Studies on Renewable Polyphenol-Based Cation Exchange Resins of Moderately High Capacity

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SYNOPSIS

Most of the commercially available ion exchange resins at present are either styrene–DVB-based or phenol-based and these are dependent on petroleum products. In view of the ever increasing demand for ion exchange resins and the petroleum crisis, the cost of these resins is going up in leaps and bounds. Although work on ion exchange resins based on naturally occurring tannins and similar materials have been reported in the literature, their low stability, insufficiently low exchange capacity, and similar other disadvantages come in the way of commercial exploitation of these products. In the present communication, studies on preparation and properties, viz., exchange capacity, hydration, swelling, stability, etc. of some effective cation exchange resins which have been obtained from a renewable natural resource of polyphenolic nature and some small proportion of phenol have been reported. The resins studied are stable and of moderately high exchange capacity (2–3 meq/g). Substituting phenol with low-priced renewable polyphenolic material, the resultant copolymer matrix after sulfonation gives ion exchange resins which are quite economic. Their properties are comparable with the commercial resins available in the market.

INTRODUCTION

Condensed tannins are flavonoids in polymer form which are extensively found in various tree barks, heartwood, and the like. They are different from hydrolysable tannins. Hydrolyzable tannins including myrobalans, chestnut extract, etc. are usually mixtures of esters of gallic acid, ellagic acid, and similar materials with a sugar (mainly glucose). They have found application as partial substitutes of phenol in the production of phenol–formaldehyde resin adhesive.[1] However, the low level of phenol substitution they allow and their low nucleophilicity have decreased their economical interest. Condensed polyphenols, on the other hand, are economically and also chemically more attractive and have found applications in the production of adhesives.[2] They include Acacia, Schinopsis (quebracho), etc. from which polyphenols are produced on a commercial scale. The decreasing availability of synthetic phenols due to petroleum crisis augmented research on the application of such naturally occurring renewable condensed polyphenols.

Condensed polyphenols are usually associated with their immediate precursors (flavan-3-ols and flavan-3,4-diols), other flavonoid analogs,[3–5] carbohydrates, and traces of amino and imino acids.[6] Tannins from wattle bark as well as from quebracho contain resorcinol units. Relatively recent studies of Anderson et al.[7] and Ayla and Parameswaran[8] showed that pine tannins from pinus ponderosa and pinus brutia are composed of resorcinolic and phloroglucinolic flavonoids.

Reaction between condensed polyflavonids and formalin is well known.[9–12] Their application as tannin–formaldehyde resin and tannin–phenol resorcinol–formaldehyde resin adhesives is being practices extensively mostly in South Africa and New Zealand in plywood and particle board industry,[13–20] but the application of the resin matrix as ion exchange resin[21,22] has not attracted so much attention, perhaps due to extensive use of styrene–
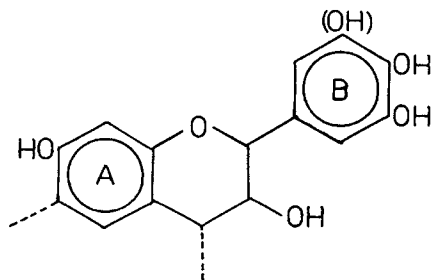
DVB copolymer as resin matrix[23] since 1944. The ion exchangers now used throughout the world are mainly of petroleum origin. In view of the rapid exhaustion of petroleum sources due to various applications of petroleum and its products on an ever increasing scale, the cost of ion exchange resins based on styrene–DVB is increasing rapidly and the need for a renewable source of ion-exchange resin can not be denied.

Randall et al.[24,25] examined the suitability of various barks as ion exchange substrates. They also studied the variations in effectiveness of barks as scavengers for heavy metal ions.

Figure 1 represents the basic structure, i.e., monomer (flavonoid) unit of wattle tannin. Recent studies[26,27] have shown that a wattle or mimosa type tannin molecule consists of 4–12 such units in which the number average mass is approximately 1250 a.m.u. It reacts with formaldehyde to give a resinous product. Marutzky and Dix[26] have condensed tannins from spruce, mimosa, and radiata pine bark with formaldehyde to have tannin formaldehyde resins of lower cation exchange capacity. They have also modified tannin resins with monochloroacetic acid. Sulfuric acid and chlorosulfonic acid were also used by them to have resins of stronger cation exchange capacity.

