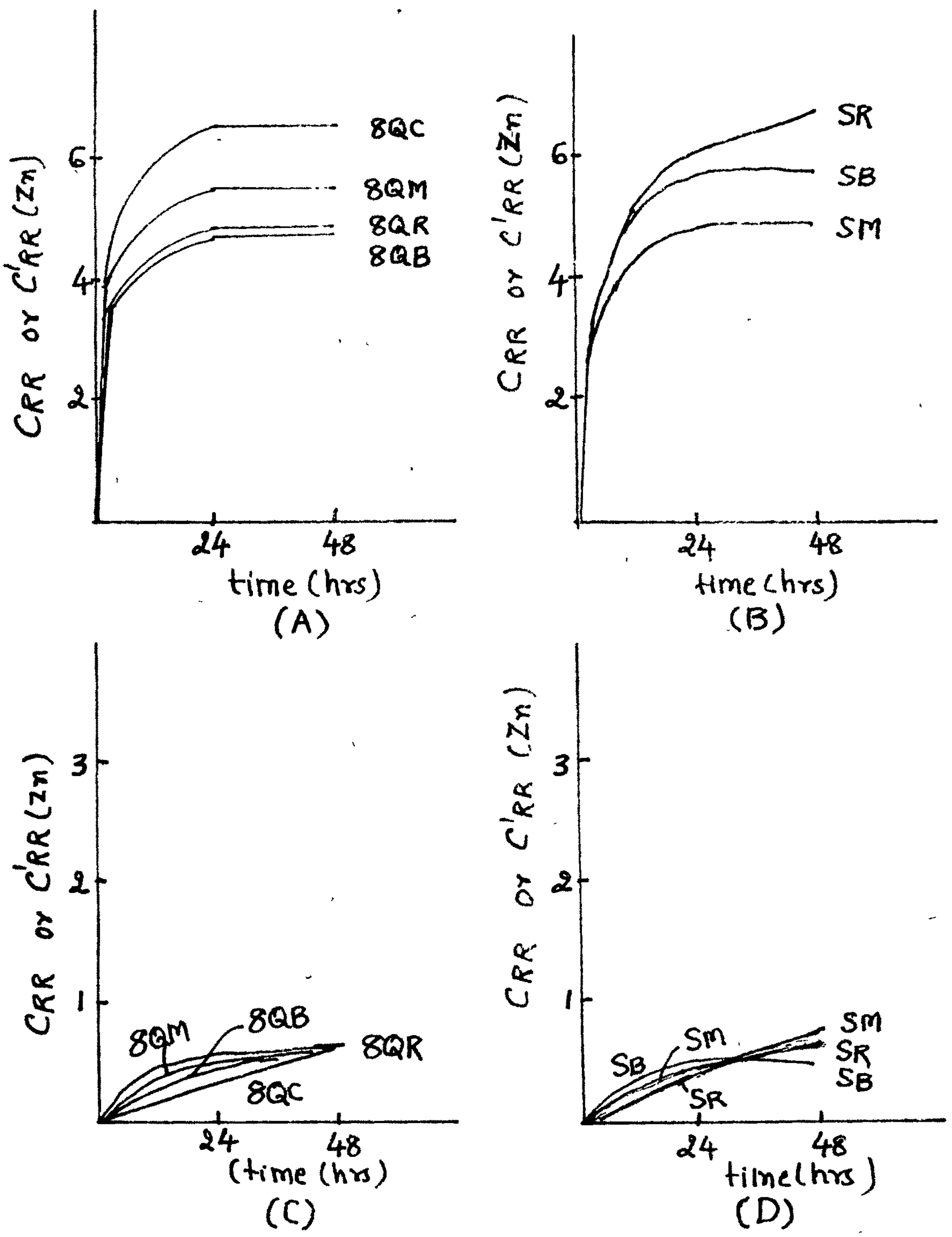


Fig III.5 Zinc (ion) exchange versus time.

Table III 8(b)

Distribution of zinc ions between resin and aqueous solution phases

(initial concentration of Zn(II) in aqueous solution : 0.076M, resin : S series)

No.	resin	concentration of zinc ion (m mole/ml)(after 48 hrs)		C'_r/C'_s	concentration of zinc ion in resin(m mole/g dry resin) (after 48 hrs) (M'_r)	M'_r/C'_s
		in resin phase (C'_r)	in aq.solution phase (C'_s)			
1	SR	5.60	0.072	77.8	4.73	65.7
2	SM	7.85	0.071	110.6	6.71	94.5
3	SB	5.70	0.071	80.3	5.65	79.6

Table III 8(c)

Distribution of zinc ions between resin and aqueous solution phases (initial concentration of Zn(II) in aqueous solution : 0.05M), resin : A series.

No.	resin	concentration of zinc ion (m mole/ml)(after 48 hours)		C'_r/C'_s	concentration of zinc ion in resin(m mole/g dery resin) (after 48 hours) (M'_r)	M'_r/C'_s
		in resin phase (C'_r)	in aq.solution phase (C'_s)			
1	MSF	7.04	0.045	156.4	5.43	120.7
2	MSB	4.75	0.046	103.3	4.39	95.4
3	MSG	5.07	0.046	110.2	4.39	95.4

III.14 ALKALI ION UPTAKE :

Na and NH_4 ion uptakes by the resins were studied under similar conditions of pH as adopted for the transition metal ion uptake. It has been found that Na- ion uptake increases in order :

8QC < 8QM < 8QB < 8QR for 8Q series
SR < SB < SM for S series
and FTB < FuA < FBHa < FCR < FA for P series

Similarly, NH_4 - ion uptake increases in order

8QC < 8QB < 8QR < 8QM for 8Q series
SR < SB < SM for S series
and FTB < FCR < FuA < FBHa < FA for P series.

III.15 MAGNESIUM ION EXCHANGE :

It was observed that Mg(II) ion exchange took place with the resins of 8Q series. Hence Mg(II) ion uptake by these resins was studied for different periods of time. Mg(II) ion uptake versus time is plotted in Fig.III.6. The plot indicates that equilibrium is established in all cases.

Molar distribution coefficients have been evaluated as C'_r/C'_s and are presented in Table III.9. The values are increasing in order :

8QB < 8QM < 8QC < 8QR

Values of M'_{λ}/C'_s are also calculated and presented in Table III.9. The values are increasing in order :

8QM < 8QC < 8QB < 8QR

III.16 COPPER ION EXCHANGE :
(dilute solution)

n Copper ion exchange from dilute solution was also studied for different period of time.

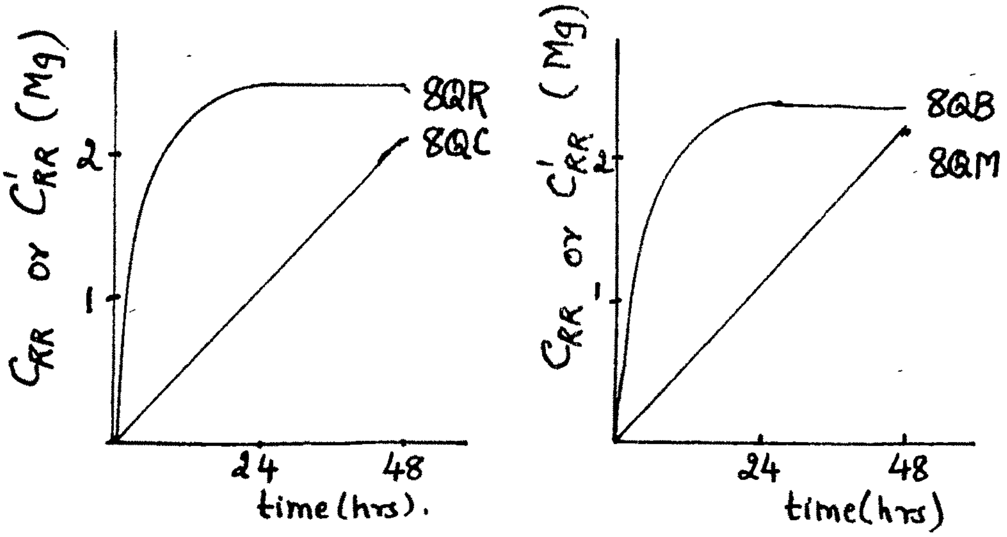


Fig III.6 Mg-ion uptake vs time.

Table III 9

Distribution of magnesium ions between resin and aqueous solution phases
(initial concentration of Mg(II) in aqueous solution : 0.058M; resin : 8Q series)

No.	resin	concentration of mg ion (m mole/ml)(after 48 hrs)		C'_r/C'_s	concentration of Mg(II) ions in resin phase (m mole/g dry resin)(after 48 hrs.) (M'_r)	M'_r/C'_s
		in resin phase (C'_r)	in aq.solution phase (C'_s)			
1	8QR	3.04	0.056	54.3	2.45	43.8
2	8QC	2.86	0.056	51.1	2.15	38.4
3	8QB	2.24	0.056	40.0	2.37	42.3
4	8QM	2.48	0.056	44.3	2.18	38.9

K_D(= C'_r/C'_s) and K_D^*(M'_r/C'_s) have been evaluated and the values are presented in Table III.10. The values of K_D are increasing in order :

8QC < 8QR < 8QM < 8QB for 8Q series

and SM < SR < SB for S series.

