disodium pyrophosphate. Thus Tammann,[7] and Karbe and Jander[8] reported that the results obtained at approximately 300° were inconsistent, but could offer no explanation. Boulle[9] found that when this heating was carried out in a stream of water vapor, his form B ($NaPO_3$ (II) was produced in a pure state. Such a condition may also be approximated by rapidly heating the monohydrate of monosodium orthophosphate in a fairly thick layer to 300°. The author has found that when the reverse is true, namely, when the vapor pressure of water was low, as when anhydrous disodium pyrophosphate was sprinkled in a very thin layer in a platinum dish and introduced into a furnace at 330°, $NaPO_3$ (III) was the principal product. Intermediate conditions, as for example slow heating to 300° using a moderately thick layer of material gave $NaPO_3$ (I) as the major product.

Quite a number of chemical compounds exhibit different polymorphic forms which, however, have the same chemical properties; the metaphosphate system appears to be unique in the fact that it comprises a number of crystalline phases, some of which in aqueous solution exhibit different chemical properties, while others behave identically when dissolved.

The diagram presents the current state of information concerning the sodium metaphosphate system.

Acknowledgments.—The author wishes to express his appreciation to Miss Catherine Hester who made most of the microscopical examinations and to Mrs. Jeanne Pfister and Mr. R. K. Scott who carried out the X-ray analysis.

Summary

1. Two new crystalline sodium metaphosphates have been produced which in aqueous solution behave like $NaPO_3$ I.

2. The sodium metaphosphate diagram of Partridge, Hicks and Smith has been revised to show more recent developments including those of the present study.

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[7] Tammann, *J. prakt. Chem.*, **45**, 463 (1892).

[8] Karbe and Jander, *Kolloid-Beihefte*, **54**, 9 (1944).

[9] Boulle, *Compt. rend.*, **206**, 915 (1938).

[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

Cuprammonium–Glycoside Complexes. I. Conductometric Measurements

BY RICHARD E. REEVES AND JULIUS R. JUNG, JR.

In the continued investigation of cuprammonium–glycoside complexes, a means other than one dependent upon optical activity was required for the recognition of these complexes. Such a method was necessary for the study of complex formation between cuprammonium and inactive glycols, as well as for those substances which, though optically active, form complexes without exhibiting large rotatory changes.

Our earlier work,[2,3] dealing exclusively with the optical method of measurements, had shown that highly active complexes form between cuprammonium and properly oriented glycol groups. It was found that such complex formation was associated with a decrease in conductivity in the cuprammonium solution; hence it was decided to follow this phenomenon by the conductometric method of measurement.

By this method many degrees of affinity for cuprammonium could be detected in the various substances tested. It was possible to distinguish the D- and L-forms of 2,3-butanediol from the *meso* variety. Various methyl α-hexopyranosides could be sharply distinguished from each other, and a difference was encountered between the complex-forming tendency of a number of α- and β-glycoside pairs. Furthermore, it was shown that the substance D-glucosan $<1,5>\beta<1,6>$ (levoglucosan) does react with cuprammonium, although on the basis of optical rotation measurements it was previously reported not to react.[4]

Experimental Part

The physical properties of all the substances employed in this investigation were in excellent agreement with the properties listed in the literature.

A stock solution containing between 5 and 8 g. of copper per liter was prepared by passing a current of air through a concentrated A. C. S. standard ammonium hydroxide solution in the presence of copper turnings. The ammonia and turnings were contained in a tall glass cylinder which was cooled in an ice-bath during the reaction. This stock solution may be preserved in the refrigerator without added stabilizer for a long time. After analysis for copper and ammonia, portions of the stock solution were diluted to contain 0.01 mole of copper (0.635 g.), 3 moles of ammonia, and 10 ml. of ethanol per liter. This standard solution, "cupra A," was employed in most of the conductivity experiments; whenever a different solution was used a notation will be made regarding its composition.

To permit the use of small amounts of glycosides very dilute cuprammonium solutions were required. The specific conductance of various ammonium hydroxide solutions with and without 0.01 molar copper are shown in Fig. 1. Inspection of this figure shows that conductance is least sensitive to ammonia concentration in the region

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] R. E. Reeves, *Sci.*, **99**, 148 (1944).

[3] R. E. Reeves, *J. Biol. Chem.*, **154**, 49 (1944).

[4] K. Hess, W. Weltzien and E. Messmer, *Ann.*, **435**, 1-144 (1924).

