

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

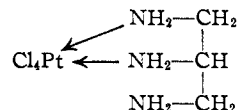
Some Coördination Compounds of Cobalt Containing Trimethylenediamine and Neopentanediamine

BY JOHN C. BAILAR, JR., AND J. B. WORK¹

The coördination compounds of ethylenediamine are well known and are very stable, the stability being due in large measure to the chelation effect involved in the formation of five-membered rings. The presence of substituents on the carbon atoms does not alter these coördination compounds in any striking way. Thus, the cobaltic compounds containing propylenediamine and 2,3-butylenediamine are similar to their ethylenediamine homologs in ease of formation, stability and color. They differ, however, in being much more soluble, both in water and in alcohol.

Several other substituted ethylenediamines, such as *meso*-stilbenediamine, *iso*-butylenediamine,² cyclopentanediamine and cyclohexanediamine³ have been used in the preparation of stable coördination compounds. A very different effect is produced, however, by increasing the number of carbon atoms between the amine groups, for this changes the ring size and introduces distortion and strain. However, six-membered rings are easily possible, as is shown by the existence of coördination compounds of trimethylenediamine. Compounds of this base with cobalt,⁴ nickel,⁵ platinum^{5c,6} and iron⁷ have been described as well as compounds of platinum with 2-methyltrimethylenediamine⁸ and of nickel^{6c} and cobalt⁹ with 2,4-diaminopentane. There is ample evidence, however, that six-membered rings are not as stable as those of five members. Thus, Pfeiffer and Haimann¹⁰ failed to obtain salts of chromium with trimethylenediamine by the same reaction that gave good yields of propylenediamine salts. Also the reaction of anhydrous ethylenediamine with anhydrous chromic sulfate constitutes a good method of preparing luteo chromic salts,¹¹ but our experiments, as well as those of Rollinson,¹² indicate that anhydrous trimethylenediamine has little tendency to react in this way. In addition, Mann and Pope¹³ have given an interesting proof that five-membered rings of this sort are more stable

than those with six members by resolving the monochelate compound [PtCl₄·α,β,γ-triaminopropane] into its optical antipodes. This is possible only if coördination is effected through the α and β positions



α,γ-coördination would give a symmetrical six-membered ring.

The present study was undertaken to test the ability of aliphatic diamines to form coördination compounds with the cobaltic ion and to compare the properties of such compounds with those of the homologous compounds containing ethylenediamine. Incidentally, some observations have been made upon methods of synthesizing cobaltic coördination compounds.

We have observed that while the action of air on mixtures of partially neutralized ethylenediamine and cobalt salts gives good yields of the [Co en₃]⁺⁺⁺ ion¹⁴ the same treatment with trimethylenediamine or diaminoneopentane gives very low yields. Among the by-products obtained with these bases are [Co tn₂CO₃]⁺ and [Co dan₂CO₃]⁺, the carbonate ion (from carbon dioxide of the air) coördinating more readily than the diamine. Only in the presence of a charcoal catalyst could [Co tn₃]⁺⁺⁺ and [Co dan₃]⁺⁺⁺ ions be formed.

It is of interest to note also that the presence of trimethylenediamine in place of ethylenediamine in cobaltic complexes produces changes which seem to depend upon strains in the molecule rather than upon the strength of the cobalt-nitrogen link. While the *cis* isomer of [Co en₂Cl₂]Cl is obtained readily and is comparable in stability to the *trans* form, the *cis* form of [Co tn₂Cl₂]Cl has not been obtained. Aquation of [Co en₂Cl₂]Cl proceeds slowly at room temperature, but that of [Co tn₂Cl₂]Cl is almost instantaneous. The mixed salt [Co en tn Cl₂]Cl is intermediate in its properties, but resembles the diethylenediamine compound more closely than it does the one containing two molecules of trimethylenediamine.

