

CATION EXCHANGE PROPERTIES OF SULPHONATED LIGNIN-FURFURAL RESIN

M. H. KHUNDKAR AND A. J. MAHMOOD

Department of Chemistry, University of Dacca, Dacca

(Received April 7, 1962)

Lignin has been condensed with furfural in the presence of acid catalyst to prepare an insoluble and infusible (highly cross-linked) resin. This on sulphonation gave a new cation-exchanger. Sulphonation has been carried out under varying conditions and best results were obtained with MnO_2 as a catalyst. Capacity values were determined with a number of standard methods and they compared well. A capacity value of 1.72 m. equiv./g. (for $-SO_3H$ group only) was obtained.

Characteristics of the resin were further studied and it is shown that, besides the $-SO_3H$ group, it also contains $-COOH$ and $-OH$ (phenolic) groups.

Introduction

For a long time, research on ion-exchange had been confined to the study of soils.¹⁻³ These ideas were developed for the preparation of natural and synthetic aluminosilicates. But the limitations of these exchangers, particularly their instability in wide pH ranges, soon became evident. This led to exploration for many years that was responsible for the synthesis of ion-exchange resins⁴ in the late thirties. These resins were so versatile that within a short time they have not only found general application in inorganic analysis, but also for various industrial uses, such as the concentration of a particular inorganic element, industrial water treatment and different problems of demineralization.

As a part of our work on lignin, the possibility of its use for the production of ion-exchange resins was investigated. Although a number of condensation products have been obtained from lignin,⁵⁻⁷ there is no reference to any earlier attempt for these being utilized for developing ion-exchange properties in them. The structure of lignin itself has not yet been settled;⁸ but the presence of a phenolic group has been confirmed. The presence of phenolic group should enable it to be condensed with aldehydes. The presence of the aromatic ring also creates the possibility of subsequent introduction in the resin of sulphonic group necessary for developing cation-exchange characteristics.

On the basis of an earlier work,⁹ after a number of preliminary trials, it was possible to establish the best conditions for the condensation of lignin with furfural giving rise to an insoluble, infusible and highly cross-linked polymer. In the present study, we were able to prepare this resin in a much shorter time; and we further studied the sulphonation of the polymer and the cation-exchange characteristics of the product. Satisfactory results have been obtained, and it is believed that the resins can be utilized for large-scale operation.

Experimental

Preparation of Lignin from Black Liquor.—About 300 c.c. of black liquor (d.1.22 at 29.0°C.) was warmed (50-60°C.) and to the liquor sufficient (400 c.c.) dilute sulphuric acid was added with constant stirring. Precipitated lignin was allowed to settle. The supernatant liquid was decanted off, filtered on a suction and washed. The dried lignin was sieved through 100 mesh sieve (B.S.S.) and stored in bottles. It contained approximately 7% ash. Acetone and dioxan are good solvents for this lignin.

Condensation of Lignin with Furfural.—Technical furfural was distilled to provide very light yellow furfural for this purpose. One hundred and eighty g. lignin was gradually added to 300 c.c. furfural with constant stirring. Almost all the lignin went into solution. Sixty g. concentrated hydrochloric acid was then added. The beaker was gradually heated to 80°C. After a few minutes the viscosity of the solution started to increase. Within half an hour it solidified into a hard mass. After cooling, the black shining lump was broken to big pieces, and dried under infra-red lamp for four hours (temp. 100-120°C.). The pieces were further broken, soaked in 2N sodium hydroxide solution (500 c.c./100 g.) overnight, washed with water, then agitated with strong hydrochloric acid, finally washed free of acid and dried. The particles between 20 and 50 mesh sizes (B.S.S.) were taken for sulphonation.

Yield of the condensation product before washing was about 95% of the total weight of lignin and furfural taken.

Sulphonation of the Resin.—The resin was sulphonated in a beaker. Dry resin was taken and sulphuric acid was added to it with stirring. When the addition of the acid was complete, it was gradually heated on an oil bath to the desired temperature. When a catalyst was used, the resin and catalyst were mixed intimately before adding

sulphuric acid. The relevant data are given in Table 1.

