SUMMARY

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In everchanging world the 'Time' demands for materials having desirable chemical, mechanical and electrical characteristics and that finds application on large scale or exhibit potential for unprecendented technological utility. The impact of this underscored truth has vividly directed the attention of investigators to polymeric system.

Seldom does one encounter a phenomenon that finds many applications in such widely divergent fields such as agriculture, biology, medicine and chemistry. In recent years, ion exchange has shown itself to be in such a position. Thus, ion exchange is firmly established as a unit operation and is an extremely valuable supplement to other procedures such as filtration, distillation and adsorption. All over the world, numerous plants are in operation, accomplishing tasks that range from the recovery of metals from industrial wastes to the separation of rare earths and from catalysis of organic reactions to decontamination of water in cooling system of nuclear reactors. The ion exchangers are used as an aid in analytical and preparative chemistry. Even a perennial challenge of purification and demineralization of water has been fulfilled by the ion exchangers.

A great deal of effort has been directed towards the syntheses of chelating or complexing resin structures and ion selective resins, amphoteric ion exchange resins, inter polymeric resins and pellicular resins, etc for various reasons. Such polymers can find use in column chromatography, membrane formation, desalination, waster water treatment etc.

Enthused by a similar objective, we planned to synthesise (a) Phenol - Epichlorohydrin-Diethylenetriamine, (b) Phenol - Epichlorohydrin - Triethylenetetramine, (c) Phenol - Epichlorohydrin - Tetraethylenepentamine, (d) Phenol - Acetaldehyde - Thiourea and (e) Phenol - Furfural - Hexamine type chelating amphoteric ion exchange resins and to characterise them with respect to their pertinent and distinguishable properties such as moisture retention ability, true density, apparent density, void volume fraction, concentration of ionogenic groups, volume capacity, total ion exchange capacity, copper exchange capacity, rate of ion exchange, pH-titrations, apparent pKa and pK_b values, isoionic point values, thermal stability of the resins in various forms (H-, Na-, K-, OH-, and Cl-forms) at various temperature, the effect of temperature of equilibration on the capacity of the resins, oxidative degradation, swelling behaviour in various solvents and absorption specificity towards pre-transitional Ca(II) and Mg(II), transitional Co(II) and Ni(II) and post-transitional Cu(II) and Zn(II) metal cations in ammonium acetate - dimethylformamide media.

Synthesis and Physico-chemical studies of Phenol-Epichlorohydrin-Polyethylenepolyamine Type Chelating Amphoteric Ion-Exchange resins

Phenol-Epichlorohydrin-Polyethylenepolyamine (Diethylenetriamine, Triethylenetetramine and Tetraethylenepentamine) type chelating amphoteric ion exchange resins have been synthesised using a gel technique. The chelate monomers employed in this investigation include catechol, 8-hydroxyquinoline, hydroquinone, salicylic acid, sulfosalicylic acid, 3-hydroxy-2-naphthoic acid, p-hydroxybenzoic acid, β-resorcylic acid and anthranilic acid.

The moisture retention of these resins have been determined. The data on percentage moisture content suggest the high degree of cross-linking in these chelating amphoteric ion exchangers. A small difference in the values of moisture content of H- and OH-form suggests that the resins can stand recycling to a good degree.

The true density, apparent density and void volume fraction of these resins were determined. A large void volume fraction of these resins infers that the resins are fairly porous and hence the diffusion of ions and the rate of ion exchange may be facilitated.

Total capacity, concentration of ionogenic groups, volume capacity have been determined. The anion exchange capacity of the resins is quite a bit higher than the cation exchange capacity. Total anion exchange capacity of some of these resins are quite comparable with those of similar type of commercial resins. In general, the total ion exchange capacity of these resins is found to be directly related to the concentration of ionogenic groups.

pH titration study reveals that the resins exhibit good anion and cation exchange capacities over the pH range 1 to 12 and are amphoteric in nature. Apparent pK_a and pK_b values and so also isoionic point values were determined. The values of isoionic point of these resins vary between 6.3 (Proline) and 7.3 (Histidine).

Data on thermal stability suggest that all the resins (H-, Na-, OH- and Cl-forms) can be safely used upto 80°C. Oxidative degradation results suggest that the anionic form of the amphoteric resin is more susceptible to oxidation in comparison to the cationic form.

The results of the effect of the temperature of equilibration on the capacity of the resin reveal that with the increasing equilibration temperature, the anion exchange capacity of the resin increases but the cation exchange capacity decreases.

Data regarding the swelling behaviour of the amphoteric resins infer that in polar solvent, the anionic form of the amphoteric resin swells more than the cationic form.

