

800. The Behaviour of Ion-exchange Resins with Mixed Solvents. Part III.¹ Dioxan-Water Mixtures.

By C. W. DAVIES and A. NAREBSKA.

Measurements are reported of the uptake of dioxan and water by sulphonic acid resins of varying degrees of cross-linking in the sodium, potassium, and nickel forms. At low molar fractions of water in the solvent, the sorption of water is *less* the more lightly cross-linked is the resin. Virtually no dioxan is taken up by a resin containing less than one mole of water per equivalent.

IN PART I² the behaviour of an anion exchanger in dioxan-water mixtures was studied. In the present work the uptake of dioxan and water by a cation exchanger in three cationic forms was measured, attention being concentrated on mixtures rich in dioxan.

EXPERIMENTAL

Materials.—Zeo-Karb 225 of 14–52 mesh, cross-linked with 1, 4.5, and 8% divinylbenzene, was used. It was washed several times with 10% hydrochloric acid, water, and 2% sodium hydroxide to remove traces of iron and other impurities, and then converted into the sodium, potassium, or nickel form by column treatment with the appropriate chloride solution, washed until free from chloride ion and dried in the air. The moisture content was determined by heating small samples to constant weight at 110–120°. The capacity of the sodium and potassium forms was determined by converting a known amount to the hydrogen form with a five-fold excess of 0.1N-hydrochloric acid and titrating the effluent with 0.1N-sodium hydroxide. The capacity of the nickel form was determined by treating a sample of the resin with N-hydrochloric acid and titrating the nickel released with EDTA in the usual way. AnalaR dioxan was distilled and the fraction boiling at 101°/760 mm. was stored in a dark bottle. Solutions with water were made up by weight.

Procedure.—A 1 g. sample of air-dried resin was weighed into a dry sintered glass filter-tube and placed into a stoppered tube containing about 15 g. of water-dioxan solution. Fourteen days were allowed for attainment of equilibrium, during which time the solution was made to percolate many times through the resin bed. Then the tube was removed, centrifuged, and weighed as described earlier.¹

The concentration of water in the mixed solvent was determined with Karl Fischer reagent; a weighed sample of solution was dissolved in methanol and titrated to the end-point colour change. It was found that the reproducibility was improved (from about 1 mg. down to 0.2 mg. of water) if, instead of applying a constant blank correction, the methanol was titrated in the vessel to the colour change before the water-dioxan solution was introduced and titrated. From the known weight of the swollen resin, the weight of the water originally contained in it, and the concentration of water before and after equilibrium, the amounts of water and dioxan absorbed were calculated.

RESULTS AND DISCUSSION

The results are in Tables 1–3.

TABLE 1.

8% Cross-linked resin.									
Sodium resin. Equiv. 217.4.					Potassium resin. Equiv. 231.5.				
N_w	0.3250	0.3245	0.177	0.0253	0.469	0.322	0.190	0.0212	
W	77.94	79.18	61.9	28.9	71.1	60.2	47.8	13.7	
D	62.95	64.54	58.7	7.0	51.7	45.9	43.3	10.7	
\bar{N}_w	0.8583	0.8572	0.838	0.953	0.871	0.865	0.844	0.863	
Nickel resin. Equiv. 244.4.									
N_w	0.323	0.192	0.0266		D	80.4	83.2	9.4	
W	86.0	68.0	33.6		\bar{N}_w	0.840	0.808	0.946	

¹ Part II, Davies and Patel, *J.*, 1962, 880.

² Part I, Davies and Owen, *J.*, 1956, 1676.

The first row of figures gives the molar fraction of water in the equilibrium solution, the second and third the weight in grams of water and dioxan, respectively, that are absorbed by one equivalent of the resin, and the fourth the molar fraction of water in the

TABLE 2.

4.5% Cross-linked resin.

