

are possible. If the constants  $K_s$  and  $K_a$  are given respectively the values of approximately  $10^{-2}$  and  $10^{-5}$  (as would appear not inconsistent with published results<sup>6,7</sup>), equation (1) predicts the observed sorption isotherm and also predicts about a two-fold increase in uptake of copper if the hydrogen ion concentration is decreased by a factor of 10 or more, as is the case in passing from 0.1 M copper sulphate to 0.1 M copper acetate (namely, sulphate pH 4.2, acetate pH 5.4). The system is obviously more complicated than depicted here, but it seems reasonable to suppose that the foregoing interpretation of the facts is essentially correct.

To sum up, therefore, the evidence now available makes it appear most probable that sorption of copper from solution by cellulose is due entirely to the action of acidic groups in, or associated with, the cellulose molecules. From this it follows that measurements of sorption of copper cannot be expected to yield any information necessarily related to the physical structure of the cellulose.

I am indebted to Dr. T. P. Nevell, of the Shirley Institute, for providing the specimens of oxycellulose used in this investigation. The work forms part of the programme of fundamental research undertaken by the Council of the British Rayon Research Association.

R. I. C. MICHIE

Department of Textile Chemistry,  
College of Science and Technology,  
Manchester 1.

<sup>1</sup> Belford, D. S., Myers, A., and Preston, R. D., *Biochim. Biophys. Acta*, **34**, 47 (1959).

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<sup>3</sup> Corbett, W. M., and Ewart, J. A. D., *Svensk. Papperstidn.*, **82**, 277 (1959).

<sup>4</sup> Davidson, G. F., and Nevell, T. P., *J. Text. Inst.*, **39**, T102 (1948).

<sup>5</sup> Nevell, T. P., *J. Text. Inst.*, **42**, T91 (1951).

<sup>6</sup> Neale, S. M., and Stringfellow, W. A., *Trans. Farad. Soc.*, **33**, 881 (1937).

<sup>7</sup> *Stability Constants of Metal Ion Complexes*, by Bjerrum, Schwarzenbach and Sillén. Special Publication No. 6, Part 1, p. 3 (Chemical Society, London, 1957).

I AM not completely certain that Dr. Michie is discussing quite the same problem as that investigated by my co-workers and me. Although we used the term 'copper-cellulose complex' in some of our papers, we were consciously using the term 'cellulose' as defined by two of us in another connexion<sup>1</sup> as a family of polysaccharides built into microfibrils of a substance which, by virtue of the extraction procedure by which it is obtained and of certain physical properties, is normally called cellulose; we were therefore not discussing those rare products—which we term 'eucellulose'<sup>1</sup>—which yield glucose only on hydrolysis.

In collaboration with Mr. Dennis, I am following up our earlier work on what should be called a 'copper-microfibril' complex. Our results and conclusions will eventually be published *in extenso* elsewhere; at the moment we can say only that the bulk of the uptake of copper is not by the 'pure' cellulose component but by pentosans so firmly bound to the microfibril that they withstand the chemical procedures normally used for the extraction of  $\alpha$ -cellulose. It is complexes with these, moreover, which give the sharp electron diffraction diagrams. We are ourselves not certain that copper adsorbed on 'pure' cellulose yields such a diagram; certainly none has been obtained with *Valonia* cellulose in spite of a measurable uptake of copper.

On the point of adsorption in 'pure' cellulose, Dr. Michie may well be correct for the materials and conditions he uses, though his interpretation rests on the straight-line relationship between uptake of copper and the so-called  $-\text{COO}^-$  content of the cellulose as determined by a method which itself depends on cation adsorption. The difference between the cotton used by him and by us was that, whereas our cotton had been treated with strong alkali in the cold, his had been scoured (that is, boiled in 1 per cent sodium hydroxide). We have reason to believe that the effect of scouring is complex, but we cannot report on this at the moment.

R. D. PRESTON

Department of Botany,  
University,  
Leeds.

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### The Borohydride Ion in the Lithium Borohydride Lattice

IN a recent communication in *Nature*, Dr. C. J. H. Schutte<sup>1</sup> has suggested that the anomalous band occurring at about  $1,250 \text{ cm.}^{-1}$  in the paraffin-oil mull spectrum of lithium borohydride at room temperature<sup>2</sup> may be assigned to the doubly degenerate frequency,  $\bar{\nu}_2(E)$ , of the tetrahedral  $\text{BH}_4^-$  ion. This frequency is normally inactive in the infra-red, but it is suggested that under the space-group  $V_h$  of crystalline, orthorhombic lithium borohydride, the  $\text{BH}_4^-$  ions occupy sites of symmetry  $C_3$ ; the degeneracy is thereby removed so that all the fundamentals are now allowed.

I suggest that confirmation of the above assignment is provided by a previous calculation of some of the vibration frequencies of the tetrahedral hydride ions<sup>3</sup>. The calculation was based on a theoretical discussion of the dynamics of binary hydrides<sup>4</sup>, in which it was shown that, with the assumption of a spherical and rigid electron distribution in the molecule, the doubly degenerate frequency,  $\nu_2(E)$ , of a tetrahedral  $\text{XH}_4$  molecule (or ion) could be determined to within 5 per cent by the formula:

$$4\pi^2\bar{\nu}_2^2 = 9(6)^{1/2}e^2/32mr_0^3$$

where  $e$  and  $m$  are the charge and mass of the proton and  $r_0$  is the equilibrium  $\text{XH}$  distance. With the value of the B-H distance obtained from proton magnetic resonance measurements on the  $\text{BH}_4^-$  ion<sup>5</sup>, namely  $1.25 \text{ \AA.}$ , the above formula gave a calculated frequency of  $1,171 \text{ cm.}^{-1}$  ( $\pm 59 \text{ cm.}^{-1}$ ) for  $\bar{\nu}_2$ . This value, therefore, gives good support to the above assignment of Schutte and is also in good agreement with the value of  $1,210 \text{ cm.}^{-1}$  obtained<sup>6</sup> from measurements of the Raman spectra of solutions of the borohydride ion in liquid ammonia.

D. A. BROWN

Department of Chemistry,  
University College,  
Upper Merrion Street,  
Dublin.

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