

# Furfural-Based Phosphonic Acid Cation Exchange Resins from *N*-Vinylcarbazole and Its Polymer. I

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## Synopsis

Crosslinked polymers based on the condensation of furfural with *N*-vinylcarbazole and poly(*N*-vinylcarbazole) were prepared. The effect of variation of furfural concentration on the condensation of furfural with *N*-vinylcarbazole and its polymer was studied. The polymers were chemically modified into phosphonic acid cation exchange resins. The effects of variation of  $\text{AlCl}_3$ ,  $\text{PCl}_3$ , and furfural amounts, reaction time, and rephosphorylation on the synthesis and capacities of cation exchange resins were also studied.

## INTRODUCTION

Furfural (F)-based polycondensates with isobutyl vinyl ether and its polymer,<sup>1</sup> tetrahydrofuran,<sup>2</sup> resorcinol,<sup>3</sup> styrene,<sup>4</sup> and  $\alpha$ -pinene<sup>5</sup> have been reported in the literature. Biswas and John<sup>6</sup> showed that furfural condenses with *N*-vinylcarbazole (NVC) and its polymer (PNVC) and the condensates on sulfonation afford cation exchange resins. Encouraged by the attractive thermal and ion exchange properties of these resins and other modified PNVC based resins,<sup>7-9</sup> detailed studies were undertaken on the synthesis of furfural-based crosslinked polymers from NVC/PNVC and their subsequent phosphorylation to resins of improved properties.

## EXPERIMENTAL

### Materials

NVC (BASF, West Germany) was purified by following the standard procedure of Biswas et al.<sup>10,11</sup> Poly(NVC) of  $\overline{DP}$  5750 supplied by BASF, West Germany, was used without further purification. Furfural (BDH) was distilled under reduced pressure and the fraction between 54 and 55°C at 17 mm Hg was collected and stored from light and heat.  $\text{PCl}_3$  (E. Merck, West Germany) and anhydrous  $\text{AlCl}_3$  (Riedel, West Germany) were used without further purification.

### Preparation of NVC—Furfural (NVCF) and PNVC—Furfural (PNVCF) Condensates

Known weights of NVC or PNVC and furfural dissolved in benzene, were mixed with anhydrous  $\text{AlCl}_3$  (20% by weight based on NVC or PNVC) in a double-necked reaction flask with a condenser and a stirrer. The reaction mixture was heated at  $50 \pm 1^\circ\text{C}$  until a gel was formed. The gel formed was stirred vigorously and kept at  $50 \pm 1^\circ\text{C}$  for 1 h. The black mass which separated out was

collected, refluxed with benzene, and filtered from unreacted NVC or PNVC and furfural. It was further refluxed with fresh quantities of methanol until the polyfurfural formed under these conditions was removed completely. Finally, the condensate was washed with acetone, followed by hot water and cured at 100–110° for 5 h.

### **Preparation of Cation Exchange Resins (NVCFP and PNVCFP)**

A known weight of NVCF/PNVCF was swollen in dichloroethane for 10 min at  $25 \pm 1^\circ\text{C}$  in a three-necked flask fitted with a condenser and a guard tube containing calcium chloride. A known amount of  $\text{PCl}_3$  containing a definite amount of anhydrous  $\text{AlCl}_3$  was added. The contents were vigorously stirred and refluxed at  $80^\circ\text{C}$  for a predetermined time interval and then allowed to cool, poured into ice-cold water, and filtered. The product was washed free of reactants, air-dried for about 12 h, and hydrolyzed with 4% NaOH solution (20 mL/g of resin) for 2 h at  $60\text{--}70^\circ\text{C}$ . The resulting resin was filtered, washed free of alkali, treated with 2N HCl (20 mL/g of resin) for 24 h at  $25 \pm 1^\circ\text{C}$ , and then washed with deionized water to remove the sorbed HCl until the wash water was free of  $\text{Cl}^-$ . The resin was air dried for about 12 h and finally cured at  $100\text{--}110^\circ\text{C}$  for 5 h.