The values of K_D^* are increasing in order :

8QC < 8QR < 8QM < 8QB for 8Q series

and SM < SR < SB for S series.

Since studies have been made at two concentrations, plots have been obtained for K_D or K_D^* versus C_s and are presented in Fig.III.7. The plots indicate that K_D and K_D^* increases with dilution for any resin of 8Q or S series.

The negative slope increases in order

8QM < 8QC < 8QR < 8QB for 8Q series

and SM < SR < SB for S series.

Table III 10(a)

Distribution of copper ions between resin and aqueous solution phases

(initial concentration of Cu(II) in aqueous solution : 0.00445M)
resin : 8Q series

No.	resin	concentration of copper ion (m mole/ml)(after 48 hrs)		C'_r/C'_s	concentration of copper ion resin (m mole/g dry resin)(after 48 hrs) (M'_r)	M'_r/C'_s
		in resin phase (C'_r)	in aq.solution phase (C'_s)			
1	8QR	0.46	0.0041	112.2	0.37	90.2
2	8QM	0.63	0.0040	157.5	0.55	137.5
3	8QC	0.36	0.0042	85.7	0.27	64.3
4	8QB	1.34	0.0033	393.9	1.42	430.3

Table III 10(b)

Distribution of copper ions between resin and aqueous solution phases

(initial concentration of Cu(II) in aqueous solution : 0.00445M)

resin : S series

No.	resin	concentration of copper ion (m mole/ml)(after 48 hrs)		C'_r/C'_s	concentration of copper ion resin(m mole/g dry resin) (after 48 hrs) (M'_r)	M'_r/C'_s
		in resin phase (C'_r)	in aq.solution phase (C'_s)			
1	SR	0.84	0.0039	215.4	0.71	182.1
2	SM	0.70	0.0040	175.0	0.60	150.0
3	SB	1.31	0.0033	397.0	1.30	393.9

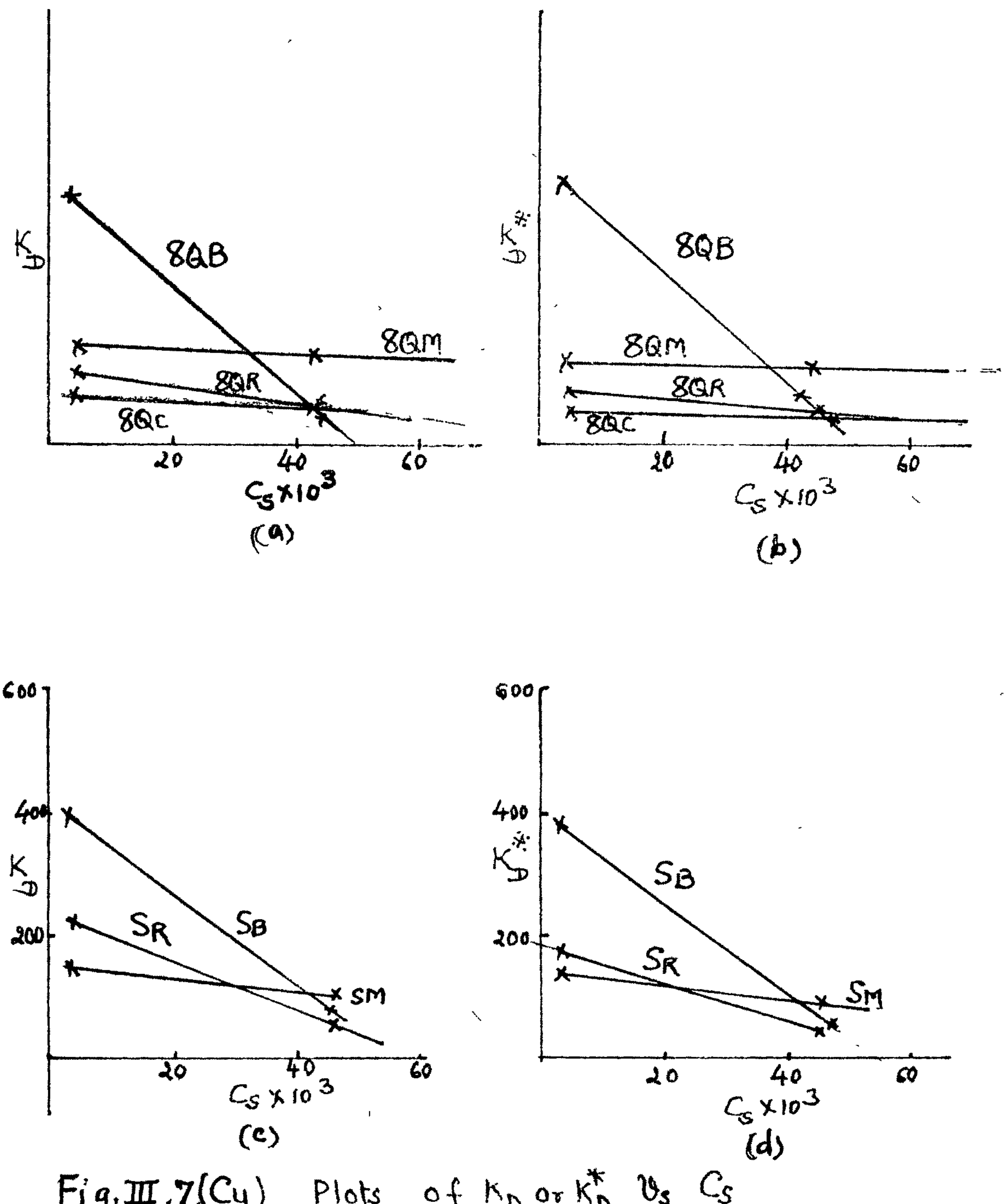


Fig. III.7(Cu) Plots of K_D or K_D^* vs C_s

III.17 NICKEL ION EXCHANGE :

Nickel ion exchange from dilute solution was also studied for different periods of time. K_D and K_D^* have been evaluated and are presented in Table III.11. The values are increasing in order :

8QR $<$ 8QC $<$ 8QB $<$ 8QM for 8Q series

SM $<$ SB $<$ SR for S series.

The values of K_D^* are increasing in order :

8QR $<$ 8QC $<$ 8QM $<$ 8QB for 8Q series

and SM $<$ SB $<$ SR for S series

Since studies have been made at two concentrations, plots have been obtained for K_D or K_D^* versus C_s and are presented in Fig.III.8. The plots indicate that K_D and K_D^* increases with dilution for any resin of 8Q or S series. The negative slope increases in order :

8QB $<$ 8QC $<$ 8QR $<$ 8QM for 8Q series

and SM $<$ SB $<$ SR for S series.

Table III 11(a)

Distribution of nickel ions between resin and aqueous solution phases

(initial concentration of Ni(II) in aqueous
solution : 0.0053M)
resin : 8Q series)

No.	resin	concentration of nickel ion (m mole/ml)(after 48 hrs)		C'_r/C'_s	concentration of nickel ion in resin(m mole/g dry resin)(after 48 hrs) (M'_r)	M'_r/C'_s
		in resin phase (C'_r)	in aq.solution phase (C'_s)			
1	8QR	0.77	0.0048	160.4	0.62	129.2
2	8QM	0.93	0.0045	206.7	0.82	182.2
3	8QC	0.86	0.0047	183.0	0.65	138.3
4	8QB	0.84	0.0045	186.7	0.89	197.8

Table III 11(b)

Distribution of nickel ions between resin and aqueous solution phases

(initial concentration of Ni(IIO in aqueous solution : 0.0053M)
resin : S series

No.	resin	concentration of nickel ion (m mole/ml)(after 48 hrs)		C'_r/C'_s	concentration of nickel ion in resin(m mole/g dry resin)(after 48 hrs) (M'_r)	M'_r/C'_s
		in resin phase (C'_r)	in aq.solution phase (C'_s)			
1	SR	1.12	0.0045	248.9	0.95	211.1
2	SM	0.55	0.0050	110.0	0.47	94.0
3	SB	0.91	0.0045	202.2	0.90	200.8

