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COORDINATION CHEMISTRY OF CHELATING RESINS AND ION EXCHANGERS

SURESH K. SAHNI and JAN REEDIJK *

Department of Chemistry, Gorlaeus Laboratories, State University Leiden, P.O. Box 9502, 2300 RA Leiden (The Netherlands)

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* Author for correspondence.

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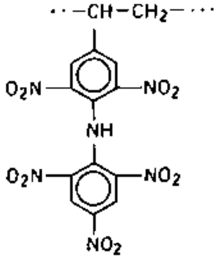
A. INTRODUCTION

(i) Purpose

The lack of selectivity of the conventional ion exchange resins has led to the discovery and development of a new class of polymers which are now known as specific and selective * ion exchange resins. These resins are in fact polymeric complexing and chelating compounds which, under certain experimental conditions, are characteristic of one ionic species only [1]. The chemistry of these new types of complexing resin began in the late 'forties when Skogseid [2,3] described the first such resin, a polystyrene derivative containing dipicrylamine groups (I) and specific for potassium ion. This was followed by the advent of chelating ion-exchange resins incorporating a variety of chelating groups on different types of polymeric matrices [4–6]. Since then, the field of chelating ion-exchange resins possessing ion-selective properties has been developing steadily, incorporating various contemporary refinements of coordination chemistry. Despite the increasing utility and application of complexing and chelating resins in transition metal, as well as in alkali and alkaline earth metal ion separations [7,8], preconcentration and recovery of trace metal ions [9,10], catalysis [11,12], organic synthesis [13,14], nuclear chemistry [15], water and waste water treatment [16–19], pollution control and industrial processes [20,21], hydrometallurgy [22,23], polymer drug grafts [24], and various miscellaneous applications in analytical chemistry [25–28], the development of their coordination chemistry has remained rather slow. The reasons for delayed interest in this aspect of chelating ion-exchange resins appear to be the following: (i) strong influence of analytical chemistry and tendency to exploit the greater ion selectivity of these new types of ion exchangers, (ii) lack of theoretical background and instrumentation for studying the physico-chemical aspects of metal com-



(I)

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* For I.U.P.A.C. recommendations for the usage of selectivity and specificity terms, see G. den Boef and A. Hulanicki, Pure Appl. Chem., 55 (1983) 554.

plexes formed by chelating ion exchangers, and (iii) there was no obvious necessity to develop this aspect of the field.

A large number of papers and several reviews on specialized aspects of complexing and chelating ion-exchange resins are available [29–62]. However, no general review on this apparently very useful and productive field has appeared since 1967 [35]. The present review is an attempt to further the various developments that took place in this field during the last two decades. Particular emphasis will be placed on the physico-chemical aspects along with other developments in the field of metal complexes of chelating ion-exchange resins. This will enable researchers working in this area to adopt a more balanced approach in the design, synthesis, characterisation and application of these industrially important polymeric chelating agents.

(ii) Scope and organisation

In the present review, we will start to summarise briefly all the aspects of the subject that have been covered in previous specialized reviews, allowing a broad and general discussion on the subject. A variety of solid supports and matrices (both organic and inorganic) have been used for anchoring various chelating groups onto them. However, in the present article synthetic ion-exchange resins derived by functionalisation of organic polymers, both linear and cross-linked, will be reviewed in detail. The metal–chelate polymers obtained by the polymerisation of organic ligands such as polymeric Schiff bases, as a result of a metal ion influence, will only be mentioned in so far as they possess ion-exchange properties. Only a brief mention of inorganic (e.g., silica) and other organic (e.g., cellulose) polymers will be made. At the appropriate places, reference will also be made to the related or similar metal complexes of the monomeric ligand systems in homogeneous medium. As a result of the industrial importance of chelating ion-exchange resins, the bulk of the literature on the subject is available only in the form of patents and coded compounds. We have nevertheless tried to include all possible details of such chelating ion-exchange resins available in the literature and reference will be made to the original source of the information. This review mainly covers literature available to the end of 1982.

The spectral and magnetic data on metal complexes of chelating ion-exchange resins will be dealt with in detail and sufficient analytical data have been included to enable a quantitative discussion of the ligating behavior of chelating ion exchangers. The nature of the bonding in such chelates and consequences of a particular geometry around the metal ion on the selectivity of chelating ion-exchange resins will also be discussed. The details of various mechanisms responsible for the action of chelating ion exchangers will be discussed in view of a relationship between the donor atoms, shape and design of the donor atoms and steric constraints of the donor atoms and the selectivity of chelating ion-exchange resins.

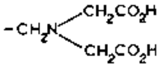
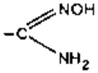
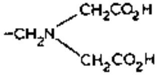
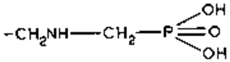
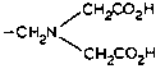
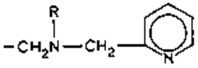
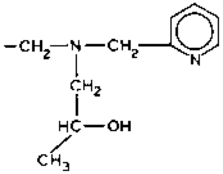
(iii) Historical development

The historical development of the complexing and chelating resins has been lucidly summarised by Millar [29] and Hering [7]. The most important initial developments in this field will be repeated here. The idea of using complexing resins originated with the observation of Erlenmeyer and Dahn [63] that mixtures of various cations could be chromatographed on a column of powdered 8-hydroxyquinoline, the suggestion of Meinhardt [64] that complexing agents could be fixed on a supporting solid, and Griessbach's concept of selective ion exchange as a function of pH [65]. Skogseid, independently from these views, described the first ion (potassium)-selective resin [2,3], and propagated the theory of ion-specific resins. This initiated a new field of industrially important and useful selective ion-exchange resins, adding new dimensions to the phenomenal success of the existing conventional ion exchangers. Mellor [66] and Gregor [67] described the preparation of several resins containing a variety of chelating groups known to form complexes with a wide range of metal ions whose selectivity and stability is pH-dependent. At this stage, the possibility of preparing specific resins as envisaged by Skogseid [2] was supported by Hale [5] who suggested, "highly selective, if not specific behavior could be expected of resins containing groups similar to those in chelating groups". The work on chelating ion exchangers continued on this premise and also on the fact that highly selective behavior could be expected of an ion exchanger that contained a chelating group capable of forming a highly stable 1:1 complex with a particular metal ion and much less stable complexes with others [29]. In fact, the high selectivity of chelating ion exchangers lies in their ability to form stable, often covalent, complexes of varying strength with metal ions, something which sulfonate groups cannot. The first work on these lines was published by Kennedy and Davies [68], who observed that thorium(IV), iron(III) and uranyl(VI) formed relatively strong complexes with phosphates and phosphonates, whereas alkaline earth and bivalent transition metal ions and lanthanides formed either weak complexes, or common salts. The resins containing phosphonic acid functional units showed similar selectivity towards various cations, but the stability constants of resins for covalently bound cations, such as uranyl(VI) and iron(III), were found to be greater by an order of 10^6 or more over that of the corresponding monomer complexes. The increase in the stability of the chelating resin complexes was attributed to a combination of factors, such as the polymer entropy effect and a lower dielectric constant of the resin matrix. It was thus shown that the affinity of the monomeric ligand systems can also be realised in the resin matrix and the essential conditions for this behavior of chelating ion-exchange resins were subsequently postulated [29]. The work of Kennedy et al. [68–70] contributed significantly in the rationalisation of these basic concepts. An increasing emphasis was given to the determination of precise data on chelate stability constants over a suitable range of cations for model (monomeric or an oligomer of low molecular weight, dimer, trimer, etc.) compounds and on other chelating characteristics of the monomeric ligands, before incorporating them into polymeric matrices. Eventually, the synthesis of a chelating resin having iminodiacetic acid as functional group anchored onto a polystyrene matrix was reported [71]. Numerous patents [72–80] were obtained for manufacturing this chelating ion-exchange resin, which became commercially available in the late 'fifties. Iminodiacetic resins became very popular despite their many drawbacks such as slow kinetics and pronounced swelling behavior. The success of this resin prompted systematic research in the area of chelating ion exchangers and many theories pertaining to the use of these new materials have been developed [7–9,81]. This resulted in the development of several selective chelating ion-exchange resins which are now available commercially (cf. Table 1). Further impetus to research in this area was provided by the improved synthetic procedures ushered in by Merrifield [82], who introduced the concept of solid-phase synthesis. At present, a large number of chelating ion-exchange resins incorporating a host of ligands, such as aminocarboxylic acids, hydroxamic acids, oxines, pyridine carboxylic acids, acid hydrazides, arsonic acids, phosphonic acids, dithiocarbamates, thiols, Schiff bases, crown ethers, cryptands etc., have been incorporated into a variety of both organic [13,51] and inorganic [83,84] polymeric supports or matrices. A number of biologically active compounds such as haemins [85,86], desferrioxamine B [24,87] and porphyrins [88,89] have also been grafted on different types of polymeric supports and their chelating properties have been studied.

(iv) Commercial chelating ion-exchange resins

A number of chelating resins containing such functional groups as iminodiacetic acid, amidoxime, aminophosphonic acid, oxine, thiols, pyridine etc., are now commercially available. The details of various commercial ion-exchange resins are available in some of the text books [8,81] on ion exchange, but Hering [7] and Saldadze and Kopylova-Valova [90] have documented the various aspects of chelating ion exchange resins in detail. A classification scheme for reactive polymers and the list of the symbols used for Soviet cation and anion exchangers is also available [91]. A selection of commercial chelating ion-exchange resins along with the details available of

TABLE 1
Details of a selection of commercially available chelating ion exchange resins

S.No.	Manufacturer	Commercial name	Active functional or chelating group	Nature of chelating group	Donor atoms	Polymeric matrix (cross-linking)	Ref. *
1.	Diamond Shamrock	IMAC GT 73	Complexing (group not known)	Weakly acidic	–	Polystyrene (X% DVB)	a
2.	Diamond Shamrock	IMAC TMR	$-SH$	Aromatic thiol	S_x	Polystyrene (X% DVB)	a
3.	Diamond Shamrock	IMAC SYN 101		Iminodiacetic acid	NO_2	Polystyrene (X% DVB)	a
4.	Diamond Shamrock	Duolite ES 346		Amidoxime	NO	Polyacrylic (X% DVB)	b
5.	Diamond Shamrock	Duolite ES 465	$-SH$	Aromatic thiol	S_x	Polystyrene (X% DVB)	b
6.	Diamond Shamrock	Duolite ES 466		Iminodiacetic acid	NO_2	Polystyrene (X% DVB)	b
7.	Diamond Shamrock	Duolite ES 467		Amino phosphonic acid	NO_2	Polystyrene (X% DVB)	b
8.	Dow Chemical, U.S.A.	Dowex A-1		Iminodiacetic acid	NO_2	Polystyrene (X% DVB)	c
9.	Dow Chemical, U.S.A.	Dowex XF-4195 Dowex XF-4196		Weakly basic groups	N_2	Polystyrene (X% DVB)	c
10.	Dow Chemical, U.S.A.	Dowex XFS-43084		Weakly basic group	N_2O	Polystyrene (X% DVB)	c

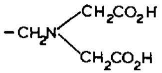
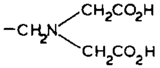
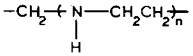
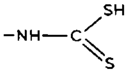
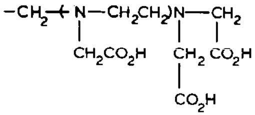
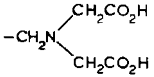
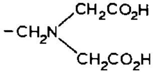
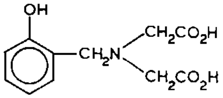
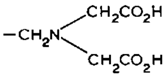
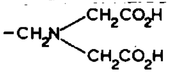
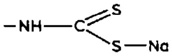
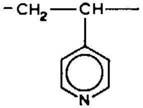
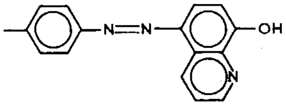
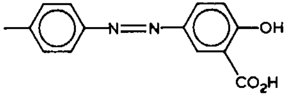
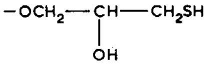
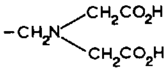
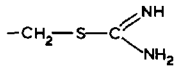
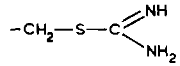
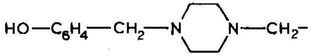
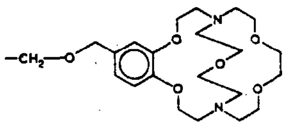
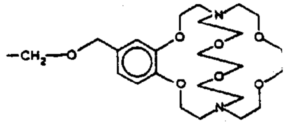
11.	Bio-rad	Chelex-100		Iminodiacetic acid	NO_2	Polystyrene (X% DVB)	d
12.	Mitsubishi	Diaion CR-10		Iminodiacetic acid	NO_2	Polystyrene	e
13.	Mitsubishi	Diaion CR-20	$-CH_2-NH-(C_2H_4NH)_n-H$	Basic (polyamine)	N_x	Polystyrene (X% DVB)	e
14.	Mitsubishi	Diaion CR-40	 $-CH_2-(N(H)-CH_2CH_2)_n-$	Ethylenimine	N_x	–	e
15.	Nippon Soda	Misso ALM-525		Dithiocarbamic acid	NS_2	–	f
16.	Reanal, Budapest	Ligandex E		Ethylenediamine triacetic acid	N_2O_4	Polystyrene (X% DVB)	g
17.	Reanal, Budapest	Ligandex I		Iminodiacetic acid	NO_2	Polystyrene (X% DVB)	g
18.	Rohm & Haas	IRC-718 (XE-318)		Iminodiacetic acid	NO_2	Polystyene (X% DVB)	h
19.	Unitika Ltd., Japan	Unicellex UR-50 (also UR-40, UR-30, UR-20 & UR-10)		(*o*-Hydroxybenzyl)iminodiacetic acid	NO_3	Phenol + formaldehyde	i
20.	VEB Chemiekombinat Bitterfeld, DDR	Wofatit MC 50		Iminodiacetic acid	NO_2	Polystyrene (X% DVB)	j

TABLE 1 (continued)

S.No.	Manufacturer	Commercial name	Active functional or chelating group	Nature of chelating group	Donor atoms	Polymeric matrix (cross-linking)	Ref. *
21.	Permutit Co. Ltd., England	Permutit S-1005		Iminodiacetic acid	NO_2	Polystyrene (X% DVB)	k
22.	Sumitomo, Japan	Sumichelate Q-10R		Dithiocarbamic acid	NS_2	Polyacrylic	l
23.	Sumitomo, Japan	Sumichelate CR-2		Basic (poly pyridine)	N_x	Polyvinylpyridine (20% DVB)	l
24.	Lachema, n.p., Brno	Spheron Oxine 1000		8-Hydroxyquinoline	NO	Poly-(hydroxyethylmethacrylate-CO-ethylenedimethacrylate)	m
25.	Lachema, n.p., Brno	Spheron Salicyl 1000		Salicylic acid	O_2	Poly-(hydroxyethylmethacrylate-CO-ethylenedimethacrylate)	m
26.	Lachema, n.p., Brno	Spheron Thiol 1000	 $-OCH_2-CH(OH)-CH_2SH$	Thiol	S_x	Poly-(hydroxyethylmethacrylate-CO-ethylenedimethacrylate)	m
27.	Bayer, A.G., West Germany	TP-207		Iminodiacetic acid	NO_2	Polystyrene (X% DVB)	n

28.	Ayalon, Haifa Israel	Srafion NMRR	 $-CH_2-S-C(=NH)NH_2$	Isothiouronium	N_2S	Polystyrene (X% DVB)	o
29.	Ionac, Sybrom Chem. Div., U.S.A.	Ionac SR-3	 $-CH_2-S-C(=NH)NH_2$	Isothiouronium	N_2S	Polystyrene (X% DVB)	p
30.	Csiro, Australia	Sirorez-Cu		Phenol-piperazine	NO	–	q
31.	Parish Chem. Co., Utah, U.S.A.	Kryptofix 221B (polymer bound)		Cryptand	NO	Polystyrene (2% DVB)	r
32.	Parish Chem. Co., Utah, U.S.A.	Kryptofix 222B (polymer-bound)		Cryptand	NO	Polystyrene (2% DVB)	r

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* Pertinent references regarding the preparation, properties and applications of these commercial ion exchange resins have been included in the appropriate places in the text. The references given here include the details of manufacturers and other useful information provided by them.

[a] Duolite International, Imacti Division (formerly Akzo Chemie), Stationstraat 48, P.O. Box 975, 3800 AZ Amersfoort, The Netherlands.

[b] Duolite (International) S.A., 107, Rue Edith Cavell, B.P. 8., F94400, Virty sur seine, Paris, France (Duolite International Ltd., is a company of Diamond Shamrock Corp.).

[c] Dow Chemical U.S.A., Functional Products and Systems Department, Midland, Michigan 48640, U.S.A.

[d] Bio.Rad Laboratories, 2200 Wright Avenue, Richmond, California 94804, U.S.A. Chelex 100 is analytical grade substitute of Dowex A-1.

[e] Mitsubishi Chemical Industries Limited, Mitsubishi Building, 5-2, Marunouchi 2-Chome, Chiyoda-Ku, Tokyo, 100, Japan.

[f] Nippon Soda, Tokyo, Japan.

[g] Reanal Fabrik Fur Feinchemikalien, Reanal Budapest, XIV., Telepes u. 53., 1441 Budapest 70. PF. 54. Ungarn (Hungary); at the time of compiling this Table, only Ligandex E was commercially offered by Reanal-Budapest.

[h] Rohm and Haas Co., Fluid Chemicals Department, Philadelphia, Pennsylvania 19105, U.S.A. The ion exchange resins supplied by Rohm and Haas Company are designated as Amerblite ion exchange resins.

[i] Unicellex Division, Unitika Limited, 23, Kozakura Uji, Uji-City, Kyoto, Japan. UR-40, UR-30, etc., correspond to sodium, calcium form of UR-50 which is the hydrogen form of the resin.

TABLE 1 (continued)

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[j] VEB Chemiekombinat Bitterfeld, DDR-44 Bitterfeld, D.D.R.

[k] The Permutitt Co. Ltd., no longer trades under that name and the original ion exchange manufacturing is now part of Diamond Shamrock and produces Duolite products. In consequence, Permutit S-1005 is no longer produced, Duolite ES 466 being supplied instead.

[l] Sumitomo Chemical Company, Limited, 15 5-Chome, Kitahama, Higashi-Ku, Osaka, Japan.

[m] Lachema, n. p., Brno, 621 33 Brno, Reckovice, Karasek 28, Czechoslovakia.

[n] Bayer A.G., Leverkusen, West Germany.

[o] Ayalon Water Conditioning Products, Haifa, Israel.

their constitution, functional groups and chromophore is given in Table 1. The chelating ion-exchange resins derived from the modification of chloromethylated styrene–divinylbenzene copolymers with iminodiacetic acid, available under different commercial names, remain the most popular and thoroughly studied class of commercial chelating ion-exchange resins [7,92]. A great deal of effort has been expended to study the various synthetic, analytical aspects, kinetics and applications of Dowex A-1 or Chelex-100, which contain iminodiacetic acid anchored onto chloromethylated styrene–divinylbenzene copolymers [92–100]. Exclusive reviews on iminodiacetic and other aminocarboxylic acid resins are available [15,94]. Another aspect of the commercialisation of chelating ion-exchange resins is the development of such compounds for specific use; many such resins have been prepared for different industrial processes, though their details remain hidden in patents. In view of this, the commercial potential of chelating ion-exchange resins must not be underestimated.

(v) Criteria for a compound to act as a selective ion exchanger

Several chelating ion exchangers have been found to be selective for one metal ion or another and thus it appears appropriate to discuss the criteria of selectivity for such ion exchangers. A chelating ion-exchange resin consists essentially of two components, i.e., a chelating group and a polymeric matrix. Thus, the properties of both components have to be taken into account when designing and synthesising a chelating ion-exchange resin. During the early stages of development of chelating ion-exchange resins, Gregor et al. [1] postulated that a suitable chelating group for incorporation into a polymeric matrix must have the following properties:

(i) It should be capable of resin formation, or be capable of substitution into a polymeric matrix.

(ii) It should be sufficiently stable to withstand the polymerisation or resinification process.

(iii) It should be compact enough so that its chelating ability is not hindered by the dense polymeric matrix.

(iv) Both arms of a chelate structure should be present on the same monomer unit in proper spatial configuration. Hale [5] pointed out that chelating ion-exchange resins, like conventional ion exchangers, should possess mechanical stability and resistance towards acids and bases used for regeneration of resin. According to Blasius and Brozio [35], many known chelating agents could lose their selectivity when incorporated into a polymeric matrix. Such unsuitable chelating ligands include all those ligands that do not form 1 : 1 complexes, e.g., anthranilic acid, 8-quinolinol and 1-

nitroso-2-naphthol. In view of these facts, long-chain molecules like ethylenediaminediacetic acid also appeared unsuitable, because of the improbability that the chelate configuration occurring in aqueous solution could be maintained on a cross-linked polymer. The selective behavior of a chelating ion-exchange resin is based on the different stabilities of the metal complexes formed by a resin at appropriate pH values and the point of maximal efficiency for separation of a given set of metal ions can be established by variation of the pH [35].

Recently, D'Alelio [101] suggested that for an effective chelating polymer the ligating behavior of the chelating group in the polymeric matrix should be similar to that of the active group in the monomeric system. He proposed the following strategy for the synthesis of a chelating polymer:

(i) Synthesis and characterisation of chelating properties of a model compound.

(ii) Synthesis and characterisation of an oligomer of low molecular weight (dimer, trimer, etc.) model compound and determination of its chelating properties.

(iii) When the results of the second step confirm chelation, a high molecular weight chelating polymer should be synthesised and characterised, and its chelation capacity should be determined.

Following this approach, D'Alelio et al. [101–106] synthesised and studied several chelating polymers containing hydroxyarylaminoacetates and other chelating groups and obtained encouraging results.

As pointed out by Nickless and Marshall [34] the final choice between selective resins is determined by the actual problem under study. They nevertheless gave some requirements for the design of a selective ion-exchange resin. The combination of conditions given in the literature allows one, in principle, to design (and synthesise) a suitable chelating resin with the desired selectivity. Nevertheless, most of the available resins have only moderate or poor selectivity and/or can only be produced by elaborate and expensive procedures. According to Hodgkin [47] the rather poor selectivity of most of the resins originates from the fact that the chelating groups normally anchored onto polymeric matrices are usually strongly chelating, and not very selective. The inhomogeneous chemical environment inside the resin also has a negative influence on the selectivity [47]. The reason for this is the fact that most modification reactions of the basic polymer are carried out in the heterogeneous phase, in which neighboring group effects can be quite important. Most early work in this area has neglected these complications, mainly because no methods were available to study the chemical and physical properties of the polymers in sufficient detail. Nowadays, Fourier NMR (^{13}C) and IR spectroscopy allow much better characterisation of polymeric chelating resins. Summarising the preceding discussion, the following essential requirements seem necessary for the synthesis of a chelating ion-exchange resin:

(i) The chelating ligand attached to a solid matrix should possess strong metal-binding properties and selectivity towards certain metal ions. The concept of "soft" and "hard" donors or "*a*" and "*b*" class metals can be a useful guide in this regard.

(ii) The chelating group should be capable of undergoing incorporation in a polymeric network and allow the process of polymerisation or resinification; in turn, the chelating polymer should be resistant to strong acids and alkalis at elevated temperature.

(iii) The chelating ligand should preferably be multidentate, permitting formation of a 1 : 1 chelate with a metal ion, and the chelating ion exchanger should be monofunctional as far as possible. The occurrence of mixed functional groups such as sulfonic, carboxylic or phenolic groups should be avoided in the same resin.

(iv) The chelating ion exchanger should possess good swelling properties and compatibility between polymer and the medium (generally aqueous) is essential; this can be regulated by the presence of hydrophilic groups on the polymer and by the extent of cross-linking. A higher degree of cross-linking results in increased mechanical strength, but the swelling properties of polymer are adversely affected.

B. THEORETICAL ASPECTS

Theoretical aspects of chelating ion-exchange resins have been discussed at length and most of the theories developed to study conventional ion-exchange resins are also applicable to chelating ion-exchange resins [7–9,33,38,81,95]. One of the most important theoretical aspects of the study of ion exchange resins is the theory of ion exchange equilibria and its application to chelating ion-exchange resins. The various aspects of the effect of complex formation on ion exchange equilibria and on the distribution of metal ions between the liquid and resin phases have been extensively studied [8,9,81,107–109]. The basis of all derivations is the expression for the stability constants, which can be evaluated by application of the law of mass action to the equilibria involving the complexes [110]. However, the high concentration of the functional groups in the macromolecular framework does not allow direct experimental measurement of the stability constants of the resin phase [35,81,111]. For simplification, some approximations are usually made to study the ion exchange equilibria of chelating ion-exchange resins. As a first approximation it is assumed that the coordination or complexation behavior of a chelating ion-exchange resin is similar to that of the corresponding monomeric repeating functional (chelating) unit in aqueous solution. Secondly, the stability constants determined for such a repeating unit (monomeric analogue) are valid for the respective equilibria inside a swollen resin gel [112–115].These assumptions are applicable only if 1 : 1 (metal to ligand) complexes are formed in the resin phase and the compact molecular structure of the chelating functional group limits the influence of the matrix on the process of complex formation [35,112]. Eger et al. [113,114] evaluated this concept by comparing the coordination behavior of *N*-benzyliminodiacetic acid and its cross-linked polymer analogue, the chelating ion-exchange resin Dowex A-1, towards some divalent transition metal ions and demonstrated that their (*N*-benzyliminodiacetic acid and Dowex A-1) coordination behavior is similar [113]. These workers also demonstrated that the thermodynamic properties of the ion exchange resin Dowex A-1 can be identified with the thermodynamic properties of its monomeric analogue, *N*-benzyliminodiacetic acid [113,114]. It is appropriate to mention here that excellent agreement between the experimental and calculated potentiometric behavior of cross-linked polymethylacrylic acid ion exchanger (Amberlite IRC-50) and the cross-linked chelating ion-exchange resin (Dowex A-1) was obtained by taking into account the polyionic interaction and the Donnan potential existing between the two phases, using the pK_a value of the basic monomer unit. It was also assumed, without detriment, that interaction between neighboring functional groups was negligible and that the cross-linked polymer was sufficiently homogeneous to support symmetry approximations. This formed the basis of the delineation of the theory for studying the ion exchange equilibria of chelating ion-exchange resins [112].

A detailed discussion of the theory of ion exchange equilibria is beyond the scope of this review article, but detailed treatises on this aspect of ion exchange resins are available in the literature [7–9,38,81,107–114].

C. SYNTHESIS OF COMPLEXING AND CHELATING ION-EXCHANGE RESINS

The synthesis of a chelating ion-exchange resin usually consists in the functionalisation of a polymeric matrix which generally consists of an irregular, macromolecular, three-dimensional network of hydrocarbon chains. Functionalisation means in our case incorporation of chelating ligands into polymeric matrices. Alternatively, a chelating monomer can be polymerised and subsequently cross-linked to obtain a chelating ion-exchange resin. The various methods of polymer modification and synthesising polymeric reagents have been reviewed [13,51,116–122] repeatedly in the recent years and Heitz [123] has critically examined the design, scope, and limitations of modified polymers and polymeric reagents. Two important aspects of the synthesis of chelating ion-exchange resins, viz. synthesis of a polymeric matrix and that of a chelating ion-exchange resin, are summarised in the following sections.

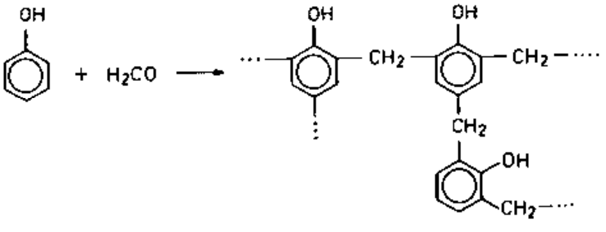
(i) Types and synthesis of polymeric matrices

Fundamentally, two types of polymeric matrices can be considered, i.e., inorganic and organic. The chemistry of inorganic supports or matrices and their functionalisation has been the subject of two recent review articles [83,84] and detailed discussion of chelating ion-exchange resins possessing inorganic supports is beyond the scope of this review. However, inorganic supports have high mechanical strength, high thermal stability, good ability to withstand high pressure and stability both towards organic solvents and to mineral acids [9]. On the other hand, there are several disadvantages associated with the use of inorganic supports, among the most conspicuous being the impossibility of a high degree of functionalisation, relatively low ion-exchange capacity and low ion-exchange rates. Silica is among the most extensively used inorganic supports [84].

The organic matrices used as supports for ion exchange resins can either originate from naturally occurring polymers or from synthetic polymers. Among the naturally occurring polymers used as supports for chelating ion-exchange resins, cellulose has been used most extensively. The chemistry of cellulose as a polymeric support, its ion exchange properties and the use of chelating celluloses for preconcentration of trace elements have recently been reviewed comprehensively by Wegscheider and Knapp [124] and Lieser [62]. Unsubstituted cellulose has a very low ion exchange capacity. In the literature, ion exchange cellulose means modified cellulose accomplished by oxidation, esterification or etherification. The ion-exchange properties of cellulose are similar to other ion exchange resins, but cellulose ion exchangers are more finely divided than ordinary ion exchange resins, present a larger surface and because of their porous structure, permit the entrance or attachment of larger molecules which are not readily adsorbed by other resins. These properties of cellulose ion-exchange resins make them useful in limited applications. The rate of exchange is also very rapid in the case of cellulose ion exchangers, although in general their capacities are smaller than those of other ion exchange resins. Cellulose-based chelating ion exchangers will not be discussed separately, but reference will be made at the appropriate places for comparing their properties with other chelating ion-exchange resins. Another important naturally-occurring chelating marine polymer is chitin, poly(*N*-acetyl-D-glucosamine) and its deacetylated derivative, chitosan, which have been useful for removing heavy metal ions from discharge water. The chelating and ion-exchange properties of chitin and chitosan have been studied in detail [125–127] and reviewed by Muzzarelli [128,129].

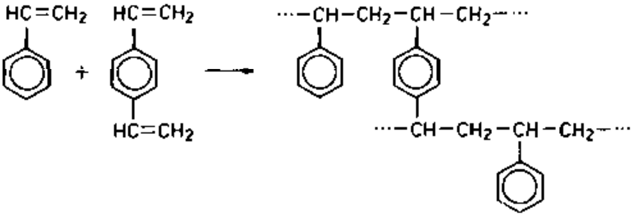
Among the synthetic organic matrices, two types of polymers can be considered, viz. condensation and addition polymers, which are extensively used as supports or matrices for chelating ion exchangers. The synthesis and properties of these polymers have been described in detail elsewhere [81,130,131], and are only briefly summarised here.

Condensation polymers are high-molecular weight cross-linked structures usually formed by an ionic organic reaction mechanism from small polyfunctional monomers through removal of small molecules such as water, alcohol, and ammonia and forming new C–C, C–N, C–O or other bonds. Phenols may thus condense with formaldehyde to give cross-linked condensation polymers having a structure of the type (**II**) depicted below. Such condensation polymers can easily undergo hydrolytic and cleavage reactions and therefore have poor chemical and mechanical stability.



(II)

Addition polymers are cross-linked structures formed by free-radical polymerisation of mixtures of olefinic and diolefinic compounds. An important example of this type of polymeric support consists in the polymerisation of styrene with difunctional divinylbenzene (DVB). A styrene–DVB copolymer possesses a structure as shown in (**III**). These addition polymers contain only C–C bonds and thus resist any hydrolytic cleavage, withstand wide variation of pH over alkaline and acidic ranges and are stable at relatively high temperatures. Among addition polymeric supports, the copolymers of acrylic acids and divinylbenzene have also been extensively used. Addition polymeric supports are preferred over condensation polymer matrices whenever possible, because of their higher chemical stability and mechanical strength.



(III)

Condensation polymers, nevertheless, continue to be popular as polymeric supports for chelating ion-exchange resins and many important chelating ion exchangers have recently been synthesised [132] on the basis of condensation polymerisation. However, the majority of commercial ion-exchange resins that find wide application possess styrene–divinylbenzene copolymer matrices. The various consequences of the nature of polymeric matrices on the properties of ion exchange resins have recently been reviewed [133,134]. A recent systematic study of styrene–divinylbenzene copolymers as matrices revealed that the homogeneity of the network or matrix has a great influence on the properties of the ion exchangers [135]. The more regular a network is built up, the better are the qualitative features the matrix exhibits.

(ii) Functionalisation and incorporation of chelating ligands into polymeric matrices

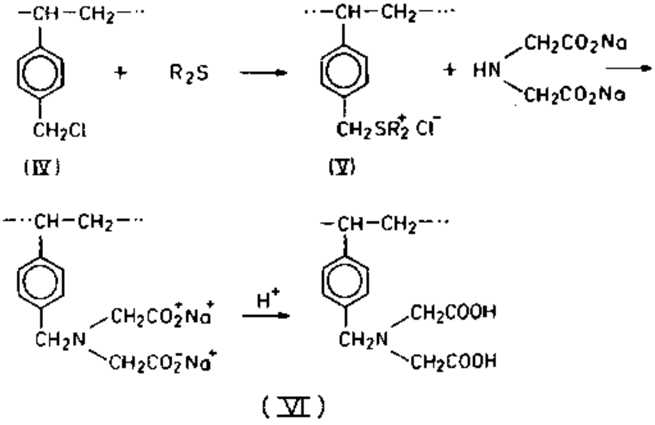
The general methods of incorporating active functional groups (in this case chelating ligands) have been summarised by Akelah and Sherrington [51]. According to them, three methods can be distinguished to incorporate active functional groups into polymer chains:

(a) direct polymerisation and copolymerisation of monomers containing the desired functional groups,

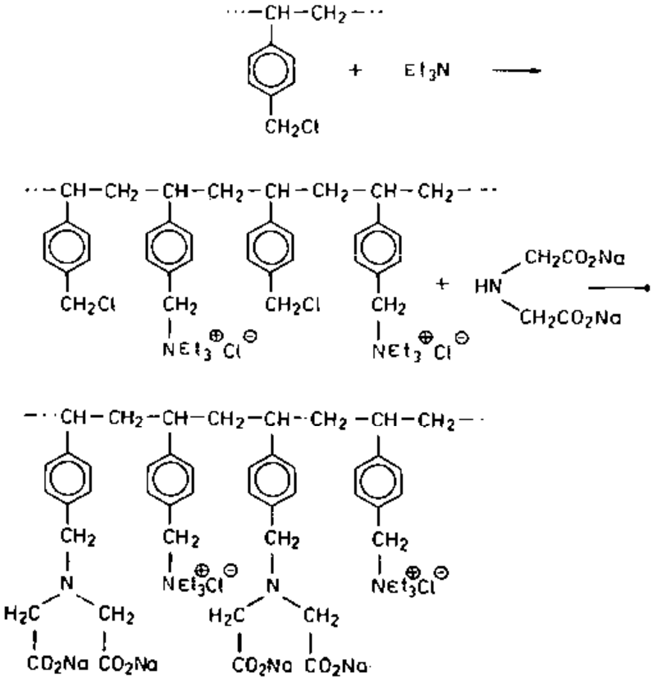
(b) chemical modification of a preformed polymer,

(c) a combination of (a) and (b).

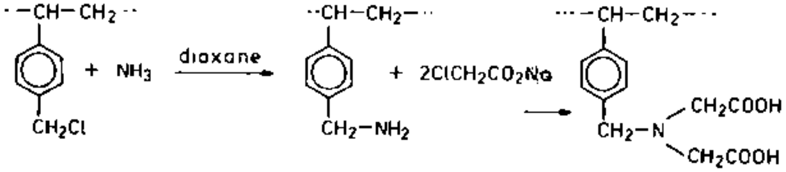
These three methods have been used in one or the other form to synthesize the majority of chelating ion-exchange resins. Some special methods have also been used to synthesise many individual resins [136]. The various methods for the synthesis of these exchange resins have been reviewed recently by several authors [11,24,34,35,42,47,51,136–139]. Some are devoted exclusively to the synthesis of chelating ion-exchange resins [42,47], whereas other articles also cover other aspects of these ion exchangers. The synthesis of polymers with macrocyclic chelating ligands as pendant or anchor groups has also been discussed by a number of authors [48,53,54,56,57,140]. The method involving incorporation of chelating ligands into preformed polymers or matrices to synthesise chelating ion-exchange resins is preferred to other methods in view of the fact that the degree of functionalisation can be controlled by varying the amount of cross-linking agents and the extent of modification in preformed matrices. The various approaches adopted for the synthesis of chelating ion-exchange resins can be illustrated by some typical syntheses. A large number of such ion exchange resins have been prepared by attaching a chelating ligand to a preformed polymer and the most extensively used preformed polymers have been the copolymers of styrene and divinylbenzene, which are unreactive as such. This material is normally first converted into its chloromethylated derivative and then treated with a chelating ligand to obtain a chelating ion exchanger. Several methods are available for chloromethylating cross-linked polystyrene [141], but a satisfactory method of chloromethylation consists in treatment of cross-linked polystyrene with chloromethyl methyl ether under Friedel–Crafts reaction conditions [142]. The conversion of chloromethylated polystyrene (**IV**) into its sulfonium salt (**V**) is an important step in the synthesis of an iminodiacetic acid chelating ion-exchange resin (**VI**); the sulfonium salt is hydrophilic whereas the chloromethylated resin is not and will not react appreciably with the sodium salt of iminodiacetic acid. Alternatively, the problem of hydrophilicity of chloromethylated polystyrene can be solved by partially converting it to a quaternary salt by treating it with triethyl amine (or any other tertiary amine) followed by reaction with a chelating group [143]. The synthesis of iminodiacetic resin by this method of partial substitution is shown in Scheme 1. Using this approach, Melby [144] synthesised several chelating ion-exchange resins. Several other functionalised derivatives of styrene–divinylbenzene copolymers, such as sulfonated [145], bromo [146], lithiated [146], hydroxyethyl [146], hydromethyl [147], phosphinated [148], thiolated [146,149], amino [150], aldehyde [151] etc., have also been prepared. A comprehensive review of functionalised polymers has recently been published [152].



