937. *Cation-exchange Resins formed by the Acid Condensation of Phenolsulphonic Acid with Formaldehyde.*

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The acid-condensation of phenolsulphonic acid and formaldehyde was examined in detail. The exchange resins varied in capacity from 0·7 to 3 milliequiv./g. The preparative technique developed allows wide variation in equilibrium swelling for any capacity from 1 to 2·8 milliequiv./g.

Under otherwise similar conditions, cross-linking depends primarily on the water content of the reaction mixture. Formaldehyde hydrolyses some sulphonic acid groups, and the unsulphonated phenyl nuclei then partake in cross-linking. With increasing excess of formaldehyde, dependence of both capacity and swelling on the duration of heating becomes more pronounced. The results agree with the Houwink concept of phenol–formaldehyde condensate structure, the resins of highest capacity carrying sulphonic acid groups on about half the phenyl rings. The condensation products are almost as stable to aqueous hydrolysis at room temperature as those of the polystyrene type but retain a certain amount of sorbed electrolyte which is difficult to remove. There is no evidence for ion-association between the fixed-ion and the counter-ion in the case of hydrogen, alkali, and alkaline-earth metal forms of the resins. Certain anomalous heat-drying phenomena and density variations observed require further study.

More than a hundred reported preparations of cation-exchange resins [1] are based on the Lederer–Manasse reaction, which was the method used by Adams and Holmes [2] to prepare

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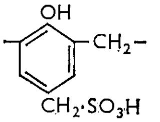
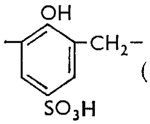
[1] Jakubovic, *Chem. Products*, 1960, **23** 457.
[2] Adams and Holmes, *J. Soc. Chem. Ind.*, 1935, **54**, 1T.

the first synthetic ion-exchange resins. Although many of these deal with the preparation of sulphonic acid resins, few, if any, detailed investigations of the acid-catalysed phenolsulphonic acid (hereafter abbreviated to PSA)–formaldehyde condensation have been published.[3] Commerical emphasis has been either on more complex phenols and aldehydes [4] or on alkali condensations [5] involving addition of sulphites or of free phenol to the reaction mixture. The sulphite-addition method became the standard for preparing resins with sulphonic groups in the side chain (formula A), and addition of phenols is necessary in preparing nuclear phenolsulphonic resins (formula B) by alkali condensation, as sodium phenolsulphonate alone will not resinify satisfactorily with formaldehyde, forming only a sticky, semicrystalline mass.[6,7] The added unsubstituted phenol can be taken to act as the cross-link-forming unit in the condensation. Thus, although the reaction system is more complicated, it can be more adequately controlled commercially.

(A)





(B)

However, for more fundamental investigations, the acid-catalysed condensation is preferable. In this, appreciable amounts of free phenol cannot be incorporated, as this results in inhomogeneity. The work reported here is a detailed examination of this reaction, its application to the preparation of homogeneous rods of the strongly acidic cation-exchange resin, and certain of the resin properties. The ionic mobilities of alkali and alkaline-earth cations in these resins have been dealt with elsewhere.[7,8]

EXPERIMENTAL

Sulphonation of Phenol.—The reaction between approximately equal parts by weight of phenol and sulphuric acid yields a mixture of *o*- and *p*-hydroxybenzenesulphonic acid.[9] At low temperatures up to 40% of the *ortho*-form is obtained, but at 100° this amounts to only 10%. A moderate excess of sulphuric acid can be used without greatly affecting the product. At temperatures above 160° di-*p*-hydroxyphenyl sulphone becomes an important by-product.[10] Disulphonation, on the other hand, occurs only when a large excess of acid is used.

The sulphonation of phenol was investigated systematically to obtain the most suitable PSA starting material. Phenol was heated with a 0·2 molar excess of sulphuric acid at 100° for a given time, and the product analysed. It was found that the percentage sulphonation varied with time of heating; *e.g.*, 5, 30, and 100 minutes' heating gave 85, 92, and 95% sulphonation, respectively. The PSA used in the resin preparations was prepared by heating 1 mole of phenol with 1·2 moles of sulphuric acid at 100° for 2 hours.