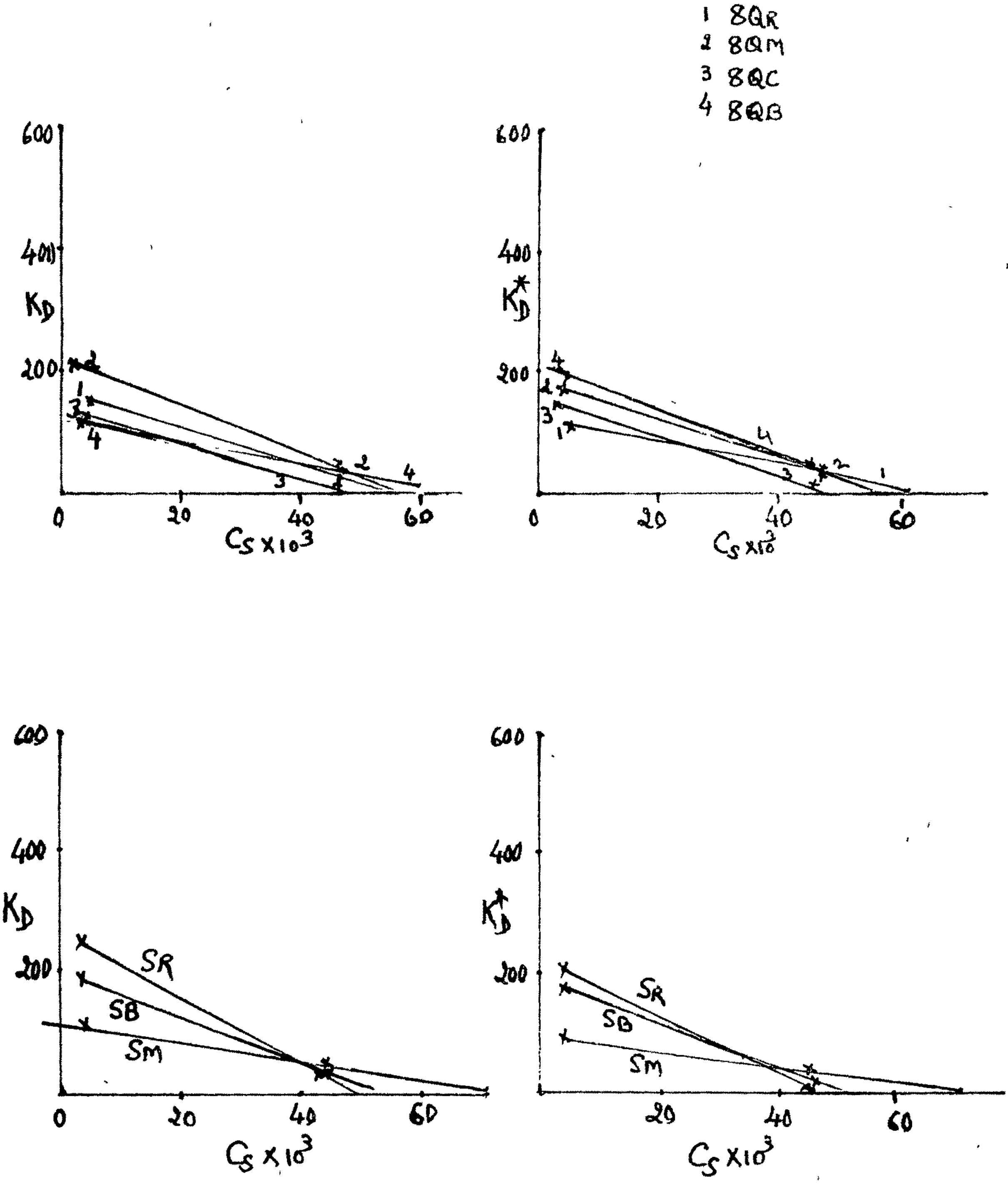


Fig III 8 (Ni) Plots of K_D or K_D^* vs C_S

III.18 ZINC ION EXCHANGE :
(dilute solution)

Zinc ion exchange from dilute solution has been studied for different periods of time. K_D and K_D^* have been evaluated and are presented in Table III.12. The values of K_D are increasing in order :

8QB < 8QC < 8QM < 8QR for 8Q series
and SB < SR < SM for S series.

The values of K_D^* are increasing in order :

8QC < 8QM < 8QB < 8QR for 8Q series
and SB < SR < SM for S series.

Since studies have been made at two concentrations, plots have been made obtained for K_D or K_D^* versus C_s and are presented in Fig. III.9. Plots are nearly horizontal or have a very small slope.

Table III 12(a)

Distrubution of zinc ions between resin and aqueous solution phases
(initial concentration of Zn(II) in aqueous solution : 0.0086M)
resin : 8Q series

No.	resin	concentration of zinc ion (m mole/ml)(after 48 hrs)		C'_r/C'_s	concentration of zinc ion in resin (m mole/g dry resin)(after 48 hrs) (M'_r)	M'_r/C'_s
		in resin phase (C'_r)	in aq.solution phase (C'_s)			
1	8QR	0.76	0.0081	93.8	0.61	75.3
2	8QM	0.61	0.0081	75.3	0.54	66.7
3	8QC	0.57	0.0082	69.5	0.43	52.4
4	8QB	0.56	0.0081	69.1	0.59	72.8

Table III 12(b)

Distribution of zinc ions between resin and aqueous solution phases

(intial concentration of Zn(II) in aqueous solution : 0.0086M)

resin : S series

No.	resin	concentration of zinc ion (m mole/ml)(after 48 hrs)		C'_r/C'_s	concentration of zinc ion in resin (m mole/g dry resin) (after 48 hrs) (M'_r)	M'_r/C'_s
		in resin phase (C'_r)	in aq.solution phase (C'_s)			
1	SR	0.70	0.0081	86.4	0.59	72.8
2	SM	0.78	0.0081	96.3	0.67	82.7
3	SB	0.56	0.0081	69.1	0.56	69.1

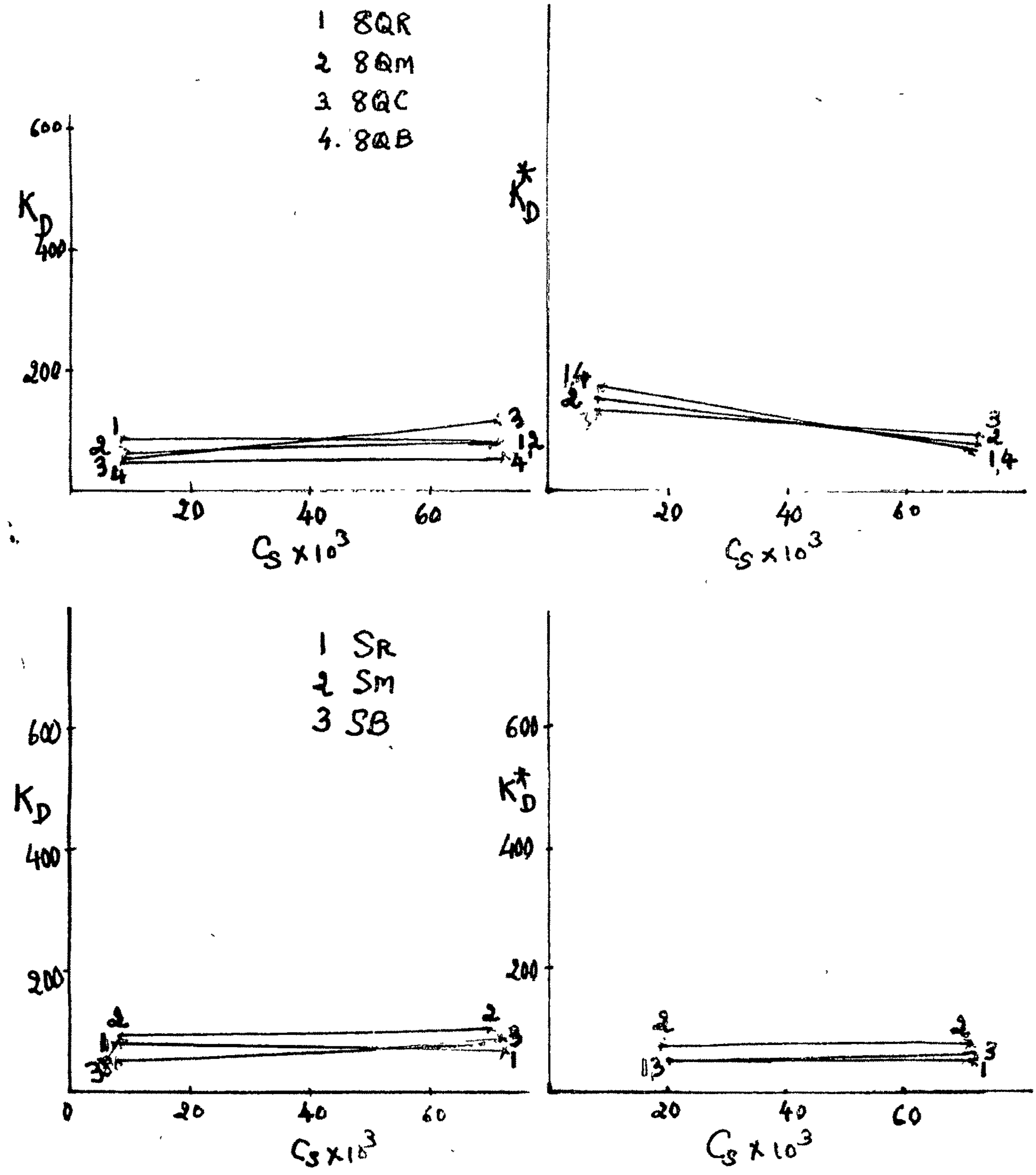


Fig III 9 (Zn) Plots of K_D or K_D^* vs C_S

III.19 MAGNESIUM ION EXCHANGE :

(dilute solution)

Magnesium ion exchange from dilute solution has been studied for different periods of time for 8Q series. K_D and K_D^* have been evaluated and are presented in Table III.13. The values of K_D are increasing in order :

$$8QB < 8QM < 8QC < 8QR$$

and the values of K_D^* are increasing in order :

$$8QB < 8QC < 8QM < 8QR \;.$$

Since studies have been made at two concentrations, plots have been obtained for K_D or K_D^* versus C_s and are presented in Fig. III.10. Plots are nearly horizontal or have a small slope.

