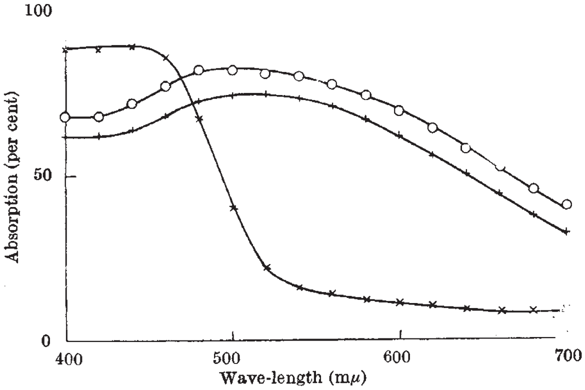

Absorption spectra of coloured pyrethrin complexes: ×—×—, blank; O—O—, synthetic pyrethrin I analogue (colour from 7·4 mgm.); +—+—, natural pyrethrin mixture, Py I : Py II = 1·6 : 1·0 (colour from 1·8 mgm.). These last two are corrected for absorption of blank

The absorption, log (I_0/I), by the coloured complexes at λ 540 mμ is proportional to the amount of ester used, and to this extent the reaction is quantitative; but as is to be expected from the results of Hestrin[1], it is also dependent upon the acidic and alcoholic components of the ester. Thus, to give the same colour intensity, the amount of the synthetic pyrethrin analogue required is 3·3 times that of the natural pyrethrin mixture (pyrethrin I : pyrethrin II = 1·6 : 1). Since the naturally occurring esters of chrysanthemum dicarboxylic acid (so-called pyrethrin II) contain two ester groupings, they may be expected to yield a more intense coloration than the esters of chrysanthemum monocarboxylic acid (so-called pyrethrin I), which is in line with the experimental results.

It is clear, therefore, that the reaction cannot be applied to the estimation of the 'pyrethrins' unless: (1) they can be first separated; or (2) the ratio in which the 'pyrethrins' occur is known to be constant. Nevertheless, the colour reaction should prove to be useful for the detection of the pyrethrins in any attempt to separate them by chromatographic methods.

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Nov. 18.

[1] Hestrin, S., *J. Biol. Chem.*, **180**, 249 (1949).

[2] Barthel, W. F., Haller, H. L., and LaForge, F. B., *Soap*, 65 (1944).

Ion Exchange Resin Membranes and Resin-Impregnated Filter Paper

Marshall[1] has prepared zeolite membranes and has used them as electrodes for the determination of ionic activities in solution in a manner analogous to the use of the glass electrode for the measurement of hydrogen ion activities. It is a logical step to attempt to use ion exchange resins in the form of membranes for similar purposes. However, the difficulties of preparing these are considerable.

These difficulties have been overcome, and we have prepared ion exchange resins in the form of membranes, rods, tubes and thimbles, containing SO_3H-, COOH- or amino- (both strongly and weakly basic) groups, and which are mechanically stable and free from cracks. A full account of the method of preparation will be published elsewhere.

The membranes consist of cross-linked resin polymers of identical composition to the well-known granular ion exchange resins and are insoluble in all aqueous and non-aqueous liquids. They are hydrated and, like the fully wetted granules, contain approximately 55 per cent of their own weight of water. The SO_3H- and COOH-resins can be converted to any desired cationic form by treating them with an excess of a solution of a salt of the appropriate cation. Similarly, anion exchange resin membranes can be converted to any desired form by treating them with the appropriate acid or base.

It is somewhat difficult to mount the membranes for use. They cannot be cemented, for example, to a glass tube as Marshall did with his zeolite membranes, since it is difficult to find a cement which will adhere to both the wet resin surface and the dry glass surface. However, the use of a resorcinol–formaldehyde resin shows promise as a cement. Modified membranes have been prepared in which difficulties of mounting are completely overcome. The membrane is formed within the pores of a sintered glass disk suitably mounted in glass, or within the pores of a paper Soxhlet thimble. Similarly, filter paper can be impregnated with the resins.

The electrical resistance of the unsupported membranes is low, and the specific resistance of a typical membrane containing sulphonic groups and in the hydrogen form is 33·2 ohms per c.c. The resistance of the supported membranes is slightly higher, depending upon the shape, but still comparatively low. The total ionic capacities of the membranes containing sulphonic and carboxyl groups are of the order of 1·5 m.eq. per (wet) gm., and those of the anion exchange membranes about 5 m.eq. per gm.

Preliminary studies indicate that the sulphonic membranes give steady and reproducible E.M.F.s in cells of the type

$$\text{Sat. calomel} \mid M^{+}(a_1) \parallel \text{membrane} \parallel M^{+}(a_2) \mid \text{sat. calomel.}$$

The resins are stable in organic solvents and we have used them to measure activities in non-aqueous solutions such as alcohol and acetone. Some resins are permeable to large organic cations[2] and can be employed for the measurements of the activities of these ions in solution.

Other resins have somewhat smaller pores, and membranes prepared from them show ionic 'sieve' effects. Electrodialysis through such resin membranes of a solution containing large and small ions indicates that in favourable cases separations can be achieved.

Datta *et al.*[3] have recently prepared and used alumina-impregnated filter paper for chromatography, and, likewise, the known methods of filter paper chromatography can be employed with the resin-impregnated filter papers. In addition, differences in ionic mobility within the resin can be exploited to separate ions by passing an electric current between electrodes clamped to the ends of the paper.

The work is being continued, and it is hoped to publish more detailed accounts of it as it progresses.

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Nov. 25.

[1] Marshall *et al.*, *J. Amer. Chem. Soc.*, **63**, 1911 (1941); *J. Phys. Chem.*, **46**, 52 (1942); *J. Amer. Chem. Soc.*, **64**, 1814 (1942); *J. Phys. Chem.*, **48**, 67 (1944); *J. Amer. Chem. Soc.*, **70**, 1297 (1948), etc.

[2] Kressman and Kitchener, *J. Chem. Soc.*, 1208 (1949).

[3] Datta, Overell and Stack-Dunne, *Nature*, **164**, 673 (1949).