to a 3-fold (stoichiometric)[3] excess of lithium aluminum hydride in ether with stirring in an apparatus adequately protected from atmospheric moisture. The reaction mixture was then further decomposed by addition of 5 ml. water followed by 45 ml. 15% sulfuric acid. The product, 3,4-methylenedioxyphenylethyl alcohol, was obtained in 62% yield by ether extraction, followed by distillation, n_{D}^{20} = 1.5500, lit.[21] n_{D}^{20} = 1.5478. The phenylurethan derivative was prepared and melted at 96.6–97.0°, lit.[22] 96.4–97.0°.

Oleic acid. Oleic acid (5.0 g., 0.018 mol.) was ozonized in 40 ml. *n*-heptane solution by a procedure similar to that described in the previous paragraph. The ozonide precipitated and ether was added to obtain a solution which was then reductively decomposed with lithium aluminum hydride. Ether extraction followed by distillation *in vacuo* afforded the two cleavage products. A 79.4% yield of 1-nonanol with n_{D}^{20} = 1.4334, lit.[16] n_{D}^{20} = 1.43347 was obtained. The infrared spectrum of the product was identical with that of an authentic specimen. 1,9-Nonanediol obtained in 49.5% yield melted at 44.2°, lit.[23] 45.5°.

1-Octene (I). 1-Octene (2.5 g., 0.022 mol.) was ozonized in 25 ml. carbon tetrachloride at 0°. The solvent was evaporated at room temperature in a current of nitrogen. The residual liquid was dissolved in dry ether and reductively decomposed as in the preceding reaction. Heptanol in 70% yield was obtained by ether extraction, n_{D}^{20} = 1.4240, lit.[14] n_{D}^{20} = 1.4245. The infrared spectrum of the product was identical with that of an authentic specimen.

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(21) F. Semmler and K. Bartelt, *Ber.*, **41**, 2752 (1908).

(22) A. L. Bluhm, Ph.D. thesis, Boston University, 1957.

(23) R. Scheuble and E. Loebl, *Monatsh.*, **25**, 1081 (1904).

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY SECTION, DIVISION OF CHEMISTRY, NATIONAL BUREAU OF STANDARDS]

Complexes of Diols with Cuprammonium Reagent

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The chelates present in cuprammonium solutions of methyl α-D-galactopyranoside, sucrose, di-D-fructopyranose 1,2′:2,1′-dianhydride, and the *cis-* and *trans*-1,2-cyclohexanediols have been studied by measurements of optical rotation and optical density, and the results evaluated by the method of continuous variation. In each case, a compound having a copper to diol ratio of 2:1 was found. Under the conditions stipulated, there is no evidence of compounds having a copper to diol ratio of 1:1.

The reaction of cuprammonium reagent and the diol groupings of carbohydrates has found extensive practical and theoretical use. Nevertheless, despite the importance of the reaction, the complexes formed have not been isolated and little has been reported on their structures.

The present investigation had its beginning in some measurements of optical rotation conducted by Isbell and Snyder on dextrans in cuprammonium solution.[1] The optical rotation varied widely with the concentrations of both the dextran and the copper reagent. In order to obtain some understanding of this behavior, it seemed desirable to investigate the composition and structure of cuprammonium–diol complexes. Isbell and his associates[2] have shown that in the carbohydrate-borate system, at least three diol-borate complexes exist. For practical and theoretical reasons, copper complexes derived from sucrose, methyl α-D-galactopyranoside, di-D-fructopyranose 1,2′:2,1′-dianhydride, and the *cis-* and *trans*-1,2-cyclohexanediols were selected for the investigation. The cuprammonium compounds from these compounds were studied by measurements of optical rotation (at 436 mμ) and optical density (at 350 mμ).

Measurements conducted with a photoelectric spectropolarimeter revealed a dependence of optical rotation on the proportions of both the diol and the copper reagent in the solution. The results indicated that *two moles of copper reagent react with each molar equivalent of the diol grouping.* This observation was substantiated by examination of optical density employing the method of continuous variation.

Discussion of previous work. Cuprammonium solution presumably contains di-, tri-, tetra-, and penta-ammonia complexes of copper. Bjerrum[3] has determined the stability constants of the four copper–ammonia cations and has shown that, in the presence of excess ammonia (as for the cuprammonium solutions used in the present study), the copper–tetrammonium complex $[\mathrm{Cu(NH_3)_4}^{++}]$ greatly predominates.