Table III 13

13

Distribution of magnesium ions between resin and aqueous solution phases

(initial concentration of Mg(II) in aqueous solution : 0.0063M)

resin : 8Q series

No.	resin	concentration of mg ion (m mole/ml)(after 48 hrs)		C'_r/C'_s	concentration of magnesium ion in resin (m mole/g dry resin)(after 48 hrs)(M'_r)	M'_r/C'_s
		in resin phase (C'_r)	in aq.soln. phase(C'_s)			
1	8QR	0.46	0.0060	76.7	0.37	61.7
2	8QC	0.28	0.0061	45.9	0.21	34.4
3	8QB	0.17	0.0062	27.4	0.81	29.0
4	8QM	0.25	0.0061	41.0	0.22	36.1

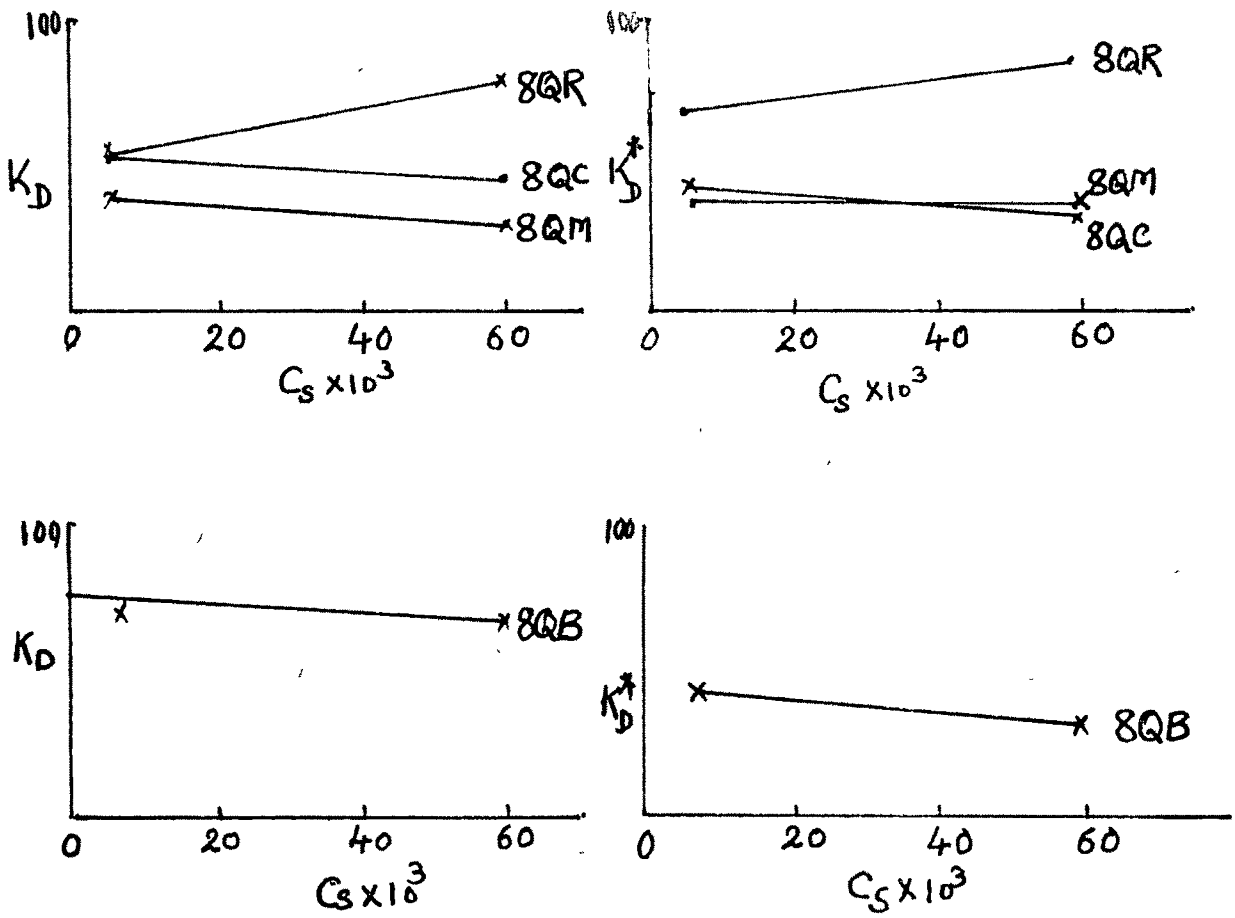


Fig III 10(Mg) Plot of K_D or K_D^* vs C_S

III.20 COPPER ION EXCHANGE :

(ammonium salt effect)

Copper ion exchange by the resins was carried out from solutions of different concentrations of Cu(II) ions in presence of 0.2M NH_4 ions. Hence values of K_D and K_D^* were calculated and are presented in Table III.14. K_D or K_D^* versus C_s has been plotted in Fig. III.11. The plots are volcano-shaped for resins of 8Q series and zigzag for resins of S series.

III.21 NICKEL ION EXCHANGE :

(ammnium salt effect)

Nickel ion exchange by the resins was carried out from solutions of different concentrations of Ni(II) ions in presence of 0.2M NH_4 ions. Hence values of K_D and K_D^* were calculated and are presented in Table III.15. K_D or K_D^* versus C_s has been plotted in Fig. III 12.

Table III 14(a)

Distribution of copper ions between resin and aqueous solution phases

(initial concentration of Cu(II) in aqueous
solution : 0.2M)
resin : 8Q series

No.	resin	concentration of copper ion (m mole/ml)(after 24 hrs)		C'_r/C'_s	concentration of copper ion in resin (m mole/g dry resin)(after 24 hrs) (M'_r)	M'_r/C'_s
		in resin phase (C_r)	in aq.solution phase(C_s)			
1.	2.	3.	4.	5.	6.	7.
1	8QR	i. 11.06	0.028	395	8.84	316
		ii. 9.91	0.020	496	7.94	397
		iii. 6.10	0.013	469	4.90	377
		iv. 3.05	0.0065	469	2.45	377

Table III 14(a)(cont.)

1.	2.		3.	4.	5.	6.	7.
2	8QM	i.	6.82	0.0315	217	5.99	190
		ii.	7.44	0.020	372	6.53	327
		iii.	3.10	0.016	194	2.72	170
		iv.	0.31	0.010	31	0.27	27
3	8QC	i.	10.01	0.028	358	7.53	269
		ii.	8.58	0.020	429	6.45	323
		iii.	3.57	0.016	223	2.68	168
		iv.	0.36	0.010	36	0.27	27
4	8QB	i.	9.51	0.025	364	10.04	402
		ii.	7.83	0.018	435	8.28	460
		iii.	4.20	0.014	300	4.44	317
		iv.	1.12	0.008	140	1.48	185

Table III 14(b)

Distribution of copper ions between resin and aqueous solution phases

(initial concentration of Cu(II) in aqueous solution : 0.2M)

resin : S series

No.	resin	concentration of copper ion (m mole/ml)(after 24 hrs)		C_r/C_s	concentration of copper ion in resin(m mole/g dry resin) (after 24 hrs) (M_r)	M_r/C_s
		in resin phase (C_r)	in aq.solution phase (C_s)			
1.	2.	3.	4.	5.	6.	7.
1	SR	i. 8.42	0.030	281	7.02	234
		ii. 8.07	0.021	384	6.64	316
		iii. 4.21	0.015	281	3.47	231
		iv. 1.05	0.009	177	0.87	97

Table III 14(b)(cont.)

1.	2.		3.	4.	5.	6.	7.
2	SM	i.	9.41	0.030	314	8.06	269
		ii.	9.87	0.020	493	8.34	417
		iii.	2.74	0.018	152	2.34	130
		iv.	1.57	0.008	196	1.34	168
3	SB	i.	10.26	0.024	427	10.12	422
		ii.	7.12	0.020	356	7.06	353
		iii.	3.70	0.010	370	3.67	367
		iv.	1.99	0.007	284	2.02	289

Table III 14(c)

Distribution of copper ions between resin and aqueous solution phases

(initial concentration of Cu(II) in aqueous solution : 0.2M)

resin : P series

No.	resin	concentration of copper ion (m mole/ml)(after 24 hrs) in resin phase (C_r)	in aq.solution phase (C_s)	C_r/C_s	concentration of copper ion in resin(m mole/g dry resin)(after 24 hrs) (M_r)	M_r/C_s
1.	2.	3.	4.	5.	6.	7.
1	FCR	i. 6.34	.0385	165	4.13	107
		ii. 2.54	.032	79	1.63	51
		iii. 1.27	.010	128	0.83	83

Table III 14(c)(cont.)