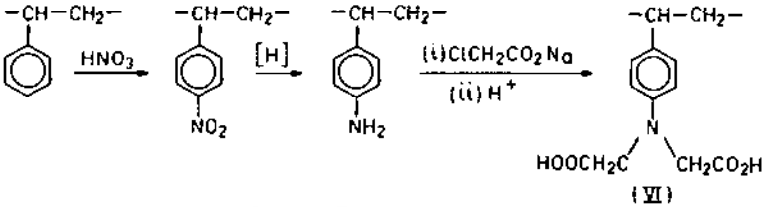
Another approach for synthesising chelating ion-exchange resins consists in the modification of a polymer through a sequence of reactions on the polymer itself. For instance, the synthesis of iminodiacetic acid resin using styrene–divinylbenzene copolymers as polymeric support can be carried out as depicted in Scheme 2 [153] and Scheme 3 [154]. Several poly(hydroxamic acid) resins have also been prepared [155] by this method. The fact that this type of synthesis involves a number of steps is a serious disadvantage because of the possibility of contamination of the end product with by-products and intermediate products due to their incomplete conversion and the



scheme 1

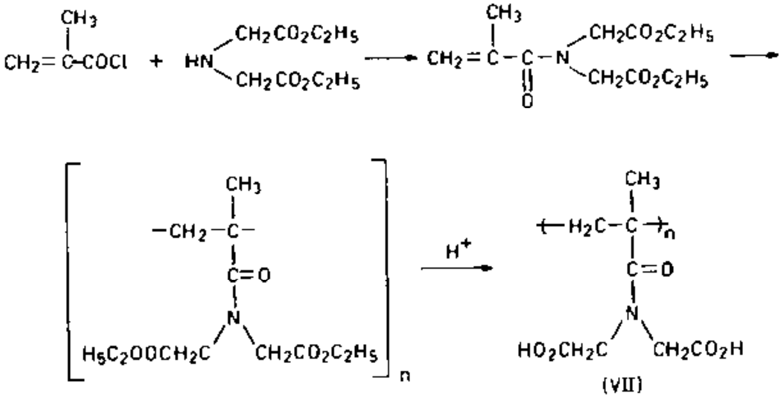


scheme 2

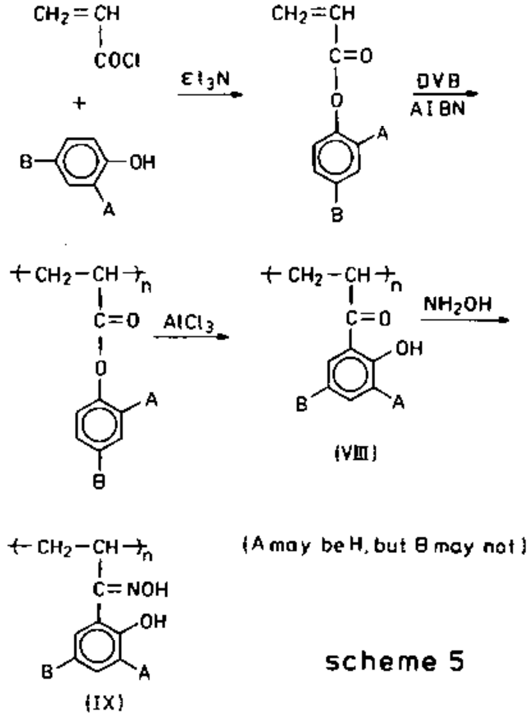


scheme 3

inherent problem of their removal. Contamination of chelating ion-exchange resins adversely affects their selectivity [47]. In view of this, the best synthesis of a chelating ion-exchange resin can be envisaged to be one which involves the minimum number of steps [47]. In recent years, a number of chelating ion-exchange resins have been prepared by the polymerisation of a monomeric unit (of chelating ligand) in the presence of a cross-linking agent. This approach of synthesising a chelating ion-exchange resin can be illustrated by the synthesis of an iminodiacetic acid resin on a polyacrylate as shown in Scheme 4 [156]. Some copper(II) specific ion exchange resins (**IX**) containing hydroxyoxime groups have also been prepared from substituted phenyl acrylate polymers (**VIII**) via the Fries rearrangement using this approach [157], depicted in Scheme 5. In this procedure considerable mani-



scheme 4

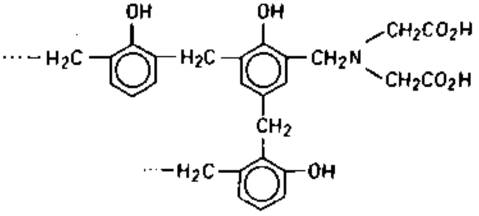


scheme 5

pulation to optimise the conditions for copolymerisation is necessary to obtain a good yield of the chelating ion-exchange resin in satisfactory physical form [51]. However, this method may lead to the formation of a relatively "purer" chelating ion-exchange resin having less contamination with by-products.

Several solvents, such as dimethylformamide, dimethylsulfoxide, dioxane, tetrahydrofuran, chlorinated alkanes, pyridine, etc., have been used for the modification of preformed polymers with chelating ligands. Dimethylformamide has been found to be most stuitable when modification of chloromethylated styrene was involved [144,158]. Though dimethylformamide reacts with chloromethylated styrene to form by-products, the extent of these side reactions is negligible when the reactions are carried out at or below room temperature [159]. These reaction conditions, however, lead to lower loading of the polymer [160].

Another important method of synthesising chelating ion-exchange resins is that of polycondensation. Many compounds that form chelates with metal ions can be copolymerised with phenols and aldehydes (generally formaldehyde), to obtain a variety of chelating ion-exchange resins [7,34,35,42,81,136]. For instance, anthranilic acid [161,162], anthranilic acid–diacetic acid [163], *m*-phenylenediamine diglycine [1], and *m*-phenylenediaminetetraacetic acid [163], among many other ligands have been copolymerised with formaldehyde and mono- or polyphenols to synthesise condensation chelating polymers. Many other chelating resins, prepared by a polycondensation method, have been found selective for different metal ions [164,165]. Recently, a quadridentate chelating ligand, *N*-(*o*-hydroxybenzyl)iminodiacetic acid, has been copolymerised with phenol and formaldehyde to obtain a new chelating ion-exchange resin (X), commercially available under the name of Unicellex UR-50 [132,166]. Some condensation chelating ion-exchange resins have been prepared by a different method in which a condensation resin matrix is first synthesised and a chelating ligand is subsequently introduced. For example, *o*-phenylenebis(oxyacetic acid) resin has been prepared by this method [167,168].



(X)

The chelating ion-exchange resins prepared as above have achieved only limited success in terms of selectivity. Recently, Efendiev and Kabanov [169] advanced a new approach based on the "memory" of monomers, to develop highly selective chelating ion-exchange resins. The idea of such selective metal sorbents originates from: the observation of the similar behavior depicted by silica gels having increased adsorption selectivity with respect to specific substrates [170–172] and the principle of the "adjustment" of macromolecular chains to the optimum tertiary structure for the adsorption of the corresponding substrates by macromolecular enzymes [173]. Such a contention is backed by the synthesis of several such polymer sorbents [174–176].

The general principle of the method of Efendiev and Kabanov [169] involves three steps in the preparation of such polymers. In the first step, the linear polymer is treated with a solution of a metal ion to be adsorbed in solution, i.e. under conditions when segments of the macromolecule are still mobile enough. The second step is fixation of the optimum conformation of the macromolecules for ion uptake by cross-linking the metal polymer complex. The final step involves removal of the template metal ion from the cross-linked sorbent. The underlying idea behind this approach is that the linear chelating ion exchanger or sorbent develops a kind of "memory" for particular metal ions, and when it is brought into contact with a mixture of metal ions, it picks up that particular metal ion, which is fixed in its "memory". In other words, it picks up that specific metal ion for which it has been trained. This approach can be illustrated by the practical example in which the diethyl ester of vinylphosphonic acid (DEVPA) and acrylic acid (AA) have been chosen as the initial monomers to pepare polymer sorbents. DEVPA and AA are copolymerised by means of photochemical initiation of the monomer mixture in the presence of 1% of cumene hydroperoxide in a sealed tube. The resulting copolymers are cross-linked using *N*,*N*′-methylenediacrylamide (MDAA) to obtain a three-dimensional structure [177,178]. For instance, a macromolecular sorbent favorably prearranged for the sorption of copper(II) was obtained by (i) mixing of the linear copolymer (derived from DEVPA and AA) with copper ions in acidic solution under conditions when sorption does not take place, (ii) slow titration of the linear copolymer with copper ammonia solution and isolation of the copper–copolymer complex precipitate, (iii) fixation of the optimal conformation for the uptake of copper ions by cross-linking of the copper–copolymer complex, and (iv) desorption of copper ions from the cross-linked sorbent with 1 M hydrochloric acid.

A few other novel methods for the synthesis of selective chelating ion-exchange resins will be discussed later.

D. CHARACTERISATION OF CHELATING ION-EXCHANGE RESINS AND THEIR METAL COMPLEXES

The characterisation of newly synthesised chelating ion-exchange resins and their metal complexes is of prime importance. In the case of chelating ion-exchange resins, characterisation has to be in terms both of its analytical and physical properties and its characterization involves the use of analytical and physical techniques. The use of physical methods in the characterisation of this type of ion exchanger is assuming greater importance as the selectivity is considered to depend on the chelating functional group. Therefore precise determination of the coordination behavior of the functional group towards metal ions and the geometry around the metal ion is essential for the further development of metal-ion selective ion-exchange resins. Thus both analytical and spectroscopic methods used for the characterisation of chelating ion-exchange resins are briefly reviewed in the following sections.

(i) Analytical methods

Various analytical methods used for the characterisation of ion exchangers and chelating resins have been described at length by several authors [7–9,33,81,95]. These analytical methods are used to determine density, grain size, water content, ash content and such parameters as capacity, distribution coefficient and selectivity coefficient. According to the simplest definition, the capacity of an ion exchanger is defined as the number of counter-ion equivalents in a specified amount of the material [81]. This simple definition of capacity has undergone many modifications and various definitions and methods for its determination have been dealt with by Inczedy [9] and Helfferich [81]. A closely related parameter is the distribution coefficient (D)

$$D = \frac{\text{amount of metal ion per g of dry resin}}{\text{amount of metal ion per cm}^3\text{ of solution}}$$

and for a very dilute solution of an ion A, the distribution coefficient for any ion exchange can be given by the expression

$$D = [\overline{\mathrm{A}}]/[\mathrm{A}] \tag{1}$$

where $[\overline{\mathrm{A}}]$ is the concentration of ion A in the resin phase and [A] is the concentration of ion A in the aqueous phase. The distribution coefficient can be evaluated by determining the metal ion concentration in an equilibrated solution by simple analytical methods. Both static and dynamic methods with or without the presence of radioisotopes have been used for the determination of distribution coefficients of chelating ion-exchange resins [9,81,97,179]. Another important parameter is the selectivity coefficient [180] for the exchange of two ions A and B, of charge a and b, respectively, given by the expression

$$K_{\mathrm{B/A}} = \frac{[\overline{\mathrm{A}}]^{b}[\overline{\mathrm{B}}]^{a}}{[\mathrm{A}]^{b}[\mathrm{B}]^{a}} \tag{2}$$

where the bars indicate the resin phase. Equation (2) is comparable to the equilibrium constant of an ionic equilibrium reaction. Thus if one considers the exchange reaction of two ions A and B with charges a and b being

$$a\,\mathrm{B}^{b} + b\,\mathrm{A}^{a} \rightleftharpoons a\,\mathrm{B}^{b} + b\,\mathrm{A}^{a}$$

the equilibrium constant for this reaction is identical to $K_{\mathrm{B/A}}$. These two expressions (1) and (2) have been defined for ion exchange resins of the conventional type only; however, these expressions can be equally well applied for chelating ion-exchange resins [181,182]. Experimental details for the determination of these parameters are well documented in the literature [7]. Both the distribution and selectivity coefficients depend on the degree of cross-linking, specific capacity (the number of equivalents of the fixed exchange groups per gram of the resin) and on the nature of the chelating group [105,182]. Detailed accounts of ion exchange selectivity and of resin selectivity have been given by Reichenberg [183] and Diamond and Whitney [184].

The heterogeneous protonation equilibria of chelating ion-exchange resins has been studied by several workers [81,97,181–187] and Szabadka [187] has recently given a general equation for the determination of protonation constants of chelating ion-exchange resins.

The swelling, which is a measure of the elastic properties of the ion exchange resins and a very important source of thermodynamic data, has been dealt with by several workers [188–191].

(ii) Physico-chemical methods

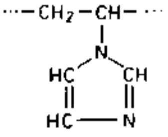
A number of physico-chemical methods mainly based on the spectral and magnetic properties of chelating ion-exchange resins and their metal complexes are now used for characterising these polymeric compounds. A detailed account of these methods have been given by Kaneko and Tsuchida [11]. These methods include all techniques used for characterisation of macrocrystalline compounds. Infrared spectroscopy provides an excellent tool for characterising chelating ion-exchange resins (in conjunction with their elemental analysis) and to locate the coordination or bonding sites in the metal complexes of chelating resins [192–194]. Attempts have also been made to study the metal–ligand vibrations in the far-infrared region [195,196]. ESR spectroscopy is being increasingly used to study the coordination structure. The interaction between the spin of the central metal ion and the coordinated ligand decides the absorption pattern and its *g*-values [197–200] which, in turn, can be used to study the metal–ligand bond. The diffuse reflectance electronic spectra provide an accurate and simple method for determining the geometry around the transition metal ions in the complexes of chelating ion-exchange resins [195,197,198,201–204]. Magnetic susceptibility measurements have been used to determine the spin-state of the metal ion in such complexes [205,206]. The extended X-ray adsorption fine structure (EXAFS) [207–209], scanning electron microscopy/electron dispersive analysis of X-rays (SEM/EDAX) and high-energy electron spectroscopy (ESCA) techniques have been used to characterise the ion exchange resins and complexes of chelating ion-exchange resins [210–214]. Thermal studies (TGA and DTA) have also been used to explore certain aspects of ion exchange resins and their metal complexes [215,216]. The possibility of using solid-state NMR to study these compounds has also been explored [217–219]. The great improvement in ^{13}C NMR techniques in recent years has made it possible to use this powerful spectroscopic method for the study of cross-linked polymers, as long as a suitable solvent can be found to swell the polymer [47,157,220,221]. Fourier-transform infrared spectroscopy has also been used to check the chemistry of cross-linked polymers and their metal complexes [47]. Mössbauer spectroscopy [166,205] has been found useful for the study of iron and some lanthanide complexes of chelating ion exchange resins. In recent years, several styrene–divinylbenzene copolymers having different functional groups have been analysed qualitatively by the combination of infrared data with the results of Curie pyrolysis–gas chromatography–mass spectroscopy [222–224]. This technique has been improved a great deal in recent years by Blasius et al. [225–227], who have amply demonstrated the use of this method for characterisation of ion exchangers with cyclic polyethers as anchor groups. Applications of these methods will be shown during the discussion of individual chelating polymers and their metal complexes. Increasing importance is now attached to the use of these methods, as various physical measurements can help in adequate characterisation of cross-linked chelating ion-exchange resins to indicate the chemical environment of the attached chelating group.

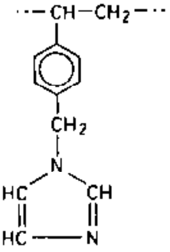
E. SURVEY OF AVAILABLE CHELATING ION-EXCHANGE RESINS

In the following sections, a brief survey of available chelating ion-exchange resins will be presented, classified according to their donor atoms.

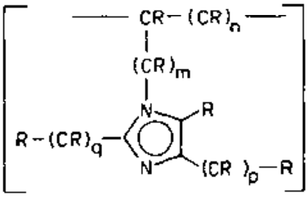
(i) Chelating ion-exchange resins containing nitrogen as the only donor atom

The number of chelating ion-exchange resins with nitrogen as the only donor atom has been growing in recent years. Blasius and Brozio [35] have reviewed the early development of such chelating ion-exchange resins. Gold and Gregor [228,229] reported the synthesis of a complexing poly(*N*-vinylimidazole) (**XI**) polymer which contains aromatic nitrogen as the only donor atoms. Chelation was found in the case of copper(I) and silver(I) [228]. Related systems containing imidazole supported on styrene–divinylbenzene copolymers have also been reported [195,230,231]. This complexing resin (**XII**) can be synthesised from chloromethylated styrene–divinylbenzene copolymers and the sodium [195] or lithium [230] salt of imidazole, using dimethylformamide or tetrahydrofuran as a solvent. Welleman et al. [195] studied the ligating behavior of this immobilised ligand (PS–Iz) with first-row transition metal ions taken in the form of their complexes with *N*-n-butylimidazole, (n-BuIz), which are soluble in chloroform. Upon reaction of the immobilised imidazole with transition metals in chloroform, a shrinking of the polymer was observed, explained in terms of additional cross-linking through the metal ions. Several metal complexes of the general formula $M(PS–Iz)_n(n\text{-}BuIz)_nX_2$ in which PS–Iz stands for polystyrene-bound imidazole ligand. X for anions such as ClO_4, NO_3, BF_4, Cl or Br, and M = Co(II), Ni(II), Cu(II) or Zn(II). The stereochemistry of the polymeric metal complexes has been established on the basis of their elemental analysis, infrared, ligand field, and ESR spectra. Spectroscopically the polymeric compounds behave like the corresponding monomeric compounds, $M(\text{benzylimidazole})_mX_2$, indicating that the imidazole ligands in a polymeric matrix are quite flexible in their coordination behavior, except in


(XI)

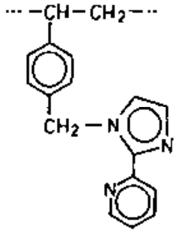

(XII)

the case of very low degrees of substitution or high degrees of cross-linking. Drago and Gaul [230] used the immobilised imidazole ligands (having varying degrees of cross-linking and loading) to examine the utility of some cobalt diphenylglyoximates, $Co(DPGB)_2 \cdot 2CH_3OH$, as a reagent to investigate the existence of isolated functionalised sites in the resins. Several polymeric ion-exchange resins composed basically of cross-linked (divinylbenzene or any other suitable cross-linking agent) recurring units of substituted imidazoles have been reported (**XIII**) capable of being utilised to separate copper, nickel and cobalt both from each other and also from other metals in solution [232,233]. These ion exchange resins have been prepared by copolymerising vinylated substituted imidazoles with divinylbenzene in β-azo-isobutyronitrile with various substituents including substituted pyridyl or amines such as bis-picolylamine. The ion exchange resins prepared by this method have been found to have higher capacity and selectivity than the similar resins prepared from polystyrene [232]. Some ion exchange resins containing pyridylimidazole (**XIV**) and pyridylimidazoline (**XV**) groups anchored onto macroporous styrene–divinylbenzene copolymers have also been evaluated for their ion-selective properties and found useful for the separation of copper and iron mixtures [234]. This work has been extended to incorporate 2-(2-pyridyl)benzaimidazole into a polystyrene matrix by treating chloromethylated styrene–divinylbenzene copolymers with the ligand

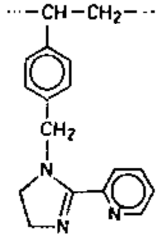


(XIII)

where $n = 1, 2$ or 3
$m = 0, 1$ or 2
$q = 0$ or 1
$p = 0$ or 1



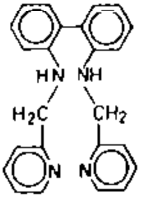
(XIV)



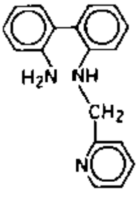
(XV)

in the presence of triethylamine in refluxing dimethylformamide. *N*-Substituted imidazoles have also been anchored onto silica and these modified silicas have been used as catalysts [235], similar to polystyrene–imidazole derivatives [236].

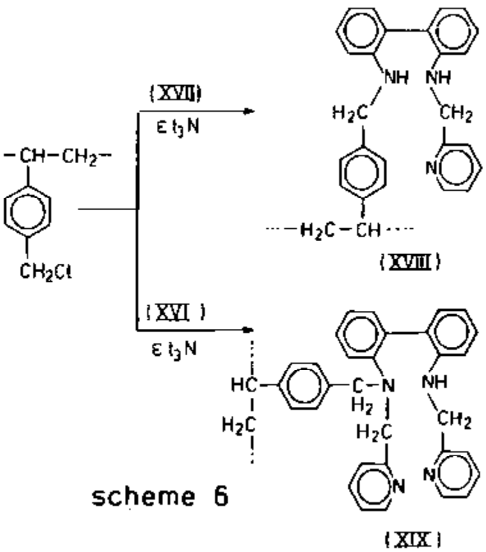
In recent years, quite a few chelating ion-exchange resins incorporating pyridine derivatives have been synthesised to evaluate their ion-selective properties. A large number of such ligands based on derivatives of *N*,*N*′-bis(2-pyridylmethyl)-2,2′-diaminophenyl (**XVI**) and *N*-(2-pyridylmethyl)-2,2′-diaminobiphenyl (**XVII**) have been prepared by Melby [144]. The chelating polymers have been prepared by alkylating the derivatives of (**XVI**) and (**XVII**) with chloromethylated cross-linked polystyrene in the presence of triethylamine as the acid acceptor and dioxane solvent as depicted in Scheme 6. These products are presumed to have structures essentially as shown in (**XVIII**) and (**XIX**), in which direct *N*-alkylation has occurred. The phenolic ligands (**XX** and **XXI**) were *O*-alkylated with the chloromethylated resin in the presence of sodium methoxide and DMF as solvent to obtain products typified by structure (**XXII**). These chelating resins were synthesised to



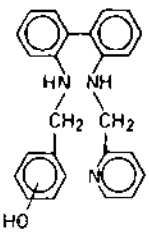
(XVI)



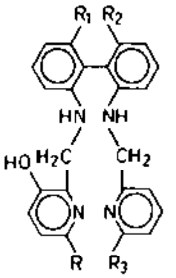
(XVII)



scheme 6

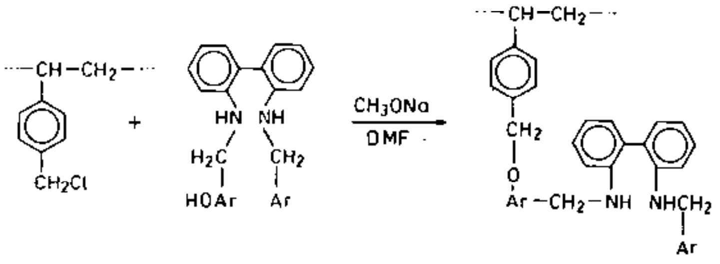


(XX)



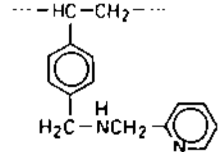
(XXI)

R, R_2, R_3 = H or CH_3

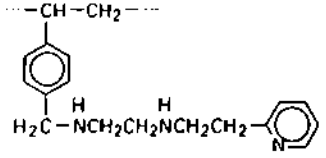


(XXII)

selectively bind copper(II) from aqueous solutions containing other metal ions, such as iron(III), based on the observation that copper(II) generally conforms to 4- or 6-coordinate structure and can exist in a variety of geometries, while iron(III) most commonly forms six-coordinate octahedral complexes. Thus a ligand with a maximum of four donor atoms and a structure, which restricts the donor lone pairs to tetrahedral disposition (obligatory tetrahedral), or which is flexible enough to permit tetrahedral disposition (facultative might be expected to favour chelation of copper(II) over iron(III). This was indeed found to be the case with the ligands studied herein. The tridentate chelating polymers derived from (XX) have been found to have relatively small capacity for copper(II) depending, for example, on the polymer attachment site, whereas the group of tetradentate chelating polymers have very high copper(II) affinities ranging up to 90% of the theoretical values despite the polymer attachment site being *ortho* to the ligand methyl amino group. These chelating polymers were found useful for selective binding of copper(II) and silver(I), or nickel(II) from acidic aqueous transition-metal ion mixtures. A group of new chelating resins, incorporating 2-picolylamine derivatives in a polystyrene matrix, has been described as selective sorbents for separation of non-ferrous transition-metal ions such as copper and nickel from acidic hydrometallurgical leach liquors, where polystyrene–iminodiacetic type resins are not applicable [237]. In addition, these resins act as catalysts for in situ reduction of iron(III) to iron(II) in the presence of suitable reducing agents, such as sulfur dioxide or formaldehyde. These chelating resins have been prepared by following the method of Grinstead and Nasutavicus [238] treating chloromethylated styrene with *N*-alkylated-2-picolylamine. These resins derived from 2-picolylamine, *N*-methyl-2-picolylamine, *N*-(2-hydroxyethyl)-2-picolylamine, *N*-(2-methylaminoethyl)-2-picolylamine and bis(2-picolyl)amine are of particular interest. Two commercial chelating resins, Dowex XF-4195 and Dowex XF-4196, possessing *N*-alkylated picolylamine functional groups (cf. Table 1) offer many interesting possibilities in the extractive metallurgy of copper, nickel and cobalt. Their selectivity for copper and nickel over iron and most other cations in acid solutions and their ability to be regenerated with sulfuric acid or ammonia solution make them useful in a number of hydrometallurgical applications [239]. The properties and hydrometallurgical applications of these two chelating ion-exchange resins have been described by Jones and Grinstead [240]. However, it may be mentioned that the chelating resins possessing 1,4′-bisimidazole and pyridyl-imidazole have been found to have improved capacity and selectivity over Dowex XF-4196 [237]. Recently, several bidentate and tridentate chelating resins incorporating 2-pyridylmethylamine (**XXIII**) and *N*-2-(2-pyridyl)ethylenediamine (**XXIV**) into chloromethylated styrene–divinylbenzene (2%) copolymer beads have been evaluated for their chelation capacity towards transition metal ions [241]. The selectivity of these resins follow the order $Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$, which is in accord with the order of the formation constants of the anchored ligands. These chelating resins with pyridine derivatives have been found to possess higher capacity and selectivity as compared to chelating resins containing salicylamine and 2-theonyl amine functional groups. These resins have been claimed to be useful for the elimination of trace amounts of harmful heavy metal ions, such as Hg^{2+} and CrO_4^{2-}.

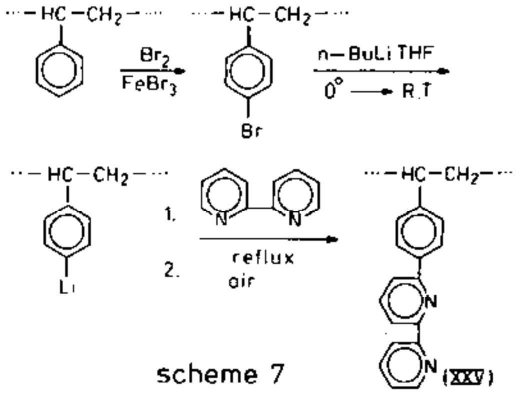


(XXIII)



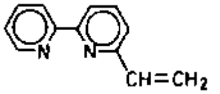
(XXIV)

A versatile bidentate ligand, 2,2′-bipyridine, has been incorporated into polystyrene–divinylbenzene copolymers by Card and Neckers [242] according to the sequence of reactions depicted in Scheme 7. The complexation of the polymer supported bipyridine with several metals in tetrahydrofuran was studied. The infrared spectra of the metal complexes were found to be very similar to each other but quite different from that of the chelating resin (**XXV**) indicating its bidentate mode of coordination. Poly(vinyl-2,2′-bipyridine) ligands have also been synthesised by the polymerisation of 6-vinyl-2,2′-bipyridine (**XXVI**) and 4-vinyl-4′-methyl-2,2′-bipyridine (**XXVII**) to study their ligating behavior towards various transition metal ions [243]. The metal complexes derived from poly(styryl)bipyridine have mainly been used as catalysts for hydrogenation [244,245]. Poly(styryl-1,8-naphthyridine) (**XVIII**) has also been prepared [246] by a similar procedure as adopted for the synthesis of poly(styrylbipyridine) [245]. Its versatility as a polymer-based chelating ligand has been demonstrated by isolating its complexes with transition metal and lanthanide ions in ethyl acetate. With copper(II) nitrate and copper(II) chloride, poly(styryl-1,8-naphthyridine took up 0.46 and 0.81 mmol Cu g^{-1} corresponding to 28 and 49% of the available 1,8-naphthyridine present in the polymer, respectively. The large difference in amount of loading observed for these two salts of copper(II) reflects the known coordination chemistry, as copper nitrate and copper chloride form 1 : 2 and 1 : 1 complexes with 1,8-naphthyridine, respectively [247,248] and supports the suggestion that the polymer is flexible enough to allow more than one

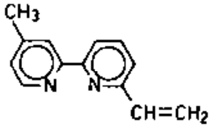


scheme 7

(XXV)

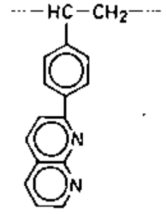


(XXVI)

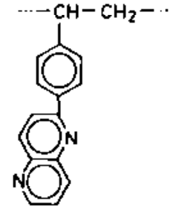


(XXVII)

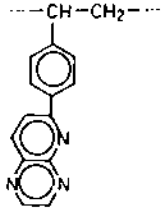
1,8-naphthyridine group to coordinate to a metal atom. The chelating polymer incorporating 1,8-naphthyridine has been found to coordinate less strongly than the corresponding bipyridine derivative (**XXV**), because of the tendency of the former to make four-membered rings on chelation. These studies have been extended to the preparation of polystyryl-1,5-naphthyridine (**XXIX**) and polystyryl-pyrido)2,3-*b*)pyrazine (**XXX**) to obtain new polymer systems which contain the potential of stepped bridging to metal ions [249]. The ligating behavior of these complexing polymers with different copper(II) salts was studied and various complexes were characterised by elemental analysis and infrared spectra. The loading ability of the three resins containing 1,5-naphthyridine, 1,8-naphthyridine and pyrido(2,3-*b*)pyrazine was compared by three different methods, establishing the superiority of polystyryl-pyrido(2,3-*b*)pyrazine (**XXX**). It was expected that the presence of both chelate and bridge sites for metal attachment contribute to making (**XXX**) the most promising metal complexing agent of these polymers. Several polymeric chelating ligands have been derived from 1,3-bis(2′-pyridylimino)isoindolines (**XXXI**) and their chelating ability was demonstrated by studying their copper(II) complexes [250]. Tridentate chelating pyrazole derivatives have recently been incorporated into a polystyrene matrix by treating chloromethylated styrene–divinylbenzene copolymers with *N*, *N*-bis(3,5-dimethylpyrazol-1-yl-methyl)(*p*-hydroxy)aniline (**XXXII**) in dimethylformamide in the presence of sodium methoxide [160]. It appears



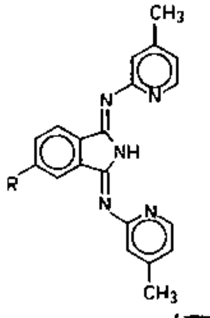
(XXVIII)



(XXIX)

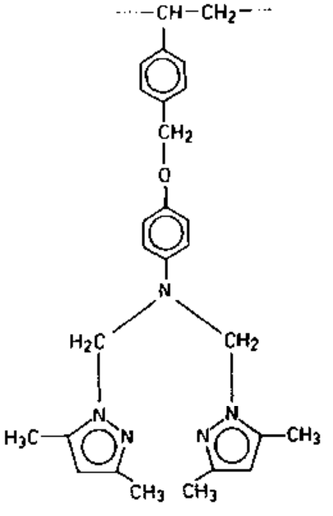


(XXX)



$R = NO_2, NH_2, NHCOCH_3,$
$NHSO_2CH_3,$
$NHCOC(CH_3) = CH_2),$
$NHCONH(CH_2)_2CO_2C(CH_3) = CH_2)$

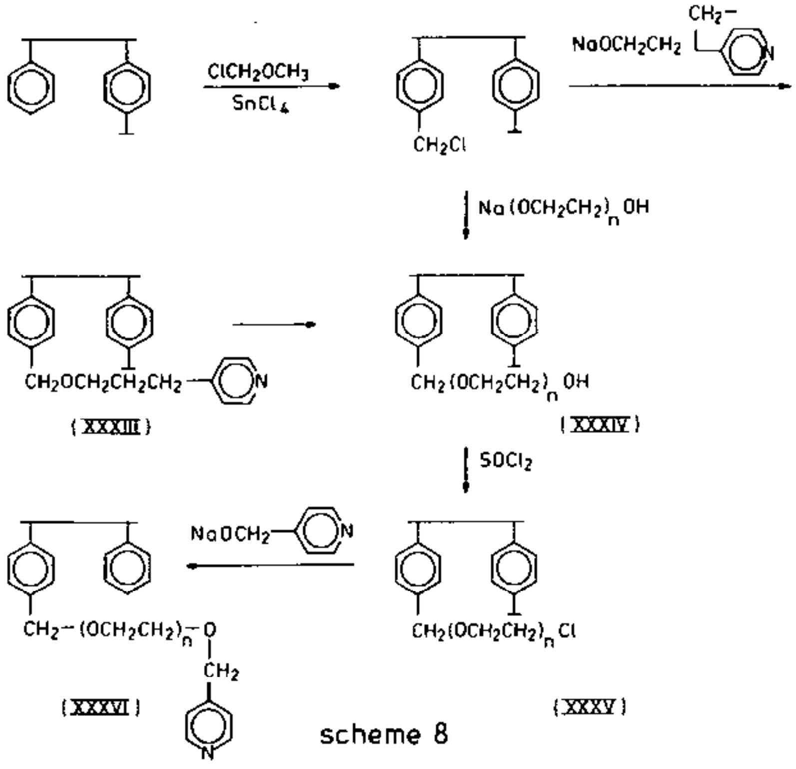
(XXXI)



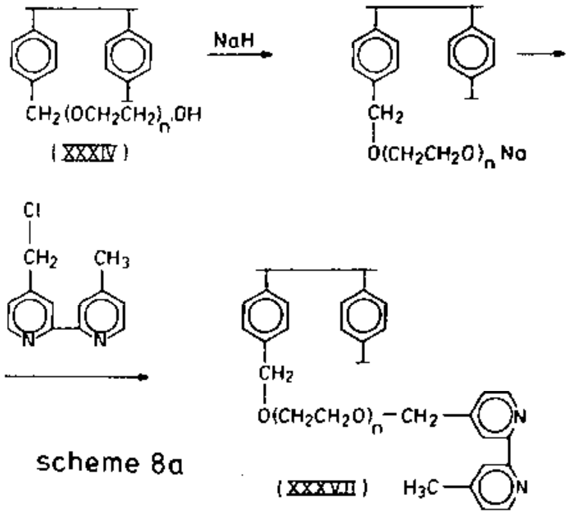
(XXXII)

that these ligands act as tridentate chelating agents both dissolved and in their immobilized form. Preliminary studies indicate that these ligands bind copper(II) strongly [251].

