I INTRODUCTION

RESINIFIED LIGANDS

I. INTRODUCTION

Literature survey and Plan of work

I.1 LIGANDS :

Ligands are characterized by the functional groups they carry. These groups may be ionic or coordinatively covalent in character. Presence of ionic groups in the ligand molecule will make the molecule acidic, basic or amphoteric and the proper distribution of two or more of these groups can make the ligand molecule to exhibit chelation. The chelating ligands will possess specificity and selectivity with reference to various ions. Because of these characteristics, chelating ligands have been explored to a large extent for the last three decades and there has been an explosive growth of literature.

Chelating ligands have a wide variety and are utilized in analytical and synthetic work. These ligands would be carrying functional groups containing O, S, N, P, etc. We restrict our discussion to the chelating ligands containing O and O/N functional groups.

I.2 RESINIFICATION OF LIGANDS :

In analytical as well as in preparative chemistry there exists considerable need for polymeric chelating ligands which combine the ease of operation of the conventional ion exchangers and specificity/ selectivity of the chelating ligands. In many of the applications the recovery of the ligands would be advantageous and the minimization of loss would be desirable. Hence various ligands have been polymerized to insoluble resins. The resinification of the ligands can be effected by the following methods in general :

(i) the ligand is inserted into a phenolic or amino resin,

(ii) the ligand is introduced into a vinyl, acryloyl, or styryl matrix,

(iii) vinyl group is attached to the ligand molecule and then polymerized,

(iv) ligand is polymerized by the polycondensation reaction, and

(v) cross-linking of linear polymeric chains is effected by using cross-linking agent or curing.

(Trapping and occlusion of the ligand by the polymeric matrix are not included in these considerations).

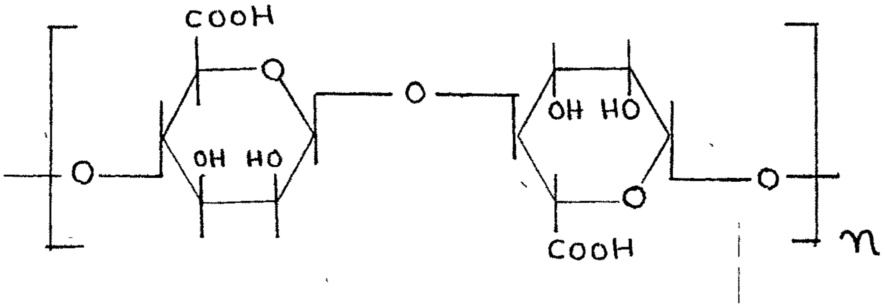
I.3 RESINIFIED LIGANDS :

The work on resinification of ligands was initiated in various schools in the fifties. The works of Bayer(1), Blasius(2), Gregor(3,4,5), Kennedy(6,7), etc, contributed considerably towards the preparation and understanding of the nature and behaviour of such polymerized ligands, and paved way for subsequent investigators. Dow Chemical Co. took the early patents(8) and marketed the product Dowex chelating resin A-1. It was followed up by the works of Bayer(9), Blasius(10), Hering(11), Manecke(12), Schmuckler(13), DeGeiso(14) etc. with reviews, dissertation, and patents(15,16,17,18) in early sixties. These products find use in column chromatography, thin layer chromatography, ligand exchange chromatography membrane - formation, desalination, mineral extraction, waste water treatment, ink compositions, etc. We briefly consider first the chelating polymeric ligands available from natural sources and then some chelating ligands polymerized by addition and condensation reactions.

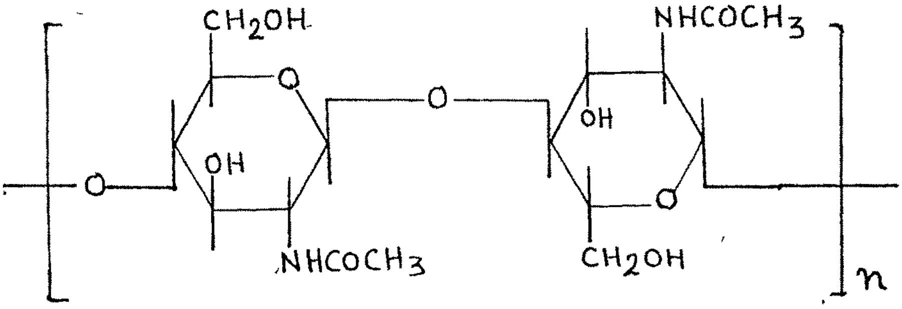
I.4 NATURAL CHELATING POLYMERS :

Alginic acid is a polyuronide found in brown sea-weeds and its chemical formula is suggested as S I 1. The alginate in sea weed behaves as a base exchange material and is present as mixed salts of cations able to render it insoluble(19,20,21). Chromatography of metal ions and organic substances on alginic acid was studied by Cozzi and coworkers(22, 23,24).

