599. *Properties of Ion-exchange Resins in Relation to Their Structure. Part IV.* Swelling and Shrinkage of Sulphonated Polystyrenes of Different Cross-linking.*

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Two methods are described for determining the weight-swelling (g. of water absorbed per g. of dry resin) of resins in bead form. In the first, a sample of swollen resin is centrifuged at 400 **g** for 30 minutes and then weighed, a correction being applied for residual water retained between the beads after centrifugation; after drying, the sample is re-weighed. The second method involves measurement of the increase in concentration which occurs when dry resin (in the hydrogen form) is added to a dilute solution of the acidic dye, Chlorazol Sky Blue FF. The results obtained by the two methods are in good agreement.

It is shown from pycnometric measurements alone that the hydrogen, sodium, and mixed forms of all the resins obey the relationship, $(V_M)_H = (W_M)_H + 0{\cdot}63$, where $(V_M)_H$ is the swollen volume and $(W_M)_H$ is the weight of water absorbed by an amount of the M-form of the resin equivalent to 1 g. of dry hydrogen form. This relationship enables volume changes to be calculated directly from weight-swelling values.

The effect on weight-swelling has been investigated for changes in the degree of cross-linking of the resin, in the cationic composition of the resin, and in the concentration of ambient hydrochloric acid solutions. The absorption of hydrochloric acid by resins in the hydrogen form has been measured.

ION-EXCHANGE resins are hygroscopic, swelling gels which undergo changes in volume in consequence of changes in environmental conditions, *e.g.*, the relative humidity of the atmosphere or the concentration of an ambient solution. Volume changes may also result from changes in the ionic composition of a resin. These effects are of importance from both practical and theoretical view-points. For example, in column applications a high exchange-capacity per unit volume of swollen resin is required; hence a resin which exhibits high swelling in water is at a disadvantage. Again, swelling and shrinkage effects may disturb the uniformity of packing of a bed of resin and thus give rise to unsatisfactory " fronts " in chromatographic separations. With ion-exchange resins derived from cross-linked copolymers of the styrene–divinylbenzene type, the swelling in water depends on the degree of cross-linking and on the nature and concentration of acidic or basic groups present as substituents. For monosulphonic acids of cross-linked polystyrenes, the swelling decreases with increasing cross-linking (Pepper, *J. Appl. Chem.*, 1951, **1**, 124). Thus, the swelling in water provides a useful criterion of the degree of cross-linking of the polymeric framework, a factor which has been shown to influence certain important ion-exchange

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* Part III, *J. Amer. Chem. Soc.*, in the press. Part II, *J.*, 1951, 493.

properties, *e.g.*, the relative affinity coefficients (Reichenberg, Pepper, and McCauley, *J.*, 1951, 493), the rates of exchange (Reichenberg, in the press), and the effective exchange-capacity for large organic ions (Kunin and Myers, *Discuss. Faraday Soc.*, 1949, **7**, 114). The importance of swelling phenomena has been emphasised also in the more recent theoretical treatments of ion-exchange equilibria. In particular, Gregor (*J. Amer. Chem. Soc.*, 1951, **73**, 642) has suggested a direct relationship between the relative affinity coefficient of two ions for a resin, the swollen resin volume, and the partial molal volumes of the hydrated ions within the resin.

For many purposes, information on the volume changes experienced by a resin is of greater interest than the corresponding data relating to changes in weight. The direct determination of the volume-swelling of particulate materials in liquids presents some difficulty but satisfactory results have been obtained by indirect methods. The true volume of a resin saturated in water may be determined pycnometrically provided the weight of water absorbed by the resin is known. Similarly, if the corresponding data are available, the true volume of the resin in contact with aqueous solutions may also be determined. For the measurement of the amount of water absorbed by a resin (the " weight-swelling ") a centrifuge method has proved convenient. Independent confirmation has been obtained in some cases by estimating the increase in concentration which occurred when dry resin (in the hydrogen form) was added to a dilute solution of an acidic dyestuff.

