

# Hydroquinone, Polyvinyl Alcohol, Formaldehyde, and Acrylonitrile (HPFA)-Based Weak Acid Electron Exchangers

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## Synopsis

A standard weak acid electron exchanger based on hydroquinone phenol formaldehyde (HPF) has been prepared by standard procedure [L. K. Edward and P. W. Richard, *Chem. Abstr.*, 49, 7780b (1955)]. Similarly, three new electron exchangers based on hydroquinone, polyvinyl alcohol, formaldehyde, and acrylonitrile (HPFA) have been synthesized and compared with the standard HPF electron exchanger.

## INTRODUCTION

Electron exchangers without any polar hydrophilic groups such as  $-\text{SO}_3\text{H}$  or  $-\text{COOH}$  are known to have poor swelling properties and consequently poor rates of exchange.<sup>1</sup> Chemical modification (e.g., sulfonation) to introduce a hydrophilic group has been tried frequently to improve the kinetic properties of the electron exchangers<sup>2</sup>; while generalizing the nature of electron exchangers based on dihydric phenol, Cassidy and Kun<sup>3</sup> have observed that during the preparative stage these materials invariably became intractable unless some polar, but otherwise inert, material is condensed with the hydroquinone. Hence it was decided to use polyvinyl alcohol as the starting material and introduce polar groups in the matrix by partial cyanoethylation of polyvinylalcohol with acrylonitrile before its condensation.

## EXPERIMENTAL

**Preparation of Electron Exchanger (HPFA<sub>1</sub>).** Poly(vinyl alcohol) 11.25 g, (0.25 mol), 50.0 ml distilled water, and 12.0-ml 10% sodium hydroxide solution were placed in a 500-ml three-necked round-bottomed flask fitted with a stirrer, a thermometer, and a condenser. The reaction mixture was heated to 70–75°C with constant stirring. To this was added 20.0-g (25.0 ml) acrylonitrile drop by drop. Then 32.4-g (1.08 mol, 90.0 ml) formaldehyde (36%) and 16.5-g (0.15 mol) hydroquinone were added with stirring. The temperature of the reaction mixture was then raised to 88°C with constant stirring for about 6 hr. When the reaction mixture became slightly viscous, the stirring and heating were discontinued, and the resulting product was removed from the reaction vessel and cured for about 24 hr in an electrically operated oven maintained at 110°C. The shiny, black mass was crushed to proper mesh size, and the sieved resin was stored for further experimental work.

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**Preparation of Electron Exchanger HPFA<sub>2</sub>.** For the preparation of HPFA<sub>2</sub>, 22.0-g (0.2 mol) hydroquinone and 41.4-g (1.38 mol, 115 ml) formaldehyde (36%) were used, all other conditions being exactly the same as in the preparation of HPFA<sub>1</sub>.

**Preparation of Electron Exchanger HPFA<sub>3</sub>.** For the preparation of HPFA<sub>3</sub>, 33-g (0.3 mol) hydroquinone and 59.4 g (1.98 mol, 165.0 ml) formaldehyde (36%) were used, all other conditions being exactly the same as in case of HPFA<sub>1</sub>.

**Conditioning.** Conditioning of the resins for the studies of ion-exchange properties, as well as redox properties, was carried out by the standard procedures.<sup>3,4</sup> The ion-exchange capacity, wet absolute density, moisture content, and pH titration curve of the synthesized electron exchangers were determined by the conventional method described by Kunin.<sup>4</sup>

**Redox Capacity.** This measurement was determined as per standard procedure (Ref. 3, p. 171), except that potassium iodide was used as a reducing agent instead of titanous sulfate, ferric chloride was used as an oxidizing agent instead of ferric sulfate, and *n*-phenylanthranilic acid was used as an indicator instead of *ortho*-phenanthroline.

**Redox Potential.** The complete apparatus for potentiometric titrations of dissolved redox couples and electron exchanger was set up as shown in Figure 1.

The oxidized form of the resin was placed in the receiver along with the mediator, and the potential difference between a platinum electrode and a calomel electrode was measured after each addition of the reducing agent (potassium iodide) from the burette to the receiver. The change in potential during the redox reactions was a convenient indicator of when the addition of titrant should be stopped.

