3–5 hours. The purification procedure requires ~30 hours.

The simplicity and rapidity of this method appear to surpass any purely chemical method so far reported for the preparation of labeled succinate. It compares favorably with the biosynthesis of carboxyl-labeled succinate using cell suspensions of *Tetrahymena gelii*[5] while possessing the advantage that predominantly methylene-labeled succinate as well as uniformly-labeled succinate can be prepared.

[5] C. B. Van Niel, J. O. Thomas, S. Ruben and M. D. Kamen, *Proc. Natl. Acad. Sci.* (*U. S.*), **28**, 157 (1942).

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The Electrophoretic Migration of Cellulose in Cupriethylenediamine Solution

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By substituting copper plates for the silver–silver chloride electrodes and filling the entire system with dilute cupriethylenediamine solution the migration of cellulose can be observed conveniently in a Tiselius electrophoresis apparatus[1] equipped with a Longsworth scanning device. In agreement with previous observations[2] cellulosic material was found to migrate slowly toward the anode under the influence of an electric current.

In eleven experiments employing cupriethylenediamine solutions of various celluloses the ascending boundaries invariably remained sharp and unresolved, while the descending boundaries usually separated into two distinguishable peaks or bands. The patterns of the descending boundaries appeared to be characteristic of the dissolved cellulose.

In view of the known interaction between cellulose and cupriethylenediamine it is not surprising that the ascending and descending boundaries are not mirror images. Such disymmetry has often been attributed to interaction among components. Smith and Briggs[3] cite many such examples, and they have obtained patterns showing a single ascending peak and multiple descending peaks from interaction between serum albumin and methyl orange.

Cupriethylenediamine exists in solution largely in the dissociated form, CuEn$_2^{++}$. In order to account for the electronegative character of the cellulose-cupriethylenediamine complex the copper-containing component must lose its strong positive charge upon combination with cellulose. This could occur through ionic linkage with cellulose as in I; or the complexing valences could be non-ionic, but of such a nature that the copper is no longer strongly basic. The complex would then exist largely in the undissociated form, II.

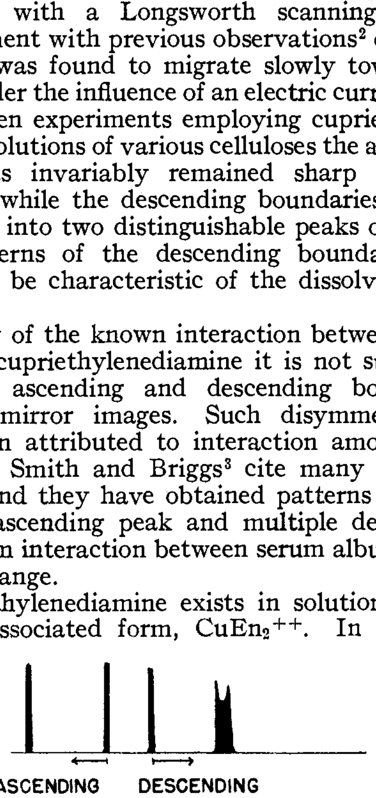
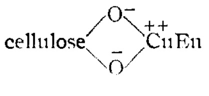
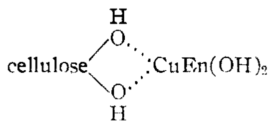


Fig. 1.—The initial and 1300-minute boundaries for methanolyzed mercerized cotton cellulose; 0.5% concentration in 0.1 *N* cupriethylenediamine solution: current, 30 ma.; field strength, 2.98 v./cm.


I


II

The *p*H of the solvent is approximately 12.7, hence a small amount of dissociation of cellulosic hydroxyl would account for the observed anodic migration.