Chiten(SI2) is a polysacharide of beta (1-4) 2-acetamido-2-deoxy-D-glucose units, some of them being deacetylated. It occurs in lower animals, fungi, etc(25).



SI-1



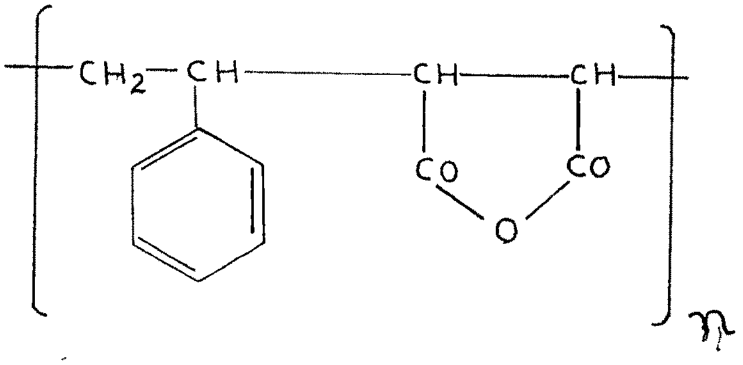
SI-2

Chitosan is deacetylated chiten and is useful as viscosity builder in solutions for rapid setting of suspended solids(26). It can also be obtained as a chelating membrane; however its capacity is less than that of its powder(27). Chitosan has been used for collecting trace metals(28).

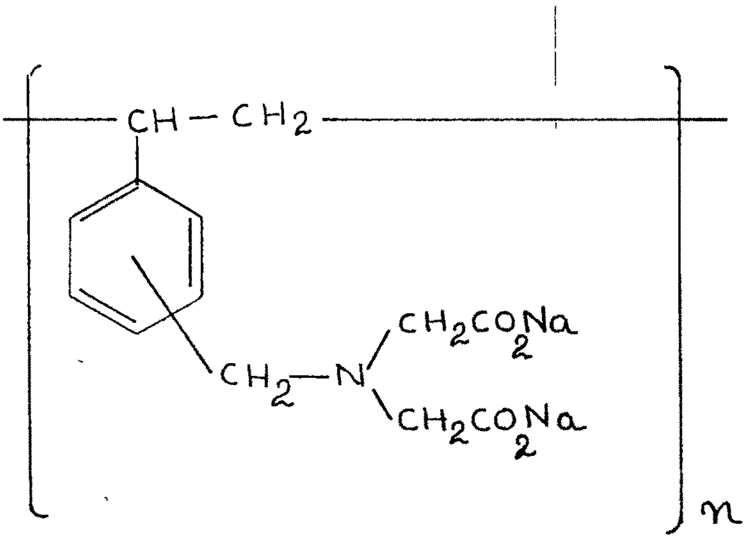
Wool is a complex protein containing various functional groups and has been studied for thin layer chromatography(29). Nucleic acids are studied for their interaction with metal ions(30,31,32,33).

I.5 SYNTHETIC CHELATING POLYMERS :

Linear addition polymers containing chelating ligands are prepared by (i) copolymerizing styrene with maleic anhydride (SI3), (ii) condensing iminodiacetate with chloromethylated polystyrene, etc. Dowex A-1 has the polymeric back-bone structure of SI4(34). Other amino acids studied for condensation were amino dipropionic acid(35), glycine(36,37), anthranilic acid(5), etc.



SI-3



SI-4

Linear condensation polymers are obtained by condensing acids, amines, aldehydes, diazonium compounds, etc with various phenols, quinones, diols, etc to yield say SI5, SI6, SI7, SI8, etc.

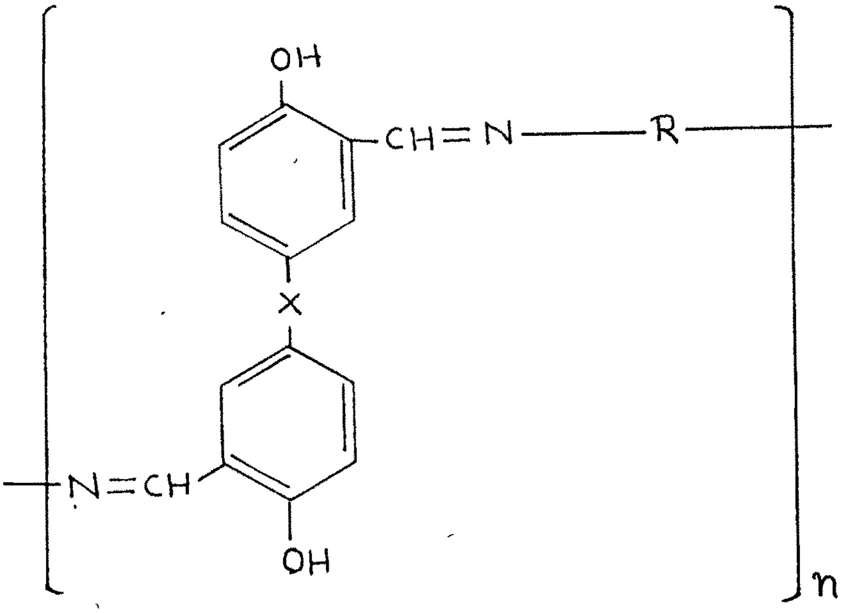
A resin containing beta-diketone and exhibiting high selectivity for copper has been synthesized by McBurney(38).