	Sodium resin. Equiv. 218.7.			Potassium resin. Equiv. 226.2.			
N_w	0.307	0.180	0.0210	0.463	0.322	0.189	0.0210
W	97.7	61.7	24.2	87.2	62.5	44.3	15.9
D	71.3	58.6	3.5	53.4	47.9	41.1	5.3
\bar{N}_w	0.870	0.837	0.971	0.889	0.865	0.841	0.936

	Nickel resin. Equiv. 246.0.						
N_w	0.313	0.180	0.0240	D	113.9	109.4	10.0
W	95.7	73.3	26.1	\bar{N}_w	0.804	0.766	0.927

TABLE 3.

1% Cross-linked resin.

	Sodium resin. Equiv. 219.8.			Potassium resin. Equiv. 231.6.			
N_w	0.299	0.183	0.0240	0.451	0.317	0.185	0.0195
W	115.1	63.2	22.6	116.0	59.2	40.1	13.5
D	111.2	70.4	13.2	84.5	58.8	52.3	11.5
\bar{N}_w	0.835	0.811	0.894	0.870	0.831	0.790	0.853

	Nickel resin. Equiv. 239.6.						
N_w	0.301	0.171	0.0212	D	146.6	146.3	13.0
W	126.0	78.8	35.4	\bar{N}_w	0.808	0.725	0.930

solvent absorbed by the swollen resin. All measurements were made in duplicate, and the first two columns of figures in Table 1 report one pair of duplicate measurements in detail and are typical of the reproducibility that could be achieved; after this mean values are shown.

The results show several points of interest. At low molar fractions, the sorption of water by the potassium and sodium resins is *less* the more lightly cross-linked is the resin. When the sorption is plotted against the molar fraction of water in the equilibrium solution, the curves for the differing degrees of cross-linking remain very close together over a considerable concentration range; they then cut one another and, at higher concentrations of water, splay out in the expected directions, with the lower cross-linked resin showing the greater swelling. The cross-over point is at a water molar fraction of 0.30 for the potassium resin and at $N_w = 0.16$ for the sodium resin, but in both cases the water sorption at the cross-over point is approximately 3.2 moles per equivalent. With the nickel resin the water sorption curves are steeper and splay out much earlier, and a cross-over point cannot be detected with certainty.

Sundheim, Waxman, and Gregor³ observed the same effect in studying the water uptake, at low relative humidities, of a range of acid resins of varying cross-linkage. They attributed it to van der Waals attractions between neighbouring polymer chains, which will be effective in a loosely cross-linked resin but will be less important at higher cross-linkings because of restrictions on the free movement of segments of the chain.

A closer comparison of the uptake of water from dioxan solutions with a similar resin's uptake of water vapour at fractional relative partial pressures can be based on the measurements of Hovorka, Schaefer, and Dreisbach,⁴ who determined the partial vapour pressure of water over the whole range of water-dioxan mixtures at 25°. In Fig. 1 the continuous lines represent the measurements of Gregor, Sundheim, Held, and Waxman⁵ at various

³ Sundheim, Waxman, and Gregor, *J. Phys. Chem.*, 1953, **57**, 974.

⁴ Hovorka, Schaefer, and Dreisbach, *J. Amer. Chem. Soc.*, 1936, **58**, 2264.

⁵ Gregor, Sundheim, Held, and Waxman, *J. Colloid Sci.*, 1952, **7**, 511.

partial pressures of water vapour. The points show our measurements plotted against the aqueous partial vapour pressure of the equilibrium solution.

The small divergences between the two sets of figures are well covered by the slight difference in the degree of cross-linking, and by the experimental uncertainty, and it seems therefore that the uptake of water from dioxan solutions is governed by the activity of the water in the equilibrium solution and is otherwise unaffected by the presence of dioxan, and by its simultaneous absorption.

