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Cation exchange resins from chemically modified poly(vinyl chloride)

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Summary

Poly(vinyl chloride) has been modified chemically to a cation exchange resin by halogen displacement reactions with phenol sulfonic acid, bisphenol-A sulfonic acid and phenolpthalein sulfonic acid. Ion-exchange capacity, salt-splitting capacity and pH-titration characteristics of these resins have been evaluated. pH-titration behaviour of these resins is consistent with that of a polyfunctional cation-exchanger having $pK_1=2$ and $pK_2=9-10$ corresponding to $-SO_3H$ and phenolic -OH groups respectively. The ion-exchange capacity values are comparable in magnitude to those of polystyrene based commercial cation-exchangers such as Amberlite IR-120 and Dowex-50.

Introduction

A recent report by Biswas and Moitra|1| described the preparation and characterization of cation-exchange resins from poly(vinyl chloride)(PVC) by the halogen displacement reaction of PVC with phenolpthalein(PHEN), bisphenol-A(BIS-A) and m-aminophenol(MAP) followed by sulfonation of the PVC-condensates. However, these resins carry -COOH and phenolic -OH groups but surprisingly no strong $-SO_3H$ groups possibly due to oxidative degradation of PVC matrix during sulfonation |1,2|.

It has now been possible to develop a modified procedure by which PVC can be converted into a polyfunctional cation exchanger containing ionogenic groups such as $-SO_3H$ and phenolic -OH by reacting PVC with sulfonic acids of phenolpthalein, bisphenol-A and phenol. This paper high-lights the procedure used for the synthesis of the resins and their characteristic ion-exchange, salt-splitting and pH-titration behaviour. A recent review on synthetic ion-exchange resins by Biswas and Pakirisamy|3| focused the rather meagre literature available on PVC-based strong acid resins in the face of which the present research with relatively simple and inexpensive experimental involvements is expected to have some interesting significance.

Experimental

Materials : Poly(vinyl chloride) NOCIL; $\overline{M}_v = 8.6 \times 10^4$) was reprecipitated from alcohol-THF mixture. Phenolpthalein (MERCK), bisphenol-A(MERCK),phenol(BDH) and fuming H_2SO_4

(8%; MERCK) were used as supplied.

Synthesis of the sulfonic acids : Phenol sulfonic acid was prepared by a standard procedure|4|. Bisphenol-A sulfonic acid and phenolpthalein sulfonic acid($X-SO_3H$ where X=BIS.A and PHEN) were prepared as follows :

In a 1-litre flat-bottomed flask 1 gm of X and 4 gm of fuming H_2SO_4 were mixed. The mixture was heated in a boiling water bath for 30 minutes with occasional shaking. The flask was then cooled in an ice-water mixture. The resultant viscous syrup, $X-SO_3H$ was then dried in a vacuum desiccator.

Synthesis of PVC-X-SO_3H resins : PVC-X-SO_3H(X=phenolpthalein, bisphenol-A and phenol) resins were prepared by the usual procedure for the polycondensation on PVC|5|. Into a 100 ml two-necked flask equipped with a stirrer, a condenser and an insert tube for N_2, 1 gm of PVC was dissolved in 25 ml of THF to which 3 gms of $X-SO_3H$ were added. The reaction was carried out for different times(Table II) at 60°C. The polymer was precipitated by adding a large excess of methanol. It was then washed with methanol and dried in vacuum for 8 hrs.

Purification : To 25 ml benzene, about 1 gm of the crude polymer was added and the mixture was allowed to stand at 55°C with occasional shaking for about 30 hrs. The insoluble resin was then filtered and dried in vacuum for 8 hrs. The dried resin was washed several times with deionized water until free from sulfate ion|6| and finally dried at 60°C for 8 hrs.

Characterization

IR-Spectra : All IR-spectra were recorded on a Perkin-Elmer 237B Grating Spectrophotometer.

Elemental analysis : Sulfur was estimated by the standard procedure|7|.

