Ion Exchange Behavior of Chemically Modified Polyvinyl Alcohol

SUSHILA AMIN and R.N. KAPADIA*

Department of Chemistry, Faculty of Science, M.S. University of Baroda, Baroda 390 002

ABSTRACT

New ion exchangers were synthesized by condensing anthranilic acid, gallic acid, p-hydroxy benzaldehyde, pyrogallol, 8-hydroxy quinoline, salicylic acid, hydroquinone, β-resorcylic acid with Poly(vinyl alcohol) in DMF solvent. The ion exchangers were characterized by their total capacity, moisture retention ability, density, void volume fraction, rate of exchanger, pH titration behaviour, apparent pK_a and pK_b and isoelectric point value, oxidation resistance, the effect of equilibration at different temperatures on the capacity of the resin, swelling behaviour in various solvents, and they were further characterised by thermogravimetric analysis (TGA).

KEY WORDS: Poly(vinyl alcohol), Ion exchanger, Ion exchange capacity

INTRODUCTION

Literature[1–5] survey shows that meagre work is reported on poly(vinyl alcohol), poly(vinyl chloride) and poly(vinyl acetate) based ion exchangers and on condensing agents other than *m*-amino phenol, bisphenol A and phenol-phthalein, formaldehyde etc. Hence we planned to synthesize exchangers from poly(vinyl alcohol)-anthranilic acid [poly-Anthra], Poly(vinyl alcohol)-gallic acid [poly-Gall], poly(vinyl alcohol)-hydroxy benzaldehyde [poly-pHyBe], poly(vinyl alcohol)-pyrogallol [poly-pyro], poly(vinly alcohol)-8 hydroxy quinoline [poly-8Hy qui], poly(vinyl alcohol)-salicylic acid [poly-sali], poly(vinyl alcohol)-hydroquinone [poly-Hyqui], poly(vinyl alcohol)-β-resorcylic acid [poly- β-Res].

EXPERIMENTAL

Synthesis of Resins

Anthranilic acid, gallic acid, p-hydroxy benzaldehyde, pyrogallol, 8-hydroxy quinoline, salicylic acid, hydroquinone or β-resorcyclic acid (1 mole) was taken in 250 mL round bottom flask and mixed with 2 moles of poly(vinyl alcohol). Solvent DMF was added in it. 4 g of p-toluene sulphonic acid was added as initiator. The mixture was vigorously stirred at 150°C for 16 h. Gel formation takes place in about 1 h. Gelling period does not vary with the amount of catalyst. A hard mass was obtained which varied in colour brown to dark brown to black for different phenolic monomers listed above. The cured hard mass was then crushed to –60 to 100 BSS mesh size as needed and washed with ethanol to remove unreacted monomers and low molecular weight products from the resins. The resins were dried in an oven at 100°C and stored in polyethylene bottles. All the resins were characterized by their elemental analyses (Table 1) and physicochemical properties following the methods described in the literature[13–20]. Also thermal studies were carried out by using methods described in literature[21–24].

The method of the estimation of the rate of ion exchange

The rate of exchange for H-form (or OH form) of the resin (0.5 g) (–60 + 100 mesh) was accurately weighed into eight to nine different stoppered bottles. 100 mL 0.1N NaOH in 1 N NaCl (or 100 mL 0.1N HCl in 1N NaCl) was added to each bottle and the resin was allowed to remain in contact for different periods of time, with intermittent shaking. At different predetermined intervals, the solutions were decanted and an aliquot was titrated against standard acid or standard alkali and from this the capacity realized at different time intervals was calculated.

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TABLE 1. Elemental Analysis of Resins

Resin	Elemental analysis, % Calculated	Found
Poly-Anthra	C = 64.04	C = 64.5
	H = 5.6179	H = 6.00
	N = 7.8651	N = 8.2
Poly-Gall	C = 54.0284	C = 54.5
	H = 4.2654	H = 4.6
Poly-pHyBe	C = 69.9386	C = 70.10
	H = 5.5214	H = 86.1
Poly-Pyro	C = 61.07	C = 61.4
	H = 5.3892	H = 5.6
Poly-8Hyqui	C = 77.5280	C = 78.1
	H = 5.6179	H = 6.1
	N = 7.8651	N = 8.1
Poly-Sali	C = 64.0449	C = 64.3
	H = 5.0279	H = 5.6
Poly-Hyqui	C = 67.5496	C = 68.0
	H = 5.9602	H = 5.3
Poly-β-Res	C = 58.4615	C = 59.0
	H = 4.6153	H = 5.1

RESULTS

The ion exchange resins are synthesized from poly(vinyl alcohol) and various phenolic derivatives (Schemes I and II). The condensate is insoluble in sodium hydroxide, hydrochloric acid and dioxane in which the individual components are miscible or soluble. Therefore, the resin appears to be a condensate product of phenolic derivative with poly(vinyl alcohol). In the series under investigation gelling time and curing period for all the resins are the same and hence we suggest that gelling time and curing period are directly related to functionality of comonomer poly(vinyl alcohol).

The ion exchangers are fairly porous with average physical stability and good chemical resistance to 3 N acids and alkali and show a change of color when converted from free acid or free base form to its corresponding salt (Na or Cl) form or vice versa. The polymers were obtained by polycondensation under mild reaction and curing conditions. The bond formation is possible through –O– or $-O-\overset{O}{\overset{\|}{C}}-$ or $-CH_2-$ bridges as evident from infrared spectra. Reversibility of ion exchangers has been established. On the basis of elemental analysis, IR spectra and physicochemical studies, we postulated the structure of resins as shown in Chart-1.

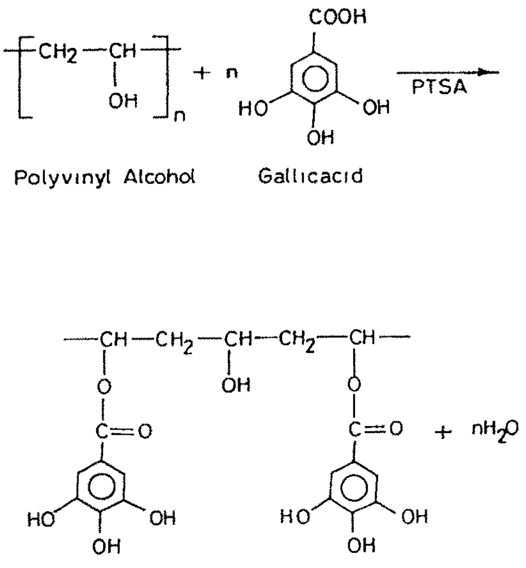
Moisture content (Table 2) of the resins is found to range from 2.27 to 7.16 for H-form and from 2.35 to 6.15 for OH-form. The resins show the following order of moisture content for cation exchangers and anion exchangers.

Cation exchangers
Poly-Gallic > Poly-Hyqui > Poly-Pyro >
Poly-β-Res > Poly-Sali > Poly-Anthra >
Poly-pHyBe > Poly-8Hyqui
Anion exchangers
Poly-8Hyqui > Poly-Anthra

The column density (Table 2) of these resins (H and OH form) is low, suggesting little swelling percentage. All the resins (H or OH forms) have large void volume fraction.