1.	2.	3.	4.	5.	6.	7.
4	FBHa	i. 4.16	.0395	105	3.59	91
		ii. 1.92	.032	60	1.60	50
		iii. 0.96	.010	96	0.82	82
5	FTB	i. 5.59	.0395	142	3.74	95
		ii. 3.01	.0315	96	2.02	64
		iii. 1.72	.0095	181	1.15	121

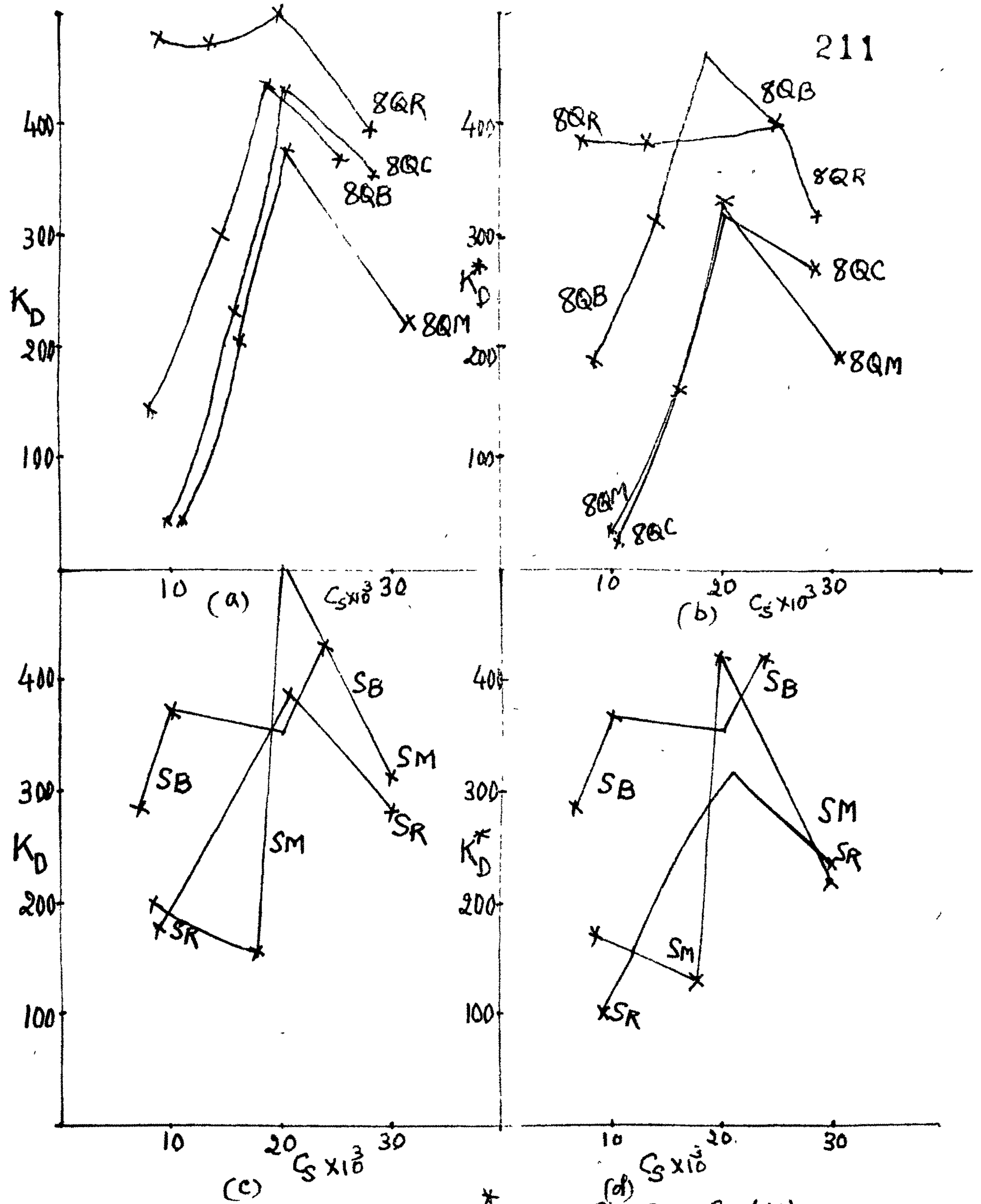


Fig III 11 Plots of K_D or K_D^* vs C_S for Cu(II)

Table III 15(a)

Distribution of nickel ions between resin and aqueous solution phases

(initial concentration of Ni(II) in aqueous solution : 0.2M)

resin : 8Q series

No.	resin	concentration of nickel ion (m mole/ml)(after 24 hrs)		C_r/C_s	concentration of nickel ion in resin(m Mole/g dry resin)(after 24 hrs) (M_r)	M_r/C_s
		in resin phase (C_r)	in aq.solution phase (C_s)			
1.	2.	3.	4.	5.	6.	7.
1	8QR	i. 8.00	0.042	190	6.13	153
		ii. 4.19	0.025	168	3.37	135
		iii. 1.15	0.0125	92	2.14	171

Table III 15(a)(cont.)

2	8QM	i.	6.20	0.0425	146	5.45	128
		ii.	4.03	0.024	168	3.54	148
		iii.	2.17	0.0125	174	1.91	153
3	8QC	i.	8.22	0.041	200	6.18	151
		ii.	4.29	0.0245	175	3.23	132
		iii.	2.86	0.012	238	2.15	179
4	8QB	i.	6.71	0.0405	166	7.10	174
		ii.	3.64	0.024	152	3.85	160
		iii.	2.52	0.0115	219	2.66	231

Table III 15(b)

Distrubution of nickel ions between resin and aqueous solution phases

(initial concentration of Ni(II) in aqueous solution : 0.2M)
resin : S series

No.	resin	concentration of nickel ion (m mole/ml)(after 24 hrs)		C_r/C_s	concentration of nickel ion in resin(m mole/g dry resin) (after 24 hrs) (M_r)	M_r/C_s
		in resin phase (C_r)	in aq. solution phase (C_s)			
1.	2.	3.	4.	5.	6.	7.
1	SR	i. 7.72	0.0415	186	6.50	157
		ii. 3.51	0.0255	138	2.96	116
		iii. 2.10	0.013	162	1.77	136

Table III 15(b)(cont.)

1.	2.		3.	4.	5.	6.	7.
2	SM	i.	8.23	0.042	196	7.05	168
		ii.	4.31	0.025	173	3.67	147
		iii.	2.35	0.013	181	2.01	155
3	SB	i.	7.41	0.013	570	7.34	565
		ii.	3.70	0.0065	569	3.67	565
		iii.	2.28	0.004	570	2.26	565

Table III 15(c)

Distribution of nickel ions between resin and aqueous solution phases

(initial concentration of Ni(II) in aqueous solution : 0.2M)

resin : P series

No.	resin	concentration of nickel ion (m mole/ml)(after 24 hrs)		C_r/C_s	concentration of nickel ion in resin(m mole/g dry resin) (after 24 hrs) (M_r)	M_r/C_s
		in resin phase (C_r)	in aq.solution phase (C_s)			
1.	2.	3.	4.	5.	6.	7.
1	FCR	i. 5.91	0.042	141	3.86	92
		ii. 5.49	0.0215	255	3.12	145
		iii. 2.96	0.0105	282	1.84	175

Table III 15(c)(cont.)

1.	2.	3.	4.	5.	6.	7.
2	FA	i. 7.70	0.038	203	6.06	160
		ii. 2.45	0.038	100	1.93	79
		iii. 1.40	0.012	117	0.83	69
3	FuA	i. 5.85	0.040	146	5.34	133
		ii. 2.92	0.0235	124	2.67	144
		iii. 0.97	0.0125	78	1.19	95

Table III 15(c)(cont.)

1.	2.		3.	4.	5.	6.	7.
4	FBHa	i.	8.96	0.035	256	8.04	230
		ii.	3.20	0.023	139	2.87	125
		iii.	1.28	0.012	107	1.15	96
5	FTB	i.	12.04	0.034	354	8.66	255
		ii.	3.87	0.0235	165	2.66	113
		iii.	1.72	0.012	143	1.15	96