As direct sulfonation of the flavonoid molecule itself with concd H_2SO_4 is rather a drastic way of introducing sulfonic acid groups into the flavonoid structure, polymerization of tannin by condensation with formaldehyde as well as of tannin–phenol with formaldehyde (in case of copolymer formation) followed by sulfonation of the resultant resin matrix was preferred by the present workers and found effective. They[28,29] have been studying for the last 10 years on the development of suitable cation exchangers using naturally occurring renewable material, tannins, as the basic raw material. Copolymer matrices prepared from polyphenol–phenol and formalin have been found to be most suitable.

Table I Technical Data of East African Wattle Spray Dried Powder (Starting Material of the Present Work)[a]

Tannins	Nontannins	Insoluble Part	Moisture
71.40%	21.60%	1.10%	5.90%

[a] Color readings: red 1.2; yellow 2.2.

Objective

Considering the facts stated above, the present work deals with the development of suitable sulfonated crosslinked tannin–formaldehyde resin and tannin–phenol–formaldehyde copolymer resins as stable and reusable cation exchangers for the application in numerous industrial processes, e.g., water softening, separation of different ions by ion exchange process, hydrometallurgy, and pollution control.

A polyphenolic extract (i.e., of wattle bark) has been collected from commercial source. This has been converted into insoluble resin material by condensing with formaldehyde capable of imparting $-CH_2-$ linkages. Some copolymers have also been prepared by varying the proportion of naturally occurring polyphenol and commercially available phenol. These resin matrices were sulfonated and the exchange capacities of the cation exchange resins so formed were investigated with respect to various cations. Some other physicochemical properties, e.g., swelling, hydration, etc. are also reported in the present paper. The study of various physical aspects of the resin materials and the different industrial applications of the resins will be presented in separate communications.

MATERIALS AND METHODS

Condensed flavonoid tannins (East African wattle extract powder), phenol, formalin, concd H_2SO_4 (98%), and NaOH were used. The technical data of the wattle extract powder used for resin formation is shown in the Table I.

Preparation of "Resin Matrix"

Resin matrices were prepared by polymerizing different proportions[29] of powdered bark extract (i.e., polyphenol) dispersed in water, phenol, and formalin (65% of the weight of the phenolic bodies used). Strong solution (10%) of NaOH was used to maintain the pH of the reaction mixture at 8. The reaction started (as indicated by the increase in vis-

Figure 1 Basic structure of condensed tannin:wattle type.

cosity) within a short while, with evolution of heat. The temperature was maintained at 70°C (using thermostat) till the total mass was resinified. The resultant mass was cooled, allowed to harden, mechanically broken into pieces, and cured at 110°C. The resin matrix without phenol was marked R-600 and the others R-601 through R-606 with increasing proportion of phenol.

Sulfonation of the "Matrix"

The resin matrix was sulfonated by 98% H_2SO_4 in the presence of a sulfonation catalyst and refluxed at different temperatures using a temperature controlled ($\pm1.0°C$) oil bath. R-603 resin matrix was sulfonated at 80, 100, 120, and 150°C separately with necessary precautions as the temperature of sulfonation was increased. All other resin matrices were sulfonated at 100°C ($\pm1°C$). The sulfonated resin was cooled, washed carefully with distilled water to remove free H_2SO_4 and converted to the Na^+ forms using NaCl solution. The Na^+ forms of the resins R-600 SO_3Na–R-606 SO_3Na were washed and dried at 100°C for a few hours in an electrically controlled oven and stored.

Sulfonation of the resin matrix by chlorosulfonic acid was also carried out. The dry resin matrix R-604 was treated with 1.5 times its weight of chlorosulfonic acid out of contact with moisture on an oil bath at 80°C (a higher temperature was not used to avoid brisk evolution of acid fumes and possible degradation of the structure of the polymer molecules) for 4 h with necessary precautions. The resultant mass was cooled in a freezing mixture (ice + NaCl) bath, and the excess $ClSO_3H$ was decomposed by ice cold water very carefully. Finally the sulfonated resin was made acid-free by washing with distilled water, converted to the Na^+ form by using NaCl solution, washed, and dried.