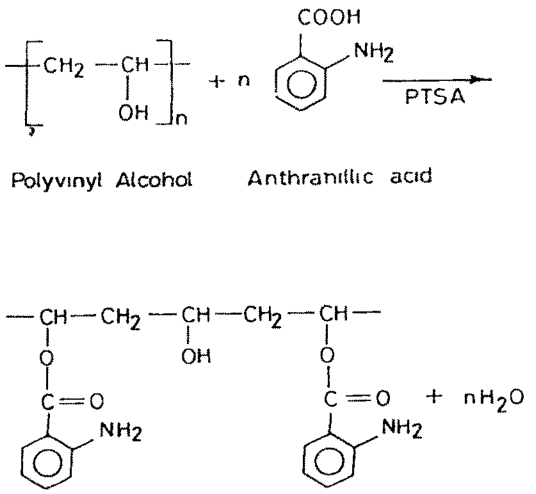
SCHEME I

REACTION MECHANISM FOR THE SYNTHESIS OF CATION EXCHANGER



SCHEME II

REACTION MECHANISM FOR THE
SYNHESIS OF ANION EXCHANGER



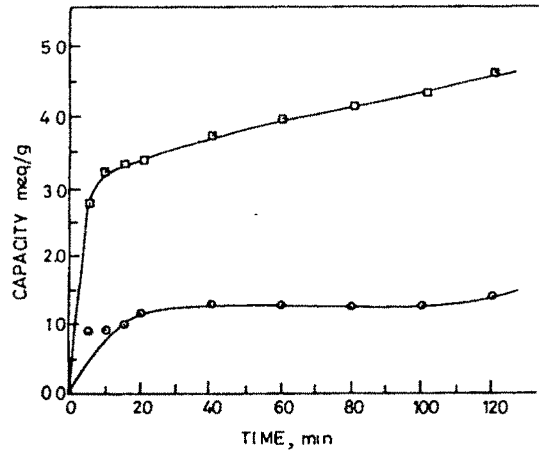


Fig. 1. Rate of cation exchange of poly-anthra (O) and poly-galli (□)

The rate of exchange for resins as cation exchanger (Figs. 1–3) as well as anion exchanger (Fig. 4) is very high (diffusion controlled). In the case of resins as cation exchanger, it is observed that (i) 50% exchange occurs in 5–10 min (ii) the rate of exchange for these resins follow the order:

Poly-8Hyqui < Poly-Anthra ≅ Poly-Sali < Poly-β Res < Poly-pHyBe < Poly- Hyqui < Poly-Pyro < Poly-Galli

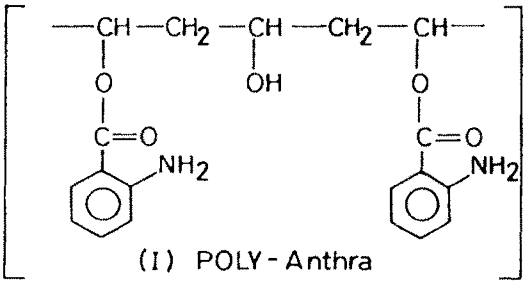
In the case of resins as anion exchanger, it is

TABLE 2. Physicochemical Characterizations of the Ion-exchange Resin

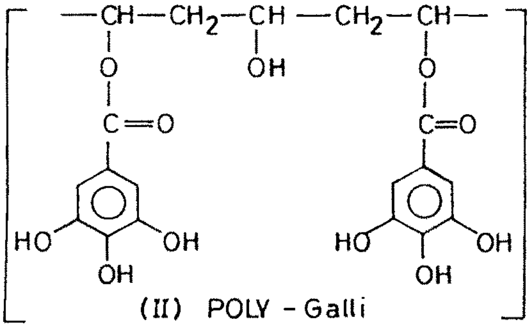
Property		Poly-Anthra	Poly-Galli	Poly-pHyBe	Poly-Pyro	Poly-8Hyqui	Poly-Sali	Poly-Hyqui	Poly-β-Res
Total capacity meq/g	CEC*	2.1651	5.6322	1.9683	4.2547	1.3278	2.2572	4.5831	2.7479
	AEC*	1.2236				1.2638			
Moisture %	H-form	5.0448	7.1605	5.2913	5.3989	2.2700	4.8291	5.9554	5.0137
	OH-form	6.1577				2.3597			
True density d_{res} g/cm3	H-form	0.4060	0.5560	0.3947	0.4440	0.4696	0.4207	0.5325	0 5096
	OH-form	0.4501				0.5027			
Apparent density d_{cal}g/ml	H-form	0.2606	0.3359	0.2941	0.3166	0.2168	0.2631	0.3125	0.2638
	OH-form	0.2528				0.3558			
Void volume fraction	H-form	0.3582	0.3959	0.2599	0.287	0.5384	0.3738	0.4132	0.4824
	OH-form	0.4960				0.7077			
pK_a		10.4148	9.8912	10.4269	11.0725	10.5699	11.4626	10.4241	10.9384
pK_b		3.3287				2.8275			
Isoionic point		6.8717				6.6986			

*CEC = Cation exchange capacity
*AEC = Anion exchange capacity

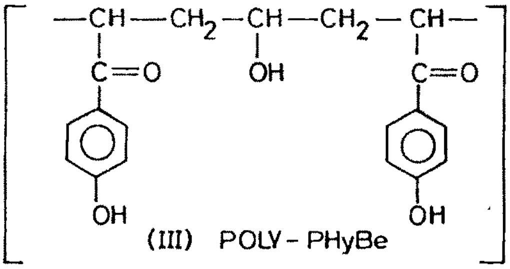
CHART 1



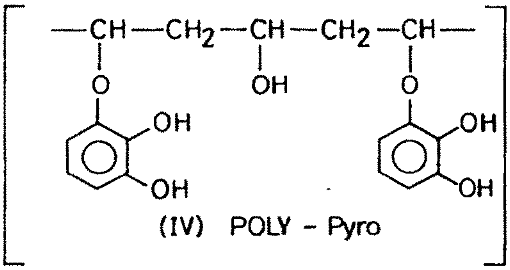
(I) POLY - Anthra



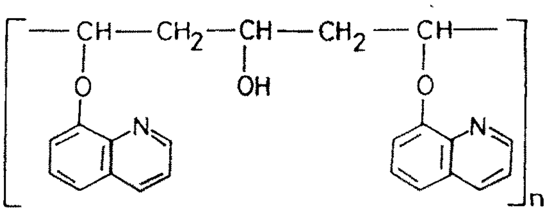
(II) POLY - Galli



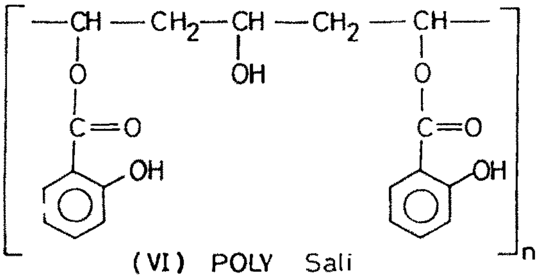
(III) POLY - PHyBe



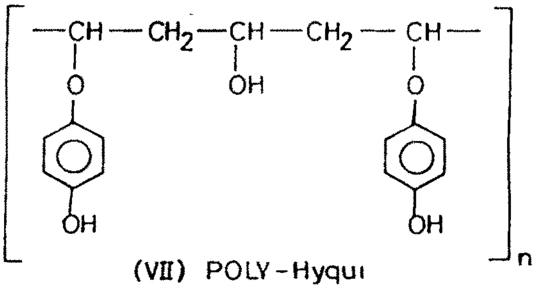
(IV) POLY - Pyro



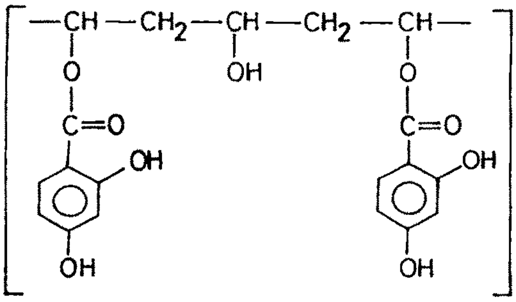
(V) POLY-8Hyqui



(VI) POLY Sali



(VII) POLY-Hyqui



(VIII) POLY - β Res

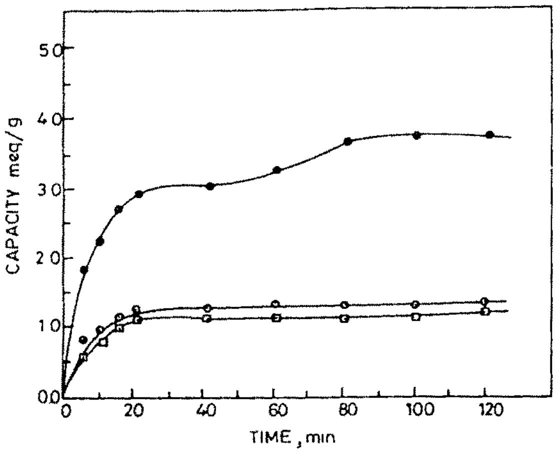


Fig. 2 Rate of cation exchange of poly-PHybe (⊙), poly-pyro (●), poly- 8Hyqui (⊡)