### **Elemental Analysis**

Nitrogen content of NVCF and PNVCF was determined by using Coleman N-Analyzer 29.

Phosphorus content of NVCFP and PNVCFP resins was estimated by the following procedure.<sup>12</sup> An accurately weighed quantity of a resin in the hydrogen form was mixed thoroughly with a mixture of  $\text{Na}_2\text{O}_2$  and  $\text{Na}_2\text{CO}_3$  (3:1) in a nickel crucible. The contents were fused to red hot for about 30 min. Thus phosphorus present in the resin was converted to sodium phosphate, which in turn was estimated gravimetrically as ammonium phosphomolybdate following a standard procedure.<sup>13</sup>

### **Evaluation of Capacity**

The total ion exchange capacity and the salt splitting capacity in equilibrium with an electrolyte like NaCl were determined after 24 h of equilibration, following a recommended procedure.<sup>14</sup>

### **IR Spectra**

IR spectra of PNVC, NVCF, PNVCF, and the phosphonic acid resins were recorded on a Perkin-Elmer 237B Spectrophotometer in nujol.

## RESULTS AND DISCUSSION

**Effect of Furfural Concentration on the Condensation of Furfural with NVC and PNVC**

Table I suggests that the gelling time increases with increase in the furfural concentration in the case of NVC, whereas it decreases in the case of PNVC. In the case of NVC no gel formation occurred, when the NVC:F ratio was increased to 1:10 (w/w), but the condensation product could be separated out by diluting the reaction mixture with benzene after 1 h. However, at an NVC:F ratio of 1:15 the condensation completely ceased.

It is observed that the furfural concentration in the final product obtained from monomer is more than that from the polymer. In the former case, the condensation of furfural may occur with the growing PNVC chain, and the NVC monomer may also undergo addition copolymerization with furfural, involving the vinyl group of NVC and the aldehyde group of furfural. Pertinently, addition copolymer of *p*-tolyl vinyl ether with furfural has been reported.<sup>15</sup> This may result in a higher amount of furfural being incorporated in the resultant polycondensate compared to the case where PNVC of  $\overline{DP}$  5750 is only present in the system. The inhibition of the reaction at 1:15 (w/w) of NVC:F may be due to the inhibition of cationic polymerization of NVC, since aldehydes are known to retard the cationic polymerization in general,<sup>15,16</sup> more particularly in the present case where the amount of  $AlCl_3$  present as a catalyst is significantly less than the furfural. Accordingly, it follows that the condensation between furfural and NVC/PNVC leading to a crosslinked matrix will occur when PNVC is present in the system. This is also borne out clearly by the data of Table I, indicating the separation of PNVC:F even at 1:15 (w/w) PNVC:F ratio.

*Gelling time:* It is seen that the gelling time increases with increase in furfural concentration in the case of NVCF, but decreases in the case of PNVC:F. However, the furfural content in NVCF and PNVC:F increases with increasing furfural concentration in the reaction mixture. This is probably due to the fact

TABLE I  
Effect of Furfural Concentration on the Condensation of Furfural with NVC and PNVC

NVC/ PNVC: F in the reaction mixture (w/w)	NVCF resin		PNVC:F resin		PNVC:F resin	
	Gelling time (min)	Nitro- gen in the final product (%)	NVC: F in the final product (w/w)	Gelling time (min)	Nitro- gen <sup>a</sup> in the final product (%)	NNVC: F in the final product (w/w)
1:2	12-13	5.79	1:0.25	8-9	6.66	1:0.09
1:5	20-22	5.38	1:0.35	5-6	6.05	1:0.20
1:10	No gel formation; the condensation product separated when reaction mixture diluted, after 1 h of reaction, with benzene	4.66	1:0.56	3-4	6.54	1:0.11
1:15	Condensation product did not separate even under above condition	—	—	3-4	5.94	1:0.22

<sup>a</sup> Nitrogen for PNVC as determined experimentally = 7.26%.

that in the case of NVCF system, the increase in furfural concentration progressively reduces the chance of simultaneous polymerization of NVC, thereby reducing the crosslinking and increasing the gelling time. The decrease in gelling time in the case of PNVCF with increase in furfural concentration is probably due to the increase in crosslinking. Finally, the gelling time for NVCF resin is more than the same for PNVCF. This is explained by the fact that the formation of the appropriate poly(NVC) chain in the former case should require some time interval.