Determination of Exchange Capacity of the Resins

The cation exchangers thus prepared were used for ion exchange studies. Weighed quantities (ca. 2 gm) of the Na^+ forms of resins were taken in burette-type exchange columns; simultaneously the moisture content of each of the samples was determined in the usual procedure.[30] Exchange capacities were studied using solution of A.R. grade chlorides or sulphates of cations under study. For Ag^+ and Pb^{2+}, nitrates were chosen. The aqueous solutions of the salts were allowed to flow downwards through the resin columns at the rate of 3 cm^3/min. Cation content of both the effluents and influents were determined analytically. The resin phase concentrations were determined, in case of monovalent ions, by measuring the exchanged H^+ ion concentration. In case of other ions, e.g., Ca^{2+}, Mg^{2+}, Cu^{2+}, etc., this was done by measuring the difference in concentrations between the influent and effluent as well as by estimating the cation content in the effluent obtained by washing down the ions "sorped"[31] on the resin phase by dil. acids. The M^{2+} ions sorped on the resin phase were taken into solution by leaching down the ions with dil. HCl or HNO_3 (0.1M). Loss of exchange capacity was found to be negligible even after 20 exchanges (Table VII). Cation exchange processes were also studied by batch method; but as concluded by earlier workers, it was found that the column method is superior to batch method.

For the study of exchange by Na^+, K^+, NH_4^+, and $(CH_3)_4^+N$ ions, the resin was converted to the H^+ ion form by 0.1N HCl or HNO_3 as influent, washed with water, and the respective halide solutions (0.1N) were then used as influent. H^+ ions thus released in the effluent were estimated by using standard alkali solution with the help of suitable indicators. Bivalent ions, e.g., Zn^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+}, etc. were determined complexometrically (using 0.01M EDTA and Erio T as indicator) and Cu^{2+} was determined iodometrically. Ag^+ ions were determined by Volhard's method using standard KSCN solution and Fe^{3+} ions as indicator.

Exchange capacities of the resins were also studied by pH-metric titrations using "Systronics" digital type pH meter and 0.1M NaOH in NaCl solution as titre.

Swelling Property

Swelling property of the resins was studied in the simple conventional way. Several measuring cylinders of 10 mL capacity were taken and weighed quantities of the dry resins of different mesh sizes were put into the cylinders, made free from air pockets by careful packing and the dry volumes of the resins noted. Then water was added to each cylinder, and the vessel with contents was shaken and allowed to settle taking care such that no air bubble was trapped in the resin mass and adhered to the side of the cylinder. The system was allowed to equilibrate and the increase in volume (if any) was noted with time.

Study of Hydration

Each sample was kept overnight under water, and filtered; the wet mass was placed into the centrifuge

tube[30] and centrifuged for 5 min at 500 rpm. The resin mass was taken in a weighing bottle, the wet weight (W_w) was taken and allowed to dry in an electric oven set at 105°C and the constant dry weight (W_d) was noted.

Contribution of SO₃H and OH Groups of the Cation Exchanger

In order to find out the contribution of SO₃H and OH (phenolic–polyphenonic) groups of the ion exchanger in the exchange process of H^+/Cu^{2+}, the following experiments were performed. The resins R-603 SO₃Na and R-604 SO₃Na having exchange capacities 2.05 and 2.43, respectively, for H^+/Na^+ exchange were converted to (i) H^+ ion form followed by (ii) Cu^{2+} ion form in resin columns, and the cycles of exchanges for H^+/Na^+ and H^+/Cu^{2+} were repeated (Table IX).