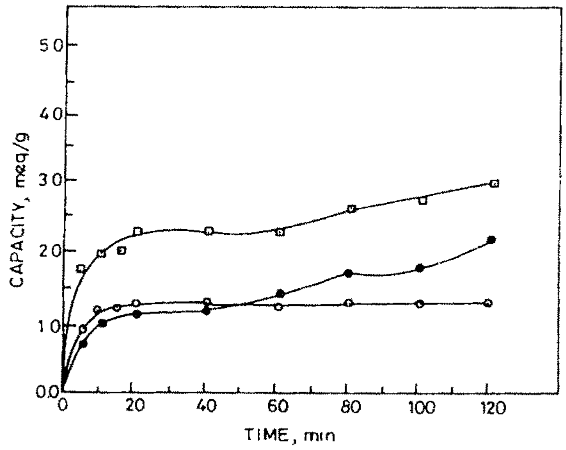


Fig. 3 Rate of cation exchange of poly-sali (⊙), poly-hyqui (⊡) poly- β-Res (●)

TABLE 3 Oxidation Resistance of Resins

Resin	% moisture untreated exchanger		% moisture H_2O_2 treated exchanger		Increase in % water content	
	H-form	OH-form	H-form	OH-form	H-form	OH-form
Poly-Anthra	5.0	6.1	7.6	16.8	2.5	10.7
Poly-Galli	7.1		16.8		9.6	
Poly-PHyBe	5.2		6.0		0.7	
Poly-Pyro	5.9		12.4		6.4	
Poly-8Hyqui	2.2	2.3	10.2	15.6	7.9	13.2
Poly-Sali	4.8		10.6		5.7	
Poly-Hyqui	5.9		10.2		4.2	
Poly-β-Res	5.0		7.2		2.1	

observed that (i) 50% exchange occurs in 10 to 40 min (ii) the rate of exchange for the resins follows the order:

Poly-Anthra > Poly-8Hyqui

The PK_a values for the resins are comparable to that of the compound having phenolic hydroxyl group (Table 1), indicating the weakly acidic nature of the matrix. The PK_b values are in the range of a base of medium strength. On oxidation these resins which are acting as anion exchangers show greater increase in percentage of water content than when they are acting as cation exchangers (Table 3). Hence, it is inferred that the cationic form is less susceptible to oxidation than the anionic form. The anion exchange capacity of the resin increase with an increase in temperature of equilibration (Table 4). This can be explained as follows:

On heating the resin, certain basic gaseous decomposition products are obtained which neutralise a part of the acid during equilibration, thus giving apparently higher value for the anion exchange capacity of the resin. The decrease in the cation exchange capacity of the resins (Table 4) with an increase in the temperature of equilibration is only due to loss of ionogenic groups.

The results of behaviour in non-aqueous solvents of these resins are reported in (Table 6). The decreasing order of porosity (polar solvents) for

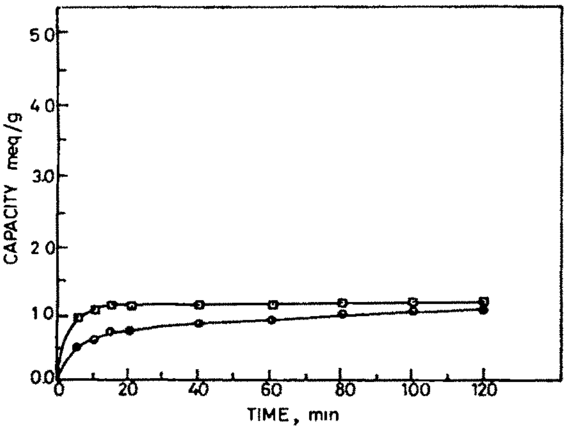


Fig. 4. Rate of anion exchange of poly-anthra (⊝), poly-8Hyquoi (⊟).

resins as exchanger is as follows:

Poly-pyro > Poly-sali > Poly-β-Res >
Poly-8-Hyqui > Poly-Hyqui > Poly-Galli >
Poly-Anthra > Poly-p-HyBe

The chelating exchangers are thermally stable up to 300°C. Decomposition of polymer start at 300°C and continue up to 900°C. For the resin Poly-Anthra, Poly-Gallic, Poly-Pyro, Poly-β-Res single stage decomposition was observed. While for resins Poly-p-HyBe, Poly-8-Hyqui, Poly-Sali, Poly-Hyqui double stage decomposition was observed. The activation energy E_A value obtained by Broido method[16] for the resin varies from 9.09 to 13.8 Kcal/mole

Their thermal stabilities were in the following order:

TABLE 4. Effect of Temperature of Equilibration on the Capacity of Resin

(Equilibration period = 2 h, amount of resin = 0.5 g)

Resin	Anion exchange capacity meq/g			Cation exchange capacity meq/g		
	30°C	50°C	70°C	30°C	50°C	70°C
Poly-Anthra	1.0215	1.2134	1.403	1.0215	1.0211	1.0210
Poly-Galli				4.6344	4.4123	4.2146
Poly-pHyBe				1.3314	1.2124	1.2130
Poly-Pyro				3.7614	3.4657	3.3615
Poly-8Hyqui	1.1655	1.3416	1.3943	1.3278	1.2440	1 1234
Poly-Sali				1.2820	1.2606	1.1093
Poly-Hyqui				2.9413	2.6171	2.0467
Poly-β-Res				2.1794	2.1646	2.1678

TABLE 5. Result of TG Data by Method of Broido

Resin	Method of Broido % wt. loss								Energy of activation Kcal
	200°C	300°C	400°C	500°C	600°C	700°C	800°C	900°C	
Poly-Anthra	2.8	5.5	22.2	37.5	57.5	77.0	93.5	99.0	10.5714
Poly-Galli	5.0	8.0	16.5	26.5	40.0	58.5	80.0	87.0	10.312
Poly-p-HyBe	2.5	8.0	17.0	24.5	43.5	79.0	93.5	93.5	13.332
Poly-Pyro	4.5	8.0	15.0	24.0	42.0	68.0	90.5	96.5	10.1886
Poly-8Hyqui	3.0	5.0	20.5	28.5	45.0	73.0	91.0	91.5	13.8/10.50
Poly-Sali	2.0	10.0	22.0	29.0	62.0	84.0	84.5	85.5	10.90/6.41
Poly-Hyqui	3.5	12.5	27.5	39.0	58.0	82.5	93.0	94.0	9.09
Poly-β-res	3.0	4.5	13.0	26.5	51.0	78.0	89.0	90.0	10.5

TABLE 6. Percentage Swelling of Resins in Various Solvents

Resin	Glacial acetic acid	Water	DMF	Dioxane	Alcohol	THF	Benzene	Acetone	Pt ether
Poly-Anthra	1.9	4.5	1.3	1.2	1.1	0.4	0.5	0.4	0
Poly-Gali	1.2	5.6	1.8	1.3	0.9	0.5	0.3	0.5	0
Poly-p-HyBe	0.7	2.9	1.1	0.8	0.9	0.2	0.3	0.2	0
Poly-pyro	1.4	7.9	1.2	1.6	1.9	0.9	0.2	0.7	0
Poly-8Hyqui	4.9	6.8	3.1	2.5	1.9	1.0	0.3	0.7	0
Poly-Sali	3.1	7.4	2.4	1.5	1.7	0.7	0.3	0.6	0
Poly-Hyqui	1.1	6.6	1.8	1.9	1.2	0.6	0.3	0.4	0
Poly-β-Res	1.8	6.9	1.8	1.3	1.1	1.0	0.4	0.5	0

Poly-Hyqui < Poly-Pyro < Poly-Gallic
< Poly-β-Res < Poly-Anthra < Poly-Sali
< Poly-p-HyBe < Poly-8-Hyqui

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Ion exchange behaviour of chemically modified polyvinyl chloride

Sushila Amin & R N Kapadia*
Department of Chemistry, Faculty of Science, M S University of Baroda, Baroda 390 002, India

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New ion exchangers were synthesized by condensing anthranilic acid, gallic acid, *p*-hydroxybenzaldehyde, pyrogallol, 8-hydroxyquinoline, salicylic acid, hydroquinone *β*-resorcylic acid, with poly(vinyl chloride) in DMF solvent. The ion exchangers were characterised by their total capacity, moisture retention ability, density, void volume fraction, rate of exchanger, *p*H titration behaviour apparent pK_a and pK_b and isoelectric point values, oxidation resistance, the effect of equilibration at different temperatures on the capacity of the resin, swelling behaviour in various solvents and they were further characterised by thermogravimetric analysis (TGA).