### Factors Affecting Phosphorylation of NVCF and PNVCF

*Effect of  $AlCl_3$  concentration:* Figures 1 and 2 show the effect of variation of the amount of  $AlCl_3$  on the phosphorylation of NVCF and PNVCF, respectively. It is seen that, with increase in the catalyst concentration, the extent of phosphorylation increases both in NVCF and PNVCF. The total capacity also follows an increasing trend. Remarkably, the resins synthesized with 25% catalyst concentration do not show any salt splitting capacity. It is seen that with increase in catalyst concentration the salt splitting capacity increases in the case of NVCFP, whereas in the case of PNVCFP it increases when the catalyst con-

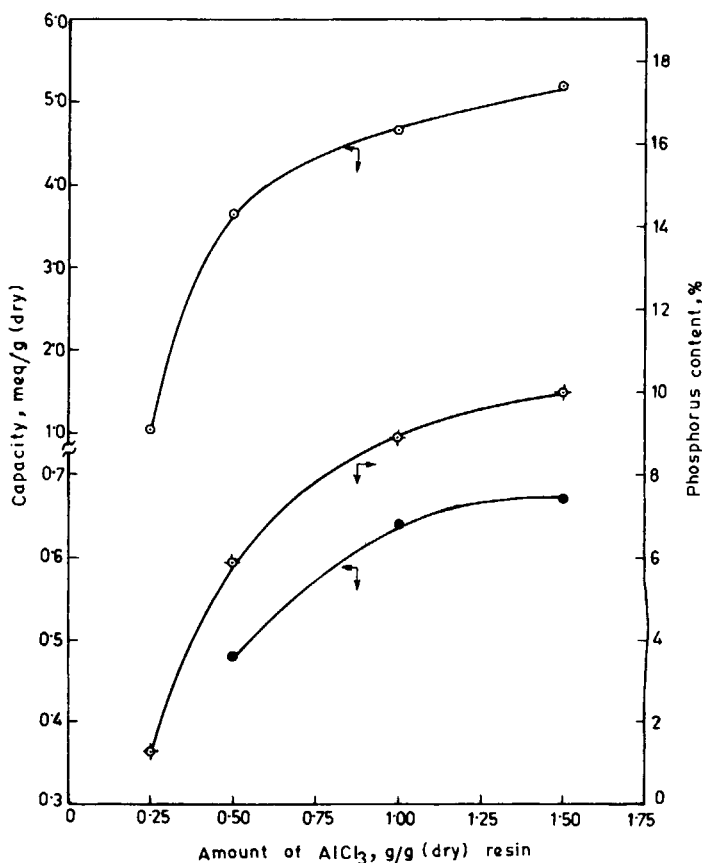


Fig. 1. Effect of  $AlCl_3$  concentration on the phosphorylation of NVCF: (○) total capacity; (●) salt splitting capacity; (◇) phosphorus content; time of phosphorylation, 5 h;  $PCl_3$ , 3 mL/g (dry) resin; dichloroethane, 10 mL/g (dry) resin; temperature, 80°C.

