

Of these the first possibility is unlikely because of steric hindrance by the alkyl groups while the second, although leading to a T_1 change in the correct direction, would not give rise to the large changes observed. The third and more likely possibility is an increase in the correlation times for rotation and diffusion of the water molecules with a resultant increase in both the intra- and intermolecular components of the relaxation rate⁴. Such an increase in τ_c would result if a significant fraction of the water molecules are partially immobilized in the vicinity of the apolar groups either by an increase in the 'ice-likeness' of water near the apolar groups or by the formation of partial clathrate hydrates about the apolar groups^{7,8}.

A qualitative interpretation of the E versus m curves can be given in terms of a simplified model in which the protons are assumed to occupy three distinct sites; that is, clathrate (or 'ice-like') water, hydrated Br^- ion and bulk water. The observed relaxation rate, $1/T_1$, is then given by the weighted average of the contributions from these sites and a preliminary calculation^{5,9} shows that approximately 30 water molecules are involved in the ordered water layer about the $(\text{C}_2\text{H}_5)_4\text{N}^+$ ion. The ordering is accompanied by a ten-fold increase in the correlation time more than that in bulk water. In comparison, tetramethyl ammonium bromide is a much less effective structure-maker orienting less than 5 water molecules about the $(\text{CH}_3)_4\text{N}^+$ ion. The deviations from linearity observed in the E versus m curves at higher concentrations indicate that the three-site model is inadequate under these conditions.

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STEVEN S. DANYLUK
ERNEST S. GORE

Department of Chemistry,
University of Toronto,
Toronto 5, Ontario.

¹ Frank, H. S., and Evans, M. J., *J. Chem. Phys.*, **13**, 507 (1945).

² Frank, H. S., and Wen, W. Y., *Disc. Faraday Soc.*, **24**, 133 (1957).

³ Samolov, O. Ya., *Zhur. Strukturnoi Khimii*, **4**, 499 (1963).

⁴ Bloembergen, N., Purcell, E. M., and Pound, R. V., *Phys. Rev.*, **73**, 679 (1948).

⁵ Fabricand, B. P., Goldberg, S. S., Leifer, R., and Ungar, S. G., *Mol. Phys.*, **7**, 425 (1963).

⁶ Danyluk, S. S., and Gore, E. (to be published).

⁷ Claussen, W. F., and Polglase, M. F., *J. Amer. Chem. Soc.*, **74**, 4817 (1952).

⁸ Jeffrey, G. A., and McMullan, R. K., *J. Chem. Phys.*, **37**, 2231 (1962).

⁹ Daszkiewicz, O. K., Hannel, J. W., Lubar, B., and Szczepkowski, T. W., *Nature*, **200**, 1006 (1963).

Detection of Divalent Sulphur Compounds on Paper and Thin-layer Chromatograms

RECENTLY a communication has been published by Thompson *et al.*¹ which describes a sensitive qualitative test for sulphoxides on paper chromatograms. The method is based on the reaction of sulphoxides with hydriodic acid to form iodine. C. De Marco² essentially extended the method of Thompson to certain other classes of partially oxidized sulphur compounds like sulphinic acids and sulphones. However, as explicitly stated in De Marco's communication, the Thompson test is of no direct use for the detection of other classes of organic sulphur compounds, especially the large number of substances containing divalent sulphur.

The publication of the two aforementioned papers^{1,2} induced us to report a method used in this laboratory, which makes it possible to detect just those classes of organic sulphur compounds giving no reaction with hydriodic acid. Our method is based on the well-known oxidation of divalent sulphur compounds by periodic acid to sulphoxides, sulphones, sulphinic acids or derivatives thereof.

A positive reaction with neutral aqueous potassium (*meta*) periodate solution is given by aliphatic thiols,

sulphides, disulphides, thioketones, thiamides and thioureas³. The aromatic thiols, sulphides, and disulphides usually do not react under these conditions⁴. However, these aromatic sulphur compounds will give satisfactory positive results with periodate in acetic acid solution, since an increase in the acidic strength of the oxidant favours the oxidation reaction^{5,6}.

The oxidation of compounds on paper chromatograms with periodate and the subsequent development of the unconsumed periodic acid with benzidine was originally used by Viscontini *et al.*⁷, in carbohydrate chemistry, where the method indicates glycol groups. In this laboratory, the application of Viscontini's method for the detection of sulphur compounds was first observed while working with sugar-amino-acid complexes, the amino-acids having been DL-methionine and L-cystine. The method was later extended to aliphatic and aromatic thiols, sulphides and thioketones. As expected, thiophene and its derivatives give no reaction, the reason being the aromatic character of these compounds.

The technical details of the periodic acid oxidation of sulphur compounds are very similar to those given in the original application by M. Viscontini. The paper or the glass-plate is sprayed with a 0.1 per cent solution of sodium (*meta*) periodate in water or in 8 N acetic acid, respectively. After 4 min the colour is developed by spraying the paper with a 0.5 per cent solution of benzidine in *n*-butanol/acetic acid (4:1 v/v). Where oxidizable substances are present on the paper, the periodate is consumed and, afterwards, the colourless benzidine is not oxidized to the dark blue compound as on the rest of the paper. The final chromatogram shows white spots on a blue background.

The procedure is readily reproducible and sensitive. In the case of methionine the sensitivity is comparable to that of ninhydrin (5–10 μg). With aromatic sulphur compounds, the sensitivity is somewhat lower and depends on the aromatic residue (20–30 μg).

A preparative periodate oxidation of methionine was performed under the conditions of the development of the chromatogram. The main reaction product was methionine sulphoxide, with a minor amount of the sulphone present.

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RUDOLF STEPHAN
J. GORDON ERDMAN

Mellon Institute,
Pittsburgh, Pennsylvania.

¹ Thompson, J. G., Arnold, W. N., and Morris, C. J., *Nature*, **197**, 380 (1963).

² De Marco, C., *Nature*, **198**, 683 (1963).

³ Boseken, J., and Arias, E., *Rec. trav. chim.*, **54**, 711 (1935).

⁴ Hargrave, K. R., *Proc. Roy. Soc., A*, **235**, 55 (1956).

⁵ Overberger, C. G., and Cummins, R. W., *J. Amer. Chem. Soc.*, **75**, 4250 (1953).

⁶ Barnard, D., Hargrave, K. R., and Higgins, G. M. C., *J. Chem. Soc.*, 2845 (1956).

⁷ Viscontini, M., Karrer, P., and Hoch, D., *Helv. chim. acta*, **38**, 642 (1955).

Production of Gallium by Continuous Electrodeposition from Acidic Solutions

As a means of production, electrolysis of gallium from only alkaline and not acidic solutions has been reported¹. The principal difficulties reported using acidic solutions are: (a) poor current efficiencies; (b) formation of solid gallium oxychloride².

Reports of acidic gallium electrolyses^{3,4} have shown it to be feasible, and the simple considerations leading to successful acidic gallium electrodeposition useful for large-scale production are outlined in this work.

Electrolysis of an aqueous solution of GaCl_3 using a molten gallium cathode and a graphite anode results in the sequence of events here.