RESULTS

I. Starting material, i.e., the bark extract used in the experiment, contained only 71.4% of the polyphenolic bodies (Table I). Table II gives the data

on the amount of polyphenolic material (in case of R-600) and polyphenolic–phenolic materials (in the cases of other resins) used in the preparation of resin matrices and the corresponding amount of the sulfonated resins produced. The amount of product obtained is quite satisfactory which suggests that most of the phenolic part in the bark extract has been substantially utilized in the resin formation. Table II points out that excessive use of phenol is not advantageous considering the amount of product obtained (see Discussion also).
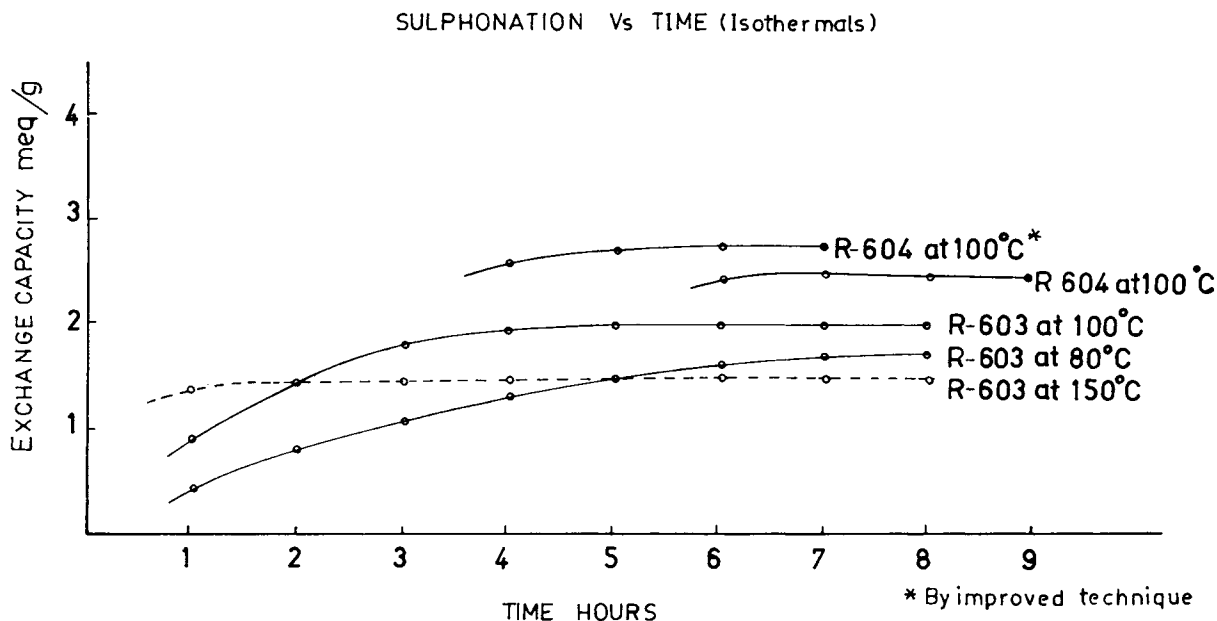
Exchange capacity of R-604 SO₃Na, using 98% H_2SO_4 as sulfonating reagent, could be raised up to 2.60 meq/g and that using chlorosulfonic acid gives the value 2.49 meq/g. Moreover, the latter shows some tendency to be dissolved in aqueous medium even. Therefore, 98% H_2SO_4 was the preferred sulfonating agent.

II(a). Sulfonation vs. time. The extent of sulfonation of the resin matrix with 98% H_2SO_4 was studied by noting the exchange capacity of the sulfonated product taken out of the reaction vessel at known time intervals, which showed that sulfonation reached an optimum value after ca. 6 h (Fig. 2).

Table II   Masses of Materials Used and Product Obtained

Resin Matrix	Total Mass of Phenolic Bodies Used (Tannin + Phenol) Excluding Formalin and Catalyst (g)	Percentage of the Total Polyphenolic and Phenolic Bodies Present in the Starting Material	Sulfonated Ion Exchanger Produced (Na⁺ Form)	Actual Dry Weight of the Sulfonated Ion Exchangers Obtained (g)	Percentage of the Na⁺ Form of the Sulfonated Ion Exchangers with Respect to the Phenolic Bodies Present in the Starting Material	Exchange Capacity H^+/Na^+ (meq/g)
R-600	100	71.40	R-600 (SO₃Na)	92	128.85	1.02
R-601	100	72.83	R-601 (SO₃Na)	93	127.69	1.60
R-602	100	74.26	R-602 (SO₃Na)	92	123.88	1.62
R-603	100	77.12	R-603 (SO₃Na)	91	117.99	2.05
R-604	100	79.98	R-604 (SO₃Na)	96	120.03	2.37[a]
R-605	100	85.70	R-605 (SO₃Na)	86	100.35	3.00
R-606	100	88.56	R-606 (SO₃Na)	82	92.59	0.86

[a] See Table IV.