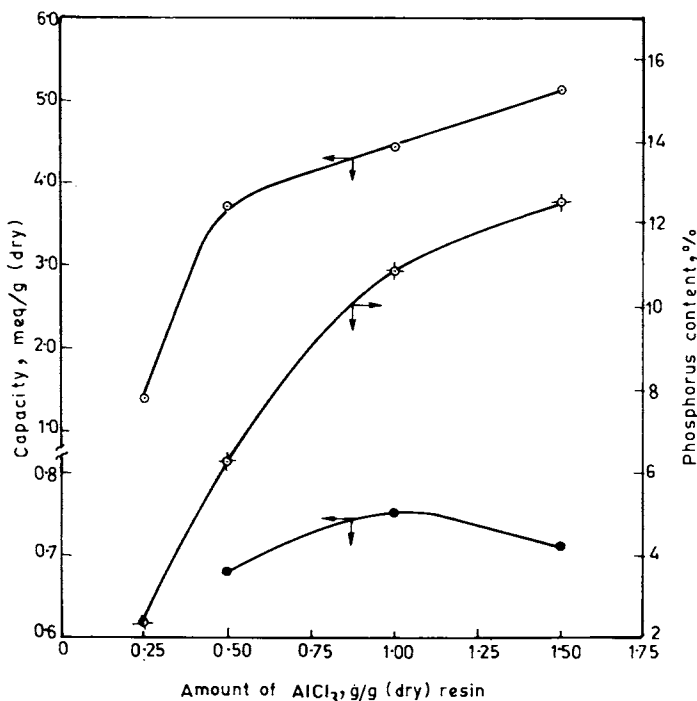


Fig. 2. Effect of  $\text{AlCl}_3$  concentration on the phosphorylation of PNVCf: (○) total capacity; (●) salt splitting capacity; (◇) phosphorus content; time of phosphorylation, 5 h;  $\text{PCl}_3$ , 3 mL/g (dry) resin; dichloroethane 10 mL/g (dry) resin; temperature, 80°C.

centration is increased from 50% to 100% and falls with further increase to 150%. It is remarkable that the extent of phosphorylation in the case of PNVCf is more than that in the case of NVCF, synthesized under identical conditions. This is due to the fact that NVCF contains more furfural than does PNVCf (Table I); hence a greater number of active sites of carbazole entities is actually occupied by furfural in the case of NVCF than in PNVCf. A decrease of active sites will imply a fall in the extent of phosphorylation.

*Effect of  $\text{PCl}_3$  concentration:* Figure 3 shows the effect of variation of the amount of  $\text{PCl}_3$  on the phosphorylation of NVCF and PNVCf and their capacities. It is seen that the phosphorus content increases from 7.60% to 8.97% in the case of NVCF and from 9.67% to 11.02% in the case of PNVCf, when the  $\text{PCl}_3$  amount is increased from 1 to 5 mL/g of resin. The total capacity increases slowly with increase in  $\text{PCl}_3$  amount. However, the salt splitting capacity increases both in the case of NVCF and PNVCf when the  $\text{PCl}_3$  amount is increased from 1 to 3 mL and thereafter remains constant with further increase of  $\text{PCl}_3$ . As with the sulfonated NVCF/PNVCf resins,<sup>6</sup> the actual values of the salt splitting capacity are much lower than the total capacity values. This is probably due to the weak acid nature of the phosphonic acid resins.

*Effect of time:* Figure 4 shows the effect of time of phosphorylation of NVCF and PNVCf. It is observed that the extent of phosphorylation of NVCF increases with time as revealed by the increase in the phosphorus content with increase in time from 1 to 3 h and thereafter tends to attain a limiting value. However, the total capacity increases from 3.85 to 4.74 meq/g (dry) when the time