**Rate of Exchange.** The reduced form of the resin was used, and the same

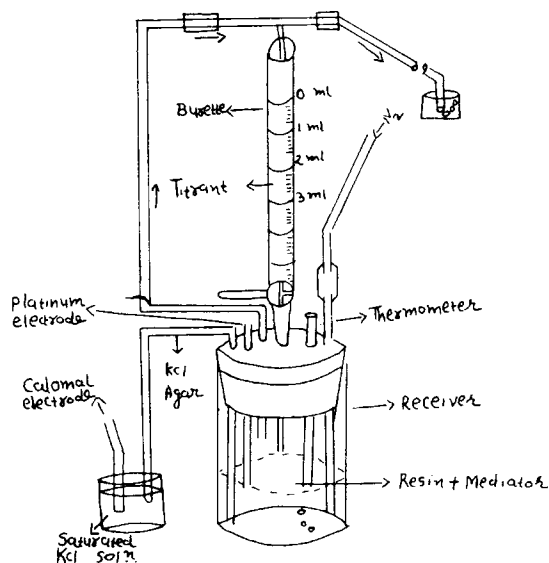


Fig. 1. Schematic drawing of the apparatus for potentiometric titration of dissolved redox couples and electron exchangers.

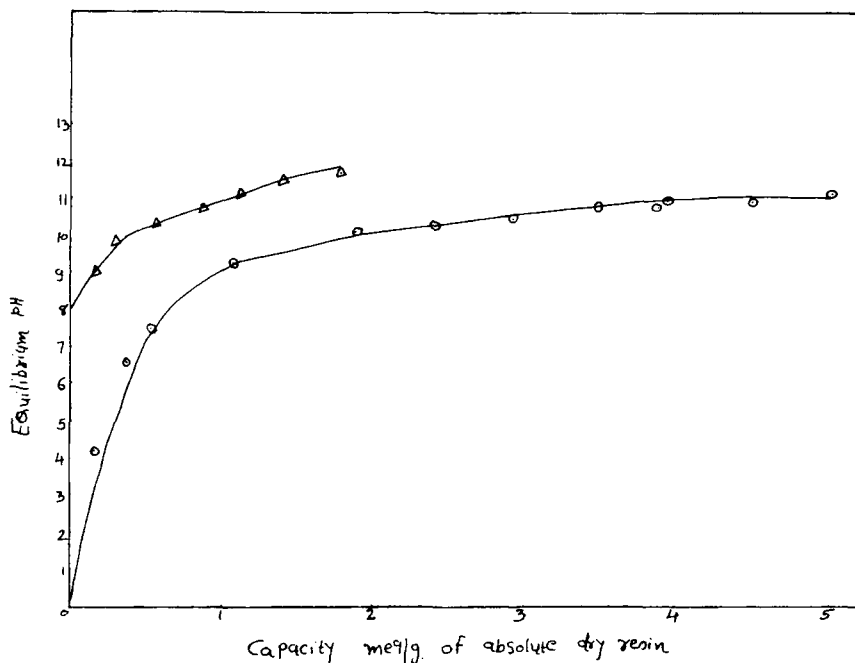


Fig. 2. pH titration curves of the HPF (○) and HPFA<sub>1</sub> (△) resins. Solutions used were 1.0N NaCl and 0.1N NaOH in 1.0N NaCl. Equilibrium was reached in 48 hr at 28°C. Quantity of resin: 0.5 g (air-dried); particle size: 20 + 40 BSS mesh.