Chelating ion exchange resins mainly suffer from two shortcomings, namely, slow uptake of metal ions due to steric hindrance of the dense polymeric matrix and lower activity of the ligands situated at the inside of resins. To overcome these limitations, Nishide et al. [252] have synthesised several chelating resins by combining various pyridine derivatives to poly(styrene) beads with a spacer group or a graft chain. Oligo(ethylene oxide) and the copolymers with 1-vinylpyrrolidone were selected as the spacer group and as the graft chain for use in water. The spacer-type pyridine beads have been synthesised as shown in Schemes **8** and **8a**. It has been found that these spacer- and graft-type beads show high rates and large stability constants and act as effective chelating resins. The pyridine residues are more labile due to spacer groups and graft chains compared with the poly(4-vinylpyridine) powder. The large stability constants of (**XXXVI**) and (**XXXVII**) and in turn, the greater stability of their copper(II) complexes can be attributed to a chelate effect. The ESR spectra of these complexes also reveal the effect of the long spacer group and the graft chain. The ESR parameters ($g_{\perp} = 2.070$, $g_{\parallel} = 2.242$, $A_{\parallel} = 150$ G) showed that the coordination structure of the copper(II) complexes is square planar based on the pyridine beads. The ESR signals were clearly split for the copper(II) compounds of (**XXXV**) and (**XXXVII**), compared with that of (**XXXVIII**), meaning that the pyridine residue of the long-spacer type (**XXXV**) and the graft-type (**XXXVII**) can complete the complexation with copper(II) while

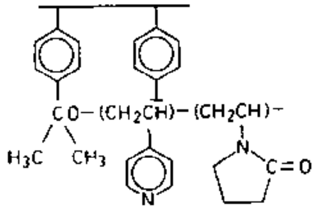


scheme 8

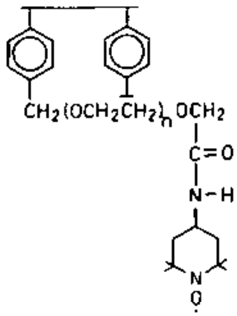


scheme 8a

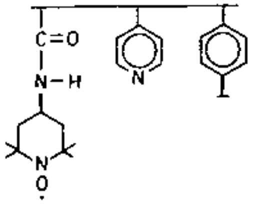
the pyridine residues of (**XXXVIII**) are immobilised and do not coordinate to copper(II). Some spin-labeled model compounds of the long-spacer type beads (**XXXIX**) and of the poly(vinylpyridine) (**XL**) have also been synthe-



(XXXVIII)



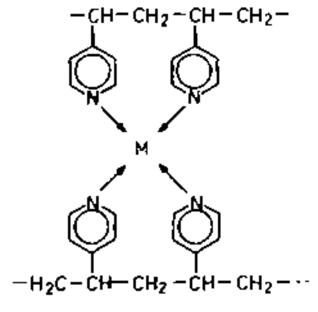
(XXXIX)



(XL)

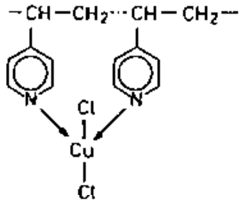
sised by Nishide et al. [252] and ESR spectra of spin-labeled beads compared with those of the copper(II) complexes of the spacer-type and graft-type pyridine beads.

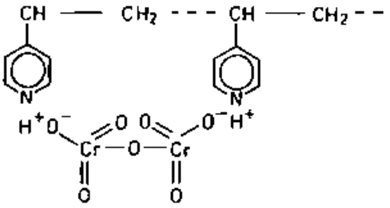
Polystyrene-bound pyridine has been prepared by a suspension technique to study the bridge-splitting reactions with dimers of the type $[Rh(C_6H_5)_3P(CO)Cl]_2$ [245], but poly(4-vinylpyridine) has been found to behave as a chelating resin [253–255]. It will form a stable intrapolymer chelate with copper ions in a fashion depicted in (**XLI**). The complexation of copper(II) with poly(4-vinylpyridine) partially quarternized in aqueous solution has been studied potentiometrically, spectroscopically (visible and ESR spectra) and viscometrically by Nishikawa and Tsuchida [253]. The overall formation constants of the polymer system were found to be much larger

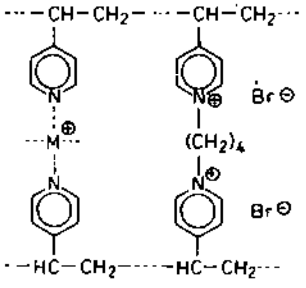


(XLI)

than those of the monomeric analogue and enhancement of the successive formation constants was attributed to the polymer effect. The copper(II) complex with poly(4-vinylpyridine) has also been shown to act as a useful catalyst for the oxidation of phenols and ascorbic acid [254,256,257]. However, it was observed that the complexed polymer was markedly contracted due to intra-polymer chelation. In view of this, the use of cross-linked poly(4-vinylpyridine) was more useful in obtaining complexes with metal ions [258]. A poly(4-vinylpyridine)–divinylbenzene (20%) copolymer is now commercially available under the name of Sumichelate CR-2 (cf. Table 1) [259]. This resin has been found to be very useful for the recovery of chromium from waste water containing hexavalent chromate which is very toxic for animals. The properties and different uses of Sumichelate CR-2 have been described in detail by Miyagawa [260]. The bonding of Sumichelate CR-2 with copper(II) chloride and chromic acid is schematically depicted in (**XLII**) and (**XLIII**), respectively. Chelate-forming resins have been prepared by cross-linking poly(4-vinylpyridine) with 1,4-dibromobutane (**XLIV**) in which free, unquaternized pyridine groups participate in coordination to a metal ion [258,261,262]. Nishide et al. [261] studied the selective adsorption of several metal ions with this type of resin using adsorption equilibrium and spectroscopic measurements. The stability constants have been found to be much larger for the Cu–**XLIV** system than for the copper–poly(4-vinylpyridine) system, indicating that the chelating resin (**XLIV**) takes up copper ions with higher efficiency. The stability constants


(XLII)


(XLIII)

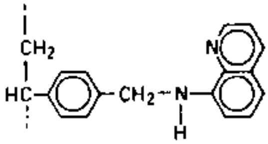

(XLIV)

and the adsorption capacity for copper(II) decreases with increasing degree of cross-linking and the same is true with iron(III), chromium(II), nickel(II) and zinc(II). The adsorption of mercury(II) is independent of the degree of cross-linking, however. Thus it appears feasible to synthesise ion-selective chelating resins by controlling the degree of cross-linking.

The structures of the copper(II) complexes of the chelating resins (**XLIV**) having a different amount of cross-linking agent have been studied with the aid of visible absorption and ESR spectra and magnetic susceptibility measurements. The absorption maxima for the copper(II) complexes lie in the range 660–700 nm and magnetic moments in the range 1.4–1.8 B.M. per copper ion at room temperature which are in the low range for monomeric copper(II) compounds. The ESR spectra of the Cu–**XLIV** complexes in aqueous solution recorded at room temperature yield the parameters ($g_{\parallel} = 2.3$, $g_{\perp} = 2.1$ and $A_{\parallel} = 150 \pm 10$ G) which are in agreement with those of the monomeric complex, $[Cu(pyridine)_4]^{2+}$, implying that the structure of copper(II) complexes with resins (**XLIV**) having a low degree of cross-linking (4–12%) is square planar, just as in the monomeric copper–poly(4-vinylpyridine) species. In the highly cross-linked resin complexes, however, the signal due to parallel orientation has been found to shift to higher magnetic field and the $g_{\parallel}$ and $A_{\parallel}$ values largely decrease to 2.2 and 60–100 G, respectively. This has been attributed to either distortion towards a tetrahedral structure or to a compression along a fourfold axis.

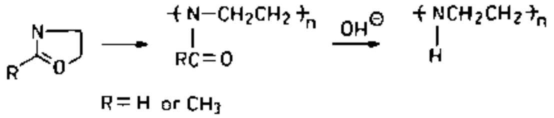
A new method for the synthesis of ion-selective chelating resins has also been developed [261] by cross-linking metal–poly(4-vinylpyridine) complexes, in which the complexed metal acts as a "template". This metal ion can be removed with acid and when free resin is dipped into a mixture of metal ions, then the "metal template" is preferentially bound. A modified procedure based on these observations has been described by Efendiev and Kabanov [169]. The complexation of metal ions with poly(1-vinylimidazole) resin prepared by radiation-induced polymerisation with template metal ion has been studied by Kato et al. [263]. The preparation and properties of polyamides prepared by the reduction of poly(4-vinylpyridine) have also been reported [264].

Several other chelating resins containing pyridine derivatives as functional groups have been synthesised and their ion-selective properties have been described [265–269]. Cross-linked polystyrenes or acenaphthene containing tertiary nitrogen, oxymethyl and aminopyridines and macroporous or gel-like resins possessing pyridine-type anion exchange resins have been used for the sorption of molybdenum, rhenium and tungsten from sulfuric acid aqueous solutions [267]. A resin (**XLV**) derived by incorporating 8-aminoquinoline into a polystyrene matrix was found to be selective for palladium and platinum [269].



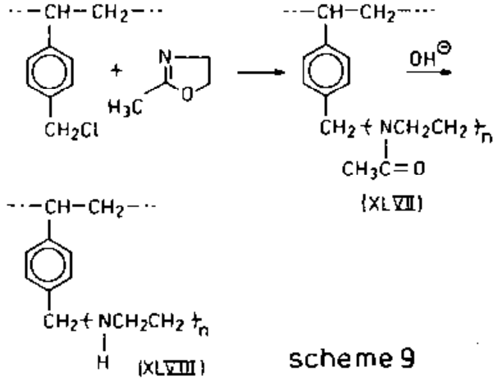
(XLV)

Recently, Saegusa et al. [270–272] reported the synthesis of crystalline poly(ethyleneimine) (**XLVI**) by the polymerisation of 2-oxazoline and the



(XLVI)

subsequent hydrolysis of the product polymer poly(*N*-formylethylenimine). A commercial resin Diaion CR-40 containing ethyleneimine is also available (Table 1). This resin has been found to be a good chelating agent for various metal ions; however, its complexes are usually soluble in water. To overcome this limitation of polyethylenimine, poly(styrene-*g*-ethylenimine) (**XLVIII**) has been prepared by the polymerisation of 2-methyl-2-oxazoline with cross-linked chloromethylated polystyrene and subsequent hydrolysis of the graft copolymer (**XLVII**) under alkaline hydrolysis as depicted in Scheme 9

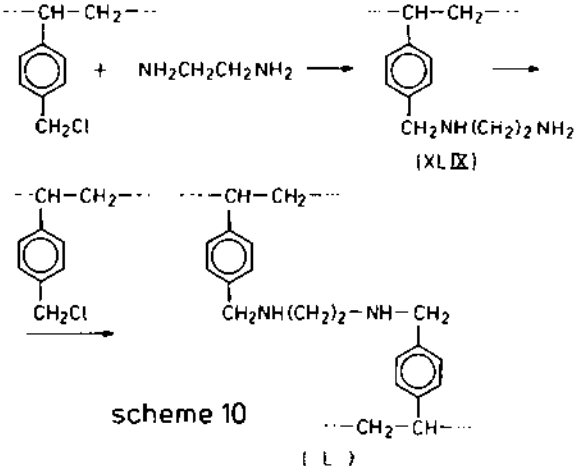


scheme 9

[273]. Direct grafting of polyethylenimine onto cross-linked chloromethylated polystyrene resulted in very poor yields of poly(styrene-*g*-ethylenimine). It was found that the direct graft polymerisation of aziridine monomer onto cross-linked polystyrene matrix is not suitable for the preparation of poly(styrene-*g*-ethylenimine) having long ethylenimine branches. Poly(styrene-*g*-ethylenimine) has been found quite effective for the adsorption of heavy metal ions, such as copper(II), mercury(II) and cadmium(II). The higher content of polyethylenimine in the graft copolymers results in the

resins having larger adsorption capacity for metal ions. The adsorption selectivity was found to follow the order $Hg^{2+} > Cu^{2+} > Cd^{2+}$, which is in agreement with the order of the stability constants of the amine complex of these metal ions [274]. The results obtained with these polyethylenimine resins were compared with a commercial polyamine-type anion exchanger (Diaion CR-20) and it was found that the graft copolymer having about 15% nitrogen possesses greater adsorption capacity for Cu^{2+} than that of the commercial resin [275–277].

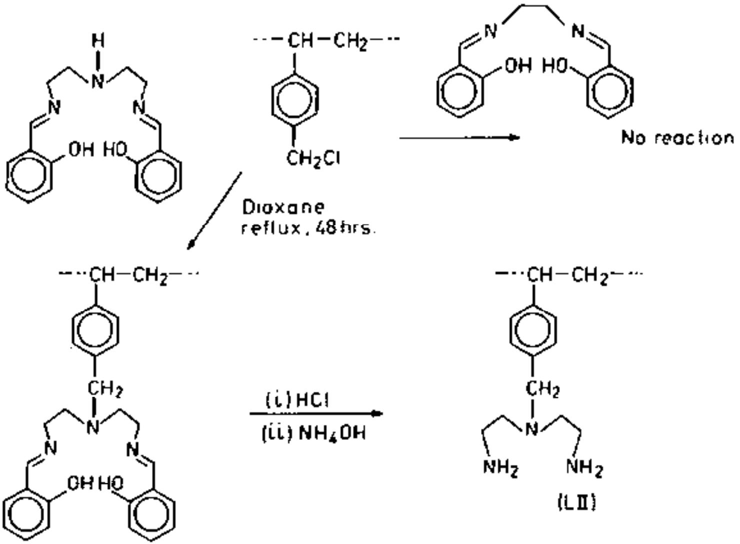
Chelating resins containing polyamine functional groups form an important class of such ligands. Several authors [278–282] have studied the modification of synthetic resins with polyamines, such as ethylenediamine, diethylenetriamine, and triethylenetetramine and conflicting claims regarding the constitution of these chelating resins have been made. Blasius and Bock [278] and Szabadka [279] studied the reactions of cross-linked chloromethylated styrene with several polyethylenepolyamines and suggested that these polyamines are linked to the matrix by one or more bridges by the amination reaction, depending upon their length. These reactions appear to proceed in a fashion depicted in Scheme 10 for amination of chloromethylated polystyrene with ethylenediamine. Two products, monoaminated polystyrene (**XLIX**) and diamineated polystyrene (**L**) are obtained [279]. Shambu et al. [280] also studied the reaction of several polyethylenepolyamines with chloromethylated "popcorn" polystyrene resins, using pyridine as reaction medium. It was observed that the rate of chloride displacement decreased with increasing molecular weight of the amine and higher degree of resin chloromethylation, while the extent of multiple attachments to the polymer matrix increased. The additional cross-linking, as a result of multiple attachments, caused the polyamine to swell to a lesser extent in pyridine and water.



scheme 10

It has been found that the capacity of the resin containing ethylenediamine with respect to its adsorption of copper(II) ions from dilute solutions increases with increasing amount of ethylenediamine. With diethylenetriamine the capacity remains unchanged, while with triethylenetetramine, the capacity was found to decrease. The complexation and protonation of chelating ion-exchange resins containing ethylenediamine functional groups have also been studied and the apparent stability constants of copper(I), copper(II), nickel(II), zinc(II) and cadium(II) complexes determined [283]. It has been suggested that with the exception of the zinc–cadmium pair, ethylenediamine resins can be used very advantageously for the separation of the metal ions studied. These chelating resins containing polyethylenepolyamine functional groups have been used as precursors for the preparation of iminodiacetic-type resins by their carboxymethylation. Such chelating resins will be discussed in detail in the section covering iminodiacetic acid resins. Leyden and co-workers [284,285] have used *N*-*β*-aminoethyl-*γ*-aminopropyltrimethoxysilane and *γ*-aminopropyltrimethoxysilane to immobilise diamino functional groups and these materials have been used for X-ray spectrometry techniques [286].

Chelating resins (**LI**,**LII**) obtained by anchoring diethylenetriamine onto chloromethylated polystyrene, as shown in Scheme 11, have been found to

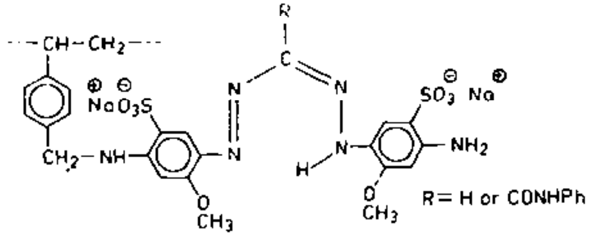


(LI)

scheme 11

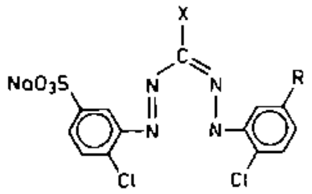
contain 3.02 mmol ligating groups g^{-1} of the resin and complex various transition metal ions. Leyden and co-workers [285,286] have used *N*-*β*-aminoethyl-*γ*-aminopropyltrimethoxysilane and *γ*-aminopropyltrimethoxysilane to immobilise diamine functional groups and these materials have been used for preconcentration of trace elements, prior to their analysis by X-ray spectrometric techniques [287]. Several partially cross-linked polyamine polymers have been synthesised for the removal of metal ions from waste water [288].

Chelating ion exchangers having formazans as functional groups incorporated into polystyrene (**LIII**) [289], silica [290] and cellulose matrix [291] have been synthesised by Kettrup and co-workers. The capacities of the ion exchangers vary from 0.05 meq g^{-1} (cellulose) to 0.6 meq g^{-1} (polystyrene). Cellulose and polystyrene-based resins show greater affinity for mercury(II), palladium(II) and silver(I) in neutral medium, but no affinity for copper(II). The low capacity of cellulose–formazans has been attributed to their hydrolysis [292]. Sulfonated formazans were loaded into quaternised aminopropyl-functionalised silica (Si–NH_2) to get the chelating supports [290]. Stability, sorption, and desorption properties of formazan-modified silica were compared with similar modified polystyrene under static and dynamic conditions. It was observed that the chelating behavior of the ligands in the presence of platinum(IV), palladium(II) and silver(I) is affected by an inorganic or organic matrix in a different way. It was shown that enrichment and separation of silver(I) is possible by flow rates up to 7 ml min^{-1} with minimum amounts of a chelating gel. Several anion exchangers were also loaded with various substituted formazans (**LIV**). Substituents (H, $CONH_2$, CONH–Ph, SO_3Na) on the ligands have been found to affect swelling, stability and sorption behavior of the chelating ligands. The uptake of



R= H or CONHPh

(LIII)



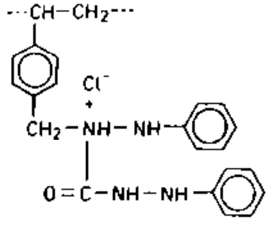
(LIV)

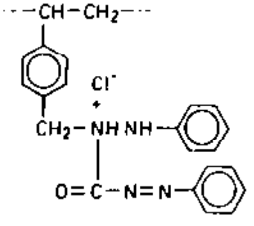
X=H,CONH₂,CONH–Ph

R=SO₃Na or H

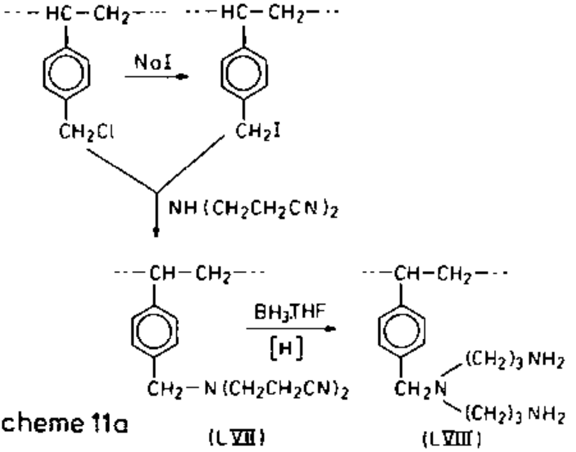
U(VI), Pt(IV), Pd(II) and Ag(I) with respect to the loaded amount of ligand, pH and shaking time was determined. At optimal conditions Ag(I) is quantitatively retained by resin columns and separated from a 1000-fold molar excess of Cu(II) [289,291].

Diphenylcarbazide and diphenylcarbazone which act as bidentate chelating ligands [293] have been incorporated into polymeric matrices to obtain chelating ion-exchange resins (**LV**) and (**LVI**) [294–296]. A resin (**LVI**) containing diphenylcarbazone as a functional group has been found specific for mercury(II) [294]. Dore et al. [295] treated a chloromethylated styrene–divinylbenzene copolymer with diphenylcarbazide in refluxing dioxane to obtain a chelating ion-exchange resin (**LV**). This resin proved to be specific for chromium(VI), which is reduced to chromium(III) during complexation in acidic medium. A mechanism has been suggested for the action of diphenylcarbazide resin. Some chelating resins have been prepared by treating macroreticular styrene–divinylbenzene and methyl methacrylate polyethylenepolyamines, e.g., triethylenetetramine, and their adsorption capacity for different metal ions evaluated [297]. The copper(II) complexes of these resins have been used for the oxidation of 2,6-dihydroxyphenylacetic acid and hydroquinone. Several chloromethylated polystyrene derivatives containing mono- and bisazo chelating ligands have been used for the selective concentration of certain metals [296]. Myasoedova et al. [298,299] studied several such chelating resins possessing amino–azo compounds. The capacity of these sorbents was determined for Cu(II) and La(III) and it has been observed that the copolymers with macroporous structure have maximum capacity, evidently due to the presence of numerous microscopic channels and pores in such copolymers, which assume more favourable conditions for the sorption of the elements.


(LV)

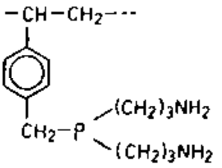

(LVI)

Recently, Drago et al. [300] described a versatile high-yield synthesis for covalently attaching multidentate chelating ligands to polystyrene matrices. Polymeric substrates containing polydentate amines as discrete units (devoid of any intra- or inter-strand bridging) can be obtained by reacting chloro- or iodo-methylated polystyrene with bis(cyanoethylamine) (**LVII**), followed by $BH_3 \cdot THF$ reduction, to provide polymer-attached bis(3-aminopropyl)amine

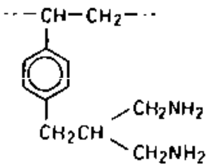


scheme 11a

(**LVIII**) as depicted in Scheme 11a. Three polydentate amines, bis(3-aminopropyl)amine, bis(3-aminopropyl)phosphine and diaminopropane have been anchored onto a polystyrene matrix to obtain three new polymer-supported multidentate chelating ligands designated by structures such as, e.g., (**LIX**) and (**LX**), respectively. These materials form the basis for the prepara-



(LIX)

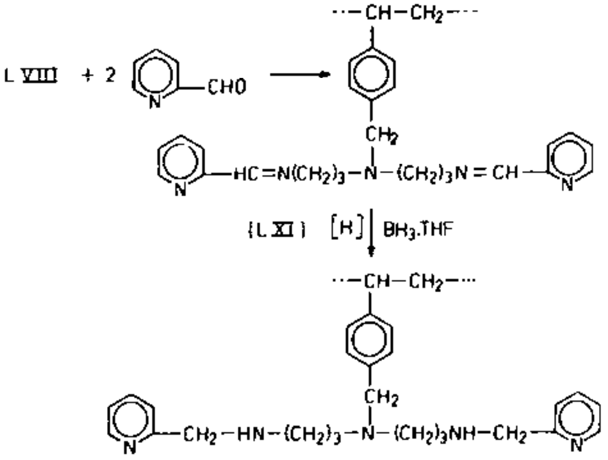


(LX)

tion of a wide variety of chelating ligands, e.g., through the Schiff base reaction with a variety of aldehydes and ketones. For instance, the polystyrene derivative derived from bis(3-aminopropyl)amine (**LVIII**) was condensed with 2-pyridinealdehyde to form the pentadentate Schiff base (**LXI**) containing two imine linkages (Scheme 12). These imine linkages were reduced with $BH_3 \cdot THF$ to yield a linear pentamine (**LXII**) capable of binding metal ions to form salt-like metal complexes. The copper(II) complex of this pentamine was prepared. None of these compounds was used as a chelating ion exchanger, but instead as polymer-supported catalysts.

(ii) Chelating ion-exchange resins containing nitrogen and oxygen as donor atoms

This forms the largest group of chelating ion-exchange resins. The important ligands possessing nitrogen and oxygen as donor atoms include

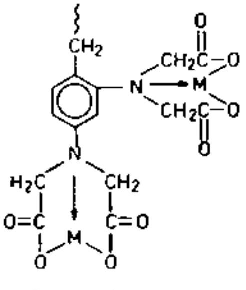


scheme 12 (LXII)

iminodiacetic acids, hydroxamic acids, oximes, hydroxyquinoline derivatives and Schiff bases, which are discussed in this section.

(a) Chelating ion exchangers containing iminodiacetic acid and related ligands

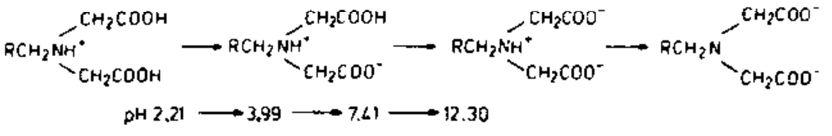
Iminodiacetic acid and its derivatives have been incorporated into a variety of matrices, including both addition and condensation resins. The first resin of this type, containing ethylenediaminetetraacetic acid as a solid solution within a phenol–formaldehyde condensate, was reported by Klyatshko [301], followed by Blasius and Olbrich [164], who prepared a condensation chelating polymer from resorcinol, (*m*-phenylenediaminedinitrilo)tetraacetic acid and formaldehyde. The latter resin was found to be useful in the chromatographic separation of cobalt(II) and nickel(II) and it appears to chelate the metal ions in the manner shown in (**LXIII**). Similarly,



(LXIII)

anthranilic acid–diacetic acid [302] and *m*-phenylene–diglycine [1] have also been incorporated into phenol–formaldehyde and resorcinol–formaldehyde condensates. Such chelating ion exchangers can easily be prepared by carboxymethylation of amino compounds with chloroacetic acid. Their ion-exchange properties were described in earlier reviews [4,5,7,34,35]. With a view to studying the effect of the benzene ring on the basicity of the nitrogen atom of iminodiacetic acid, several workers used cross-linked polystyrene as starting materials for the synthesis of iminodialkanoic acids [34], Gregor [302] and Pepper and Hale [154] proposed synthetic routes for attaching iminodiacetic acid directly to a benzene ring, as shown in Scheme 4. This was followed by the introduction of iminodiacetic acid into cross-linked polystyrene through a methylene group. Soon after the publication of the first report on the synthesis of this chelating resin, several other routes were proposed for the synthesis of such resins and reviews are available [165,303]. The best route for the synthesis of iminodiacetic acid resin on a polystyrene matrix consists in the treatment of cross-linked polystyrene with iminodiacetate and its subsequent hydrolysis. The resins containing iminodiacetic acid as functional group are now commercially available under different trade names (cf. Table 1). This chelating resin was first manufactured by Dow Chemical Company and was marketed as Dowex A-1. The Company's manual [80] describes the properties and various applications of this versatile chelating ion-exchange resin. This is probably the most extensively studied chelating ion-exchange resin and by now so much has been done on this chelating resin that an exclusive review article would be useful. We can only give here a brief description of the properties of this resin.

Schmuckler et al. [96] have briefly reviewed the structural and other fundamental properties of iminodiacetic acid resins. It has been found that on average out of every 8 rings in the resin 5 are substituted with iminodiacetic acid. A qualitative analysis of Dowex A-1 was made by Schwartz [304] at various pH values with the resin immersed in a buffer solution of acetic acid–sodium acetate at constant ionic strength. The locations of the various groups as a function of pH, supported by the infrared spectrum, are given in Scheme 13. The chelating properties of Dowex A-1 clearly indicate that it behaves as a solid complexing agent, forming mainly stable 1 : 1 complexes with different metal ions, though the possibility of 1 : 2 metal to ligand complexes may occur [113]. These results obtained from analytical studies were later confirmed with the aid of electronic and ESR spectra of



$$RCH_2\overset{+}{N}H\begin{smallmatrix}CH_2COOH\\CH_2COOH\end{smallmatrix} \longrightarrow RCH_2\overset{+}{N}H\begin{smallmatrix}CH_2COOH\\CH_2COO^-\end{smallmatrix} \longrightarrow RCH_2\overset{+}{N}H\begin{smallmatrix}CH_2COO^-\\CH_2COO^-\end{smallmatrix} \longrightarrow RCH_2N\begin{smallmatrix}CH_2COO^-\\CH_2COO^-\end{smallmatrix}$$

$$\text{pH } 2.21 \longrightarrow 3.99 \longrightarrow 7.41 \longrightarrow 12.30$$

scheme 13

the metal complexes of Dowex A-1. It has been established that the resin acts as a tridentate ligand coordinating through the imino nitrogen atom and bonding through two carboxylic oxygen atoms involving deprotonation [166,197,199,201]. The influence of the medium on the adsorption behavior of this resin is analogous to the effect of the medium in competing equilibria in soluble chelates [33]. The electrolytic dissociation [305] and kinetics of several exchange processes with Dowex A-1 have been studied [98,99]. In the case of metal ions which form chelates with Dowex A-1, the rate of exchange was not diffusion-controlled (as is common with conventional resins) but rather was governed by the rate of the chelation reaction itself [98]. However, Heitner-Wirguin and Markovits [99] reported that the exchange rates are governed by diffusion processes under conditions of low pH, where the resin is considerably more shrunken than in the studies of Turse and Rieman [98]. The effect of pH and ionic strength on the distribution coefficients of alkaline earth and transition metals have been reported by several workers [97, 182, 306]. Leyden and Underwood [97], who also studied the effect of temperature on distribution coefficients, concluded that most of the divalent metal ions show similar behavior, exhibiting D values which became maximal at pH 4.5. It has been observed that an increase in ionic strength causes a decrease in the distribution coefficients of alkaline-earth metal ions, but has little effect on nickel or copper [306,307], presumably due to their tendency to form very stable complexes once the ion has entered the resin. Equations for the calculation of the distribution coefficients of the alkaline earth metals at various pH and ionic strengths have been reported [306]. Leyden and Underwood [97] estimated that apparent pK values of the resin lie in the range 2.37–3.45 for pK_1 and between 8.15 and 8.58 for pK_2, being close to those reported by Krasner and Marinsky [115]. In general, all these values reported in the literature are in agreement with those reported for benzyliminodiacetic acid [113,114] and iminodiacetic acid [308]. Chatterjee and Chatterjee [309] have studied thermodynamic properties such as enthalpy and entropy changes with a view to ascertaining the nature of the metal–resin complex and the effect of swelling on the reaction.

The commercial resins Dowex A-1 and Chelex-100 have been used for several selective separations of various metal ions, particularly those of transition metal ions from alkali and alkaline-earth metal ions as a function of pH, even from high ionic strength solutions [310–312]. The selectivity coefficients for this resin relative to calcium, $K_{\mathrm{Ca}}^{\mathrm{M}}$, are 4.9 for Mn^{2+}, 20.5 for Co^{2+}, 19.8 for Zn^{2+}, 52 for Ni^{2+}, and 500 for Cu^{2+} [313]. The selectivity order for the macroreticular iminodiacetate resin, gel-type iminodiacetate resin and Dowex A-1 have been determined and compared. The selectivity order for the macroreticular resin is $\mathrm{K}^+ < \mathrm{Mg}^{2+} < \mathrm{Mn}^{2+} < \mathrm{Ni}^{2+} < \mathrm{Co}^{2+} < \mathrm{Zn}^{2+} < \mathrm{Cu}^{2+}$ [314]. Hering [315] determined the following order for a gel-type resin: $Na^+ < Mg^{2+} < Ca^{2+} < Co^{2+} < Zn^{2+} < Ni^{2+} \ll Cu^{2+}$ and Rosset [313] determined the selectivity order for Dowex A-1 as $Mg^{2+} < Mn^{2+} < Co^{2+} < Zn^{2+} < Ni^{2+} \ll Cu^{2+}$. This indicates that during the chromatographic separations, the elution order with macroreticular chelating resin is similar to that previously observed with a microreticular chelating resin [314]. Recently, the characterisation of the calcium form of Chelex-100 for trace metal studies has been carried out, since the calcium form does not shrink, as do the sodium or ammonium forms, when divalent metal ions are taken up; this greatly facilitates a steady flow without the column channelling [316].

The coordination behavior of cobalt(II), nickel(II), copper(II) and zinc(II) towards the chelating ion-exchange resin Dowex A-1 and its monomeric analogue, *N*-benzyliminodiacetic acid, has been examined potentiometrically by Eger et al. [113,114]. A comparison of the sets of potentiometric titration curves for the monomer and the gel-type resin system clearly demonstrated that the coordination behavior of these metal ions is similar. The 1 : 1 and 1 : 2 complexes of the transition metals mentioned above are observed in both systems. The anomalous behavior of copper(II) observed with *N*-benzyliminodiacetic acid, i.e., the removal of an extra H^+ ion [308,317] is not apparent in the resin system, probably because of the inability of the system to reach equilibrium within the time allowed for each experiment. These results have been quantified by comparing the values of the first dissociation constants of various transition metal chelates of *N*-benzyliminodiacetic acid and Dowex A-1 at different temperatures. The thermodynamic properties are similar to its repeating monomer units [114].

The sorption characteristics of Dowex A-1 in the presence of such strong ligands as 1,10-phenanthroline and sodium triphosphate have been studied [318,319]. The possibility of mixed-ligand metal complexes in the case of 1,10-phenanthroline has been proposed [318] and divalent metal ions have been found to adsorb more strongly on this resin in the presence of sodium triphosphate [319]. The possibility of separation of some trivalent lanthanides on a calcium-saturated Dowex A-1 resin has also been explored [320]. The equilibration and kinetics of ion-exchange adsorption of plutonium at extremely low concentrations (1.5×10^{-7} mol l^{-1}) have been reported [321]. A comparative study of separation of nickel(II) and cobalt(II) by ion-exchange filtration through carboxylic acid and several commercial chelating resins revealed the following order of efficiency: Chelex-100 > Dowex A-1 > Wofatit A-20 > Wofatit MC-50 > Diaion CR-10 > Lewatit TP-207 > Duolite ES 466 > Zerolit S-1006 [322]. Among several uses of iminodiacetic acid resins, the use of Chelex-100 or Dowex A-1 as preconcentration agents for trace elements in the analysis by X-ray spectrometric techniques [25,286], to establish and maintain known ionic activities of metals at a constant pH [26] and for the recovery of metal ions from the secondary effluent of petrochemical plants and industrial waste water [323,324] appear very promising. The use of Chelex-100 or Dowex A-1 for separation and preconcentration of transition metal ions from natural and sea water has been extensively examined [325–338]. These resins are particularly suited to this application because optimum metal binding occurs in the pH range 6–8, where distribution coefficients of the order of 10^5 have been measured [95–97,339]. Riley and Taylor [335] compared the separation and preconcentration capabilities of two iminodiacetic acid resins, Chelex-100 and Permutit-S1005, towards trace metal ions from sea water. They obtained similar results with both resins except for manganese(II), which was only retained with 60% efficiency at the optimum pH of 9 on Permutit-S1005, whereas it was completely retained by Chelex-100. Permutit-S1005 was found to be less stable chemically, but it did not change its dimensions when its counter ion was changed. The efficiency of Chelex-100 in concentrating metals in the presence of cationic, anionic and non-ionic detergents, washing powder and sodium triphosphate at a concentration as high as 100 mg l^{-1} has been examined by Riley and Taylor [335]. They found that the metal retentions are better than 92%, but are poor in the presence of soap or the potential detergent additive, nitriloacetic acid. Using radio-tracer techniques it appeared that total metal content, present in natural water, is not adsorbed by Chelex-100, unless the metal ions are first released from colloids or fortuitously present chelates.

The spectral and magnetic properties of metal loaded Dowex A-1 or Chelex-100 have been studied [166,197,199,201–205] to establish the coordination sites (of the chelating resins), stereochemistry of metal complexes, spin-state and configuration, in order to further knowledge of the relationship between geometry around a metal ion and the ion-selectivity of the chelating ion-exchange resin. Hoek and Reedijk [197] studied the structural features of cobalt(II), nickel(II) and copper(II) complexes of Chelex-100 and concluded that the iminodiacetate functional group in this resin coordinates as a tridentate chelating ligand to these metal ions. The coordination polyhedra (distorted octahedron) is completed either by water molecules or by carboxylate oxygen atoms from neighboring iminodiacetate groups resulting in an MO_5N chromophore. The posssibility of formation of significant amounts of MO_6 and MO_4N_2 chromophores as observed with iminodiacetic acid, is highly unlikely as deduced from the crystal field parameter values of cobalt and nickel complexes. Similar conclusions were drawn regarding the chelating behavior and stereochemistry of these metal ions by Heitner-Wirguin [201] and Nakashima et al. [166] on the basis of spectroscopic studies. The EPR spectra of vanadyl(II), chromium(III), iron(III), manganese(II) and gadolinium(III) complexes of Dowex A-1 and Mössbauer spectra of iron(III) complexes have also been studied in relation to their stereochemistry in the resin phase [166]. Magnetic susceptibilities of iron(III), cobalt(II), nickel(II) and copper(II) complexes of Chelex-100 measured between 90 and 300 K revealed high-spin complexes in the resin phase, similar to their monomeric iminodiacetic and benzyliminodiacetic acid analogues [205]. Some relevant spectral and magnetic parameters of transition metal complexes of iminodiacetic acid resins Chelex-100 and Dowex A-1 are given in Tables 2, 3 and 4.