Preparation of Resins.—So as to facilitate the subsequent investigation of certain physicochemical properties,[8] the resins were prepared in the form of cylindrical rods, about 4 mm. in diameter and at least 10 cm. in length. In this form the clarity and transparency of the resulting resin rods also gave a good indication of the uniformity of the preparation and the microhomogeneity of the product.

The accepted linear structure for acid-condensed phenol–formaldehyde resins is an alternation of phenyl nuclei and methylene bridges.[11] A certain minimum ratio of the aldehyde to

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[3] B.P.P. 515,517, 654,487.

[4] U.S.P. 2,319,359, the manufacture of Wofatit base exchange resins is reported in B.I.O.S. Report, 1946, No. 621, 22.

[5] B.P. 588,380; Moralli, *Compt. rend.*, 1951, **232**, 332; Kuwada, Misono, Yoshikawa, and Osawa, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1952, **55**, 625.

[6] Kressman and Kitchener, *J.*, 1949, 1190.

[7] Jakubovic, Ph.D. Thesis, London, 1958.

[8] Jakubovic, Hills, and Kitchener, *J. Chim. phys.*, 1958, 263; *Trans. Faraday Soc.*, 1959, **55**, 1570.

[9] Obermiller, *Ber.*, 1907, **40**, 3623.

[10] Zehenter and Fauser, *J. prakt. Chem.*, 1927, **117**, 233.

[11] Vanscheidt, Itenberg, and Andreeva, *Ber.*, 1936, **69**, 1900; Müller and Müller, *Kunststoffe*, 1948, **38**, 221; Meggson, *Trans. Faraday Soc.*, 1936, **32**, 336.

the phenolic constituent is required to produce cross-linking; very little branching or cross-linking occurs if the phenol is even in slight excess.[12] First signs of gelation appear when the molar ratio of formaldehyde is increased from 0·863 to 0·869 to one of phenol.[13]

In the preparations reported here, the molar ratio of formaldehyde to PSA was kept above 1. A systematic investigation of the influence of the ratio of PSA to formaldehyde and water was undertaken. So as to eliminate any variation in the composition of the reactants other than that caused by the actual reaction, the preparations were carried out in sealed tubes. The proportion of sulphuric acid to PSA was kept constant, as the course of the reaction and the products could be controlled and varied more readily by changes in the other components and in reaction conditions.

The standard mixture of PSA and sulphuric acid was diluted with the requisite amount of water, and the formaldehyde solution added. After thorough mixing the whole was transferred to a glass tube about 20 cm. long, having an internal diameter of 3 mm. Throughout the preceding dilution, mixing, and transfer, the solutions were kept below 10°. The open end of the tube was drawn out before filling, so that a momentary application of a fine jet of flame at the tip sealed off the tube. A space of at least 2 cm. was left between the surface of the reaction mixture and the sealing-off point. Nevertheless, about 0·5 cm. at each end of the resin rods was cut off and discarded. It was found that displacing the air remaining in the tube with nitrogen had no detectable effect on the course of the reaction or on the product. The condensations were carried out by heating the tubes in an oven at the required temperature.

Determination of Ion-exchange Capacity.—The resin rod was repeatedly equilibrated with N-hydrochloric acid and then washed with de-ionised water until the washings gave no reaction for chloride ions and had pH 5—7. The resin, now in the pure hydrogen form, was weighed in a stoppered tube, excess of water being removed from its surface by rapidly mopping the rod between two hard filter-papers. It was then equilibrated successively at least three times with the neutral salt solution concerned, the portions being collected for titration with standard alkali. The exchange capacity was expressed as milliequiv. of H^+ per g. of swollen resin in the hydrogen form. The results were reproducible to $\pm 0{\cdot}5\%$ or better. An alternative method tried consisted of titration *in situ*, the resin being equilibrated with the salt solution and the liberated acid back-titrated at intervals; however, this was not normally used, for the several titres required made it less accurate and the indicator tended to be sorbed by the resin.

