KINETIC BEHAVIOUR OF THE SULPHONATED LIGNIN-FURFURAL RESIN

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The breakthrough capacity of the sulphonated lignin–furfural resin depends on the condition of sulphonation. This capacity as well as the capacity determined by the dynamic method are influenced by different cations. No other anions, except the acetate, can influence the capacity determined by the dynamic method. Concentration also has marked effect on the sorption of a cation. This effect is much more prominent than the effect produced by the change in the flow rate. The value of the breakthrough capacity does not change even if the resin is taken in the Na^+ form instead of the H^+ form. Moreover, $2M$ NaCl can elute Ca^{2+} ions quantitatively.

Values of the distribution coefficient with different cations increase with the increase of pH up to certain range and then tend to approach limiting values.

The sulphonated lignin–furfural resin is a polyfunctional cation exchanger.[1] Its characteristics as a cation exchanger may not be the same as those expected from a monofunctional cation exchange resin. The present investigation was undertaken to obtain further information on the characteristics of the sulphonated lignin–furfural resin so as to explore its utility for different purposes.

When a salt solution is added to a resin containing sulphonic acid group, the cation of the salt is sorbed and the ions on the resin are eluted according to the following equilibria:

$$R—SO_3H + NaCl \rightleftharpoons R—SO_3Na + HCl$$
$$2R—SO_3Na + CaCl_2 \rightleftharpoons (R—SO_3)_2Ca + 2NaCl$$
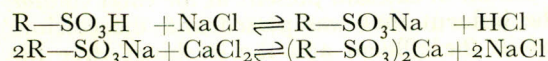
where $R—SO_3H$ and $R—SO_3Na$ represent H^+ and Na^+ forms of the resin. If sufficient amount of the resin is taken in the salt solution it may take considerably long time for the completion of the exchange of the cations of the salt. On the other hand, if the resin is taken in a column, soaked with water, and the salt solution (influent) is dropped from the top and the solution that comes out of the resin bed (effluent) is collected at a reasonable rate the cations will be exchanged much more quickly. The ions removed from the resin (eluate) pass down the column and the equilibria as shown above are shifted towards the right. While passing down the column, the influent is gradually depleted of the cations due to its contact with fresh resin. In this way the influent becomes completely free from the metal ions present in it. At the point of leakage breakthrough occurs. The breakthrough capacity is the total amount of the metal ions sorbed just up to the point of leakage. This is generally expressed in milliequivalents per gram dry resin in the desired form.

In the present paper the ion exchange properties of sulphonated lignin–furfural resin have been studied with different cations and anions and at different pH values. Regeneration characteristics of the resin have also been studied. These studies reveal many characteristics of the resin that appear favourable for the application of the resin in the laboratory as an analytical tool as well as in the relevant industries.

Experimental

Column Specification.—The column was made from a Jena glass tube (48 cm long, 2.36 cm in diameter) having a two-way stopcock attached at the end. The column is continuous through one of the ways of the stopcock with a glass tubing drawn into a nozzle. To the other way was joined another glass tubing through which was supplied water for back-wash. The stopcock not only regulated the water-flow for back-wash but also helped regulate the rate of collection of the effluent. This column was used for studying the breakthrough and the regeneration characteristics. For other purposes smaller columns (1 cm $\times$ 15–20 cm) were used.

Pre-treatment of the Resin.—The sulphonated resins were taken in the column. The resin rested on glass wool in the column and it was washed free of the sulphuric acid. A 10% sodium chloride solution was dropped on the resin and the effluent was collected at the rate of 30–50 ml/hr. When no acid was detected (tested with methyl red) Na^+ form of the resin was washed free of the chloride ions, taken out of the column and sucked dry on a Buchner funnel. The air dried Na^+ form resin was sieved and the particles between 20–50 mesh size (B.S.S.) were taken. The sieved resin was oven-dried at $100\pm5°C$ for constant weight, cooled in a desiccator and 50.0 g of this resin was taken in the column, soaked in water overnight and back-washed to remove air voids. The resin bed was 27 cm long.

When desired, the Na^+ form resin was converted to the H^+ form by dropping 2M hydrochloric acid at the above rate until no Na^+ was detected in the influent. The column was then washed free of the excess acid.