TABLE I  
Characteristics of the Synthesized Electron Exchangers

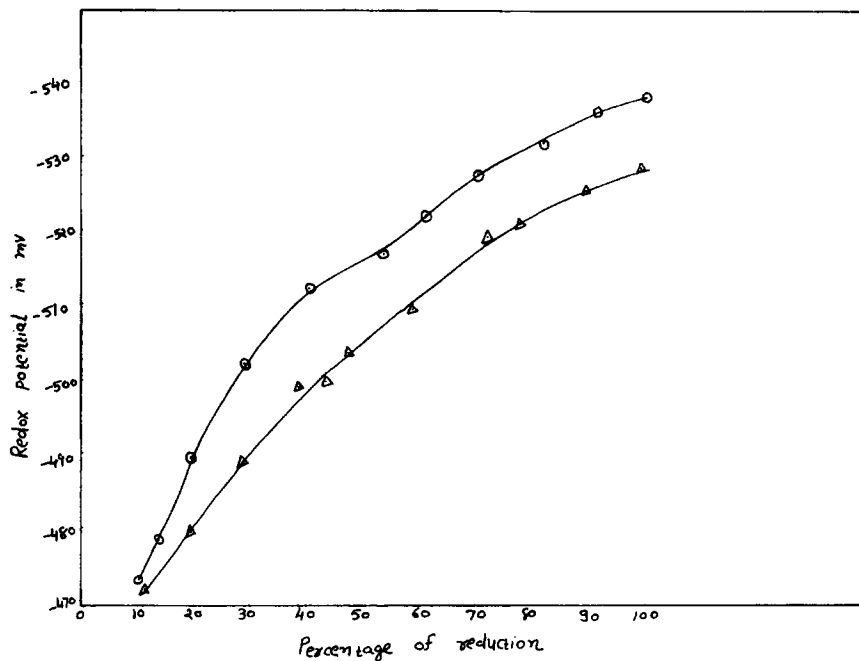
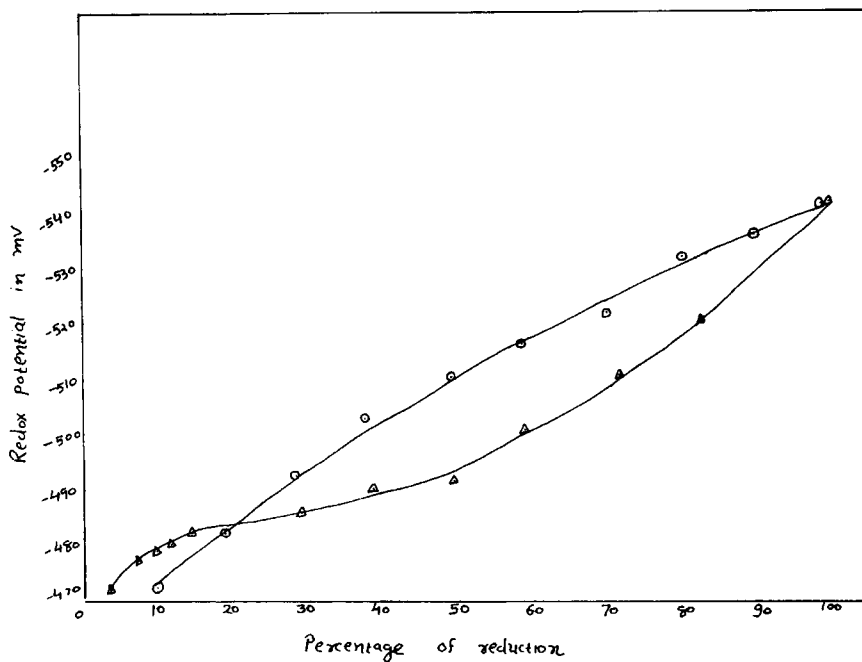
No.	Property	Electron Exchanger			
		HPF	HPFA <sub>1</sub>	HPFA <sub>2</sub>	HPFA <sub>3</sub>
1	Appearance	Shiny, black particles	Shiny, black particles	Shiny, black particles	Shiny, black particles
2	Moisture content	8.30–11.40	12.06	13.91	16.06
3	Total capacity (meq/g dry resin)	4.59	1.76	2.35	2.55
4	Wet absolute density (g/ml)	1.13	1.16	1.18	1.16
5	Dynamic redox capacity (meq/g dry resin)	0.23	0.54	0.28	0.03
6	Redox capacity (meq/ml)	0.11	0.27	0.14	0.015
7	Static redox capacity (meq/g dry resin)	0.44	0.59	—	0.19

procedure was applied as per the standard method (Ref. 4, p. 177), except for measuring redox potential during the experiment and using ferric chloride as an oxidizing agent instead of ferric sulfate.

## RESULT AND DISCUSSION

All the resins synthesized were a lustrous black, and the pH titration curves (Fig. 2) of HPF and HPFA<sub>1</sub> resins show their weakly acidic nature.

In case of the HPFA<sub>1</sub>, HPFA<sub>2</sub>, and HPFA<sub>3</sub> electron exchangers, the ion-ex-

Fig. 3. Redox potential curves of the HPF (○) and HPFA<sub>1</sub> (△) resinsFig. 4. Redox potential curves of the HPFA<sub>2</sub> (△) and HPFA<sub>3</sub> (○) resins.