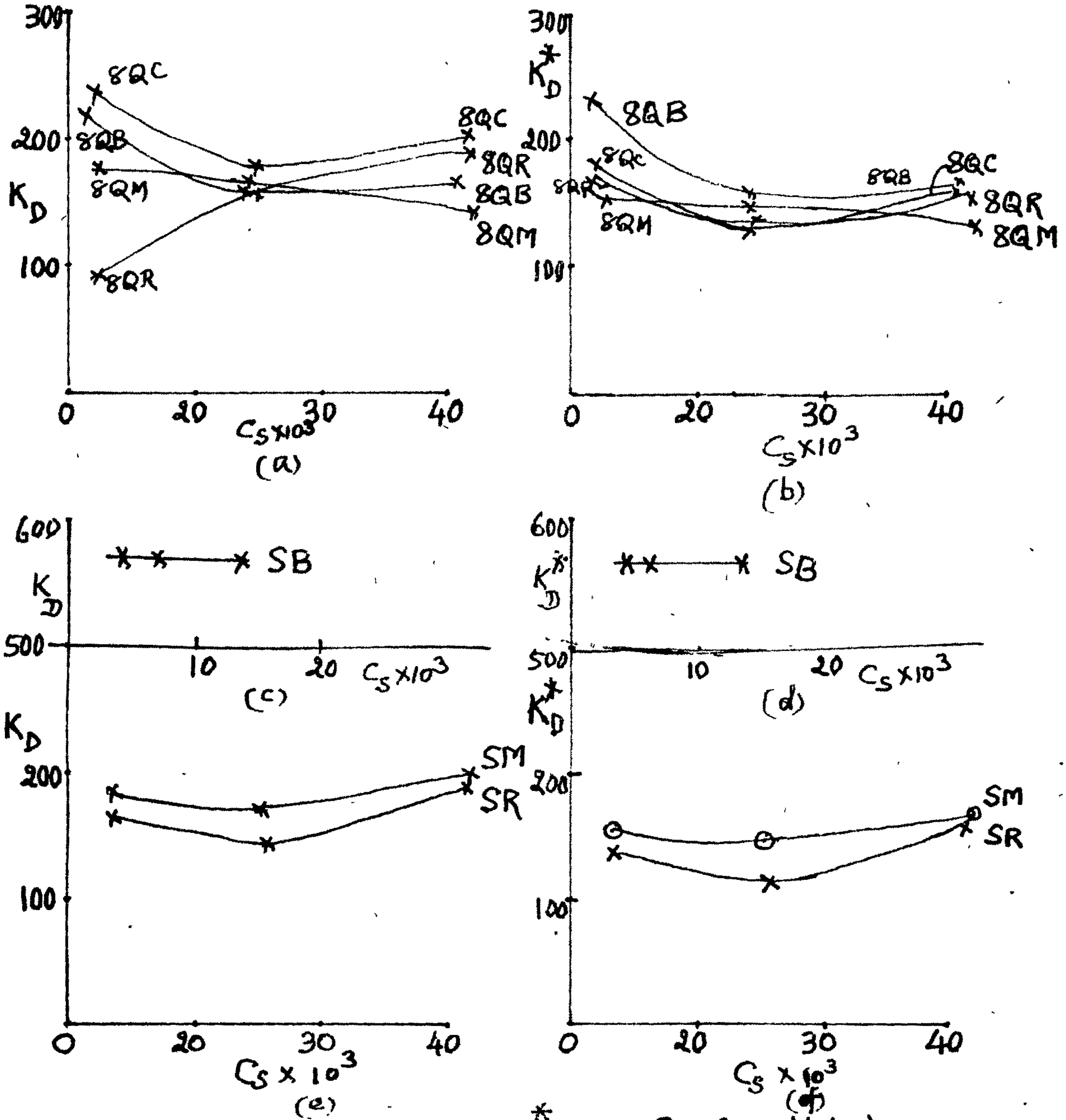


Fig III 12 Plots of K_D or K_D^* vs C_S for Ni(II)

The plots are concave in general except for SB which is horizontal and for 8QR which is convex.

III.22 ZINC ION EXCHANGE :

(ammonium salt effect)

Zinc ion exchange by resins was carried out from solutions of different concentrations of Zn(II) ions in presence of 0.2M NH_4 ions. Hence values of K_D and K_D^* were calculated and are presented in Table III.16. K_D or K_D^* versus C_s has been plotted in Fig. III.13. The plots generally indicate increase in K_D or K_D^* with dilution.

III.23 DISTRIBUTION COEFFICIENT :

We now consider the dependence of distribution coefficient on various factors.

Table III 16(a)

Distribution of zinc ions between resin and aqueous solution phases

(initial concentration of Zn(II) in aqueous solution : 0.2M)

resin : 8Q series

No.	resin	concentration of zinc ion (m mole/ml)(after 24 hrs)		C_r/C_s	concentration of zinc ion in resin (m mole/g dry resin)(after 24 hrs) (M_r)	M_r/C_s
		in resin phase (C_r)	in aq.solution phase (C_s)			
1.	2.	3.	4.	5.	6.	7.
1	8QR	i. 1.91	0.049	39	3.06	62
		ii. 1.52	0.037	41	2.45	66
		iii. 1.33	0.025	53	2.14	85
		iv. 1.33	0.012	110	2.14	179

Table III 16(a)(cont.)

2	8QM	i.	1.55	0.049	32	2.72	55
		ii.	1.08	0.038	28	1.90	50
		iii.	1.08	0.025	43	1.90	76
		iv.	0.93	0.012	77	1.63	136
3	8QC	i.	1.43	0.050	29	2.15	43
		ii.	1.07	0.038	28	1.61	42
		iii.	0.71	0.012	60	1.07	89
		iv.					
4	8QB	i.	1.68	0.049	34	3.55	72
		ii.	1.40	0.037	38	2.96	80
		iii.	1.26	0.024	52	2.66	111
		iv.	0.98	0.012	82	2.07	172

Table III 16(b)

Distribution of zinc ions between resin and aqueous solution phases

(initial concentration of Zn(II) in aqueous solution : 0.2M)

resin : S series

No.	resin	concentration of zinc ion (m mole/ml)(after 24 hrs)		C_r/C_s	concentration of zinc ion in resin (m mole/g dry resin)(after 24 hrs) (M_r)	M_r/C_s
		in resin phase (C_r)	in aq. solution phase (C_s)			
1.	2.	3.	4.	5.	6.	7.
1	SR	i. 2.75	0.047	59	5.92	126
		ii. 2.10	0.036	58	3.55	99
		iii. 1.40	0.024	58	2.37	99
		iv. 1.05	0.012	88	1.77	148

Table III 16(b)(cont.)

1.	2.	3.	4.	5.	6.	7.
2	SB	i. 2.56	0.047	55	5.08	73
		ii. 2.05	0.036	57	3.39	94
		iii. 1.14	0.024	48	2.26	94
		iv. 0.86	0.012	71	1.69	141
3.	SM	i. 2.35	0.049	48	4.02	82
		ii. 1.96	0.037	53	3.36	91
		iii. 1.76	0.024	73	3.02	126
		iv. 1.37	0.012	114	2.35	196

Table III 16(c)

Distribution of zinc ions between resin and aqueous solution phases
(initial concentration of Zn(II) in aqueous solution : 0.2M)
resin : P series

No.	resin	concentration of zinc ion (m mole/ml)(after 24 hrs)		C_r/C_s	concentration of zinc ion in resin(m mole/g dry resin) (after 24 hrs) (M_r)	M_r/C_s
		in resin phase (C_r)	in aq. solution phase (C_s)			
1.	2.	3.	4.	5.	6.	7.
1	FCR	i. 2.54	0.049	52	1.65	34
		ii. 2.11	0.037	57	1.38	37
		iii. 1.90	0.024	79	1.38	52
		iv. 1.48	0.012	123	0.10	8

Table III 16(c)(cont.)

1.	2.		3.	4.	5.	6.	7.
2	FA	i.	1.92	0.049	39	1.51	31
		ii.	1.57	0.037	42	1.30	35
		iii.	1.22	0.025	49	0.10	4
		iv.	1.05	0.012	81	0.08	17
3	FuA	i.	1.95	0.049	40	1.78	36
		ii.	1.62	0.037	44	1.48	40
		iii.	1.30	0.0245	53	1.19	48
		iv.	1.14	0.012	95	1.04	87

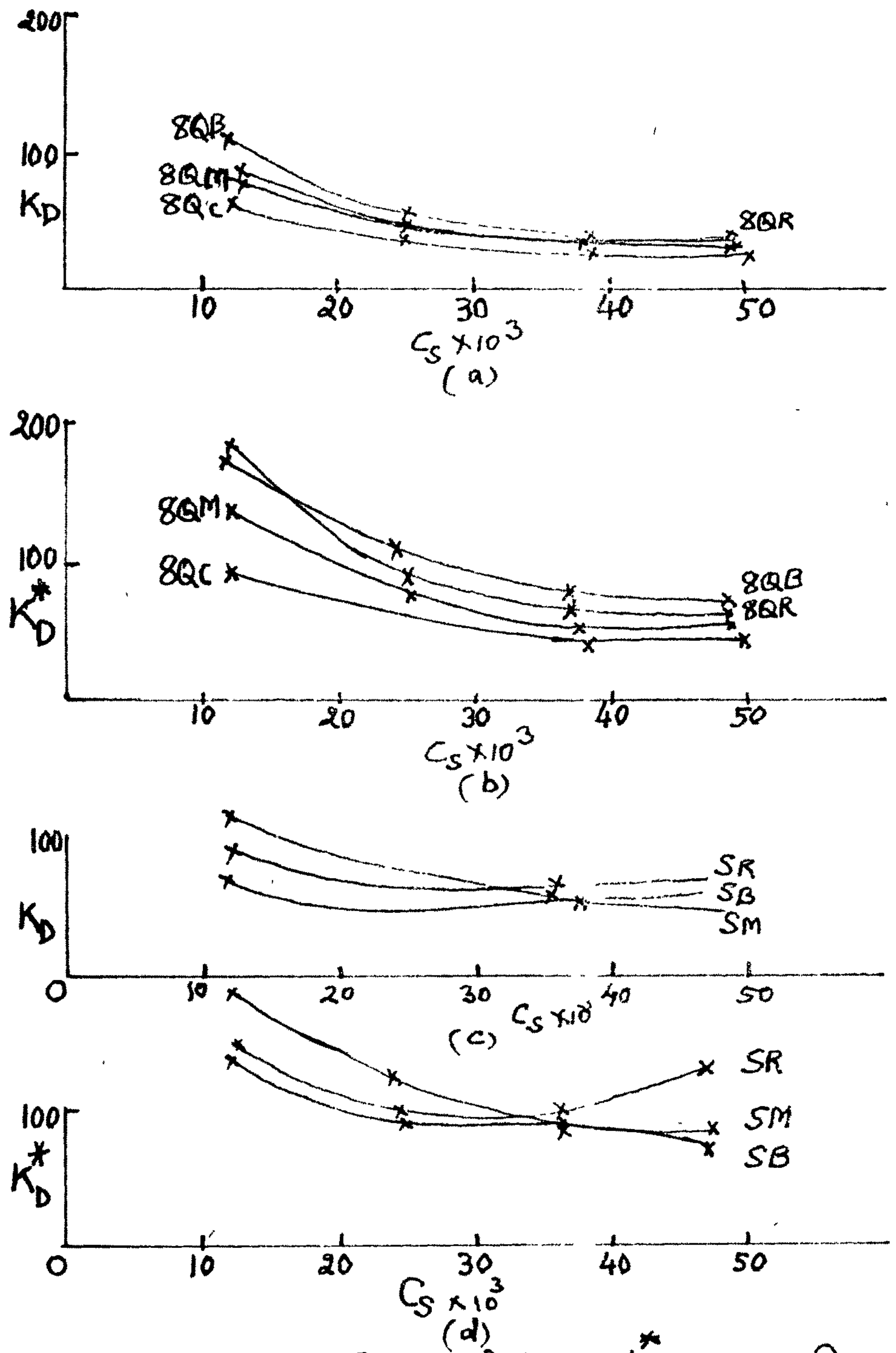


Fig III 13. Plots of K_D or K_D^* versus C_S for Zn(II)

