261. *Cation Exchange with a Synthetic Phenolsulphonate Resin. Part III. Equilibria with Large Organic Cations.*

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The affinity of some large organic cations, *viz.*, quaternary ammonium salts and the quininium ion, for a phenolsulphonate resin increases with increasing size of the ion. This is in contrast to the simple inorganic cations and suggests that van der Waals forces contribute largely to the affinity, the Coulomb forces being less important. This is supported by the greater affinity for the resin of the trimethyl-*n*-amylammonium ion than of the isomeric tetraethylammonium ion. The rates of exchange, on the other hand, decrease with increasing ionic size.

The saturation capacity is the same for the largest of the quaternary ions studied, *viz.*, phenylbenzyldimethylammonium, as for inorganic ions, indicating that all the molecular pores within the resin are larger than the effective diameter of this ion. The quininium ion, however, appears to be larger than some, at least, of the pores, as it exhibits an apparently lower affinity than its size would suggest.

No physical adsorption is observed from solutions of highly dissociated salts of large cations.

The exchange of organic cations from aqueous solutions of their hydrochlorides with a calcium zeolite was studied by Ungerer (*Kolloid-Z.*, 1925, **36**, 228). However, his results were complicated by a simultaneous exchange of hydrogen ion, produced from the hydrolysis of the salts and, accordingly, seem inconclusive. This factor was eliminated in the present work by using neutral salts only of the organic cations.

Experimental.

The present study was carried out at 25° with the same phenolsulphonate resin (— 10 + 20 mesh) and the same technique as used in Parts I and II (preceding papers). Quaternary ammonium salts were used, as they have the advantage of being readily prepared in a pure state and the quaternary ion can be built up and modified at will. In addition, with the exception of the tetramethylammonium and possibly tetraethylammonium ion, they are completely unhydrated in solution (J. O'M. Bockris, private communication), and the ionic size can be calculated with fair accuracy from the known C–C, C–N, and C–H bond lengths.

The parent ammonium ion was used as the reference ion in the resin, which was allowed to come to equilibrium with the quaternary bromide in every case, for, although it has been shown in Part I that equilibria among univalent inorganic cations are largely independent of the anion, it was considered more satisfactory to maintain the same anion with these hitherto unstudied ions.

It was found that, as the ion was made larger, the rate of attainment of equilibrium became less and, accordingly, it was necessary to allow prolonged periods for equilibrium to become established.

True equilibrium was considered to have been attained when two identical experiments showed the same amount of exchange when allowed to remain for different periods of time.

The tetramethylammonium ion in 0·1N-solution reached equilibrium in a matter of hours, although about 5 days were, in fact, allowed; on the other hand, the phenylbenzyldimethylammonium ion required a minimum of 6 weeks. When the study was extended to quinine hydrochloride, a 0·05N-solution had not reached equilibrium even after 20 weeks (see Fig. 2).

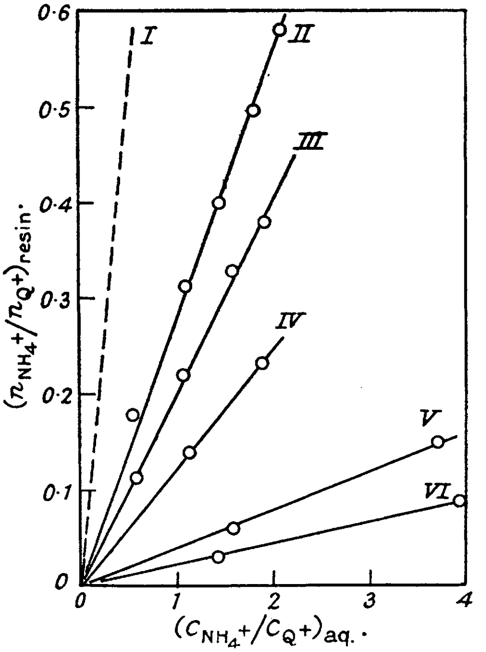
RESULTS AND DISCUSSION.

The equilibria attained are plotted in Fig. 1 in terms of the mass-action functions, and the equilibrium constants, obtained from this graph, are given in the table. The equilibrium constant is defined by

$$K = [C_{NH_4^+}/C_{Q^+}]_{aq.}/[n_{NH_4^+}/n_{Q^+}]_{resin} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

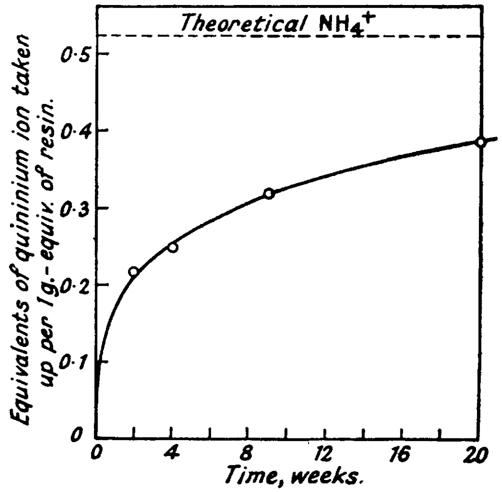
where the n terms are the numbers of the specified ions in the resin phase at equilibrium, and the C terms are the corresponding aqueous concentrations.

