

I. INTRODUCTION

1.10 GENERAL INTRODUCTION

The topic of synthetic ion-exchange resin is a fascinating and challenging field in the polymer research. The growth, which started in 1935 with the discovery by two English chemists, Adams and Holmes (59) still continues unabated. Today, ion-exchange is firmly established as a unit operation and is extremely valuable supplement to other procedures such as filtration, distillation and adsorption (60). The ion-exchange resins are extensively used for the recovery of metals from industrial wastes, for separation of rare earth, for decontamination of water in cooling system in nuclear reactor and also as catalyst in organic reactions. In the laboratory ion-exchangers are used as an aid in analytical and preparative chemistry. The aims of scientific research with ion-exchanger membranes extend far into physiological chemistry and biophysics. Depending upon their applications ion-exchange resins are classified as (1) cation exchange resins, (2) anion exchange resins, (3) amphoteric ion-exchange resins, (4) specific ion-exchange resins, (5) chelating ion-exchange resins and (6) redox ion-exchange resins and (7) electron exchange resins.

1.20 SOME GENERAL ASPECTS OF SYNTHETIC ION-EXCHANGE RESINS VIS-A-VIS POLYMER INFRASTRUCTURE

Ion-exchange process is normally defined as the

stoichiometric interchange of cations or anions from an insoluble solid material commonly known as ion-exchangers kept in contact with an electrolyte solution.

The synthetic ion-exchange resins which are most important class of ion-exchangers implied to synthetic cross-linked polymers containing particular functional group. The polymeric backbone, the so called 'matrix' consists of irregular three-dimensional net works of hydrocarbon chains. The matrix carries ionic groups, e.g. $-\text{SO}_3^-$ (sulphonic acid), $-\text{COO}^-$, $-\text{PO}_3^{2-}$, ASO_3^{2-} in cation exchangers and $-\text{NH}_3^+$, >NH_2^+ , >N^+ , >S^+ in anion exchanger, and when the matrix consists of both class of the above ions are called amphoteric exchangers, obviously cation exchangers exchange cations, anion exchangers exchange anions and amphoteric exchanger both with the electrolyte solution in application. Ion-exchange resins thus are cross-linked polyelectrolytes.

Synthetic ion-exchange resins which are essentially insoluble in all solvents act like one single macromolecule and are elastic in nature in contrast to inorganic ion-exchangers (e.g., zeolite).

A schematic representation of an ion-exchanger is given in the Fig. 1.20.

A cation exchange resin (e.g., containing sulphonic acid group) Swells limitedly in water due to the cross-linking, the negatively charged sulphonate anions are attached firmly to the framework. Those fixed negative charges are balanced by an