Evaluation of ion-exchange capacity: The total ion-exchange capacity was evaluated|8| by the following procedure. A known weight of the dried resin(about 0.3 gm) was crushed and placed in a stoppered pyrex conical flask. About 50 ml of NaOH solution(0.1N) was added; the mixture was kept with occasional shaking for 40 hrs to attain equilibrium. An aliquot(25 ml) of the supernatant liquid was withdrawn and titrated for alkalinity against standard HCl solution(0.1N). A blank experiment was also performed for determining the acid equivalent. From these data, the ion-exchange capacity of the resin was calculated|9| in meq/gm.

Evaluation of salt splitting capacity : A known weight of the dried resin(0.1 gm) was crushed and placed in a stoppered pyrex flask. About 25 ml of 1.0M NaCl solution|8| was added to it and the mixture was kept with occasional shaking for 40 hrs to attain equilibrium. An aliquot(5 ml) of the supernatant solution was withdrawn and titrated against standard NaOH solution(0.1N). From these data, the salt-splitting capacity was evaluated in meq/gm.

pH-metric titration of PVC-X-SO_3H resins : The pH-metric titration of PVC-X-SO_3H resins was evaluated as follows. A known amount of the dried resin(0.1 gm), 10 ml of 1.0M NaCl solution and incremental quantities of NaOH solution(0.07N) were added, keeping the total volume as 50 ml by adding deionized water. The flasks were equilibriated by keeping for 40 hrs with occasional shaking. The equilibrium pH of the supernatant solution was measured by a digital pH-meter and the capacity of each solution was evaluated as before with 25 ml aliquot of the supernatant solution from each flask.

Control solutions (without resin) were prepared using the same procedure, equilibrated for 40 hrs and were subsequently analysed. pK-values were calculated from the inflections in pH-capacity curves by the procedure of Helfferich and others |8-10|.

Results and Discussions

Table I presents some data on the synthesis and characterization of X-SO_3H. Table II represents the corresponding data on PVC-X-SO_3H resins.

All the PVC resins synthesized as above are colored solids, insoluble in all typical solvents for PVC. The presence of absorbtion bands due to O-H bending and C-O streching for phenolic -OH and S=O streching for -SO_3H groups is consistently observed in all the resins. The general insolubility of the resins may be due to the incorporation of the bulky groups in the PVC chains. With bifunctional moieties such as phenolpthalein and bisphenol-A there is an added chance of intramolecular crosslinking (Fig.1) which would further enhance the insolubility of the resins.

Table III summarises ion-exchange characteristics of the PVC-X-SO_3H resins. Remarkably, ion-exchange capacity values in all three resins are significantly higher than those realised with these resins prepared by the earlier procedure |1|. Likewise, the salt splitting capacity|8| values that is, the capacities in the presence of a constant concentration of NaCl, are also significantly higher than the same obtained by the earlier procedure. The presence of -SO_3H groups is further endorsed by the pH-metric titration behaviour (Fig.2). In fact, except for the PVC-phenol-SO_3H-resin, the other two resins exhibit a similar pH-titration pattern, typical of polyfunctional ion-exchangers. In these two resins, the pK_1 and pK_2 values calculated from Fig.2(Table III) by the procedure of Helfferich|9| confirm the presence of -SO_3H(pK=2) |9| and phenolic -OH(pK = 9 - 10)|9| groups. Significantly, for PVC-phenol-SO_3H, pH-titration behaviour is typical of a monofunctional strong acid resin with one inflection with pK = 2 corresponding to the -SO_3H group. The occurrence of phenolic -OH in PVC-PHEN/BIS-A-SO_3H resins is due to the possibility that some of the -OH groups in X-SO_3H actually remain unreacted |1| as condensation may occur through either or both of the two phenolic -OH groups. Such a