FIG. 1.



I, NH_4^+. IV, $(NMe_3Am^n)^+$.
II, NMe_4^+. V, $(NMe_2EtPh)^+$.
III, NEt_4^+. VI, $(NMe_2Ph{\cdot}CH_2Ph)^+$.

FIG. 2.



These figures show that the affinities (as measured by the equilibrium constant) *increase* with increasing ionic size. This clearly indicates that the ion is held on the resin by a different set of forces from those binding simple inorganic ions, where the affinity decreases with increasing size, and suggests that van der Waals forces are contributing very considerably to the affinity (cf. also Hendricks, *J. Physical Chem.*, 1941, **45**, 65). The Coulomb forces, which are predominant in determining the affinity of the inorganic cations, are here playing a minor rôle. In this respect the behaviour of the large ions towards the resin is similar to that of dye ions towards a textile fibre.

It is not readily possible to calculate van der Waals contributions quantitatively; nevertheless, it is clear qualitatively that the interaction between the large ion and the surface on which it is bound should increase with the number of atoms in the ion which are able to come within a few Ångstrøm units of the surface. In agreement with this view, the trimethyl-*n*-amylammonium ion is seen (Fig. 1 and table) to have a higher affinity than the isomeric tetraethylammonium ion : models show that the former can be arranged with a larger number of atoms within a few A. of a surface than the latter.

TABLE I.

Ion.	Equilm. const.	No. atoms in contact with surface (not counting hydrogen).	Major diam. A.
Ammonium	1·00	0	2·4 *
Tetramethylammonium	3·67	3	4·6
Tetraethylammonium	5·0	6	7·2
Trimethyl-*n*-amylammonium	8·24	7	9·5
Phenyldimethylethylammonium	25·2	9	8·5
Phenylbenzyldimethylammonium	44·4	14	11·2

* Hydrated size, calculated from mobility (73·7) by the formula given by Walden (" Elektrochemie nichtwassriger Losungen," 1924 edn., p. 189). The sizes of the (unhydrated) quaternary ions are calculated from models, using the bond lengths given by Pauling (" The Nature of the Chemical Bond," 1944 edn., pp. 160 *et seq.*).

All the quaternary ions so far studied are of a size less than that of the smallest molecular channel within the resin, since the saturation capacity (or equivalent weight) is the same for the largest of them, *viz.*, phenylbenzyldimethylammonium, as for the simple inorganic ions (see also Part I). As already mentioned, however, the *rate* of exchange of the large ions is very much less in spite of the higher affinity, because of the difficulty of diffusing into the resin.

Presumably, if the ion were larger than some, at least, of the molecular channels, certain parts of the resin would be inaccessible and a lower saturation capacity would be observed, as well as an apparently lower affinity. The quininium ion may be an example of this effect, for its large size should cause it to exhibit a very high affinity, whereas, in fact, it was found to exchange from a solution of its monohydrochloride (pH 7) not only exceedingly slowly but also to an apparently limited extent. This is clear from Fig. 2, where it is seen that the rate curve begins to level out, and the extent of the exchange after 20 weeks (*i.e.*, approaching the flat portion of the curve) is still very low, being less even than for NH_4^+ itself (see broken line in Fig. 2).

In spite of the overall slowness of the exchange, about one-half of it takes place relatively rapidly, showing that some sites are readily accessible even to very large ions. This may indicate the presence of a few molecular channels of very large diameter, or it may represent exchange occurring on the " external surface " only of the resin. In either case it is to be expected that a faster rate and a higher exchange would occur as the particle size of the resin was reduced. As described in Part I, the position of equilibrium is normally independent of particle size, and this is to be expected where all the sulphonate groups are accessible to the ion, as proved by a normal saturation capacity or equivalent weight.

The normal equivalent weight exhibited towards the phenylbenzyldimethylammonium ion indicates that even the smallest of the molecular pores within the resin have diameters greater than the effective diameter of this ion, *viz.*, 6—11 A., while a few pores have diameters as large as that of the quininium ion. This is in contrast with the diameters of the pores in a zeolite studied by Wiegner and Russell (*J. Soc. Chem. Ind.*, 1931, **50**, 65T), which were shown to lie between 3 and 5 A., even such relatively small ions as NH_3Me^+, $NH_2Me_2^+$, and $NHMe_3^+$ exhibiting a progressively reduced affinity for the zeolite. The pores are also larger than those in a polyhydric phenolic resin studied by Akeroyd and Broughton (*J. Physical Chem.*, 1938, **42**, 343), many of which were less than about 9 A., in diameter, as indicated by the considerably reduced affinity for the benzyltrimethylammonium ion.

No physical adsorption of the salts or organic cations occurs, even when the cation is as large as phenylbenzyldimethylammonium, presumably because of the nearly complete dissociation of these salts.

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