Figure 1 shows initial and final boundaries for a low molecular weight methanolyzed cellulose derived from cotton linters. The ascending boundary moved as a single component, while the descending boundary split into two well-defined peaks having mobilities of 0.72 and 0.85×10^{-5} sq. cm./volt/sec. To obtain this result, a sample containing 250 mg. of methanolyzed cotton cellulose[4] was dissolved in 5.0 ml. of stock cupriethylenediamine solution (one molar in copper, 2.01 molar in ethylenediamine) and diluted to exactly 50 ml. with water. This solution was placed in the bottom and descending leg of the 92-mm. electrophoresis cell and the remainder of the cell and electrode chambers were filled with about 1500 ml. of cupriethylenediamine solution of the same concentration. The assembly was brought to temperature equilibrium at 0° and the boundaries were formed and moved into position for observation by the usual procedures. The boundaries were photographed by the schlieren technique employing a mercury vapor light source. A current of 30 ma. was then passed through the cell for 1300 minutes and the final position of the boundaries was recorded.

There was no evolution of gases at either electrode during the experiment. The solutions in the anode and cathode chambers were analyzed separately for copper and nitrogen at the end of the run. The results of these analyses are compared in Table I with the composition of the initial diluted cupriethylenediamine solution. It is apparent that some change in composition of the solutions in the electrode chambers occurred during the run. There was a migration of ethylenediamine toward the cathode and an observable plating out of copper on this electrode. Some of the migration of cellulose toward the anode might have arisen from displacement due to the transport of ethylenediamine and copper to the closed cathode compartment; however, it is difficult to explain the splitting of the descending boundary on this basis.

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[1] L. G. Longsworth, *Chem. Revs.*, **30**, 323 (1942).

[2] W. A. Sisson, *Contrib. Boyce Thompson Institute*, **10**, 113 (1938).

[3] R. F. Smith and D. R. Briggs, *J. Phys. and Colloid Chem.*, **54**, 33 (1950).

[4] This material was prepared by autoclaving purified, mercerized cotton linters for one hour at 120° with methanol containing, initially, 3.6 per cent. anhydrous hydrogen chloride. Its intrinsic viscosity was 0.35 in A. C. S. cuprammonium.

TABLE I

THE COMPOSITION OF CUPRIETHYLENEDIAMINE INITIALLY AND AT THE END OF AN ELECTROPHORESIS RUN

Cupriethylenediamine solution	Cu, g./l.	N, g./l.
Initial	6.35	5.64
Anode chamber after 1300 minutes	6.25	5.51
Cathode chamber after 1300 minutes	5.37	5.90

A descending boundary quite different from the preceding in appearance was obtained with hydrolyzed cotton cellulose. Shown in Fig. 2 are initial and 1,352 minute boundaries for a hydrocellulose produced by autoclaving mercerized Empire cotton fiber with 0.5 *N* aqueous hydrochloric acid for 2 hours at 120°; the intrinsic viscosity of this preparation was 0.52 in cuprammonium. The descending boundary developed two peaks, corresponding to mobilities of 0.57 and 0.91 × 10^{-5} sq. cm./volt/sec. Not only the mobilities of the peaks but the distribution of material appears to be different from those of the methanolyzed sample.

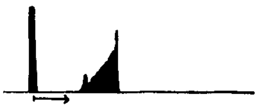

Fig. 2.—The initial and 1352-minute descending boundaries for hydrolyzed cotton cellulose; 0.5% concentration in 0.1 *N* cupriethylenediamine solution: current, 30.5 ma.; field strength, 2.97 v./cm.

In an attempt to enhance the rate of anodic migration of the hydrocellulose the reducing end groups of the above preparation were oxidized at 0° with sodium hypoiodite solution buffered to *p*H 10.6, conditions favorable for producing end-group carboxyls. Titration of the acid form of the oxidized material showed the presence of 0.061 mole of carboxyl per gram. This oxidized hydrocellulose, subjected to electrophoresis, gave a descending boundary pattern (Fig. 3) similar to the preceding one; but the mobilities of the two components were greater, 0.71 and 0.99 × 10^{-5} sq. cm./volt/sec., respectively.