TABLE - I

Synthesis and Characterization of X-SO_3H

Synthesis				Characterization			
X	X : SO_3H	Condensation hr	Condensation ^oC	Yeild (%)	Physical state	Color	IR-absorbtion bands common to all compounds (cm^{-1})
PHEN	1 : 4	0.5	80	85	Viscous	Brown	(1)1410-1310(strong) O-H bending and C-O streching vibrations for phenolic -OH. (2) 1210-1030(strong) S=O streching vibration for -SO_3H
BIS-A	1 : 4	0.5	80	80	Highly viscous	Blackish brown	
PHENOL	1 : 1.5	0.5	80	82	Viscous	Deep brown	

TABLE - II

Sunthesis and Characterization of PVC-X-SO_3H Resins

Synthesis				Characterization			
X	PVC:X-SO_3H	Condensation hr	°C	Yeild (%)	Color	Solubility[a]	IR-absorbtion bands common to all the condensates, (cm^{-1})
PHEN	1 : 3	10	60	30	Gray	(-)	(1) 1410-1310 (Strong) O-H bending and C-O streching vibrations for phenolic -OH. (2) 1210-1030 (medium) S=O streching vibration for -SO_3H.
	1 : 3	20	60	79	Grayish brown	(-)	
	1 : 3	22	60	80	Grayish brown	(-)	
BIS-A	1 : 3	10	60	28	Grayish white	(-)	
	1 : 3	20	60	70	Brown	(-)	
	1 : 3	22	60	72	Brown	(-)	
PHENOL	1 : 3	10	60	25	White	(-)	
	1 : 3	20	60	74	Grayish white	(-)	
	1 : 3	22	60	75	Grayish white	(-)	

[a] (-) insoluble in all solvents.

TABLE - III

Ion-Exchange Properties of PVC-X-SO_3H Resins a)

Resin	X	Ion-exchange capacity (meq/gm)	Salt-splitting capacity (meq/gm)	pK-values b)		% of S
				pK_1	pK_2	
PVC-X-SO_3H	PHEN	4.95 (3.08) c)	1.10 (0.52) c)	2.35	8.10	4.7
	BIS-A	4.82 (3.20) c)	1.20 (0.55) c)	2.30	8.20	4.5
	PHENOL	4.64	0.91	2.26	-	4.3
Amberlite IR-120	-	4.3-5 d)	-	-	-	-
Dowex d)-50	-	4.9-5 d)	-	-	-	-

a) All capacity measurements and sulfur estimations have been done with the resin obtained by condensing PVC and X-SO_3H at 60°C for 20 hrs (Table-II).

b) pK-values were calculated from the data of Fig. 2.

c) Figures in parenthesis represent the corresponding values for the resins prepared by the earlier procedure|2|.

d) Polystyrene based commercial resins; manufacturer's data compiled by Helffrich|9|.