Procedure for Determining the Breakthrough Capacity.—In order to find out the breakthrough of the exchange of H^+ on the resin and Na^+ of the solution $10^{-2}M$ sodium chloride solution was used as the influent. The resin, though weighed in the Na^+ form, was converted to H^+ form in the column. Sodium chloride solution was dropped from the top of the column and the effluent was collected at a constant rate. The acid liberated in different samples of constant volume were determined by titration with standard sodium hydroxide. Breakthrough capacities for Li^+ and K^+ ions were determined similarly. But for other metal ions samples were collected and tested for the metal ions in the effluent, that is, for the leakage. Samples were collected until there was leakage. The column was then washed

free of the metal ions and metal ions sorbed on the resin were eluted with 2N hydrochloric acid at the rate of 30–50 ml per hr. From the amount of the metal ions eluted, the breakthrough capacity was determined. The results are presented in Table 2.

Capacity by Dynamic Method for Different Ions.—The resin taken in the column was converted into the H^+ form. For Na^+, K^+, and Li^+ ions the influent was passed till there was no acid liberated (tested with methyl red indicator). The effluent was collected and the liberated acid was determined with standard sodium hydroxide solution. A blank titration was performed with equal volume of water and the alkali consumed was subtracted from the volume needed for the determination of the total acidity. From the strength of acid the capacity was determined. For other cations the influent was passed till the effluent concentration was the same as that of the influent. The column was washed free of the metal ions and the sorbed cations were eluted with 2N hydrochloric acid. From the total amount of the eluted metal ions the capacity was determined. The results are presented in Table 3.

Regeneration Characteristics.—The regeneration characteristics were studied with the calcium ions only. The resin in the column was in the Na^+ form and the calcium solution was passed through the column. The total calcium solution passed through was always greater than that needed by the theoretical calculation. The column was washed free of the unsorbed ions. The effluent and the washings were collected and analysed for calcium. The difference between the amount of calcium present in the total volume of the influent that was passed and the calcium found in the effluent and the washings gave the total amount of the calcium sorbed on the resin.

TABLE 1.—THE EFFECT OF CONDITIONS OF SULPHONATION ON THE BREAKTHROUGH CAPACITY.

Resin taken=50.0 g; temp=28-29°C; 0.05N NaOH; volume of each sample collected=200 ml (at 10-min intervals).

Conditions of sulphonation	Breakthrough capacity (mequiv/g)
Sulphonation at 120–130°C with conc. H_2SO_4	0.24
Sulphonation with conc. H_2SO_4 and oleum mixture at 120–130°C	0.24
Sulphonation with conc. H_2SO_4 at 120–130°C (catalyst Ag_2SO_4)	0.32
Sulphonation with conc. H_2SO_4 at 120–130°C (catalyst MnO_2)	0.48

TABLE 2.—THE INFLUENCE OF DIFFERENT CATIONS ON THE BREAKTHROUGH CAPACITY.

Resin taken=50.0 g; temp=28-29°C; concentration of influent=0.01M; volume of each sample collected=200 ml (at 10-min intervals).

Resin in the form	Cation in the influent	Breakthrough capacity (mequiv/g)	Time for reaching breakthrough point (min)
H^+	Na^+	0.48	240
,,	K^+	0.48	240
,,	Li^+	0.22	120
,,	Ag^+	0.79	380
,,	NH_4^+	0.59	240
,,	Ca^{2+}	0.73	380
Na^+	,,	0.73	380
H^+	Cu^{2+}	0.93	240
,,	Fe^{3+}	0.81	140

The sorbed calcium was eluted with either 2M sodium chloride or 2M hydrochloric acid. The results are presented in Table 4.

Distribution Coefficient.—The distribution co-efficient of a cation with respect to a cation exchange resin is defined by Tompkins and Mayer[2] as equal to the concentration of the cation in the resin phase divided by its concentration in the liquid phase, or

$$\lambda = \frac{M_R/\text{mass of resin in g}}{M_L/\text{volume of solution in ml}}$$

$$\lambda = \frac{M_R}{M_L} \times \frac{\text{volume of solution in ml}}{\text{mass of resin in g}} \qquad (i)$$

where M_R and M_L are the fractions of the cation M in the resin and liquid phase respectively, and λ is the distribution coefficient at equilibrium.

Expression (i) can be expressed as:

$$\lambda = k\frac{M_R}{M_L} = k.\frac{M_O - M_L}{M_L} \qquad (ii)$$

where k is a constant and equal to the ratio of the volume of the solution in ml to the mass of the resin in g, and M_O is the amount of metal ions present in the feed solution and proportional

TABLE 3.—THE INFLUENCE OF DIFFERENT CATIONS AND ANIONS ON THE CAPACITY (BY THE DYNAMIC METHOD).

Resin taken=5.0 g; concentration of the influent=0.01M; rate of flow=30 ml/hr; temp=28-29°C.