The sorption of dioxan depends on its concentration in the mixed solvent, on the cationic form of the resin and on its cross-linking, and, owing to the large difference in the

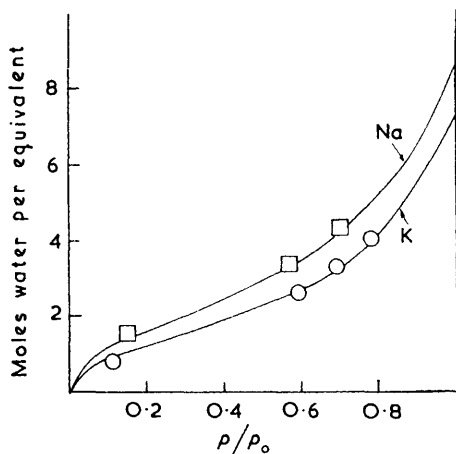


FIG. 1.

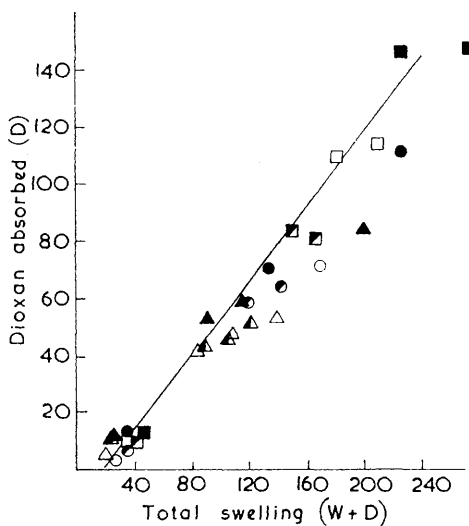
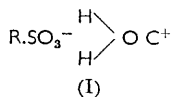


FIG. 2.

1%	4.5%	8%	Cross-linked resin in
●	○	◐	Sodium form
▲	△	◑	Potassium form
■	□	◒	Nickel form

molal volumes of dioxan and water, on the resin's volume. A complete theory would be complicated, but Fig. 2 gives a broad picture of our measurements. Here the weight of dioxan absorbed per equivalent is plotted against the total weight swelling ($W + D$). It is clear that virtually no dioxan is taken up by a resin containing less than one mole of water per equivalent; a resin will not swell at all in pure dioxan, as the dioxan molecule is unable to overcome the polymer-polymer interactions postulated by Gregor *et al.* The Tables also illustrate this effect, where it will be seen that in every case \bar{N}_W rises rapidly from a minimum value as N_W is reduced, and tends to $\bar{N}_W = 1$ for $N_W = 0$.

According to Glueckauf and Kitt,⁶ the first molecule of water taken up by a cation exchanger is attached to the sulphonate ion, although the structure (I) may not perhaps be wholly excluded. However this may be, it seems significant that according to our results this monohydration must proceed to completion and all polymer-polymer contacts be broken before the interior of the resin becomes accessible to dioxan molecules. Once this stage of hydration has been passed, dioxan enters the resins freely in amounts by weight approximately equal to the weight of water absorbed. This continues until the resins approach their maximum swelling, when the curves bend over, partly as a result of the increasing molar fraction of water in the equilibrium solutions, and partly because of the



⁶ Glueckauf and Kitt, *Proc. Roy. Soc.*, 1955, *A*, **228**, 322.

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increased importance of the restoring force in the stretched resin, which will tend to exclude the larger dioxan molecule.

Grunwald, Baughman, and Kohnstam⁷ concluded that the potassium ion forms a mixed solvate in dioxan-water mixtures, being bound to two dioxan and (probably) two water molecules. Such a structure, if easily dissociated, would not be looked for in a resin on account of its size; there is certainly no evidence for it in our results, where even in the 1% cross-linked resin a molecular ratio D : K⁺ of 1 : 1 is not attained.

BATTERSEA COLLEGE OF TECHNOLOGY, LONDON S.W.11.

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⁷ Grunwald, Baughman, and Kohnstam, *J. Amer. Chem. Soc.*, 1960, **82**, 5801.