TABLE 2
Ligand field spectral data of metal complexes of commercial ion exchange resins containing iminodiacetic acid

Complex	Band maxima (cm^{-1})	*Dq* (cm^{-1})	*B* (cm^{-1})	Ref.
$CuCl_2$–Chelex-100 (50–70% load.)	14,200	–	–	197
$CuCl_2$–Chelex-100 (0.5–30% load.)	14,500	–	–	197
$Cu(ClO_4)_2$–Chelex-100 (50–70% load.)	14,500	–	–	197
$Cu(ClO_4)_2$–Chelex-100 (0.5–30%)	14,300	–	–	197
Cu–Dowex A-1 wet	14,850	–	–	199
Cu–Dowex A-1	14,000	–	–	
Cu–ES 466 (ca. 70% load.)	13,000	–	–	unpub. results
Cu–ES 466 (ca. 50% load.)	13,000	–	–	unpub. results
Cu–ES 466 (ca. 25% load.)	13,000	–	–	unpub. results
$CoCl_2$–Chelex-100 (50–70% load.) wet	8470 (ν_1), 19,120 (ν_3)	925	780	197
$CoCl_2$–Chelex-100 (0.5–30% load.) wet	8620 (ν_1), 19,300 (ν_3)	940	785	197
$Co(ClO_4)_2$–Chelex-100 (50–70% load.)	8470 (ν_1), 19,080 (ν_3)	925	780	197
$Co(ClO_4)_2$–Chelex-100 (0.5–30% load.)	8600 (ν_1), 19,300 (ν_3)	940	785	197
Co–Dowex A-1	8500 (ν_1), 19,500 (ν_3)	930	805	
$CoCl_2$–ES 466 (ca. 70% load.)	8440 (ν_1), 18,180 (ν_3)	922	718	unpub. results
$CoCl_2$–ES 466 (ca. 50% load.)	8660 (ν_1), 18,520 (ν_3)	946	727	unpub. results

TABLE 2 (continued)

Complex	Band maxima (cm^{-1})	Dq (cm^{-1})	B (cm^{-1})	Ref.
$CoCl_2$–ES 466 (ca. 25% load.)	8450 (ν_1), 18,520 (ν_3)	923	741	unpub. results
$NiCl_2$–ES 466 (ca. 70% load.)	9090 (ν_1), 14,700 (ν_2), 25,000 (ν_3)	909	829	unpub. results
$NiCl_2$–ES 466 (ca. 50% load.)	9200 (ν_1), 15,800 (ν_2), 25,000 (ν_3)	920	880	unpub. results
$NiCl_2$–ES 466 (ca. 25% load.)	9090 (ν_1), 14,700 (ν_2), 25,000 (ν_3)	909	829	unpub. results
$NiCl_2$–Chelex-100 (50–70% load.)	9500 (ν_1), 15,600 (ν_2), 25,300 (ν_3)	950	830	197
$NiCl_2$–Chelex-100 (0.5–30% load.)	9500 (ν_1), 15,400 (ν_2), 25,500 (ν_3)	950	830	197
$Ni(ClO_4)_2$–Chelex-100 (50–70% load.)	9440 (ν_1), 15,300 (ν_2), 25,400 (ν_3)	945	825	197
$Ni(ClO_4)_2$–Chelex-100	9500 (ν_1), 15,500 (ν_2), 25,600 (ν_3)	950	840	197

TABLE 3

E.S.R. parameters of metal complexes of some commercial chelating ion exchange resins containing iminodiacetic acid

Complex	E.S.R. parameters				Ref.
	$g_{av.}$	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (in G)	
Cu–Dowex A-1					
(in conc. HCl) wet	–	2.27	2.09	–	166
dry	–	2.29	2.08	–	166
Cu–Dowex A-1					
(at pH = 4.32) wet	–	2.29	2.07	186	166
dry	–	2.31	2.09	184	166
Cu–Dowex A-1					
(at pH = 9.30) wet	–	2.27	2.08	180	166
dry	–	2.29	2.08	191	166
$CuCl_2$–Chelex-100 (50–75% load.)	2.14	–	–	–	197
$CuCl_2$–Chelex-100 (0.5–30% load.)	2.14	–	–	–	199
$Cu(ClO_4)_2$–Chelex-100 (50–70% load.)	2.14	–	–	–	197
$Cu(ClO_4)_2$–Chelex-100 (0.5–30% load.)	2.14	–	–	–	197

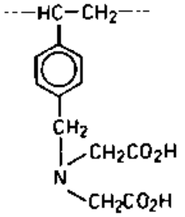
TABLE 3 (continued)

Complex	E.S.R. parameters				Ref.
	$g_{av.}$	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (in G)	
$CuCl_2$–Chelex-100 (0.5–30% load. in 0.3M HCl)	–	2.25	2.06	180	197
$CuCl_2$–Chelex-100 (0.5–30% load. in 0.3M NH_3)	–	2.25	2.10	180	197
$Cu(NO_3)_2$–Chelex-100 (0.3% load.)	–	2.28	2.08	165	197
$Cu(NO_3)_2$–Chelex-100 (1% load.)	–	2.26	2.09	172	197
$Cu(NO_3)_2$–Chelex-100 (2% load.)	–	2.26	2.10	168	197
Cu–Dowex A-1 wet	–	2.28	2.09	151	199
dry	–	2.28	2.07	149	199
Cu–ES 466 dry (ca. 70% load. at pH = 5.5)	–	2.30	2.11	150	unpub. results
Cu–ES 466 dry (ca. 50% load. at pH = 5.5)	–	2.29	2.10	150	unpub. results
Cu–ES 466 dry (ca. 25% load. at pH = 5.5)	–	2.28	2.11	150	unpub. results
Mn–Dowex A-1	2.0	–	–	–	166
Fe(III)–Dowex A-1	g values: 4.41 and 2.02				166
VO(+2)–Dowex A-1 (in conc. HCl) dry	–	1.95	1.98	178	166
VO(+2)–Dowex A-1 (at pH = 3.82)	–	1.94	1.99	179	166
Cr–Dowex A-1 (in conc. HCl) dry	g values: 4.34 and 1.99				166
Cr–Dowex A-1 (at pH = 3.9)	g values: 5.16 and 1.99				166
Cr–Dowex A-1 (at pH = 8.50)	g values: 4.14 and 1.98				166
Gd–Dowex A-1 (at pH = 3.90)	g values: 5.80, 3.37, 2.81 and 1.98				166
Gd–Dowex A-1 (at pH = 8.5)	g values: 5.87, 3.51, 2.83 and 1.98				166

Yamada et al. [340] has recently synthesised a water soluble ligand, bis(carboxymethyl)iminomethylene derivative of oligostyrene ($Pn = 6.8$) through a reaction between chloromethylated oligostyrene and dimethylim-

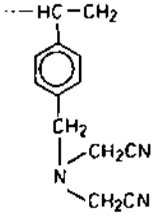
TABLE 4
Magnetic and Mössbauer spectral data of metal complexes of some commercial chelating ion exchangers containing iminodiacetic acid

Complex	$\mu_{eff.}$ (BM)	Mössbauer spectral parameters			Ref.
		I.S. (mm s^{-1})	Q.S. (mm s^{-1})	L.W. (mm s^{-1})	
Fe(III)–Dowex A-1 (in conc. HCl)	–	0.19	0.36	0.24	166
Fe(III)–Dowex A-1 (at pH = 4.0)	–	0.37	0.63	0.72	166
Fe(III)–Dowex A-1 (at pH = 9.0)	–	0.37	0.80	0.53	166
Fe(III)–Chelex-100 (at pH = 6)	5.20	0.64	0.63	–	205
Fe(III)–Chelex-100 (at pH = 4 and 10)	–	0.64	0.63	–	205
Co(II)–Chelex-100	5.21	–	–	–	205
Ni(II)–Chelex-100	3.09	–	–	–	205
Cu(II)–Chelex-100	2.02	–	–	–	205

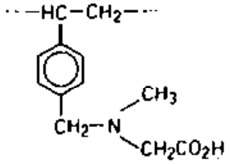


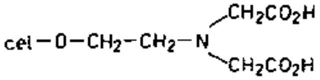
(LXIV)

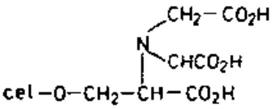
inodiacetate in dimethylformamide, followed by the alkaline hydrolysis of an intermediate iminodiacetate(**LXIV**). A potentiometric investigation of this water soluble ligand in the presence and absence of metal ions revealed that its chelating behavior is similar to that of benzyliminodiacetic acid, which is the monomeric unit of the polymeric ligand. As expected, the pK_a values of the ligand are similar to that of benzyliminodiacetic acid ($pK_{a(1)} = 2.8$ and $pK_{a(2)} = 9.56$). The fact that the n value equals unity indicates that a very slight intramolecular interaction is operative among the neighboring functional groups during the first protonation step. On the contrary, a higher n' value indicates the occurrence of weak interactions among the neighboring functional groups during the second proton dissociation. However, the n and n' values of this ligand are much smaller than those observed for polymethacrylic acid ($pK_a = 7.3$, $n = 2.3$) or polyacrylic acid ($pK_a = 6.3$, $n = 2.2$). The order of chelate stability constants have been found to follow the order Ni(II) > Zn(II) > Co(II) > Ca(II) > Mg(II), and is similar to those of benzyliminodiacetic acid or iminodiacetic acid [308]. In the cases of iron(III) and copper(II), precipitation or turbidity was observed when 1×10^{-3} M ligand solution was mixed with metal ion solution in a 1 : 1 or 1 : 2 ratio, and for nickel(II) and zinc(II) in a 1 : 1 ratio. This precipitation has been ascribed to cross-linking of the polyelectrolyte by the metal ion and not to hydrolysis of the metal ion [340]. The preparation of the water soluble polymeric ligand (**LXIV**) has also been reported to be achieved by the hydrolysis of an iminodinitrile intermediate (**LXV**) [9]. However, it has recently been shown that on treating chloromethylated polystyrene with iminodinitrile in pyridine, a pyridinium derivative is obtained instead which is also soluble in water [340]. The ion-selective properties of a chelating resin (**LXVI**) derived from chloromethylated polystyrene and *N*-methylaminoacetic acid have been studied [7].


(LXV)

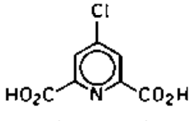
Iminodiacetic acid has also been anchored on a cellulose matrix in different forms, such as iminodiacetic acid–ethyl cellulose (IDA–cellulose) (**LXVII**) [341] and iminodiacetic acid–propionic acid–cellulose (**LXVIII**) [342]. The two pK_a values of the IDA–cellulose (**LXVII**) were 2.65 ± 0.08 and 9.1 ± 0.2. The stability order of the different metal ions investigated follow the order: Cu(II) > Ni(II) > Co(II) > Ca(II) > Mg(II). Iminodiacetic acid–propionic acid–cellulose (**LXVIII**) is capable of removing trace species, such as Fe^{3+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Cd^{2+}, from aqueous solution containing up to 10% NaCl, $MgSO_4$ or $CaCl_2$ [343].

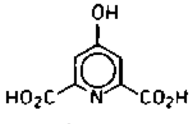

(LXVI)

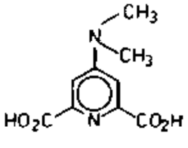

(LXVII)


(LXVIII)

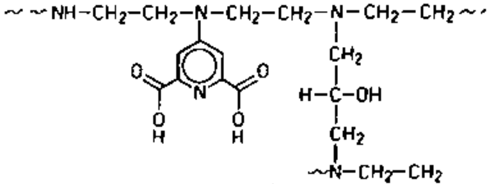
An analogue of iminodiacetic acid, 2,6-pyridinedicarboxylic acid or dipicolinic acid has also been incorporated into several types of matrices such as formaldehyde and resorcinol, polyethylimine (polyaziridine) and polystyrene using different derivatives of dipicolinic acid, namely, 4-chloro (**LXIX**), 4-hydroxy (**LXX**), and 4-(dimethylamino) (**LXXI**) pyridine-2,6-dicarboxylic


(LXIX)


(LXX)

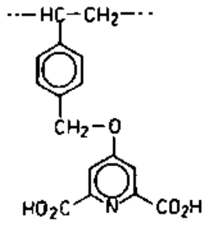

(LXXI)

acids [345–347]. The complexing behavior of these chelating resins is comparable to those of the corresponding iminodiacetic acids. However, it has been found that the influence of this matrix is relatively small because of the compact and inflexible coplanar structure. In addition, the possibility of increasing the difference in the stabilities of the complexes of a given pair of metal ions is offered by substitution in the 4-position of the pyridine ring of this acid. The resins incorporating 4-(dimethylamino)- and 4-hydroxy derivatives have been found to possess the largest difference in the stabilities of their calcium(II) and strontium(II) complexes. Thus, these resins are useful for the separation of the elements of the alkaline earth series, particularly for the separation of trace amounts of calcium(II) and strontium(II) [346]. The separation efficiency of the polyaziridine-based resin is even better than that based on formaldehyde and resorcinol and the greater separation capability of the former resin has been attributed to the additional coordination ability of the aziridine chain, whose structure is depicted in (**LXXII**) [345]. The


(LXXII)

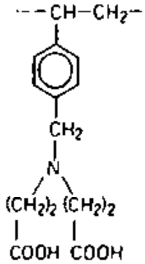
polystyrene-based resin has been obtained by treating chloromethylated polystyrene with the dimethyl ester of 4-hydroxy-2,6-pyridinedicarboxylic acid in dimethylformamide and hydrolysing the ester with sodium methoxide in dioxane, or by treating chloromethylated polystyrene with 4-hydroxy-2,6-pyridinedicarboxylic acid in the presence of triethylamine [347]. The intermediate anion exchanger reacts with the pyridine acid (**LXX**) to give a chelating ion exchanger (**LXXIII**). This chelating ion-exchange resin has been characterised on the basis of elemental analysis and IR spectroscopy. The detailed ion-exchange properties of this resin are under study [347].

Following the success of iminodiacetic acid resins, a large number of

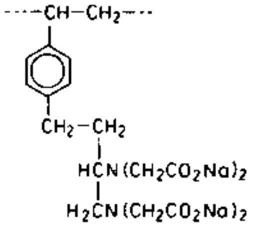


(LXXIII)

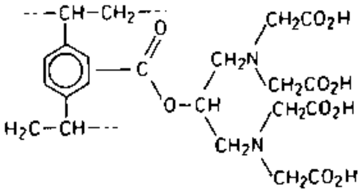
chelating ion-exchange resins incorporating similar functional groups have been studied. An example of such a resin is that obtained from the condensation of $\beta\beta'$-iminopropionic acid on chloromethylated styrene–DVB (divinylbenzene) copolymer through its dimethyl ester [348]. This resin (**LXXIV**) possesses more amphoteric than chelating properties, compared to those resins incorporating iminodiacetic acid and iminoacetic–propionic acid [349]. These observations are consistent with the behavior of monomeric *N*-substituted iminodipropionic acid. This resin has been claimed to be useful for the separation of alkali and alkaline earth metal ions [350]. A phenol–formaldehyde condensate containing *N*-phenyliminodiacetic acid as a chelating group has also been reported to be effective for the separation of calcium and magnesium from sodium between pH 6 and 12 [351]. Polystyrene-based exchangers (**LXXV**) with pendant groups containing EDTA moieties have been found capable of absorbing heavy metal ions [352]. Diaminetetraacetic acids form stronger complexes with metal ions that does iminodiacetic acid and also the former reacts with metal ions to form 1 : 1 complexes. Thus a resin containing a diaminepolyacetic acid functional group is expected to react and retain the metal ions more strongly than the resins containing an iminodiacetic acid functional group [353]. Some tetraacetic acid [164] and triacetic acid [278] resins have been evaluated for their ion-exchange properties, but the synthetic procedures used to obtain these resins generally lead to products with uneven properties [35,278]. This led Moyers and Fritz [353] to synthesise a new chelating resin containing a propylenediaminetetraacetic acid functional groups (**LXXVI**) attached to a



(LXXIV)

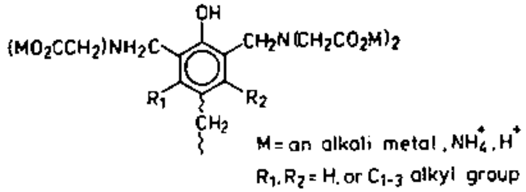


(LXXV)



(LXXVI)

carboxylic acid divinylbenzene resin (XAD-4) via an esterification reaction. The resin is rather easily prepared by reacting a carboxylated divinylbenzene resin (carboxylated XAD-4) with 1,3-diamine-2-hydroxypropane-*N,N,N′,N′*-tetraacetic acid. This resin possesses a macroporous matrix and has favourable kinetics for chelating reactions with metal ions. It has been found to be highly selective for uranium(VI), thorium(IV) and zirconium(IV) and reasonably selective for copper(II) below pH 2.5. The first three ions are separated from other metal ions by complexation on the resin in 0.01 M hydrochloric acid and once retained, they are separated from each other by sequential elution with 0.1 M hydrochloric acid, 4.0 M hydrochloric acid and 1.0 M sulfuric acid. Distribution coefficients of various metal ions with the resin at several pH values have been determined by a column elution method by using the relationship: $D_g = V'_R/W$, where V'_R is the adjusted retention volume and W is the weight (grams) of resin in the column. The selectivity order of metal ions is Mg(II) < Mn(II) < Cd(II) < Co(II) < Zn(II) < Fe(III) < Ni(II) < Bi(III) < Cu(II) < UO_2^{2+} < Th(IV) < Zr(IV), in good agreement with the selectivity order of the propanediaminetetraacetic acid. The resin has also been shown to retain quantitatively a number of trace elements from simulated sea water. *m*-Phenylenediglycine–formaldehyde condensate [1] and a formaldehyde condensate containing *m*-phenylenediamine-tetraacetic acid [164] have been found to be suitable for selective separation of transition metal ions from alkali and alkaline-earth metal ions. A phenolic resin (**LXXVII**) possessing two iminodiacetic moieties shows selectivity for iron(III) and copper(II) at pH 3 [354]. Another tetraacetic acid, carboxymethyl(imino)bis(ethylenenitrilo)tetraacetic acid (diethylenetriamine-*N,N,N′,N′,N*-pentaacetic acid, DTPA), is coupled to an affinity chromato-

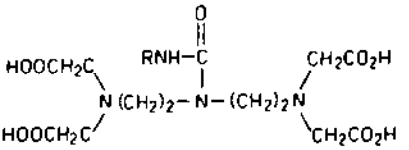


M = an alkali metal, NH_4^+, H^+

R_1, R_2 = H or C_{1-3} alkyl group

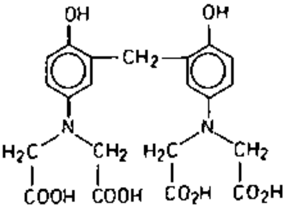
(LXXVII)

graphic gel, AH-Sepharose 4B, via a carbodiimide coupling reaction to obtain a new chelating gel (**LXXVIII**) which has been claimed to be easier to handle and more selective for trace metal ions than Chelex-100 (Chelex-100 has an affinity for alkali and alkaline-earth metal ions) [355]. This chelating gel has successfully been used for extracting copper from sea water with high selectivity over alkaline earths such as magnesium. It has been shown to be useful over a wide pH range (4–9), and is stable and reversible over a long period of time. The effect of cross-linking of the resin upon separation of rare earth metals with *trans* 1,2-diaminocyclotetraacetic acid has also been reported [356]. Several chelating ion-exchange resins containing 3,3′-methylenebis-*N*-(hydroxyphenyl)iminodiacetic acid (**LXXIX**) and its methoxy derivative have been studied by D'Alelio et al. [102,106].



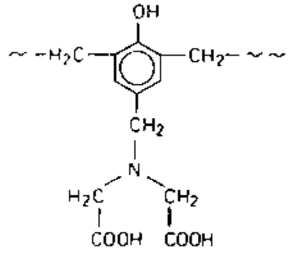
R= AH - sepharose 4B gel residue

(LXXVIII)

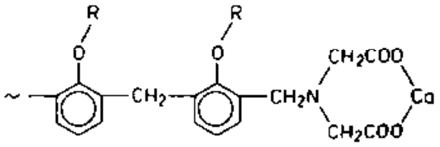


(LXXIX)

Recently, a versatile chelating ion-exchange resin (**X**) has been prepared by copolymerising *N*-(*o*-hydroxybenzyl)iminodiacetic acid with phenol and formaldehyde [132,166]. This resin is now commercially available under the name of Unicellex UR-50 (cf. Table 1 for details). A chelating ion-exchange resin incorporating *N*-(*p*-hydroxybenzyl)iminodiacetic acid (**LXXX**) has also been prepared and its ion-selective properties have been compared with Unicellex UR-50 and Dowex A-1 [132,166]. It has been observed that the order of decreasing stability is Cu(II) > Ni(II) > Zn(II) > Co(II) regardless of the chelating resin involved. The stability for a given metal ion is of the same order for the three resins, except for iron(III). Only the resin (**X**) shows a strong affinity towards iron(III) and this unusually high stability of monomeric *N*-(*o*-hydroxybenzyl)iminodiacetic acid and its resin (**X**)–iron(III) complexes in acidic solution is attributed to participation of a hydroxyl group in the chelating process, whereas in the case of the *N*-(*p*-hydroxybenzyl)iminodiacetic acid resin (**LXXX**) and Chelex-100 (or Dowex A-1) only the iminodiacetic acid group is responsible for chelation [132]. The tetradentate mode of coordination of *N*-(*o*-hydroxybenzyl)iminodiacetic acid resin (**X**) has been confirmed by spectroscopic (IR, electronic, ESR and Mössbauer) studies of the metal complexes of this resin (with chromophore NO_3) [166]. The ESR spectra of VO(IV), Cr(III), Mn(II), Fe(III), Cu(II) and Gd(III) complexes of Unicellex UR-50 have been compared with those of the metal complexes of Dowex A-1 and a study of spin–spin exchange interaction indicates that the iminodiacetate groups present in the coordination pores of Unicellex UR-50 are closer to one another than those in Dowex A-1 or Chelex-100. The order of decreasing chelate stability is Cu(II) > Ni(II) > Zn(II) > Co(II), regardless of the chelating resin. A derivative of UR-50 containing ether groups (**LXXXI**) instead of phenolic groups has also been described [357].



(LXXX)

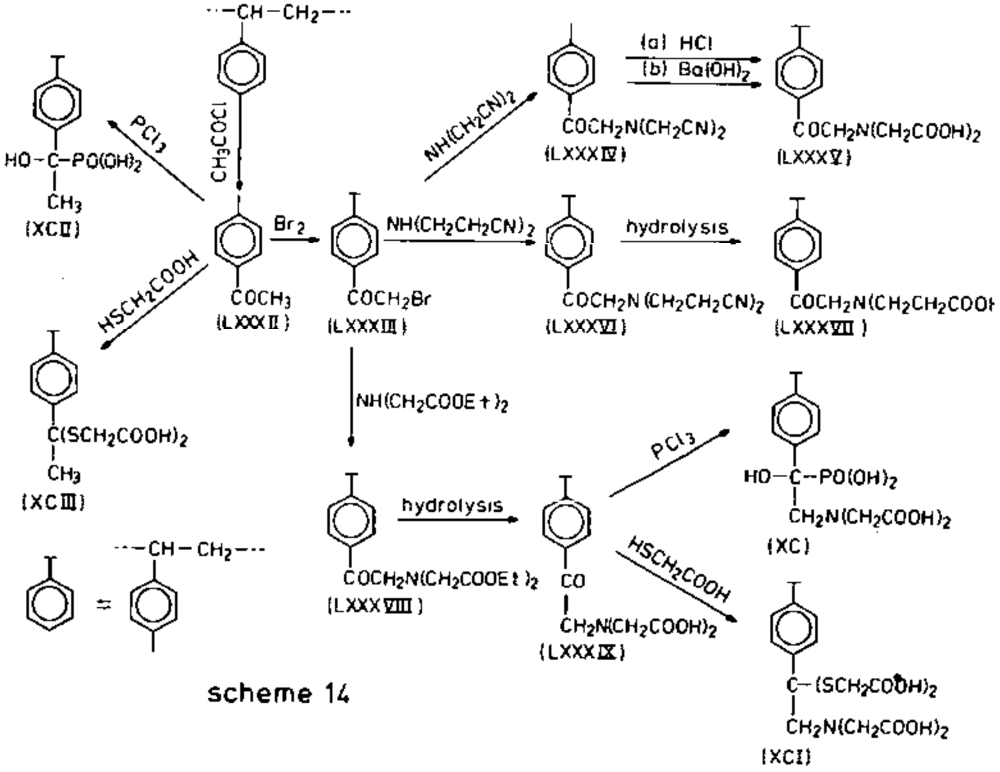


R = an alkyl group

(LXXXI)

Hering et al. [358–361] have carried out extensive work on different aspects of iminodiacetic acid and related resins, e.g., sarcosine, methylaminopropionic acid, and iminodiacetic propionic acid resins. The characterisation and ion-selective properties of such resins have been described at length in several earlier reviews [7,30–35,38]. Moieseeva et al. [362] have studied the magnetic properties of manganese(II), cobalt(II), nickel(II), copper(II), iron(III) and chromium(III) complexes of poly(*p*-biscarboxymethyl)amino styrene and found that these complexes have the same type of coordination bonds as their low-molecular weight analogues, viz. the metal complexes of phenylglycine or *N*-(carboxymethyl)aminoacetic acid. NMR studies of the interaction of water molecules with complexes of soluble polystyrene amino acids have also been carried out [363]. A strong signal on the strong-field side of the free water signal in the NMR spectra of the chelating ion exchanger of iminodiacetic acid resin containing Na^+, Cd^{2+} or Ca^{2+} is observed and assigned to water molecules coordinated to these metal ions. The synthesis and ion-exchange properties of several resins containing aminocarboxylic groups have been reported [364–370].

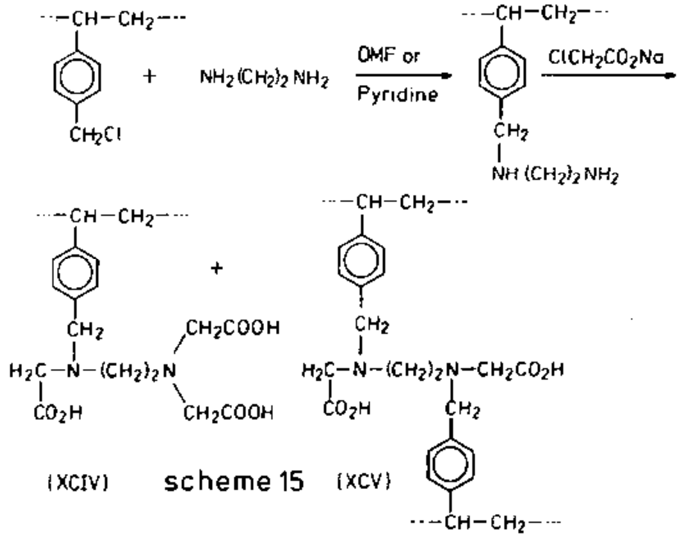
In view of the high stability of the monomeric compounds, *N*-acetoiminodicarboxylic acid [372] and aminoacetone-*N,N*-diacetic acid [373], attributed to the contribution of carbonyl coordination, a series of ion exchangers containing ketoiminocarboxylic acids $-COCH_2N[(CH_2)_m-COOH]_2$ as functional groups has been synthesised by Marhol and Cheng [371]. An acetylated styrene–DVB copolymer (**LXXXII**) is converted into its bromo derivative (**LXXXIII**) and used as starting material for several modification reactions. Several chelating ion-exchange resins containing iminodinitrile functionalities (**LXXXIV, LXXXVI**), ketoiminodicarboxylic acid groups (**LXXXV, LXXXVII, LXXXIX**), phosphonic–iminodicarboxylic acid groups (**XC, XCII**) and thioglycolloic–iminodicarboxylic acid groups (**XCI, XCIII**) have been synthesised by a sequence of reactions, shown in Scheme 14. However, a low-exchange capacity resin was obtained when iminodiacetonitrile instead of an iminodiacetic acid dimethyl ester (**LXXXVIII**) was used to obtain the resin (**LXXXV**). The content of nitrogen, phosphorus, and sulfur was lower than the theoretical values of these elements, calculated from the structural formulae of the resins. The mechanical stability of the



scheme 14

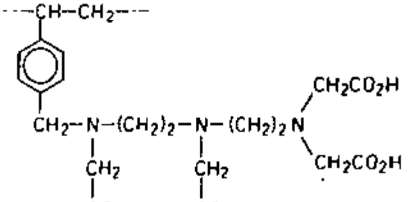
resins is very good and their chemical stability varies with the type of resin. With the exception of the resins (**XCI** and **XCIII**), all exchangers have been found to be stable in neutral or acidic solution at room temperature. In alkaline solution, slight degradation was observed. In the presence of Cu^{2+} ions at elevated temperature (80°), changes in the resin (**LXXXIX**) were observed, attributable to possible interaction between the carbonyl group and Cu^{2+} ions, as no such change was observed with Ca^{2+}. A qualitative order of selectivity of the ketoiminodicarboxylic acids has been found to be slightly different. For resin (**LXXXVII**) at pH 3.0, it is: $Th > UO_2^{2+} > Pb > La > Zn > Ni > Co > Ca > Sr > Mg$ and for the resin (**LXXXIX**) at pH 3, it is: $Th > Pb > Ni > UO_2^{2+} \gg Ca > Zn > Cd > Co > Ca > Sr > Mg$. It has been observed that the swelling volumes are in good agreement with the selectivity series of these resins. The ions for which the functional group has the lowest selectivity (Mg^{2+}), give the highest swelling volume.

Chelating ion-exchange resins possessing polyaminocarboxylic groups can also be prepared by carboxymethylation of polyethylenepolyamine chelating polymers [278,374–376]. Blasius and Bock [278] condensed a number of polyethylenepolyamines such as ethylenediamine, diethylenetriamine and triethylenetetraamine, with chloromethylated polystyrene–DVB copolymers and subsequently carboxymethylated them to obtain chelating ion-exchange resins containing iminodiacetic and aminoacetic acid units. They observed that the polyethylenepolyamines are linked to the polymeric matrix by one or more bridges according to the length of the polyethylenepolyamine and they found that the subsequent carboxymethylation of the polyamine resins remains incomplete. Therefore, the chelating groups of a given ion exchanger do not have the same repeating unit and it is difficult to give an exact description of the complex formation of these resins. However, Szabadka et al. [279,374,375] have shown that the chelating ion-exchange resins of well-defined and reproducible composition containing polyaminopolycarboxylic acids can be synthesised by careful amination and subsequent carboxymethylation of chloromethylated polystyrene–DVB copolymers [374]. For instance, ethylenediamine reacts with chloromethylated polystyrene to give rise to two products in which one amino group is attached to a polymeric matrix (**XLIX**) and in the other, both the amino groups are attached to the polymeric matrix (**L**) (Scheme 10). Thus, two chelating ion exchangers are obtained on carboxymethylation of resin (**XLIX**) and resin (**L**) which are depicted as resin (**XCIV**) and (**XCV**) respectively (Scheme 15) [279,374]. Following this method, Szabadka and Inczedy [279] have exclusively prepared a chelating ion-exchange resin containing ethylenediaminetriacetic acid functional groups (**XCIV**). This chelating ion exchanger is now commercially available as Ligandex E (cf. Table 1). The protonation constants of this chelating ion-exchange resin have been calcu-

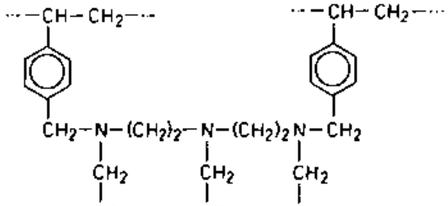


(XCIV) scheme 15 (XCV)

lated in aqueous solutions at different ionic strengths and constant values are obtained independent of the ionic strength [374]. Similarly, a chelating ion-exchange resin with diethylenetriaminetetraacetic acid as a functional group (**XCVI**) has been prepared [375], though the possibility of formation of a related product, depicted in (**XCVII**) during the reaction of chloromethylated polystyrene with diethylenetriamine cannot be completely ruled out [278]. The protonation constants of the resin containing diethylenetetraacetic acid functional groups have also been determined by batch titration and the values agree well with the theoretical titration curve [375]. A Japanese patent [376] also describes the preparation of a resin containing a diethyleneamine-



(XCVI)

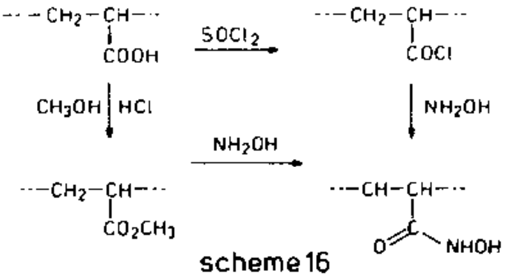


(XCVII)

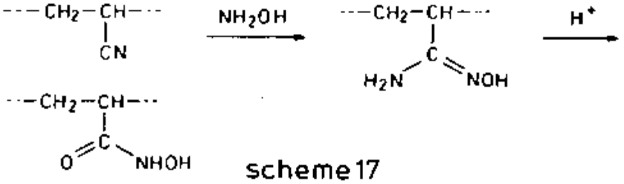
tetraacetic acid functional group, anchored on chloromethylated polystyrene and this resin has been claimed to be resistant to oxidation.

(b) Hydroxamic acid, oxime and oxine-containing ion exchange resins

The coordination chemistry of these classes of ligands is well established, as is evident from the fact that metal coordination compounds of hydroxamic acids [377,378], oximes [379] and oxines [380] have repeatedly been reviewed in recent years. Development of polymeric ligands incorporating hydroxamic acids can be attributed to their ability to form stable complexes with heavy metals, particularly with iron(III), their occurrence in nature as trihydroxamic acids called siderochromes, which are known to play an important role in biological pathways involving iron transport [381] and powerful catalytic activities of *N*-methylhydroxamic acids in the hydrolysis of certain active esters [382]. Winston and Mazza [383] and Vernon [155] have partially reviewed some aspects of the development of polymeric hydroxamic acids. Most of the research on polyhydroxamic acid has been concentrated on primary or *N*-unsubstituted compounds [384], with very few exceptions [383,385–387]. Several synthetic routes are known for the synthesis of monomeric hydroxamic acids and its derivatives. Vinyl monomers bearing hydroxamic acid groups have been reported to polymerise under a variety of conditions. The monomers, acrylo-, methacrylo-, crotono-, and cinnamohydroxamic acids have been prepared by reaction of the corresponding ester with hydroxylamine [388,389]. Initial attempts to prepare poly(hydroxamic acids) deal with the conversion of conventional weak-acid cation exchangers to acid chlorides which, in turn, were treated with hydroxylamine. However, results obtained by this method were discouraging, because of poor conversion of the acids into acid chlorides [390–392]. In many instances, better results have been obtained by employing the method involving the reaction of an ester with a hydroxyl amine [393–395]. In this regard, the work of Kern and Schulz [395] merits special mention; they reported that a reaction between poly(methyl acrylate) and hydroxylamine results in the formation of a polymer containing 80% acrylohydroxamic acid, 14% acrylic acid and 6% methyl acrylate, and which formed the characteristic red-brown iron(III) complex. The ratio of iron to the hydroxamic acid in this complex has been found to be 1 : 3. Several other ion exchange resins containing hydroxamic acid groups have been prepared from Amberlite IRC-50 (containing –COOH groups on a vinyl-addition polymer) by conversion of the carboxyl groups to the acid chloride [396,397] or to an ester [398], followed by treatment with hydroxylamine (Scheme 16). Another approach consists in the treatment of polyacrylonitrile with hydroxylamine followed by hydrolysis of the intermediate amidoxime to synthesise chelating ion-exchange resins containing pendant hydroxamic acid groups [399–402]. The


scheme 16

same approach has been used by Kyffin [403] to convert amidoxime polymers into poly(hydroxamic acids), including one commercial resin, ES 346 (cf. Table 1), which contains an amidoxime chelating group on a polyacrylic matrix. This method appears to give satisfactory yields [155]. The sequence of reactions used to prepare poly(hydroxamic acids) by this procedure is depicted in Scheme 17. Marshall [404] adopted a different approach for

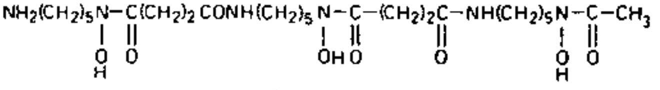

scheme 17

synthesising a poly(hydroxamic acid) polymer, by using a one-step reaction involving sodium hydroxide and hydroxylamine treatment of poly(acrylonitrile). The resins prepared by this process possess capacities of 1.3 and 5.0 mmol g^{-1} for iron(III) and Cu(II), respectively. A similar approach was used by Schouteden [405] to convert poly(acrylonitrile) to poly(hydroxamic acid) by treating the starting material with hydroxylamine in dimethylformamide. Vrancken and Smets [406] also synthesised a poly(hydroxamic acid) by treating poly(acryloyl chloride) with hydroxylamine in dimethylformamide. The conversion of polymeric carboxylic acids, however, poses many problems. Other disadvantages of this type of resin are that they are unstable towards relatively concentrated acids and bases and undergo rearrangements during regeneration [407]. However, the poly(hydroxamic acids) prepared from the hydrolysis of cross-linked poly(acrylonitriles) and subsequent condensation with hydroxylamine show high stability towards concentrated acids and bases during regeneration and, in turn, retain their high capacity for iron(III) ions (3.5 mmol g^{-1}) [407]. This type of chelating ion exchanger is cheaper and easier to prepare than Dowex A-1, and the swelling, equilibration rates, and total capacities are comparable; they possess higher selectivity, which makes them more versatile ion exchangers for analytical purposes. Vernon and Eccles [386] recently prepared two chelating ion exchangers containing *N*-substituted hydroxylamine functional groups. One chelating ion exchanger contained *N*-benzoyl-*N*-phenyl-hydroxylamine, prepared by condensation of phenylenedihydroxylamine and terphthaloyl chloride, was soluble in alkaline solution and the other chelating resin was prepared by a reaction between *p*-(bromoethyl)benzoyl-phenylhydroxylamine with poly(ethyleneimine). The chelating properties of these polymers were studied with iron, cobalt, copper, vanadium and uranium, along with the effect of a competing ligand on the resin capacity. The linear oxime–carbonyl polymer has a pH-dependent chelating capacity analogous to chelates formed by the monomer BPHA, whereas the poly(ethyleneimine)-based resin had high capacities for the metal ions studied. The absence of a co-ion in metal–ion capacity studies indicates the possible formation of 1 : 2 and 1 : 3 metal complexes with the resin. This behavior of the resin is comparable to that of the monomer when solvent extraction of the metal ion with a ligand in solution is carried out. In view of the interesting results obtained with *N*-aroylphenylhydroxylamines, this work was extended to the preparation of cross-linked *N*-acyloxime resins. In one of the preparations, beads of a commercial resin Zeocrab 226 (a cross-linked methacrylic acid) were first converted into an acid chloride which was treated with phenyl hydroxylamine at room temperature for several days. According to another approach, an acryloyl chloride, styrene and divinylbenzene were copolymerised by irradiation with ultra-violet light and the polymer so obtained reacted with phenylhydroxylamine in dimethylformamide for 14 days at 5 °C, followed by treatment with methanol. This approach is better than other methods employing acryloyl chloride, since the resulting cross-linked acid chloride polymers are not contaminated by carboxylic acid or anhydride groups. The properties of aroyl oxime and acyl oxime ion-exchange resins have been compared. It was found that the two types of resins possess comparable capacities for different metal ions studied. Anomalously, high capacities for cobalt(II) and copper(II), ranging between 1.2–2.1 mmol g^{-1} and 3.1–3.6 mmol g^{-1}, respectively, have been explained in terms of the residual carboxylic acid content of the two resins. The *N*-acyloxime resin (PMA) is capable of separating mercury(II) and lead(II) at low pH with preferential retention of mercury by the column [387].