SULPHONATION Vs TIME (Isothermals)

Figure 2 Extent of sulfonation (related to exchange capacity) vs. time (isothermals).

II(b). Effect of temperature on sulfonation was also studied. The sulfonation experiments on R-603 resin matrix show that the exchange capacity is changed to 1.71, 2.05, 1.60, and 1.53 meq/g for H^+/ Na^+ exchange by sulfonating the resin matrix at 80, 100, 120, and 150°C, respectively, using 98% H_2SO_4 as the sulfonating reagent. These results shown in Figure 3 indicate that the sulfonation reached its optimum value near about 100°C. Temperature higher than 100°C is not suitable due to too much evolution of oxides of sulfur resulting in the lower exchange capacity of the product.

III(a). Swelling property of R-604 SO_3Na is shown in Table III.

III(b). Study of hydration of the resins is shown in Table IV.
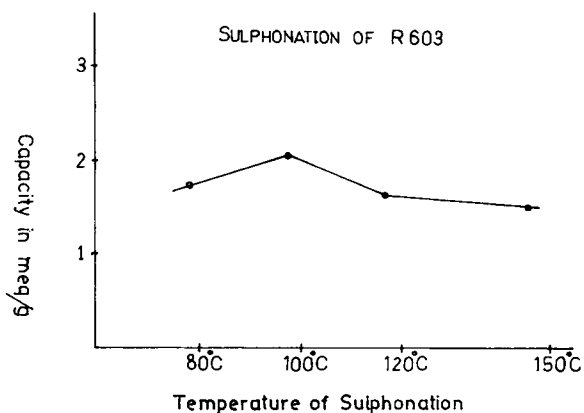
Figure 3 Effect of temperature on sulfonation of R-603 with 98% H_2SO_4.

IV. Stability of the resin sulfonates: The sulfonic acid cation exchange resins discussed are quite stable towards acid and salt solutions. The deterioration of exchange capacity is negligible with time. Even after storing the dry Na^+ form of the sulfonic acid resin for long 10 years, the exchange capacity remains unchanged (Table VIII). In the column also, the exchange capacity of the Na^+ form when kept under water remained almost constant even after 2 years. The exchange capacity is reproducible even after 20 (Table VII) or more exchanges (except for Ag^+, Cu^{2+}, etc. cations, which has been discussed later).

V. Exchange capacity of the resin sulfonate: Exchange capacities with respect to different cations are shown in Tables V and VI.

VI. pH vs. volume of NaOH (in NaCl) titration curves are shown in Figure 4 which shows that the resin in acid form behaves like a strong acid in a solution of high ionic strength.

VII. Cycles consisting of the consecutive exchanges for H^+/Na^+ and H^+/Cu^{2+}, are shown in Table IX.

DISCUSSION

Simple tannin formaldehyde resin (e.g., R-600) has been found to possess ion-exchange capacity, although of lower value. This is due to the presence of weak acidic character of the phenolic hydroxyl group present in it.

Table III   Swelling vs. Mesh Size

Resin	Size of the Resin Particles	Dry Volume (mL)	Wet Volume (mL)	Swelling (%)
R-604 SO$_3$Na	20–30 mesh	2.55	4.00	56.86
	30–72 mesh	3.30	5.20	57.58
	72–100 mesh	3.20	5.05	57.81
	100–120 mesh	1.80	2.85	58.33

In order to produce a resin of better ion-exchange capacity effective in the neutral and acidic range, the introduction of strong acid groups in the tannin–formaldehyde or modified tannin–phenol–formaldehyde resin (TPF resin) is needed. Sulfonation with 98% concd H$_2$SO$_4$ (the cheapest sulfonating agent) has been carried out to get exchangers having reasonable exchange capacity and with high stability in neutral and acid medium. The process adopted here resulted in giving a stable product of long shelf-life too (Table VIII).