In 1857, Schweizer[4] published the observation that cellulose disperses in cuprammonium solution. Since then, many practical applications of this reaction have been made.[5] The cuprammonium ion exists only in solutions having a high concentration of ammonia. Therefore, the conditions for forming a complex with a diol are restricted to a limited range of *p*H. Upon acidification, the com-

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(1) H. S. Isbell and C. F. Snyder, unpublished work (contained in NBS Report 2400, March 31, 1953).

(2) H. S. Isbell, J. Brewster, N. B. Holt, and H. L. Frush, *J. Research Natl. Bur. Standards*, **40**, 129 (1948).

(3) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

(4) E. Schweizer, *J. prakt. Chem.*, **72**, 109, 344 (1857).

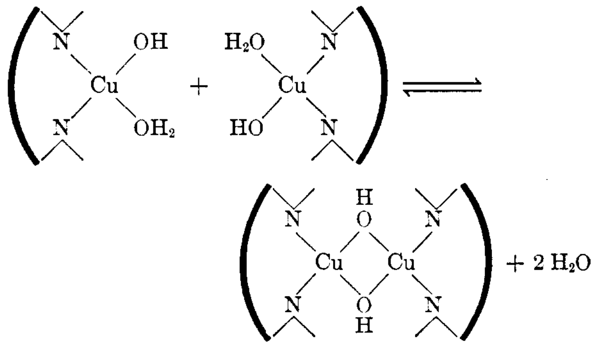
(5) E. Heuser, *The Chemistry of Cellulose*, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 161.

plex of the diol with the copper–ammonia is decomposed, usually with regeneration of the unchanged diol. [However, in some cases, side reactions occur. Thus, when a cellulose–cuprammonium complex is exposed to air and ultraviolet light (especially light in the range of 300 to 400 mμ), the viscosity smoothly decreases, and the solubility of the regenerated "cellulose" is found to have increased. The change seems to be associated with an effect on groups other than "the diol grouping" (the hydroxyl groups on carbon atoms 2 and 3 of the D-glucose residues), since comparable effects are not observed with the complexes of nonreducing monosaccharides.]

Traube and associates[6] determined the amount of copper removed from copper hydroxide solution by the addition of a known weight of cellulose together with a known weight of ethylenediamine. On the basis of their findings, they proposed the formula $[(C_6H_8O_5)_2Cu]$ $[Cu(NH_3)_4]$, having a 1:1 ratio of copper to diol, for the cellulose-cuprammonium compound. Subsequent workers have tacitly assumed a 1:1 copper-diol ratio for all other diols so studied.

Reeves[7] used the reaction of pyranoid sugars (and derivatives) with cuprammonium to study pyranoid conformations. He found that reaction takes place readily when the two oxygen atoms of a diol are separated by 2.51 Å, but that no reaction occurs when they are more than 3.45 Å apart. He found[14] that equilibrium constants for the reaction of $0.01M$ cuprammonium reagent with 1,6-anhydro-β-D-mannopyranose ("D-mannosan") support "a simple bimolecular association of the form mannosan + cupra $\rightleftharpoons$ [mannosan-cupra]."

In recent studies[8,9] on the hydrolytic tendencies of metal chelate compounds, it is suggested that Cu(II) chelates of a series of diamines form monohydroxo complexes that are in equilibrium with binuclear compounds.



Similar compounds have not been reported for carbohydrate complexes, but their formation might be anticipated. Copper–diol complexes of this type (each diamine of the above equation being replaced by a diol), as well as those represented by Reeves' equation, require a 1:1 copper-diol proportion.

Discussion. Sucrose, methyl α-D-galactopyranoside, and di-D-fructopyranose 1,2':2,1'-dianhydride were selected as representative carbohydrates containing at least one active diol grouping per molecule and various numbers of extra hydroxyl groups. In order to be sure that the results did not reflect the reactions of the single hydroxyl groups, *cis*- and *trans*-1,2-cyclohexanediol were included in the study. Kwart and Gatos[10] have shown by conductivity measurements that the latter two compounds react with the cuprammonium reagent.