Skogseid(39) prepared a resin by condensing polyaminostyrene with picryl chloride and found it specific for K ion.

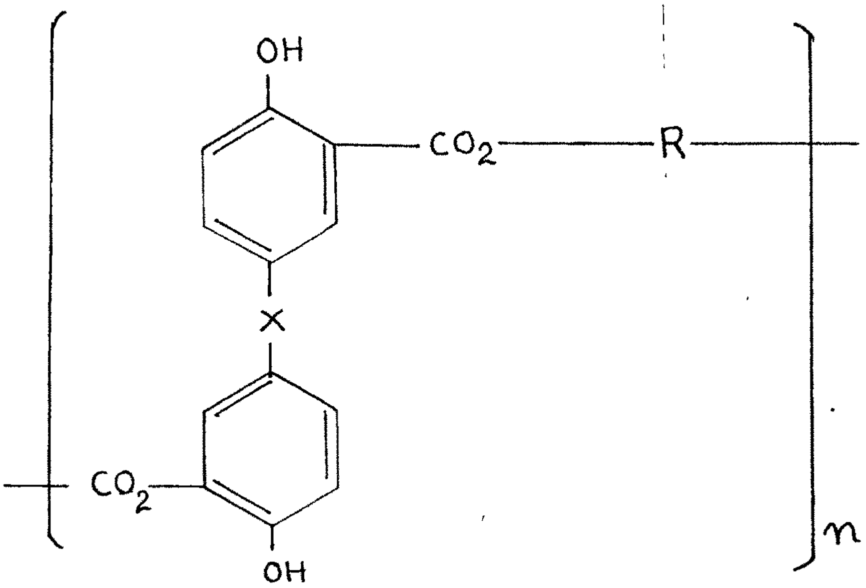
O-aminophenol(40,41), m-phenylene diglycine(40), m-phenylenediamino tetracetic acid(42), etc have been polycondensed with phenols and formaldehyde.

Hydroxamic acid groups have been introduced into a resin with carboxylic acid groups(43,44).

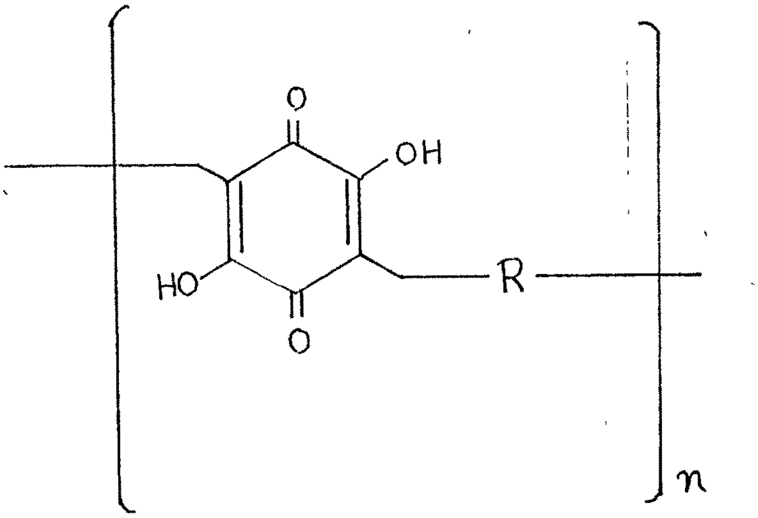
Resins containing chlorophyll and haemin derivatives possess specificity for Fe(III)(45,46).