Centrifuge methods have been widely used for determining the weight-swelling of textile fibres (Preston, *J. Text. Inst.*, 1949, **40**, P674). In principle, a sample of material of known dry weight is saturated with water and then re-weighed after being centrifuged to remove excess of liquid. The chief difficulty encountered is that centrifuging—at least at moderate speeds—fails to remove all the water held by capillary forces *external* to the material. In this work, the amount of residual water was estimated from control experiments with surface-sulphonated resins which swelled to a negligible extent.

A similar approach to the determination of the swelling of resins has been described by Gregor, Held, and Bellin (*Analyt. Chem.*, 1951, **23**, 620), who, however, made no correction for the residual water.

EXPERIMENTAL

Materials.—Sulphonated polystyrenes of different cross-linking were prepared in bead form by methods previously described (Pepper, *loc. cit.*). The cross-linking agent was divinylbenzene, which was supplied commercially in the form of a solution in ethylstyrene. During the course of the work, two series of resins, differing with respect to the divinylbenzene solution employed, were prepared. The first series was made from a divinylbenzene solution supplied by Monsanto Chemicals Ltd. containing approximately 33% of divinylbenzene; these resins were used for the studies of relative affinity coefficients previously reported (Reichenberg *et al.*, *loc. cit.*). The second series was made from a solution containing approximately 50% of divinylbenzene, obtained from the Dow Chemical Co. The two series were matched on the basis of the swelling of the unsulphonated copolymers in toluene. The divinylbenzene contents of the monomer mixtures required to give copolymers of equal swelling were found to be in fair agreement. After sulphonation, corresponding members of the two series exhibited the same swelling in water within experimental error.

Surface-sulphonated resins were prepared by treating cross-linked polystyrene beads with sulphur trioxide vapour at 0° for 20—25 minutes. The exchange-capacity of the products decreased with increasing particle diameter; thus, for fractions 100—200 μ and 300—400 μ in diameter, the capacities were 0·03 and 0·01 mg.-equiv. per g. (compared with 5·2 mg.-equiv. per g. for fully sulphonated resin). The surface-sulphonated resins were readily wetted with water and clearly present a hydrophilic surface comparable with that of the fully sulphonated materials.

Determination of Weight-swelling.—*Centrifuge method.* A sample of resin (approx. 1 g. wet weight) was introduced into a glass filter-tube (Fig. 1) fitted with a sintered-glass disc of porosity 2, 3, or 4. The tube and resin were immersed in de-ionised water at 25° for about 1 hour and then placed in a glass centrifuge tube (15 ml.) which was closed with a rubber cap in order to prevent evaporation of water during centrifuging. Since the rubber cap became deformed during centrifuging and tended to seal the filter-tube, two small holes were blown in the filter-tube to equalise pressure inside and outside. The tube was centrifuged at 400 **g** for 30 minutes, the temperature being maintained at 25° by running the laboratory centrifuge (with the lid open) in an air-thermostat. The filter-tube was weighed and re-immersed in water, and the operation repeated. The filter-tube was finally heated at 110° overnight and then dried to constant weight by heating it at 110° at a pressure of 1 mm. Hg with a trap containing phosphoric oxide in the vacuum line. Previously, the weight of the empty filter-tube had been obtained after drying it at 110° and after centrifugation with water alone. These data give the dry weight of the sample of resin and also the wet weight, uncorrected for residual water.

The wet weight of resin was reproducible to ±2 mg. for periods of centrifuging from 30 minutes to 6 hours; losses due to evaporation were completely prevented by the rubber caps. Within the same limits, the wet weight of all the resins examined was constant for centrifuge speeds varying from 1500 to 2300 r.p.m., corresponding to 225 to 530 **g**. Some deswelling with increase in the centrifugal field might be expected with very lightly cross-linked resins. Calculation indicates, however, that the effect is insignificant at the speeds used even with a resin of 2% nominal divinylbenzene content, which was the most lightly cross-linked resin examined. It may be noted, however, that Preston (*J. Text. Inst.*, 1951, **42**, T79) has observed that the amount of residual water decreases linearly with the reciprocal of the centrifugal field at much higher speeds (1000—5000 **g**).

