Ethanolamine Forms of a Cation Exchanger

By **C. W. Davies** and **B. N. Patel,** Department of Chemistry, University of Surrey, London S.W.11

Data are reported for the swelling in water of the mono-, di- and tri-ethanolammonium forms of a cation-exchange resin. The results suggest that some association occurs between the organic cation and the resin, and that this is least for the mono- and greatest for the tri-ethanolammonium ion.

THE data in the Table have been obtained for the mono-, di-, and tri-ethanolammonium forms of the cation-exchange resin, Zeo-Karb 225, when fully swollen in water. M, D, and T stand for mono-, di-, and tri-ethanolamine, respectively; W is the number of grams of water taken up by one g. equivalent of the resin, V is the volume in c.c. of one g. equivalent of the swollen resin, R is the volume of one g. equivalent of the resin salt, and R^- is one g. equivalent of the resin anion.

% Cross-linked resin		$[MH]^+R^-$	$[DH]^+R^-$	$[TH]^+R^-$
8	W	153·7	139·7	124·5
	V	337·3	356·5	376·0
	R	183·6	216·8	251·5
4·5	W	278·5	262·8	242·5
	V	456·5	475·7	489·6
	R	178·0	212·9	247·1
2	W	828·1	786·6	735·5
	V	1005·0	994·2	974·0
	R	176·9	207·6	238·9

EXPERIMENTAL

The resin samples, of 14—52 mesh, were backwashed to remove the lightest particles, exhaustively treated with 2N-hydrochloric acid until free from iron, washed with deionized water, and air-dried. The water content of the product was obtained by heating samples to constant weight at 120°. The capacity was then determined by passing a large excess of 0·5M-sodium chloride through a weighed sample, and estimating the acid liberated by titration.

For the swelling measurements a 1 g. sample of the air-dry resin in the hydrogen form, contained in a filter tube with a sintered-glass base, was equilibrated with a suitable aqueous solution of the ethanolamine. The filter tube containing the resin was then centrifuged at 2000 revs./min. for 30 seconds, and weighed. The ethanolamine concentration of the equilibrium solution was determined by titration. The weight of solvent taken up by the ethanolamine form of the resin can be calculated from these results, and when these figures are plotted against the ethanolamine concentration of the equilibrium solution a short extrapolation to zero concentration gives the maximum value of W. Concordant values of W were also obtained directly by quickly washing the swollen resin with deionized water before centrifuging.

Equivalent volumes were determined by experiments in which a known quantity of the swollen-resin salt was con-

tained in a density bottle which was filled with water at 25° and weighed. From the known weight and capacity of the resin sample, together with the appropriate value of W, the total weight of the swollen-resin phase was known, and hence, by subtraction, the weight of free water. The volume of the resin phase is obtained by difference, since the capacity of the weighing bottle is known, and the equivalent volume, V, of the swollen resin can be calculated. Several workers have established that the swelling water in resins of this type retains its normal density, so the difference, $V - W = R$ represents the equivalent volume of the resin salt itself.

DISCUSSION

A comparison of the values of R in the Table shows that within experimental error (the results for the heavily swollen 2% resin are the least accurate) each hydroxyethyl group adds 34 c.c. to the volume. The results of the swelling suggest the presence of two opposing influences. For the 8% resin the amount of water taken up decreases from the $[MH]^+$ to the $[TH]^+$ form, but the total volume of the swollen resin increases. The same is true of the 4·5% cross-linked resin, but the 2% resin differs, in that both the swelling and the total volume of the resin decrease from the $[MH]^+$ to the $[TH]^+$ form.

On simple considerations the behaviour of the more highly cross-linked resins would be expected. Swelling equilibrium is reached when the osmotic pressure of the swelling liquid is balanced by the restoring force exerted by the stretched resin network. The larger the volume of the cation contained in the resin the larger will be the total volume when this equilibrium is reached, and the greater the restoring force exerted by the resin. The osmotic pressure of the swelling liquid is therefore higher when equilibrium is reached and the volume of swelling liquid taken up is correspondingly lower.

In the 2% resin some other effect is manifestly present. It might be peculiar to this resin; but it is more probable that it is present in every case, and becomes evident with the lightly cross-linked resin merely because the size of the cation is relatively unimportant in these highly swollen resins. This second effect reduces the swelling tendency from the $[MH]^+$ to the $[TH]^+$ form. It is suggested that van der Waals attraction between the resin network and the organic radicals of the ethanolammonium ion will favour some association between the cation and resin anion, and that the extent of this will be greatest with the triethanolammonium ion.