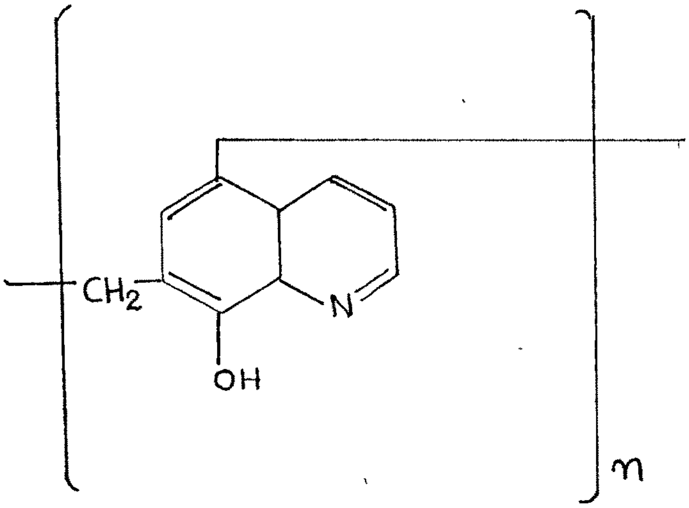
SI-5



SI-6



SI-7

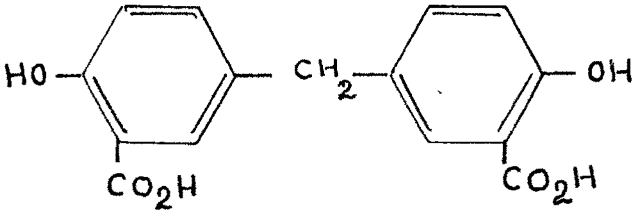


SI-8

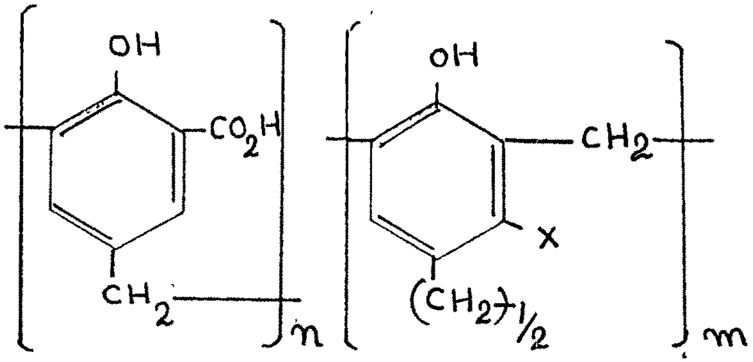
We consider resinified salicylic acid, resinified salicylaldehyde and resinified 8-quinolinol below.

I.6 RESINIFIED SALICYLIC ACID AND SALICYL ALDEHYDE :

Salicylic acid forms a dimer (SI9) when condensed with formaldehyde in the proportion of 2:1 under acidic conditions(47). Three dimensional networks containing salicylic acid (SI10) were prepared and studied for their ion exchange properties by many investigators. Ashida(48) prepared weakly acidic resins by condensing salicylic acid with formaldehyde in presence of acid catalyst and studied its ion exchange characteristics. Moriguchi and Miura(49) condensed salicylic acid with formaldehyde using sulphuric acid catalyst and prepared copper complex of the product. Condensation copolymers of salicylic acid with phenol, resorcinol, bisphenol-A, etc. were prepared and studied (i) as ion exchangers by Umezawa and Ohtsuka(50), Matsumura and Komiya(51),



SI-9



SI- 10

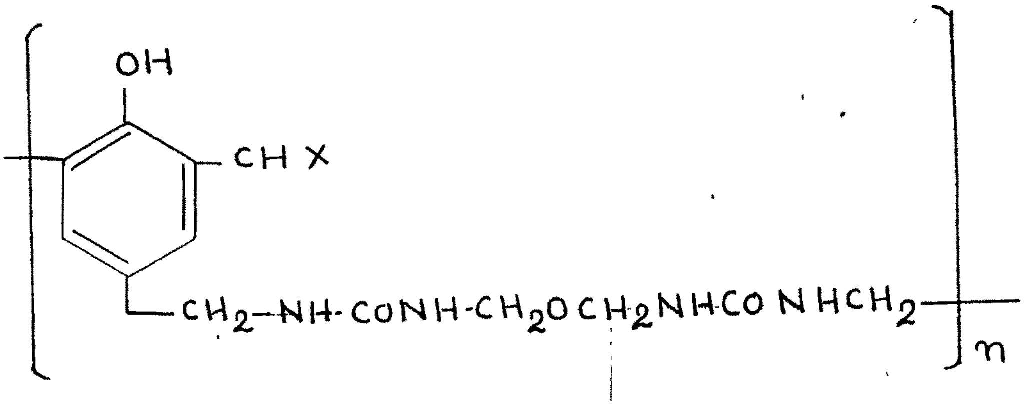
Kennedy and coworkers(52), Virasoro(53), Rabek et al (54,55), Julien et al(56), Trivedi and Krishnaswamy (57), Meshcheryakova et al(58), Rozhanovaskaya and Zasova(59), Kuz'michev and Filippychev(60), Joshi and Patel(61), Topp(62), Komiya(63), Rabeck(64), Soloway(65), Manecke(66), Izoret(67), etc. and (ii) for the separation of U and Th by Petit and Lumbroso(68), DeGeiso et al(69), etc. Structural studies have been made by DeGeiso et al(69), and spectral studies by Umapathy et al(70). These resins have been studied (and patented) (i) for photographic materials(71), (ii) for purifying proteases(72), (iii) as tanning agents(73), (iv) in printing ink compositions(74), (v) in surface coating compositions(75,76,77,78), (vi) as lake former for dyes(79), etc. Condensation polymers of salicylic acid and urea, melamine, etc have been prepared and studied as lacquers in surface coating compositions and ink compositions(80,81,82,83,84). Petrov and Tsvetkova(85) and Parikh(86) prepared both linear and cross-linked resins from salicylic acid, urea, melamine, etc and studied their ion exchange behaviour. Parikh(86) further prepared linear polymers (SI11) from salicylaldehyde, salicylaldoxime, urea and formaldehyde and studied their exchange reactions.