Literature survey on chemical modification of polymer[1-3], reveals that the chlorine displacement reaction between poly(vinyl chloride) and suitable aromatic hydroxy acids bearing appropriate functional groups, yields modified poly(vinyl chloride) with improved thermal stability and ion exchange behaviour relative to unmodified poly(vinyl chloride). Encouraged by these findings we explored the possible application of these polymers as ion exchangers. Hence, we report the synthesis of ion exchangers from poly(vinyl chloride)-anthranilic acid [poly-anthra], poly(vinyl chloride)-gallic acid [poly-gallic], poly(vinyl chloride)-*p*-hydroxybenzaldehyde [poly-*p*-hybe], poly(vinyl chloride)-pyrogallol [poly-pyro], poly(vinyl chloride)-8-hydroxyquinoline [poly-8-hyqui], poly(vinyl chloride)-salicylic acid [poly-sali], poly(vinyl chloride)-hydroquinone [poly-hyqui], poly(vinyl chloride)-*β*-resorcyclic acid [poly-*β*-res].

Synthesis of Resins

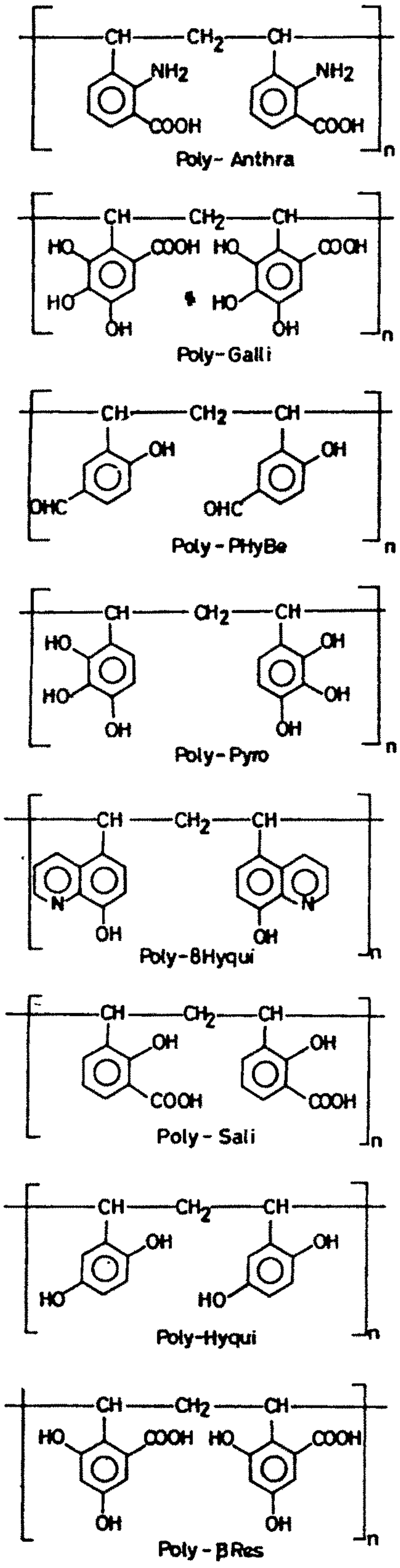
Anthranilic acid, gallic acid, *p*-hydroxybenzaldehyde pyrogallol, 8-hydroxyquinoline, salicylic acid, hydroquinone or *β*-resorcyclic acid was taken in 250 mL round bottom flask and mixed with poly(vinyl chloride) (*K* value = 55-57). 4 g of *p*-toluene sulphonic acid (PTSA) was added as initiator. Solvent DMF was added in it. The mixture was vigorously stirred. The whole reaction mixture was refluxed at 150°C for 4 h. Gel formation takes place in about 1 h. A hard mass was obtained which varied in colour from brown to dark brown to black for different phenolic monomers listed above. The cured hard mass was then crushed to −60 to 100 BSS mesh size as needed and washed with ethanol to remove unreacted monomers and low molecular weight products from the resins. The resin was dried in an oven below 100°C and stored in polyethylene bottles. All the resins were characterised by their physicochemical properties following the methods described in the literature[4-18]. Thermal studies were carried out by using methods reported in literature[19-22].

Results

The ion exchange resins are synthesised from poly (vinyl chloride) and various aromatic hydroxy acids derivatives. In the series under investigation gelling time and curing period for all the resins are the same and hence we suggest that gelling time and curing period are directly related to the functionality of comonomer poly(vinyl chloride).

The ion exchangers are fairly porous with average physical stability and good chemical resistance to 3*N* acids and alkali and show a change of colour when converted from free acid or free base form to its corresponding salt (Na or Cl) from or vice-versa. The high molecular weight polymers were obtained by poly condensation under mild reaction and curing conditions. On the basis of elemental analysis and IR spectra and other physicochemical studies, we may postulate the structure of resins as shown in Scheme 1.

Moisture contents (Table 1) of the resins have low values. The total cation exchange capacity is higher than anionic exchange capacity for these resins (Table 1). The resins show the following decreasing order for cation exchange capacity.



Scheme 1

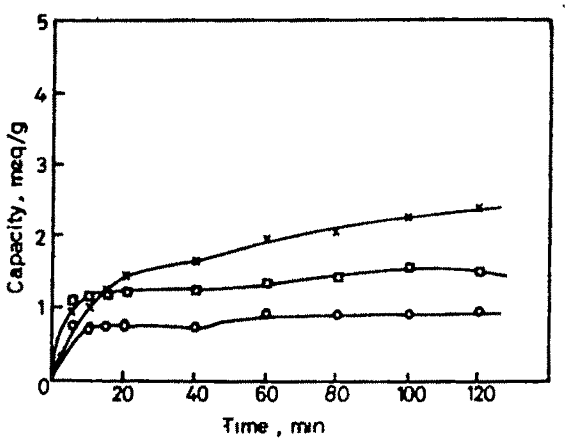


Fig 1—Rate of cation exchange of poly-anthra (⊙), poly-gallic (×) and poly-*p*-hybe (□)

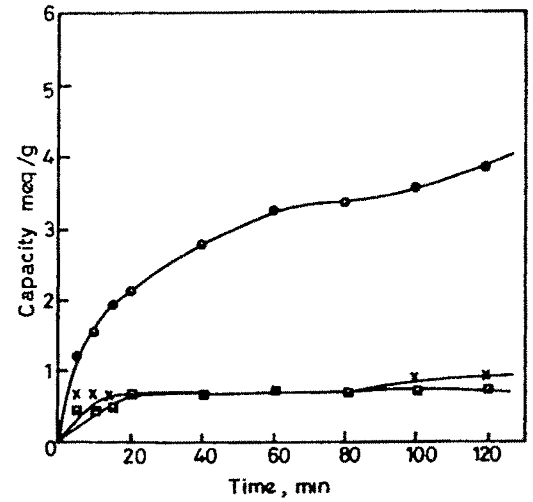


Fig 2—Rate of cation exchange of poly-pyro (⊙) poly-8-hyqui (×) and poly-sali (□)

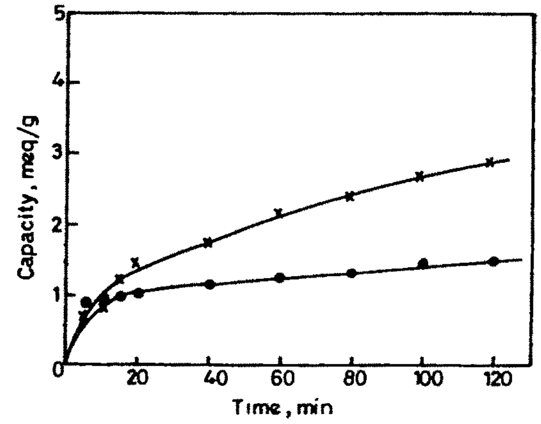


Fig. 3—Rate of cation exchange of poly-hyqui (⊙) and poly-*β*-res (×)

Poly-sali < poly-anthra < poly-8-hyqui < poly-hyqui
< Poly-*p*-hybe < poly-gallic < poly-*β*-res
< poly-pyro

The resins show the following decreasing order for anion exchange capacity.

poly-8-hyqui < poly-anthra

The column density (Table 1) of the resins (H and OH-forms) is low, suggesting large swelling percentage in the resin. Also the resins (H and OH-forms) have large void volume fraction.