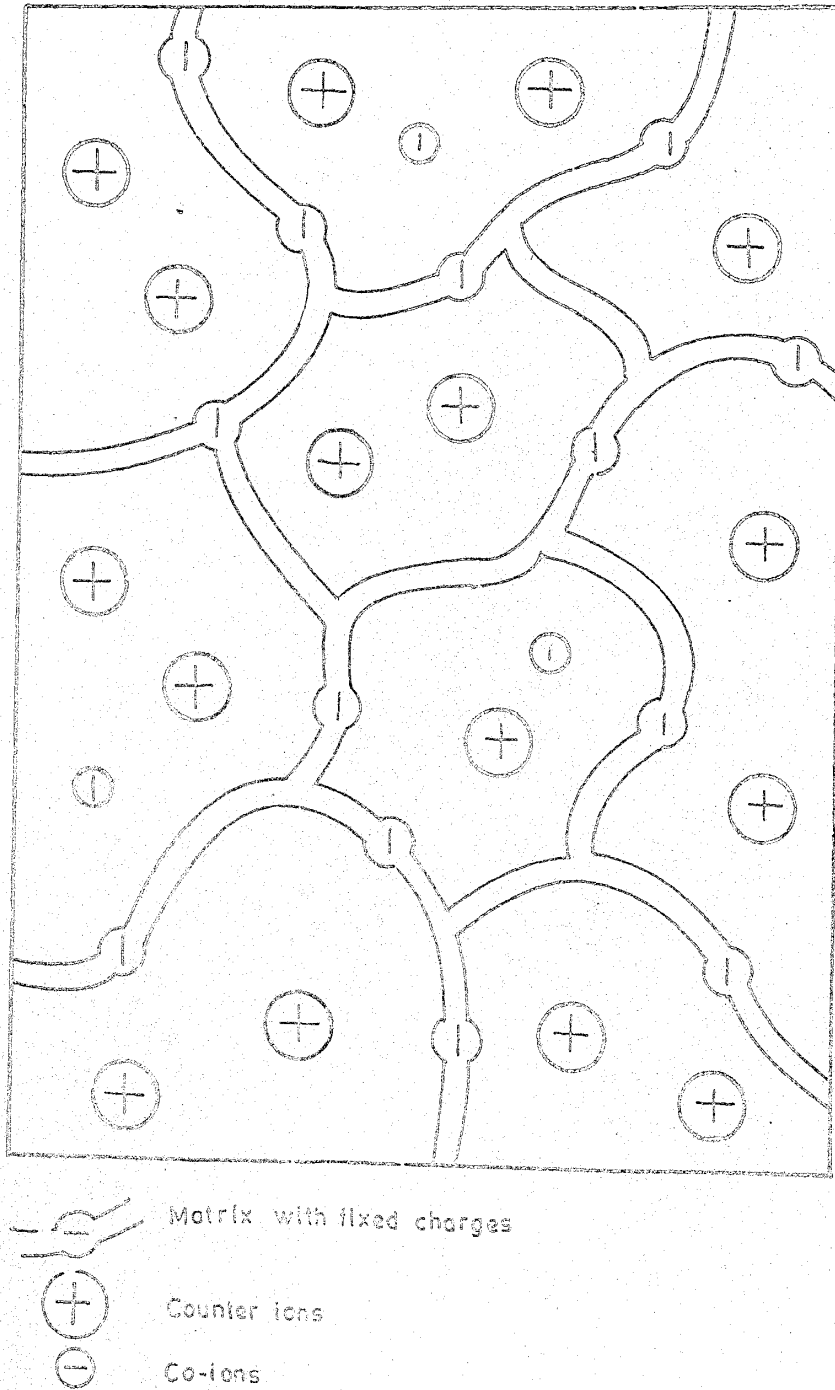


FIG. 120. SCHEMATIC REPRESENTATION OF THE STRUCTURE OF AN ION EXCHANGE RESIN (REPRODUCED FROM HELFFERICH⁶⁰)

equivalent number of hydrogen ions in the hydrogen form of the resin ; in the sodium form of the resins these ions will be sodium ions, etc. These cations move freely within the water filled pores, and are generally known as mobile ions and these ions exchange with cations containing in an electrolyte solution kept in contact with the resin until an equilibrium is attained reversibly. The same mechanism operates in case of an anion exchanger.

1.30 GENERAL SURVEY OF THE VARIOUS CATION EXCHANGE RESINS

1.31 Some aspects of chemical modification of polymers

The properties of polymers can be improved either by copolymerization of two different monomers or by subjecting the homopolymer to transformation reactions involving the addition or substitution of functional groups in backbone polymer. The copolymerization as mentioned above can give rise to a condensation product or simply an addition copolymer. It has also been observed that chemically modified polymers have improved physical and chemical properties and are better adaptable to new technical uses. These copolymerization or transformation reactions involving monomers or polymers are generally governed by their chemical reactivity which is indirectly related to their structure, and the nature of the functional groups attached to these compounds. For polymers which are chemically identical but differ in physical structure, the reactivity also appears to be different. This

is considered as the effect of polymer morphology and reactivity, which is attributed to steric hindrance. This morphological effect on reactivity is more frequent and pronounced in linear high polymers. In addition to steric hindrance and gross structure, morphology of polymers includes factors of fine structure such as fibrils and micelles, accessible and nonaccessible regions, amorphous and crystalline areas, and other supermolecular agglomeration. These factors can exist only when the polymer is in the solid state and so the effect of morphology on the reactivity of polymers is restricted to heterogenous systems. Reactivity is therefore, the ability of the polymer chain molecule to react with other molecules, while accessibility defines the ease by which the functional groups of the polymer molecule can be reached by the reactant molecule.

Conventional reactions such as addition, cyclization, substitution and reactions of the functional groups - characteristic of organic compounds are generally performed on polymers for converting them into appropriate end products. In most instances the modified polymers are characterized by many improved properties which make them useful for various applications.

A brief outline of the various reactions are summarized below

1.311 . Cyclization

Cyclization of polymers is effected in presence of

catalysts such as H_2SO_4 , $SnCl_4$, BF_3 , $TiCl_4$ and $FeCl_3$. Natural rubber in presence of acids or Friedel-Crafts Catalysts and poly(acrylonitrile) on heat treatment undergo cyclizations (99-101).

1.312 Addition Reactions

These comprise reactions including the addition of thiols (102-104) to unsaturated polymers and hydrogenation of unsaturated polymers under suitable condition of temperature and pressure in presence of suitable catalysts (105-112).

1.313 Chlorination

Chlorination of aromatic polymers such as poly(styrene), in the side chain is usually accompanied by nuclear chlorination also, but the latter can be suppressed by complexing metal ions (113-115).

1.314 Chloromethylation

Nuclear substitution involving chloromethylation are well known in bringing about chemical modification of vinyl aromatics. The substitution of a chloromethyl group in a polymer molecule provides some modification of its properties (116-117).

1.315 Amination

Amination of chloromethylated polymers and copolymers with suitable aminating agents introduces quaternary ammonium group into the polymer chain (118)

1.316 Sulphonation

Sulphonation of polyvinyl aromatics is usually accompanied by cross-linking due to the formation of sulphone groups in addition to the formation of sulphonic acid group. The common sulphonating agents used are conc. H_2SO_4 , SO_3 or chlorosulphonic acid in presence or absence of solvent. It may not be possible to introduce more than one sulphonic acid group per benzene ring without going to conditions which decompose the polymer (102,103,119).

1.317 Phosphorylation

Phosphorylation of polyvinyl aromatics has been effected by PCl_3 in presence of a Friedel-Crafts Catalyst. Phosphonic acid groups are obtained from the condensed product either by oxidation with nitric acid or by oxidation with hot aqueous caustic soda (4,5,19,120).