He also prepared ion exchange resins from salicylaldehyde, melamine, urea, thiourea and formaldehyde and studied their ion exchange characteristics.

I.7 RESINIFIED 8-HYDROXY QUINOLINE :

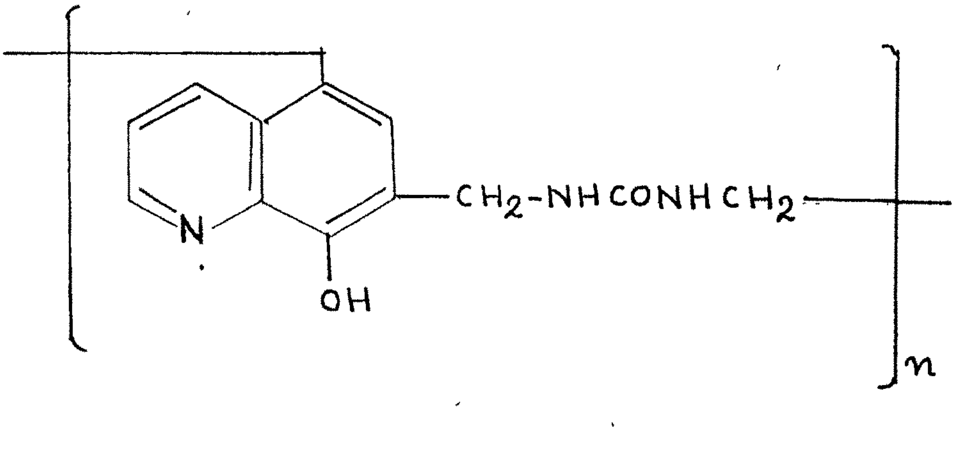
Poly-oxines and copolycondensates of 8-hydroxy quinoline with phenols have been prepared and studied by Gregor et al(40,87), Pennington and Williams(41), Varnon and Eccles(88), Zhou and Pan(89), etc.

Anion exchange resin loaded with 8-quinolinol-5-sulphonic acid has been studied for the selective removal of the trace amount of chalcophile elements from natural water prior to neutron activation analysis(90).



X = O, NOH

SI – 11



SI- 12

Potentiometric titration was used for the examination of the complex-forming capacity of polyaminostyrene condensate with 5-chloromethyl 8-quinolinol and the calculation of the formation constants of metal complexes formed by the resin(91).

Oxine-based resins were prepared by condensing metal oxinates with resorcinol and furfural(92).

Condensation polymers from 8-quinolinol, formaldehyde, etc were prepared and used as chelating agents for Mn(II), Cu(II), Co(II), etc.(93,94).

A lightly cross-linked, macroporous, polystyrene azo-oxine resin showed properties superior to oxine-resorcinol condensates and was suggested for isolating Hg(II) and U(VI)(88).

Membranes were prepared by grafting oxine-phenol condensate on partly hydrolysed cellulose acetate and used for sorption of Cu(II), Ni(II) and Zn(II)(95).

Ion uptake by oxine-based condensates and other ion exchange resins has been compared by Jones et al(96).

Oxine-phenol copolycondensates have been prepared and studied for their chelation with metal ions(97,98,99).

Parikh(86) prepared linear polymer (SI12) from oxine, urea and formaldehyde and studied its exchange reactions with metal ions.

He also prepared ion exchange resins from oxine, melamine or thiourea and formaldehyde and studied their ion exchange properties.

I.8 ION EXCHANGE SELECTIVITY :

Taking into consideration an ion exchanger and its equilibrium with two monovalent counter ions A and B, present both in the ion exchanger and in the solution in contact with it, we may write

$$\bar{A} + B ======== A + \bar{B}$$

where the bars indicate the exchanger phase. The selectivity coefficient $K_{B/A}$ is defined as :

$$K_{B/A} = (\bar{X}_B/\bar{X}_A)\,(X_A/X_B)$$

where $\bar{X}_A$ and $\bar{X}_B$ represent the equivalent fractions of the counter ions in the exchanger and X_A and X_B corresponding equivalent fractions in solution ($\bar{X}_A + \bar{X}_B = 1;\ X_A + X_B = 1$)

Any value of $K_{B/A}$ that is different from unity measures the relative difference in prefrence of the solution and exchanger phases for the two competing ions.