The amount of residual water held externally to the beads of resin after centrifuging was estimated from control experiments with surface-sulphonated polystyrene. A filter-tube was filled with water, centrifuged under the standard conditions described above, and weighed. A known weight of surface-sulphonated resin was added to the tube, which was then immersed in water, centrifuged, and re-weighed. The amount of residual water was found to be proportional to the weight of resin taken. The experiment was repeated with surface-sulphonated resins of different particle diameter. Within the range 100—400 μ, no trend with size was observed, a mean value of 50 ± 5 mg. of water per g. of resin being obtained. This value corresponds to 53 mg. per ml. of resin, the density of the resin being 1·06 g. per ml.

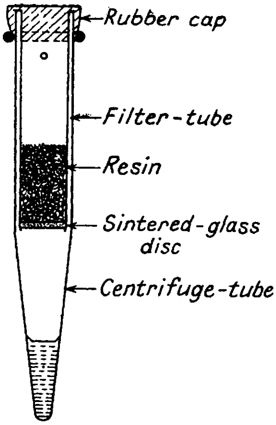


FIG. 1. *Centrifuge-tube assembly.*

An upper limit for the amount of residual water was obtained, independently, from experiments on the absorption of hydrochloric acid by a very highly cross-linked resin (see below). Experiments with samples of different particle diameter again showed no trend within the range 150—400 μ and gave a mean value of 58 ± 4 mg. per ml. of resin. This is in reasonable agreement with the previous value obtained gravimetrically, which was therefore applied as a correction to the weight of wet resin. This correction, which is about 4% of the wet weight, is known to an accuracy of ±10%; the error from this source may therefore be ±0·4% of the weight of wet resin. The overall accuracy of the wet weight per g. of dry resin is 1—2%. For clarity the results are expressed as g. of water absorbed per g. of dry resin.

The centrifuge method was used for the determination of the weight-swelling of resins of different cationic composition. The resin sample in the filter-tube was converted into a known cationic composition by treatment with an appropriate " conditioning " solution (Reichenberg *et al.*, *loc. cit.*). The weight-swelling of the conditioned resin in contact with the solution was obtained by centrifuging it immediately; alternatively, the sample was washed with water and then centrifuged, thus giving the weight-swelling of the conditioned resin in contact with water.

The weight of water absorbed per g. of dry conditioned resin is obtained directly; knowing the cationic composition of the resin and its specific exchange-capacity, the weight of water absorbed by an amount of conditioned resin equivalent to 1 g. of the dry hydrogen form may be calculated.

" Negative absorption " method. Weight-swellings were also determined by measuring the increase in concentration of a dilute solution of a reference solute on addition of the dry resin. The acidic dye Chlorazol Sky Blue FF was selected as reference solute since it may be determined colorimetrically in very dilute solution, and the anion diffuses very slowly and to an extremely small extent into cation-exchange resins (Kressman and Kitchener, *Discuss. Faraday Soc.*, 1949, **7**, 90). A 0·05% solution of the pure dye (Colour Index No. 518) was prepared. The dye had been purified by precipitating the commercial product with sodium acetate and washing the precipitate with boiling ethyl alcohol. This procedure had been repeated three times and the dye dried at 100° overnight.* When this solution was passed through a column containing sulphonated cross-linked polystyrene (hydrogen form), there was no indication of any absorption of dye by the resin. The solution of the dye in the free acid form was then diluted to a concentration of 0·01% (wt./vol.). An accurately weighed sample (0·5—2·0 g.) of the sulphonated cross-linked polystyrene (hydrogen form) which had been dried at 110° as described above was treated with 5 ml. of the 0·01% solution. After 2 hours with occasional shaking, the solution was filtered off from the resin, and the concentration of the dye was measured colorimetrically, a Hilger Spekker absorptiometer being used. The filtrate sample was diluted with water and pyridine to give a final pyridine concentration of 25% (v/v) and a dye concentration of about 0·001% which was found suitable for an accurate determination.