Cations	Anions	pH	Capacity (mequiv/g)
Na+	Cl⁻	6.32	1.20
	CH₃COO⁻	—	3.80
	Cl⁻	5.20	1.18
K+	NO₃⁻	5.72	1.19
	SO₄⁻⁻	6.14	1.20
Ag+	NO₃⁻	6.90	1.60
Li+	Cl⁻	6.14	1.00
Ca2+	Cl⁻	6.30	1.60
	NO₃⁻	6.10	1.60
	CH₃COO⁻	6.90	4.20
Ba2+	Cl⁻	6.50	1.60
	NO₃⁻	6.60	1.60
Cu2+	Cl⁻	3.66*	1.75
	NO₃⁻	4.30*	1.80
	SO₄²⁻	2.40*	1.80
	CH₃COO⁻	5.00	4.30
Fe3+	Cl⁻	2.20*	2.20
	NO₃⁻	1.76*	2.22
	SO₄²⁻	1.94*	2.18

*Acetic acid was added to prevent hydrolysis.

to the volume, V_O, of the titrant needed for V ml of the feed solution; M_L is proportional to the volume, V_e, of the same titrant needed for the V ml of the solution after the equilibrium is established. If $V_O - V_e = V_d$, (ii) becomes

$$\lambda = k.V_d/V_e \qquad (iii)$$

Expression (iii) was used to calculate the distribution coefficient.

The Na⁺ form of the resin was oven-dried and cooled. 1.000(±0.002) g of this resin was taken in the Jena reagent bottle provided with a stopper. 100 ml of the 10^{-2}M desired metal ion solution was added to the bottle and shaken intermittently for 48 hr (equilibrium was established within this period). The pH values of the feed solutions were adjusted previously by the addition of acetic acid or sodium hydroxide. 50.0 ml of the feed solution and the same volume of the supernatant liquid after the equilibrium was established were titrated with the same titrant.

Calcium was determined with EDTA using murexide as the indicator. Copper and iron were determined in the usual way.

Results and Discussion

Table 1 shows that when sodium chloride solution was used as the influent the breakthrough capacity was the highest for the resin sulphonated in presence of manganese dioxide as catalyst. In the subsequent runs, therefore, the resin sul-
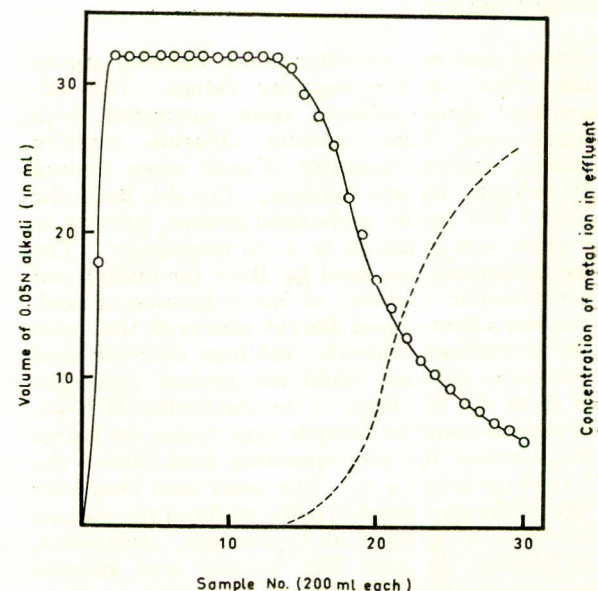

Fig. 1.—Breakthrough characterists of sulphonated lignin-furfural cation exchange resin.

phonated under this condition was used. Figure 1 is the breakthrough curve for the resin sulphonated in presence of manganese dioxide. The nature of the curves for other cases is also the same. Figure 1, a representative of the breakthrough curves, can be explained on the basis of the experimental observations. The amount of the acid liberated in the first sample is not much because the sodium chloride solution displaces most of the water in the column in the beginning. The straight portion of the curve indicates that during this period the exchange (of Na$^+$ by H$^+$ on the resin) has been quantitative. The falling section of the curve is due to the leakage of the sodium ions in the samples of the effluent. As the sodium ions pass down unexchanged the acidity in samples gradually decreases. When the effluent was analysed for the eluting cations the shape of the breakthrough curve was as indicated by the dotted lines in Fig. 1. The straight portion stands for those samples where the eluting cation could not be detected. The sigmoid rise of the curve indicated the gradual appearance of the cations with time. The dependence of the breakthrough capacity on different cations (influents) is similar to the dependence of the capacity by the dynamic method for corresponding cations (compare Tables 2 and 3). When one run was performed at a considerably low rate (5 ml/min) the breakthrough capacity rose to 0.84 mequiv/g. Lowering the rate even to 2 ml/min the breakthrough capacity could not be increased to more than 0.98 mequiv/g. Although the capacity values were relatively higher these rates were considered too slow for practical purposes.