1.318 Nitration

Nitration is an example of a reaction in which the polymer dissolves with increasing substitution. The nitration and reduction of vinyl aromatic polymers offer several ways to the preparation of electron exchange resins (121).

1.40 A BRIEF OUTLINE OF THE VARIOUS CATION EXCHANGE RESINS

1.41 Styrene Based Resins : Most important class of the

cation exchange resin has been prepared from the polymerization of styrene in presence of divinyl benzene as a cross-linking agent, then different functional groups are introduced. Cation exchange resins with sulphonic (29), phosphonic (26), phosphinic (26-28) and arsonic (30) groups have been prepared from styrene divinyl benzene copolymer.

A typical representation of styrene - divinyl benzene is sulphonated copolymeric cation exchanger. Sometimes polystyrene is cross-linked by other cross-linking agents like formaldehyde, adipoyl chloride, chlorofumaroyl chloride, malonyl chloride, succinoyl chloride, dichloromaleoyl chloride to give various type of cation exchange resins of different properties (31-34).

1.42 Acrylic Based Copolymeric Resins The copolymerization of acrylic or methacrylic acid and a cross-linking agent such as divinylbenzene or ethylene dimethacrylate gives weak acid cation exchange resins (35-37). Polyelectrolytes useful as ion-exchange resins have been prepared by heating a mixture of acrylonitrile, acetone, formaldehyde and sodium bisulphate in a strongly alkaline aqueous solution and then saponifying the resulting polymers (38).

1.43 Vinyl Chloride Polyene sulphonic acid cation exchange resin has been prepared from polyvinyl chloride (PVC) by sulphonating with chlorosulphonic acid in 1,2 dichloro ethane solvent. The cation exchange resins contain both sulphonic acid and carboxylic acid (39-43).

1.44 Vinyl Alcohol Cation exchange resins have been prepared from polyvinyl alcohol by sulphonation and phosphorylation using concentrated sulphuric acid and phosphorus oxychloride respectively (44,45-49).

Besides above mentioned resins phenol, resorcinol, cyclohexanone shellac, lignin have been used to give cation exchanger with cross-linking agents like formaldehyde or furfural (48,49-51,52-54).

1.45 Composite Cation Exchange Resins Blending of two independent ion-exchange resins during the polymerization process would result in the development of a composite ion-exchange resin. However, the incorporation of inert materials in ion-exchange resins would also result in composite ion-exchange resins (55-58).

1.46 Synthetic Cation Exchange Resins Containing N-Vinyl Carbazole in the Polymer Backbone

Biswas and his School (1-16), pioneered in the study of the synthetic cation exchange resins containing N-vinyl carbazole in the polymer backbone. Poly NVC has a unique combination of thermal, chemical and fire retarding properties and with a view to improving these properties the chemical modification of the resins has been performed either during the polymerization of N-vinyl carbazole monomer in presence of different agents furfural (2,4,5), divinyl benzene (6) , at different conditions or by treatment of poly N-vinyl carbazole with same type of above

mentioned agents at various conditions. The higher thermal stability of N-vinyl carbazole based polymers has promoted to investigate the feasibility of synthesizing ion-exchange resins from these polymers with higher thermal stability.

Table 1.46 represents the reported NVC-based cation exchange resins along with their pertinent physico chemical characteristics and ionogenic groups.

The sulphonated cation exchange resins of the N-vinyl carbazole based polymers are moderately fast ion exchangers (1). Pielichowski and Morawiec (19) reported the synthesis of a phosphonic acid cation exchange resin from poly N-vinyl carbazole. Sulphonic acid resins obtained from the modified N-vinyl carbazole are more thermally stable than the unmodified poly N-vinyl carbazole (2,3). Phosphonic acids are more thermally stable than the corresponding sulphonic acid resins having N-vinyl carbazole moiety (4,5).

Syntheses of phosphonic acid resin from N-vinyl carbazole divinyl benzene copolymer and of a sulphonic acid resin and a phosphonic acid resin have also been accomplished from NVC/Poly NVC Formaldehyde copolymer by Biswas and Bagchi (77-79). Details of these syntheses and characterization being a part of the thesis will be described in due course.

Table 1.46 shows some of the reported NVC-based cation exchange resin along with their ionogenic groups. A brief review of the cation exchange resins synthesized and characterized from N-Vinyl carbazole based polymers is given below.

1.461 Phosphonic Acid Cation Exchange Resin
From Virgin PNVC

PNVC has been phosphorylated in presence of different phosphorylating reagents and in the presence of various Friedel Crafts catalysts, PCl_3 and AlCl_3 has given the most satisfactory results. The value of total capacity amounts 3.2 meq/g. The pH metric curve of the ion-exchange resin shows no sharp inflection whereas the differential curve shows two inflections indicating that there were two degrees of dissociation (19).