FIG. 2. *Comparison of the results obtained by two methods of determination of weight-swelling.*

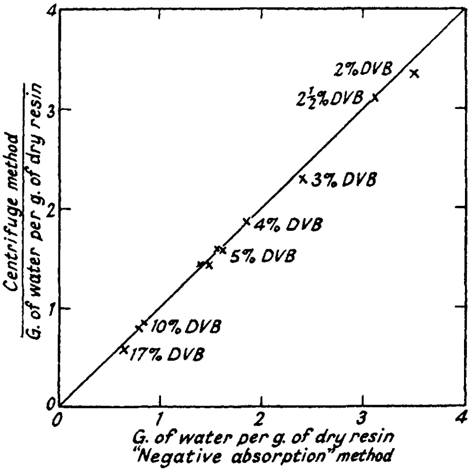
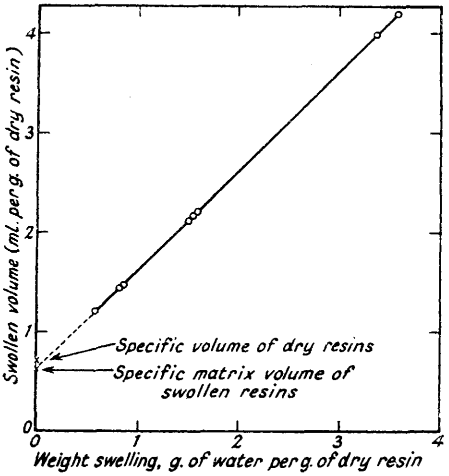


FIG. 3. *Relationship between swollen volume and weight-swelling (hydrogen-form resins).*



Variation in the concentration of dye solution from 0·002% to 0·05% caused no significant difference in the values obtained for weight-swelling.

Comparison of Results Obtained by Centrifuge and " Negative Absorption " Methods.—The weight-swellings of a number of samples of sulphonated polystyrenes of different degrees of cross-linking and particle-size were determined by the two methods, which, as shown by Fig. 2, gave results in good agreement. Also, for a given degree of cross-linking, the values of weight-swellings obtained were independent of particle-size. It may be noted that the results obtained by the " negative absorption " method must represent minimum values for the weight-swelling, since, if the dye is absorbed by the resin or if the swelling of the resin is affected by the concentration of the dye in solution, a low result would be given.

Determination of Volume-swelling.—The weight of water displaced by a sample of swollen resin of known cationic composition was determined at 25·00°±0·02°, a 5-ml. density bottle being used. The dry weight of the sample was obtained by transferring the resin quantitatively to a small filter-tube and then heating it at 110° *in vacuo* to constant weight as described pre-

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* The pure Chlorazol Sky Blue FF was kindly supplied by Imperial Chemical Industries Limited, Dyestuffs Division.

viously. The weight of the swollen sample can be calculated from this dry weight and the weight-swelling, and hence the true swollen volume per g. of dry resin can be obtained.

Specific volumes of the dry resins were determined directly, dry *n*-heptane being used as displacement medium.

Absorption of Hydrochloric Acid by Resins in the Hydrogen Form.—Resin samples in filter-tubes were conditioned with hydrochloric acid solution of known concentration until equilibrium was reached with respect to the weight-swelling and also the amount of hydrochloric acid absorbed. A 30-fold excess of acid relative to the capacity of the resin sample was normally used at a flow-rate of 100 ml. per hour. After conditioning, the resins were centrifuged and weighed; all the acid was then washed out with de-ionised water, and the washings titrated with standard sodium hydroxide solution. The operation was repeated with hydrochloric acid solutions of different concentrations, and finally the resins were dried to constant weight.

From these measurements, it was possible to calculate both the weight of water and the amount of hydrochloric acid absorbed per g. of dry resin for each acid concentration. Corrections were applied for the amounts of water and acid left in the sintered disc of the filter-tube and also retained between the resin beads after centrifugation.

RESULTS AND DISCUSSION

Relationship between Weight-swelling and Swollen Volume.—It was originally intended to measure volume changes indirectly by first determining weight-swellings and then combining these values with pycnometric data. However, the pycnometric data alone indicate that a simple linear relationship between weight-swelling and swollen volume is applicable over a wide range, and hence, within this range, changes in weight-swelling are a reliable measure of volume changes. From the pycnometric measurements *per se* we obtain directly the quantity A given by

$$A = \frac{\text{Weight of swollen resin} - \text{Weight of equal volume of water}}{\text{Weight of dry resin}}$$

The mean values of A_H obtained from pycnometric measurements on the hydrogen forms of different resins are given below :

Nominal % of divinylbenzene	2	5	10	15
A_H (Monsanto DVB solution)	0·373	0·373	0·376	—
A_H (Dow DVB solution)	0·378	0·373	0·373	0·377

Statistical analysis confirmed that there was no significant variation in the values of A_H either with divinylbenzene content or with source of the divinylbenzene solution; the grand mean of all results was 0·374 (standard deviation 0·004).