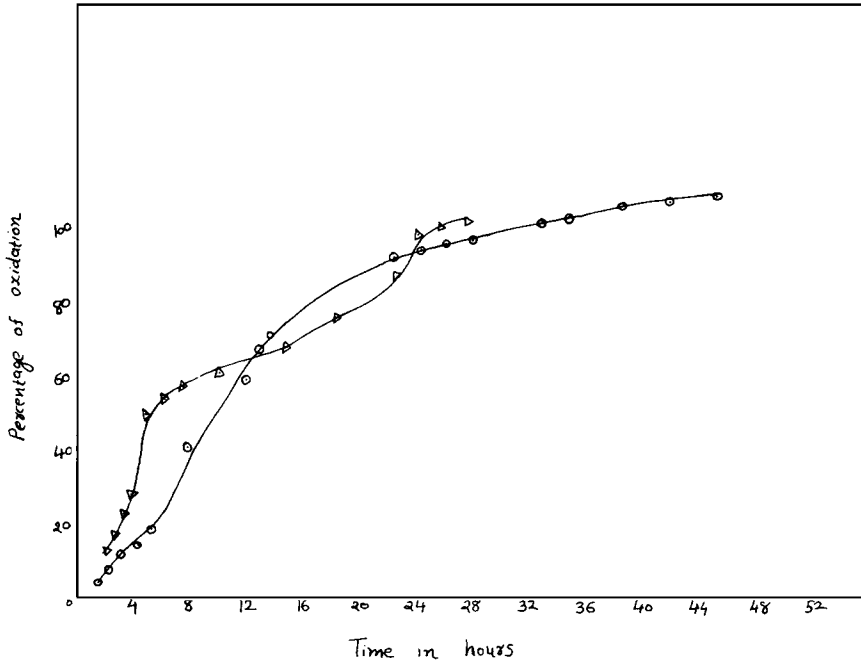


Fig. 5. Exchange rate of the HPF (O) and HPFA<sub>3</sub> (Δ) resins.

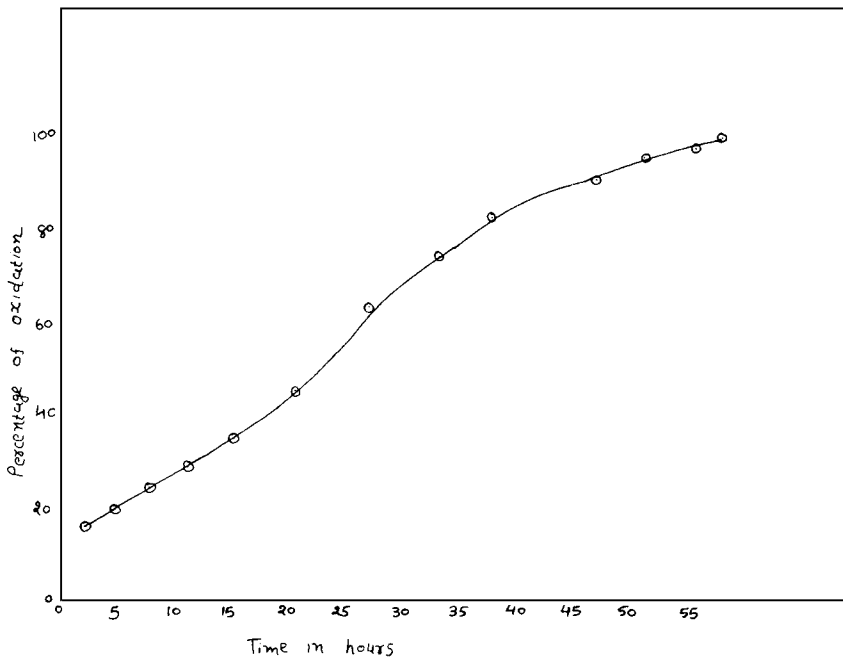


Fig. 6. Exchange rate of the HPFA<sub>1</sub> resin.

change capacity increased as the amount of hydroquinone increased, but there was a definite decrease in the redox capacity (Table I). The increase in the percentage of phenolic hydroxy groups (HPFA<sub>1</sub>-A<sub>3</sub>) resulted in the increase of the ion-exchange capacity (Table I).

The redox potential curves and the midpoint redox potential values of the HPFA<sub>1</sub>, HPFA<sub>2</sub>, and HPFA<sub>3</sub> resins are similar to those of HPF resin (Figs. 3 and 4). Due to the slow rate of reaction, the HPF, HPFA<sub>1</sub>, and HPFA<sub>3</sub> resins required 37, 54, and 26 hr, respectively, to realize their full redox capacity (Figs. 5 and 6). The HPFA<sub>3</sub> resin showed a faster rate of exchange compared to HPFA<sub>1</sub> resin because HPFA<sub>3</sub> was obviously more swollen.

### References

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