The resin was sulphonated¹⁰ under the following conditions:

- (i) With concentrated sulphuric acid at 120-130°C.
- (ii) With concentrated sulphuric acid at 155-165°C.
- (iii) With concentrated sulphuric acid and oleum (containing 80% H₂SO₄ and 20% free SO₃) mixture (3:1 v./v.) at 120-130°C.
- (iv) With concentrated sulphuric acid in presence of 1% silver sulphate catalyst at 120-130°C. and
- (v) With concentrated sulphuric acid in presence of 8% manganese dioxide catalyst at 120-130°C.

After sulphonation the product was converted into the sodium form by treating with 10% sodium chloride solution. It was dried and sieved to get particles between 20 and 50 mesh sizes. For subsequent operations the resin was regenerated with 2N hydrochloric acid.

Capacity Determination.—For capacity determination, hydrogen-form, oven dry (100±5°C.) resin was taken and the following methods were employed:

- (i) Titration Curve Method: For this 1.0 g.

resin was soaked overnight in 0.1 M potassium chloride solution. The liberated acid was titrated with decinormal sodium hydroxide solution by following the change of pH. As higher values of pH approached stirring of the resin suspension became necessary to facilitate equilibrium.

pH was plotted against milliequivalents of sodium hydroxide added and the capacity was obtained by extrapolation of the inflexion point. Figure 1 represents two titration curves of the resin.

- (ii) Dynamic Method: Five g. resin was taken in a neutral glass column provided with stop-cock and glass-wool. The resin was kept immersed in water overnight, air voids were removed and washed with water. 2N sodium chloride solution was then added from the top of the column and effluent was collected at 10-15 drops per minute till no more acid was liberated. The total acid in the effluent was determined with standard sodium hydroxide solution and from this the capacity per gram of resin was calculated.

- (iii) Limiting Exchange (Barium-Adsorption) Method: One g. resin was shaken with 2N barium chloride solution repeatedly till there was no further liberation of acid. From the total volume of the acid liberated the capacity was obtained as above. This represented the capacity for exchange by sulphonic groups only.

Results are given in Table 1.

TABLE 1.—EFFECT OF SULPHONATING CONDITIONS ON CATION-EXCHANGE CAPACITY OF LIGNIN-FURFURAL RESIN. WT. OF RESIN TAKEN = 60.0 G.

Condition of sulphonation	Ratio of resin to acid (w:v)	Time for complete sulphonation (hrs.)	Capacity (m. equiv./g. dry resin)		
			Titration curve method	Dynamic method	Ba-adsorption method
1. Conc. sulphuric acid at 120-130°C. ..	1:3.0	4.0	1.25	1.10	1.16
2. Conc. sulphuric acid at 155-165°C. ..	1:3.0	5.0	1.12	0.91	1.04
3. Conc. sulphuric acid and oleum mixture at 120-130°C. ..	1:3.0	3.0	1.45	1.14	1.25
4. Conc. sulphuric acid in presence of silver sulphate catalyst at 120-130°C. ..	1:4.0	3.5	1.65	1.17	1.45
5. Conc. sulphuric acid in presence of manganese dioxide catalyst at 120-130°C. ..	1:4.5	4.0	1.72	1.20	1.55

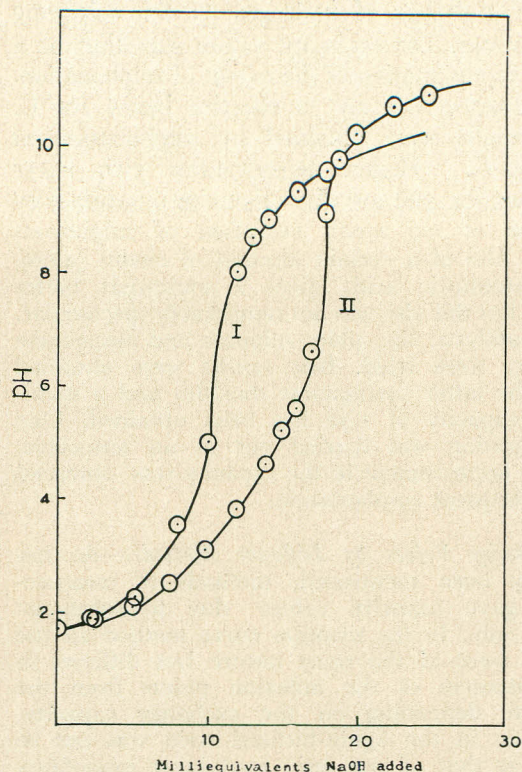


Fig. 1.—Titration curves of sulphonated lignin furfural resin. I. Sulphonated without catalyst. II. Sulphonated in presence of MnO_2 .