Neopentanediamine (2,2-dimethyltrimethylenediamine) forms compounds which are similar to those of trimethylenediamine itself, but they are more readily formed and are more stable toward heat and the dichloro salts are more stable toward

- (1) From a portion of the doctorate thesis of J. B. Work, 1942.
- (2) Mills and Quibbell, *J. Chem. Soc.*, 839 (1935); Lidstone and Mills, *ibid.*, 1754 (1939).
- (3) Jaeger and ter Berg, *Proc. Acad. Sci. Amsterdam*, **40**, 490 (1937); Jaeger and Bijkerk, *ibid.*, **40**, 12, 116, 316 (1937); *Z. anorg. allgem. Chem.*, **233**, 97 (1937); many earlier articles by Jaeger.
- (4) Werner, *Ber.*, **40**, 61 (1907).
- (5) (a) Tschugaeff, *ibid.*, **39**, 3190 (1906); (b) *J. prakt. Chem.*, [2] **75**, 159 (1907); (c) [2] **76**, 89 (1907).
- (6) Drew and Tress, *J. Chem. Soc.*, 1935 (1933).
- (7) Breuil, *Compt. rend.*, **199**, 298 (1934).
- (8) Mann, *J. Chem. Soc.*, 1261 (1928).
- (9) Dippell and Jaeger, *Rec. trav. chim.*, **50**, 547-581 (1931).
- (10) Pfeiffer and Haimann, *Ber.*, **36**, 1064 (1903).
- (11) Rollinson and Bailar, *This Journal*, **65**, 250 (1943).
- (12) Rollinson, Thesis, University of Illinois, 1939.
- (13) Mann and Pope, *Nature*, **119**, 351 (1927); Mann, *J. Chem. Soc.*, 1224 (1927).

(14) The following symbols are used to represent the diamines: en, ethylenediamine; tn, trimethylenediamine; dan, diaminoneopentane; hn, hexamethylenediamine; dn, decamethylenediamine.

aquation. Attempts to prepare the *cis* form of $[\text{Co dan}_2\text{Cl}_2]\text{Cl}$ have been partially successful, but it is evident that the *trans* isomer is much more stable than the *cis*. As might be expected, $[\text{Co dan}_2\text{Cl}_2]\text{Cl}$ is more soluble in alcohol than is $[\text{Co tn}_2\text{Cl}_2]\text{Cl}$.

The luteo salts $[\text{Co tn}_3]\text{Cl}_3$ and $[\text{Co dan}_3]\text{Cl}_3$ are pinkish yellow, which is quite in contrast to the brownish yellow color of most cobaltic luteo salts. The pink cast is evidently inherent in the crystal structure rather than in the structure of the luteo ion, for it is not evident in solution, but reappears upon recrystallization. At -77° , the color is lemon yellow which, however, reverts to pink as the temperature rises. The iodide $[\text{Co tn}_3]\text{I}_3$ is brownish-yellow even at room temperatures. Jaeger¹⁵ has observed a similar case in the salts of *trans* cyclopentylenediamine; $[\text{Co cptdin}_3]\text{Cl}_3$ is pink, but the iodide is lemon yellow.

The water solubility of the luteo cobalt chlorides also is striking, as it seems to increase with increasing carbon content. Hexammine cobaltic chloride, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is very slightly soluble,¹⁶ 0.05 g. dissolving in one gram of water at 17.5° . The ethylenediamine salt dissolves to the extent of 0.35 g. per gram of water at 25° , while one gram of water will dissolve 1.08 g. of the trimethylenediamine salt at 32° . The propylenediamine salt is also very soluble.

Attempts to prepare chelate compounds with aliphatic diamines having more than three methylene groups in the chain have not been successful. Tetramethylenediamine (putrescine) and pentamethylenediamine (cadaverine) have been studied extensively.^{4,5a,5b,6,10,17} Decamethylenediamine and octadecamethylenediamine have been studied by Pfeiffer and Lübke¹⁷ and the former of these also by McReynolds,¹⁸ who obtained cupric coordination compounds, but found no evidence that they were of cyclic nature. The success which has attended the use of decolorizing charcoal as a catalyst in the preparation of cobaltic amines¹⁹ gave rise to the hope that such catalysis might permit the formation of coordination compounds containing long chain diamines. Since the coordinately bound chlorine atoms in $[\text{Co en}_3\text{Cl}_2]\text{Cl}$ are readily replaced by amine groups, the reaction of this salt with hexamethylenediamine and with decamethylenediamine to give $[\text{Co en}_2\text{hn}]\text{Cl}_3$ and $[\text{Co en}_2\text{dn}]\text{Cl}_3$ was attempted. There was some evidence that coordination took place in the presence of charcoal but the only compound isolated was $[\text{Co en}_3]\text{Cl}_3$.

(15) Jaeger, "Optical Activity and High Temperature Measurements," Cornell University Press, Ithaca, N. Y., 1930, p. 143.

(16) Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd ed., Vol. I, D. Van Nostrand Co., New York, N. Y., 1940, p. 425.

(17) Pfeiffer and Lübke, *J. prakt. Chem.*, [2] **136**, 321 (1933).