1.462 Sulphonated Cation Exchange Resin From
Poly N-vinyl Carbazole

The cation exchange resin containing N-vinyl carbazole moiety has been reported from the sulphonation of poly N-vinylcarbazole. Poly-N-vinyl carbazole was sulphonated using 98.8% concentrated sulphuric acid. The total capacity 4.5 meq/g, salt-splitting capacity 3.9 meq/g has been realized. The pH-metric titration curve shows a typical mono-functional cation exchange resin with strong $-\text{SO}_3\text{H}$ group. The suggested reaction scheme was given in the Fig. 1.462. For every carbazole unit one $-\text{SO}_3\text{H}$ group at the 3-position is introduced (1).

1.463 Furfural-Based Sulphonic Acid Cation-Exchange
Resins From N-vinyl Carbazole and its Polymer

A sulphonated synthetic cation exchange resin based on the condensation of furfural with N-vinyl carbazole or poly-N-vinylcarbazole in presence of anhydrous aluminium chloride

has been reported. Maximum total capacity and salt-splitting capacity 4.6 and 4.0 respectively have been shown. Furfural here acts as a cross-linking agent forming a polycondensate with N-vinyl carbazole or poly N-vinylcarbazole. The pH metric titration of the resin shows two inflections one has been attributed for a strong $-\text{SO}_3\text{H}$ group and the other for a weak $-\text{COOH}$ group arising from the oxidation of furfural during oxidation. The capacity values are close to the capacity values of resin as described in 1.462 (2).

1.464 Phthalic Anhydride-Based Cation Exchange Resin From N-vinyl Carbazole

In this work a phthalic anhydride based sulphonated cation exchange resin from N-vinyl carbazole has been reported. Phthalic anhydride is treated with N-vinylcarbazole in presence of anhydrous AlCl_3 in dry benzene. First the polymerization of N-vinyl carbazole to poly-N-vinylcarbazole takes place and then followed by condensation of phthalic anhydride with carbazole moiety of the polymer. In both the cited reaction anhydrous aluminium chloride acts as a catalyst. The reaction scheme is shown in the Fig. 1.464.

With concentrated sulphuric acid both cyclization reaction of the keto acid and sulphonation of the aromatic ring take place. Total capacity 4.73 meq/g and salt-splitting capacity 2 meq/g are realised. The pH metric titration curve shows only one inflection and that is for a strong $-\text{SO}_3\text{H}$ group (3).

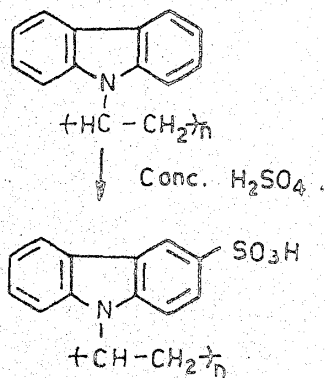
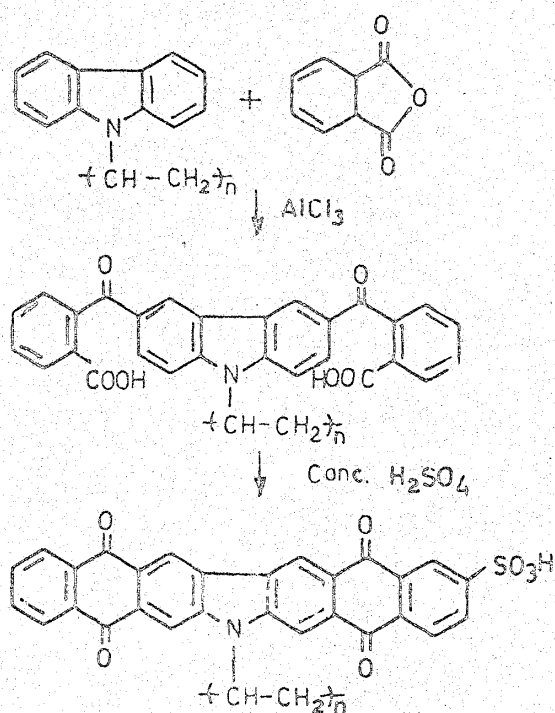


FIG. 1462 SULPHONATION OF PVC

FIG. 1464 REACTION SCHEME FOR THE FORMATION OF
SULPHONATED PHTHALIC ANHYDRIDE BASED
CATION EXCHANGE RESIN FROM PVC.

1.465 Sulphonated Poly [N-vinyl Carbazole - 3,6-Bis(4 Keto-1Naphthol)] Polyfunctional Cation Exchanger

First poly-N-vinylcarbazole is condensed with benzoyl chloride in presence of anhydrous $AlCl_3$ as catalyst and nitrobenzene as solvent to poly(3,6 dibenzoyl-N-vinylcarbazole) and this is then converted to poly(N-vinylcarbazole-3,6 dicarboxylic acid) by potassium hydroxide and heat to obtain the desired resin from the above prepared compound it is then further treated with 1-naphthol and concentrated sulphuric acid in presence of nitrobenzene as solvent. Figure 1.465 represents the reaction scheme.

The resin shows a total capacity values of 5.12 meq/g. The salt-splitting capacity is 2.03 meq/g is little lower value in compare to other similar resins. From the pH metric titration curve the polyfunctionality of the resin has been revealed and is attributed to the presence of $-SO_3H$, $-COOH$ and phenolic $-OH$ group (8).