Characterization.—Topp and Pepper's¹¹ method was followed. Eight Jena reagent bottles were taken. In each 1.0 g. of the oven-dry (H-form) resin was added. Different volumes of decinormal sodium hydroxide solution, followed by water to make the total volume 100 c.c., were taken in the bottles (Tables 2 and 3). One bottle contained 100 c.c. water only. Sodium chloride was added in each bottle to make the solutions 0.1M with respect to sodium chloride. Bottles were well-stoppered and shaken intermittently for 48 hours. Equilibrium pH as well as milligram equivalents of sodium ions adsorbed in each bottle was determined.

Figure 2 shows the characteristic curves of resin sulphonated in the presence of manganese dioxide catalyst and sulphonated without catalyst at 120-130°C.

Results and Discussion

Information regarding structure of lignin is insufficient to allow putting forward any definite mechanism for the lignin-furfural condensation. Nevertheless, it can be tentatively suggested that the condensation should be of the phenol-aldehyde

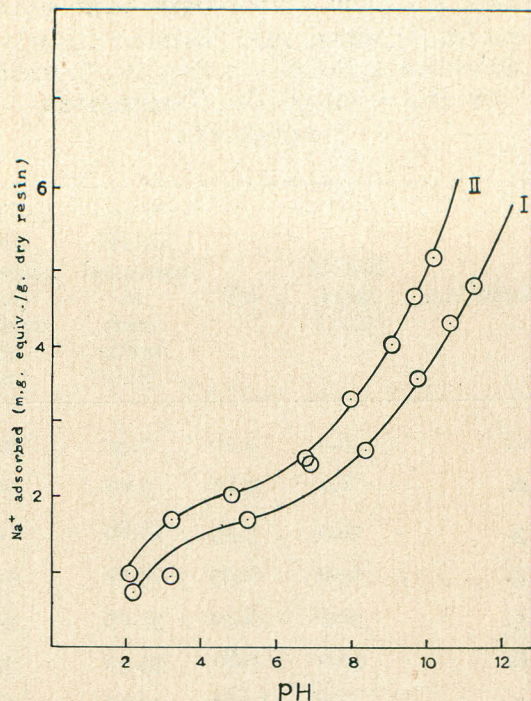


Fig. 2.—Characteristic curves of sulphonated lignin-furfural resin. I. Sulphonated without catalyst. II. Sulphonated in presence of MnO_2 .

type through the formation of reactive intermediates, leading to the formation of highly cross-linked thermosetting resins. Such reactive intermediates are known¹² to result when phenol is condensed with furfural in acidic medium.

In the present investigation also, with concentrated hydrochloric acid as catalyst, condensation was possible within a short time and needed milder operating conditions, and consumed higher proportions of furfural. But with basic catalysts, drastic conditions and higher proportions of lignin were required and the products were of soluble types. Products from condensation in presence of acid was infusible and insoluble. A small amount of low molecular weight polymers that were formed could be easily removed by washing with alkali. This also prevented the resin from throwing colour in solutions of higher pH values.

Sulphonation was carried out in an open vessel on an oil bath. Temperatures recorded were bath temperatures. Reaction started with considerable frothing which subsided towards the end. The effects of variation of conditions of sulphonation on the cation-exchange capacities were studied and results are given in Table 1.

The capacity values (by the different methods) given in Table 1 may be taken to be virtually due

TABLE 2.—RESIN SULPHONATED WITH CONCENTRATED SULPHURIC ACID (WITHOUT CATALYST). STRENGTH OF NaOH = 0.1005 (N). STRENGTH OF HCl = 0.1066 (N). TEMPERATURE = 29.0-30.0°C.

Bottle No.	NaOH taken (c.c.)	pH	(N/10) NaOH consumed in each bottle (c.c.)	Sodium ions adsorbed (m.g. equiv./g dry resin)
1.	0.0	2.20	7.40	0.74
2.	8.0	3.20	9.60	0.96
3.	16.0	5.25	16.60	1.67
4.	24.0	6.95	24.10	2.42
5.	32.0	8.40	31.05	3.12
6.	40.0	9.80	35.40	3.56
7.	48.0	10.65	43.00	4.32
8.	56.0	11.30	47.80	4.80

TABLE 3.—RESIN SULPHONATED WITH CONCENTRATED SULPHURIC ACID IN PRESENCE OF MANGANESE DIOXIDE CATALYST. STRENGTH OF NaOH = 0.1020 (N). STRENGTH OF HCl = 0.1030 (N). TEMPERATURE = 29.8-30.0°C.