(18) McReynolds, Thesis, University of Illinois, 1938.

(19) Bailar and Work, *This Journal*, **67**, 176 (1945).

Experimental

The neopentanediamine used in this investigation was given to us by Dr. J. L. Martin and the Commercial Solvents Corporation, to whom we express our sincere thanks. The other diamines were obtained from commercial sources.

Preparation of Dichloro Di-trimethylenediamine Cobaltic Chloride, $[\text{Co tn}_2\text{Cl}_2]\text{Cl}$.—This salt has previously been prepared from potassium cobaltinitrite by Werner and Lindenberg.²⁰ We were able to repeat their synthesis without difficulty and also to prepare the compound directly from cobaltous chloride. Oxidation of an aqueous solution of cobalt chloride and trimethylenediamine, either by air or by hydrogen peroxide does not give the desired product. Side reactions in which water is involved are evidently the cause of the difficulty, for when alcohol was used as the solvent, a yield of 43% of purified material was obtained.

Seven grams of 85% trimethylenediamine (0.08 mole) was added to a solution of 6.9 g. of anhydrous cobalt chloride (0.053 mole) in 250 cc. of absolute alcohol and the mixture was oxidized by a stream of air (freed from carbon dioxide) for thirty hours. After filtration, the residue was dissolved in 40 cc. of water and reprecipitated by the addition of 30 cc. of concentrated hydrochloric acid and the alcoholic mother liquid which had been filtered off. The precipitate weighed 7.9 g., but contained some cobalt chloride. It was purified by dissolving in a small quantity of warm water and reprecipitating with an equal volume of concentrated hydrochloric acid. The purified bright green product weighed 5.5 g. It was dried at 80° . *Anal.* for chloride. Calcd. for $[\text{Co tn}_2\text{Cl}_2]\text{Cl}$: Cl, 33.93. Found: Cl, 33.86.

The filtrate from this recrystallization was mixed with an equal volume of alcohol, but no further precipitate formed. On slow evaporation, however, large square plates deposited. Analysis for chloride and loss in weight on heating showed the formula to be $[\text{Co tn}_2\text{Cl}_2]\text{Cl}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$.

Anal. Calcd.: Cl, 36.79; loss, 18.8. Found: Cl, 36.22; loss, 19.5.

Jørgensen²¹ has described an analogous ethylenediamine compound, $[\text{Co en}_2\text{Cl}_2]\text{Cl}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$.

The trimethylenediamine salt is a green crystalline material, soluble in alcohol and extremely soluble in water. In water, however, it aquates at once, giving a red solution. The salt is much less stable to heat than is the corresponding ethylenediamine salt, decomposing completely in three days at 110° . Action of concentrated ammonium hydroxide and decolorizing charcoal, or of liquid ammonia, converts it to a yellow crystalline material, presumably $[\text{Co tn}_2(\text{NH}_3)_2]\text{Cl}_3$. Silver carbonate converts it to the highly soluble red compound, $[\text{Co tn}_2\text{CO}_3]_2\text{CO}_3$. These salts were not analyzed, but seem to be entirely analogous to the corresponding ethylenediamine salts. Attempts to convert the carbonate salt to the *cis* dichloro salt by the action of hydrogen chloride in ether were not successful.

Preparation and Properties of Dichloro Di-neopentanediamine Cobaltic Chloride.—This compound was prepared by direct oxidation of a mixture of neopentanediamine and cobalt chloride, just as with trimethylenediamine, but in this case water was used as the solvent. Apparently neopentanediamine has a greater coordination tendency than has trimethylenediamine.

Anal. Calcd. for $[\text{Co dan}_2\text{Cl}_2]\text{Cl}$: C, 32.47; H, 7.58. Found: C, 32.47; H, 7.68.

The complex salt resembles the corresponding trimethylenediamine compound closely, but seems to be somewhat more stable, for a sample of it showed no signs of decomposition when heated to 110° for three days. Also $[\text{Co dan}_2\text{Cl}_2]\text{Cl}$ aquates in water solution a little more slowly than does $[\text{Co tn}_2\text{Cl}_2]\text{Cl}$, but the rate of aquation is still very much faster than for *trans* $[\text{Co en}_2\text{Cl}_2]\text{Cl}$. The solubility of $[\text{Co dan}_2\text{Cl}_2]\text{Cl}$ in alcohol is even greater than

(20) Werner and Lindenberg, *Ann.*, **356**, 265, 269 (1912).