1.466 Cation Exchange Resin From Sulphonated N-Vinyl Carbazole and Divinylbenzene Copolymer

A copolymer from N-vinylcarbazole and divinyl benzene is first prepared and then the N-vinylcarbazole-divinyl benzene copolymer is sulphonated with concentrated sulphuric acid to give the desired resin.

The total capacity and the salt-splitting capacity is

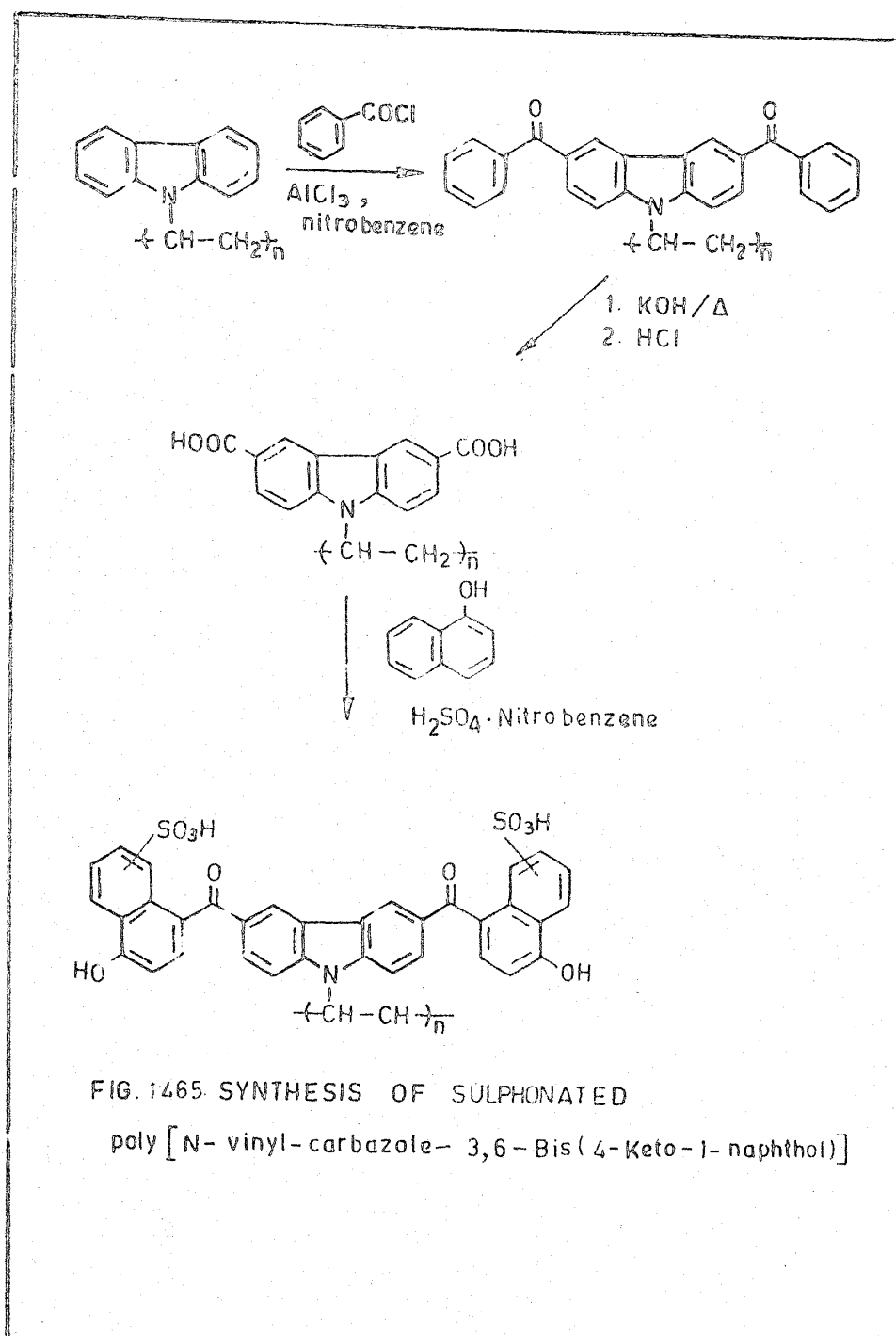


Table 1.46

Cation Exchange Resins Based on Poly(NVC) and its Copolymers

Sl. No.	Ion-exchange Resins	Ionogenic groups	Total capacity meq/g(dry)	Reference
1.	PNVCS Poly N-vinyl carbazole sulphonated	$-\text{SO}_3^- \text{H}^+$	4.5	Biswas and John (1)
2.	PNVCP Poly N-vinyl carbazole phosphorylated	$\text{PO}_3^{2-} (\text{H}^+)_2$	3.2	Piclichowski and Morawiec (19)
3.	NVC-PAS N-vinyl carbazole- phthalic anhydride sulphonated	$\text{SO}_3^- \text{H}^+$	4.7	Biswas and Packirisamy (13)
4.	NVCFS N-vinyl carbazole- Furfural sulphonated	$\text{SO}_3^- \text{H}^+$ $\text{COO}^- \text{H}^+$	4.62	Biswas and John (2)
5.	PNVCFS Poly N-vinyl carbazole- furfural sulphonated	$\text{SO}_3^- \text{H}^+$ $\text{COO}^- \text{H}^+$	4.01	Biswas and John (2)
6.	NVCFP N-vinyl carbazole- furfural phosphorylated	$\text{PO}_3^{2-} (\text{H}^+)_2$	5.18	Biswas and Packirisamy (4,5)
7.	PNVCFP Poly N-vinyl carbazole- furfural phosphorylated	$\text{PO}_3^{2-} (\text{H}^+)_2$	5.12	Biswas and Packirisamy (4,5)

Contd...