Except acetate, no other anion has any appreciable effect on the capacity values. The sulphonated lignin–furfural resin saturated with calcium ions from calcium chloride solution liberated further quantity of acid when treated with calcium acetate solution. On this basis the capacity due to the carboxylic groups, present in the resin, was found to be 1.70 mequiv/g.[1] The same procedure was used by Roy[3] for finding out the carboxylic capacity of the sulphonated coal. Moreover, Kunin and Barry[4] observed that salts such as sodium chloride, calcium chloride and magnesium chloride could not replace hydrogen ions from the H$^+$ form of the Amberlite IRC-50, a monofunctional carboxylic type cation exchange resin; because the corresponding acid caused the pH to drop below 4.0. The weak acid character of the exchanger restricted the study of the cations that could be present as hydroxides, carbonates, bicarbonates or salts like borates and silicates whose corresponding acids were not too strong to decrease the pH below 4 or 5. We observed that once the exchange groups, sulphonic and car-

boxylic or only carboxylic, were converted to the metal ion form, regeneration with hydrochloric acid to corresponding acid group could be effected readily.

While salt solutions are passed through the H$^+$ form of the sulphonated lignin furfural resin the acid liberated from the sulphonic group lowers the pH considerably and possibly depresses the dissociation of the weak carboxylic group, and the metal ions cannot replace the carboxylic hydrogen ions. When this resin is saturated with calcium ions and the excess acid liberated is washed off, the carboxylic groups in the resin are predominantly exchangeable. When this resin is treated with calcium chloride solution the pH may drop considerably due to the formation of hydrochloric acid and the competitive activity of the hydrogen ions may be such that ultimately the metal ions pass down unsorbed. On the other hand, the acetic acid formed from the acetates may not lower the pH to such extent as to initiate this competitive process and the metal ions are sorbed. Since the metal ions form strong electrolytes with carboxylate ions of the resin the hydrogen ion is capable of replacing these cations.

The high capacities for the cupric and ferric ions may be due to the inherent affinity of the cation exchanger of the present type[5-7] and also due to the addition of the acetic acid to prevent hydrolysis in these two cases. The acetates that may have formed contributed towards the enhancement of the sorption of these ions. Shah and Bafna[8] have observed greater affinity of some industrial resins for alkaline earth metal ions. The characteristics of the lignin–furfural resin are comparable to those studied by these workers. But the present resin has affinity for calcium and barium ions intermediate between those of alkali metal ions and cupric ions.

No obvious correlation between the cationic charge and the approach of the breakthrough point was noted in the present case (Table 2). The breakthrough capacity for the cupric ion exchange was the highest, whereas the capacity (by the dynamic method) is the highest for the ferric ions.

Table 4 shows that as the concentration of the calcium ions in the influent increases, their sorption decreases. With 0.1M calcium solution the capacity by the dynamic method is 1.6 mequiv/g, the rate of elution being 0.5 ml/min. On this basis the column of 50.0 g resin should take up 1.76 g calcium. But at a still lower concentration (0.05M) and at the same rate the calcium uptake is only 1.27 g. Lowering this concentration to

one-tenth and increasing the rate by tenfold the uptake could be increased to only 1.60 g. While determining the capacity by the barium or calcium sorption method[1] a 10% solution was used. The data in Table 4 suggest that the capacity due to the sulphonic acid group could have been higher had a still dilute solution been used. This table also gives us some idea regarding the suitability of the lignin–furfural resin as an industrial "water softener". The calcium sorbed by the Nah form resin could be quantitatively eluted wit[+] 2M sodium chloride solution. Another series of identical operations were carried out and the calcium sorbed was eluted with 2M hydrochloric acid solution. It appears that 2M sodium chloride solution is equally efficient like 2M hydrochloric acid for eluting the sorbed calcium ions. These observations may point to more suitability of the present resin than other resins[9] containing both carboxylic and phenolic acid groups only and having very high selectivity for calcium and magnesium ions.

From the last column of Table 3 the carboxylic capacity was calculated to be about 2.6 mequiv /g. Unlike the capacity due to the sulphonic acid group this capacity appears to remain unaffected by the cations that have been studied. In addition to these two groups, the resin also contains phenolic group.[1] The Na^+ form resin may have only the sulphonic hydrogen ion replaced by the sodium ion and it may have softened water predominantly in this form. Under the present experimental conditions it may be quite unlikely that phenolic group is participating in the water-softening operation. The participation of the carboxylic group in this operation is doubtful on the basis of the experimental data and arguments already put forward.