Determination of Water Content at Equilibrium Swelling.—The weighing of the resin was carried out as described in the previous section. The technique of mopping by rolling the rods between hard filter-paper was investigated and found to give water content results reproducible within $\pm 0{\cdot}2\%$. Two methods of drying were used.

(a) *Heat-drying.* Drying below 100° was unsatisfactory as constant weight was not reached for many days. Heating at 115—120° gave good results in several hours. The resins could generally not be re-swollen, however. To ascertain whether this was due to further reactions (see p. 4826) which could affect the water content, an alternative drying technique was investigated.

(b) *Vacuum-drying.* This was carried out for 10 days in a vacuum-desiccator over phosphoric oxide, the pressure being kept below 1×10^{-3} mm.

The results obtained with several resins by these two methods were in good agreement, the differences being not more than $\pm 0{\cdot}2\%$. However, as the resin rods generally shattered during the desiccation, re-swelling could not be examined readily, but again did not seem to occur.

Determination of Density.—The dry weight and volume of the resin rods were measured, and the density obtained in the usual way. The volumes were determined by displacement of light petroleum in a micro-burette. The results were irreproducible; this may be connected with the irreversibility of drying and re-swelling.

RESULTS AND DISCUSSION

The results are given in the Tables. The molar proportions of PSA and sulphuric acid are not quoted in Table 1 as they were kept constant, being 1·0 and 0·2 throughout.

General Considerations.—Some overall trends which can be discerned from the results will be discussed first. When the PSA : formaldehyde ratio is kept constant, under similar

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[12] Bettleheim and Nihlberg, *Svensk kem. Tidskr.*, 1947, **59**, 31.

[13] Pollack and Riesenfeld, *Z. angew. Chem.*, 1930, **43**, 1129.

reaction conditions the cross-linking is greater the smaller the water content of the reaction mixture. This could be due to several causes, such as retardation of the reaction between formaldehyde and PSA by the dilution effect, or attenuation of hydrolysis of the sulphonic acid groups necessary for cross-linking to occur (see below). However, it has been shown that under acidic conditions the condensation of phenol and formaldehyde leads directly to methylene bridging [11] and, therefore, the lessened cross-linking caused by increasing amounts of water would be a direct consequence of the shift to the left in the equilibrium

TABLE 1. *Molar composition of the reactants, reaction conditions and characteristics of resins.*

Resin no.	CH_2O	H_2O	Hours of heating		H_2O content (%) at eq. swelling of H^+ form	Molar ratio, water to phenol, at eq. swelling	Exchange capacity (meq./g.)	
			At 85°	Addl. at 100°			Swollen resin	Dry resin
1	1·3	8	2·0		65·0	12	0·963	2·75
1S			0·5	1·5	63·7			
1H			16·0		65·1		0·963	2·76
2	1·3	15	4·0		75·7	25	0·681	2·81
2S			0·5	3·0	73·7			
2H			34·0		73·7		0·709	2·70
3	1·3	30	10·0		88·5	63	0·328	2·84
3S			0·5	9·5	84·5			
3H			61·0		84·4		0·422	2·70
4	1·7	9	2·0		63·3	13	0·849	2·31
4S			0·5	1·5	60·2			
4H			16·0		60·7		0·767	1·95
5	1·7	16	4·0		74·7	23	0·603	2·38
5S			0·5	3·5	71·6			
5H			34·0		71·2		0·584	2·03
6	1·7	31	10·0		86·2	47	0·319	2·32
6S			0·5	9·5	82·4			
6H			61·0		81·6		0·379	2·05
7	3·5	11	2·0		71·3	17	0·441	1·54
7S			0·5	1·5	66·9			
7H			32·0		63·9		0·263	0·73
8	3·5	20	4·0		87·8	51	0·229	1·89
8S			0·5	3·5	86·4			
8H			55·0		84·2		0·263	1·02
9	3·5	37	15·0		89·4	57	0·190	1·80
9S			0·5	14·5	84·5			
9H			75·0		83·9		0·195	1·21
10	1·58	24	5·0		81·9		0·476	2·64
11	3·38	31	8·0		86·7		0·234	1·76
12	3·38	31	30·0		82·3		0·274	1·55
13	4·23	26	10·0		82·8		0·259	1·50
14	2·06	25	8·0		81·2		0·422	2·22
15	2·05	38	146·0		86·7		0·177	1·33
16	2·06	25	60·0		82·9		0·246	1·42

$$2HO{\cdot}C_6H_4{\cdot}SO_3H + CH_2O \rightleftharpoons [HO{\cdot}C_6H_3(SO_3H)]_2CH_2 + H_2O$$