The synthesis of a macroporous cross-linked poly(hydroxamic acid) has been achieved through the hydrolysis of a cross-linked poly(acrylonitrile)–DVB copolymer to an amide on treatment with hydroxylamine [408]. This polymeric ligand has been reported [408] to be superior to those previously reported and found selective for iron(III), vanadium(V) and mercury(II). These types of resins are completely stable towards 5 M HCl or H_2SO_4 and also to 1 M NaOH. The main advantage of such types of resin appears to be their ability to separate multivalent ions, e.g., iron(III) from

Cu(II) at pH 1.5 and Cu(II) from Co(II) at pH 3.5, whereas iminodiacetic acid resin is most useful for blanket extraction of these metal ions at pH > 5. Several ion exchange separations with such resins have been described [409]. These types of resin have also been found to be useful for recoveries and separations of iron(III) and uranium(VI) from sea water. Sorption and desorption of gold and silver by this exchanger and separation from each other are reported [409]. A patent [410] describes the preparation of several poly(hydroxamic acid) resins by the hydrolysis of polyamidoximes having $-CH(CN)CH_2CH[C{=}(NOH)NH_2]CH_2-$ recurring units. A poly(hydroxamic acid) sodium salt of this resin has been used for water softening.

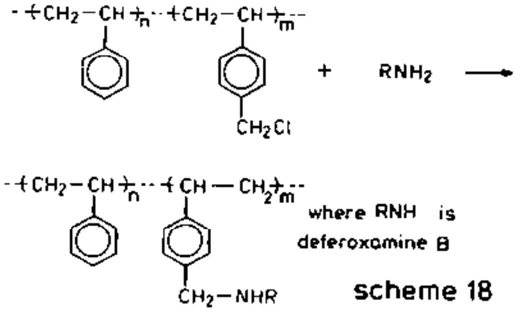
Initial attempts by Narita et al. [411] to convert styrene–DVB copolymers containing ethyl acrylate or *p*-nitrophenyl methacrylate either failed, or resulted in polymers containing a considerable fraction of carboxylic acid groups in spite of vigorous treatment with hydroxylamine. Similar observations have been made in this laboratory when an attempt was made to convert an ethylacrylate–styrene derivative into a hydroxamic acid resin [412]. However, Winston and Mazza [383] have shown that such hydroxamic acid resins could be prepared through reaction of the active ester substituted with *O*-benzylhydroxylamine followed by treatment with hydrogen bromide. Recently, in the course of a search for polymeric chelating agents for treating cases of extreme iron poisoning, Ramirez and Andrade [413] grafted the trihydroxamic acid, deferoxamine-B (**XCVIII**) to several polymers through



$$NH_2(CH_2)_5\underset{OH}{N}-\underset{O}{\overset{\|}{C}}(CH_2)_2CONH(CH_2)_5\underset{OH}{N}-\underset{O}{\overset{\|}{C}}-(CH_2)_2\underset{O}{\overset{\|}{C}}-NH(CH_2)_5\underset{OH}{N}-\underset{O}{\overset{\|}{C}}-CH_3$$

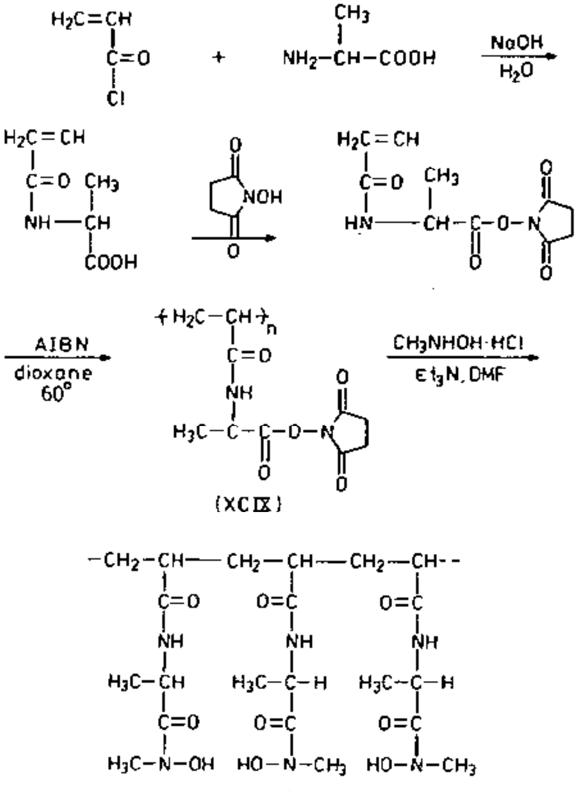
(XCVIII)

the free amino group. The reaction used for attaching deferoxamine to chloromethylated polystyrene and commercially available chloromethylated Amberlite XAD-2 and XAD-4 is depicted in Scheme 18. Attempts have been



scheme 18

made to prepare the synthetic analogues of deferoxamine-B, to obtain a hydroxamic acid polymer with a structure designed to permit facile formation of an octahedral iron(III) complex of high stability, utilizing neighboring hydroxamic acid groups [383]. Winston and Mazza [383] prepared such a polymer bearing hydroxamic groups and having high affinity for iron(III) through the sequence of reactions shown in Scheme 19 to obtain a



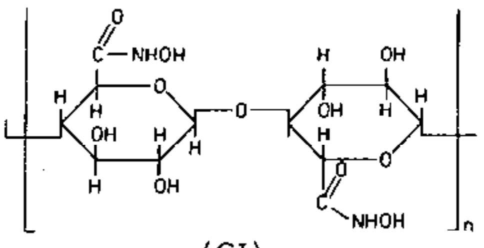
scheme19

polymer (**XCIX**) which on treatment with hydroxylamine in DMF gives a hydroxamic polymer (**C**) as confirmed by elemental analysis and IR spectra.

Iron-binding studies with this polymer reveal the formation of both FeA_3 and FeA_2^+ species. However, an FeA_3 complex would be expected to have lower stability as a result of either bond angle strain and atomic compression, or a lower probability in bringing a third hydroxamic group into a position to form the octahedral complex. Winston and McLaughlin [414] extended these studies to two related polymers having the hydroxamic groups separated by 11 and 3 atoms, respectively. The iron binding properties of these polymers along with earlier reported polymers having hydroxamic groups separated by 9 atoms [383] have been compared with those of the model compound desferrioxamine B (DFO). The order of stability of iron complexes with these three resins is: DFO, 11, 9 and 3 atoms, respectively.

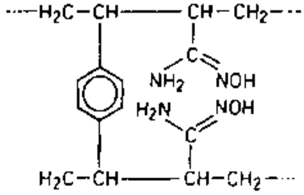
Philips and Fritz [384] described synthetic methods for attaching *N*-phenyl- and *N*-methylhydroxamic acid groups to a macroporous polystyrene–divinylbenzene copolymer by the acetylation of a commercial resin XAD-4 [386], followed by oxidation to carboxy XAD-4. Chloroformyl XAD-4 was obtained by treating the carboxy XAD-4 with thionyl chloride which on treatment with *N*-methylhydroxylammonium chloride gives the required polymer. Use of hydroxyammonium chloride leads to the synthesis of *N*-unsubstituted hydroxamic acid resins. The extraction of 19 metal ions was studied as a function of pH with the *N*-methylhydroxamic acid resin and several analytical applications (including the purification of chemical reagents, concentration of trace metal ions etc.) and chromatographic separations of metal-ion mixtures with this resin have been demonstrated.

A hydroximated cellulose powder (**CI**) with a low content of hydroxamic groups has been prepared from a starting material of carboxy-cellulose, containing about 6 wt.% of carboxyl groups [415] and recently, hydroxamic cellulose fibres with a high content of hydroxamic acid group have also been reported [415]. The preliminary results show that this hydroxamic cellulose, having a sorption capacity about 2.1 mmol g^{-1}, may be used for environmental analytics. A new chelating ion-exchange resin named "hydroximised Sephadex" (H-Sephadex) has been prepared by treating carboxymethyl Sephadex (4.27 mmol COOH g^{-1} gel) with hydroxylamine. Lead(II), copper(II), cadmium(II), mercury(II), zinc(II) and manganese(II) were collected completely from 50 ml of 1×10^{-5} M solution of each metal salt over different pH ranges [416].



(CI)

A related group of ligands, amidoximes, is the basis of the synthesis of some very useful chelating ion-exchange resins. Amidoxime resins are being increasingly studied because of their ability to selectively bind to several metal ions such as iron(III), copper(II) and uranyl(2+) at very low pH range. The chemistry of amidoximes has been reviewed [417]. Schouteden [418] synthesised a polymeric amidoxime by treating poly(acrylonitrile) with hydroxylamine. Amidoximes have amphoteric character and thus polymeric amidoximes swell significantly in dilute acids and bases, rendering these polymers unsuitable for column packing [419]. Colella et al. [419] synthesised a poly(acrylamidoxime) metal-chelating resin and cross-linked with divinylbenzene to improve its mechanical stability. The proposed structure of poly(acrylamidoxime) resin is depicted in (**CII**). The infrared spectrum of the poly(acrylamidoxime) resin shows characteristic absorptions of amidoximes [417,418]. The amine stretching frequency at 3400 cm^{-1}, broad absorption of the OH stretching frequency at 3325 cm^{-1}, broad absorption at 1650 cm^{-1} due to C=N stretching vibration of the oxime group and a broad band at 900 cm^{-1} has been assigned to N – O stretching of the oximes. The amidoxime content of the resin has also been determined by analytical methods. The resin shows no affinity for the alkali and alkaline earth metals tested over the pH range 2–8; the resin selectivity has been determined at pH 5 for several metal ions. The order of decreasing selectivity is: Cu(II), Ni(II), Co(II), Zn(II) and Mn(II). The kinetics of the resin–metal interaction have been found to be sufficiently rapid in most cases for application in packed columns for the collection of trace metals. The uptake of trace metals was found to be 90% or more for most metals over a range which encompasses the pH of most natural water systems. This resin has been used for determination of Fe(III), Cu(II), Cd(II), Pb(II) and Zn(II) from sea water and pond water [420]. Metal concentrations as determined by this resin are in good agreement with the values determined directly on samples by either differential pulse polarography or differential-pulse anodic-stripping voltammetry. In comparison with Chelex-100 and a poly(dithiocarbamate) resin [421], poly(acrylamidoxime) resin (**CII**) has been shown to possess a distinct advantage in the full recovery of sequestered metals. A commercial resin, ES 346, containing an amidoxime functional group is also available. This resin, containing a cross-linked polyacrylic matrix, strongly binds iron(III), uranium(VI), vanadium(V) and copper(II), and binds moderately with cobalt(II) and nickel(II), whereas metals like chromium(III) also form relatively stable complexes with this resin at relatively low pH [422]. Using this chelating resin, the separation of iron(III), copper(II) and uranium(VI) ions, using pH control, was studied by Vernon and Kyffin [423]. These metals can be quantitatively recovered from cobalt and nickel salt solution at pH ≈ 3.

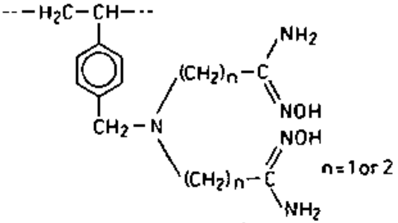


(CII)

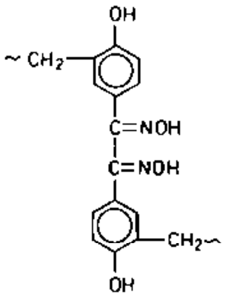
Iron(III) may be separated from copper(II) by selective desorption with sodium carbonate solution as eluent. Gold and platinum group metals may also be separated with these types of resin [423]. Schwochau et al. [424] employed a cross-linked poly(acrylamidoxime) resin for the extraction of uranium from sea water at natural pH. The resin presents an uranium loading of > 3000 ppm and it has higher selectivity, uptake, and attrition ability than hydrous titanium oxide. Another advantage of this resin is that it accumulates less calcium and sodium than hydrous titanium oxide. Uranium can be eluted from the complexing resin with hydrochloric acid. This resin, besides containing an amidoxime functional group, may also contain other related functional groups [424].

The chelating properties of a poly(acrylamidoxime) resin prepared from acrylonitrile–divinylbenzene copolymer and its reaction with hydroxylamine has also been described [425]. The pH dependence of its chelating capacity for metal ions, such as Sb(III), Sb(IV), Bi(III), Te(IV), Se(IV) and Se(VI), have been determined. Another amidoxime-containing cation exchanger has been prepared by the reaction of a polyalkylene glycol dimethacrylate unsaturated nitrile (e.g., acrylonitrile) copolymer with hydroxylamine [426]. Recently, chelating resins containing (di)amidoxime groups on a polystyrene–divinylbenzene matrix (**CIII**) have been reported [427]. The chelating behavior of this resin has been compared with several similar polymeric ligands containing amidoxime as functional group. It has been observed that the adsorption of copper(II) by chelating resin (**CIII**) increased with the increasing concentration of Cu(II) ions in water solutions and gradually approached the equilibration with the shape of a Langmuir adsorption isotherm. The adsorption stability constants between copper(II) and the chelating resins decreased in the order: $-N(CH_2CN)_2 > -N(CH_2CH_2CN)_2 > NaCN >$ acrylonitrile derivatives (amidoximes) [427].

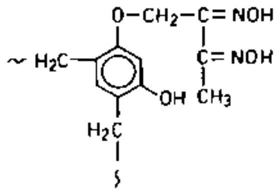
Chelating ion-exchange resins incorporating oxime functionality form an interesting and useful class of polymeric ligands because of their strong chelating properties. Chelating resins derived from hydroxyoximes find extensive application in hydrometallurgy of copper(II) [23]. The earlier developments of oxime-containing resins have been reviewed [30–32,34,35]. Stamberg, Seidel and Rahm [428] reported the synthesis of three chelating ion-exchange resins containing vicinal dioxime groups. These resins have different matrices, such as formaldehyde with the dioxime (**CIV**), resorcinol–formaldehyde (**CV**) and cross-linked polystyrene (**CVI**). These chelating polymers selectively extract nickel(II). The chelating resin containing cross-linked polystyrene possesses good mechanical stability, whereas two other chelating resins (**CIV** and **CV**) suffer from lack of mechanical stability and also instability at high pH range. Manecke and Danhauser [429] synthesised a similar chelating ion-exchange resin (**CVII**) by propionylating,



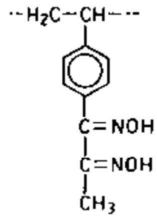
(CIII)



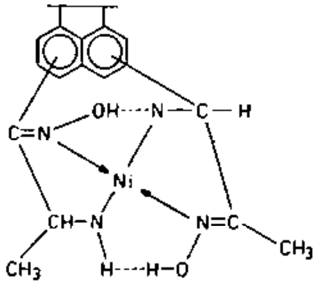
(CIV)



(CV)



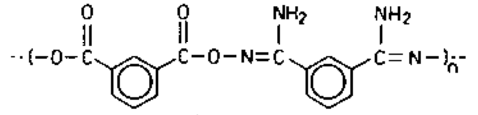
(CVI)



(CVII)

nitrosating and finally dioximating a copolymer of polyacenaphthylene and divinylbenzene. This resin also suffers from poor mechanical stability. Very recently, Walsh et al. [157] prepared a series of chelating resins containing *o*-hydroxyoxime functional groups from substituted phenyl acrylate polymers by a Fries rearrangement as depicted in Scheme 5. These chelating resins containing *o*-hydroxyoximes as the functional group have been found to be specific for copper(II) ions. Warshawsky [430] used a polystyrene resin impregnated with β-diphenylglyoxime as a reagent for selective separation of palladium(II). De Geiso et al. [431] synthesised the monomeric *O*-methacroyl and *O*,*O'*-dimethylacroyl derivatives of dimethylglyoxime and each of these ligands was polymerised to yield cross-linked chelating resins.

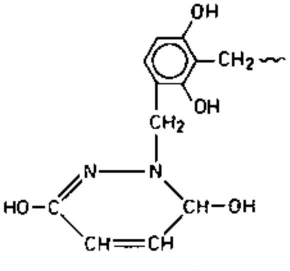
Sykora and Dubsky [432] reported that resacetophenonoxime condenses in an alkaline solution either alone or in the presence of resorcinol with formaldehyde, giving rise to a new selective cation exchanger. This resin has been found to be highly selective for Cu^{2+}, having a maximum capacity at pH 6 (6.4 mmol g^{-1} dry weight). The resin also possesses a high capacity for iron(III) and aluminium(III), but this high capacity and swelling power of the resin results in poorer mechanical properties (wear and volume changes during the change of form). The resin possessing resorcinol has better mechanical properties, but slightly diminished capacity. Two Czech patents describe the preparation and properties of condensation polymers containing oxime functional groups [433,434]. A number of 2-hydroxyaryloximes have been impregnated physically into polymeric matrices such as macroporous styrene–divinylbenzene copolymers, and these impregnated resins find use in hydrometallurgy of copper [435]. These resins are, in fact, solvent impregnated resins (SIR) and differ from the conventional chelating ion-exchange resins, which contain chelating ligands covalently bonded to a polymeric matrix. The properties of conventional and impregnated chelating ion-exchange resins have been compared [436]. The synthesis and chelating properties of a soluble chelating polymer, poly(*O*-isophthaloylisophthalamide oxime) have been described in detail by Lehtinen et al. [437]. The polymer has the structure (**CVIII**) and it forms intense green to dark brown complexes with copper(II). The structure of chelating copper polymers were studied using infrared spectra and X-ray diffraction data. For establishing the structure of these polymeric chelates, a copper(II) complex of a model compound, *O*,*O*′-dibenzoylisophthalimide oxime was studied. The infrared spectra of chelating polymers resemble that of the complexed model compound and, therefore, these polymers have been considered to have almost the same structure as the model compound. Thermal properties of copper chelates do not differ from that of the polymer itself. A related class of polymers is that of the polyhydrazides. The synthesis and chelating properties of polyhydrazides have been studied in detail by Frazer et al. [438]. Compared to poly(*O*-isophthaloylisophthalamide oxime), the reaction rate and degree of chelation are much higher for polyhydrazides [438,439]. Several mono- and dihydrazides and their corresponding hydrazones have been anchored on styrene–DVB copolymers. Several bi-, tri-, and tetradentate hydrazides such as benzoic acid, salicylic acid, malonic acid, succinic acid, adipic acid, dipicolinic acid, furan-2,5-dicarboxylic acid hydrazides have been incorporated into a styrene matrix by a general reaction using dimethylformamide as solvent and triethylamine as proton acceptor [440]. Some of the resins incorporating hydrazides appear to be selective for



(CVIII)

copper(II) ions. Blasius and Brozio [441] found that a chelating resin, prepared by the mixed condensation of pyridine-2,6-dicarboxylic acid dihydrazide, resorcinol and formaldehyde, possesses pronounced affinity for transition metal ions. An intense red-colored resin prepared by polycondensation of iminodiacetic acid dihydrazide with formaldehyde and resorcinol in alkaline medium has been found to behave in the same way; it selectively takes up copper(II) ions.

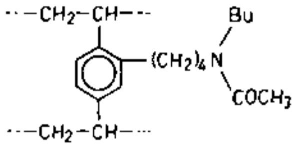
Egawa et al. [442] prepared chelating resins containing hydrazide groups by treating divinylbenzene–methylmethacrylate copolymers with hydrazine hydrate. The so-prepared hydrazide selectively binds Hg^{2+} and Cu^{2+} at pH 4, and metals were eluted by 6 N inorganic acids. Alkali metal ions did not effect the adsorption of the heavy metal ions by the resins. Blasius and Laser [443] synthesised a resin having cyclic maleic acid hydrazide groups (**CIX**).



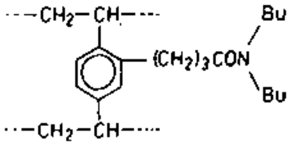
(CIX)

This resin has been found to bind both mercury(I) and mercury(II). Resins prepared from an aromatic derivative of ethylene, a dihydrazide of 1,2-ethylenedicarboxylic acid and divinylbenzene show good chelating properties [444]. The complex-forming properties of such resins can be intensified by adding 2-methyl-5-pyridine as an aromatic derivative. These resins have been found to bind divalent copper, nickel, cobalt and magnesium but fail to form complexes with alkali metal ions [445]. A number of acrylic acid hydrazide polymers have been synthesised from polyacrylamide and hydrazine hydrate [446]. Orf and Fritz [447] have described the preparation and chromatographic application of three resins incorporating tertiary amide group as shown in **CX**, **CXI** and **CXII**. Among these resins, the resin **CX** has been found to be most successful and it retains uranium(VI), thorium(IV) and zirconium(IV) selectively from aqueous solution, pH 3.0. Gold(III) and palladium(II) can also be retained by the resin from aqueous solutions containing hydrochloric acid. The resin has a capacity for gold of 1.7 mmol g^{-1}.

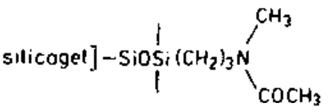
The chelating ion-exchange resins incorporating 8-hydroxy quinoline (oxine or 8-quinolinol) form an important and extensively studied class of selective ion exchangers. A large number of resins with oxine as a functional



(CX)



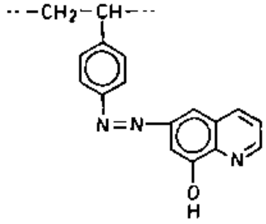
(CXI)



$$\text{silicogel}]-\text{SiOSi}(\text{CH}_2)_3\text{N}(\text{CH}_3)\text{COCH}_3$$

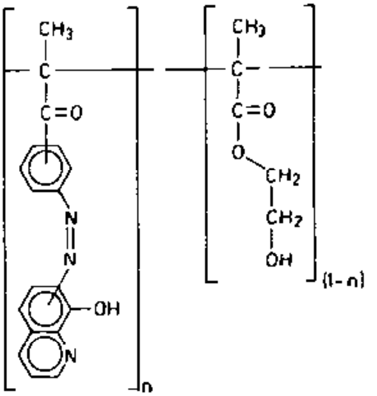
(CXII)

group having different types of matrices have been synthesised. The oxine resins studied so far can be divided into four groups: (i) cross-linked polystyrene resins with oxine groups attached to a styrene ring via an azo linkage, (ii) condensation resins derived from formaldehyde, phenol and oxine, (iii) resins derived from poly(5-vinyl-oxine) and (iv) oxine attached to silica gel and porous glass beads. The synthesis and ion-exchange properties of all these types of resins incorporating oxine or substituted oxines will be reviewed briefly here. The bulk of the work on chelating ion-exchange resins containing 8-hydroxyquinoline has been carried out by Vernon and Nyo [448,449]. Vernon and Eccles [450] have briefly reviewed the development of this class of chelating ion-exchange resins. To start with, Von Lillin [451] and Parrish [452] were first to prepare a phenol–formaldehyde condensate containing 8-hydroxyquinoline. These resins exhibited chelating properties similar to oxine itself, but the capacity of the resin was very low, presumably due to high degree of cross-linking. To improve this resin, Parrish synthesised an oxine resin using cross-linked polystyrene as a matrix in which the chelating group is linked through an azo group and the resin, polystyrene-(4-azo-5)-8-hydroxyquinoline, was synthesised (**CXIII**). The polystyrene-based ion exchanger was found to absorb copper, nickel and cobalt strongly in the pH range 2–3. Following this report on oxine resin, several other reports appeared on the chelating and analytical properties of this resin [453,454]. A



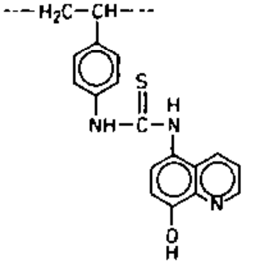
(CXIII)

commercial resin containing 8-quinolinol as a chelating group is now available commercially as Spheron Oxine-1000(**CXIV**) (Table 1). This resin consists of a matrix of a copolymer of hydroxyethyl methacrylate and ethylenedimethyl acrylate and the functional group is bound to the polymeric matrix via an azo-group [455]. Spheron Oxine-1000 does not interact with ammonium and alkali metal ions or (in acidic media) with ions of alkaline earths. This resin thus differs from classical chelating resins containing iminodiacetic acid groups, which also possess the non-selective properties of weak carboxylic cation exchangers. In contrast, the affinity of Spheron Oxine is remarkably high for heavy metal ions and is only slightly influenced by ionic strength. The exchange capacity of this resin for most heavy metal ions amounts to 0.2–0.3 mmol g^{-1} at pH 5. Spheron Oxine-1000 is useful for group-selective separation of metal ions like Mn^{2+}, Al^{3+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Cu^{2+}, UO_2^{2+} [456].

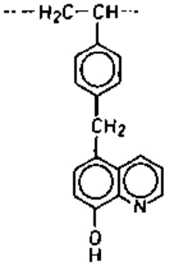


(CXIV)

Sugii et al. [457] prepared two macroreticular polystyrene resins containing 8-hydroxyquinoline groups. Resin (**CXV**) with an oxine group attached to polystyrene via a thioureido linkage was prepared by treating aminopolystyrene with 8-hydroxyquinolyl isothiocyanate in a mixed solution of triethylamine and dioxane. Resin (**CXVI**) was prepared by the reaction of

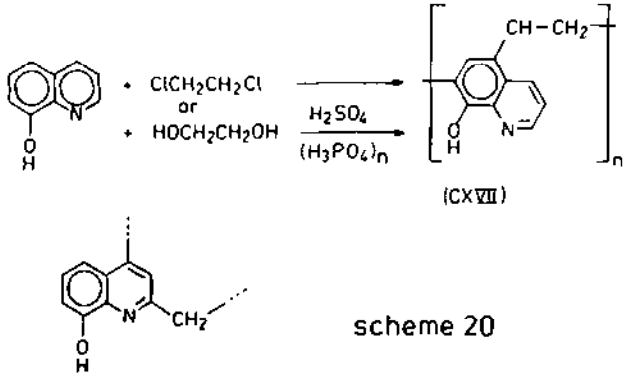


(CXV)



(CXVI)

chloromethylated polystyrene with zinc oxide chelate in nitrobenzene. Resin (**CXVI**) has been found to be selective for Hg(II) and Cu(II), whereas the resin (**CXV**) is selective only for Hg(II) in the pH range below 5. The resin (**CXV**) has high selectivity and capacity for mercury(II), but it is rather unstable in strong acidic media, and its capacity is lower than the resin (**CXVI**) [457]. Patel and Patel [458] studied the chelating and ion exchange properties of poly(8-hydroxyquinolinediylethylene) (**CXVII**) (Scheme 20)



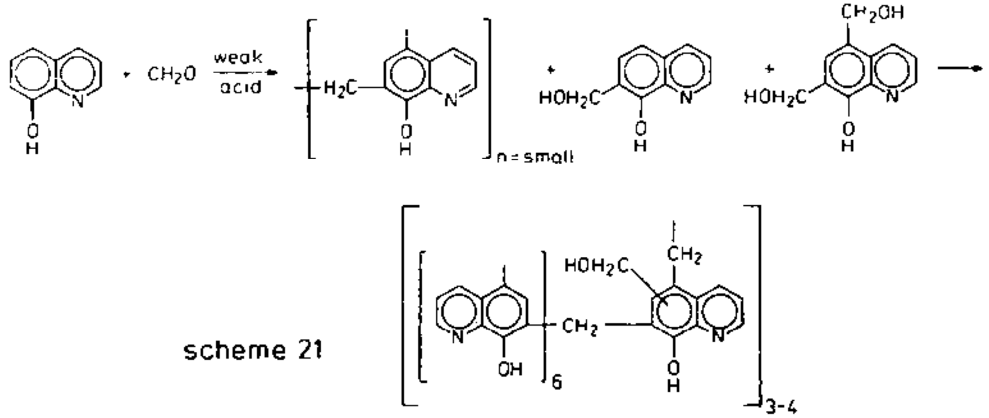
(CXVII)

(CXVIII)

scheme 20

because the larger separation of the 8-hydroxyquinolinediyl units in this type of resin should make a better chelating ion exchanger. Distribution coefficients for several metal ions were determined over a wide range of pH in media of different ionic strengths. The resin has been found to take copper(II) more selectively than many other divalent ions. Using this resin, a mixture of copper(II) and magnesium(II) could be separated at pH 3. The observed order of distribution ratios of divalent metal ions in the pH range 3–8 is: Cu(II) > Ni(I), Co(II) > Zn(II), Cd(II), which matches partly with the possible order of selectivity of a cation exchanger based on the Irving and Williams order of stability constants. A series of poly(8-hydroxyquinolinediylmethylene)s was prepared by a method based on Friedel–Crafts polyalkylation of 8-hydroxyquinolinol, with dichloromethane in the presence of anhydrous aluminium chloride varying the molar ratios of two monomers. These polymers have been characterised on the basis of their infrared and ultraviolet spectra and a structure shown in (**CXVIII**) has been assigned to this type of polymer. The thermal properties of these ion exchangers have also been studied and compared with that of the oxine–formaldehyde polymer [459].

Vernon and Eccles [460] prepared a series of ion exchanger resins containing 8-hydroxyquinoline as chelating group (**CXIX**) reported earlier by Pennington and Williams [461], De Geiso et al. [462] and Davies et al. [454] (Scheme 21). Some more resins were prepared by polycondensation of

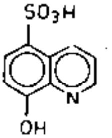


scheme 21

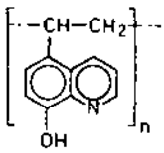
(CXIX)

4-nitroresorcinol–formaldehyde with varying amounts of phenol, reduction, diazotising and coupling to oxine. Capacities were determined for several elements such as copper, nickel, zinc, aluminium and uranium (i.e., as uranyl(2 +)) and for column separation of various cation mixtures the macroporous polystyrene-azo-oxine were found to be far superior to the formaldehyde polycondensates. The resins derived from 4-nitrosoresorcinol exhibited a capacity of roughly twice that of the polystyrene-based resin [453]. Similar conclusions were arrived at by Parrish and Stevenson [463], who found that polystyrene-based resins of the gel type were less satisfactory than the condensation resins, with optimal swelling properties and made by control of water content during curing of the resin. The resins have a high capacity and selectivity and a fast exchange rate, which resulted from the incorporation of a proportion of sulfonic groups in condensation resins. During their studies, Vernon and Eccles [460] found that both 1 : 1 and 1 : 2 complexes are formed with divalent metal ions, when different resins containing oxine functional groups are employed. Hoek and Reedijk [198] isolated the copper(II), cobalt(II), nickel(II) and zinc(II) complexes of Spheron Oxine-1000 and studied them with the aid of electronic and ESR spectra to confirm the formation of 1 : 1 and 1 : 2 metal complexes by oxine resins. Through these studies, it has been concluded that the 8-hydroxyquinoline group in Spheron Oxine-1000 coordinates as a bidentate chelating ligand to copper(II), which preferentially binds to two oxine groups although coordination to only one oxine group, probably due to steric reasons, has also been observed. The coordination polyhedra of the 1 : 2 complex is square planar, as evidenced by electronic spectra (13900 cm^{-1}) and EPR parameters ($g_{\parallel} = 2.23$–2.24 and $A_{\parallel} = 181$–195 G) which agree well with those spectral data obtained for $Cu(oxine)_2$ complexes having a chromophore CuO_2N_2 [461]. The coordination polyhedron of the copper(II) ion, bound in a 1 : 1 ratio, is completed by water molecules resulting in a chromophore MO_5N. The EPR spectral data also indicated the presence of species having the chromophore CuO_4N_2. In fact, the spectral data support the presence of two kinds of species in some of the resins, as indicated by a second set of $g_{\parallel}$ and $A_{\parallel}$ parameters computable from ESR spectra ($g_{\parallel} =$ 2.29–2.32 and $A_{\parallel} = 148–160$ G). The data agree well with copper complexes possessing the chromophore CuO_4N_2 (two water molecules present in the axial positions). No definite conclusions could be drawn in the case of cobalt and nickel complexes which seem to bind preferentially in a 1 : 2 ratio. However, in the presence of excess of ligands, the presence of 1 : 2 species has not been excluded.

The properties of Spheron Oxine-1000 having azo groups and flexible side chains of a hydrophobic macroporous copolymer of glycoldimethacrylate and glymonomethacrylate (**CXIV**) have been compared with other oxine-containing resins prepared from macroporous copolymers of styrene and divinylbenzene [464]. It has been found that Spheron Oxine-1000 is susceptible to hydrolysis with alkali (due to the presence of ester linkage) and its water regain capacity is reduced on drying, whereas the polystyrene-based resin is stable towards both alkali and acid. However, the polystyrene-based resins have been found to exhibit slow exchange rates [464]. Recently, chelating resins containing 8-hydroxy-5-sulfonic acid (**CXX**) have been studied [465–467]. These resins have been found useful for preconcentration of several transition metal ions. A conventional anion exchanger loaded with 7-iodo-8-hydroxyquinoline-5-sulfonic acid has been applied to the selective and quantitative separation of Fe(III), Cu(II), Cr(VI), and Pb(II) from aqueous solutions [468]. Bernhard and Grass [469,470] reported the preparation of seveal oxine-containing chelating resins, which were cross-linked with furfural and resorcinol. It has been shown that the selectivity of these chelating resins depends on the addition during preparation of certain metal ions, such as barium and aluminium. An oxine resin prepared from poly-5-vinyl-8-hydroxyquinoline (**CXXI**) has been found to be an excellent reagent for fast, quantitative removal of trace metals from saline matrices [471].



(CXX)



(CXXI)

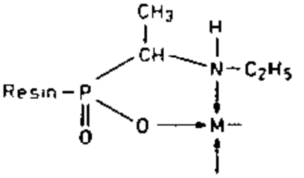
8-Hydroxyquinoline immobilized on silica gel has been prepared and used for the preconcentration of Cd, Pb, Zn, Cu, Fe, Mn, Ni, and Co from sea water prior to their determination by graphite furnace atomic absorption spectrometry [472,473]. A column loaded with such a resin permitted large enrichment factors, while providing processing of large volume samples, quantitative recovery of these metal ions and a matrix-free concentrate suitable for elemental analysis [472]. Recently, in a comparative study of 8-hydroxyquinoline immobilised on cross-linked polyvinyl pyrrolidone, a macroreticular styrene–DVB (XE-305) and methylated polystyrene (Merrifield resin) have been used for the preconcentration of metal ions from sea water prior to their measurement by electrothermal atomic absorption spectrometry and optimal results were obtained with XE-305 [473]. Several other reports are available on the immobilised controlled Pore Glass–oxine resins [474,475].