The exchange capacity as well as the percentage of hydration of the ion exchangers increase with the increase in the proportion of pure phenolic bodies in the resin matrix (Tables II and IV). It is also quite interesting that the exchange capacity falls off suddenly if the percentage of pure phenol in the resin matrix is increased beyond a certain limit. The increase in exchange capacity with increase in phenol percentage in the copolymer resin matrix may be explained as follows:

i. The structure of the precursor to condensed tannin (wattle) molecule so far known has been mentioned earlier (Fig. 1). The resin (e.g., R-600) formed with tannin molecule alone and formalin restricts the number of sites available for sulfonation due to its par-

ticular conformation in the resin matrix (Fig. 5) as also steric hindrances.

ii. The tannin–phenol–formaldehyde resin may be represented[32] as in Figure 6 which clearly shows that the introduction of phenol units into the tannin–formaldehyde matrix (e.g., R-601–R-605) allows more and more sites for sulfonation as the percentage of pure phenolic bodies is increased and thereby causes greater exchange capacities. As a rule, during polymerization phenol is added to facilitate condensation[30] of the molecules, leading to the formation of resin matrix from phenolic bodies. Tannin molecules being separated by phenol units provide more sites of sulfonation for (a) phenol as well as for (b) tannin units.

iii. When the percentage of phenol exceeds a certain limit (e.g., R-606) the resultant product perhaps becomes more rigid/compact due to high degree of crosslinking leading to some unfavorable structure of the whole copolymer molecule which allows only less number of available sites of sulfonation.

The percentage of hydration varied from 70.4 to 278.6 for R-600 SO$_3$Na–R-605 SO$_3$Na; but in case of R-606 SO$_3$Na it falls off appreciably. The increase of hydration with increase of phenol percentage fol-

Table IV   Study of Hydration

Resin	Percentage of Hydration = $[(W_w - W_d)/W_d] \times 100$	Percentage of Actual Polyphenolic and Phenolic Bodies Present in the Resin Matrices	Exchange Capacity H$^+$/Na$^+$ (meq/g)
R-600 SO$_3$Na	70.4	71.40	1.02
R-601 SO$_3$Na	122.8	72.83	1.60
R-602 SO$_3$Na	119.7	74.26	1.62
R-603 SO$_3$Na	197.0	77.12	2.05
R-604 SO$_3$Na	226.4	79.98	2.37–2.60[a]
R-605 SO$_3$Na	278.6	85.70	3.00
R-606 SO$_3$Na	62.8	88.56	0.86

[a] Exchange capacity of R-604 SO$_3$Na has been increased up to 2.60 meq/g by improved sulfonation process.

lows the same sequence as mentioned above, which also substantiates the assumptions regarding the structural variation due to the variation of phenol content and available sites for sulfonation (hence exchange positions) in the resin matrices (R-600–R-605). Hydrophilic character is increased with degree of sulfonation which is reflected in the exchange capacity. It may be noted that hydration falls off in the resin, R-606 SO_3Na in the sequence, where exchangeable sites are less as pointed out earlier. The hydrophilic character is jeopardized due to high degree of crosslinking which results in a low degree of sulfonation.

Swelling of the resins in aqueous medium is inversely proportional to the particle size for any particular ion exchange resin; the lower the particle size the higher the swelling (Table III). Higher surface area of the resin particles facilitates more water absorption.

The sulfonated resin matrices mainly based on phenolic bodies are susceptible to alkali[33] and behave as strong acids only at higher ionic strengths which is substantiated by pH neutralization curves (Fig. 4). Resins discussed being based on polyphenolic/phenolic bodies are also susceptible to strong alkali. Solubility of the resin in $2N$ or stronger HNO_3 only is also in line with the Amberlite IR-1 type resin[34] (sulfonated phenolic).
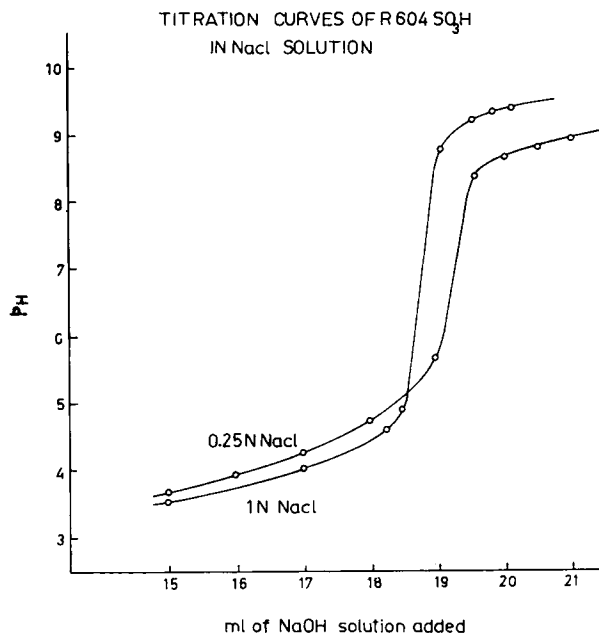