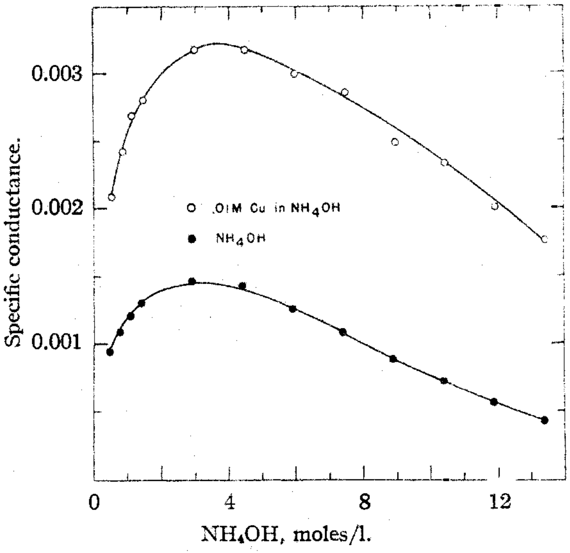

Fig. 1.—The specific conductance of ammonia solutions with and without copper.

of 3 molar ammonia (the region of maximum conductance) hence this concentration was chosen. The reason for the incorporation of ethanol is illustrated by the ethanol curve of Fig. 2. By its incorporation a "hydroxyl effect" is considerably levelled off, and only true complex-forming substances show a pronounced change in conductance.

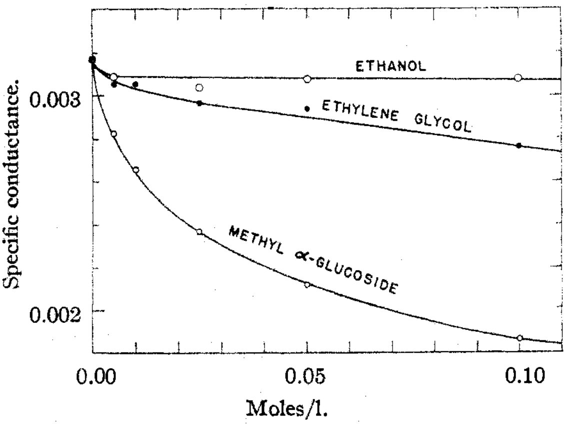

Fig. 2.—The change in specific conductance upon adding various substances to a solution containing 0.01 mole of copper and 3 moles of ammonia per liter.

Substances which ionize in solution, or esters which may decompose into ionizable substances, cannot be used in the conductometric method without obscuring the effect of the conductance change due to complex formation.

Conductivity measurements were made with a commercial 1000-cycle conductivity bridge using a dip-type cell capable of operating with 14 ml. of solution. The readings were made in terms of resistance (ohms, Ω), and specific conductance (L) was calculated by the formula $L = c/\Omega$. The cell constant, c, determined with 0.1 M potassium chloride, was found to be 0.116. The temperature at the time of measurement was controlled by immersion of the tube containing the liquid in a water thermostat held at 25 ± 0.2°. Except while measurements were in progress the tubes were stoppered to prevent loss of ammonia and the attendant cooling of the cuprammonium solution. The small amounts of material were added directly to the cupra and concentrations were calculated upon the original volume of solution.

Results

Aliphatic Glycols.—In Fig. 3 are shown the resistance *versus* glycol concentration relationships for the three forms of 2,3-butanediol dissolved in the standard cuprammonium solution. The D- and L-forms are, of course, indistinguishable from each other, by this method, but they show a marked difference from the *meso* variety, the latter giving a smaller change in resistance. The behavior of ethylene glycol (not shown in the figure) was almost identical with that of the *meso* form of the butanediol. A type of behavior believed to be different is illustrated in Fig. 3 by trimethylene glycol. This substance has two hydroxyl groups separated by a methylene group and the data are regarded as indicating no significant change in conductivity. From this it is deduced that trimethylene glycol belongs in the group of substances which fail to form a copper complex.

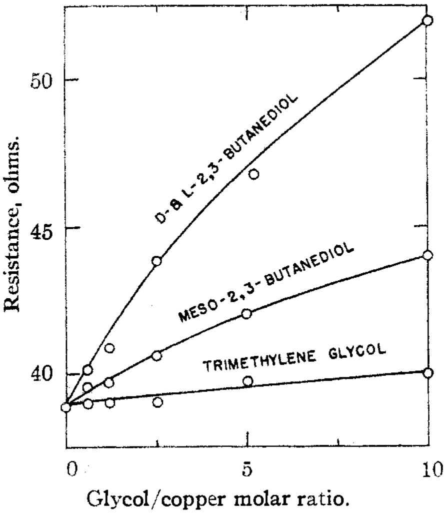

Fig. 3.—The resistance *versus* concentration relationships of various aliphatic glycols in cupra A.