Nevertheless, the results also support the retardation of the hydrolysis of sulphonic acid groups. Thus, resin 9, produced by 15 hours' heating, had a higher exchange capacity than resin 7, which has been heated for only about 2 hr., but which was formed in the presence of less than a third of the water present in the condensation of resin 9.

For equimolar ratios of PSA to water, the formaldehyde concentration, particularly at the lower ones investigated, has only a small influence on the equilibrium swelling of the resultant resin, but a marked effect on its capacity. This indicates that the formaldehyde takes part in the hydrolysis of the sulphonic acid groups, which is confirmed by the fact that the rate of loss of capacity during the reaction is greater the greater the formaldehyde concentration. It is also significant that this rate is lowered by increasing the water content of the reaction mixture.

In the preparations where a high PSA : formaldehyde ratio was used, the duration of heating (from 2 to 60 hr.) was without much influence on the capacity of the product throughout the wide range of water contents employed. This is a further indication that the formaldehyde is operative in the hydrolysis of the sulphonic acid groups and, once exhausted, the polyacid is stable to hydrolysis under the experimental conditions. The additional cross-linking produced on prolonged heating is on the whole negligible, being significant only in the case of resin 3, which has the highest water content in the reaction mixture.

Use of intermediate PSA : formaldehyde ratios at corresponding water contents results invariably in resins of lower capacity and swelling. Heating prolonged by a factor of about 8 causes a decrease of some 15% in exchange capacity and an approximately 5% decrease in equilibrium swelling. These findings further confirm the view that the formaldehyde not only links and cross-links the aromatic rings, but also hydrolyses sulphonic acid groups from some of the phenolic nuclei.

The results for the lowest PSA : formaldehyde ratio show a marked dependence of both capacity and swelling on the time of heating. Thus heating for 75 hr. instead of 15 hr. decreases the capacity by a third, and increases the solid content of the swollen resin by more than a half. However, the first signs of the onset of inhomogeneity could be detected with resins obtained after prolonged heating and having very low capacities.

Cross-linking, as measured by equilibrium swelling changes, proceeds much more rapidly at the higher curing temperature. This can be seen be comparing the various S and H resins, particularly those of 2—6. To bring about similar cross-linking requires 6—10 times as much heating at 85° as at 100°. This does not hold for the resins 7, 8, and 9 prepared with a high formaldehyde ratio, again illustrating the more complicated nature of the reaction in presence of a large excess of formaldehyde.

The exchange capacity of the resins varied between 0·7 and 3 milliequiv./g. As the phenolic hydroxyl groups do not take part in exchange reactions at a pH below 10, and all the exchange data were obtained at a pH not exceeding 8, the capacity represents the exchangeable hydrogen ions of the sulphonic acid groups, provided it is independent of factors such as counter-ion valency, resin particle size, and electrolyte solution concentration. As noted elsewhere, this was shown to be the case. Considered as for a sulphonic acid, the capacities correspond to equivalent weights between 300 and 1000. These results are comparable with those of Kressman and Kitchener,[6] who used an alkali-condensation technique for preparing a PSA exchanger.

The resin structure being considered to consist of phenyl nuclei linked by methylene bridges, the number of phenyl nuclei per unit weight of the resin can be calculated from the equivalent weight. Thence, the molar ratio of water per phenyl unit can be obtained. Comparison of this value with that for the reaction mixture shows that in all cases the resin as prepared was below its equilibrium swelling. This was borne out by the increase in volume on washing and water equilibration of the resin rods after preparation.