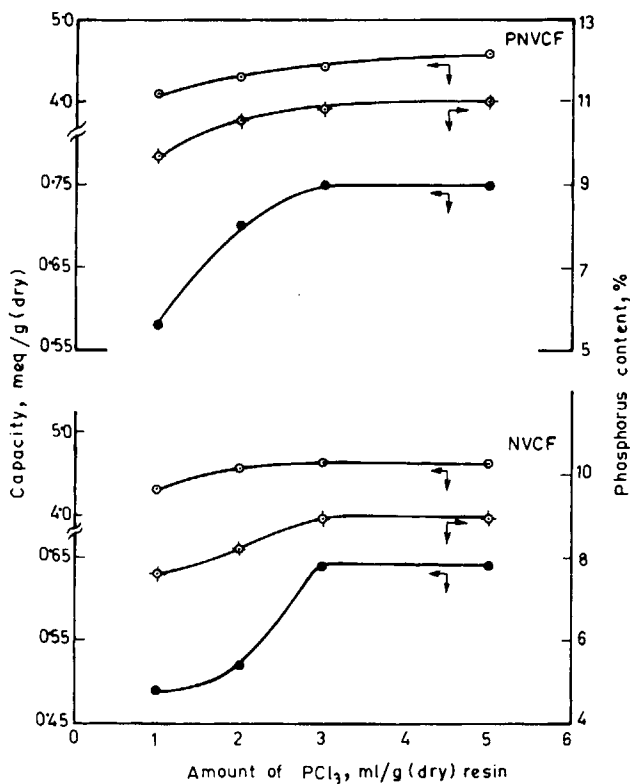


Fig. 3. Effect of  $\text{PCl}_3$  concentration on the phosphorylation of NVCF and PNVCF: (○) total capacity; (●) salt splitting capacity; (◇) phosphorus content; time of phosphorylation, 5 h;  $\text{AlCl}_3$ , 1 g/g (dry) resin; dichloroethane, 10 mL/g (dry) resin; temperature,  $80^\circ\text{C}$ .

of phosphorylation is increased from 1 to 2 h, and with further increase to 3 h it falls to 4.43 meq/g (dry) and finally attains a value of 4.64 meq/g (dry). With increase in time from 2 to 3 h some phosphorus links are likely to be formed between two molecules of carbazole, resulting in the loss of activity of the phosphonic acid groups of the resins in ion exchange process. Formation of inactive sulfone groups during the sulfonation of NVCF and PNVCF and of phosphorus links during the phosphorylation of PNVC has been reported by Biswas and John<sup>6</sup> and by Pielichowski and Morawiec.<sup>17</sup>

It is remarkable that at 1 h of phosphorylation the percentage of phosphorus in PNVCFP is much greater than that of NVCFP, although the capacities of the resins remain the same. As discussed earlier, NVCF matrix is thought to be more crosslinked than the PNVCF matrix. Accordingly, the later will provide more active sites for phosphorylation as also for crosslinking through phosphorus. In view of this, higher phosphorus content in PNVCFP resin need not imply higher total capacity values.

Unlike other NVC based sulfonic acid cation exchange resins,<sup>7,9</sup> the salt splitting capacity undergoes a significant change both in the case of NVCFP and PNVCFP with the variation of time. As the salt splitting capacity is attributed to the sorption of the solute followed by salting out,<sup>14</sup> the sorption characteristics of the resins are probably affected very much with the phosphorylation conditions.