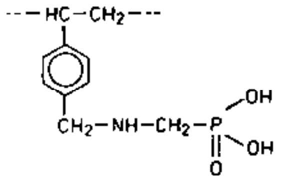
(c) Aminophosphonic acid ion exchangers

Like α-aminocarboxylic acids, their phosphonic acid analogues also possess strong complexing properties. For example, under neutral non-aqueous conditions phosphoramides $(RO)_2P(O)/NR'R''$ show strong solvating properties for heavy metal salts, such as iron(III) chloride and uranyl nitrate. Besides, complexing resins containing phosphates and phosphonates have been found to be useful for separation of such cations as Th^{4+}, Fe^{3+}, UO_2^{2+} (which form relatively strong complexes) from alkaline earths, divalent and trivalent lanthanides ions (which form weak complexes with these type of resins) [476]. Several such resins based on cross-linked polystyrene and different condensation matrices have been described by Kennedy and Walsh [477,478]. As a sequel to their work on complexing resins containing phosphate and phosphonate functional groups, Kennedy et al. [479,480] extended this work to the synthesis of chelating resins with α-amino phosphonates and phosphonamide with a view to investigating their coordinating properties. Resins containing amphoteric α-amino acidphosphonate functional units have been synthesised by the reaction of polymerised diallyl hydrogen phosphonate with acetaldehyde ethylimine, followed by hydrolysis, as shown below

$$(RO)_2P(O)H + CHMe{=}NEt \rightarrow (RO)_2P(O)(CHMe{-}NHEt)$$

This type of resin, however, has greater affinity for divalent transition metal ions than for the uranyl ion. Their behavior is also similar to that of α-aminocarboxylic acid resins in following the Irving–Williams order of metal chelate stability to form complexes of the type shown in (**CXXII**). Following this, a series of α-aminophosphonate resins containing the amphoteric complexing unit $-NR-CR-P(O)(OH)_2$ have been synthesised by various routes and shown to have adsorption capacities of the order of 1 to 2.5 meq g^{-1} of dry resin (sodium form) for copper(II) ions [476]. A commercial resin (Duolite ES 467) containing α-aminophosphonate group-ing on a cross-linked polystyrene matrix is known to form very stable complexes with low-atomic mass cations. This chelating resin presumably contains the structure (**CXXIII**). The order of selectivity of ES 467 is: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ca^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+}$ [16]. Thus this resin is particularly useful for the separation of copper from other divalent transition metals. Among the principal uses of ES 467, decalcification, metal separations and recovery of such metal ions as zinc, lead, etc. are recommended by its manufacturer [481]. The cobalt(II), nickel(II), copper(II), and zinc(II) complexes of this resin (isolated at various pH) have been studied by spectroscopic methods to establish the precise nature of the polyhedron around the respective metal ion. It appears that the cobalt(II) complexes possess a tetrahedral geometry, the electronic spectra of the nickel complexes correspond with tetragonally distorted nickel(II) and ESR spectra of copper complexes indicate the presence of two types of chromophores in the polymeric chelating ligand [482].

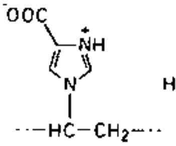

(CXXII)


(CXXIII)

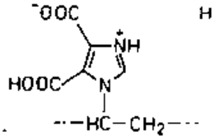
Recently, the preparation and ion-exchange properties of several chelating resins containing aminophosphonic acid groups have been reported [483]. The resin capacity lies in the range 2.6–3.4 meq g^{-1} and the limiting stage of amination was diffusion of the aminating agent. The selectivity of these ion exchangers for cobalt(II), nickel(II), copper(II), zinc(II), iron(II), lanthanum(III) and thorium(IV) has been found to be better than that shown by ion exchangers containing carboxylic acid groups only. Two Japanese patents [484,485] claim the synthesis and applications of chelating resins containing aminophosphate type functional groups. One such resin has been prepared by aminating PVC beads with diethylenetriamine and treatment of the resulting product with H_3PO_3, HCl and formaldehyde [484]. Interestingly, a metal-ion adsorbed aminophosphate-type chelating resin has been found to be effective for the removal of fluoride ions from water [485]. Recently, a new chelating resin, Sumichelate MC-90, a divinylbenzene–styrene copolymer containing an aminoalkylphosphonic acid functionality, has been developed for purification of feed brine for chloro-alkali cells. Sumichelate MC-90 has an adsorption capacity of about twice that of commercial iminodiacetic-type chelating resins and is used for the removal of Fe^{3+} or trace levels of Ca^{2+} and Mg^{2+} in brine [486]. Preparation of several other aminophosphoric acid-type resins has also been described [487]. It consists in the treatment of amino resins, containing amine reactive group, with amino compounds (such as diethylenetriamine) containing primary or secondary amino groups, and treating the resulting compound with H_3PO_3 or methylphosphite or other phosphorus-containing compounds and alkylating agents. Such a resin, prepared from diethylenetriamine, has been found to take up substantial amounts of calcium when immersed in a solution containing 100 mg calcium per liter, when calcium leakage reached 3 ppm in the treated solution [487]. Manecke and Heller [488] also reported the preparation of copolymers of diethyl-2-(1-aziridinyl)ethylphosphonate and 2,2′-bis(1-aziridinyl)ethylbenzene. By saponification of the ester groups of the copolymers, new amphoteric ion-exchange resins of aminophosphonic acid having uniform and high exchange capacity are obtained. The binding ability of these resins for magnesium(II), nickel(II), copper(II) and zinc(II) ions as a function of pH and uptake of these metal ions as function of time were investigated [488].

(d) Other chelating ion-exchange resins containing nitrogen and oxygen as donor atoms

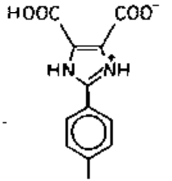
There are several other chelating ion-exchange resins incorporating nitrogen and oxygen donor functional groups which could not be covered in the preceding sections. Such chelating resins are discussed below. A number of chelating polymers derived from imidazolecarboxylic acids have been described by Manecke and Schlegel [489]. Homopolymers of some vinyl-substituted imidazole–carboxylic acid esters were obtained by radical-solution polymerisation and their properties were examined. Methyl 1-vinylimidazole-4,5-dicarboxylate and dimethyl-2-(*p*-vinylphenyl)imidazole-4,5-dicarboxylate were polymerised with *p*-divinylbenzene and by saponification of these copolymers, three new chelating resins as depicted in **CXXIV**, **CXXV**, and **CXXVI**, respectively, have been obtained. These chelating ion-exchange resins have been characterised on the basis of their IR spectra. All these polymers showed a strong band at ca. 1710–1720 cm^{-1} characteristic of carboxylic groups. The apparent dissociation constants, the swelling



(CXXIV)

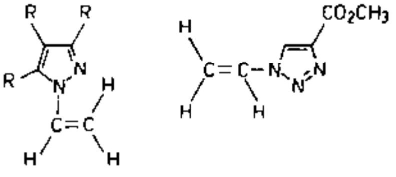


(CXXV)



(CXXVI)

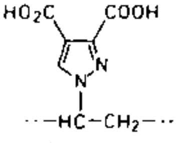
behavior at different pH values, the binding ability of the resins for copper(II) at pH 5, and uptake of copper(II) ions as a function of the time have reported [490]. Following their work on imidazolecarboxylic acid resins, Manecke and Ruhl [491] extended this work on pyrazolecarboxylates and triazolecarboxylates, based on **CXXVII** and **CXXVIII**, respectively. The



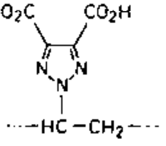
R=H, CO_2CH_3 or $CO_2C_2H_5$

(CXXVII)

N-vinyl derivatives are first converted into homopolymers by radical polymerisation and on copolymerisation with *p*-divinylbenzene leads to the formation of chelating ion-exchange resins [491,492]. The syntheses of cross-linked poly-1-(3,4-dicarboxy-pyrazol-2-yl)ethylene and 1-(4,5-dicarboxy-1,2,3-triazol-2-yl)ethylene have been described and the proposed structures of these chelating ion exchangers are depicted in **CXXIX** and **CXXX**,



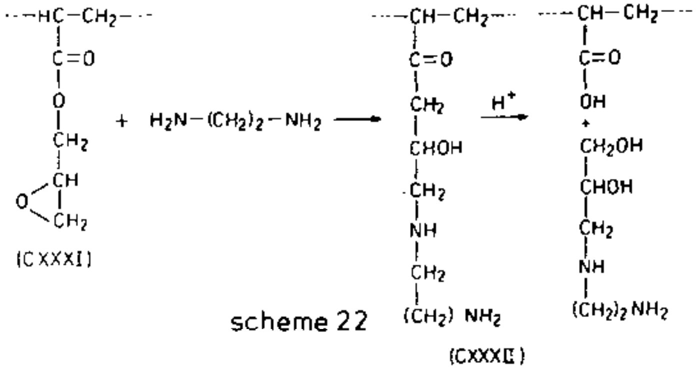
(CXXIX)



(CXXX)

respectively. These resins have been characterised on the basis of their elemental analysis and IR spectra. A band characteristic of the vinyl group is observed at ca. 910–935 cm^{-1}. The swelling behavior and time dependence of the uptake of copper(II), zinc(II) and magnesium(II) ions of these chelating ion exchangers have been reported [491,492].

A series of polymeric chelating ligands have been prepared by incorporating ethylenediamine functional groups into copolymers of glycidalacrylate–ethylenediamethacrylate and glycidalacrylate–methylene-bis-acrylamide (**CXXXI**). These glycidal acrylates were prepared by suspension radical polymerisation [493]. The model compound, *N*-(2-aminoethyl)-3-amino-1,2-propanediol was synthesised and the procedure for incorporating ethylenediamine into this cross-linked polymer was also described [494]. It was shown that the ester bond in (**CXXXII**) can be hydrolysed (Scheme 22). The preparation of copper(II), zinc(II), cobalt(II) and nickel(II) complexes with these ligands was described. The kinetics of these chelating ligands have also been studied [494–498]. The ligating behavior of these chelating polymers with copper(II) salts in water has been studied and it was

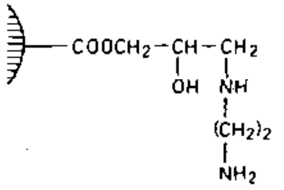


(CXXXI)

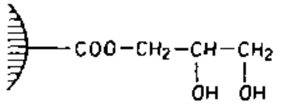
scheme 22

(CXXXII)

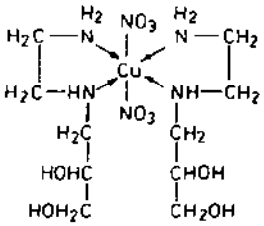
found that stable chelates could be obtained. The formation of the $Cu[R-CH_2-CH(OH)\cdot CH_2NH(CH_2)_2NH_2]_2(NO_3)_2$ chelate, where R is a polymeric matrix, has been confirmed by carrying out similar studies on a model compound. The donor group of the polymeric ligand is represented in (**CXXXIII**). The metal can be coordinated both by the nitrogen atoms from the primary and secondary amine groups and by the oxygen atom of the hydroxyl group. Direct evidence for the participation of the hydroxyl group in the bonding with the metal ion has been provided by the conductometric titration with the hydrolysed copolymer (**CXXXIV**). It has been shown that no reaction takes place between Cu^{2+} ions and hydroxyl groups at pH 5–6. The copper(II) complex of the model compound, *N*-(2-aminoethyl)-3-amino-1,2-propanediol has been shown to possess the structure (**CXXXV**) in the polymeric matrix [498]. The pattern of UV and visible spectra of copper(II) ions (the presence of a band at ca. 545–580 nm) indicated a tetragonally



(CXXXIII)



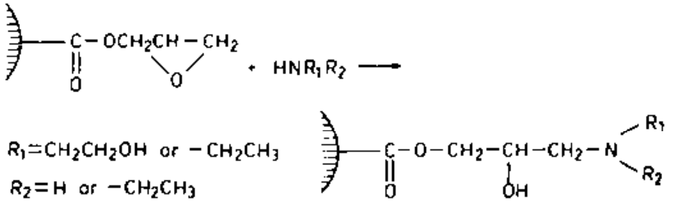
(CXXXIV)



(CXXXV)

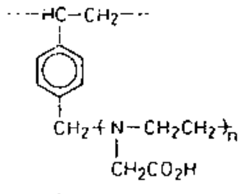
distorted geometry around the copper(II) ions, such as the copper(II) nitrate–ethylenediamine complex, which has a similar chromophore, viz. CuN_4O_2.

Kalalova et al. [499] extended these studies to new macroporous complexing resins of the type shown in the structure (**CXXXVI**) which have been prepared by the reaction of the copolymers of glycidal methacrylate–ethylenedimethacrylate with ethyl amine, diethyl amine and 2-hydroxy ethylamine (Scheme 23). The chelating behavior of these resins with copper(II), zinc(II), iron(II), nickel(II) and cobalt(II) has been studied and it has been found that the amount of bound metal, as well as the selectivity of the resins, drops remarkably in the above-mentioned order in all the polymers studied. The kinetic measurements showed that the reaction of 2-hydroxy ethylamine with copper ions was the fastest; however, the reaction was slower in the case of the ethylenediamine ligand described earlier [493]. The sorption ability in terms of the capacities of these resins differ from each other. The amount of metal bound to the polymer decreases remarkably in the following order: $Cu^{2+} > Zn^{2+} > Fe^{2+} > Ni^{2+} > Co^{2+}$. This fact has been used for separating the individual metals from their mixtures, e.g., Cu–Co, Cu–Ni, Zn–Co and Fe–Co. Measurement of the hydrolytic stability of the complexes indicated that with respect to stereochemical requirements of the metal, different complexes have been formed, utilising further –OH groups or water molecules contained in the resin. The complex formation has been demonstrated by IR spectroscopy. Several similar resins with a polystyrene matrix have been prepared by treating chloromethylated polystyrene with different amines and hydroxy amines and ion-exchange properties of these chelating polymers have been evaluated [500–502].

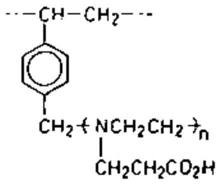


scheme 23 (CXXXVI)

Saegusa et al. [270–273] reported the preparation of several cross-linked poly(styrene-*g*-ethylenimine) resins which were found to be quite effective for the adsorption of heavy metal ions such as Cu^{2+}, Hg^{2+}, and Cd^{2+} However, these resins could not be used for the adsorption of metal ions which do not form stable amine complexes, because the site for coordination in poly(ethyleneimine) is the secondary amine group. To overcome this poor adsorption capacity of poly(ethylenimine) chelating polymers, carboxyalkyl groups have been introduced in such polymers, in analogy with carboxymethylation of several carboxymethylated polyamine polymers [278], in order to explore the ion-chelating properties of these new types of resin, poly(styrene-*g*-*N*-carboxymethylethylamine) (**CXXXVII**) and poly(styrene-*g*-*N*-carboxyethylethylenimine) (**CXXXVIII**). These resins have been prepared



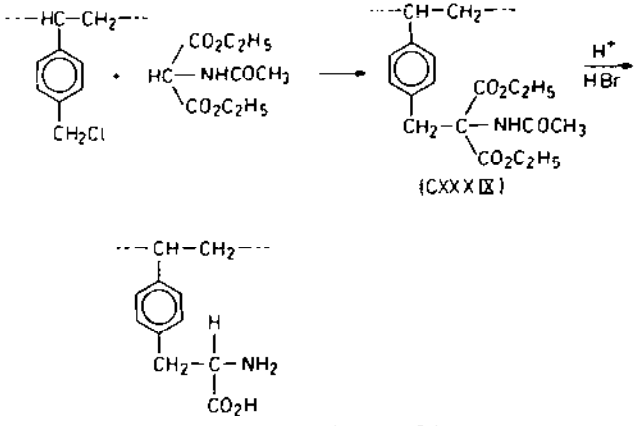
(CXXXVII)



(CXXXVIII)

by carboxyalkylation of poly(styrene-*g*-ethylenimine) under alkaline conditions [503]. Carboxyethylation of polyethylenimine has also been performed by its reaction with acrylic acid and the structure of the product so obtained is depicted in (**CXXXVIII**). The extent of the reaction was determined by change in the nitrogen content of the resin [503]. The adsorption of metal ions such as copper(II), cadmium(II), mercury(II), nickel(II), and calcium(II) by all these resins has been examined and the following order: $Hg^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+} > Ca^{2+}$ at pH 6 has been found for adsorption of these metal ions. The dependence on pH of the adsorption was larger with the carboxymethylated derivative and this has been attributed to the smaller stability constant of β-carboxylamine chelate than that of α-carboxylamine chelate [504]. It is worth noting that with the introduction of carboxyalkyl groups, the adsorption capacity for metal ions (per gram of resin) decreased, whereas the affinity of the resins for these metal ions increased. These resins can be used for the separation of Cu^{2+} ions from a mixture of metal ions at pH 6 [503].

Related to these resins are the chelating polymers derived from amino acids, which are expected to be more selective than the corresponding aminocarboxylic acid resins. Schlogl and Fabitschowitz [505] reported the preparation of glycine resin based on a polystyrene matrix. Sugii et al. [506] prepared a macroreticular phenylalanine resin (**CXL**) which has essentially the same functional group as that of the glycine resin and possesses similar metal-sorption properties. The resin (**CXL**) has been synthesised according to Scheme 24. Spherical macroreticular styrene–divinylbenzene copolymer beads were chloromethylated and allowed to react with diethyl acetoamimalonate followed by hydrolysis of the resulting product (**CXXXIX**) with hydrobromic acid in the usual way [506]. The IR spectra of the intermediate resin (**CXXXIX**) showed no band at ca. 670 cm^{-1} (due to νC–Cl) but the characteristic absorption of the carbonyl (ester) group appeared at ca. 1740



(CXXXIX)

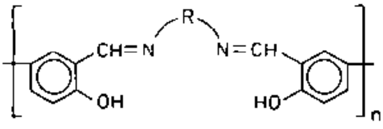
(CXL)

scheme 24

cm^{-1}. A characteristic feature of the phenylalanine resin was the presence of the bands for the carboxylate group at 1600–1660 cm^{-1} and for the amino group at 3300–3400 cm^{-1}. The phenylalanine resin shows high selectivity for mercury(II) and copper(II) in the pH range 2–3. The important characteristics of the resin are the fast equilibrium, high selectivity and small volume changes on conversion of its hydrogen form to other metal forms. These characteristics make this resin suitable for rapid concentration of trace amounts of copper(II) in the presence of large amounts of different metal ions. This resin may also be used for the determination of copper in sea water and for the separation of copper–cobalt and copper–nickel mixtures. The analytical properties of this phenylalanine resin has been compared with those of Dowex A-1 and it has been found to be superior to Dowex A-1 for trace concentrations of copper at a high flow rate, even in the presence of iron which strongly interferes with the recovery of copper on a Dowex A-1 column. A patented process [507] describes the preparation of several cation exchange resins incorporating nitrogen-containing ligands on an epoxy resin and polyethylenimine and cross-linked with glutaraldehyde, tetraethylene pentamine, glyoxal, etc. These resins can be used for the separation of multivalent metal ions in the presence of monovalent ions. Some amphoteric ion-exchange resins based on pyridine carboxylic acids have been reported [508]. Lieser et al. [509,510] have described several nitrogen- and oxygen-containing chelating cellulose ion exchangers. The ligands used for these studies include 1-(2-hydroxyphenyl-azo)-2-naphthene and 4-pyridyl-(2)-azo-resorcinol. These chelating polymers have been used for separation of heavy metal ions (copper, iron) from solutions containing ammonium sulfate, alkali and alkaline earth metal ions and also from a concentrated zinc chloride solution. The separation of Fe, Cu, Pb, Co, Zn, Cd and Cr at the 1 ppm level from methanol has also been investigated [509].

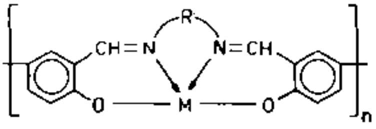
Dingman et al. [511] reported a series of polyamine–polyurea resins for separating heavy metal ions from dilute solutions. These resins are prepared by polymerising and cross-linking various polyethylenimines with toluene-2,4-dithiocyanate. The effects of pH, equilibration time, resin cross-linking, and monomer units are considered in a batch equilibration study on the chelation of copper(II), nickel(II), zinc(II), and cobalt(II). The various monomers used in this study include ethylenediamine, triethylenetetramine, tetraethylenepentamine and polyethylenimines. By using one of these resins in a column, copper, cobalt, and nickel ions have been quantitatively concentrated, recovered, and determined from known aqueous solutions having concentrations as low as 4 parts in 10^{10} with concentration factors as high as 10^3. High concentrations of alkali and alkaline earth metal ions do not compete with the complexation of heavy metal ions, since they are not complexed by these resins. The order of stabilities of the chelates formed on the resin is much the same as their respective soluble metal–ammonia complexes. These complexing resins can be used for trace metal analysis in both fresh and saline natural water systems [511]. Recently, chelation ion-exchange properties of salicylic acid–thiourea–trioxane terpolymers have been studied [512]. A batch equilibration method has been used for evaluating the distribution coefficients over a wide range of pH and in media of various ionic strengths. The terpolymers showed a higher selectivity for copper(II), iron(III), and uranyl(2 +) ions, than for manganese(II), cobalt(II) and zinc(II) ions.

A number of polymeric Schiff bases have been synthesised and studied for their ion-selective properties. This type of polymeric ligand has been introduced by Bayer [513,514]. The relative stability of complexes formed by copper, nickel, cobalt, zinc, cadmium, manganese and uranium with bis-*o*-hydroxyanil of glyoxal were studied and it appeared that the metals can be displaced by one another in the following sequence: $Cu > UO_2 > Ni > Co > Mn > Zn > Cd$]513,514]. Bayer reported several such chelating polymers with *N*,*O*-donor atoms which have been described in detail in earlier reviews [7,29–35]. Some of these chelating polymers possess high selectivity over a pH range 0–7. These polymers would not bind to alkali and alkaline earth metal ions at all and would retain ions such as copper(II), uranyl(VI) and nickel(II) the best, even in the presence of a large excess of other heavy metal ions [515,516]. A renewed interest in this type of chelating polymer for selectively binding transition and other heavy metal ions, developed in recent years. The preparation and properties of Schiff bases such as 5,5′-methylene-disalicyaldehyde-1,2-propanediamine copolymer have been described by Bottino et al. [517]. The selectivity of this copolymer has been found to decrease through the metal series: Ni ≈ Cu, Co, Fe, Zn, Mn, Pb and Cd. Nickel(II) was found to be complexed preferentially from any metal couple except in the presence of copper. Several polymeric Schiff bases having the structure (**CXLI**) have been prepared by polycondensation reactions of 5,5′-methylene-bis-salicyaldehyde with the appropriate diamines in DMF [518–521] and reacted with different metal ions to obtain the complexes of the general formula depicted in (**CXLII**). Woehrle has very recently reviewed the synthesis, properties and applications of such chelating polymers, which form planar metal chelates [522]. This type of polymer possesses high selectivity, and capacity, but the mechanical and chemical stability is very poor.



$R = -CH_2-CH_2-, (CH_2)_4, (CH_2)_6$

(CXLI)



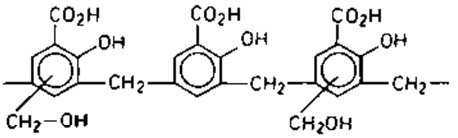
(CXLII)

(iii) Chelating ion exchange resins containing oxygen as the only donor atom

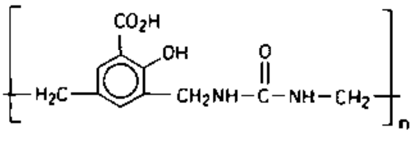
Several types of ligands containing oxygen as the only donor atom have been incorporated into different types of polymeric matrices. Some of the ligands used for such studies include polyphenols, polycarboxylic acids, 1,3-diketones, phosphonic acids, arsonic acids, polyphenolic carboxylic acids, fluorones, flavones and related compounds.

(a) Chelating ion exchange resins containing phenolic and carboxylic acid groups

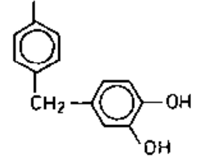
The important developments of chelating ion-exchange resins containing polyphenols and polycarboxylic acids have been described in earlier review articles [7,29–35]. Compounds containing phenolic groups can easily be converted into polymeric compounds by condensing them with formaldehyde (or any other aldehyde), with or without an appropriate phenol, in the presence or absence of a cross-linking agent to obtain a gel-type resin. The resins obtained from pyrogallol [523,524], salicylic acid [179,525], resorcinol [526], 2,3,4-trihydroxybenoic acid [527], 2,4-dihydroxybenzaldehyde [527] and 2′,4′-dihydroxyacetophenone [526] by this procedure have been described in the literature. The resins obtained from salicylic acid and formaldehyde were first described by De Geiso et al. [179,525] and Davies et al. [528]. The analyses and neutral equivalents suggest that the structure of the polymer is like (**CXLIII**) [525]. A chelating resin containing salicylic acid, chemically bound via the side-chain azo groups to hydrophilic glycol methacrylate gels, has been reported by Slovak et al. [529]. This resin, which is now commercially available under the trade name of Spheron Salicyl-1000 (cf. Table 1) shows high selectivity for iron(III) and aluminium(III) ions above pH 2.5. It has been shown that the enhanced sorption of heavy metals by complex formation is accompanied by non-specific ion exchange arising from dissociation of the carboxyl group of salicylic acid. The sorption capacity for heavy metals was found to exceed 0.35 mmol g^{-1} and sorption equilibration was achieved within two min. Recently, the chelation ion-exchange properties of salicylic acid–urea–formaldehyde resin (**CXLIV**) have also been described [530]. The copolymer showed higher selectivity for uranyl(VI), copper(II) and iron(III) than for manganese(II), cobalt(II) and zinc(II). Several transition metal complexes of this chelating resin have been prepared and studied by spectroscopic methods [531]. The IR spectra of the complexes showed that urea present in the copolymer is not involved in the complexation, and it only improves the stability of the copolymer [531]. A synthetic chelating resin, a polycondensation product of pyrogallol and formaldehyde, has been developed and characterised for use as a substrate for a $^{68}Ge-^{68}Ga$ generator [532]. The distribution constants between this resin and 0.3 N HCl are 0.5 for gallium and higher than 5000 for germanium. Similar observations have been made by Schuhmacher et al. [533]. It was shown that the resin is radiolytically stable and the generator eluate is non-toxic, and can be used for the preparation of intravenous injectates [532]. Warshawsky and Kahana [534] prepared a catechol derivative of polystyrene (**CXLV**) by a Friedel–Crafts reaction. This catechol derivative can be used as an intermediate for the preparation of new chelating ion exchange resins. Several cation exchangers (**CXLVI**) with improved selectivity have been prepared by treating chloromethylated styrene–divinylbenzene copolymers with sodium malonic acid monoester followed by hydrolysis [535]. Poly(aldehyde carboxylic acids), useful as complexing agents, can be prepared by polymerising



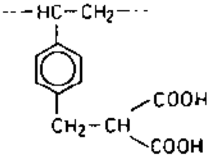
(CXLIII)



(LXLIV)

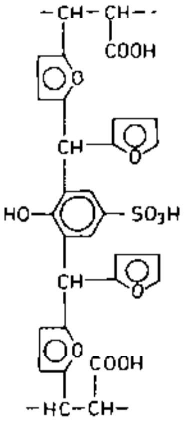


(CXLV)



(CXLVI)

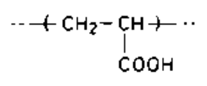
maleic anhydride or acrylic acid with acrolein [536]. These polymers are particularly useful for complexing calcium(II) and iron(III). A number of chelating resins having the structure of the type (**CXLVII**), with both



(CXLVII)

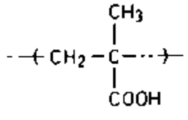
sulfonic and carboxylic groups, have been evaluated for their ion-exchanging properties [537]. The infrared spectra of metal complexes of carboxylic acid resins have been studied in detail by Chuveleva et al. [538–540] and a mechanism of the sorption of metal ions on complex-forming carboxylic resins has been suggested [538,539]. The electronic spectra of nickel(II), cobalt(II), copper(II) and neodymium(III) ions adsorbed on a carboxylate resin Zeo-Karb 226 from dilute solutions have been compared with the spectra of the same metal ions adsorbed on a sulfonic acid resin, Dowex-50 WX8 and with the spectra of the solid metal malonates [541]. The spectra show that the metal ions are at least partly coordinated with the carboxylate groups at 100% loading of the resin. The ESR spectra of the metal complexes of carboxylic resins have also been studied [542–544]. Meleshko et al. [544] studied the sorption and desorption of copper(II) ions on carboxylic acid resins by ESR spectra and showed that it is possible to trace the oxidation state and coordination mode of a paramagnetic ion on an ion exchange resin. Umezawa and Yamabe [199] have also studied the interactions of copper(II) ions with carboxylic acid resins and compared the results with other cation exchange resins, including an iminodiacetic-type chelating resin. It was found that the movement of copper ions within the network of the ion exchange resin is restricted and the mobility of copper ions is closely connected with chemical interaction of the copper ions with the fixed ionic groups of the resins. The mobility of the copper ions follows the sequence: sulfonic group > phosphonic group > carboxylic acid group > iminodiacetic acid group [199].

A number of polycarboxylic acid resins have been synthesised from acrylic or methacrylic acids [545–547] or by saponification of maleic anhydride polymers [548]. Recently, Nishide et al. [549] prepared poly(acrylic acid) (**CXLVIII**) and poly(methacrylic acid) (**CXLIX**) by radical polymerisation; they also prepared a copolymer of maleic acid and styrene by hydrolysis of the alternating copolymer of maleic anhydride and styrene (**CL**). A cross-linked poly(acrylic acid) has been prepared by copolymerising acrylic acid with acrylamide and di(ethylene glycol) (**CLI**). The complexation of uranyl(2 +) in aqueous solution with these carboxylic acid resins has been studied potentiometrically. The overall formation constants of the uranyl complexes with poly(methacrylic acid) and cross-linked poly(acrylic acid) have been found to be much larger than those with low-molecular weight acids. This phenomenon appears to be general with the polymeric complexing systems and has been explained by "concentration" in the polymeric domain, i.e., once the metal ion is attached to one group on the polymer chain, the other ligand coordinates more readily [549]. The maximum amount of uranyl(2 +) has been found to be 0.31 and 1.94 mmol g^{-1} polymer for (**CL**) and (**CLI**), respectively. It has been observed that the resin (**CLI**) takes up uranyl ions at higher efficiency as compared with the strongly acidic and weakly anionic exchange resins.



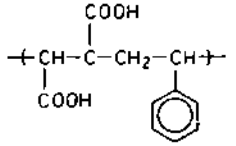
$$\cdots\!-\!\!(CH_2-\underset{COOH}{CH})\!\!-\!\cdots$$

(CXLVIII)

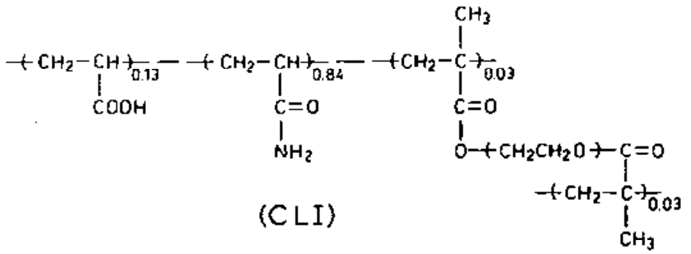


$$\cdots\!-\!\!(CH_2-\overset{CH_3}{\underset{COOH}{C}}\cdots)\!\!-$$

(CXLIX)



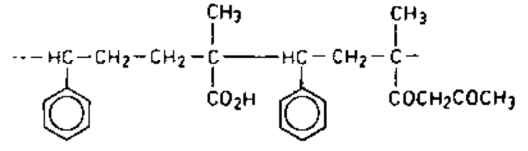
(CL)



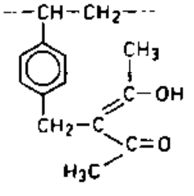
(CLI)

(b) Other chelating ion exchange resins containing ligands with oxygen as the only donor atom

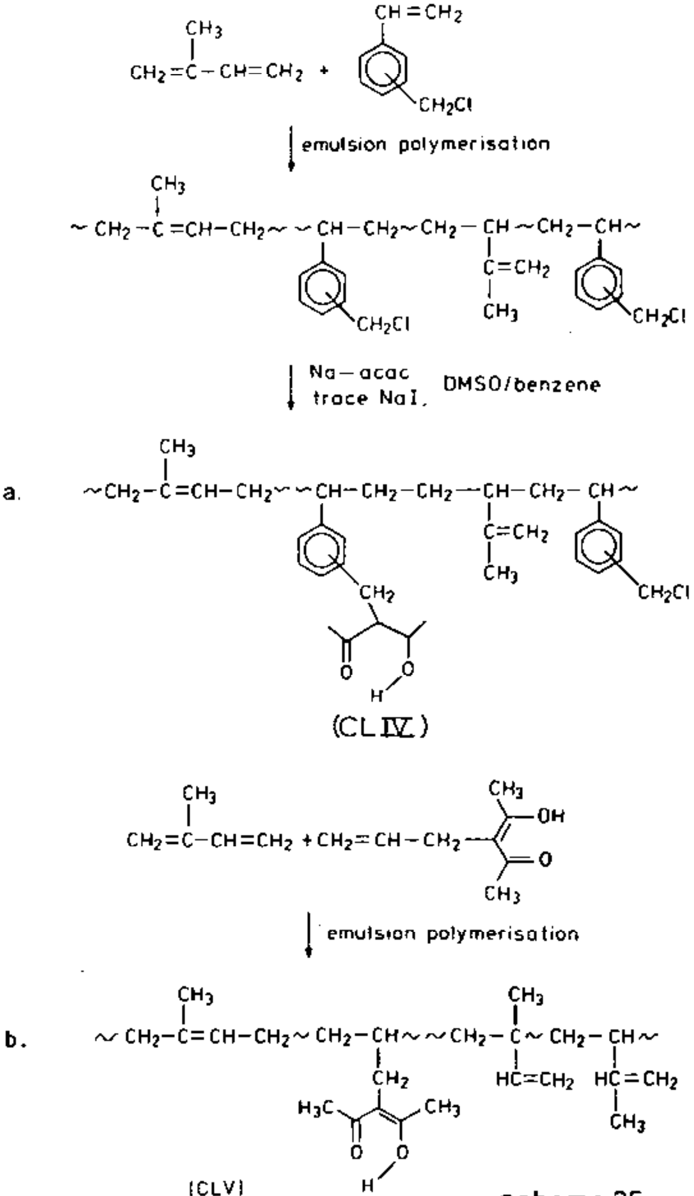
The other important ion exchange resins incorporating oxygen-containing ligands have been derived mainly from 1,3-diketone phosphonic and arsonic acids. Resins containing 1,3-diketones have been prepared both by vinyl-type polymerisation of the corresponding monomer and by direct incorporation of 1,3-diketones in pre-formed cross-linked polymer. De Geiso et al. [550] reported the synthesis of a copolymer of 5-methyl-5-hexane-2,4-dione and styrene (**CLII**). These resins produced an intense red colour with iron(III) salts, a characteristic reaction of β-diketones. This type of resin has been found to be selective for iron(III). Several other reports are available on the synthesis and chelating properties of monomers of 1,3-diketones [551], 5-hexene-2,4-dione [552], its methyl derivative [553] and polymers containing ethyl-2-vinylacetoacetate [554]. Recently, Bhaduri et al. [555,556] incorporated acetylacetone into a styrene–divinylbenzene (8%) copolymer by chloromethylation and treatment with acetylacetone in the presence of a catalytic amount of sodium ethoxide in a swelling solvent such as tetrahydrofuran (**CLIII**). The IR spectra of the modified beads and soluble functionalised derivative of acetylacetone show a medium and high intensity band at 1700 cm^{-1}, respectively; this band can be assigned to the νC=O vibration of acetylacetone. The intense νC=O band in the linear styrene derivative can be attributed to a higher degree of functionalisation. The synthesis and characterisation of Co(II), Cu(II), Fe(III), VO(2 +), and Zr(IV) complexes of polymer-supported acetylacetone have also been described [555]. Yeh et al. [557] have also reported the preparation of diene-based copolymers such as polystyrene and polydimethylsiloxane containing a measurable number of acetylacetone groups along the polymeric chains. Acetylacetone-substituted diene–styrene derivatives (**CLIV**) have been prepared by two methods: (a) emulsion polymerisation of diene–costyrene–CH$_2$Cl using a standard polymerisation method and subsequent introduction of a small amount of acetylacetone through a displacement reaction at the chloromethyl group as shown in Scheme 25; (b) by direct emulsion polymerisation of a monomeric acetylacetone, i.e., vinylbenzylacetylacetone with styrene, using the conventional emulsion system (**CLV**) or by bulk polymerisation using azobisisobutyronitrile (AIBN) as solvent and irradiating the monomer by UV radiation. Method (a) was found to be better than method (b) because the amount of acetylacetone can be adjusted in the former. The proportions of acetylacetone can be adjusted or controlled at two stages, by varying the stoichiometric amounts of diene and styrene–CH$_2$Cl monomers and by controlling the conversion of chloromethyl derivative to functionalised polymer (–CH$_2$acac).