Table 1.46 (Contd.)

Sl. No.	Ion-exchange Resins	Ionogenic group	Total capacity meq/g(dry)	Reference
8.	Sulphonated[NVC-3,6-bis (4-keto-1-naphthol)]	$\text{SO}_3^- \text{H}^+$ $\text{COO}^- \text{H}^+$ Phenolic -OH	5.1	Biswas and Das (8)
9.	NVC-DVBS N-vinyl carbazole- divinyl benzene copolymer sulphonated	$\text{SO}_3^- \text{H}^+$	4.9	Biswas and Mishra (7)
10.	NVC-DVBP N-vinyl carbazole- divinyl benzene copolymer phosphorylated	$\text{PO}_3^{2-} (\text{H}^+)_2$	5.4	Biswas and Bagchi (This work)
11.	Poly N-vinyl carbazole- Formaldehyde copolymer sulphonated	$\text{SO}_3^- \text{H}^+$	5.2	Biswas and Bagchi (This work) (78)
12.	NVC/PNVC - FOP N-vinyl carbazole/Poly- N-vinyl carbazole copolymer phosphorylated	$\text{PO}_3^{2-} (\text{H}^+)_2$	3.7/4.7	Biswas and Bagchi (This work) (79)

4.9 meq/g and 4 meq/g respectively. The pH-metric curve reveals the presence of one inflection and that is for $-SO_3H$ group (7).

1.467 Furfural-Based Phosphonic Acid Cation Exchange Resin
From N-Vinyl Carbazole and its Polymer (NVCFP, PNVCFP)

First a polycondensation is made between N-vinylcarbazole-furfural or poly-N-vinylcarbazole-furfural in presence of anhydrous aluminium chloride. The polycondensate is then phosphorylated in presence of phosphorus trichloride and aluminium chloride as a catalyst. The proposed reaction mechanism is described in the Fig. 1.467.

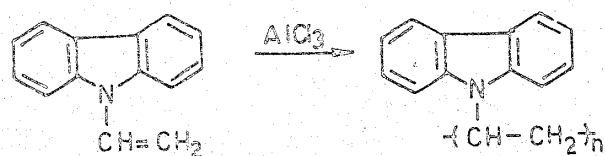
Furfural here acts as a cross-linking agent. The total capacity and the salt-splitting capacity of the resins are realized 4.64 meq/g and 0.74 meq/g respectively (4,5).

The thermal behaviour and other pertinent characteristics of the above mentioned resins as well as the cation exchange resins synthesized in course of the present work - and a comparative comprehensive accounts of those resins with other commercial resins will be duly described in subsequent pages.

1.50 OBJECT AND SCOPE OF THE PRESENT WORK

The work presented in this dissertation is primarily concerned with the syntheses and evaluation of pertinent physico-chemical properties of some novel copolycondensed polymer system based on N-vinyl carbazole/poly N-vinyl carbazole, which can be processed into cation exchange resins with different functional

Homopolymerization :



Condensation reaction and phosphorylation reaction:

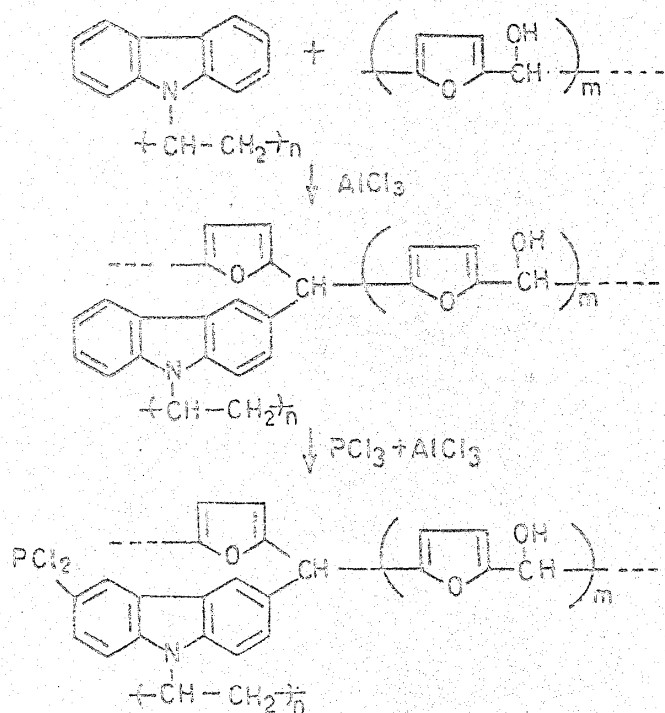


FIG. 1467. TENTATIVE REACTION MECHANISM FOR THE FORMATION OF NVCFP AND PNVCFP.

groups. In the light of the discussions made in the earlier section it appears that the cation exchange resins derived from various polymer systems based on N-vinyl carbazole/poly N-vinyl carbazole possess different thermal stability and ion-exchange capacity depending on the nature of ionogenic groups vis-a-vis polymer matrix. Mention may be made in specific of the syntheses of a large variety of ion-exchange resins from N-vinyl carbazole based polymers by Biswas et al. (1-5,7,8).