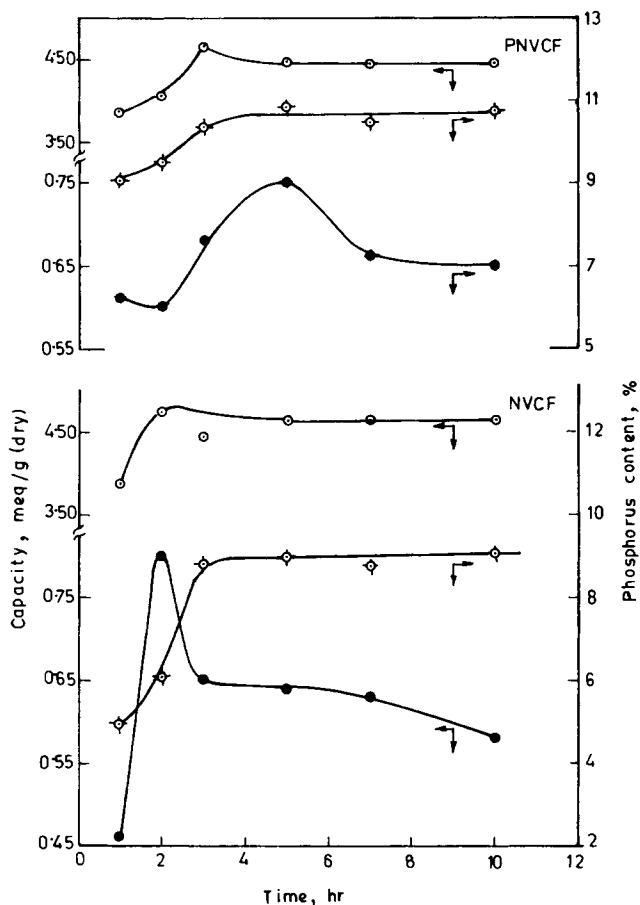


Fig. 4. Effect of time of phosphorylation of NVCF and PNVCF: (○) total capacity; (●) salt splitting capacity; (◇) phosphorus content;  $\text{AlCl}_3$ , 1 g/g (dry) resin;  $\text{PCl}_3$ , 3 mL/g (dry) resin; dichloroethane, 10 mL/g (dry) resin; temperature,  $80^\circ\text{C}$ .

*Effect of furfural:* In Figure 5, total capacity, salt splitting capacity, and phosphorus content of NVCFP and PNVCFP resins have been plotted as a function of the amount of furfural used for the condensation. As seen from Figure 5, the total capacity does not undergo any significant change with increase in furfural concentration. However, an increase of 1% phosphorus content is observed in the case of NVCFP when NVC:F is increased from 1:2 to 1:10 (w/w), whereas a decrease of 1% phosphorus in PNVCFP is observed when the PNVC:F ratio is increased from 1:2 to 1:15 (w/w). This also supports the earlier conclusion that with increase in furfural concentration the extent of crosslinking is decreasing in the case of NVCF system and increasing in the case of PNVCF system, which would result in an increase of active sites for phosphorylation in the former case and a decrease of active sites in the latter case.

There is a sudden fall in the salt splitting capacity of NVCFP when NVC:F is increased from 1:2 to 1:5 (w/w) and then remains the same with further increase to 1:10 (w/w). A similar, though somewhat less conspicuous, fall occurs with PNVCF resin when PNVC:F is increased from 1:2 to 1:5 (w/w), after which the value remains constant. The initial fall in NVCFP and PNVCFP is probably

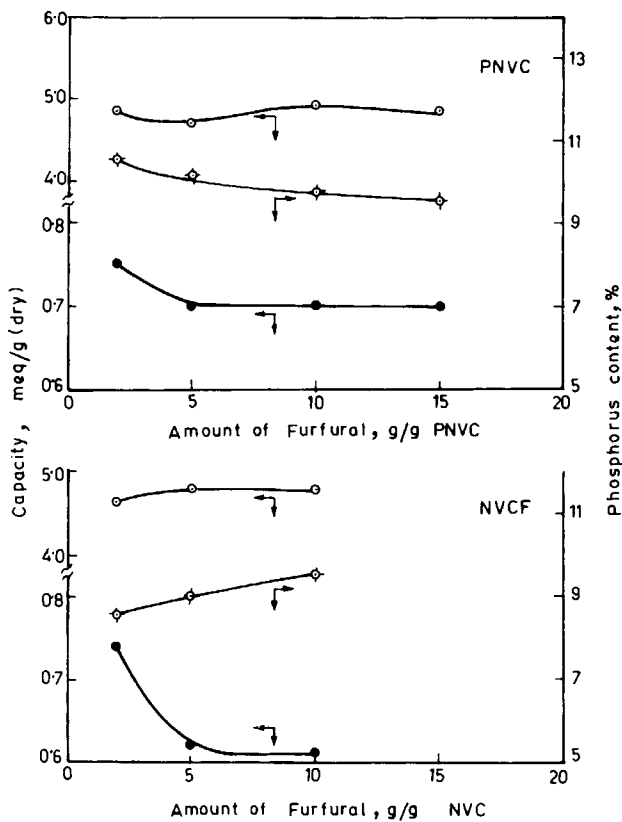


Fig. 5. Effect of furfural concentration on the phosphorylation of NVCF and PNVC: (○) total capacity; (●) salt splitting capacity; (◇) phosphorus content; time of phosphorylation, 7 h;  $\text{AlCl}_3$ , 1 g/g (dry) resin;  $\text{PCl}_3$ , 3 mL/g (dry) resin; dichloroethane, 5 mL/g (dry) resin; temperature,  $80^\circ\text{C}$ .

due to a change in the sorption characteristics of either resins with incorporation of more furfural in NVCF and PNVC condensates.

