

There appears to be no adequate analogy to the facile reduction of a nitro- to azo-compound, which occurs in this and presumably the cinnoline series, and the explanation is probably to be found in the fact that both reactant and product are present in aqueous solution. The azo-compound is unlikely to be an intermediate in the reduction to amine, for it is highly resistant to further reduction. More probably the nitroso-compound is intermediate and, if it is not itself rapidly reduced further to amine, condenses with amine already present. The proportion of amine (III; $R = \text{NH}_2$) formed appears to increase at the expense of (IV) as the efficiency of stirring improves, and this suggests that for reduction of (III; $R = \text{NO}_2$) to (III; $R = \text{NH}_2$) an adequate concentration of ferrous ions is required throughout the reaction solution. With a colloidal suspension of ferrous hydroxide this condition is more likely to be fulfilled, and (IV) is therefore not produced. This explanation is, of course, incomplete in that it does not account for the great variation of yield of azo-salt from different nitro-quaternary salts.

In view of the results of Lourie and his collaborators and the known efficacy of 'double' molecules as trypanocides², our biological results with (IV) are of considerable interest. Against *T. congolense* in mice it is only one-hundredth as active as either (III; $R = \text{NO}_2$) or (III; $R = \text{NH}_2$), these results being in striking contrast to those obtained by 'doubling' the aminoquinoline or aminocinnoline molecules. On the other hand, it exerts a more prolonged prophylactic action in mice than any other phenanthridinium salt we have examined and its toxicity by the subcutaneous route is low, mice surviving a subcutaneous dose of 1 gm. per kgm. body-weight for ten days. These results suggest slow absorption, perhaps due to depot formation; but other properties of (IV) do not necessarily support such an explanation. Thus its solubility in water (6 gm. per litre at 20°) is practically the same as that of (III; $R = \text{NO}_2$), and its activity against *T. rhodesiense* in mice amounts to one-third of that of (III; $R = \text{NH}_2$), which is the most active member of the series yet known against this species. Thus against *T. rhodesiense* the activity of (IV) ranks high in the series⁶. That (IV) separates from aqueous solution as a gel suggests that the solution is colloidal, and it is significant that the notable prophylactic properties of suramin, which also is a large molecule, have been attributed *inter alia* to the colloidal nature of its solution. It is possible also that (II) and (III) represent optimum molecular patterns for *T. congolense* activity, and that the area of the molecules is critical.

L. P. WALLS
E. BEVERIDGE

Chemical Division,
Wellcome Research Laboratories,
Beckenham, Kent.

Wellcome Laboratories of Tropical Medicine,
183-193 Euston Road,
London, N.W.1.
April 17.

¹ Kenneford, J. R., Lourie, E. M., Morley, J. S., Simpson, J. C. E., Williamson, J., and Wright, P. H., *Nature*, **161**, 603 (1948).

² Lourie, E. M., Simpson, J. C. E., and Walker, J. M., *Brit. J. Pharmacol.*, **6**, 643 (1951).

³ Walls, L. P., *J. Chem. Soc.*, 299 (1945).

⁴ Caldwell, A. G., and Walls, L. P., *J. Chem. Soc.*, 193 (1948).

⁵ Walls, L. P., and Whittaker, N., *J. Chem. Soc.*, 43 (1950).

⁶ Brownlee, G., Goss, M. D., Goodwin, L. G., Woodbine, M., and Walls, L. P., *Brit. J. Pharmacol.*, **5**, 261 (1950).

Relation between Intrinsic Viscosity and Degree of Polymerization

It is generally agreed that the relation between intrinsic viscosity and degree of polymerization (D.P.), for the majority of polymer systems, is of the form $[\eta] = K (\text{D.P.})^\alpha$; but there appears to be no slackening in the controversy as to the numerical values of K and α for a particular system. Most of the values have been obtained from measurements of the intrinsic viscosity and osmotically determined degree of polymerization on nearly homogeneous fractions. Apart from experimental error, there is a number of ways in which discrepancies can arise. High intrinsic viscosities may not be free from the influence of the non-Newtonian behaviour of the solutions from which they are derived; fractions may not be sufficiently homogeneous; and membranes may not be strictly semi-permeable¹.

There is, however, an additional source of error, more often than not neglected. It has been pointed out² that in osmometry the osmotic pressure in cm. of water is not simply the difference in height between the menisci of the solution and solvent, multiplied by the density of the solution; it is actually the difference in pressure between the column of solvent and the column of solution, when the column length is measured from the centre of pressure of the cell, in the case of a vertical membrane, or from the membrane, when it is horizontal, to the meniscus. For dilute solutions, the correction to be added requires an approximate measurement of the vertical distance between the solvent meniscus and the centre of the membrane, and a knowledge of the densities of the solvent and solution.

The correction is much larger for the Fuoss-Mead³ than for the Schulz⁴ osmometer. For a solution of given concentration in a particular osmometer, the correction to the osmotic pressure is of the same order whatever the degree of polymerization of the solute. The effect on the absolute value of the osmotic pressure is then greatest for solutes of high degree of polymerization, and hence the relation between intrinsic viscosity and degree of polymerization is altered.

The relation between the intrinsic viscosity (dl./gm.) in butyl acetate at 25° C., and the degree of polymerization, measured in an osmometer of the Fuoss-Mead type, has recently been determined in these laboratories for a series of fractions of cellulose nitrate, containing 14 per cent of nitrogen, derived from viscose rayons and covering the range of degrees of polymerization from 100 to 1,800. The uncorrected values for K and α were 0.0154 and 0.93 respectively, but on making the correction they became 0.0108 and 1.0. This startling change stresses the importance of the density of the solution in osmotic pressure measurements.

W. G. HARLAND

British Cotton Industry Research Association,
Shirley Institute,
Didsbury,
Manchester 20.
April 18.

¹ Philipp, H. J., and Bjork, C. F., *J. Polymer Sci.*, **6**, No. 4, 383 (1951).

² Boissonas, C. G., and Meyer, K. H., *Helv. Chim. Acta*, **20**, 783 (1937). Higginbotham, R. S., Shirley Institute Mem., **24**, 221 (1950); or, *J. Text. Inst.*, **42**, No. 6, T235 (1951). Gilbert, G. A., Graff-Baker, C., and Greenwood, C. T., *J. Polymer Sci.*, **6**, No. 5, 585 (1951). Lang, H., *Kolloid-Z.*, **122**, 165 (1951).

³ Fuoss, R. M., and Mead, D. J., *J. Phys. Chem.*, **47**, 59 (1943).

⁴ Schulz, G. V., *Z. physik. Chem.*, **A**, **178**, 317 (1936).