The rate of exchange for ion exchange resins as cation exchanger (Figs 1-3) as well as anion exchanger (Fig. 4) is very high (diffusion controlled). In the case of ion exchange resins as cation exchanger, it is observed that (i) complete exchange occurs in 20-60 min and (ii) the rate of exchange for these resins at the same density follows the order.

poly-8-hyqui ≅ poly-sali ≅ poly-anthra < poly-*p*-hybe
≅ poly-hyqui < poly-gallic ≅ poly-*β*-res < poly-pyro

In the case of ion exchange resins as anion exchanger it is observed that (i) complete exchanger

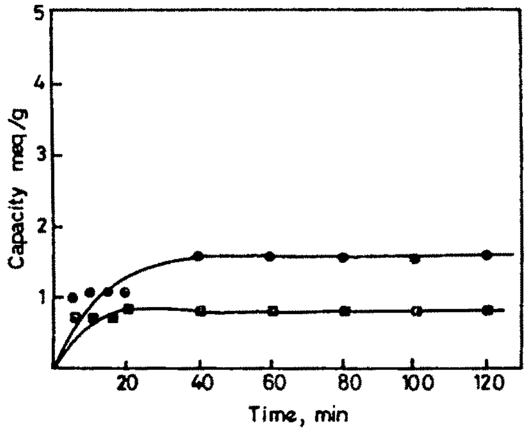


Fig 4—Rate of anion exchange of poly-anthra (⊙) and poly-8-hyqui (□)

Table 1 – Physicochemical characteristics of the ion-exchange resin

Property		poly-anthra	poly-galli	poly-*p*-hybe	poly-pyro	poly-8-hyqui	poly-sali	poly-hyqui	poly-*β*-res
Total capacity	CEC*	2.2269	3.9409	2.2461	4.9065	1.7986	1.0723	1.8912	3.9823
meq/g	AEC*	2.1246				1.5346			
Moisture%	H-form	3.7015	4.1722	4.0229	4.9836	4.3114	3.0122	4.9627	4.0112
	OH-form	2.3320				2.5779			
True density	H-form	1.3520	1.3793	1.3096	1.3974	0.3967	0.5091	1.1031	0.5205
d_{re}, g/cm^3	OH-form	1.5429				1.2580			
Apparent density	H-form	0.3140	0.4027	0.3155	0.3615	0.2659	0.4175	0.2751	0.3956
d_{cal}, g/cm^3	OH-form	0.3243				0.5611			
Void volume	H-form	0.7678	0.7081	0.7594	0.7414	0.8097	0.1800	0.7507	0.2400
fraction	OH-form	0.7899				0.5540			
pK_a		10.6130	10.3291	10.4714	9.7432	10.1181	9.8908	10.5191	10.5771
pK_b		3.9638				4.0343			
Isoionic point		7.2884				7.0762			

*CEC = cation exchange capacity *AEC = anion exchange capacity

Table 2 – Oxidation resistance of resin

Resin	% Moisture untreated exchanger		% Moisture H_2O_2 treated exchanger		Increase in % water content	
	H-form	OH-form	H-form	OH-form	H-form	OH-form
Poly-anthra	3.7015	2.332	7.2000	10.2	3.4985	7.8680
Poly-gallic	4.1722	—	7.6000	—	3.4278	
Poly-*p*-hybe	4.0229	—	13.6000	—	9.5771	
Poly-pyro	4 9836	—	14.4000	—	9.9164	
Poly-8-hyqui	4.3114	2.5779	7.0020	10.4	2.6906	7.8221
Poly-sali	3.0122	—	8.2000	—	5.7878	
Poly-hyqui	4.0627	—	8.4000	—	3.4373	
Poly-*β*-res	4.0112	–	7.6000	—	3.5888	

occurs in 20-60 min and (ii) the rate of exchange for these resins at the same density follows the order:

Poly-8-hyqui < poly-anthra

Table 1 reveals that pK_a values of the resins are comparable to that of the phenolic hydroxyl group, indicating the weakly acidic nature of the matrix. The pK_b values are in the range of a base of medium strength. On oxidation these resins acting as cation exchangers show greater increase in percentage water content than when they are acting as anion exchanger (Table 2). Hence, it is inferred that the anionic form is less susceptible to oxidation than the cationic form. The anion exchange capacity of the resin increase with an increase in temperature of equilibration Table 3.

On heating the resin, certain basic gaseous de-

Table 3 – Effect of temperature of equilibration on the capacity of the resin

Equilibration period = 2 h
Amount of resin = 0.5 g

Resin	Total AEC (meq/g) of absolutely dry resins as determined at temp., °C			Total CEC (meq/g) of absolutely dry resins as determined at temp., °C		
	30	50	70	30	50	70
Poly-anthra	1.5649	1.7234	1.8213	1.07951	1.06313	1.0601
Poly-gallic				2.4542	2.42120	2.4146
Poly-*p*-hybe				1.6351	1.6021	1.5912
Poly-pyro				3.9239	3.8123	3.8121
Poly-8-hyqui	0.8068	0.9131	1.0136	0.9680	0.9612	0.9512
Poly-sali				0.8269	0.9212	0.8143
Poly-hyqui				1.8912	1.8901	1.8814
Poly-β-res				2.8583	2.8393	2.8412

Table 4 – Result of TG data by method of Broido

Resin	Method of Broido% wt. loss								Energy activation E_a, kcal/mol
	200°C	300°C	400°C	500°C	600°C	700°C	800°C	900°C	
Poly-anthra	1.2	9.5	16.2	23.5	41.0	69.5	80.5	80.5	22.17
Poly-gallic	3.5	5.5	8.5	14.5	17.5	45.5	66.5	87.0	23.49
Poly-*p*-hybe	11.5	10.0	26.0	32.5	38.0	48.5	55.5	63.5	17.32
Poly-pyro	8.5	10.5	17.0	25.0	58.0	68.5	75.0	80.5	22.86
Poly-8-hyqui	2.5	3.5	11.5	16.0	19.0	24.0	36.0	51.5	41.57
Poly-sali	2.0	6.0	18.0	26.5	35.5	51.0	77.0	58.0	31.67
Poly-hyqui	12.5	22.0	41.0	48.5	15.5	66.0	74.0	80.0	28.44
Poly-β-res	5.0	6.5	11.0	20.5	49.0	90.0	98.0	99.0	23.49

Table 5 – Per cent swelling of resin in various solvents

Resin	Glacial acetic acid	Water	DMF	Dioxane	Alcohol	THF	Benzene	Acetone	Pet. ether
Poly-anthra	3.3	18.4	4.0	3.0	4.1	1.7	0.3	2.5	0
Poly-gallic	1.5	7.2	1.9	1.4	2.2	0.9	0.9	0.8	0
Poly-*p*-hybe	1.6	9.2	1.8	2.0	2.5	1.6	1.2	2.1	0
Poly-pyro	2.1	9.7	2.6	1.4	3.0	1.9	1.1	2.1	0
Poly-8-hyqui	3.8	9.7	3.0	2.2	4.5	0.7	0.7	2.7	0
Poly-sali	1.9	6.7	2.7	1.4	2.4	1.0	0.8	2.3	0
Poly-hyqui	4.9	16.7	4.0	2.5	5.6	2.4	0.8	2.5	0
Poly-β-res	2.0	9.4	2.5	2.3	2.8	2.0	1.3	2.5	0

Table 6 – Elemental analysis of resin

Resin	% required			% obtained		
	C	H	N	C	H	N
Poly-anthra	60.71	5.32	7.45	60.08	5.72	7.29
Poly-gallic	51.75	3.85	—	51.88	3.81	—
Poly-*p*-hybe	66.18	4.93	—	66.18	4.89	—
Poly-pyro	57.87	4.82	—	57.77	4.74	—
Poly-8-hyqui	70.49	7.24	7.15	70.59	7.24	7.25
Poly-sali	60.18	4.93	—	66.18	4.93	—
Poly-hyqui	63.65	5.30	—	63.83	5.45	—
Poly-β-res	55.81	4.16	—	55.89	4.24	—

composition products are produced which neutralise a part of the acid during equilibration, thus giving apparently higher value for the anion exchange capacity of the resin. The decrease in the cation exchange capacity of the resins (Table 3) with an increase in the temperature of equilibration is only due to loss of inorganic groups.

