

These recovery curves are in good agreement with the earlier results¹ of one of us (F. T. F.).

The magnitude of the induced current accords well with the results of Armistead, Pennock and Mead², and of Coleman and Bohm³, if equation (1) is used to extrapolate the present measurements to the higher dose-rates used by them.

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¹ Farmer, F. T., *Nature*, 150, 521 (1942).

² Fowler, J. F., and Farmer, F. T., *Nature*, 171, 1020 (1953).

³ Fowler, J. F., and Farmer, F. T., *Nature*, 173, 317 (1954).

⁴ Fowler, J. F., and Farmer, F. T., *Nature*, [174, 136 (1954)].

⁵ Rose, A., *R.C.A. Rev.*, 12, 362 (1951).

⁶ Armistead, F. C., Pennock, J. C., and Mead, L. W., *Phys. Rev.*, 76, 860 (1949).

⁷ Coleman, J. H., and Bohm, D., *J. App. Phys.* 24, 497 (1953).

Anomalies in Osmotic Pressure Measurements

IN the course of a study of the molecular weights of coal-tar pitch fractions, we have observed unusual anomalies with two samples in benzene solution. A large number of fractions have been examined in benzene and in other solvents using modified Zimm-Meyerson osmometers fitted with specially prepared polyvinyl alcohol membranes¹ of the lowest possible permeability. We and other workers² have found samples of average molecular weight as low as 250 to be retained by the membranes, and nearly all our samples have followed van't Hoff's law almost exactly. As the full results of the investigation are being published elsewhere, attention is now directed only to the behaviour of two fractions produced by molecular distillation of that part of a coke-oven tar pitch which is insoluble in petroleum ether of boiling range 100–120° C. but soluble in benzene.

These two samples are believed to consist predominantly of condensed polycyclic aromatic hydrocarbons and to contain also limited quantities of compounds containing oxygen, nitrogen or sulphur in the ring structure or oxygen in phenolic form. Both have a number average molecular weight of about 400. The anomalous behaviour is a marked

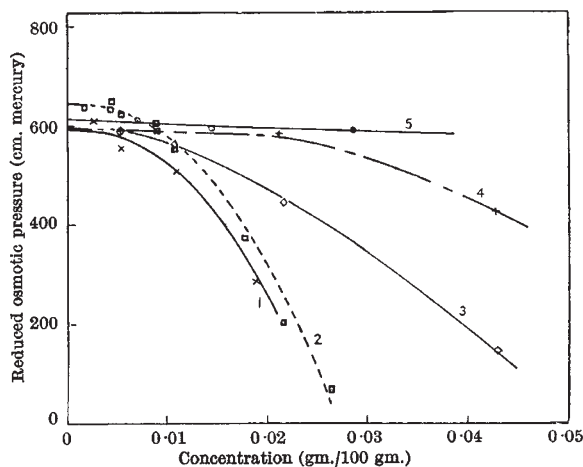


Fig. 1. Reduced osmotic pressure curves for pitch fractions. Curves 1-4, in benzene at 20°, 25°, 30°, 40° C. respectively. Curve 5, in nitrobenzene at 30° C.

reduction of the reduced osmotic pressure, when measured at 25° C. in benzene solution, with increasing concentration. In both instances the actual osmotic pressure passed through a maximum and fell again as the concentration was raised. One of the samples was found to yield no detectable pressure at all at a concentration of 0.065 gm. per 100 gm. solvent. The other sample was examined at each of several temperatures in benzene and at 30° C. in nitrobenzene, the results being shown in Fig. 1. The phenomenon tends to disappear at elevated temperatures and does not occur at all in nitrobenzene solution.

At first sight this behaviour seems to be most readily explained by assuming association of the solute molecules in a weak solvent, and the effect of raising the temperature and of changing to the stronger polar solvent seems to support this view. That association should occur to the extent indicated by the results, however, and at so low a concentration, is difficult to imagine.

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¹ Hookway, H. T., and Townsend, R., *J. Chem. Soc.*, 3190 (1952).

² Report of the Chemistry Research Board for 1953, 48 (H.M. Stationery Office, London, 1954).

Structural Changes in Boiling Solutions of Sugar with Reference to Chromatography of Carbohydrates

THE sensitivity of the chromatographic method in detecting sugars has made possible a greater appreciation of the labile character of many monosaccharides, and has emphasized the significance, in quantitative work, of degradation in sugar solutions at the boil¹ and of accelerated epimerization attributable to trace alkalis in chromatographic paper². It does not seem to be so fully appreciated, however, that structural changes in sugar solutions can occur during heating for periods comparable with those frequently used in polysaccharide hydrolyses, and that such changes might give rise to misinterpretation of the results of qualitative paper-chromatography studies.

The effect referred to may be illustrated by the chromatograms reproduced in Fig. 1, which were obtained by applying the appropriate syrups to the paper without heat-drying, developing with butanol/acetic acid/water solvent, and spraying with aniline hydrogen phthalate. The hydrolysate of the water-soluble fraction of chlorite-treated *Urena lobata* fibre, after neutralization and concentration to a syrup at 50° C., was applied, without heating, along a line on a sheet of filter-paper. A spot of the syrup was used to indicate the positions of the separated fractions in the main chromatogram (Fig. 1,a). Half the section of the paper which contained the rhamnose fraction of the hydrolysate was extracted with distilled water in a micro-Soxhlet apparatus, and the solution in the flask was maintained at the boil for 12 hr., a period in excess of that required for complete extraction, yet considerably less than many hydrolysis-times quoted in the literature. On chromatographic development the concentrated solution yielded not only a spot corresponding to rhamnose but also another spot for a sugar with an R_f value approximating to that of xylose (Fig. 1,b). The other half of the section of the paper, with the remainder of