(CLII)

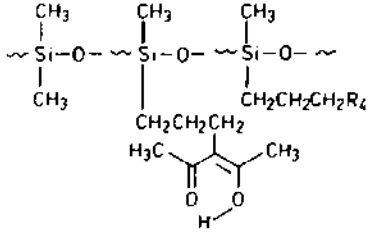


(CLIII)

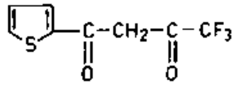


scheme 25

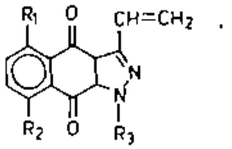
The IR spectra of the monomers show a band at ca. 1710 (*keto*) and 1590 (*enol*) cm^{-1}. The NMR spectra showed the various diene copolymers prepared in the emulsion polymers consisted of 20–25% styrene units in the polymer chain, based on the integrated peaks of aromatic protons. The polydimethylsiloxane (**CLVI**) carrying acetylacetonate groups distributed along the polymer chain was also prepared. These polymers were converted into insoluble gels by treating them with metal complexes in non-aqueous solutions. The complexes of copper(II), chromium(III) and iron(III) prepared in this way have been characterised with the aid of IR and electronic spectra. The kinetic stability of the chelate cross-links has been studied by a unique ligand exchange-gel solubility relationship. Griesbach and Lieser [296] incorporated 1-theonyl-(2′)-3,3,3-trifluoroacetone (**CLVII**) into a styrene–DVB copolymer. A German patent [558] has described the chelate-forming ion exchange resins with 1,3-diketone anchor groups obtained by treating hydroxylated or aminated resins with diketone or other 1,3-diketone precursors. The distribution coefficients of this resin for uranyl(2+), copper(II) and iron(III) has been found to be 10^4, 10^3, and 10^3 ml g^{-1}, respectively at pH 5, and $10^{3.5}$, $10^{2.8}$, and $10^{3.4}$, respectively at pH 7. Recently, Sugii et al. [559] prepared two macroreticular resins containing β-diketone groups anchored on a styrene–DVB–copolymer. These resins have been found to be highly selective for iron(III) in the pH range 1–4, but no significant affinity was observed for Cd(II), Co(II), Cu(II), Mg(II), Mn(II), Ni(II), Zn(II) and U(VI). The β-diketone resin prepared from styrene–DVB–copolymer and was found to be suitable for the separation of ^{59}Fe and ^{60}Co by a column separation [559]. Some β-diketones prepared by the polymerisation of methacrylate methacrylacetone have also been found to possess profound complexing affinity for iron(III) ions [560]. The ion-exchange properties of poly(5-acetyl-4-hydroxyl-1,3-phenylene)-1,2-ethandiyl prepared from *o*-hydroxyacetophenone and 1,2-dichloroethane by formaldehyde condensation have been studied and the resin is found to be selective for copper(II), cobalt(II), manganese(II), zinc(II) and iron(III) [561]. A condensation polymer incorporating 5,8-dihydroxy-1,4-naphtochinon (naphtharazin) into formaldehyde and a phenol matrix has also been evaluated for its ion-exchanging properties [562]. Manecke and Graudenz [563] studied the chelating properties of 5,8-dihydroxy-3-vinyl-1H-benz[f]indazole-4,9-dione (**CLVIII**), its 1-methyl derivative and its 2-methyl derivative (**CLIX**) and found that these ligands form 1 : 1 polymeric chelates of gradual stability with divalent metal ions such as Mg, Cd, Ni, Zn and Cu. The resin cross-linked with 3,7-divinyl-pyrazolo-5,4-indazole-4,8-dione (**CLX**)



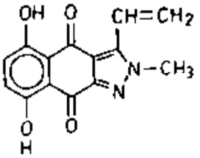
(CLVI)



(CLVII)



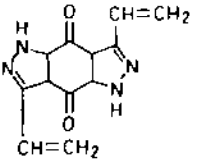
(CLVIII)



(CLIX)

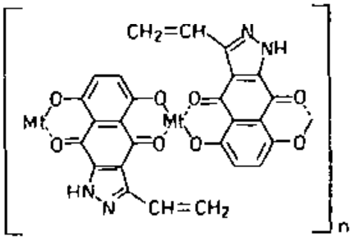
$R_1, R_2 = OH, H, OCOCH_3$

$R_3 = H, CH_3$



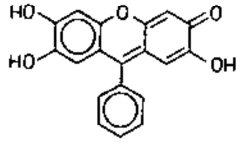
(CLX)

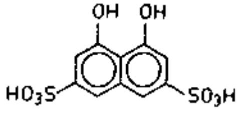
has been found to take up rapidly, in its alkali form, divalent cations from buffered solutions, showing a high specificity for cadmium and copper ions. Experiments with these resins in a column gave a clear separation of a Cu^{2+}/Ni^{2+} mixture. It was indicated that polymerisation of the monomers on the surface of silica gel might result in resins with improved properties [564]. The structure of metal complex of a polymeric ligand obtained from a monomeric system like (**CLVIII**) is depicted in (**CLXI**). The chelating properties of some chelating resins incorporating into silica gel have also been explored [564,565]. Supports carrying 1,3-diketones have been found to be highly selective for the preconcentration of uranyl(2 +) from dilute aqueous solutions [566].

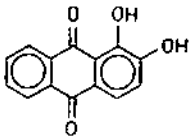


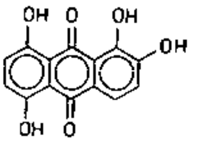
(CLXI)

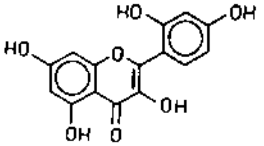
Stamberg and Seidl [567] described the preparation of a condensation chelating polymer incorporating 2,6,7-trihydroxy-9-phenyl-3H-xanthene-3-one (phenylflurone), (**CLXII**), which is highly selective for germanium. Griesbach and Lieser [296] prepared several ion exchangers, incorporating 4,5-dihydroxynaphthalindisulfonic acid (**CLXIII**), alizarin (**CLXIV**), 1,2,5,8-tetrahydroxyanthrachinon (chinalizarin) (**CLXV**) and morin (**CLXVI**) into a polystyrene matrix. The synthetic route involved the nitration of cross-linked polystyrene, followed by reduction, diazotisation and coupling with the appropriate ligand. The capacities of these resins are relatively low and lie in the range 0.4–0.7 mmol g^{-1}. The flavone resin has been found to be selective for iron [568]. A chelating polymer incorporating a 3-acetyl-4-hydroxybenzyl group in the side chain has been prepared by Hauta et al. [569]. Some novel resins have also been synthesised by condensing phenols and aldehydes with 2-(hydroxymethyl)-5-hydroxy-4H-pyran-4-one (**CLXVII**) [570]. These weak cation exchangers do chelate several metal ions.

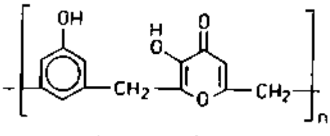

(CLXII)


(CLXIII)

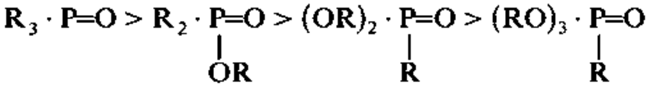

(CLXIV)


(CLXV)


(CLXVI)

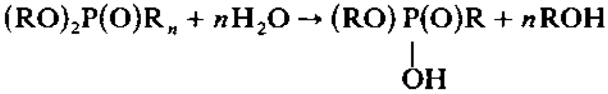

(CLXVII)

The phosphonic acid ion exchangers containing oxygen as the only donor atom form an important type of chelating polymer. In recent years, an increasing number of chelating ion exchangers incorporating arsonic acids (containing oxygen as the only donor atom) have also been studied. Kennedy and co-workers, while looking for some specific resins for uranyl ion, synthesised several such resins by phosphorylating styrene or chloromethylated styrene–divinylbenzene copolymers [477,478]. They selected phosphorus-containing ligands, because phosphorylated organic compounds by virtue of the electron donating phosphoryl oxygen have the strongest complexing properties for inorganic salts, such as uranyl nitrate and ferric chloride. The complexing strength of the phosphoryl ligand is governed by the inductive effect of the attached groups and follows the sequence



$$R_3 \cdot P{=}O > R_2 \cdot \underset{OR}{\underset{|}{P}}{=}O > (OR)_2 \cdot \underset{R}{\underset{|}{P}}{=}O > (RO)_3 \cdot \underset{R}{\underset{|}{P}}{=}O$$

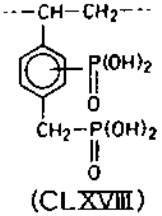
where R is a hydrocarbon radical [477]. Accordingly, di-allyl-allylphosphonate $(C_3H_5O)_2 \cdot P(O)C_3H_5$ was synthesised and polymerised with benzoyl peroxide. Alkaline hydrolysis of a diallyl-allylphosphonate polymer removes only one allyl group



$$(RO)_2P(O)R_n + nH_2O \rightarrow (RO)\,\underset{OH}{\underset{|}{P}}(O)R + nROH$$

where R is an allyl group.

In potentiometric titrations the resulting polymer showed one equivalence point and possessed an acid/base capacity of ca. 4.3 meq g^{-1} of the dry resin. Phosphorylation of polystyrene–divinylbenzene copolymer and its chloromethylated derivative, first reported by Idris-Jones [571], was repeated by Kennedy [572] and it was found that the dibasic polymer possesses the ion-exchange capacity of 4.0–4.5 meq g^{-1} of the dry resin. Reaction of a cross-linked chloromethylated styrene derivative with phosphorous trichloride and subsequent hydrolysis and oxidation resulted in a highly phosphorylated dibasic polystyrene phosphonate (**CLXVIII**) with a total sodium/hydrogen capacity of 8 meq g^{-1} of the resin [379]. A commercial resin Duolite C-63 possessing the similar functional group is also available. Persoz and Rosset [573] have carried out a detailed study on the complexing behavior of this resin with various transition and other heavy metal ions. The exchange capacity of Duolite C-63 has been found to be 5.1 meq g^{-1} (sodium). It has been shown that the resins containing phosphonic acid units show the same order of selectivity towards various cations as do the monomers with the following order of decreasing affinities: thorium(IV) > uranium(IV) > uranyl(2 +) > iron(III) > lanthanides(III) > hydrogen(I) > copper(II) > cobalt(II) > barium(II) > sodium(I). A comparison of the gen-

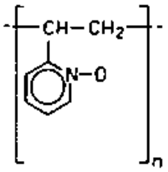


(CLXVIII)

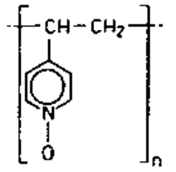
eral behavior of these resins with conventional sulfonate resins indicates that the uranyl ion and most of the trivalent cations are bound by linkages to the phosphonate functional units in the resin matrix via four-membered rings. Binding of several divalent metal ions by a phosphorylated ion-exchange resin has been studied by Horyna and Vesely [574] and the kinetic behavior of chelating resins with phosphonic functional groups has also been reported [575]. The rate-determining step for exchange of univalent and bivalent cations with this resin was found to be diffusion through the particle bead, whereas with strong complex-forming trivalent cations, the slow step was the chemical reaction at the reaction site. Diffusion coefficients, rate constants, activation energies and equilibrium half-time values are compared for forward and reverse reactions. It has been found that in buffered solutions, the effect of pH did not account for the slow rates obtained with cations which formed chelates with the phosphonic groups [575]. New phosphorus-containing ion exchangers have been prepared by first treating cross-linked chloromethylated polystyrene copolymer with a cyanide salt solution in an organic solvent and treating the product with a mixture of H_3PO_3 or a carboxylic acid and a phenoxide [576]. Kadlec and Matejk [577] obtained the separation of uni- and multivalent cations and selective deionisation by cationic phosphonic acid exchangers from a solution of salts of strong acids. Phosphorus-containing ion exchangers with increased selectivity have also been prepared from chloromethylated polystyrene–divinylbenzene copolymer through phosphorylation with phosphonitrile chloride followed by treatment of the resulting product with aliphatic amines or urea [578]. A successful phosphorylation of a formaldehyde–phenol matrix has been achieved [579] by means of a general reaction introduced by Kenner and Williams [580] for the phosphorylation of phenols. Recently, sorption properties of a phosphonated cation exchanger for uranyl ions have been studied [581]. The sorption of uranium increased with an increase in pH due to increase in number of dissociated phosphonic groups. The anomalously high $H^+–UO_2^{2+}$ exchange constant has been related to the simultaneous ion exchange and chelating processes. The resin has been found to be suitable for recovery of uranium from sea water [581]. A number of chelating ion exchangers having *β-keto* phosphonate groups have also been reported [582].

The first arsonic acid resin was prepared by Parrish [583] from poly(aminostyrene) using a Bart reaction. Davies et al. [454] have also reported the synthesis of polystyrene-azo-*o*-hydroxy-phenylarsonic acid by treating polystyrene–diazonium chloride with a solution of *o*-hydroxyphenylarsonic acid in an alkaline medium. Fritz and Moyers [584] prepared a series of macroporous arsonic acid resins by a synthetic method advanced by Parrish [583]. The effect of varying pore diameter and surface area on the properties of the final polymers has been studied. One of the resins was used for the concentration of trace metal ions from demineralised water, tap water and sea water. A method for separation of uranium(VI) and thorium(IV) from each other and also from other metal ions has been developed. Hirsch et al. [314] prepared a macroreticular arsonic-acid ion exchanger, following the procedure of Parrish [583]. The arsonite resin has a hydrogen capacity of 3.00 mmol g^{-1} and capacity for copper(II) has been found to vary with pH, being 1.3 mmol g^{-1} at pH 11 and 0.8 at pH 3.5. This resin showed the selectivity order as: Mg < Ca < Mn < Co < Ni < Zn < Cu, which is different from the one reported for a phosphonate resin, Duolite C-63: Mg < Ca < Ni < Co < Mn < Zn < Cu [573]. The shift in the position of the nickel and manganese has been attributed to the difference in coordinating properties between arsono and phosphono groups [245].

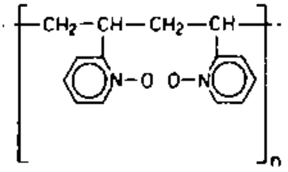
Another type of ligand containing oxygen as the only donor atom is derived from *N*-oxides of bases like pyridine. The metal complexes of such ligands have been studied at length and reviewed repeatedly in recent years [585]. Some metal complexes of poly(4-vinylpyridine-1-oxide) (**CLXIX**), poly(4-vinylpyridine-1-oxide) (**CLXX**) and 2,2′-trimethylenedipyridine-1-oxide (**CXXI**) have been studied by Kadir and Holt [586,587]. Due to steric reasons, these three ligands form different type of complexes as depicted in **CLXII**, **CLXIII** and **CLXIV**. The structures of these metal complexes have been established on the basis of their elemental analysis and IR spectra.



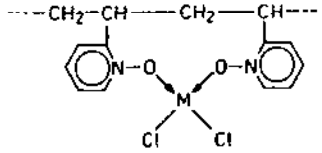
(CLXIX)



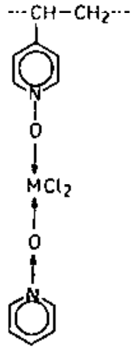
(CLXX)



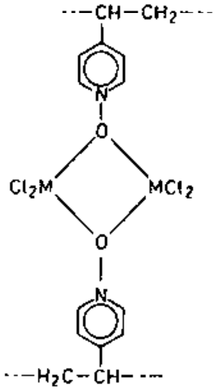
(CLXXI)



(CLXXII)



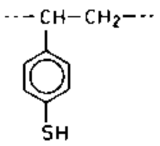
(CLXXIII)

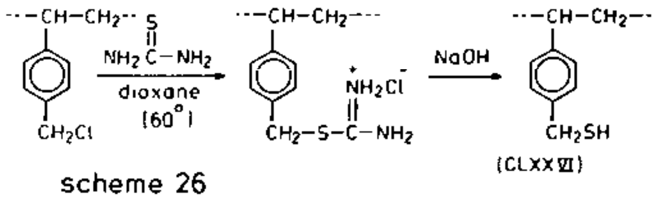


(CLXXIV)

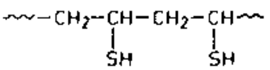
(iv) Chelating ion-exchange resins containing sulfur or nitrogen and sulfur as donor atoms

Polythiostyrene is the first sulfur-containing complexing ligand to be discussed. Gregor et al. [588] and Overberger and Lebovits [589] reported the synthesis of polythiostyrene almost at the same time through related routes. Gregor et al. [588] synthesised polythiostyrene by treating the diazonium chloride of polystyrene with potassium xanthate and hydrolysing the resulting product. Overberger and Lebovits [589] obtained polythiostyrene (**CLXXV**) by converting *p*-aminoacetophenone to a xanthate by diazotization followed by its reaction with potassium xanthate. The product was not isolated but was directly reduced with sodium borohydride in ethanol followed by saponification to obtain *p*-thiol-α-methyl benzyl alcohol. The benzyl alcohol derivative was converted to a diacetate which was then deacetylated by passing through a hot tube at 450 °C yielding *p*-vinylphenylthioacetate; this was polymerised with 2,2′-azo-bis-isobutyronitrile as catalyst to yield polyphenylthioacetate which on saponification with dilute base yielded polythiostyrene. Frechet et al. [147] prepared polythiostyrene by reaction of cross-linked polystyryllithium with elemental sulfur, followed by reduction of the resulting polymer with $LiAlH_4$. The polystyryllithium can be prepared directly from polystyrene by treatment with *n*-butyllithiumtetramethylethylenediamine [146,590], or via the bromination–lithiation route [146]. The second route is generally preferred because it allows better control of the degree of functionalisation. Parrish [583] synthesised a cross-linked poly-thiomethylstyrene (**CLXXVI**) by treating chloromethylated polystyrene with thiourea to yield an exchanger (Scheme 26) containing the isothiourea hydrochloride group, followed by hydrolysis with alkali. This cross-linked poly-thiomethylstyrene was found to take up mercury quantitatively, when a solution of mercuric nitrate in dilute


(CLXXV)


scheme 26

nitric acid was allowed to pass through a column of this resin. An improved synthesis of this resin containing thiomethyl groups attached to polystyrene rings, and involving three-phase systems and the use of a phase-transfer catalyst, has been developed [147]. In this method, the degree of functionalisation could be controlled and the product obtained was free of disulfide bonds. It has been observed that the resin, containing aliphatic groups, ionises less than the resin containing thiol groups directly attached to polystyrene rings. The resin with thiomethyl groups is specific for mercury(II), whereas resins of the "polythiostyrene" type can selectively bind iron(II), cobalt(II) and nickel(II). A linear, soluble poly(mercaptostyrene) (**CLXXVII**)

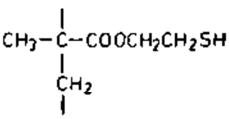


$$\sim CH_2-\underset{SH}{\underset{|}{CH}}-CH_2-\underset{SH}{\underset{|}{CH}}\sim$$

(CLXXVII)

prepared by Braun [591] is specific for mercury. In general, these resins containing thiol groups might be used to remove those metals which form mercaptides from a mixture of metal ions [583]. Two commercial resins, Duolite ES 465 and IMAC-TMR (cf. Table 1) contain thiol groups and are stated to be specific for mercury(II) [592]. Attempts to bind significant amounts of first-row transition metal ions at different pH values with Duolite ES 465 failed [593].

The adsorption capacity of all the thiol resins mentioned above is affected adversely by the hydrophobic nature of the polymeric matrix. Recently, the metal uptake behavior of thiol derivatives of the polystyrene and methacrylate-type resins have been compared and better results were obtained with the latter [594]. Slovak et al. [595,596] prepared some thiol derivatives from macroporous hydrophilic hydroxyethyl methacrylate gels (Spheron). One such resin has been prepared by modification of Spheron gel and contains β-mercaptoethyl methacrylate units (**CLXXVIII**). This resin was found to



$$CH_3-\overset{|}{\underset{\underset{|}{CH_2}}{\underset{|}{C}}}-COOCH_2CH_2SH$$

(CLXXVIII)

take up 95% mercury from a very dilute solution of the metal salts within 10 min under static conditions. However, prolonged shaking of the mixture resulted in a decrease in the amount of metal sorbed. This behavior has been explained by β-elimination of the mercaptoethyl group from the resin [597]. This observation led to the preparation of another type of chelating resin (Spheron thiol) as depicted in Table 1. This material is now commercially available under the trade name of Spheron Thiol-1000 (cf. Table 1). This chelating resin, having hydrophilic glycomethacrylate gels with sides containing thiol groups shows high sorption selectivity for Hg, Sb, Bi, As, Ag, Cu, and Pt, even in 1–3 M solutions of sulfuric or hydrochloric acid. The sorption capacity of the resin reached ca. 0.5–1.00 mmol g^{-1} in 0.05 M HCl and equilibration was achieved within 5 min, except for arsenic and platinum in weakly acidic solutions. For the analytical determinations of small amounts of elements, especially when batch sorption methods are used, the direct sampling of aqueous suspensions of Spheron thiol, after sorption, into the AAS electrothermal atomiser proved to be advantageous [598] and, hence, desorption was not needed.

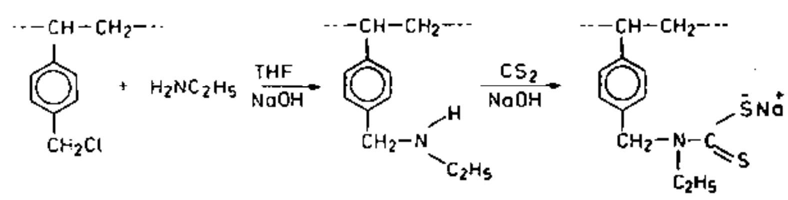
One of the most important and thoroughly studied classes of ligands containing sulfur as donor atoms are the dithiocarbamates and related ligands [598]. Dithiocarbamates have been used extensively in analytical chemistry for the determination of traces of heavy metals [599–602]. Dithiocarbamates form exceptionally strong, insoluble complexes with a large number of metal ions, with the notable exception of alkali and alkaline earth metal ions [603]. One possible advantage of the chelating ability of polymer-supported dithiocarbamates could be their ability to quantitatively concentrate a large number of metal ions simultaneously, while not complexing alkali and alkaline earth metal ions [603]. In recent years, a number of dithiocarbamates have been anchored onto a variety of polymeric supports and the ion-selective properties of these chelating resins have been evaluated. Siggia et al. [603,604] synthesised several dithiocarbamate resins by treating polyamine–polyurea resins [511] containing some available secondary amine groups with carbon disulfide as shown below

$$-\mathrm{NH(CH_2CH_2NH)}_x\mathrm{CH_2CH_2NH}- + \mathrm{CH_3C_6H_3(NCO)_2}$$

$$\rightarrow -[\mathrm{NH(CH_2CH_2NH)}_x\mathrm{CH_2CH_2NHCONHCH_3C_6H_3NHCO}]_y-$$

$$\rightarrow -[\mathrm{NH(CH_2CH_2NCS_2H)}_x\mathrm{CH_2CH_2NHCONHCH_3C_6H_3NHCO}]_y-$$

Among the various metal ions studied, a color change was observed only for Cu^{2+} (blue) and Ag^{+} (yellow-brown). The capacity of the resins for the various metal ions tested appears to follow the order: $Ag^{+} > Hg^{2+} > Cu^{2+} > Sb^{3+} > Pb^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+}$ and Ca^{2+} was not taken up. These dithiocarbamate chelating resins form mainly 1 : 1 (metal to ligand) complexes, whereas monomeric diethyldithiocarbamate has been found to form both 1 : 1 and 1 : 2 complexes. The predominant formation of 1 : 1 complexes in polymeric systems has been ascribed to steric constraints in the ligand [603]. Poly(dithiocarbamate) resins are ideally suited for trace metal collection and analysis [604]. Recently, poly(dithiocarbamates) have been used for the determination of trace elements in coal and other energy-related materials [605]. The poly(dithiocarbamate) resins also find applications in concentration and separation of trace elements from complex matrices [606,607]. Okawara and Sumitomo [608] briefly described the preparation of dithiocarbamate resins using chloromethylated polystyrene as the starting material. Recently, Hirtani et al. [609] reported the preparation of four kinds of polystyrenedithiocarbamate resins containing *N*-methyl-*N*-carboxymethyldithiocarbamate (resin **1**), *N*-methyl-*N*-carboxymethylamino (resin **2**) *N*,*N*-di(α-hydroxymethyl)dithiocarbamate (resin **3**) and di(β-hydroxyethyl)amino groups. They used styrene–divinylbenzene (2%) as a polymeric matrix and synthesised these chelating polymers by treating chloromethylated polystyrene with the sodium salt of the corresponding dithiocarbababamic acid in dimethylformamide. On reaction with copper(II) ions, the reaction reached a maximum of 4.17 meq g^{-1} for resin (**1**) and 4.75 meq g^{-1} for resin (**2**). The polymers containing sulfur show a larger reactivity towards metal ions in comparison to polymers without sulfur atoms. The reactivity of resin (**1**) towards metal ions decreased in the order: Ag(I) > Cu(II) > Zn(II) > Ni(II) > Co(II). The other metal ions, except Ag(I) and Cu(II), barely reacted with resin (**2**). Thus resin (**2**) has remarkable selectivity for Ag(I) and Cu(II). The ligands and the complexes have been characterised on the basis of IR spectra. In the infrared spectra of metal complexes of resins (**1**) and (**2**), absorption at 1480 cm^{-1} assigned to the thione amide group and at 990 cm^{-1} assigned to the thiocarbonyl group, shifted towards lower frequencies. This indicates that nitrogen and/or sulfur atoms participate in the coordination. The anchored dithiocarbamate ligands are unaffected by γ-irradiation. Bhaduri and Khwaja [610] have also synthesised some polymer-supported dithiocarbamate ligands (**CLXXIX**) from chloromethylated styrene–divinylbenzene (8%) copolymers, using the sequence of reactions given in Scheme 27. They synthesised molybdenum(V) and rhodium carbonyl complexes with

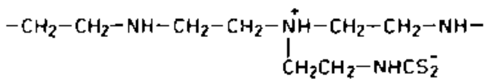


scheme 27

(CLXXIX)

polymer supported diethyldithiocarbamate and studied them with the aid of infrared and EPR spectra, (for use as catalyst) [610,611], whereas Hirtani et al. [609] used the anchored dithiocarbamate ligands for ion-selective studies. Several dithiocarbamate–cellulose derivatives have been prepared by reaction of ethylenediamine-, 2,2′-diaminodiethylamine-, and triethylenetetramine cellulose (trien) derivatives with sulfur dioxide in ammonia solution [612]. The metal uptake behavior of these amine and dithiocarbamate–cellulose derivatives have been compared for Cu(II), Cd(II), Pb(II), Hg(II), Co(II) and $UO_2(2+)$. The dithiocarbamate derivatives showed better metal-uptake capacity and trien–cellulose could also take up silver(I), selenium(IV) and antimony(V) over a wide range of pH values. The trien–dithiocarbamate–cellulose was used to preconcentrate Cu(II), Cd(II), Hg(II), and Pb(II) from sea and tap water. Dithiocarbamate chelating groups anchored to silica have been used as preconcentration aids for X-ray analysis [613,614]. Wing et al. [615] reported the preparation of several water-insoluble starch xanthates by xanthation of highly cross-linked starches under various conditions. These products have been found to be very effective in removing various heavy metals from water to concentrations below established discharge limits.

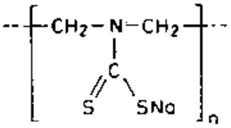
The binding of the transition metal ions VO(IV), Fe(III), Fe(II), Co(III), Co(II), Ni(II) and Cu(II) by a poly(iminoethylene)dithiocarbamate copolymer has been investigated by uptake studies, IR, electronic, EPR spectra and magnetic susceptibility measurements [616]. Poly(iminoethylene)dithiocarbamate copolymer is a zwitterion with both nitrogen and sulfur donor sites (**CLXXX**). This dithiocarbamate derivative has been synthesised by



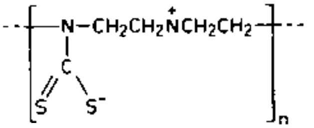
$$-CH_2-CH_2-NH-CH_2-CH_2-\underset{\displaystyle CH_2CH_2-NHCS_2^-}{\overset{+}{N}H}-CH_2-CH_2-NH-$$

(CLXXX)

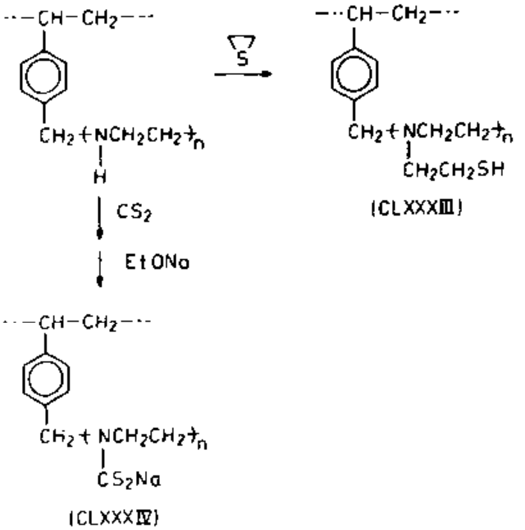
reaction between poly(iminoethylene) and carbon disulfide in ethanol, substitution taking place at the primary and secondary amino groups of poly(iminoethylene) to the extent of 35%. In the IR spectrum of the polymer, by analogy with simple dithiocarbamate $R_2NCS_2^-$, a band occurring at 1460 cm^{-1} and a strong band at 965 cm^{-1} have been assigned to $\nu(NCS_2)+\delta(CH_2)$ and $\nu(CNC)+\nu(CS_2)$ vibrations, respectively. In the spectra of the metal complexes, the band occurring at 1480 cm^{-1} moved to higher frequencies and the lower band at 965 cm^{-1} broadened and showed a splitting of less than 20 cm^{-1}, indicating the bidentate coordination mode of the CS_2 group. Weak to medium intensity bands observed in the range 352–384 cm^{-1} have been assigned to ν(M–S) vibrations by comparison with the low molecular weight complexes. The magnetic moments of vanadyl(2+), iron(III), iron(II), cobalt(II), nickel(II) and copper(II) complexes lie at ca. 1.39, 5.40, 5.19, 0.87, 1.86 and 2.26 B.M., respectively. These magnetic moments, except copper(II), are lower than usually observed for high-spin complexes of these metal ions. The cobalt complex contains mainly cobalt(III), whereas in the case of the nickel(II) complexes the presence of both diamagnetic and paramagnetic species was shown. The electronic spectra, magnetic moments, and EPR spectra show that the structures of metal complexes were not always the same as found in the analogous low molecular complexes. Cobalt(III) and iron(III) dithiocarbamates are coordinated by six sulfur atoms and so the degree of reaction depends on the accessibility of the three dithiocarbamate groups for coordination, whereas the requirements for vanadyl(2 +), iron(II), nickel(II), and copper(II) are two dithiocarbamates. Okawara and Nakai [617] reported the reaction of commercial poly(iminoethylene) with carbon disulfide in the presence of sodium hydroxide to form a chelating resin of possible structure **CLXXXI**. This polymer could chelate metals though no quantitative data have been given. Barnes and Esselment [618] attempted a reaction between poly(iminoethylene) and carbon disulfide in the absence of a base under very mild conditions and obtained a novel product, poly(*N*(dithiocarboxylato)iminoethylenehydrogeniminoethylene). They assigned a zwitterion structure (**CLXXXII**) by analogy with a structure assigned to the product obtained from the reaction of aliphatic diamines and carbon disulfide in ethanol. This new polymer shows two bands at 1385 and 970 cm^{-1} characteristic of dithiocarbamates and assigned to ν(N–C=S) and ν(C=S) vibrations, respectively. This resin chelates iron(II), cobalt(II), nickel(II), zinc(II), copper(II), mercury(II), and silver(I). However, it did not bind manganese(II). Iron(II), cobalt(II), nickel(II) and zinc(II) appear to be bound to this resin in a similar fashion, as do copper(II) and mercury(II). Binding to silver, for which it can be selective, is likely to be different. Analysis of these complexes indicated that anions are present in the polymeric matrices. Following their own work on the modification of poly(styrene-*g*-ethylenimine), Saegusa et al. [619] introduced sulfur-containing functional groups into poly(styrene-*g*-ethylenimine) by reaction with ethylene sulfide and carbon disulfide (Scheme 28), producing new chelating resins of the aminoethylmercaptan (**CLXXXIII**) and diethyldithiocarbamate type (**CLXXXIV**). These resins have been characterised on the basis of their IR spectra and estimation of thiol groups. The chelating polymer (**CLXXXIII**) forms stable complexes with heavy metal ions and is effective for the adsorption of mercury(II); the order of adsorption capacity of the resin (**CLXXXIV**) is: $Hg^{2+} > Cu^{2+} > Cd^{2+}$, agreeing well with the stability constants for dithiocarbamates complexes of these metal ions [620]. The order of adsorption capacities of these two resins and poly(styrene-*g*-ethylenimine) (**XLVIII**) follows the order: (**XLVIII**) > (**CLXXXIII**) > (**CLXXXIII**) > (**CLXXXIV**) [620]. The mercaptomethylation of a highly branched poly(ethylimine) has also been described [621].



(CLXXXI)

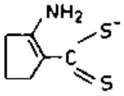


(CLXXXII)



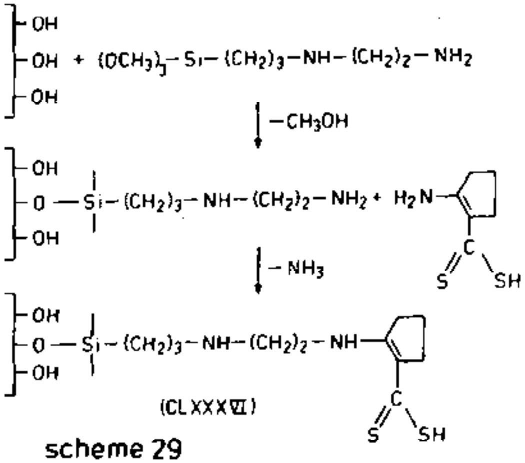
scheme 28

Some nitrogen- and sulfur-bearing chelating groups have been incorporated into polymeric matrices. Seshadri and Kettrup [621] incorporated 2-amino-1-cyclopentene-1-dithiocarboxylic acid (**CLXXXV**), which is known



(CLXXXV)

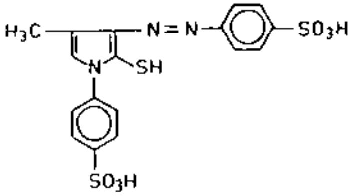
to form intense colored complexes with noble metals, silver and mercury, into silica gel. This potential bidentate (SS or SN) ligand can be attached to silica gel by the sequence of reactions shown in Scheme 29 [622,623]. The



scheme 29

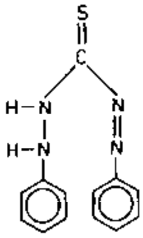
silica-supported ligand possesses the structure (**CLXXXVI**). A method has also been described for the preparation of filter papers containing this chelating ligand (**CLXXXV**) by silylating Whatman filter paper SG 81 through a sequence of reactions used for the functionalisation of the solid support. Parameters such as the effect of pH, and effect of time on extraction efficiency of (**CLXXXVI**) on different metal ions have been evaluated. This resin possesses greater affinity for Ag(I), Hg(II), and Pd(II) (having an exchange capacity ca. 1 mmol g^{-1}) than for other metal ions like Cu(II), Cd(II), Zn(II), and Pt(IV) (0.2–0.6 mmol g^{-1}). The capacity of this resin for different metal ions follows the order: Ag > Hg > Pd > Pt > Cu > Cd > Fe > Zn > Ni > Rh. In most cases the kinetics were fast. Copper(II), nickel(II), zinc(II), mercury(II), uranyl(2 +) and platinum(IV) extracted at least 90% in less than 1 min and only palladium(II) required 5 min to reach a level of 90% extraction. Most of the properties of this resin are comparable to other conventional chelating ion-exchange resins and both functionalised silica and filter papers have potential for removal of heavy metal ions such as silver, mercury and palladium [622,623]. Leyden et al. [283–285] have also anchored several bisdithiocarbamates onto silica gel or controlled pore glass beads and found that such materials, after homogenisation and pelletising, can be used for X-ray spectrometric determinations without any interference from calcium or magnesium.