The results of behaviours in non-aqueous solvents of these resins are reported in Table 5. The decreasing order of porosity (polar-solvent) for resins as exchanger is as follows:

poly-anthra < poly-hyqui < poly-8-hyqui
< poly-pyro < poly-β-res < poly-p-hybe
< poly-gallic < poly-sali

The ion exchangers are thermally stable up to 300°C (Table 4). Decomposition of polymer start at 300°C and continue up to 800°C. The activation energy (E_a) value obtained by Broido method[19-22] for the resin varies from 17.32 to 41.57 kcal/mol.

Their thermal stabilities were in the following order:

poly-p-hybe < poly-anthra < poly-pyro
< poly-gallic ≅ poly-β-res < poly-hyqui
< poly-sali < poly-8-hyqui

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Short Communication

Ion exchange behaviour of chemically modified poly vinyl acetate

Sushila Amin & R N Kapadia*

Department of Chemistry, Faculty of Science, M S University of Baroda, Baroda 390 002, India

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New ion exchangers have been synthesized by condensing anthranilic acid, gallic acid, *p*-hydroxybenzoic acid, pyrogallol, 8-hydroxyquinoline, salicylic acid, hydroquinone and *β*-resorcylic acid with poly vinyl acetate in glacial acetic acid as a solvent. All the resins have been characterised for their various physico-chemical properties.

The present communication reports the syntheses of different ion exchangers by condensing poly vinyl acetate with anthranilic acid [poly-Anthra], poly vinyl acetate gallic acid [poly-Galli], poly vinyl acetate-*p*-hydroxy benzoic acid [poly-*p*HyBe], poly vinyl acetate-pyrogallol [poly-pyro], poly vinyl acetate-salicylic acid [poly-sali], poly vinyl acetate-hydroquinone [poly-Hyqui] and poly vinyl acetate-*β*-resorcylic acid [poly-*β*-res].

Experimental procedure—Anthranilic acid, gallic acid, *p*-hydroxybenzoic acid, pyrogallol, salicyclic acid, hydroquinone, and *β*-resorcylic acid (1 mol) each one was taken in 250 mL round bottom flask and mixed with 1 mol of poly vinyl acetate. ($\bar{M}w = 45{,}000$). Glacial acetic acid (approx. 100 mL) was added in it. Two grams of *p*-toluene sulphonic acid was added as initiator. The mixture was vigorously stirred and refluxed on low flame sand bath for 24 h. Gel formation takes place in about 1 h and a hard mass was obtained which varied in colour from dark brown to black for different phenolic monomers listed above. The cured hard mass was then crushed to -60 to 100 BSS mesh size as needed and washed with ethanol to remove unreacted monomers and low molecular weight product from the resins. The resins were dried in an oven at 100°C and stored in poly-ethylene bottles. All the resins were characterised for their various physico-chemical properties, by the reported methods[1-3]. Thermal studies were also carried out by using reported procedure[4,5].

To estimate the rate of ion exchange the H-form (or OH-form) of the resin (0.5 g and -60 to 100 BSS mesh) was accurately weighted into eight to nine different stoppered bottles. 100 mL 0.1 N NaOH in 1N NaCl (or 100 mL 0.1N HCl in 1N NaCl) was added to each bottle and the resin was allowed to remain in contact for different periods of time, with intermittent shaking. At different predetermined intervals, the solutions were decanted and an aliquot was titrated against standard acid or alkali and from this the capacity realized at different time intervals was calculated.

Results and discussion—The ion exchange resins were synthesized from poly vinyl acetate and various phenolic derivatives. The condensate is found to be insoluble in sodium hydroxide, hydrochloric acid and dioxane in which the individual components are misible or soluble. Therefore, the resin appears to be a condensate product of phenolic derivative with poly vinyl acetate. The gelling time and curing period for all the resins are same and hence it can be said that the gelling time and curing period are directly related to functionality of comonomer, poly vinyl acetate.

The exchangers are fairly porous with average physical stability and good chemical resistance to 3N acids and alkali. Moreover, a colour change is observed during conversion from free acid or free base form to its corresponding salt (Na or Cl) form or vice-versa. As the poly condensation was carried out under mild reaction and curingionditons, the bond formation is possible through $-CH_2-$ and $-C=O$ bridge, as evident from infrared spectra (Table 1). Reversibility of ion exchangers has also been established. On the basis of elemental analysis, IR spectra and other physico-chemical studies, the possible structure of resins are predicted and shown in Fig. 1..

The various physico-chemical characteristics of the resins are presented in Table 2. Moisture contents of the resins are found to be from 0.01 to 0.20, for the H-form and 0.04 for OH-form (Table 2). The resins show the following order of moisture content for cation exchangers.

Poly-Hyqui < Poly-Anthra < Poly-*p*HyBe

Poly-*β*-Res < Poly-sali < Poly-pyro < Poly-Gallic

The column density (Table 2) of these resins (H and OH-form) is low, suggesting little swelling percentage. All the resins (H or OH form) have large void volume fraction.

Table 1—Major peaks observed in the infrared spectra of resins

Resin	Wave number cm^{-1}	Nature of peak	Probable assignment
Poly-Anthra	1660	medium	N – H bending
	1320-1280	weak	C-N vibration
	1150	sharp	$-O-$ ether linkage
	1710-1730	broad	$-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-$ conjugated carbonyl group
Poly-Galli	3600-3000	broad	– OH stretching
	1720-1680	medium	$-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-$ conjugated carbonyl group
	1550-1610	sharp	C = C Aromatic ring
Poly-*p*-HyBe	3500-3200	broad	– OH stretching
	1740-1700	medium	$-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-$ conjugated carbonyl group
	1590	sharp	C = C Aromatic ring
Poly-pyro	3600-2800	broad	– OH stretching vibration
	1350-1550	broad	– O- ether linkage stretching
Poly-Sali	3600-3000	broad	– OH stretching vibration
	1720-1680	medium	$-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-$ conjugated carbonyl group
Poly-Hyqui	3600-3000	broad	– OH stretching vibration
	1740-1700	medium	$-O-C-$ ester group stretching
	1620-1580	medium	C = C Aromatic ring
Poly-*β*Res	3600-2500	broad	– OH stretching
	1740-1700	medium	$-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-$ conjugated carbonyl group
	1620-1580	medium	C = C Aromatric ring

Table 2—Physico-chemical characteristics of the ion-exchange resions

Property		Poly-Anthra	Poly-Galli	Poly-*p*-HyBe	Poly-Pyro	Poly-Sali	Poly-Hyqui	Poly-*β*-Res
Total Capacity	CEC*	2.39	7.04	3.97	7.88	3.18	3.90	4.63
meq/g	AEC*	1.02						
Moisture	% H-form	0.02	0.20	0.04	0.13	0.01	0.06	0.05
	% OH-form	0.04						
True density	H-form	0.71	0.56	0.62	0.42	0.79	0.77	0.65
d_{res}, g/cm^3	OH-form	0.61						
Apparent density	H-form	0.44	0.44	0.35	0.42	0.44	0.44	0.42
d_{cal}, g/mL	OH-form	0.46						
Void volume	H-form	0.34	0.20	0.29	0.17	0.47	0.43	0.35
fraction	OH-form	0.26						
pK_a		8.57	9.27	10.37	9.20	10.37	10.09	10.15
pK_b		2.47						
Isoionic point		5.52						
Increase in	H-form	10.78	18.20	5.76	10.07	6.99	8.14	3.95
% water content	OH-form	8.37						
Effect of temp. of	H-form							
equi. on	30°C	2.46	6.98	3.95	7.74	3.29	3.61	4.25
capacity of	50°C	2.43	6.88	3.89	7.70	3.20	3.60	4.06
resin (CEC*)	70	2.40	6.79	3.87	7.67	3.11	3.51	4.00
	OH-form							
	30°C	1.23						
(AEC*)	50°C	1.34						
	70°C	1.39						