The hydroxyl groups of sucrose are so arranged that the cuprammonium reagent can react with either the 3,4-diol or the 4,5-diol of the D-glucose residue; the D-fructofuranose residue contains no reactive diol grouping. Methyl α-D-galactopyranoside is similar to the D-glucose residue of sucrose in that the hydroxyl groups of both C3-C4 and C4-C5 could be involved in the reaction. Since one hydroxyl group (at C4) is common to both these diol groupings, both compounds contain only one active diol grouping per molecule. Di-D-fructopyranose 1,2':2,1'-dianhydride, however, contains two active diol groupings per molecule. Hydroxyl groups at C4 and C5 of each D-fructopyranose residue form an active diol grouping, but the hydroxyl group at C3 would not be expected to enter into the reaction.

It is well known that the interaction of many carbohydrates with cuprammonium produces a large shift in their specific rotation at 436 mμ. Measurement of the optical rotation of the blue solutions with visual polarimeters is unsatisfactory, but accurate values were obtained with a photoelectric spectropolarimeter. Cuprammonium solutions of the selected carbohydrates were prepared in which the copper-diol ratio was varied. In each case, the specific rotation (calculated on the basis of carbohydrate content) changed rapidly, until a copper-diol ratio of 2:1 was reached; it then became relatively stable. These results indicated that *two* copper atoms are required for the complexing of one diol group.

The optical rotation of varying concentrations of di-D-fructopyranose 1,2':2,1'-dianhydride is typical of these reaction changes (see Table 1). Observations made after the solutions had been stored for twenty-four hours are included with those made at the time of preparation. The small difference in specific rotation for the two series of observations indicates that the complexing reaction takes place with great rapidity.

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[6] W. Traube, G. Glaubitt, and V. Schenck, *Ber.*, **63**, 2083 (1930); W. Traube and A. Funk, *Ber.*, **69**, 1476 (1936).

[7] R. E. Reeves, *Advances in Carbohydrate Chem.*, **6**, 107 (1951).

[8] R. Gustafson and A. Martell, *J. Am. Chem. Soc.*, **81**, 525 (1959).

[9] R. Courtney, R. Gustafson, S. Chaberek, and A. Martell, *J. Am. Chem. Soc.*, **81**, 519 (1959).

[10] H. Kwart and G. Gatos, *J. Am. Chem. Soc.*, **80**, 881 (1958).

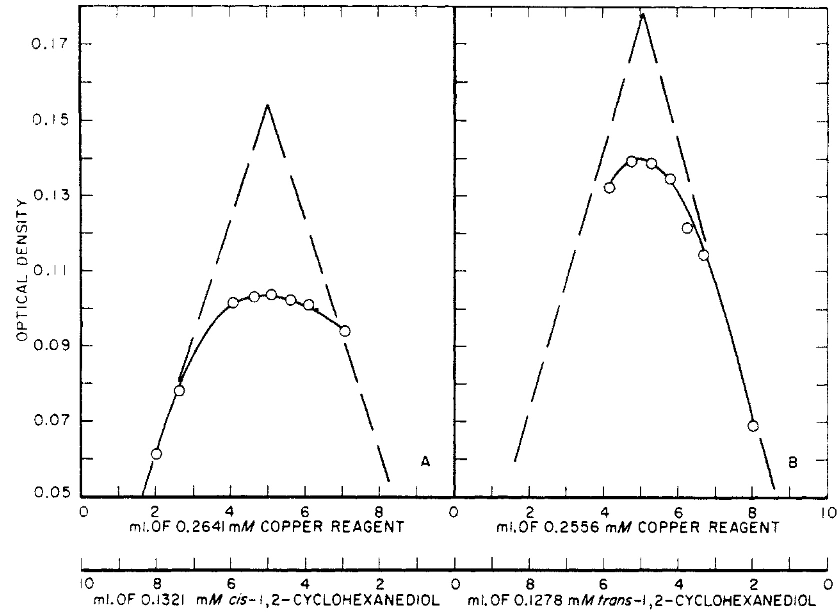

Fig. 1. Experimental observations on the reaction of *cis*-and *trans*-1,2-cyclohexanediols and cuprammonium reagent. (In curve A, the maximum at 5 ml. of 0.2641 mM copper and of 0.1321 mM *cis*-1,2-cyclohexanediol indicates a 2:1 ratio of copper to diol in the reaction product. In curve B, the maximum at 5 ml. of 0.2556 mM copper and of 0.1278 mM *trans*-1,2-cyclohexanediol indicates a 2:1 ratio of copper to diol in the reaction product.)