Structural Considerations.—Although the very low pH at which the reactions have been carried out favours the formation of 4,4′-dihydroxydiphenylmethane,[14] as the PSA used was mainly the *para*-compound, the 2,2′-isomer is probably the major initial chain former. This accords well with the findings of Koebner,[15] who isolated compounds with up to 7 nuclei in the condensation of *p*-cresol.

It has been shown [16] that in all types of phenol–formaldehyde condensations the phenolic hydroxyl group remains virtually unaffected, with the possible exception of certain quinone methide transition compounds, which may also account for the coloration of these condensates. No conclusive evidence was found in this work for any decrease in the content of phenolic hydroxyl groups. Within the limits of the accuracy of the determination of the capacity of these resins at high pH, the total capacity so determined

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[14] Finn and Musty, *J. Soc. Chem. Ind.*, 1950, **69**, 49.

[15] Koebner, *Z. angew. Chem.*, 1933, **46**, 251.

[16] *E.g.*, Martin, "Chemistry of Phenolic Resins," Wiley, New York, 1956.

was found to coincide with the sum of the sulphonic acid capacity (as determined below pH 8) and the phenolic capacity as calculated. However, experimental difficulties associated with the pH range at which the phenolic hydroxyls act as exchange sites, coupled with alkali-absorption effects, precluded detailed quantitative examination.

Setting aside this aspect, it can be assumed that the resin matrix of the exchange materials is essentially hydrophobic and remains substantially unaffected throughout. This is particularly likely in acid condensations, for it has been shown that under these conditions negligibly few hydroxymethyl groups are formed.[17] The equilibrium swelling of a given counter-ionic form therefore depends solely on the cross-linking and the exchange capacity, the latter representing the only strongly hydrophilic groups present and, in fact, being responsible for the aqueous gel nature of these cation-exchange materials.

As the capacities of resins 1, 2, and 3 are equal within ±3%, the differences in swelling can be ascribed to cross-linking alone. To illustrate this more clearly, regain values rather than equilibrium swelling can be quoted. Whilst resin 1 has a regain of 2 (two parts of water for each part of resin in the swollen resin), resin 3 has a regain of about 7. Similarly, resins 4 and 6 have the same capacity, yet regains of 1·7 and 6·2, respectively. These very large differences show the wide variation in nominal cross-linking available by the preparative technique used. Comparison with polystyrene-sulphonic acid exchange resins is difficult, however, for the condensation products are more complex, whilst the cross-linking of the styrene resin corresponds closely to the bifunctional agent (usually divinyl benzene) added in the polymerisation. Nevertheless, the highest "cross-linking" which could by such a comparison be assigned to these materials would be 15%. If the structure of these resins consisted of chains of phenyl nuclei linked by methylene bridges, such cross-linking should produce resins of much higher capacity, provided all phenyl nuclei not taking part in bridging the chains retained their sulphonic acid groups. Although chain branching is possible and the structure is probably more complex than is represented by such an orderly arrangement of chains, this would not account for the relatively low capacities. Calculations show that the final products invariably contain more unsulphonated phenyl nuclei than PSA units, whilst if those forming the cross-links were the only unsulphonated units there should be at least five PSA residues for each unsulphonated phenol ring. Clearly, considerable hydrolysis has occurred, but whether more than the above proportion of the freed phenols has taken part in cross-linking or other three-dimensional linkages is speculative. The results obtained provide overall support for a structure of Houwink's " isogel " type; [18] evidence for a somewhat similar " microgel " structure of a PSA–formaldehyde resin has recently been put forward by Koschel and Schlögl.[19]

Hydrolytic Stability of the Resins.—The nuclear phenol sulphonic–formaldehyde cation-exchange resins are said to be less stable than the corresponding materials with side-chain sulphonic acid groups. Conductometric studies of the release of electrolyte (assumed to be sulphuric acid) into an aqueous layer in contact with the resins showed an apparent loss of capacity which was initially high, as compared with that for a polystyrene resin, but which decreased after prolonged washing, as shown:

Loss of capacity per day (% × 10^2).