Figure 4 pH neutralization curve of R-604 SO_3H.

The exchange capacity of the resins under discussion is due both for sulfonic acid groups introduced and weakly acidic phenolic OH groups already present, in the resin matrix. Marutzky and Dix[26] tried to estimate the exchange capacity of the resins

Table V Exchange Capacities with Respect to M^+ Ions

Resin	H^+/Na^+ (meq/g)	H^+/K^+ (meq/g)	H^+/NH_4^+ (meq/g)	$H^+/(CH_3)_4^+N$ (meq/g)	H^+/Ag^+ (meq/g) (Apparent)
R-600 SO_3Na	1.02	0.89	—		2.30
R-601 SO_3Na	1.60	1.65	1.57		3.31
R-602 SO_3Na	1.62	1.61	1.52		3.01
R-603 SO_3Na	2.05	2.00	1.91		3.29
R-604 SO_3Na	2.43	2.44	2.33		3.12
R-605 SO_3Na	3.00	3.00	2.98	2.85	3.99
R-606 SO_3Na	0.86	0.91	0.70		1.67

Table VI Exchange Capacities with Respect to M^{2+} Ions

Resin	H^+/Pb^{2+} (meq/g)	H^+/Ca^{2+} (meq/g)	H^+/Mg^{2+} (meq/g)	H^+/Cu^{2+} (meq/g) (Apparent)
R-600 SO_3Na	0.53	0.91	0.79	1.30
R-601 SO_3Na	2.12	1.48	1.58	2.00
R-602 SO_3Na	—	1.63	1.46	—
R-603 SO_3Na	2.40	1.95	1.90	2.42
R-604 SO_3Na	—	—	—	2.83
R-605 SO_3Na	2.32	2.97	2.97	3.15
R-606 SO_3Na	0.75	0.69	0.63	0.59

Table VII Study of Deterioration of Exchange Capacity with Number of Exchanges

Resins	Exchange Capacity H^+/Na^+ (meq/g)				
	1st Exchange	5th Exchange	10th Exchange	16th Exchange	20th Exchange
R-603 SO_3Na	2.05	2.04	2.01	2.01	2.01
R-604 SO_3Na[a]	2.57	2.55	2.56	2.55	2.54

[a] A sample from the improved products.

prepared by them from the sulfur content of the pulverized resins and to compare the exchange capacities so obtained with those determined by titration method. The present work being more concerned with the experimental exchange capacities, the column method of determination was adopted and reproducible results were obtained.

The cation exchange capacities as obtained by estimating the exchanged H^+ ions of the sulfonic acid forms of the resins in the cases of monovalent and some bivalent ions are comparable (Tables V and VI) but the values for Ag^+ and Cu^{2+} ions are somewhat higher. Determination of exchange capacity by estimating the liberated acid is not applicable in the latter cases. Exchange capacity in these cases has been estimated by difference of the influent and effluent concentrations and the capacity based on the "sorped" cations has been termed as "apparent exchange capacity." The higher "apparent" values (Tables V and VI) may be explained as due

to chelation of these metal ions with the other active sites of the resin matrix containing OH (phenolic–polyphenolic) groups, in addition to the normal exchange of the H^+ ions of sulfonic acid groups. In the cases of H^+/Cu^{2+} exchange, the sorped Cu^{2+} ions were released by leaching with $1N$ HCl and the same was estimated and found to be equivalent to that of the apparent exchange capacity, given in Tables VI and IX.