Different values of the distribution coefficient were plotted against the corresponding values of

pH of the feed solution (Fig. 2). The plots are linear up to certain value of the pH. The dotted lines show the departure from linearity, which is significant. This may indicate that the distribution coefficient approaches a limiting value with the rise of pH. When this value is reached the distribution coefficient may not increase even if the pH increases. The distribution coefficient is directly proportional to the amount of the cation sorbed under identical experimental conditions. Similar rise in the extent of sorption of cations with the increase in pH has also been observed by Walton[10] for ZeoKarb 225. But ZeoKarb 225 should have larger values of the distribution coefficient for the same amount of the resin because of its higher capacity.

Table 5 may indicate that the trend the values of the distribution coefficient follows in the calcium, cupric and ferric ions is the same as that observed in the capacity values of these three ions. The distribution studies may, therefore, indicate that the sorption of a cation by the lignin–furfural resin increases linearly with pH only up to certain limit.
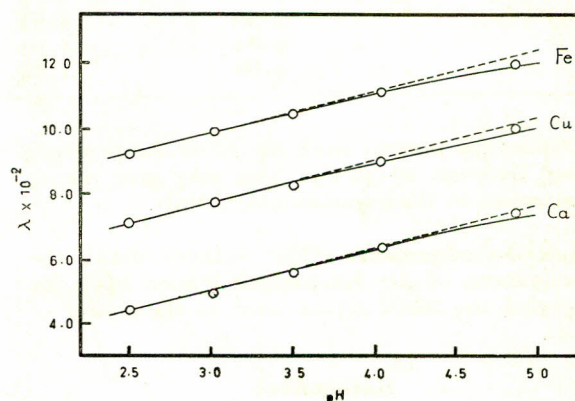

Fig. 2.— Distribution coefficient of different cations for sulphonated lignin-furfural resin at different pH.

TABLE 4.—COMPARATIVE STUDY OF THE ELUTION OF CALCIUM ION BY SODIUM CHLORIDE AND HYDROCHLORIDE ACID SOLUTIONS.

Resin taken=50.0g; temp=28-29 C; concentration of eluant=2M; the rate of collection of the effluent=30 ml/hr (regeneration).

Conc. of Ca^{2+} (M)	Rate of collection effluent (ml/min)	Ca^{2+}soln passed (ml)	Calcium sorbed (g)	Calcium eluted with	
				NaCl (g)	HCl (g)
1.00	0.5	250	0.659	0.660	0.658
0.550	0.5	500	0.847	0.847	0.849
0.275	0.5	1200	1.226	1.227	1.226
0.050	0.5	5000	1.273	1.272	1.273
0.005	5.0	10225	1.604	1.604	1.600

TABLE 5.—DISTRIBUTION COEFFICIENT OF CALCIUM, CUPRIC AND FERRIC IONS AT DIFFERENT pH VALUES.

Resin taken $= 1.000 \pm 0.002$ g; mean value of $k = 100$; volume of feed solution used $= 100.0$ ml; temp $= 29$–$30°C$ V_0 for each of the calcium, cupric and the ferric system is 21.50 ml, 21.9 ml and 23.50 ml, respectively; concentration of EDTA soln $= 2.09 \times 10^{-2}M$; concentration of $Na_2S_2O_3 = 4.38 \times 10^{-2}N$; concentration of $K_2Cr_2O_7 = 5.20^{-2}N$.

Cations		$pH \pm 0.02$	Volume of titrant needed after equilibrium (V_e) (ml)	Difference (V_d) (ml)	V_d/V_e	λ
Ca^{2+}	..	2.50	4.00	17.50	4.38	438
		3.02	3.65	17.85	4.89	489
		3.50	3.25	18.25	5.62	562
		4.04	2.90	18.95	7.43	743
Cu^{2+}	..	2.50	2.70	19.25	7.14	714
		3.02	2.50	19.45	7.77	777
		3.50	2.33	19.60	8.30	830
		4.04	2.20	19.75	8.98	898
		4.86	2.00	19.95	9.98	998
Fe^{3+}	..	2.50	2.35	21.15	9.22	922
		3.02	2.15	21.35	9.90	990
		3.50	2.05	21.45	10.48	1048
		4.04	1.95	21.55	11.10	1110
		4.86	1.80	21.70	12.05	1205

During the present work the room temperature varied between 28–30°C. This may give rise to some errors in the experimental results.

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