Sorption behaviour of some bivalent metal cations [Ca (II), Mg (II), Co (II), Ni(II), Cu(II) and Zn(II)] on cationic form (NH_4^+ - form) of the amphoteric resins from ammonium acetate - dimethylformamide media was studied. In general, the sorption of the metal cations was found to be decreasing with the increasing concentration of ammonium acetate. Due to selective sorption exhibited by these resins, some of the chromatographic separations of the metal cations from their synthetic binary mixture were successfully achieved while few other possibilities of chromatographic separations of various metal cations under study, employing a particular resin (NH_4^+ - form) have been suggested.

Synthesis and Physico-chemical studies of Phenol-Acetaldehyde - Thiourea Type Chelating Amphoteric Ion Exchange Resins

Phenol-Acetaldehyde - Thiourea type chelating amphoteric ion exchangers have been synthesised adopting a gel technique. The chelating monomers employed were salicylic acid, hydroquinone, 3-hydroxy-2-naphthoic acid, anthranilic acid, pyrocatechol, 8-hydroxyquinoline, β-resorcylic acid and gallic acid.

Data on moisture content are indicative of high degree of cross-linking in these resins. The true density, apparent density and void volume fractions of these resins have been determined. Since the difference between true density of H- and OH-form of the resins is small, these resins can stand recycling to a good degree. The void volume fraction values reveal the porous nature of the ion exchangers.

The total ion exchange capacities of the resins are indicative of weakly basic anion exchangers and weakly acidic cation exchangers. Also, total ion exchange capacity, in general, is found to be directly related to the concentration of ionogenic groups.

The rate of ion exchange of these resins have been determined and the results are studied graphically. The results reveal that,

(i) complete cation exchange occurs within 24 hours as against 48 hours for complete anion exchange by the resins under investigation,

(ii) more than 50% of the total cation exchange capacity is realized in about 1 hour as against about 3 hours for more than 50% of the total anion exchange capacity and,

(iii) since the rate of ion exchange is fast, continuous stirring is essential.

pH titration studies reveal that the resins behave as anion exchangers over the pH range 1-7 while as cation exchangers over the pH range 7-11.3. This infers the amphoteric nature of these resins. The pH-titration curves are similar to those of weakly acidic and weakly basic anion exchangers. Apparent pK_a and pK_b values and isoionic point values have been determined. Isoionic point values vary between 6.3 (Proline) and 7.3 (Histidine).

Thermal stability study reveals that the anionic form of the resins are stable upto 40°C while cationic forms are stable upto 60°C. Salt forms are more stable than the free acid or free base form of the resins. The stability over is Na-form > K-form > H-form

and

Cl-form > OH-form

Data on oxidative degradation reveal that the anionic form of the resins are more susceptible to oxidation than the cationic forms.

Synthesis and characterization of Phenol- Furfural-Hexamine Type chelating Amphoteric ion exchange resin.

This ion exchanger has been synthesised using a gel technique. As a chelate monomer, salicylic acid was used.

The moisture content of the resin suggests high degree of cross-linking. The difference in the moisture content and the density of the resin in H- and OH- forms is small and hence the resin can stand a recycling to a good degree.

A void volume fraction values reveal the porous nature of the ion exchanger. Total ion exchange capacity is related directly to the concentration of ionogenic groups. A little higher observed cation exchange capacity than the expected one may be due to the contribution of weakly acidic -CooH group.

A faster achievement of more than 80% of the total anion exchange capacity within 25 minutes as against 540 minutes for cation exchange capacity of the resin may be attributed to the diffusion of ions inside the matrix. The shape of the rate of exchange curve reveals the porous nature of the matrix.

A pH-titration behaviour of the resin is a characteristic of weakly acidic and weakly basic monofunctional exchanger. The apparent pK_a and pK_b values and isoionic point value have been calculated. Isoionic point value is comparable with that of Proline.

No change in total capacity of the resin in free acid or free base form and salt forms is observed upto 100°C, but increase in capacity is found beyond temperature 100°C. Oxidation resistance test reveals that the anionic form is more susceptible to oxidation than the cationic form of the resin. A study of sorption behaviour of certain bivalent metal cation on cationic form (NH_4^+- form) from NH_4OAc - DMF media reveals that sorption of metal ions decreases with the increase in the concentration of NH_4OAc [Concentration (v/v) of DMF being constant]. From the view point of small differences in K_d values for different metal cations at different concentration of NH_4OAc, the resin appears to be unable to differentiate significantly between the divalent metal ions under investigation.

The study not only brings forth some very thrilling aspects neither to less accounted for but also highlights the supporting as well as deviating features. The light thrown by this investigation will surely be turned out to be quite fruitful.