Table III 17(a)

Ratio of distribution coefficient

(8Q series)

No.	resin	D_2/D_1			
		Cu(II)	Ni(II)	Zn(II)	Mg(II)
1	8QR	1.7	3.2	1.1	1.4
2	8QM	1.1	3.8	0.9	0.9
3	8QC	1.4	6.0	0.6	0.9
4	8QB	6.3	3.8	1.1	0.7

Table III 17(b)

Ratio of distribution coefficient

(S series)

No.	resin	D_2/D_1		
		Cu(II)	Ni(II)	Zn(II)
1	SR	3.5	8.4	1.1
2	SM	1.6	2.1	0.9
3	SB	4.3	5.4	0.9

Further we consider the dependence of the distribution coefficient on the presence of salt in solution. For the purpose we calculate D_s/D for C_s = 0.01, 0.02, 0.03 and 0.04 from the figures presented earlier.(D represents the distribution coefficient and D_s that in presence of 0.2M NH_4 for the same concentration of metal ion in solution). These values are evaluated and plots of log D_s/D versus C_s are presented in Fig. III.14. The results indicate that the curves are linear, in general, in case of Zn and Ni ions and nearly linear in some cases of Cu ions. Hence we can suggest that

$$\log D_s / D = K' + pC_s$$

where K' and p are constants. We can evaluate K' and p from the graphs. This expression correlates D_s/D with C_s for a definite relative concentration of salt in solution. Similarly one can express the variation of D_s/D with the concentration (C) of salt in solution for a definite concentration of metal ion as

$$\log D_s/D = KC$$

Where K is termed as salting out constant.

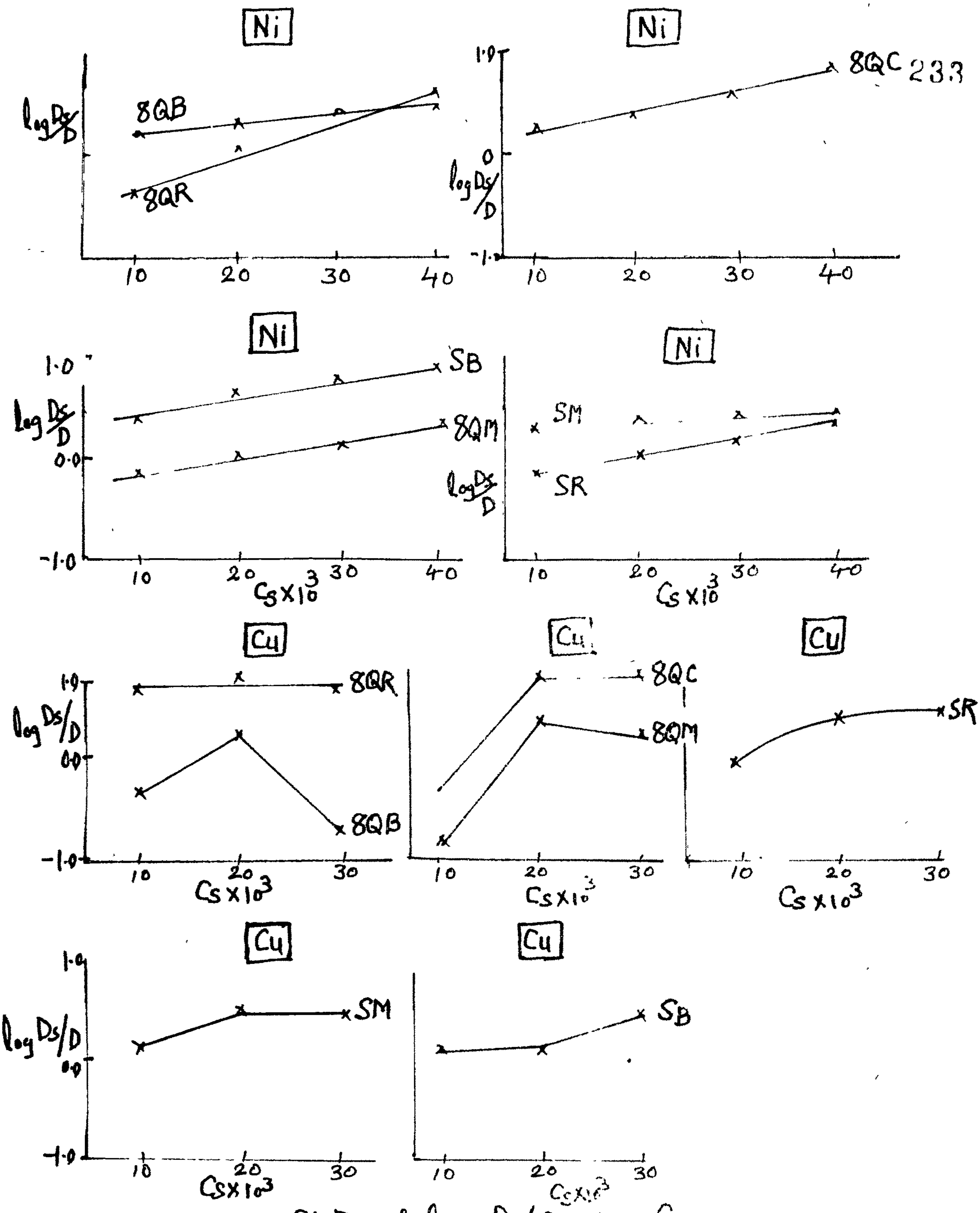


Fig III 14 (a) Plots of log Ds/D vs C_s

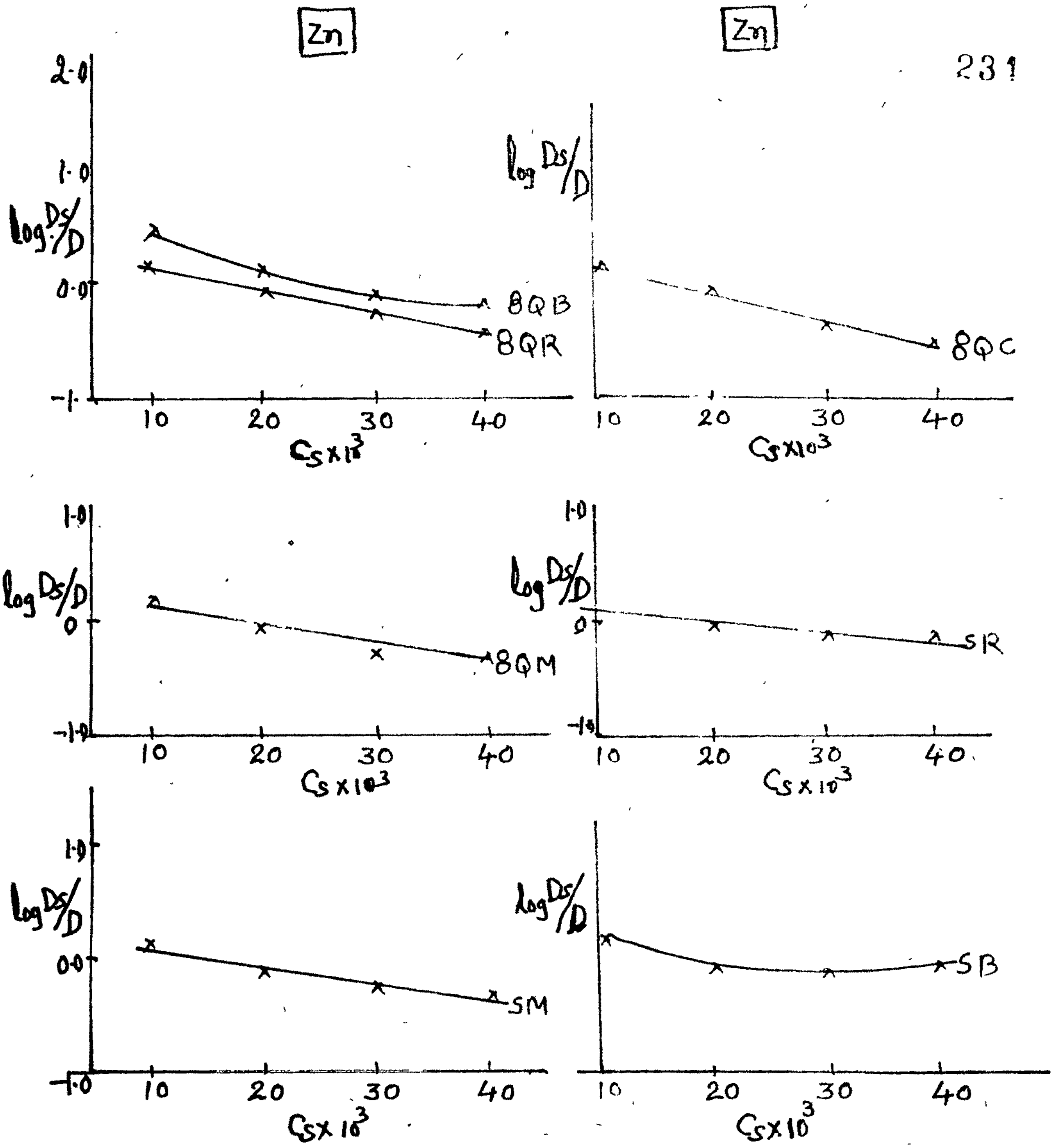


Fig III.14 (b) Plots of log D_s/D Vs. C_s

Thus

$$K' = KC$$

We suggest from the curves that (i) the slopes of the curves for Ni are opposite in sign to those for Zn and (ii) K' is positive for Zn and negative for Ni for the resins studied and NH_4 ions.