Further,

$$\Delta G^{\circ} = -RT\ \ln K_{B/A}$$

If we are dealing with bivalent ions we may write for Na^+ and M^{2+} ions,

$$M^{2+} + \overline{2Na^{+}} === \overline{M^{2+}} + 2Na^{+}$$

and

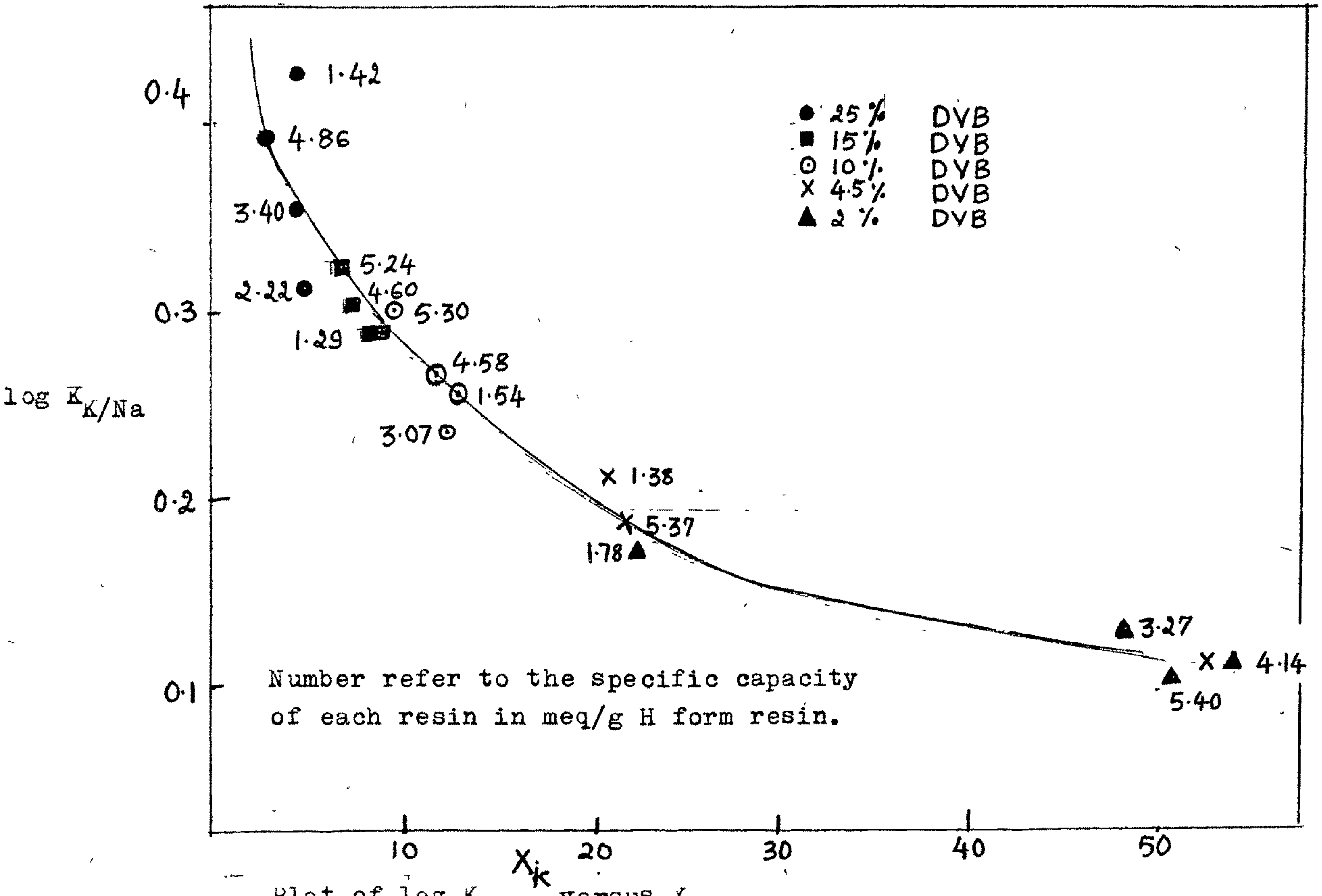
$$K_{M/Na} = \left(\overline{X_{M^{2+}}} \;/\; X_{M^{2+}}\right)\left(X_{Na^{+}} \;/\; \overline{X_{Na^{+}}}\right)$$

For resins having styrene DVB matrix, there are three parameters affecting ion exchange :

(i) the nature of the exchange grouping,
(ii) the number of exchange groupings per unit amount of exchanger and
(iii) the degree of cross-linking.

The results obtained for sulphate resins are shown graphically in Fig. I.1, where log $K_{K/Na}$ is plotted against the average amount of water taken by the resin per miliequivalent of exchange capacity (X_k)(100). Each point plotted represents a different resin.

The understanding of ion exchange selectivity has been based on the mechanistic approach. Gregor(101,102) postulated a model in which the exchange is regarded as consisting of two parts, an un-crosslinked polyelectrolyte with solvent and the cross-linking. Selectivity is considered to arise primarily because of differences in the partial volume of the hydrated counter ions in the resin and is related to the elastic counter pressure in the resin, tending to oppose the swelling of the resin. Equilibrium is reached when the elastic



Number refer to the specific capacity of each resin in meq/g H form resin.

Plot of log $K_{K/Na}$ versus X_K

Fig. I.1

counter pressure is equal to the resistant osmotic pressure(103). Gregor's theory has been strongly criticized by Glueckauf(104).