	Initially	After prolonged washing
Typical resin of present work	2	0·5
Zeo-Karb 215 (nuclear sulphonic)	5	0·5
Zeo-Karb 315 (side-chain sulphonic)	3	0·5
Zeo-Karb 225 (polystyrenesulphonic)	0·2	0·2

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[17] Finn, James, and Standen, *Chem. and Ind.*, 1954, 188.

[18] Houwink, *J. Soc. Chem. Ind.*, 1936, **55**, 247.

[19] Koschel and Schlögl, *Z. phys. Chem.* (*Frankfurt*), 1957, **11**, 137.

It seems that there is always some electrolyte strongly sorbed in the resin, which is responsible for the initial increase in conductivity. Further, it was found that the ammonium form of PSA–formaldehyde resins was also quite stable, less than 0·001% hydrolysing in water per day, and the alkali and alkaline-earth metal forms can be taken to be at least as stable. This agrees with the results of Heyman and O'Donnel,[20] who found no hydrolysis of the alkali-metal forms of a similar resin.

Exchange-capacity, Swelling, and Counter-ionic Form.—Use of lithium, sodium, potassium, rubidium, and cæsium chlorides for capacity determination gave identical results. It was also found that variation in the anion was without influence, chloride, nitrate, sulphate, and others being examined. The exchange capacity was also independent of the concentration of the salt solution, as no difference was found with 2N- and 0·05N-solutions. Capacity determinations using barium and calcium chloride solutions gave the same results as those obtained with alkali-metal salts, even with the highly swollen low-capacity exchange resins. This seems to indicate that the cation is not directly associated with the exchange sites, for the small ion (having a radius of a few Å) could hardly span the mean distance of separation between neighbouring sulphonic acid groups (at least 20 Å). This was further confirmed by the swelling of the resins in the various salt forms. The swelling is an indication of the extent to which the different cations are bound to the anionic groups, this aspect of ion-exchange having received considerable attention.[21] In the resins discussed here, little difference was found in the equilibrium-swelling water contents of the various forms. The alkali-metal forms were swollen to within a fraction of a percent of the hydrogen form, differences between the various cationic forms themselves being insignificant (see Table 2).

TABLE 2. *Swelling of the resins in the alkali-metal forms.*

Resin no.	Counter-ionic form	Equil. swelling (% water)	Alkali-metal content (%)
10	H	81·9	
	Li	81·7	0·327
	Na	80·7	1·10
	K	79·7	1·894
	Cs	75·8	6·278
11	H	86·7	
	Li	86·6	0·161
	Na	86·1	0·538
	K	85·6	0·925
13	H	82·8	
	Li	82·6	0·180
	Na	82·3	0·593
	K	81·8	1·012
	Rb	80·6	2·210
14	H	81·2	
	Li	81·1	0·290
	Na	80·3	0·965
	K	79·4	1·660
	Rb	77·7	3·582
	Cs	75·8	5·548
16	H	82·9	
	Li	82·8	0·170
	Na	82·4	0·562
	K	82·0	0·959
	Rb	81·2	2·090
	Cs	79·9	3·217

The fact that the resins could not generally be re-swollen after drying indicates the occurrence of some irreversible process. One explanation could be that some hydroxymethyl groups formed in the resin condense to methylene or ether bridges. Alternatively, sulphonic acid groups could be split off during the heating, the consequent decrease in the content of hydrophilic groups reducing the capacity for re-swelling. Such losses have been observed by other workers; for instance, heating Dowex 30, which is of the PSA–formaldehyde type, for 16 hr. at 135° halved its exchange capacity, and a loss of about 23% in capacity was sustained at 120°.[22] More recently, this irreversible change on drying of

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[20] Heymann and O'Donnell, *J. Colloid Sci.*, 1949, **4**, 405.

[21] *E.g.*, Kitchener, " Ion-exchange Resins," Methuen, London, 1957.

[22] Bauman, Skidmore, and Osmin, *Ind. Eng. Chem.*, 1948, **40**, 1350.

PSA resins has been observed by Holdoway, Lane, and Willans,[23] who state it to be the object of their further studies.

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[*Received, May 4th*, 1960.]

[23] Holdoway, Lane, and Willans, *Chem. and Ind.*, 1959, 483.