It follows from the definition of A above that if W is the weight of water absorbed per g. of dry resin (the weight-swelling) and V is the volume of swollen resin per g. of dry resin, then $A = 1 + W - 0{\cdot}997V$, where 0·997 g. per ml. is the density of water at 25°. Since A_H is a constant (equal to 0·374), $V_H = 1{\cdot}003W_H + 0{\cdot}628$. This equation covers the swollen hydrogen forms of all resins of divinylbenzene content from 2 to 15%. On consideration of the variation in swelling with decrease in cross-linking, it appears that the absorption of each additional gram of water is accompanied by an increase in volume of almost exactly 1 ml., *i.e.*, the partial specific volume of water in the swollen resins is the same as in the free state.

It is of interest to consider how far this concept can be extended to cover the variation in swelling of an individual resin with change in relative humidity. If the linear relationship were valid over the whole moisture isotherm, the specific volume of all the dry resins would be 0·63 ml. per g. The densities of the dry resins (hydrogen form) are in fact the same within experimental error; the observed value of 1·43 ± 0·03 g. per ml., however, corresponds to a specific volume of 0·70 ml. per g., which is 0·07 ml. per g. greater than the previous figure. Hence, when a dry or nearly dry resin is allowed to swell in water, there is a contraction in the total volume of the system and at low swellings the volume must increase by less than 1 ml. for each gram of water absorbed. A similar effect is observed with cellulosic materials and other swelling gels. The value of 0·63 ml. per g. will be referred to as the *specific matrix volume* of the swollen resins in the hydrogen form, it being understood that this includes the volume of the sulphonic acid groups. These results are illustrated in Fig. 3, where the individual points have been calculated by combining the mean value of A_H for each resin with the value of W_H obtained by the centrifuge method.

The linear relationship is obeyed by different resins possessing weight-swellings ranging from 3·5 to 0·6 g. of water per g. of dry resin; hence for an individual resin, although the linear relationship is not valid over the whole isotherm, it is probably applicable down to weight-swellings of 0·6 g. of water per g. of dry resin or less. For most resins this corresponds with a relative humidity of about 75% (Pepper, *loc. cit.*).

FIG 4.

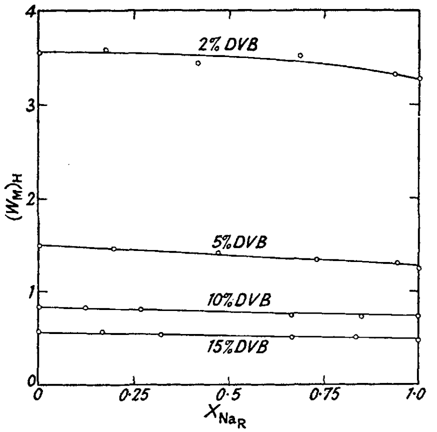
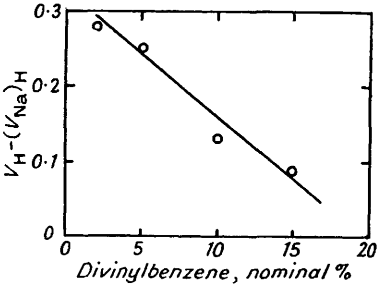


FIG. 5. $V_H - (V_{Na})_H$ *for resins of different divinylbenzene content.*



Pycnometric measurements on the sodium forms of different resins gave a constant value for A_{Na} with a mean of 0·432 (standard deviation 0·006). Hence the specific matrix volume of the swollen sodium salts of all the resins is 0·569 ml. per g. This value is referred to 1 g. of dry sodium resin and cannot be compared directly with the previous figure, which relates to 1 g. of dry hydrogen resin. Taking the specific exchange-capacity as 5·2 mg.-equiv. per g. of dry hydrogen resin, we calculate that 1 g. of dry hydrogen resin is equivalent to $1{\cdot}11_5$ g. of dry sodium resin. The decrease in capacity (5·4 to 5·0) observed with increase in cross-linking affects this factor by less than 1%. Hence the matrix volume of an amount of swollen sodium resin equivalent to 1 g. of dry hydrogen resin is $0{\cdot}569 \times 1{\cdot}11_5 = 0{\cdot}633$ ml., which differs very slightly from the value of 0·628 ml. obtained on the hydrogen resins. The mixed sodium–hydrogen forms of different resins gave a similar result. Hence, we conclude that the hydrogen, sodium, and mixed forms of all the resins obey the relationship