Bottle No.	NaOH taken (c.c.)	pH	(N/10) NaOH consumed in each bottle (c.c.)	Sodium ions adsorbed (m.g. equiv./g dry resin)
1.	0.0	2.10	9.60	0.98
2.	8.0	3.20	16.60	1.69
3.	16.0	4.80	19.65	2.00
4.	24.0	6.80	24.40	2.49
5.	32.0	8.00	32.10	3.27
6.	40.0	9.10	39.35	4.01
7.	48.0	9.70	45.75	4.67
8.	56.0	10.20	50.60	5.16

to the exchange of hydrogen in the sulphonic acid groups. The exchange values may thus be a direct representation of the extent of sulphonation. Sulphonation was not so effective below 100°C. Best results were obtained by sulphonation at 120-130°C. Higher temperatures give lower sulphonation and are also otherwise unsatisfactory because of too much evolution of sulphurous fumes. Use of a certain amount of oleum (along with sulphuric acid) gives a somewhat better result, but this also was not remarkably spectacular. Two catalysts, viz., silver sulphate and manganese dioxide, were tried. Best results were obtained with the latter (manganese dioxide) and a maximum capacity of 1.72 has been obtained. One condensation was carried out in an autoclave, but no improvement in the capacity was observed on subsequent sulphonation.

Capacity Values by Different Methods.—As has already been mentioned, methods of measurement gave capacity values due to sulphonic group only. In the titration curve method all the curves were of the same nature but differed in the distances of the inflexion points from the ordinate depending on the exchange capacity. Inflexion in the lignin-furfural resin was not so sharp as that of any resin containing monofunctional sulphonic acid group. Influence of some other groups, probably carboxylic group (active in the pH range 4-10¹³) might be the cause. This will be discussed later on.

A somewhat lower capacity by the dynamic method was evident from the fact that adsorption depended here upon the concentration of the influent, rate of collection of the effluent and particle size of the resin. With lower effluent rate higher exchange may be achieved.

Barium adsorption method gave higher results than sodium adsorption method indicating greater affinity of the resin towards barium ions. Exchange capacity of the lignin-furfural resin can be well compared with that of Amberlite IR-100.¹⁴

Characterization of the Resin.—Determination of the capacity particularly by the pH- titration method indicated that the resin may not be purely a monofunctional sulphonic acid type cation-exchanger. It was, therefore, necessary to characterize the resin, that is, to find out the presence of any other functional groups that might be operative in the cation-exchange process under different pH conditions.

It was found that the characteristic curves for resin sulphonated under different conditions were

of similar nature (Fig. 2). Data presented here were obtained with resin sulphonated with concentrated sulphuric acid without catalyst (Table 2) and with manganese dioxide catalyst (Table 3).

The curves (Fig. 2) show that adsorption starts at about pH 2. The curves consist of three portions. First portion, where adsorption seems to increase without appreciable increase in pH. This part is due to adsorption by sulphonic group. During next phase adsorption increases with pH. But the increase is not very sharp. Had there been only sulphonic group present, adsorption should have increased from the start to the extent depending upon capacity, then remain constant even with increase with pH. Carboxylic group is known to be active in the pH range 4-10 and the effect of phenolic group does not start till pH reaches 8. The second portion of the curve, therefore, appears to be due to combined adsorption by sulphonic and mainly carboxylic groups. If there were only sulphonic and carboxylic groups, adsorption beyond pH 10 should not have been so sharp as shown by the last portion of the curve. This sharp rise is only due to the phenolic group. This sharpness in adsorption started much earlier than usual. This is because, before the effect of carboxylic group stops, the activity of the phenolic group becomes operative.

A critical analysis of the curves and its comparison with the individual curves given by Topp and Pepper for $-\text{SO}_3\text{H}$, $-\text{COOH}$ and $-\text{OH}$ (phenolic) groups justifies the conclusion that the sulphonated lignin-furfural resin is of the poly-functional type containing all these three groups. Further, it may be stated that the exchange capacity of 1.72 was mainly due to the $-\text{SO}_3\text{H}$ group.