A somewhat different theory was proposed by Harris and Rice(105). They produced a sophisticated treatment of the mechanisms governing the degree of swelling of ion exchange resins. Their basic assumption was that some of the counter ions were 'bound' to the fixed ionic groupings. They deduced the values for the degree of swelling of resins in aqueous solutions. Unfortunately, their treatment of selectivity was entirely non-mechanistic.

The theory of Eisenman(106,107) differs from the previous theories in a number of respects, of which two merit emphasis :

(i) Hydration of ions is recognized as of key importance; however, hydration is considered in terms of its energatics rather than in terms of hydrated volume;

(ii) electrostatic interactions are regarded as the primary cause of affinity reversals.

They suggested that

$$\Delta G^{o}_{B/A} = - RT \ln K_{B/A}$$

The general agreement between the theoretical predictions and experimental results is quite good for sulphonate resins but much different for carboxylate resins.

Ling(108) introduced an approach whose basic assumptions are similar to those of Eisenman but which is more sophisticated in the detailed calculations. Ling's model was designed primarily in relation to biological systems and with emphasis on the carboxylate group as the fixed grouping.

I.9 RESIN SELECTIVITY IN AQUEOUS SOLUTIONS :

Variations in the resin selectivity occur as the external phase goes from a dilute solution to a concentrated one. For understanding ion exchange selectivity, the following points are to be taken into consideration :

(i) water-water interaction(109,110,111,112, 113,114)
(ii) ion-water interaction(115,116,117,118, 119,120),
(iii) ion-ion interaction(121,122,123),
(iv) ion-resin matrix interaction(124,125,126),
(v) swelling of the resin(100,127,128,129),
(vi) Donnan potential(130),
(vii) exclusion of coions from the resin phase(131, 132,133,134),
(viii) competitive solvating of the ions(135),
(ix) non-uniformity of exchange sites(136,137, 138,139,140,141),
(x) degree of cross-linking of the resin(125, 142,143,144),
(xi) sieving effect of the matrix pores(124,125 145,146), etc.

9(a). Dilute solution selectivities :

The dilute solution case is simpler than the concentrated solution case, in that the resin invasion by non-exchange electrolyte is negligible as are changes in swelling and cation - anion interactions.

If the ion exchange resin is treated as a concentrated electrolyte soltuion, the following differences emerge with reference to dilute external solution :

(i) one speices of ion in the resin phase, the matrix - fixed ion, is relatively immobile, but the matrix itself can swell when in contact with external solution.

(ii) There is less unbound or 'free' water per ion in the resin phase and electrostatic interactions are stronger there than in dilute external solution.

(iii) The 'free' water that remains in the resin phase has less cooperative structure.

The first difference leads to the treatment of the resin as a Donan membrane and accounts for the exclusion of coions from the resin phase when in contact with dilute solutions. It is the special feature emphasized by the model basing selectivity on osmotic pressure - volume effect(101). This model as pointed out earlier, yields the right selectivity order for hydrated ions on a qualitative basis but fails quantitatively.

It is believed that electrostatic ion - pairing of the counter and resin ions influences the selectivity, especially of weak acid and weak base resins, whereas, effects on ion-water and water-water interactions play a major role in resin selectivity particularly for strong acid and strong base exchangers. In addition to the osmotic pressure-volume and electrostatic ion-pairing models, other approaches take into consideration

(i) polarizability of the ion(147,148,149,150,151),
(ii) clustering of ion pairs(152,153), etc.

9(b). Concentrated solution selectivities :

(i) As the water activity decreases and the ion concentration increases, the hydration of the ions becomes less complete and the ion-water interactions become less important. Also, the resin shrinks, making the resin phase more concentrated and decreasing the average pore size so that sieve effects may become significant.

(ii) The water structure is increasingly damaged by the higher concentrations of ions. It results in a lower dielectric constant for the medium.