Purified Empire cotton fiber, after methanolysis for 96 hours at 15° in methanol containing 0.5 *N* hydrogen chloride, gave a methanolyzed cellulose having an intrinsic viscosity of 1.45 in cuprammonium solution. Two hundred and fifty milligrams of this material was dissolved in 10 ml. of the stock cupriethylenediamine solution and diluted to 50 ml. giving a solution 0.2 molar in copper. This solution was run against solvent of the same concentration and the boundaries were photographed initially and after 2,760 and 4,200 minutes. The descending boundaries are shown in Fig. 4; the mobilities of the slow and fast moving components were calculated to be 0.72 and 0.80 × 10^{-5} sq. cm./volt/sec., respectively.

Native cotton cellulose does not remain dissolved in cupriethylenediamine upon dilution to 0.1 molar copper concentration. However, celluloses having intrinsic viscosities as great as 2.88 in A.C.S. cuprammonium were run successfully with the 0.1 molar cupriethylenediamine. Runs made with 0.2 molar cupriethylenediamine solution yielded results essentially the same as those obtained with the 0.1 molar solvent; hence it is possible that even less degraded celluloses can be investigated with the stronger solvent.

Fig. 3.—The initial and 1400-minute descending boundaries for hypoiodite oxidized hydrolyzed cotton cellulose; 0.5% concentration in 0.1 *N* cupriethylenediamine solution: current, 30 ma.; field strength, 3.01 v./cm.

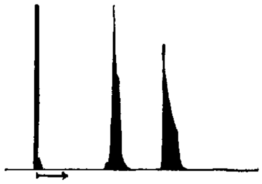

Fig. 4.—The initial, 2760-minute and 4200-minute descending boundaries for a methanolyzed native cotton cellulose; 0.5% concentration in 0.2 *N* cupriethylenediamine solution: current, 30 ma.; field strength 1.74 v./cm.

In the seven other experiments not reported in detail there are indications that increasing ethylenediamine concentration may increase the rate of cellulose migration; also that the mobilities may increase slightly during the course of a run. The latter may be due to oxidative degradation occurring during the experiment, since no particular precautions have yet been employed to exclude air from the system. It should be mentioned that δ and ϵ boundaries were not observed in any of these experiments.

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Alkyliodosilanes: Methyl, Propyl, Butyl and Amyl

BY HERBERT H. ANDERSON

Six new alkyliodosilanes—methyltriiodosilane, dimethyldiiodosilane, *n*-propyltriiodosilane, *i*-propyltriiodosilane, *n*-butyltriiodosilane and *n*-amyltriiodosilane prepared by the Ruff method[1] are described. Some information concerning the reaction of aniline with a variety of silicon halides and pseudo halides is also presented.

Preparation of Compounds.—Our earlier paper[2] describes the synthetic process in detail; the equations are illustrative

$$RSiCl_3 + 6C_6H_5NH_2 \longrightarrow RSi(HNC_6H_5)_3 + 3C_6H_5NH_3Cl\downarrow$$
$$RSi(HNC_6H_5)_3 + 6HI \longrightarrow RSiI_3 + 3C_6H_5NH_3I\downarrow$$

A similar set of equations is valid for dimethyldiiodosilane. The method is not suitable for preparing trialkyliodosilanes.

***n*-Propyltriiodosilane.**—On mixing 43 g. of *n*-propyltrichlorosilane, 170 ml. of aniline and 250 ml. of benzene, there was spontaneous warming from 25 to 68°, and much precipitation took place. The material was processed as described earlier[2] to yield 44 g. of *n*-propyltriiodosilane.

***i*-Propyltriiodosilane.**—An initial temperature rise of only 16°, accompanied by only slight precipitation, occurred when 17 g. of *i*-propyltrichlorosilane, 64 ml. of aniline and 100 ml. of benzene were mixed. Even after three days the precipitate was small; the addition of another 25 ml. of aniline and another period of two days did not force the reaction more than one third of the way to completion, and it was necessary to reflux the mixture two hours to produce proper precipitation. The mixture was allowed to cool overnight, and processed as usual to give 14 g. of *i*-

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[1] O. Ruff, *Ber.*, **41**, 3738 (1908).

[2] H. H. Anderson, D. L. Seaton and R. P. T. Rudnicki, THIS JOURNAL, **73**, 2144 (1951).