

suspensions and sedimentation in May 1949, and reported in these columns<sup>10</sup>.

A. J. HUGHES

John and E. Sturge, Ltd.,  
1 Wheelleys Road, Birmingham 15.

<sup>1</sup> Einstein, A., *Ann. Physik*, **19**, 289 (1906).

<sup>2</sup> Einstein, A., *Ann. Physik*, **34**, 591 (1911).

<sup>3</sup> Bingham, E. C., and Durham, T. C., *Amer. Chem. J.*, **46**, 278 (1911).  
Bingham, E. C., "Fluidity and Plasticity" (McGraw-Hill, 1922).

<sup>4</sup> Hughes, A. J., M.Sc. thesis, Univ. of Wales (1949).

<sup>5</sup> Oliver, D. R., and Ward, S. G., *Nature*, **171**, 397 (1953).

<sup>6</sup> Brinkman, H. C., *J. Chem. Phys.*, **20**, 571 (1952).

<sup>7</sup> Eirich, F., Bunzl, M., and Margaretha, H., *Kolloid Z.*, **74**, 276 (1936).

<sup>8</sup> Eilers, H., *Kolloid Z.*, **97**, 313 (1941).

<sup>9</sup> Vand, V., *J. Phys. Coll. Chem.*, **52**, 277 (1948).

<sup>10</sup> Ward S. G., *Nature*, **164**, 220 (1949).

WE are indebted to Mr. Hughes for directing our attention to the fact that the equation given by Bingham for the fluidity of a suspension may be developed to give the relationship

$$\eta_r = 1 + kc + k^2c^2 + k^3c^3 \dots$$

as in the M.Sc. thesis of Hughes, a copy of which he has kindly allowed us to peruse. In the equation,  $\eta_r$  is the relative viscosity of a suspension having a volumetric concentration  $c$  of the solid phase;  $k$  is a constant.

In our opinion it is not justifiable to expand equation (2) in Hughes's communication to terms beyond the first power of  $c$  and to expect it to apply to higher concentrations than that postulated by Einstein, especially as he deliberately neglected the effects of interparticle collisions. Accordingly, any agreement for concentrations higher than that considered by Einstein, between the expanded version of Einstein's equation and those developed by Vand, Brinkman, Roscoe and others, appears to be fortuitous.

Hughes found that the equation

$$\eta_r = 1 + kc + k^2c^2 + k^3c^3 \dots$$

is applicable to certain slowly settling suspensions. We have found that it holds only for stable suspensions of spheres, for which the value  $k$  depends upon the type of viscometer used but does not differ greatly from 2.5. For unstable (settling) suspensions we have found that a relationship of the form

$$\eta_r = (1 + k_1) + (1 + 2k_1)kc + (1 + 3k_1)k^2c^2 \dots$$

appears to hold for solid concentrations between 10 and 30 per cent by volume. The numerical coefficient  $k_1$  depends upon the instability of the suspension. It is hoped that detailed results will be published shortly.

DONALD R. OLIVER  
STACEY G. WARD

University, Edgbaston,  
Birmingham 15.

### A Study of Manganous Complexes by Paramagnetic Resonance Absorption

THE paramagnetic resonance absorption of unstable metal complexes in aqueous solution has been explored and has been applied to the measurement of dissociation constants of such complexes. The method has the obvious limitation, in common with other magnetic methods, that direct measurements are confined to those ions and molecules which are paramagnetic. On the other hand, the method, in

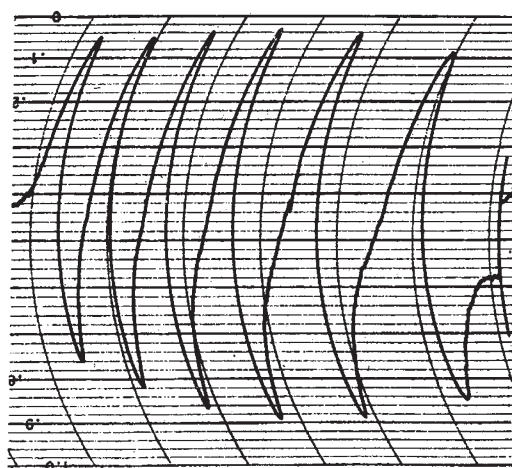


Fig. 1. Record of the derivative of the paramagnetic resonance absorption versus magnetic field of an aqueous solution of manganous chloride (0.005 M)

common with other spectroscopic methods, has the advantage that it can measure directly and rapidly the concentration of the free metal ion in solution without disturbing any pre-existing equilibrium state.

Manganous ion in dilute solid or liquid solution exhibits a hyperfine structure in its absorption when investigated by the paramagnetic resonance absorption method<sup>1</sup>. The existence of this hyperfine structure with its sensitive dependence on the chemical environment of the manganous ion and on type of bond in the molecule, coupled with the widespread biochemical activity of manganous ion, led us to initiate our studies with this ion.

The apparatus used in these studies records the derivative of the absorption curve with respect to magnetic field as a function of the field. Fig. 1 shows a typical record of the spectrum of an aqueous solution of manganous chloride (0.005 M), which was scanned from approximately 2,950 to 3,450 gauss in 5 min. with a modulation of 4 gauss and a microwave frequency of 9,000 Mc./s. Similar spectra can be obtained at concentrations ranging from 0.001 M to 0.5 M with approximately 0.1 ml. solution. The height of the derivative curve from the maximum to the minimum was found to be a linear function of the concentration of manganous ion in the range investigated, namely, 0.001–0.01 M, and it was therefore unnecessary to integrate the curves to obtain the concentration.

The phenomenon which made it possible to calculate dissociation constants was the disappearance of the hyperfine spectrum when the manganese formed a complex; the height of the peaks corresponded to the concentration of free manganous ion. When an equimolar concentration of ethylenediamine tetraacetic acid was added to a manganous chloride solution at pH 7.5, the peaks disappeared completely. A group of phosphate esters was investigated and it was found, for example, that with a series of increasing concentrations of glucose-6-phosphate, progressively smaller peaks were obtained corresponding to progressively lower concentrations of free manganous ion, as shown in Table 1. From these results, a dissociation constant  $4.76 \times 10^{-3}$  M/litre for a complex of one manganese ion with one divalent glucose-6-phosphate ion can be calculated. The dissociation constant for glucose-1-phosphate was found to be  $5.18 \pm 0.10 \times 10^{-3}$ , and those of other mono-