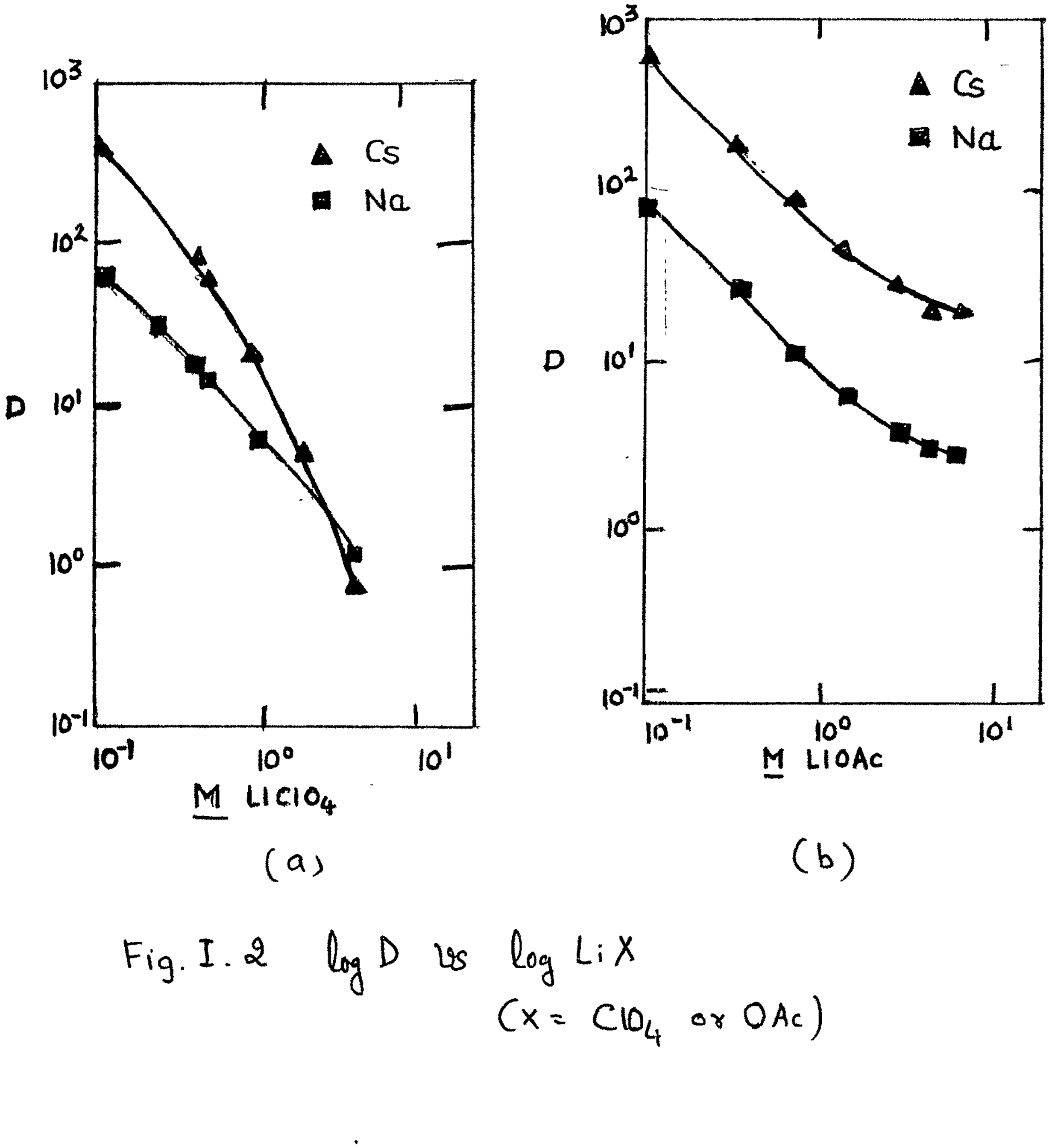
(iii) The number of ions of opposite charge in the vicinity of a chosen ion increases rapidly, so that anion-cation contacts become more frequent and ion-ion interactions become more important in both phases.

(iv) Non-exchange electrolyte enters the resin phase, With increasing electrolyte concentrations, the Donan potential falls and the resin becomes more susceptible to the entrance of coion.

The ion exchange equilibria deviate from the ' mass action law ' behaviour which is well followed in dilute solution. Cation - anion associations occur as competing complexing equilibria. The curves of log D for Na and Cs ion vs log LiX concentrations shown in Fig.I.2 indicate that inversion of Na and Cs curves is observed in case of $LiClO_4$ but not in case of LiOAc(154,155,156).

I.10 PRESENT WORK :

Considerable work has been carried out in our laboratories on chelates, chelate polymers, etc. Work has been carried out by (i)Patel(157) and (ii)Shah(158) on metal chelates of vic - oxime - semicarbazones, etc. (iii) Mistry(159) on semiconductivity of chelate polymers, (iv) Kapadia(160) on coordination polymers, (v) Parikh(86) on linear and cross-linked copolymers of chelating ligands (vi) Sheth(161) on amphoteric ion exchange resins, (vii) Vyas(162) on pyrolysed polymeric chelates, (viii) Godhwani(163) on redox



(a) (b)

Fig. I.2 log D vs log LiX
($X = ClO_4$ or OAc)

polymers, etc. Work is in progress in our laboratories on various polymeric ligands and their properties. As a part of this work, it was proposed to study resinified chelating ligands. Hence it was planned :

(i) to prepare condensation copolymers from the ligands such as oxime imines, oxine, salicylaldehyde, etc. using comonomers such as resorcinol, m-cresol, bis phenol A, melamine, polyvinyl alcohol etc.

(ii) to study their general and ion exchange properties such as solubility, water content, density, pH titration, ion uptake etc.

(iii) to obtain IR spectra, magnetic moment etc. of some of the resins and their cation - loaded products.

(iv) to consider structural characteristics, magnetic behaviour, etc from the data obtained.

Experiments carried out and results obtained are presented and discussed in the following pages.