$$(V_M)_H = (W_M)_H + 0{\cdot}63$$

where $(V_M)_H$ is the swollen volume and $(W_M)_H$ is the weight of water absorbed by an amount of the M-form of the resin equivalent to 1 g. of the dry hydrogen form.

Gregor, Gutoff, and Bregman (*J. Colloid Sci.*, 1951, **6**, 245) have given the swollen weights and swollen volumes of various cationic forms of Dowex-50. This commercial resin is believed to be a sulphonated polystyrene containing about 8% of divinylbenzene. From their data we calculate the following values of $(V_M)_H - (W_M)_H$:

H	Li	Na	K	Rb	Cs	NH_4	NEt_4
0·644	0·634	0·656	0·700	0·729	0·745	0·738	1·325

The agreement between their results and our own for the sodium form is not good; it appears, however, that the above relationship may be valid for the mixed forms of the resin involving hydrogen, lithium, and sodium, but not for the other univalent cations.

It may be noted that our results were obtained on resins possessing approximately the same specific exchange-capacity. If the capacity were less than that corresponding to monosulphonation, the linear relationship might still hold but the matrix volume would be greater than 0·63 ml.

Effect of Degree of Cross-linking and Cationic Composition of the Resins on Swelling.—Weight-swellings of the hydrogen forms of resins prepared from the Dow divinylbenzene solution are shown in the following table; similar data for resins prepared from the Monsanto divinylbenzene solution have been reported (Pepper, *loc. cit.*, Fig. 7).

Nominal % of divinylbenzene	2	2½	4½	5	7½	10	15	25
Weight-swelling	3·55	3·10	1·78	1·50	1·10	0·82	0·58	0·38

The above swelling values are means obtained from a number of preparations at each nominal divinylbenzene content; individual preparations showed some variation from these means (cf. next table). It will be seen that weight-swelling is a sensitive criterion of the degree of cross-linking up to a nominal divinylbenzene content of about 10% but that the sensitivity of this test falls off at higher divinylbenzene contents. However, in this latter range, the relative affinity coefficients of the resins for sodium and hydrogen are markedly affected by divinylbenzene content and provide a satisfactory criterion (Reichenberg *et al.*, *loc. cit.*).

FIG. 6. *Absorption of hydrochloric acid.*

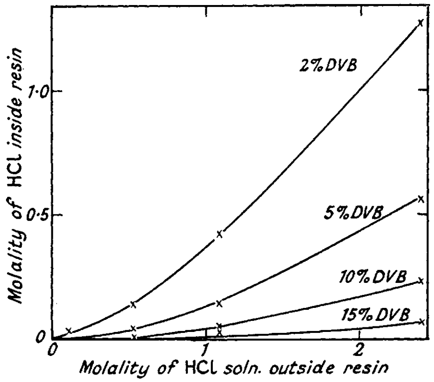
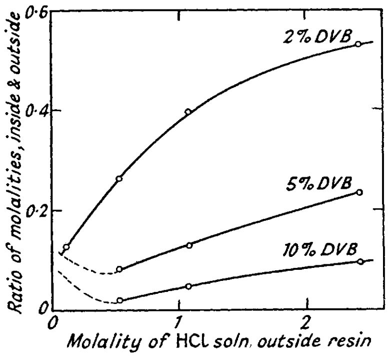


FIG. 7. *Ratio of molalities inside and outside resin as a function of molality outside.*



Swelling changes resulting from variation in the cationic composition of the resin have been determined for the sodium–hydrogen system. In Fig. 4, $(W_H)_M$, *i.e.*, the weight of water absorbed by an amount of the mixed sodium–hydrogen resin equivalent to 1 g. of dry hydrogen form, is plotted against the equivalent fraction of sodium on the resin, X_{Na_R}. The data presented refer to resins in contact with water. Somewhat lower values were obtained in contact with the 0·1N-conditioning solutions, but this effect was appreciable only with the 2% divinylbenzene resin where the difference was 0·2 g. of water per g. of dry resin.