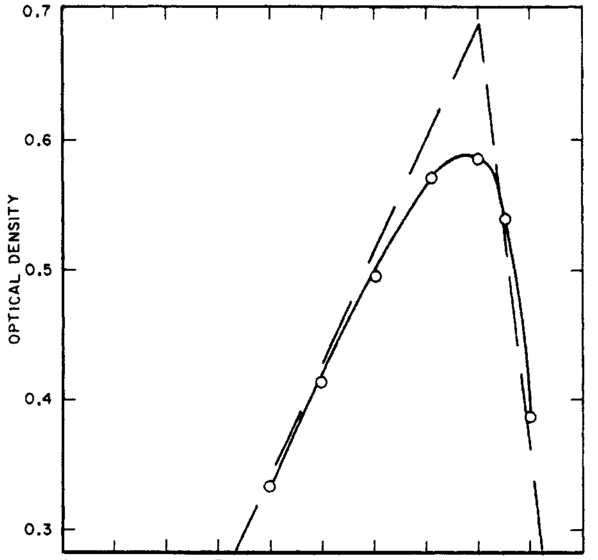

Fig. 2. Experimental observations on the reaction between di-D-fructopyranose 1,2':2,1'-dianhydride and cuprammonium reagent. (The maximum absorption observed when 8 ml. of 0.1 mM copper reagent and 2 ml. of 0.1 mM di-D-fructopyranose 1,2':2,1'-dianhydride react indicates combination of eight molecules of copper per two molecules of the disaccharide for the reaction product. This is equivalent to two molecules of copper per molar equivalent of diol grouping.)

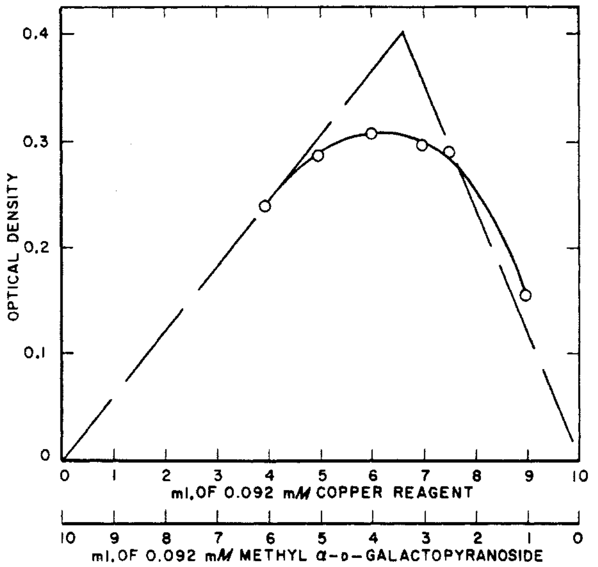

Fig. 3. Experimental observations for the reaction of methyl α-D-galactopyranoside and cuprammonium reagent. (The maximum absorption observed in the region of 6.7 ml. of 0.092 mM copper reagent and 3.3 ml. of 0.092 mM methyl α-D-galactopyranoside indicates two molecules of copper per molecule of glycoside in the reaction product.)

The composition of the complex was further studied by the method of continuous variation.[11-13] By this method, measurements of some physical property of the reaction product are made on a

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[11] P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

[12] W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

[13] A. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds*, Academic Press Inc., New York, N. Y., 1952, p. 29.