In recent years, a number of other chelating ligands containing nitrogen and sulfur as donor atoms have been used for functionalising polymeric matrices. A chelate-forming resin bearing mercapto and azo groups has been prepared from a commercial resin, Amberlite IRA-400 (8% DVB) by treatment with azothiopyrine disulphonic acid, namely disodium-4,4′-(4-diazenediyl-5-mercapto-3-methyl-1,2-diazacyclopenta-2,4-dien-1-yl)dibenzenesulfonate (**CLXXXVII**) [624,625]. This resin has been found to be very effective for the collection of mercury(II) both by batch and column. In the column method, the amount of mercury(II) in solution could be reduced below 0.5 μg l^{-1}. The mercury(II) adsorbed could be eluted with thiourea solution and the resin could be used repeatedly. The resin of (**CLXXXVII**) can be regarded as a valuable sorbent for the treatment of waste water, containing mercury(II). It has advantageous features for the preconcentra-



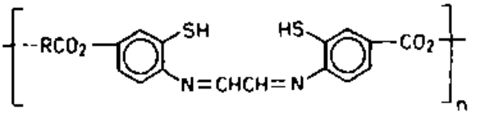
(CLXXXVII)

tion of some trace metal ions, such as copper(II) and cadmium(II) in trace analysis. Tanaka et al. [626] and Griesbach and Lieser [296] incorporated 1,5-diphenylthiocarbazone (**CLXXXVIII**), a versatile *S*,*N*-bidentate ligand,



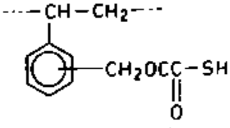
(CLXXXVIII)

into a polystyrene matrix by two different routes. Tanaka et al. treated an anion-exchange resin (Amberlite IRA-400, a strong basic anion exchanger having a styrene–DVB copolymer matrix) with a sulfonic acid derivative of dithizone, whereas Griesbach and Lieser treated diazotised polystyrene with dithizone to obtain the resin. The spectral properties of these resins were examined and found to be similar to dithizone itself. The capacity of the resin prepared from the sulfonic acid derivative of dithizone was 1.9 mmol g^{-1} of dry resin. This resin is quite effective for the adsorption of mercury(II), with which it forms 1 : 2 complexes. Recently, Nakazato et al. [627] described the preparation of acrylamide chelating resins containing thiosemicarbazide by condensation of a spherical porous copolymer with thiosemicarbazide (a S,N-bidentate chelating ligand known for its strong complexation with heavy metal ions [628]) and studied metal ion adsorption. The mechanism of sorption of platinum(IV) on S,N-containing sorbents (e.g., CH_2–S–$(CH)_2NEt_2$ and CH_2SEt functional groups) in an aqueous solution of hexachloroplatinate has been reported. The IR and X-ray fluorescence revealed that sorption on polymeric sorbents involves chelation of platinum by the S-containing bidentate functional group [629]. A complex-forming ester containing sulfur and nitrogen as donor atoms, having the structure (**CLXXXIX**) has been prepared by treating glyoxal bis(2-mercapto-4-hydroxyanil) with a dicarboxylic acid dichloride such as terphthaloyl or adipoyl chloride. This resin has been used to recover gold from gold salts to the extent of 96%, with 1.5% copper and negligible amount of other ions.



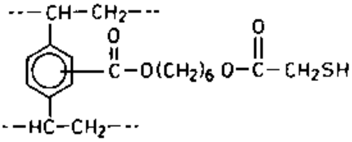
(CLXXXIX)

Hering and Haupt [630] recently reported the properties of ion exchangers prepared by treating chloromethylated polystyrene with $HS(CH_2)_nCOOC_2H_5$ ($n = 2$ or 3) in the presence of alcoholic potassium hydroxide. Phillips and Fritz [631] reported the synthesis and properties of a resin (**CXC**) containing



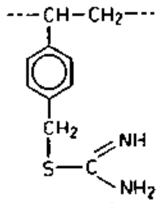
(CXC)

a thioglycoloyloxymethyl functional group. This resin retains Ag(I), Bi(III), Sn(IV), Sb(III), Hg(II) and Au(III) from 0.1 M mineral acid and Cd(II), Pb(II) and U(VI) from a solution of pH 3.5. Chelating resins with thioglycolate anchor groups have been synthesised by treating sucrosemethacrylate gels with thioglycolic acid [632]. The capacities of these gels are extremely high for silver(I) (5.3 mmol g^{-1}) and mercury(II) (4.9 mmol g^{-1}). A resin containing hexylthioglycolate groupings (**CXCI**) has been developed by



(CXCI)

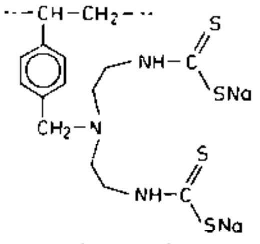
Moyers and Fritz [633] by stepwise reactions of 1,6-hexenediol and thioglycolic acid with a macroporous styrene–divinylbenzene copolymer containing carboxylic acid groups (XAD-4). It is evident from the structure of the hexylthioglycolate resin that it contains unreacted carbonyl groups, which impart general ion-exchange properties and thus this resin exhibits strong selectivity towards certain metal ions only in highly acidic solutions. It is specific for silver(I), mercury(II), bismuth(III) and gold(III) in 0.1 M mineral acid. Another resin (**CXCII**) is selective for gold(III) [634]. This resin



(CXCII)

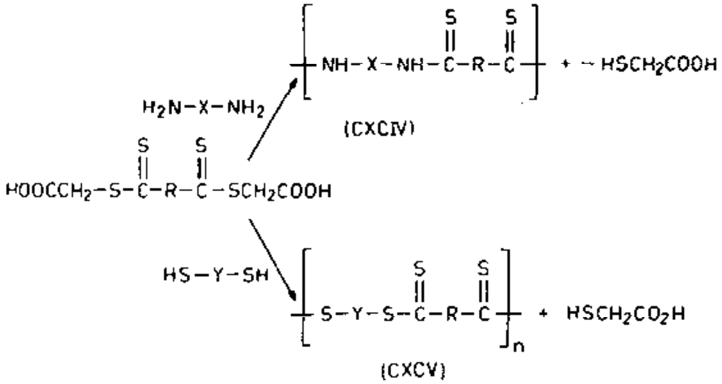
contains isothiouronium groups anchored to cross-linked chloromethylated polystyrene, and is also very selective for the platinum metals; its capacity for gold is very high, i.e., 5.58 mmol g^{-1}. A resin containing isothiouronium chelating groups is also available commercially under the names of Srafion

NMRR and Ionac SR-3 (see Table 1). A number of chelating resins having either sulfur, or sulfur and nitrogen along with carboxylic donor groups ligands attached to a polystyrene matrix have been reported by Mahrol and Cheng [371] (Scheme 14). The synthesis of these ligands goes through acetoxypolystyrene. In a comparative study with Chelex-100 and similar resins, the resins containing sulfur as one of the donor atoms have a lower chemical stability. In water slight hydrolysis of the functional groups was observed at room temperature. When the resins were washed with 2 N sulfuric acid, the sulfur content of the resins decreased considerably. Nevertheless, these resins may be used for separation of metal ions in slightly acidic and neutral solutions. Some soluble macromolecular complexing agents have been synthesised by copolymerising acrylic acid and *N*-allylthiourea [635]. Naumova et al. [636], while studying the interaction between divalent metal ions and sulfur-containing ion exchangers found that when sulfur is present in the copolymer matrix, it can attract metal ions away from the carboxyl groups and prevent their reaction. The adsorption of Cu^{2+}, Cd^{2+} and Zn^{2+} on this resin has been studied by IR spectroscopy. Very recently, Suzuki and Yokoyama [282] proposed a novel route for synthesising polystyrene resins containing pendant multidentate ligands having two dithiocarbamate groups (**CXCIII**). Such chelating resins form complexes with copper(II), nickel(II), cobalt(II) and zinc(II); most of these complexation reactions were accompanied by an obvious change in color of the polymer beads. A new class of novel polymers containing thiocarbonyl groups have been synthesised by the polycondensation of dicarboxymethyl dicarbodithioates with diamines and dithiols (Scheme 30) and polymers (**CXCIV**) and (**CXCV**), respectively, are obtained [637]. The polymers were characterised by elemental analysis and IR and ^1H NMR spectra.

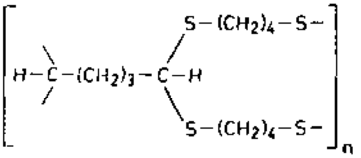


(CXCIII)

A number of solid thio-ether based polymers have been prepared by the condensation of a dialdehyde and a dithiol in the presence of HCl as a catalyst, a reaction type previously used to prepare low molecular weight chelating agents with high selectivity for mercury(II) [638,639]. Of the various polymers (**CXCVI**) prepared by this method, the polymer prepared from glutaraldehyde and butanedithiol in a 1:2 mole ratio proved to have

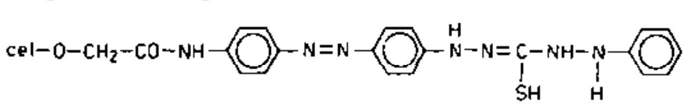


scheme 30



(CXCVI)

the most satisfactory physical properties. This resin has been found to be highly selective for mercury(II) [638]. The therapeutic potential of this resin has also been explored [639]. Several hydrophilic chelating gels with sulfur-containing anchor groups have been prepared from sucrose metharylates and their ion exchanging properties evaluated [640,641]. Starting from carboxymethylcellulose Bauman et al. [642] have prepared diazonium cellulose and coupled it with potassium dithizonate (**CXCVII**); the capacity of the freshly

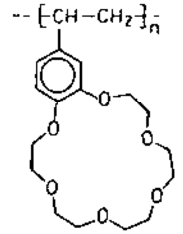


(CXCVII)

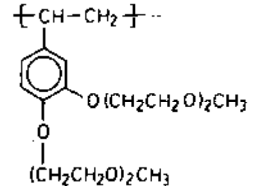
prepared resin is 0.58 meq g^{-1}. In the column experiments, this material gave complete recovery of Cu^{2+}, Zn^{2+} and Ag^{+} at pH 5 and ions were eluted quantitatively with nitric acid. The columns were reusable and this chelating resin was also used for trace metal collection from sea water [642].

(v) Chelating ion-exchange resins containing macrocyclic and related ligands

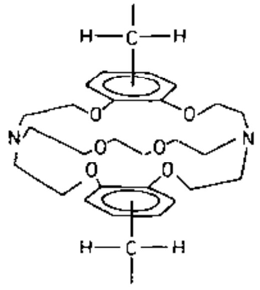
Crown ethers and related ligands have found increasing application in a number of areas such as liquid–liquid extraction for separation or enrichment of trace metals or isotopes, of neutral solutes and of optically active isomers (using chiral macrocycles), in ion-selective electrodes and membranes, thin layer chromatography, electrophoresis, and in anion-activated catalysis and models for enzyme systems [57]. These crown ethers can also bind a variety of other solutes including transition metal ions [643], lanthanides [644], organic cations, such as ammonium and diazonium cations [645,646] and even neutral molecules [647]. The crown ethers and related macroheterocyclic ligands are generally obtained in low yields through relatively long reaction sequences, which prompted workers engaged in this field of research to look for economical ways to use such versatile but expensive compounds. The natural choice was the use of polymeric supports to incorporate macroheterocyclic ligands, so that these expensive materials could be retrieved and recycled. The use of macrocyclic ligands on a polymeric support or a linear polymer may result in the modification of binding properties of such ligands, due to possible coorperative effects with other ligands, or to environmental effects. A variety of macroheterocycles, such as crown ethers (**CXCVIII**) (including cyclic compounds containing nitrogen, sulfur or phosphorus atoms instead of oxygen atoms), acyclic polyethers (**CXCIX**) or cavitands [648] and cryptands (**CC**) (bicyclic crown ethers) have been incorporated into different types of polymeric matrices including both addition and condensation polymeric supports. The complexes, formed by the polyethers and the metal salts, are held together by interactions between cations and C–O dipoles of the polyethers, indicating that these macroheterocycles are usually neutral ligands. Thus an anion has



(CXCVIII)



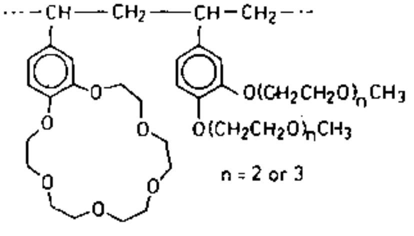
(CXCIX)



(CC)

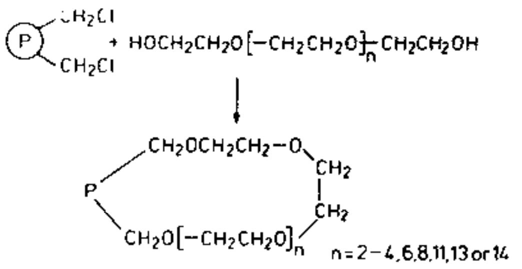
also been taken up together with the cation to maintain electroneutrality of the resin. Secondly, the variable ring sizes, the number and positions of the donor atoms in the ether ring permit the selective adaption to a certain cation [48,140]. Such attractive features of crown ethers and related systems aroused tremendous interest and much work has been done on the synthesis and characterisation of polymeric macroheterocyclic ion exchangers in a short span of time, so much so that the various aspects of polymeric crown ethers have repeatedly been reviewed in the recent years [48,51–54,140]. Blasius et al. [48,140] have prepared a large number of polymeric or polymer-supported crown ethers, including cryptands and reviewed their synthesis, properties and applications. Similarly, Smid et al. [649,650] have worked on poly(vinylbenzene–crown ethers) and have reviewed this and related work [54,651]. Gramain et al. [652–654] have studied a variety of condensation polymers containing diazacrown ethers and cryptands [57]. Warshawsky et al. [655] introduced the concept of polymeric pseudocrown ethers. Functional metal–porphyrazine derivatives and their polymers have been studied by Shirai et al. [656]. It is obvious from the preceding delineation that most of the work done on ion exchangers containing macroheterocyclic ligands has been reviewed in recent years and thus, the development and recent advances in this area will only be briefly described here.

The first contributions to this field of crown ethers were made by Kopolow, Hogen-Esch and Smid [649,650], who studied various poly(crown ethers) obtained by the polymerisation of vinyl crown ether derivatives. Two of the compounds, poly(vinylbenzo-15-crown-5) and poly(vinylbenzo-18-crown-6) have similar structures, but a marked difference was observed in their properties. Similar behavior is shown by polymers with a polystyrene backbone containing short glyme chains ($O(CH_2CH_2O)_nCH_3$) attached to benzene rings [657]. The synthesis and their behavior towards various cations and anions have been reviewed by Smid [54,651]. Some mixed crown glyme-containing polymers (**CCI**) have also been studied [658]; such poly-



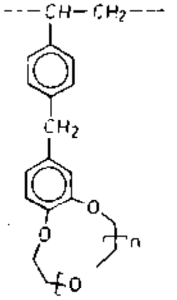
(CCI)

mers show strong hydrophobic interactions with organic solutes and cations and can be used to enhance electrostatically the binding of anionic organic solutes. Fritz and Miller observed that a polymer incorporating pendant ester groups (Amberlite XAD-7) strongly binds gold as $AuCl_4^-$ [659] while studies on the coordination of platinum group metal thiocyanates suggest that metal ion coordination is accomplished by a cooperative effect of many esters groups, the close proximity of the polymer backbone not being deleterious. This led Warshawsky et al. [655] to assume that the synthesis of macrocyclic ethers incorporating a part of the macromolecular network would result in polymers of high coordinating power. To verify this hypothesis, Warshawsky et al. [655,660–662] synthesised a range of such polymers described as "polymeric pseudocrown ethers" (PPCE) based on a one-step in-situ cyclisation reaction between a chloromethylated styrene–divinylbenzene copolymer and polyoxyalkylene under Williamson ether-synthesis conditions, as shown in Scheme 31. A typical structure of a pseudocrown ether



scheme 31 (CCII)

is shown in (**CCII**). It was shown that the slightly cross-linked polymers with intermediate flexibility are best suited for this type of synthesis, because they offer several advantages, such as good accessibility (good swelling and diffusion) to large polyether molecules, good conformational adaptability and minimal further cross-linking. For instance, a chloromethylated styrene–divinylbenzene copolymer having 4% DVB was considered a suitable precursor for the synthesis of PPCE and high cyclisation yields were obtained with this copolymer, even when an excess of a diol was used. A detailed study of coordination of transition metals, including Au^{3+}, Fe^{3+} and Zn^{2+} as chlorides, bromides or iodides in acidic NaX solutions show that PPCE coordinate MX_4^- or MX_4^{2-} complexes (M = Au, Fe, Zn and X = Cl, Br or I) without competition from a large excess of hydrogen or X^- ions. The coordination patterns of the various PPCE show that coordination is most effective when the anion will fit well in the PPCE cavity. The coordination of MX_4^- or MX_4^{2-} anions (ionic diameter 10.5–13 Å) is most effective with PPCE-14 (incorporating 14 oxygen atoms with cavity diameter of 10.5–13 Å) and falls off to zero with PPCE-4 (incorporating only four oxygen atoms). It was shown that a macroreticular polystyrene derivative incorporating polyoxyethylene (14 units) (PPCE-14) complexed strongly with both protic and Lewis acids [655]. The distribution coefficients were found to depend on the dielectric constant of the solvent and followed the order: $D_{\text{benzene}} > D_{\text{chloroform}} > D_{\text{dioxane}} > D_{\text{water}}$. These authors also studied the complexation of PPCE with iron(III) (in the form of $FeCl_4^-$) in phosphoric and hydrochloric acid mixtures [660]. Complexation depends on the hydrochloric acid concentration and became efficient only when the concentration of hydrochloric acid exceeded 4 M. Column tests have shown that iron can be separated very effectively and efficiently from phosphoric acid and regeneration of the polymers could be accomplished with water. Warshawsky and Kahana [534] extended this method of preparation of PPCE for synthesis of polymeric crown ethers carrying pendant macrocyclic rings. Thus, the alkylation of catechol with chloromethylated styrene–divinylbenzene copolymer produces the polymer bound catechol (**CXLV**), which upon reaction with a series of polyglycol dihalides affords macrocyclic polymeric benzocrown ethers (**CCIII**) in fairly good yields. The ion-coordination patterns for



(CCIII)

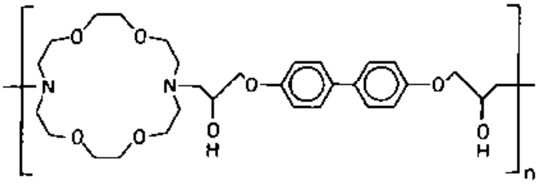
polymeric crown ethers were studied by using distribution and equilibrium distribution values in the temperature range 20–60 °C for the perchlorate, thiocyanate or bromide and indicated that:

(i) the spheric recognition patterns, typical of crown ethers in solution, are fully reproduced in the polymeric analogues;

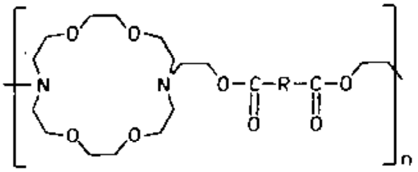
(ii) the highest binding constants are obtained for the polymeric benzocrown-6, as anticipated from data for the corresponding monomeric benzocrown-6;

(iii) the polymers bind alkali metal cations via two types; the residual catechol groups allow an ion-exchange mechanism and crown ether groups by a salt coordination mechanism; the latter is temperature dependent [534].

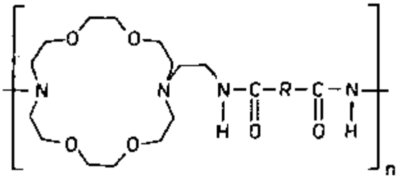
Gramain and Frere [652] have studied a number of polymeric crown ethers obtained by polycondensation of diazacrown ethers. The polymers are readily prepared by reacting the cyclic diamines (1,4,10-trioxo-7,13-diazacyclopentadecane (diamine [21] H) or 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (diamine [22] H) or a cryptand with epichlorohydrin, dioxyoctane or diglycidic ether of 2,2-bis(4-hydroxyphenyl)propane; the structure of the repeating unit of one of these is shown in (**CCIV**). The cation complexation properties of these polymeric ligands have been studied by potentiometric titrations, liquid–liquid extraction, NMR and UV spectra and compared with the properties of corresponding monomeric analogues. The stability constants for polymeric complexes are comparable to those of the monomeric analogues independent of the ratio of complexation, indicating that the polymeric structures have no influence on the structures of the complexes. With various cations studied (alkali, alkaline earth, and Cu^{2+}, Cd^{2+} and Pb^{2+}), the 1:1 metal to ligand stoichiometry was observed in chloroform. The selectivity was governed by the respective size of the cation and of the internal cavity of the macrocycle in the case of alkali and alkaline earth metal ions. With copper(II), cadmium(II) and lead(II), higher stabilities were obtained with larger macrocycles [653]. These studies have been extended to the synthesis of polyesters (**CCV**) and polyamides (**CCVI**) containing diazacrown ethers in the backbone [654]. Polymeric macrocyclic ion exchangers have been prepared by polycondensation of *N,N'*-diethylene alcohol and *N,N'*-diethylene amine of cyclic diamines with various acid dichlorides. The cation binding properties of these polymers have been



(CCIV)

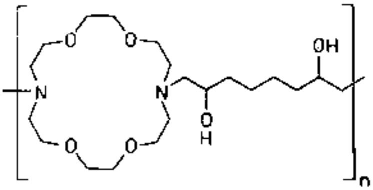


(CCV)

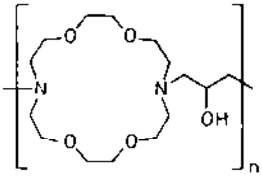


(CCVI)

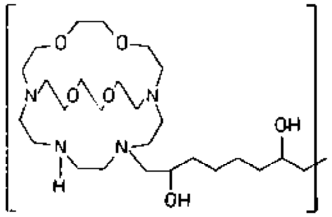
studied by water–chloroform extraction using picrate salts and compared with the properties of the corresponding monomeric ligands. The binding properties are strongly dependent on the polymeric structure and the observed decrease in the stability of the metal complexes has been attributed to the presence of an ester or amide group in close proximity to the ring. Some water-soluble polymeric crown ethers containing a [*22*] diazacrown ether in the backbone have also been synthesised by the polycondensation of the cyclic diamine [*22*] with diepoxyoctane (**CCVII**) or epichlorohydrin (**CCVIII**) [653]. The cation-binding properties of these polymeric ion exchangers have been studied with the aid of ^{13}C NMR spectroscopy and potentiometry. In general, formation of 1 : 1 (metal : ligand) complexes with all the cations (Ca, Ba, Sr, Cu, Zn) in water has been observed except for the barium complex of the diepoxyoctane polymer (**CCVII**) which possesses a 2 : 1 sandwich polymeric structure. The formation of this unique type of complex was attributed to the particular geometry of the ligand [653]. The synthesis and ion-binding properties of a water soluble polycryptate, poly(4,7,13,16-tetraoxa-1,10,21,24-tetraazabicyclo[8.8.8.]hexacos-21,24-ylene-2,7-dihydroxyoctamethylene) (**CCIX**) obtained by the condensation of tetraoxatetrazamacrobicycle with 1,2,7,8-diepoxyoctane have also been described [663]. Such a polymeric macrobicyclic ligand was chosen in view of the observation



(CCVII)



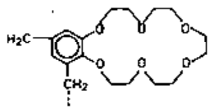
(CCVIII)



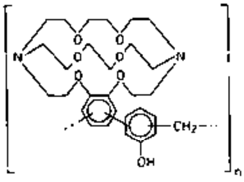
(CCIX)

of Lehn and Montavon [664] that macrobicyclic polyether ligands containing nitrogen and oxygen atoms bind selectively to transition and heavy, toxic metal ions. Thus, by combining the effects of cavity size and nature of the binding sites, ion exchangers with high selectivities can be obtained. In the polymeric crown ether (**CCIX**) these factors were combined with steric effects; this ion exchanger is highly selective for copper(II) and cadmium(II) [663].

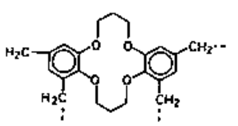
Blasius et al. [665–669] have prepared a large number of polymeric macrocylic crown ethers by polycondensation of a crown ether, a cryptand or a glyme with formaldehyde in formic acid. Additional cross-linking agents such as toluene, xylene, phenol, and resorcinol have been used in many cases; silica has also been used as a polymeric support [669]. All types of crown ethers containing oxygen, oxygen and nitrogen, or sulfur and cryptands have been used in these studies. Some typical examples of such macrocyclic crown ethers are depicted in the structures **CCX**, **CCXI**, **CCXII**, and **CCXIII**. Since synthesis, properties and applications of all these polymeric macroheterocycles have been reviewed comprehensively by Blasius et al. [48,140], this type of ion exchanger is not discussed here. Richard et al. [670] have recently studied the interaction between univalent cations (Li, Na, K and Ag) and bivalent cations (Ba, and Ca) with kryptofix (2,2)-substituted polyacrylamide using ^{13}C NMR. The grafting of linear polyacrylamide was achieved by a Mannich reaction with kryptofix and the structure of the polymer is shown in **CCXIV**.



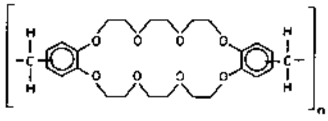
(CCX)



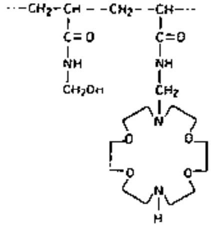
(CCXI)



(CCXII)

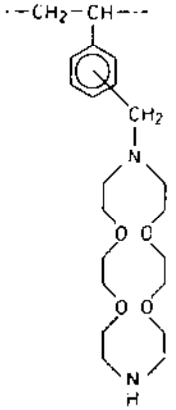


(CCXIII)

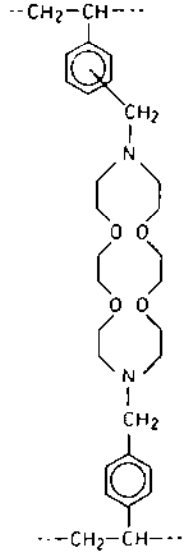


(CCXIV)

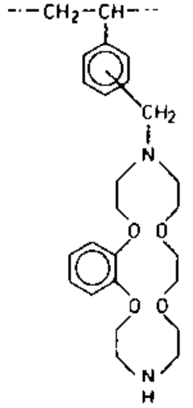
A number of presynthesised crown ethers, cryptands or glymes have been grafted into polystyrene–divinylbenzene copolymers [671–673]. Some of the ion exchangers of this type are shown in **CCXV**, **CCXVI**, and **CCXVII**. The bulk of the work on this type of macroheterocyclic ion exchangers was carried out by Blasius et al. who recently reviewed their own work [48,140]. In addition to various conventional methods, these ion exchangers with cyclic polyethers as anchor groups have also been characterised by pyrolysis gas chromatography and pyrolysis mass spectrometry [140]. This technique, earlier used for the characterisation of several styrene–divinylbenzene copolymers having various functional groups, can be used, in conjunction with IR spectroscopy for simple and definitive characterisation of cross-linked functionalised polymers [222]. Pyrolysis gas chromatograms and pyrolysis mass spectra (in conjunction with IR spectroscopy) with different cyclic polyethers as anchor groups show characteristic fragments and these patterns can be used as structural details for the identification of ion exchangers of unknown structures [225–227].



(CCXV)

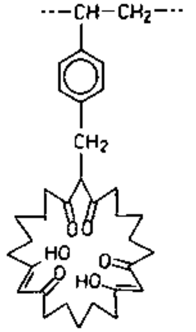


(CCXVI)



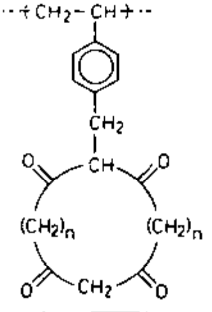
(CCXVII)

A macrocyclic hexaketone which is a very strong host for the uranyl cation (UO_2^{2+}) has been anchored onto chloromethylated polystyrene in dimethylformamide using potassium carbonate as condensing agent [674]. The IR spectrum of the resulting polymer (**CCXVIII**) contained no band characteristic of the CH_2Cl group; instead, new bands appeared at 1720 and 1600 cm^{-1} corresponding to the *keto* and *enol* forms, respectively, of the hexaketone. This polymer-bound macrocyclic hexaketone has been used for extracting uranium directly from sea water in chloroform. The extracted

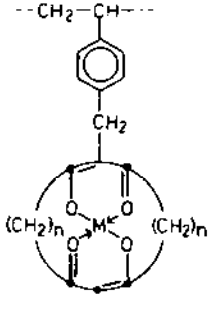


(LCXVIII)

uranium could be separated from the polymer-bound hexaketone by treating it with 1 M HCl. It was possible to extract 36% of uranium present in the original sea water. Recently, Ito and Saegusa [675] anchored 22- and 26-membered macrocyclic bis-1,3-diketones on chloromethylated polystyrene in dimethylformamide in the presence of sodium hydride to obtain new chelating polymers of the structure shown in (**CCXIX**). The 22- and 26-membered macrocyclic bis-1,3-diketones were synthesised by a method which involved $FeCl_3$-induced ring expansion of the corresponding tetrakis(trimethylsilyloxy)tricycloalkanes [676]. The IR spectra of the polymer of the type (**CCXIX**) exhibited a strong absorption band at 1710 cm^{-1}, but did not show any band at ca. 1600 cm^{-1} characteristic of enolizable 1,3-diketone, indicating that the polymeric bis-1,3-diketone is present in the *keto* form. This was supported by the UV spectrum of the polymer, which showed no absorption band at 275 mm due to the *enol* tautomer [675]. The chelating behavior of these cyclic polymers towards several transition metal ions such as copper, nickel and cobalt has been studied. These ligands chelate these metal ions in a fashion shown in (**CCXX**) with two ketonic groups under-



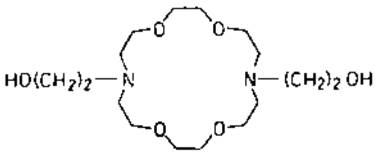
(CCXIX)



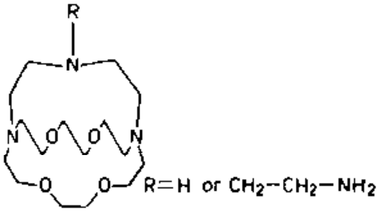
(CCXX)

going enolization and subsequent deprotonation. Copper(II) could be eluted from these polymers with 10% hydrochloric acid.

Frere and Gramain [677] have recently described the preparation of three macrocyclic ion exchangers grafted on chloromethylated styrene–divinylbenzene copolymers. These three macrocycles included one diazacrown ether (**CCXXI**), one cryptand (**XXCCII**) and a polymeric cryptand (**CCIX**). These

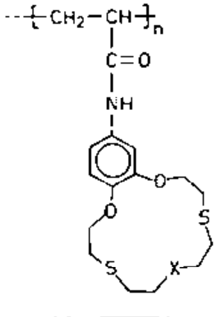


(CCXXI)



(CCXXII)

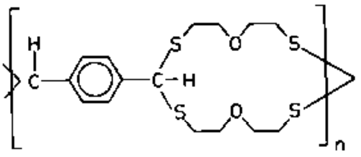
cation exchangers were used to separate alkali and alkaline earth metal ions by liquid column chromatography in water. The separations occurred according to the binding properties of the ligands in solution with an increase of the binding constants in the resin phase. The resolutions obtained were limited by the relatively low capacities of the resins (0.4–0.9 mmol g^{-1}) and mainly by slow diffusion of the cations inside the resins. Recently, some new poly- and bis(thiacrown ether)s as depicted by **CCXXIII** have been



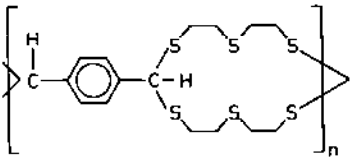
(CCXXIII)

developed for the extraction of silver picrate [678]. Nishimura et al. [679] developed a new method for the synthesis of polyamine macromers by lithium alkylamide-catalysed addition reactions of *N*,*N*′-diethylenediamine and 1,4,10,13-tetraoxa-7,16-diazacyclodecane to 1,4-divinylbenzene, respectively, to prepare some new polymeric ion exchangers having crown ethers as anchor groups. Some crown ether-modified polyethylenimines were synthesised for selective extraction of alkali metals from aqueous to organic phase [680]. Gramain has recently reviewed these new types of ion exchangers and their potential applications as catalysts [681]. Two cryptands, Kryptofix 221B and Kryptofix 222B bound to Merrifield resin (chloromethylated styrene–DVB copolymer with 2% DVB) are now commercially available (cf. Table 1).

Recently, Nakajima et al. [682] have investigated the chromatographic behavior of several alkali and alkaline earth metal halides on crown ether modified silicas with water or water/methanol as the mobile phase. Alkali metal halides, LiX, NaX, KX, RbX, and CsX (X = Cl, Br, or I) could be successfully separated on poly(benzo-15-crown-5)- or bis(benzo-15-crown-5)-modified silica by elution with water or water/methanol mixtures. The separation of alkali metal halides having a common cation is also possible on the modified silicas. The chromatographic behavior of the modified silicas was found to reflect the excellent cation selectivity of poly- and bis(benzo-15-crown-5)s [682]. The selectivity of the cation binding of insolubilised non-cyclic poly(oxyethylene) derivatives has been described by Fujita et al. [683]. These non-cyclic poly(oxyethylene) beads have been synthesised from chloromethylated cross-linked poly(styrene) and poly(oxyethylene) derivatives having various oxyethylene units. Their distribution coefficients and separation factors for alkali and alkaline earth metal salts were determined in acetone, 10% water–acetone, and methanol. The polymer-supported poly(oxyethylene) derivative with more than 5 oxyethylene units is highly selective for potassium in the latter two solvents. It has been found that the metal–salt selectivity depends not only on metal cations but also on their counter anion [683]. Several chelating polymers having sulfur in place of oxygen or sulfur and oxygen both as ether linkages have been reported by Nyssen et al. [684]. Two of the typical polymers synthesised for the removal of toxic metal ions are represented by **CCXXIV** and **CCXXV**. All of these



(CCXXIV)



(CCXXV)

compounds containing mercaptal linkages show high selectivity for mercury(II). However, their selectivity for binding mercury(II) in preference to other metal ions varies considerably as the structures are varied. The polymers which have been prepared from terephthaldicarboxaldehyde and polythiols tend to be fairly selective for mercury(II), while one prepared from glutaraldehyde and pentaerythrito tetrathioglycolate is less selective and tends to bind lead, cadmium and copper, as well as mercury [684].

F. CONCLUDING REMARKS

It is evident from the preceding discussion that the chemistry of chelating resins and ion exchangers is well established and the art of design, synthesis, characterisation and applications of such compounds has reached a developed state. The usefulness of chelating ion exchangers can be imagined from the fact that about 32 of them incorporating different chelating groups such as polyamines, polyalkylenimines, pyridine derivatives, iminodiacetic acids, amidoximes, oxines, aminophosphonic acids, phosphonic acids, carboxylic acids, thiols, dithiocarbamic acids, isothiouronium, phenol–piperazine and cryptands, are now commercially available. They are used for applications as diverse as separation of a mixture of metal ions [685], removal and preconcentration of metal ions, hydrometallurgy of copper and nuclear chemistry. Some highly selective chelating-ion exchangers are available for copper, mercury, iron, uranium and chromium, but the concept of "tailor-made" selective ion exchangers is still far away. Most of the chelating ion exchangers developed so far lack the desired degree of selectivity and to some extent the mechanical strength, and chemical stability to a general solvent system.

It appears that the successful design of highly selective chelating ion exchangers can be realised if careful consideration is given to steric constraints and the nature of the donor atoms of the ligand, besides following the other criteria mentioned in the preceding text. Thus, there is a further need to develop highly selective chelating-ion exchangers with high capacity, favorable kinetics, and reasonable mechanical strength and chemical stability. The task does not appear too difficult in view of the advanced techniques available for the synthesis of heterogeneous systems and spectroscopic means of their characterisation. There are a number of ligand systems containing different types of donor atoms available and they can be attached to or incorporated into different types of polymeric matrices, such as condensation and addition copolymers, to obtain new chelating ion exchangers. However, detailed evaluation of new chelating ion exchangers would need stability constant data on the metal complexes of monomeric systems, which unfortunately is lacking. More effort in this direction would be useful in view of the fact that chelating ion exchangers are capable of removing trace amounts of toxic metals from the environment and natural water systems and recovery of precious metals from different sources including sea water. To conclude, it may be said that the task of developing highly selective and efficient chelating ion exchangers remains difficult, but the results described in this review are encouraging for further research.

ACKNOWLEDGEMENTS

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