III.24 SOLVENT UPTAKE :

Solvent uptake is useful in studying the solubility parameter of the resins. Taking the solubility parameter as 23.4 for water, 14.5 for methanol, 9.2 for benzene and 9.9 for acetone, we plot solvent uptake versus solubility parameter in Fig.III.15. The maximum in the curve gives us an idea of the solubility parameter of the resin. The values are increasing in order :

8QB < 8QM < 8QC < 8QR for 8Q series

and SB < SR < SM for S series.

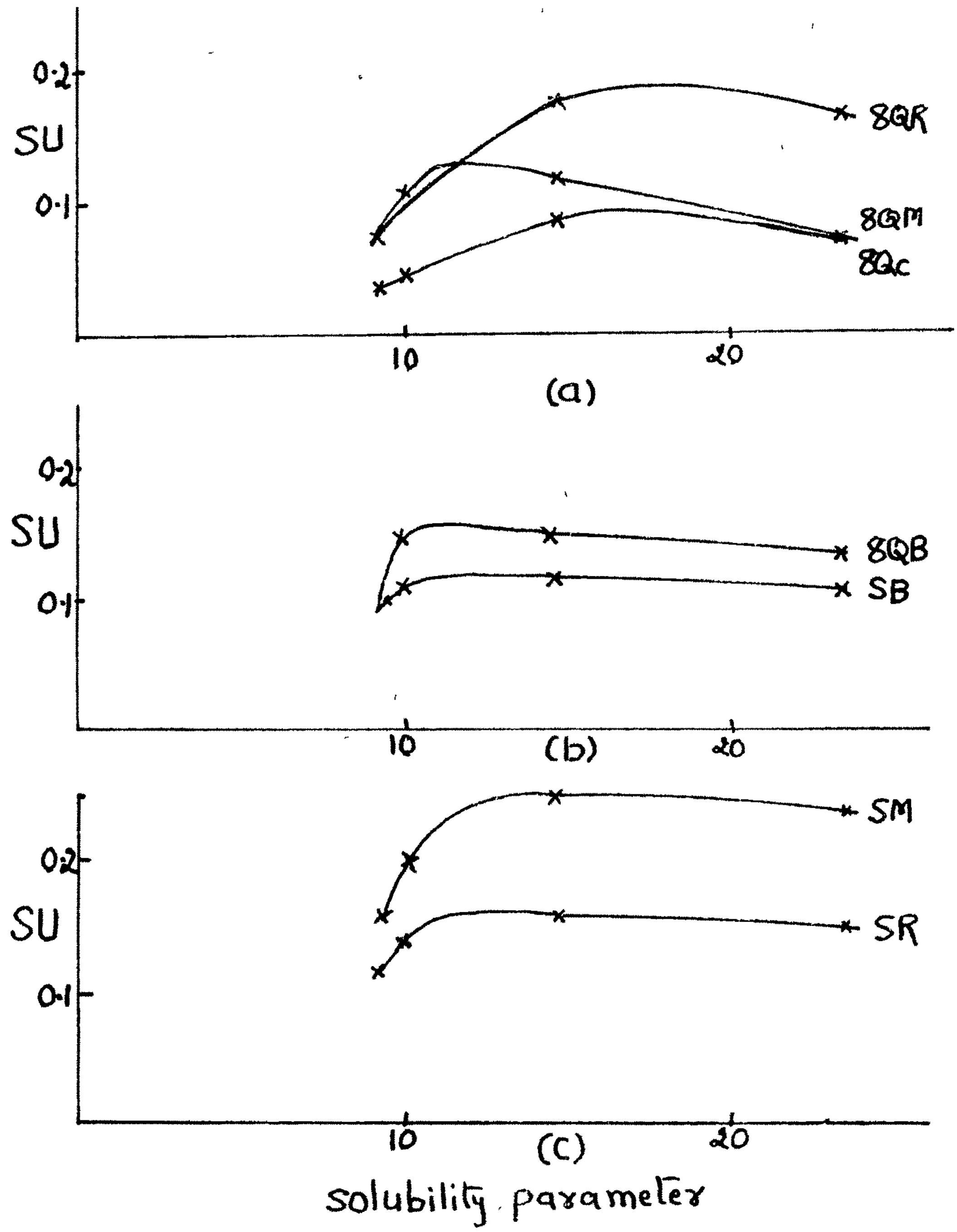


Fig III.15. solvent uptake versus solubility parameter,

III.25 MAGNETIC MOMENT :

Parikh(86) observed that oxine-urea resin is quite similar to the chelating ligand in behaviour in its monomeric and polymeric forms(169) and forms complexes with Cu(II), Ni(II) and Co(II) ions of the same structure irrespective of the nature of the anion used. On the other hand, he observed that salicylaldehyde-urea-resin formed complexes with Cu(II), Ni(II) and Co(II), whose nature depended on the nature of the anions used.

We have prepared Cu(II) loaded resin - 8QR. We consider that basic Cu(II) complex with the resin is formed. Its mol.wt. is suggested as 1388.5 per Cu atom. Hence molar mass susceptibility is calculated as 1410×10^{-6}. Applying the diamagnetic correction of 754, we obtain the corrected molar mass susceptibility as 2164×10^{-3}. Hence the magnetic moment of the copper(II) ion in the complex is evaluated as 2.26 B.M. It may be noted that the chelating resin chelex 100 forms - MX complexes(170).

III.26 IR SPECTRA :

IR spectra of phenol - formaldehyde condensates have been studied by Bender(171), Hunter and Grisenthwaite(172), Nakamura(173), Conley and Bieron(174), etc. They show one or more bands in 700-900 cm^{-1} region indicating the number and position of substituents on the ring. Charles et al (175) have noted that C-O stretching frequency near 1100 cm^{-1} dcreases slowly as the mass of the metal increases along the series Mg, Ca, Zn, Cd and Pb. Since 8QR resin is a hard mass difficult to grind, the spectra have less intense bands than expected. Further, since 8QR contains only a small proportion of oxine in relation to resorcinol, the bands related to resorcinol will be in prominance and the bands related to oxine or its chelate would be weak or absent.

In 4000-3000 cm^{-1} region, a broad band has been observed which may be related to the water present in the resin.

A band observed at 1490-1485 cm^{-1} in these spectra is characteristic of the phenyl ring.

A band at 1105-1100 cm^{-1} is attributed to C-O-group.

Bands observed at 520 and 1835 cm^{-1} in acid form of the resin are not observed in its salt forms.

III.27 CONCLUDING REMARKS :

We consider the following as some important results and conclusions of this work :

(i) vic-oxime-imines of 2,3-dioxobutyranilide could not be resinified.

(ii) Oxine and salicylaldehyde were resinified (a) using acidic comonomers such as resorcinol, etc (b) using basic comonomers such as melamine, etc (c) using condensing agents such as formaldehyde, etc. and (d) employing acetal copolymerization.

(iii) The resins have low column density and high void volume fraction in general,

(iv) It is concluded from the pH titration curves that ion uptake at higher alkali concentrations involves ion exchange and electrolyte sorption.

(v) pK_a values of the resins which are treated as very weak acids are evaluated.

(vi) Ion uptake of Cu(II), Ni(II), Zn(II) and Mg(II) ions by these resinified ligands has been studied under different conditions. It has been observed that (a) eventhough oxine would precipitate Cu(II), Ni(II) and Zn(II) ions under acidic conditions also, resinified oxine can take up these ions under basic conditions only, (b) distribution coefficient of these metal ions varies with its concentration but nature of variation depends on the specific metal ion and (c) when salt effect is studied by the addition of ammonium salt to the solution, the nature and extent of salting out of the metal ion depends on the specific nature of the metal ion. It is noted that anomalous behaviour is observed for Cu(II) ions.

(vii) Magnetic moment of a Cu complex of resinified oxine is calculated on the basis of a consideration that 1:1 complex of Cu with oxine in resin is formed as is observed with chelax-100.

(viii) IR spectra have bands of relatively weak intensity because of the hardness (and immiscibility) of the resin and its complexes.