The results of Table IX show that the capacities for each of the H^+/Na^+ and H^+/Cu^{2+} exchanges remain the same in all the cycles studied. The data also indicate that H^+/Cu^{2+} exchange capacity is considerably higher than that of H^+/Na^+ in each cycle, which might be due to the dual contribution of SO_3H and OH (phenolic/polyphenolic) groups in the total apparent exchange capacity for H^+/Cu^{2+}; the role of SO_3H group being common in both the cases, the excess capacity of 0.37 over 2.05 meq/g for R-603 SO_3Na and that of 0.40 over 2.43 meq/

Table VIII Study of Deterioration of Exchange Capacity with Time

| Resin and Its Initial Capacity (H^+/Na^+ Exchange)	Condition of Storage	Exchange Capacity, H^+/Na^+ (meq/g)			
		6 Months	1 Year	2 Years	10 Years
R-603 SO_3Na	When stored dry	2.01	2.02	2.05	2.02
(2.05 meq/g)	When placed under water	2.00	1.99	—	—
R-604 SO_3Na	When stored dry	2.56	2.57	2.57	—
(2.57 meq/g)	When placed under water	2.55	2.54	2.54	—

Table IX Exchange Capacities in meq/g for H^+/Na^+ and H^+/Cu^{2+} [a] Exchange Cycles

| Resin	1st Cycle		2nd Cycle		3rd Cycle		4th Cycle	
	H^+/Na^+	H^+/Cu^{2+} [a]	H^+/Na^+	H^+/Cu^{2+} [a]	H^+/Na^+	H^+/Cu^{2+} [a]	H^+/Na^+	H^+/Cu^{2+} [a]
R-603 SO_3Na	2.05	2.42	2.04	2.42	2.05	2.42	—	—
R-604 SO_3Na	2.43	2.83	2.43	2.83	2.43	2.83	2.43	2.83

[a] Apparent exchange capacity.
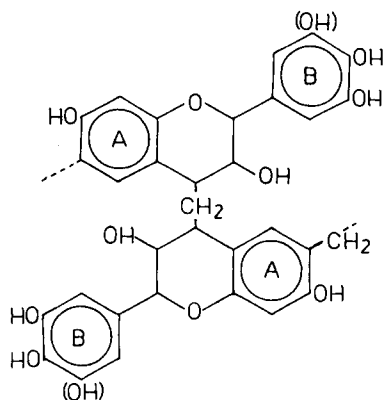
Figure 5 Tannin–formaldehyde resin matrix (showing two crosslinked monomer units—one of the possibilities).

g for R-604 SO_3Na (Table IX) are thus perhaps due to the chelation by the OH groups along with other factors in the exchange process. That the apparent higher exchange capacity value for H^+/Cu^{2+} is not due to the higher valency of Cu^{2+} over Na^+ ion may be corroborated by the fact that the exchange capacities for H^+/Ca^{2+} and H^+/Mg^{2+} are nearly the same (Tables V and VI) as that of H^+/Na^+ exchange.

CONCLUSION

A comparison of the exchange capacities of some of the major commercial cation exchange resins[31] with those obtained from the sulfonated copolymer resins[29] show that the latter resins are quite potentially viable substitutes, considering their long shelf-life, stability under wet condition, low cost, and the like. Standing at the critical juncture of the crisis of petroleum products and search for some renewable sources for ion-exchange resins, the present attempt is found to be successful to a large extent in providing one of the relatively inexpensive as well as renewable sources of cation exchange resins. The
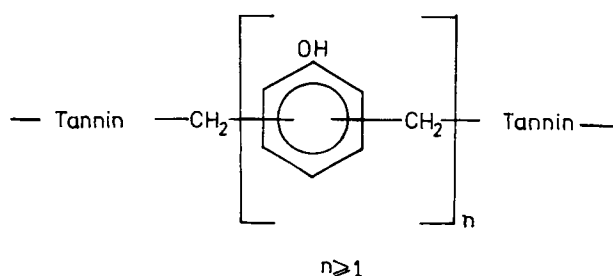
Figure 6 Tannin–phenol formaldehyde copolymer resin.

results on the work in the fields of water softening, treatment of "brackish" water, acid catalysis, hydrometallurgy, dissolution of insoluble electrolytes, etc., with the above resins will be reported in the next communication.

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