Glycopyranosides.—In Fig. 4 are shown the resistance *versus* glycoside concentration relationships for a number of methyl α-hexosides. That these glycosides are much more actively complex-forming substances than the aliphatic glycols is indicated by the lower concentrations required to produce similar conductivity changes. The glycosides exhibited affinities for cuprammonium increasing in the order glucoside, galactoside, altroside, mannoside and guloside. In Fig. 5 comparison is made between a number of α- and β-pyranoside pairs. It will be noted, in each of these instances, that the curve for the β-glycoside lies above that of the corresponding α-glycoside.

D-Glucosan$<1,5>\beta<1,6>$.—The behavior of this substance in cuprammonium solution was first examined by Hess, Weltzien and Messmer,[4] who concluded that there was no reaction

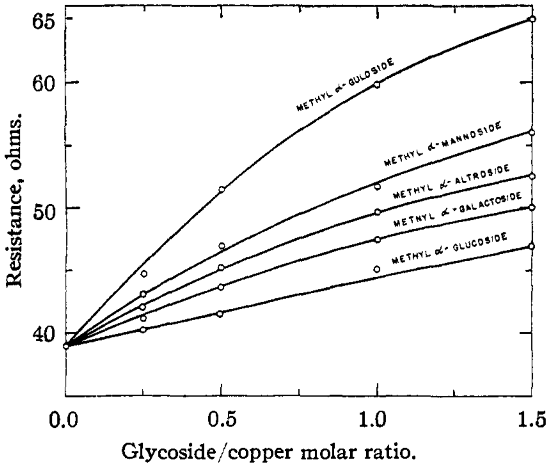

Fig. 4.—The resistance *versus* concentration relationships of various methyl α-D-hexopyranosides in cupra A.

between it and cuprammonium, since the optical rotation in this solvent was practically the same as in a copper-free solution. Their finding in regard to lack of rotatory shift was later confirmed,[3] but the conclusion that no complex formation occurred was shown to be incorrect by the data given in Fig. 6. The effect on conductivity of levoglucosan is at least equivalent to that of methyl α-glucoside, a substance known to be complex-forming because of its optical behavior, as well as because of the conductivity effect noted above.

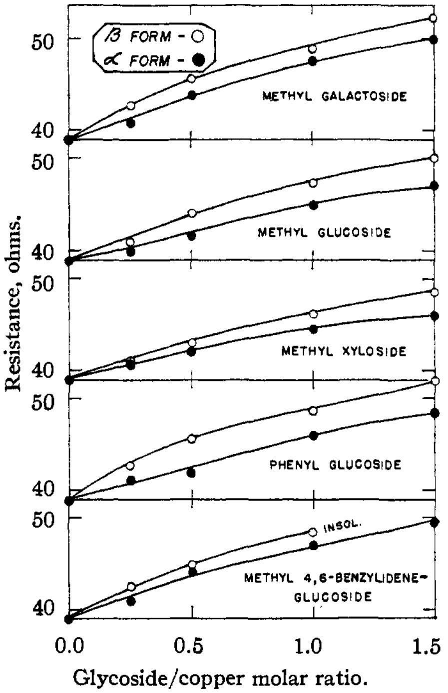

Fig. 5.—Comparison of resistance–concentration relationships of various α- and β-D-glycopyranoside pairs in cupra A.

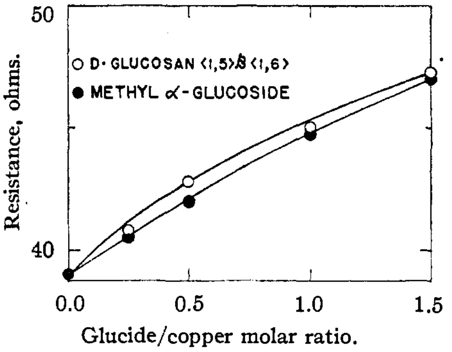

Fig. 6.—Comparison of the effect on resistance of D-glucosan<1,5>β<1,6> (levoglucosan) and methyl α-D-glucoside in cupra A.

Our studies to date indicate that complex formation is always accompanied by a marked decrease in the conductance of a dilute cuprammonium solution unless the effect is obscured by decomposition or ionization of the substance being examined. Complex formation may or may not be associated with a large shift in optical rotation. The conditions which determine the rotatory behavior will be considered more fully in subsequent communications.

Acknowledgment.—We are indebted to Dr. R. D. Coghill, Professor C. S. Hudson and Dr. H. S. Isbell for supplying some of the substances employed in this investigation.

Summary

A conductometric method is described that is capable of measuring the relative affinities of various substances for cuprammonium. Differences in affinity were observed for the optically active and *meso* forms of 2,3-butanediol. Differences were noted in the behavior of various methyl α-hexosides, and between various α- and β-pyranoside pairs. The substance D-glucosan<1,5>β<1,6> was shown to react with cuprammonium solution.

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