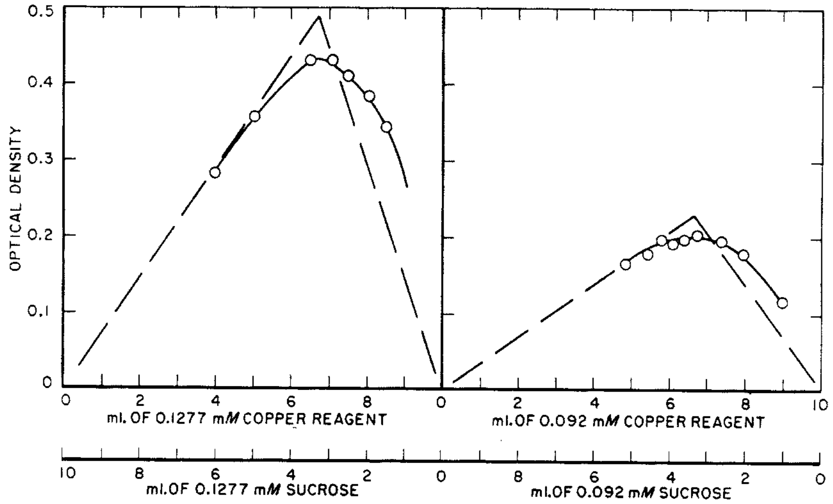

Fig. 4. Experimental observations on the reaction between sucrose and cuprammonium reagent. (The maximum absorption observed in the region of 6.7 ml. of cuprammonium reagent and 3.3 ml. of sucrose solution of equal molality indicates two molecules of copper per sucrose molecule in the reaction product)

TABLE I

Optical Rotation of Di-D-Fructopyranose 1,2′:2,1′-Dianhydride in Cuprammonium Reagent

Di-D-fructopyranose 1,2′:2,1′-dianhydride (g./100 ml. of sol.)	Molar Ratio Cu[a]/disaccharide	Cu/diol	α_{436}[b,c]	$[\alpha]_{436}$[c]	$[\alpha]_{436}$[d]
8.062	1.02	0.51	1.638	81.3	81.1
6.542	1.26	0.63	1.983	121.2	120.2
4.236	1.95	0.97	2.436	230.0	227.0
2.030	4.07	2.00	2.015	397.1	394.1
1.274	6.48	3.20	1.387	403.8	443.3
0.784	10.50	5.20	0.801	408.6	429.5
0.257	32.10	16.00	0.268	417.1	442.0

[a] The reagent contained 1.6181 g. of copper per 100 ml. [b] The solutions were contained in a 0.25-dm. polarimeter tube. The zero point was observed on the cuprammonium reagent. All rotations were measured by use of a photoelectric spectropolarimeter (manufactured by O. C. Rudolph and Sons), in a room maintained at 20°. [c] After 24 hours. [d] Initial.

series of reaction mixtures in which the sum of the molar proportions of the reactants is kept constant. Measurements of optical density were made on (a) the cuprammonium reagent and (b) reaction mixtures containing the cyclohexanediols at wave lengths from 320 to 400 mμ. It was found that increased optical density accompanies the copper–diol complexing. This observation is in agreement with Reeves' results on D-mannosan–cupra solution.[14] The wave length 350 mμ was selected as suitable for making observations during the present study.

At each concentration, the optical density of the cuprammonium reagent-blank was subtracted from that of the reaction mixture. The values resulting represent the increase in optical density produced by the copper-diol complex. They are, therefore, proportional to the concentration of copper-diol complex. Graphs obtained by plotting the optical densities observed at each concentration against the concentration of copper are shown in Figs. 1–4. In these applications of the method of continuous variation, the maximum absorption occurs when the amounts of diol and copper used are in the same ratio as that in which they occur in the reaction product.

Absorption data observed when 0.1321 m*M* *cis*-1,2-cyclohexanediol reacted with 0.2641 m*M* cuprammonium reagent, and when 0.1278 m*M* *trans*-1,2-cyclohexanediol reacted with 0.2556 m*M* copper reagent are shown in Fig. 1. Ammonia concentration remained constant throughout each series. In both cases, the optical density reaches a maximum when the concentration of diol used is one half that of the copper, thus giving a 2.1 ratio of copper to diol.

Experimental data presented in Fig. 2 indicate maximum concentration of the complex when an 8:2 ratio of copper to di-D-fructopyranose 1,2′:2,1′-dianhydride exists. Again, the copper-diol ratio is 2:1 because each molecule of anhydride contains two diol groupings.

Sucrose and methyl α-D-galactoside contain one active diol grouping per molecule. Figs. 3 and 4 show that the maximum optical density occurs when the molar ratio of copper to carbohydrate is 2, *i.e.*, copper to diol is 2:1.

When a large excess of copper is present, some reaction appears to take place with hydroxyls not included in the active diols. This is indicated by the dissymmetry of the absorption curves in Fig. 4, based on the reaction of sucrose with its six additional hydroxyl groups. In contrast, the experimental curves of Fig. 1, representing the reaction of

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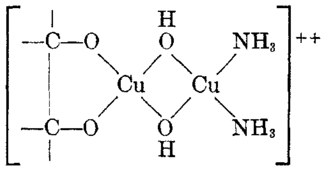
(14) R. E. Reeves, *J. Am. Chem. Soc.*, **73**, 957 (1951).

cyclohexanediols with cuprammonium reagent, more nearly approach the theoretical curves.