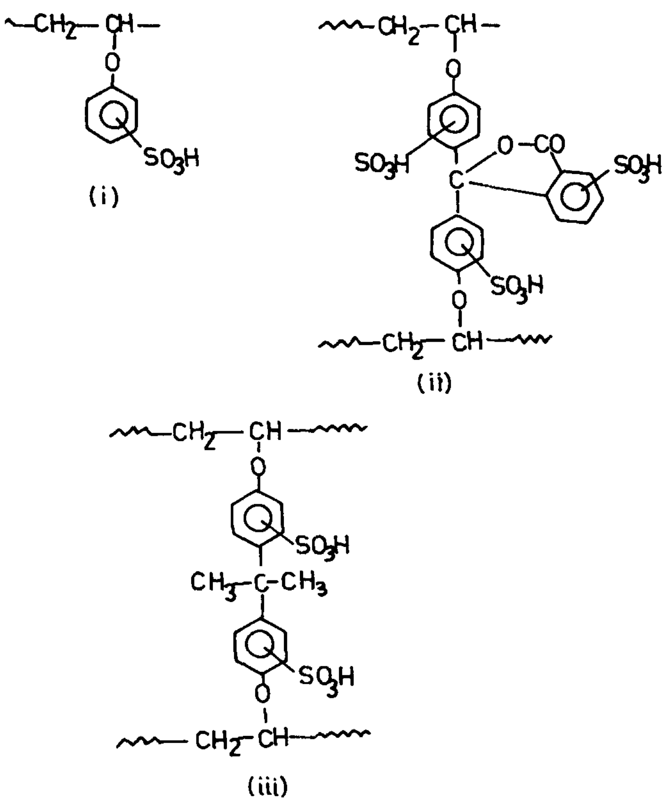

Fig. 1. Tentative structures of PVC-X-SO$_3$H resins.

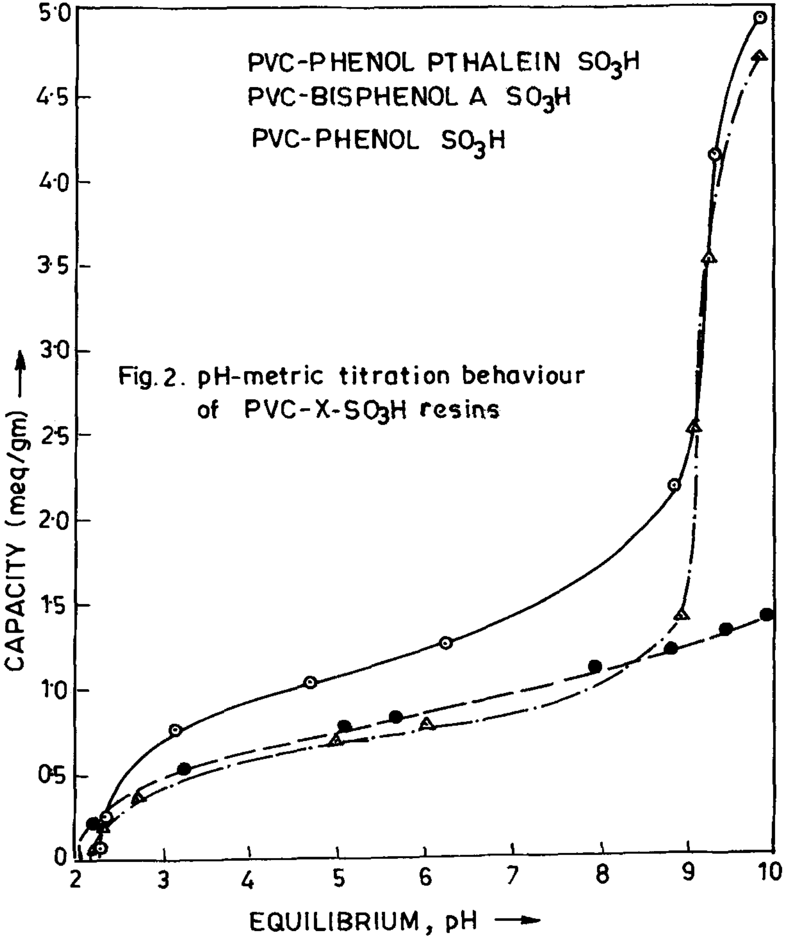

Fig. 2. pH-metric titration behaviour of PVC-X-SO$_3$H resins

possibility would be expected to be unimportant in PVC-phenol-SO_3H resin (one -OH group) so that the question of a free or unreacted -OH group does not arise in this system. This is also endorsed by the characteristic difference in the pH-titration behaviour of PVC-phenol-SO_3H resin relative to the other two resins.

The observed ion-exchange capacities of PVC-X-SO_3H resins are quite comparable to the corresponding data for the polystyrene based commercial cation exchanger resin(Table III). Helfferich|9| has compiled the capacity values of a variety of commercial polystyrene-based and miscellaneous other polymer-based resins which fall in the range 4.3 - 5 meq/gm. It is particularly significant that the PVC-X-SO_3H resins compare favourably with these commercially accepted resins in ion-exchange capacity values.

Acknowledgement

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