That the resin definitely contains some phenolic groups has been further confirmed by studying the characteristics of the resin prior to sulphonation. And the nature of the characteristic curve so obtained (Fig. 3) is exactly of the same type as obtained for phenolic cation-exchangers. Presence of phenolic groups in the resin are only to be expected, and is indicative of the fact that they are not destroyed during sulphonation.

Presence of carboxylic groups in the resin is interesting. These carboxylic groups probably came from the aldehyde groups of the resin during sulphonation.¹³ During condensation all the aldehyde groups of furfural may not be used up. These carboxylic groups were actually determined. Sulphonic groups of the resin were first saturated with calcium ions from calcium chloride

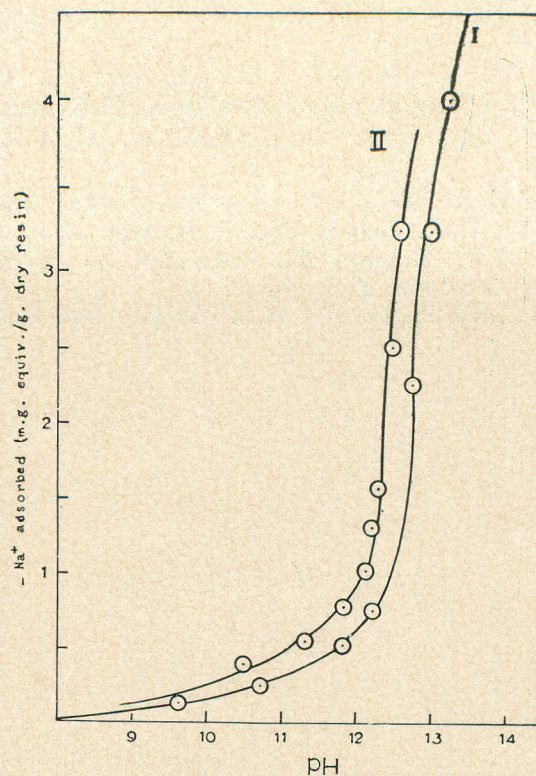


Fig. 3.—Characteristic curves of the unsulphonated resin. I. Phenol-formaldehyde resin. II. Unsulphonated lignin-furfural resin.

solution. The calcium form of the resin was washed free of adhering acid, dried and 1.0 g. was taken. This was shaken with calcium acetate solution until the acid liberation was complete. The liberated acid (by calcium acetate) gave the measure of the exchange for carboxylic groups per gram resin. For resin sulphonated in presence of manganese dioxide catalyst it was 1.70 mequiv./g. for $-\text{COOH}$ groups alone.

Acknowledgement.—The authors wish to record their indebtedness to the Karnaphuli Paper Mills for their constant co-operation in supplying the black liquor used for the preparation of lignin.

References

1. H. S. Thomson, *J. Roy. Agr. Soc. Engl.*, **11**, 68 (1850).
2. J. T. Way, *ibid.*, **11**, 313 (1850); **13**, 123 (1852).
3. E. Z. Lemberg, *Deut., Geol. Ges.*, **22**, 335 (1870); **28**, 519 (1876).
4. B. A. Adams and E. L. Holmes, *J. Soc. Chem. Ind. (London)*, **54**, 1-6T (1935) and other patents.

5. Hermann Bureister, U. S. 2,1920 (Feb. 27, 1940).
6. S. N. Ushakov, I. I. Matveev, Ya. M. Lukomski and O.M. Klimova, *Informatsi-no, Tech. Byull. Glavkhim*, Plant No. 3, 5-16 (1940).
7. A. Wacek and H. Daubner, —Tellenbacher (Univ. Vienna) *Monatsh*, **8**, 266-273 (1951).
8. F.E. Brauns, *The Chemistry of Lignin*, Academic Press (1952).
9. Max Phillip and H.D. Weighe, *Ind. Eng. Chem.*, **23**, 286-287 (1931).
10. M.H. Khundkar and A. J. Mahmood, Pakistan Patent (Application No. 912/61).
11. N.E. Topp and K. W. Pepper, *J. Chem. Soc. (London)* 3299 (1949).
12. A.P. Koschutz, Kudryanzeff and B. Maschkilieson, *Kunststoffe*, **23**, 97 (1933).
13. N. E. Topp and K.W. Pepper, *J. Chem. Soc. (London)* 3301 (1949).
14. H. A. Shah and S. L. Bafna, *J. Indian Chem. Soc.*, **29** (No. 3) 190 (1952).