

SUMMARY

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 unprecedented technological utility. The impact of this under scored 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 demineralisation of water has been fulfilled by ion-exchangers.

A great deal of effort has been directed towards the synthesis of chelating on 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, waste water treatment etc..

Enthused by a similar objective, we planned to synthesis the following :

- (1) Poly(vinyl alcohol) - Aromatic phenolic derivatives
- (2) Poly(vinyl chloride) - Aromatic phenolic derivatives
- (3) Poly(vinyl acetate) - Aromatic phenolic derivatives
- (4) Furfural - 1,4-phenylenediamine - Aromatic phenolic derivative
- (5) Furfural - Benzidine - Aromatic phenolic derivative

Chemical modified polymeric resins and to characterize 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, pH titrations, apparent pK_a and pK_b values, isoionic point values, the effect of a equilibration at different temperature on the capacity of the resin, thermal analysis [TGA], the dielectric properties, oxidative degradation and swelling behaviour in various solvents.

In the First Chapter of the thesis poly(vinyl alcohol) - aromatic phenolic acid type ion-exchange resins have been synthesised using a gel technique. The monomers employed in this investigation are anthranilic acid , gallic acid, p-hydroxy-benzaldehyde, pyrogallol, 8-hydroxyquinoline, salicylic acid, hydroquinone, β -resorcylic acid.

A small difference in the value of moisture retention content of H^+ and OH^- form suggest that the resins can stand

recycling to a good degree. 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 ^{li}facilitated. The anion exchange capacity of the resins is higher than cation exchange capacity, and 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 capacity over the pH range 1 to 12. Oxidation degradation results suggest that the cationic form of the ion-exchange resin is less susceptible to oxidation in comparison to the anionic form. The results of the effect of the temperature on the capacity of the resin reveals that with the increasing equilibration temperature, the anion exchange capacity of the resin increases and the cation exchange capacity decreases. Data regarding the swelling behaviour of the ion-exchange resins infer that in polar solvent resins swell more than in the non polar solvent.

In the Second Chapter of the thesis, synthesis and physico-chemical behaviour of poly(vinyl chloride) - aromatic phenolic acid derivative have been studied by using gel technique. The monomer employed were same as described in Chapter 1.

The void volume fraction reveals the porous nature of the ion exchangers. The total ion exchange capacities of the resins are directly related to the concentration of ionogenic groups. The rate of exchange results reveal that the complete exchange occurs in 20-60 min. pK_a values of the resins are comparable to that of the phenolic group, indicating weakly acidic nature of

the matrix. The pK_a values are in the range of a base of medium strength. On oxidation these resins act as cationic exchangers showing greater increase in percentage water content than when they are acting as anionic exchangers. Swelling of these resins in various solvent was found out.

In the Third Chapter of the thesis synthesis and physico-chemical behaviour of poly(vinyl acetate) - aromatic phenolic derivatives type resins have been discussed. The monomers employed in this investigation include anthranilic acid, gallic acid, p-hydroxy-benzoic acid, pyrogallol, 8-hydroxyquinoline, salicylic acid, hydroquinone and β -resorcylic acid.

The moisture retention of these resins is very low. The void volume fraction was found to be low. The total ion-exchange capacity of these resins is directly related to the concentration of ionogenic group pH titration study reveals that the resin exhibit good exchange capacities over the pH range of 1 to 12. Apparent pK_a and pK_b and isoionic point were determined. A raise in the temperature increases the capacities of anion resins. The capacities decrease as temperature is increased for cationic resins. Data regarding swelling behaviour of ion-exchange resins infer that in polar solvents resins swell more. The rate of ion-exchange reveals that complete exchange occurs in 20 to 60 minutes.

The synthesis of resins using schiff bases derived from furfural and aromatic diamines have been discussed in the Fourth Chapter. The physico-chemical properties of the resins were

carried out as described in the earlier chapters. Schiff bases synthesised from furfural -1,4-phenylenediamine and furfural-benzidine. The monomers employed in the synthesis of resins are same as described in chapter 3.

The resins are amphoteric in nature. The moisture retention of these resins have been determine. The data on percentage moisture content suggest the high degree of crosslinking in their amphoteric ion exchangers. The true density, apparent density and void volume fraction of these resins were determined. We find large void volume fraction. Hence the diffusion of ions and the rate of ion-exchanger may be facilitated. Total capacity, concentration of ionogenic groups and volume capacity have been determined. 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 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 results of the effect of the temperature of equilibrium on the capacity of the resin reveal that with increasing equilibration temperature, the anion exchange capacity of the resin increases, the cation exchange capacity decreases. Data regarding swelling behaviour of the amphoteric resins infer that in polar solvent, resins swells more. The rate of ion-exchange of these resins have been determined and the results are studied graphically, complete exchange occurs in 10 to 20 minutes for amphoteric resins.

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The fifth chapter of the thesis deals with thermogravimetric analysis of resins. The TG data are analysed by the method of Broido to estimate the value of activation energy of the degradation reactions.

The last chapter of the thesis deals with electrical properties of resins. In case of electrical properties of resins, volume resistivity of the resins, dielectric dissipation factor ($\tan \delta$) at 1000 Hz frequency of applied voltage and electric strength are studied.

The study brings forth some thrilling aspects and also highlights the supporting as well as deviating features of the chemically modified polymers. The light thrown by this investigation will surely turn out to be fruitful.