

The qualitative separation has also been made applicable to the simple mono- and di-carboxylic acids and is being extended to cover the sugar acids.

It is apparent that the method should be of wide application as a micro-method of investigation in the carbohydrate group.

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Colour of Iodine Solutions

THE dependence of the colour of iodine solutions upon the nature of the solvent is generally believed to be due to the presence of loosely bound iodine-solvent complexes, or 'solvates', in the brown solutions (for example, in ethanol) and of 'unsolvated' diatomic iodine molecules in the violet solutions (for example, in carbon tetrachloride)¹. The nature, however, of this 'solvation' remains obscure. It is obviously not a simple electrostatic solvation, for it has little to do with the dielectric constant of the solvent; nor would such a solvation serve to account for the marked difference in chemical properties between the violet and brown solutions.

An explanation may be found in the amphoteric nature of iodine. There is some evidence to show that the symmetrical ionic structures $\text{Hal}^+\cdot\text{Hal}^-$; $\text{Hal}^-\cdot\text{Hal}^+$ may contribute more to the actual normal state of the halogen bond, especially in bromine, and still more in iodine, than has been commonly supposed. Moreover, since the univalent positive iodine ion contains an unoccupied $5p$ orbital in the free state, the proximity of an electron-donor, for example, an oxygen, sulphur or basic nitrogen compound, would stabilize one of the ionic structures and thus destroy the electrical symmetry of such an iodine molecule, bringing about what is, in effect, a partial ionization of the iodine, with the positive end of the molecule stabilized by co-ordination with the donor molecule. The essential difference, therefore, between a violet solution and a brown one is that whereas in the former the iodine is present as symmetrical non-polar diatomic molecules, in the latter the iodine molecules are polarized by co-ordination with an electron donor molecule.

That it is principally the electron-donor character of the solvent and not its dipolar character which is operative is shown by the fact that iodine forms brown solutions in very weakly polar solvents which have some donor character, but violet solutions in such strongly polar solvents as nitro-compounds, which have little or no donor or 'basic' properties.

This theory is supported by the magnitude of the dielectric polarization of iodine in violet and brown solutions respectively. A new series of measurements has been made, and is being extended, of the dielectric polarization of iodine in a number of solvents of small or zero polarity and in the presence of electron-donor groups. The results, details of which will be published in due course, leave no doubt that the

formation of a red or brown solution of iodine is accompanied by a polarization of the molecule. For example (to the nearest 0.1 D), the *apparent* dipole moment of iodine in benzene (reddish-violet solution at 25°) is 0.6 D , in *p*-xylene (deeper red), 0.9 D , in 1:4-dioxane (brown), 1.3 D , and in di-isobutylene (red-brown solution), 1.5 D .

No less interesting, however, than this solvolytic ionization of iodine itself is the light which it throws on the donor or basic properties of aromatic and ethylenic hydrocarbons.

A similar explanation to that offered above may without doubt serve also to account for the parallel phenomena of the dichroism observed in solutions of iodine monochloride and iodine monobromide^{2,3}.

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¹ Lachmann, *J. Amer. Chem. Soc.*, **25**, 50 (1903).

² Gillam and Morton, *Proc. Roy. Soc., A*, **132**, 152 (1931).

³ Gillam, *Trans. Farad. Soc.*, **23**, 1132 (1933).

Partition Chromatography of Organic Acids on a Paper Sheet Support

By so-called 'one-dimension partition chromatography' on a paper support (first used successfully by Conden, Gordon and Martin¹ for the separation of amino-acids, and recently adapted by Partridge² for the separation of reducing sugars), we have succeeded in separating the individual members of a mixture of carboxylic acids of the types commonly occurring in plant tissues.

Attempts to exploit this sort of procedure, with water as the fixed phase in the paper and a neutral mobile phase (*n*-butanol), were unsuccessful for the following reasons. (a) From the positions at which the 'spots' of aqueous solutions of the individual acids were applied to the paper, the acids left long, diffuse 'tails' behind the 'heads' as the heads travelled down the paper with the mobile phase; and, moreover, (b) the excursions of the heads were found to vary with the concentrations of the acids, being less at the lower concentrations. The diffuse tails made it impossible to separate the members of a mixture, and the variation of excursion with concentration precluded the possibility of identifying an acid by the excursion of its head relative to the excursion of the mobile phase.

Under the above conditions of experimentation, it is possible that the acids are adsorbed to some extent by the paper. Be that as it may, a serious difficulty must, in any event, arise from the increase in dilution of an acid in the neighbourhood of the initial spot as it is withdrawn therefrom into the mobile phase for transmission down the paper. From consideration of the dielectric constants of water and of *n*-butanol, it is reasonable to suppose that the 'gross' partition of an acid between the aqueous and the mobile phase will change markedly in favour of the aqueous phase as dilution proceeds. The diffuse tails and the reduction in extent of excursion with reduced concentration of the acids in the applied spots are, therefore, to be expected, even if adsorption of the acids by the paper is not an important factor.

One method of overcoming the difficulty is to use, as mobile phase, a solvent strongly acidified with a volatile acid. The mobile phase (we have used