A remote possibility is that another (soluble) copper-containing compound (not involving a diol) is formed simultaneously with the copper-diol complex. Should this occur, the copper–diol ratio in the complex could be 1:1.

The structure of a probable cuprammonium–diol complex having a copper–diol ratio of 2:1 is as follows. Coordination compounds of copper are planar; thus, the ammonia groups must be located at the four corners of a square, with the copper atom in the middle. A possible interpretation is that a binuclear complex of the form



exists in the strongly ammoniacal solution. Occurrence of such a reaction would account for (a) the decrease in conductivity that accompanies formation of the copper–diol complex and (b) the 2:1 copper–diol ratio.

EXPERIMENTAL

The cuprammonium reagent was prepared, and analyzed for copper and ammonia, according to the procedure described by TAPPI.[15] Each diol was dissolved in concentrated ammonia water in which the ammonia concentration was the same as that in the cuprammonium reagent. An appropriate amount of the cuprammonium reagent and of the respective diol solution were placed in a 10-ml. flask, and the solution was made up to 10 ml. with concentrated ammonia water. All solutions were kept in an ice bath until each reaction mixture had been brought to final volume. Each was then transferred to a capped vial and allowed to warm up to room temperature. Ammonia analyses on a series of sucrose–cuprammonium reaction mixtures showed that a uniform ammonia concentration was still present after 24 hr. Absorption observations were made with a Beckman spectrophotometer at room temperature; cell depths of 0.4 cm. were used. In all experiments, the absorption values of the blanks, which contained the cuprammonium reagent plus ammonium hydroxide, were found to follow Beer's law. The experimental points shown in Figs. 1–4 were obtained by subtracting the absorption of the blank cuprammonium solution from that of the reaction mixture at each concentration.

cis-1,2-Cyclohexanediol was prepared by oxidation of cyclohexene with permanganate, according to the procedure of Clarke and Owen,[16] m.p. 98°. *trans*-1,2-Cyclohexanediol was prepared by oxidation of cyclohexene with performic acid, as described by Roebuck and Adkins,[17] m.p. 104–105°.

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[15] Recommended Practices of the Technical Association of the Pulp and Paper Industry, T 206 m-55.

[16] M. Clarke and L. Owen, *J. Chem. Soc.*, 318 (1949).

[17] A. Roebuck and H. Adkins, *Org. Syntheses*, **28**, 35 (1948).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF LITHIUM CORP. OF AMERICA]

Analysis and Stability of *n*-Butyllithium Solutions in *n*-Heptane

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The purity of the ether has been shown to have a marked effect when the "double titration" procedure is used in analyzing solutions for *n*-butyllithium content. Results of these studies show that a reasonably accurate determination of the *n*-butyllithium content in *n*-heptane solutions is obtained by a single, direct acid titration of a hydrolyzed sample of the solution. Determination of the *n*-butyl chloride content by use of the disodium biphenyl reagent has been shown to be suitable for direct analysis of *n*-butyllithium solutions in *n*-heptane. Essentially no change in *n*-butyllithium content occurred on storing *n*-heptane solutions at room temperature for over three months. The density at 26° of a 2.59 molar solution of *n*-butyllithium in *n*-heptane was found to be 0.697 ± 0.001.

The analysis and stability of organolithium solutions have been of continuing interest for many years. Stability studies have been complicated by the necessity of determining the amount of an organolithium compound present in the presence of compounds formed during its deterioration. Any one of several methods can be used for such an analysis with varying degrees of accuracy and convenience. The "double titration" or "indirect titration" procedure developed by Gilman and Haubein[1] probably has been used the most widely. This procedure involves hydrolyzing directly one sample of the organolithium solution followed by acid titration to determine the total base present. A second sample is treated with benzyl chloride then hydrolyzed and titrated with acid. As most organolithium, particularly, alkyllithium, compounds react rapidly with benzyl chloride to form non-alkaline products, this titration determines the residual alkalinity due to materials originally present which did not contain carbon-lithium bonds. The difference between the total alkalinity and the residual alkalinity should provide an accurate measure of the amount of organolithium compound present. Certain difficulties encountered in obtain-

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[1] H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, 66, 1515 (1944).