Earlier studies have disclosed that furfural based sulphonic acid cation exchange resins from N-vinyl carbazole and its polymer have significantly lower thermal stability as well as lower ion-exchange capacity than the corresponding phosphonic acid cation exchange resin from the same above mentioned polymer system. In the light of these observations it would be expected that phosphorylation of N-vinyl carbazole divinyl benzene copolymer would result in improved thermal property. Accordingly, the first phase of the work concerns the preparation and characterization of the cation exchange resin from the phosphorylation of NVC-DVB copolymer. The major objective behind the synthesis of phosphonic acid cation exchange resins from NVC-DVB copolymer matrix has been to highlight the effect of phosphorylation on the improvement or otherwise of the properties of NVC-DVB copolymer resin. Detailed studies have, therefore, been undertaken to establish the optimum conditions for the synthesis of phosphorylated materials. The characterization of the resin has been done by the standard techniques like capacity measurements total and salt splitting, pH metric

titration, stability measurement of the resin in water at different temperatures, rate of exchange. Finally a comparison has been drawn between this resin and the corresponding sulphonic acid resin as reported by Biswas et al, in regard to the various desirable properties of the resins (3,7).

The essential requirement of a cation exchange resin is that the polymer matrix should be cross-linked. Generally divinyl benzene is used as a cross-linking agent in vinyl polymerization and that may be either free radical or cationic copolymerization. Biswas and Mishra (6) have reported the use of divinyl benzene as a cross-linking agent in the cationic copolymerization of N-vinyl carbazole and divinylbenzene using anhydrous aluminium chloride as catalyst.

Divinyl benzene can only be used as a cross-linking agent in the polymerization system of a vinyl monomer (e.g. N-vinyl carbazole, styrene) but it can not be or at least has not been used as a post cross-linking agent to form a three-dimensional network from any polymer system like polystyrene or poly N-vinyl carbazole. Since divinyl benzene is a costly material and not perhaps suitable as a post-cross-linking agent for polymer system a suitable alternative is warranted which is cheaper than divinyl benzene and also simultaneously satisfy other conditions of network formation.

The second phase of work has therefore been concerned with attempts to find a replacement for divinyl benzene as a cross-

assessment of the synthesized copolymers is also made with other NVC-based polymer in respect of thermal stability (77).

The subsequent aim of the next phase of work has been to modify the synthesized formaldehyde -N-vinyl carbazole based copolymer from the earlier phase of the work to cation exchange resins. Both sulphonation and phosphorylation of the resins have been carried out. Detailed physico-chemical studies of the cation exchange resins thus produced have been undertaken (78,79). The comparison of the above formed resins with similar type of resins has revealed certain interesting characteristics and those are highlighted in the present thesis.

1.60 CHARACTERIZATION OF RESINS

The synthetic cation exchange resins are characterized through evaluation of ion-exchange capacity, functionality, rate of exchange, and chemical and thermal stability. These parameters reveal the nature of the resins and also their accessibility to various operations under different conditions (60).

1.61 Ion-exchange Capacity

Ion-exchangers are characterized in a quantitative manner by their capacity which is generally defined as the number of counter ion equivalents or ionogenic groups in a specified amount of material and is usually expressed in milliequivalents per gram of the resin (meq/g) (61). It is a characteristic constant

of the material and is independent of the experimental conditions. For practical purposes, the term capacity is further known as scientific weight capacity, technical volume capacity, apparent capacity and sorption capacity etc. The various capacities are expressed in different concentration units. The characteristic constants obtained by taking the weight of a given amount of the ion-exchanger is called the (scientific) weight capacity. The apparent capacity is defined as the number of exchangeable counter ions in the material and is important for practical applications. In resins with strong acid or strong base groups, the number of exchangeable counter ions is practically equivalent to the number of ionogenic groups (62). So the term total capacity referred in the present study represents the (scientific) weight capacity as well as the apparent capacity.

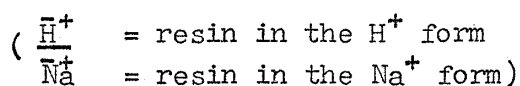
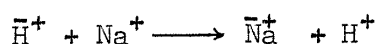
In the usual practice, the total capacity of a resin is measured with standard alkali solution. If it is measured in presence of a standard electrolyte solution, then it is called the salt-splitting capacity of the resin.

Though the capacity relates to the concentration of the fixed ionic groups, which refers to the particular state of the resin under the given experimental conditions, it inherently varies rather than remain a characteristic constant (62). The value of the capacity may change with factors such as swelling, cross-linking, degree of ionization of the ionogenic groups, that is their pK value and on the pH in the resin.

