CHELATING POLYMERS

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Modern technological demands for materials having desirable chemical, mechanical and electrical characteristics have directed the attention of investigators to polymeric systems. Besides the usual addition and condensation polymers, polymers having coordination sites for metal atoms and those carrying coordinated metal atoms are being studied widely from various angles. Polymers capable of chelation are designated as chelating polymers and polymers carrying chelated metal atoms as chelate polymers. Chelating polymers are known to occur in nature and can be synthesised as linear chains or cross-linked networks. The present investigation includes (a) preparation of linear condensation polymers as chelating polymers and their reaction with some transition metal salts, and (b) preparation of cross-linked condensation polymers as chelating polymers and the study of their ion exchange behaviour towards acid, alkali and copper(II) ion.

A. Linear Condensation Polymers

A wide range of chelating polymers occurs in nature. Alginic acid, chitin, chitosan, pectic acid, humic acid, nucleic acids, proteins, etc. are some examples of them. Synthetically, linear chelating polymers can be obtained by addition or condensation reactions. The commercial resin DOWEX A-1 has polystyrene backbone structure obtained by addition reaction. Various chelating ligands can be linked to styrene unit. Linear chelating polymers can also be obtained by condensing chelating ligands by suitable reactions. In the present investigation, linear condensation polymers were prepared by condensing chelating ligands, containing phenolic group, with a bifunctional condensing agent obtained from urea and formaldehyde, and their reaction with transition metal ions (Cu, Ni, Co, Zn, Mn) in presence of sulphate, chloride and acetate ions was studied.

We find that the presence of a specific anion has a definite influence on the reaction of a salt with the polymer obtained from salicylic acid (SADU). Thus in presence of sulphate or chloride ion, substitution reaction takes place and a fraction of metal valency is satisfied by the polymer anion. On the other hand, in presence of acetate ion, substitution reaction is observed for Cu(II) and Co(II) salts, whereas addition reaction is observed for Mn(II), Ni(II) and Zn(II) salts.

In case of the polymer obtained from salicylaldehyde (SDU) substitution reaction is observed in presence of acetate, chloride and sulphate ions. Both valencies of the metal ion are satisfied by the polymer anion in presence of sulphate ion, one of the metal valencies is satisfied by the polymer anion in presence of acetate ion and complex behaviour-complete substitution of anion, partial substitution of anion or partial substitution of anion followed by secondary chemical reactions is observed in presence of chloride ion.

In case of the polymer obtained from salicylaldoxime (SODU) substitution reaction is observed in presence of acetate ion, wherein one of the metal valencies is satisfied by the polymer anion.

In case of the polymer obtained from 8-hydroxy quinoline (OQDU) both valencies of the metal ion are satisfied by the polymer anion in presence of acetate, chloride or sulphate ion.

When both valencies of the metal ion are satisfied by the polymer anion, it is considered that the metal ion forms a bridge between two different polymeric chains and that cross-linking of different chains by metal ions takes place.

To our knowledge, the linear chelating polymers based on urea-formaldehyde resin reaction are reported for the first time.

B. Cross-linked Polymeric Networks

Chelating ion exchange polymers have a wide scope of applications in analytical and preparative chemistry. They combine the ease of operation of the conventional ion exchangers and the specificity/selectivity of the ligands. Bayer, Blasius, Gregor, Kennedy, Manecke, and Hering have contributed considerably towards the preparation and understanding of the nature and behaviour of the chelating polymers. Such polymers can find use in chromatography, membrane formation, desalination, hydrometallurgy, waste-water treatment, etc. We undertook the investigations on the chelating polymers possessing amphoteric ion exchange behaviour. Our attempts to cross-link the linear condensation polymers obtained in Part A were unsuccessful as products did not give reproducible results. Hence we prepared amphoteric ion exchange resins using different phenols, amines/amides and formaldehyde and studied their ion exchange behaviour with acid, alkali and copper ion.

Chelating polymers formed from different phenols, melamine and formaldehyde do not melt, are insoluble in water and various organic solvents and exhibit amphoteric ion exchange behaviour. Their structures, based om analysis, show certain regularities in the molar ratio of phenol to melamine. It is considered that sulphonic, carboxylic and a aldehyde groups present in phenolic compounds have condensed with the amino group of melamine directly. Their moisture content varies from 10% to 23% in H- and OH- forms. Their cation and anion exchange capacities were determined. Their cation exchange capacity is attributed mainly to the phenolic group. By adopting pH titration technique the apparent dissociation constants (pK_C and pK_A) and the isoionic point (IP) for these resins are evaluated. Further, exchange isotherms are plotted and deviation from the expected nature of the curves is attributed to the polyfunctional nature of the resins, their inhomogeneity, selectivity, etc. The rate of ion exchange for these resins was also studied, and was found to vary over a wide range. The exchange capacity of these resins for copper ion was determined and exchange isotherms were obtained from copper titrations. Selectivity of these resins for copper ion is evidenced.

The chelating polymers were also prepared from (1) phenols, urea and formaldehyde, (2) phenols, thiourea and formaldehyde, (3) phenols, p-phenylene diamine and formaldehyde and (4) phenols, o-amino pyridine and formaldehyde, and studied. Similar observations were made with these chelating polymers also.

Further, amphoteric ion exchange behaviour of soil and kienetics of ion exchange are considered and various factors affecting the rate of ion exchange are discussed.