*CEC = Cation Exchange Capacity *AEC = Anion Exchange Capacity

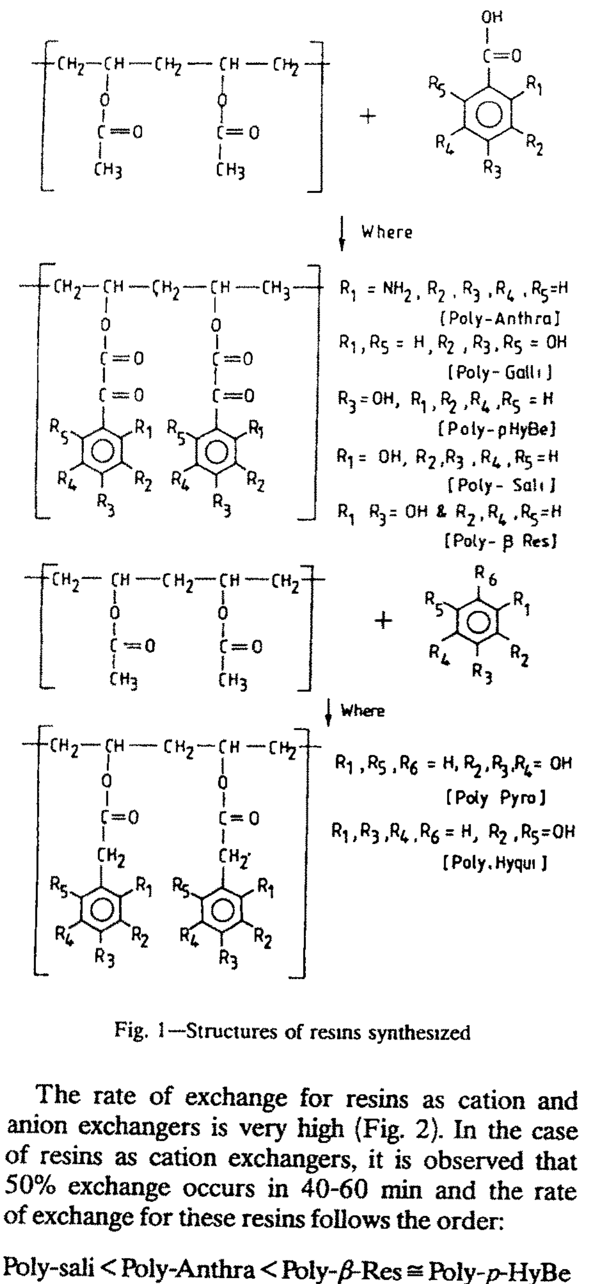

Fig. 1—Structures of resins synthesized

The rate of exchange for resins as cation and anion exchangers is very high (Fig. 2). In the case of resins as cation exchangers, it is observed that 50% exchange occurs in 40-60 min and the rate of exchange for these resins follows the order:

Poly-sali < Poly-Anthra < Poly-β-Res ≅ Poly-p-HyBe
< Poly-Hyqui < Poly-Gallic ≅ Poly-pyro

On the other hand in the case of resins as anion exchanger 50% exchange occurs just in 5-10 min.

The apparent pK_a and pK_b values are calculated from pH titration carves using relation (i) and (ii), respectively.

$$pK_a = pH + \log[Na^+]_s \frac{\log[R^-]+RH}{2} \quad \ldots (i)$$

$$pK_b = pH - \log[Cl^-]_s \frac{+\log[H^+RH+RH]}{2} \quad \ldots (ii)$$

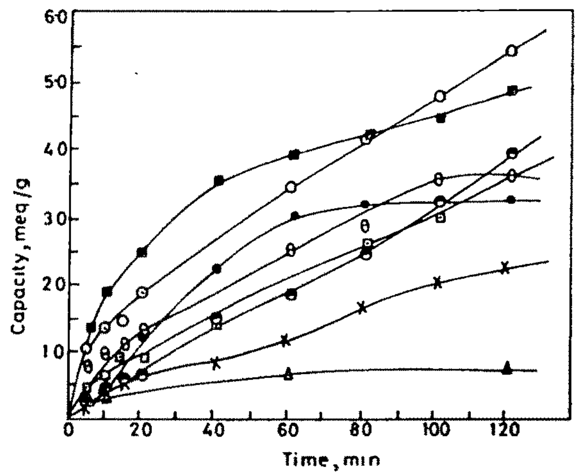

Fig. 2—Rate of cation exchanger of (●) Poly-Anthra, (■) Poly-Gallic, (□) Poly-p-HyBe, (⊙) Poly-Pyro, (×) Poly-Sali, (○) Poly-Hydro, and (⊖) Poly-β-Reso and rate of anion exchanger of (△) Poly-Anthra

It is observed that the pK_a values for the resins are comparable to that of the compounds having phenolic hydroxy group (Table 2), indicating the weakly acidic nature of the matrix. The pK_b values are in the range of a base of medium strength.

The results of behaviour in non-aqueous solvents of these resins showed the deceasing order of porosity and is as follows:

Poly-pyro < Poly-β-Res < Poly-Galli < Poly-Anthra
< Poly-Hyqui < Poly-p-HyBe < Poly-Sali

From the TGA data the ion exchangers were found thermally stable up to 300°C and decomposition of the polymer starts at 300°C and continues up to 900°C. The activation energy (E_A) obtained by Broido method for the resins varies from 20.79 to 40.50 kcal/mol. Their thermal stabilities are found to be following order:

Poly-Hyqui < Poly-pyro < Poly-β-Res
< Poly-p-HyBe < Poly-Sali ≅ Poly-Galli
< Poly-Anthra.

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R.K. Khanna(RI843C/D3NN/On 512 system)

Synthesis and characterisation of amphoteric ion exchangers

Sushila Amin & R N Kapadia
Department of Chemistry Faculty of Science M S University of Baroda, Baroda-390 002

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Furfural - Benzidine - Phenolic derivative type amphoteric resins have been synthesized using gel technique The monomers employed included gallic acid, phydroxy benzoic acid, salicylic acid and hydroquinone Physico-chemical properties such as the total capacity, moisture retension ability, density, void volume fraction, rate of exchange, *p*H titration behaviour, apparent PK_a, PK_b and isoelectric point values oxidation resistance, the effect of equilibration at different temperature on the capacity of the resin, and swelling behaviour in various solvent have been investigated

R K. Khanna(RI843A/D3NN/On 512 system)

Literature[1,2], throw some light on the type of the work done on furfural type resins. In continuation of our work on furfural type resins[3], we now report synthesis of new resins using Schiffbase (furfural - Benzidine), with gallic acid, phydroxy benzoic acid, salicylic acid, and hydroquinone.

These are:
Furfural - benzidine - gallicacid (Fu-Ben-GA)
Furfural - benzidine - Phydroxybenzoic acid (Fu-Ben-PHy)
Furfural - benzidine - Salicylic acid (Fu-Ben-SA)
Furfural - benzidine - hydroquinone (Fu-Ben-Hy)

Synthesis of Resin

Schiffbase[1,2] was synthesised by using furfural and benzidine, 2 moles of gallic acid, phydroxy benzoic acid, salicylic acid or hydroquinone was taken in a 250 ml round bottom flask and dissolved in DMF solvent, 1 mole of Schiff base added to it PTSA was used as initiater and refluxed for 3 hours Gel formation takes place in about 1 hour. A hard mass was obtained, which was dark brown to back colour for different phenolic monomers listed above. The cured hard mass was then crushed to − 60 to 100 BSS mesh size as needed and washed with ethanol to remove unreacted monomers and low molecular weight products from the resins. The resins was dried in an oven below 100°C and stored in polyethylene bottles All the resins were charactensed by their physicochemical properties following the method described in the literature[4-9].