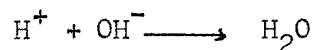
1.62 Functionality of the Resin From the pH-metric Titration

The best way of characterizing ion-exchange resins is from a knowledge of the pK values of their ionogenic groups which can be determined by the pH titration. Thus, pH titration curves reveal whether the resin is monofunctional or polyfunctional in nature. Each functional group has a characteristic pH titration curve (66) and also possesses apparent pK values (67,68) (Table 1.62).

Cation exchangers in H^+ form and anion exchangers in OH^- form can be considered as insoluble acids and bases. They usually act like their soluble counterparts and as usual can be titrated with standard bases and acids. The ion-exchanger remains insoluble in such a titration and at the same time attains equilibrium with the solution to which the titrant is added. When NaOH is added to the cation exchanger, ion-exchange takes place as follow



The H^+ ions released by the resin combine at once with OH^- ions of the added base,



The resin acid or base gets neutralized and is observed by the change in pH of the supernatant solution while the titration is

in progress. The evaluation of such a pH titration curve gives the nature of ionogenic groups and their pK values.

Ion-exchangers are usually titrated in presence of a dissolved salt like NaCl. Such a salt changes the titration curves of resins but has little effect on the titration curves of dissolved acids and bases. In such cases the ion-exchange begins even before the addition of NaOH. At this stage, the pH of the solution depends on the amount of NaCl added, on the ratio of solution volume to resin weight, the capacity and nature of the resin. The solution is progressively neutralized with the addition of NaOH and at the same time the ion-exchange is driven to completion. So the titration curve shows a gradual rise in the early stages of the titration and a steep rise at the point of complete neutralization of the resin. The presence of the salt results in a lower and slightly more sloping curve in the early stages of titration. Otherwise the curve is unchanged. The capacity of the resin can be calculated from the amount of titrant added corresponding to each pH measurement. The plot of equilibrium pH versus capacity reveals the functionality of the resin.

The titration curve of strong-acid resin (66,67) is similar to that of a dissolved strong acid, except that the initial pH of the aqueous phase is much higher since the H^+ ions of the acid groups are in the resin rather than in the aqueous phase. A monofunctional weak-acid resin has a different titration curve. The initial pH of the aqueous phase

is slightly higher because the acid groups are weakly dissociated. So the resin is reluctant to exchange its H^+ ions for Na^+ ions and hence the ion-exchange remains incomplete. With increasing concentrations of Na^+ and OH^- ions in the solution, the ion exchange is driven to more and more completion. When the resin is completely converted to Na^+ form, the pH rises sharply. Thus a sharp rise is seen in the case of weak-acid resins at higher pH of the solution.

The titration curve of a polyfunctional cation exchanger containing both strong-acid and weak-acid groups show two inflections. In the early stages of the titration the pH in the resin is low since the weak-acid groups are undissociated and hence inactive. The initial part of the titration curve resembles that of a monofunctional strong-acid resin. The pH in the aqueous phase rises steeply as soon as the strong-acid groups are completely converted in the Na^+ form. Further increase in Na^+ and OH^- , the ion-exchange takes place with the weak-acid group of the resin, so much so, a second sharp increase can be observed in the titration curve which corresponds to the weak-acid group of the resin.

The pK value of cation-exchange resin at 50% conversion may be calculated from the relation given by Helfferich (69).

$$pK = pH + \log [Na^+] - \log \frac{[\bar{X}]}{2} \quad \dots(1)$$

where, pH = pH of the external solution in contact with the resin at 50% conversion of the resin.

$[Na^+]$ = concentration of sodium ions in the external solution at 50% conversion of the resin (expressed in molarity) (70).

$[\bar{X}]$ = the total concentration of dissociated and undissociated ionogenic groups (expressed in milliequivalents per gram of the resin) (70).

For strong-acid group, the equation gives only an upper or lower limit for the pK value. However, the exact pK is of little practical significance in this case, since the groups are almost completely ionized even at very low and high pH. The pK values of the different groups in polyfunctional ion-exchange resins can also be calculated using the above equation provided that values differ sufficiently so that the titration curve shows distinct steps (70). Here, the point of half conversion of the respective groups, i.e., the half height of the respective step must be located (70).

1.63 Rate of Exchange

The rate of ion-exchange is determined by diffusion processes (71). Its mechanism is in a redistribution of counter ions by diffusion. The exchange rate depends on the nature of the ionogenic groups and also on the degree of cross-linking. The degree of cross-linking determines the mesh width of the matrix and thus the swelling ability of the resin and the mobilities of the counter-ions in the resin which affect the rate of exchange. A highly cross-linked matrix reduces the fast exchange of ionogenic groups (72).

1.64 Stability of the Resins

The chemical, thermal and mechanical stability of the resin mainly depend on the structure, the degree of cross-linking of the matrix, and on the nature and number of ionogenic groups (72). The thermal degradation of the matrix usually takes place by the oxidation and loss of fixed ionogenic groups by thermal hydrolysis (73). Most of the resins withstand temperatures upto slightly more than 100°C except strong-base anion exchange resins which begin to deteriorate above 60°C. Inorganic ion exchangers have higher thermal stability. However, the synthetic ion-exchange resins are definitely superior to other materials in their chemical and mechanical stability, ion-exchange capacity, ion-exchange rate and versatility.