It will be seen from Fig. 4 that more water is absorbed by the hydrogen form of the resins than by an equivalent amount of the sodium form. Moreover, the swollen volume of the hydrogen form is greater than that of the sodium form, which is in accord with other evidence that the hydrated hydrogen ion is larger than the hydrated sodium ion (Boyd, Schubert, and Adamson, *J. Amer. Chem. Soc.*, 1947, **69**, 2818; Kressman and Kitchener, *J.*, 1949, 1190; Gregor, Gutoff, and Bregman, *loc. cit.*). The difference between the swollen volumes of the two forms, *i.e.*, $V_H - (V_{Na})_H$, decreases with increasing cross-linking, tending to a value of 0·3 ml. per g. of dry resin at low divinylbenzene content and to zero at high divinylbenzene content (Fig. 5). This effect is consistent with Gregor's treatment of the swelling of ion-exchange resins (*J. Amer. Chem. Soc.*, 1951, **73**, 642). He suggests that some of the water in a swollen resin is bound fairly strongly to the various ions whilst the rest is " free " water. When one cation is replaced by a larger cation, the resin expands but the elastic forces of the polymer network (which tend to resist any increase in total volume) are increased. As a result, " free " water is squeezed out. Hence the net increase in volume is less than the difference between the volumes of the two hydrated cations. The elastic forces, and hence the amount of " free " water squeezed out, increase with increasing cross-linking.

Swelling in Hydrochloric Acid Solutions and Absorption of Hydrochloric Acid.—The amounts of water absorbed by resins of different divinylbenzene content (hydrogen form) in contact with hydrochloric acid solutions of varying concentration, and the corresponding amounts of hydrochloric acid taken up by the resins, are given below. In both cases, the greatest effect is observed with the resin of lowest cross-linking. Absorption of hydrochloric acid by the 25%-divinylbenzene resin was negligible; the amount of acid washed out was equal within experimental error to the correction for residual solution retained between the beads after centrifugation.

	Nominal % of divinylbenzene				
	2	5	10	15	25
Weight-swelling (g. of water per g. of dry resin) :					
H_2O	3·26	1·57	0·88	0·60	0·36
0·11N-HCl	3·14	1·52	0·88	0·60	0·36
0·52N-HCl	2·80	1·48	0·86	0·60	0·35
1·05N-HCl	2·41	1·38	0·84	0·59	0·35
2·30N-HCl	1·81	1·24	0·78	0·57	0·35
Absorption of hydrochloric acid (mg.-equiv. of HCl per g. of dry resin) :					
0·11N-HCl	0·04	0·02	0	0	0
0·52N-HCl	0·39	0·06	0·01	0·01	0
1·05N-HCl	1·03	0·19	0·04	0·02	0
2·30N-HCl	2·31	0·70	0·18	0·04	0

From these data we obtain the number of mg.-equiv. of hydrochloric acid taken up per g. of water absorbed, *i.e.*, the molality of hydrochloric acid inside the resin. These values are plotted in Fig. 6 against the molality of the outside solution. The applicability of Donnan membrane concepts to ion-exchange resins has been discussed by several authors in recent years (Bauman and Eichhorn, *J. Amer. Chem. Soc.*, 1947, **69**, 2830; Gregor, *loc. cit.*). It would appear from the simpler treatments, at least, that the ratio of hydrochloric acid molality inside the resin to that outside should tend to zero at zero external concentration and to unity at high external concentrations. Our data for the 2%-divinylbenzene resin, which are the most reliable, are consistent with this concept (Fig. 7). With the other resins, there appears to be a minimum at low external concentrations; however, a small experimental error would account for the effect. Where little reliance can be placed on the shape of the curves in Fig. 7, broken lines have been used.

The work described above has been carried out as part of the research programme of the Chemical Research Laboratory, and this paper is published by permission of the Director of the Laboratory.

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