Estimation of the rate of ion exchange— ~~Rate of exchange at room temperature~~ 0.5g (− 60 to 100 mesh) of resin was accurately weighted into each of nine different stoppered bottles. 10ml of 0.1N NaOH in 1N NaCl was added to each bottle and the resin allowed to remain in contact for different periods of time, with intermittent shaking At definite predetermined intervals, the solutions were decanted and an aliquot was titrated against standard acid or alkali and from this the capacity realized at different time intervals was calculated.

Results and Discussion

The amphoteric ion-exchange resins were synthesized from Schiff base and various phenolic derivatives. The resins are insoluble in sodium hydroxide, hydrochloric acid and dioxane in which the individual components are miscible or soluble Therefore the resin appears to be a condensate products of phenolic derivative with Schiffbase.

The ion exchangers are fairly porous with average physical stability and good chemical resistance to 3N acids and alkali and shows a change of colour when converted from free acid or free base form to its corresponding salts (Na or Cl) form or viceversa. The resins were obtained by poly-condensation under mild reaction and curing conditions. The bond formation is possible through − C - C − bridge as evident from Infrared spectra.

Reversibility of ion exchangers has been established. On the basis of elemental analysis (Table 1). IR spectra, and physico-chemical studies, we have postulated the structure of resins as shown in Fig. 1.

Moisture content (Table 2) of the resins are found to range from 4 02 to 5 22 for the H-form and 5 0 to 14 0 for OH form The resins shows the following order of moisture content for cation and anion exchangers

Fu-Ben-Sa < Fu-Ben-PHy < Fu-Ben-Hy < Fu-Ben-Ga and for anion exchangers the order were as above.

The column density (Table 2) of these resins (H and OH form) is low, suggesting little swelling percentage All the resins (H or OH) form has large void volume fraction.

The rate of exchange for resins as cation exchanger (Figs. 2,3) as well as anion exchanger (Fig. 4,5) is very high diffusion controlled). In the case of resins as cation exchanger, it is observed that (i) 50 percent exchange occurs in 5 to 20 min (ii) the rate of exchange for these resins follows the order
Fu-Ben-SA < Fu-Ben-Phy < Fu-Ben-GA < Fu-Ben-Hy

In the case of resins as anion exchanger it is observed that 50 percent exchange occurs in 5 to 10 min (ii) the rate of exchange for these resins follows the order
Fu-Ben-SA < Fu-Ben-Hy < Fu-Ben-PHy < Fu-Ben-GA

pK_a The PK_a values for the resins are comparable to that of the compounds having phenolic hydroxy group (Table 2), indicating the weakly acidic nature of the matrix. pK_b The PK_b values are in the range of a base of medium strength. On oxidation these resins acting as cation exchanger show greatest increase in percentage water content than when they are acting as anionic form is less susceptible to oxidation than the cationic form (Table 3). The anion exchange capacity of the resin increase with an increase in temperature of equilibrium (Table 4)

On heating the resin, certain basic gaseous decomposition products are produced which neutralise a part of the acid during equilibration, thus giving apparently higher value for the anion exchange capacity of the resin. The decrease in the cation exchange capacity of the resin (Table 4) with increase in the temperature of equilibrium is only due to loss of inorganic groups.

The results of behaviour in non-aqueous solvents of these resins are reported in (Table 5) The decreasing order of porosity (polar solvents) for resins as exchangers is as follows:
Fu-Ben-SA < Fu-Ben-GA < Fu-Ben-PHy > Fu-Ben-Hy

R.K. Khanna(RI843A1/D3NN/On 512 system)

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R.K Khanna(RI843A2 D3NN On 512 system)

Fig 1 Structures of resins

Fig 2—Rate of exchange for cation
○ Fu-Ben-GA, □ Fu-Ben-PHy

Fig 3 –Rate of exchange for cation
○ Fu-Ben-SA □ Fu-Ben-Hy

Fig 4 - Rate of exchange for anion
○ Fu-Ben-GA, □ Fu-Ben-PHy

Fig 5 - Rate of exchange for anion
○ Fu-Ben-SA □ Fu-Ben-Hy

R K Khanna(RI843A3 D3NN On 512 system)

Table 1—Elemental analysis

Resin	Per cent required			Per cent obtained		
	% C	% H	% N	% C	% H	% N
Fu-Ben-PHy	67 08	3 72	4 34	67 72	5 04	4 03
Fu-Ben-Py	74 48	4 13	4 82	73 98	5 08	3 98
Fu-Ben-Sa	74 48	4 13	4 82	73 79	5 35	4 46
Fu-Ben-Hy	73 38	4 31	5 03	73 09	5 16	5 23

R K Khanna(R1843C1 D3NN On 512 system)

Table 2 Physico-chemical characteristics of the ion-exchange resin

Property		Fu-Ben-Ga	Fu-Ben-PHY	Fu-Ben-SA	Fu-Ben-Hy
Total capacity	CEC*	5.45	4.65	4.13	5.01
(meq g)	AEC*	5.99	5.51	5.38	5.41
Moisture (%)	H-form	5.22	4.9	4.02	5.01
	OH-form	14.0	8.0	5.0	13.6
True density	H-form	1.12	1.31	1.00	1.02
(dres g cm^{3})	OH-form	1.10	1.23	1.01	1.28
Apparent density	H-form	0.29	0.32	0.28	0.24
dcol g ml^{1}	OH-form	0.30	0.29	0.31	0.25
Void volume fraction	H-form	0.74	0.75	0.72	0.76
	OH-form	0.73	0.76	0.71	0.80
	PK$_a$	11.26	10.70	11.13	11.24
	PK$_b$	3.84	3.76	3.82	4.12
Isoionic point		7.55	7.23	7.48	7.68

*CEC = cation exchange capacity *AEC = anion exchange capacity

R K Khanna(R1843C2 D3NN On 512 system)

Table 3—Oxidation resistance of resin

Resin	Per cent moisture untreated exchanger		Per cent moisture H$_2$O$_2$ treated exchanger		Increase in per cent content	
	H-form	OH-form	H-form	OH-form	H-form	OH form
Fu-Ben-Ga	5.22	6.26	14.03	16.93	8.81	10.97
Fu-Ben-PHY	4.90	5.15	12.48	15.43	7.58	10.28
Fu-Ben-Sa	4.02	4.93	11.59	15.03	7.57	10.01
Fu-Ben-HY	5.01	5.98	13.56	16.34	8.55	10.36

R K Khanna(R1843C3 D3NN On 512 system)

Table 4—Effect of temperature of equilibration on the capacity of the resin

Resin	Equilibration period = 2 hr (Amount of resin = 0.5 g) Total AEC (meq g) of absolutely resins as determined at temp °C			Total CEC (meq g) of absolutely dry resins as determined at temp °C		
	30	50	70	30	50	70
[Fu-Ben-PHY]	5.21	5.22	5.31	5.34	5.31	5.29
[Fu-Ben-PY]	5.13	5.14	5.23	4.62	4.34	4.23
[Fu-Ben-Sa]	5.23	5.34	5.43	4.13	4.09	4.08
[Fu-Ben-HY]	5.31	5.43	5.54	5.04	4.93	4.81

R K Khanna(R1843C4 D3NN On 512 system)

Table 5—Per cent swelling of resin in various solvents

Resin	Glacial Acetic Acid	Water	DMF	Dioxane	Alcohol	THF	Benzene	Acetone	Pet Ether
Fu-Ben-PHy	2.62	6.61	1.49	1.47	2.46	1.50	0.74	1.56	0.00
0	Fu-Ben-Py	3.33	6.26	0 2.26	9.33	2.47	1.64	0.69	1 1.35
Fu-Ben-Sa	2.74	6.66	2.89	1.87	2.87	1.57	0.93	1.39	0.00
Fu-Ben-Hy	1.77	6.24	1.13	0.84	1.49	0.81	0.61	1.03	0.00