*Effect of rephosphorylation:* Rephosphorylation studies<sup>5</sup> were carried out with a view to improve the capacity and the phosphorus content of the resins. Figure 6 shows the effect of rephosphorylation of NVCFP and PNVCFP resins. NVCFP resin of total capacity 4.64 meq/g (dry) (phosphorus content 8.56%) and PNVCFP resin of total capacity 4.84 meq/g (dry) (phosphorus content 10.52%) were used for rephosphorylation studies. An overall increase in total capacity of 0.27 and 0.21 meq/g (dry) has been realized for NVCFP and PNVCFP resins, respectively, after three rephosphorylations. The third rephosphorylation causes a decrease in phosphorus content, in both cases, and the decrease is more pronounced in the case of PNVCFP. However, the total capacity tends to increase on the contrary. Significantly, after the third rephosphorylation of NVCFP/PNVCFP a brown coloration was observed in the supernatant solution, when the reaction mixture was poured into ice-cold water. This possibly indicates that the resins undergo slight decomposition after the second rephosphorylation.

The sorption characteristics of the resins are also likely to be affected under



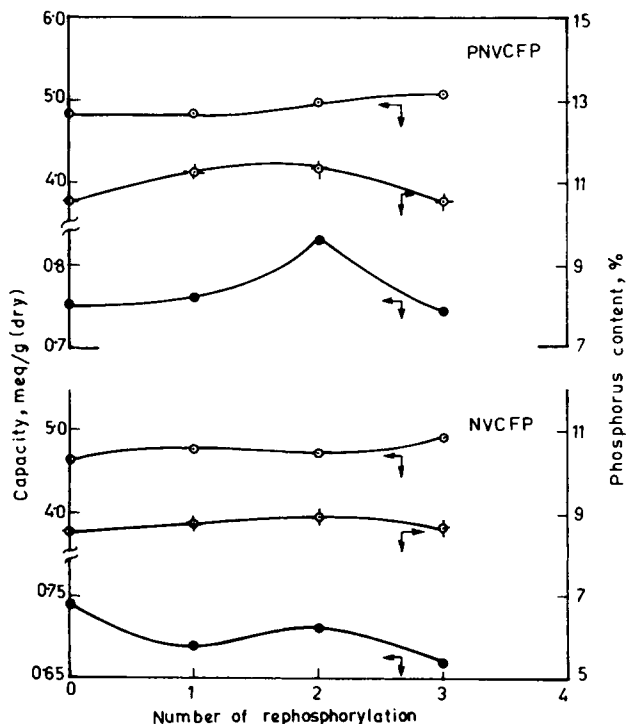


Fig. 6. Effect of rephosphorylation of NVCFP and PNVCFP: (○) total capacity; (●) salt splitting capacity; (◇) phosphorus content; time of phosphorylation, 5 h;  $\text{AlCl}_3$ , 1 g/g (dry) resin;  $\text{PCl}_3$ , 3 mL/g (dry) resin; dichloroethane, 10 mL/g (dry) resin; temperature,  $80^\circ\text{C}$ .

these conditions, which are, however, reflected in the variation of the salt splitting capacities (Fig. 6).

### IR Spectra

The IR spectra (Fig. 7) of the crosslinked polymers NVCF and PNVCF are not much informative since the absorption characteristic of the furan ring at  $740\text{ cm}^{-1}$  is masked by the absorption due to NVC moiety. No absorption indicative of aldehyde is found in the spectra of NVCF/PNVCF. Therefore, furfural apparently has taken part in the condensation reaction, through the aldehyde group.<sup>15</sup> As for the IR spectra of NVCFP/PNVCFP, the distinct band at  $909\text{--}1040\text{ cm}^{-1}$ , otherwise absent in the IR spectra of NVCF/PNVCF, is attributable to the presence of the P—OH group.<sup>17</sup> A wide band appearing in the range of  $1075\text{--}1200\text{ cm}^{-1}$  seems to be caused by the superposition of P—O bond vibrations and asymmetric vibrations of  $\text{PO}_2^-$  groups.<sup>17</sup>

### Physical Properties

NVCF and NVCFP are black, while PNVCF is brown and PNVCFP is snuff in color. The crosslinked polymers as well as the phosphonic acid resins are insoluble in organic solvents including aliphatic and aromatic hydrocarbons, alcohols, acetone, acetonitrile, nitrobenzene, and halogenated hydrocarbons and also in inorganic acids and alkalis.

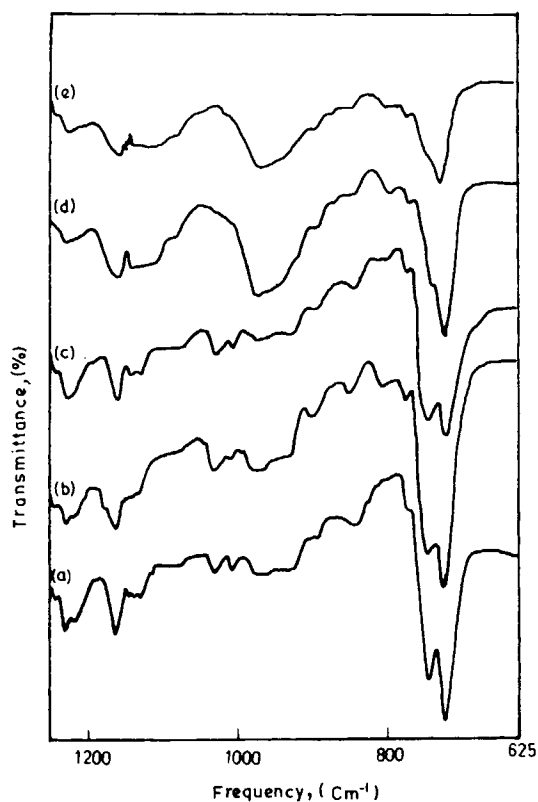


Fig. 7. IR spectra of: (a) PNVC; (b) NVCF; (c) PNVCF; (d) NVCFP; (e) PNVCFP.

### Comparison of Capacities of Phosphonic Acid Cation Exchange Resins Based on Furfural and NVC/PNVC

As revealed in Table II, NVCFP and PNVCFP resins, compare favorably with the other reported phosphonic acid resins based on furfural and PNVC in regard to capacities. Pertinently the present resins are better in respect of their capacity than phosphorylated PNVC resin.<sup>17</sup>

TABLE II  
Comparison of Capacities of Phosphonic Acid Cation Exchange Resins Based on Furfural and NVC/PNVC

Resin	Capacity [meq/g (dry)]	Reference
NVCFP <sup>a</sup>	5.18	this work
PNVCFP <sup>a</sup>	5.12	this work
PNVCF	3.20	17
PFP ( $\alpha$ -pinene-furfural)	3.01	5
SFP (styrene-furfural)	4.33	4

<sup>a</sup> Phosphorylation time: 5 h; AlCl<sub>3</sub>, 1.5 g/g (dry) resin; PCl<sub>3</sub>, 3 mL/g; dichloroethane, 10 mL/g (dry) resin; temperature, 80°C.

## CONCLUSIONS

Condensation of furfural with NVC/PNVC, followed by the subsequent chemical modification through phosphorylation, affords phosphonic acid cation exchange resins of improved capacity relative to the other furfural- or PNVC-based phosphonic acid resins.

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