(21) Jørgensen, *J. prakt. Chem.*, [2] **39**, 24 (1889).

that of $[\text{Co}(\text{tn}_2\text{Cl}_2)\text{Cl}]$. All efforts to convert *trans* $[\text{Co}(\text{dan}_2\text{Cl}_2)\text{Cl}]$ to the *cis* form by repeated evaporation of the neutral solution met with failure.

The addition of ammonium hydroxide to $[\text{Co}(\text{dan}_2\text{Cl}_2)\text{Cl}]$ produced a red compound which was not isolated, but which was assumed to be $[\text{Co}(\text{dan}_2(\text{NH}_2)\text{Cl})\text{Cl}_2]$.

Preparation and Properties of Carbonato Di-neopentanediamine Cobaltic Salts.—The brick red carbonato chloride $[\text{Co}(\text{dan}_2\text{CO}_3)\text{Cl}]$, was obtained accidentally in an attempt to prepare the luteo salt, $[\text{Co}(\text{dan}_3)\text{Cl}_3]$ by aerial oxidation of an aqueous solution of cobalt chloride and neopentanediamine. Enough carbon dioxide was absorbed from the air to give a small yield of the carbonato salt. Eight grams of cobalt chloride hexahydrate (0.0336 mole), 12 g. of 95% neopentanediamine (0.112 mole), and 150 ml. of water were mixed with 3.4 g. of concentrated hydrochloric acid (0.0354 mole) and a stream of air was bubbled through the solution for fifteen hours. The solution was then evaporated in a stream of air at room temperature until a red-black mush was formed. When this was placed in a vacuum desiccator for a week, it dried to a pinkish-orange residue. This was dissolved in a minimum volume of water at room temperatures and then twice this volume of alcohol was added. Ether was then added until a red precipitate formed. This was removed by filtration, washed with alcohol and with ether, and dried in air. It weighed 4.8 g. It was dissolved in 50 ml. of water and reprecipitated with alcohol. The final product weighed 2.1 g. This salt is extremely soluble in water and could not be obtained completely free from impurities.

Anal. Calcd. for $[\text{Co}(\text{dan}_2\text{CO}_3)\text{Cl}]$: C, 36.8; N, 15.6; Cl, 9.68. Found: C, 35.9; N, 14.8; Cl, 9.69.

The carbonato carbonate was obtained by the action of silver carbonate on the dichloro salt $[\text{Co}(\text{dan}_2\text{Cl}_2)\text{Cl}]$. This carbonate was treated with alcoholic hydrogen chloride in an attempt to prepare the *cis* dichloro salt. The product was gray, as might be expected if it were a mixture of the green *trans* and the purple *cis* forms. One sample had a pale purple color, which changed to green in two days. It is evident that the *trans* form is much more stable than the *cis*.

Dichloro Trimethylenediamine Ethylenediamine Cobaltic Chloride, $[\text{Co}(\text{en}(\text{tnCl}_2)\text{Cl}]$.—This salt was obtained through the dinitro nitrite $[\text{Co}(\text{en}(\text{tn}(\text{NO}_2)_2)\text{NO}_2)]$ which was prepared by an adaptation of Werner's method for the preparation of the corresponding compound containing propylenediamine and ethylenediamine.²²

A mixture of 20 g. of $[\text{Co}(\text{en}(\text{NH}_2)(\text{NO}_2)_2)]$ (0.073 mole), 6.35 g. of 85% trimethylenediamine (0.073 mole) and 300 cc. of water was warmed with frequent stirring until the solid completely dissolved (about an hour). It was then evaporated to 25 cc. and treated with 100 cc. of alcohol and 75 cc. of ether. The yield of $[\text{Co}(\text{en}(\text{tn}(\text{NO}_2)_2)\text{NO}_2)]$ was 19.7 g. or 80%. The salt is quite soluble in alcohol.

Three grams of the dinitro compound was converted to the *trans* dichloro salt by heating it with 20 cc. of concentrated hydrochloric acid for an hour and a half. The salt was then precipitated by the addition of 20 cc. of alcohol. The yield was 2.5 g. (92%) of a bright green crystalline powder.

Anal. Calcd. for $[\text{Co}(\text{en}(\text{tnCl}_2)\text{Cl}]$: Cl, 35.52. Found Cl, 35.46.

The properties of this salt are of course intermediate between those of $[\text{Co}(\text{en}_2\text{Cl}_2)\text{Cl}]$ and $[\text{Co}(\text{tn}_2\text{Cl}_2)\text{Cl}]$, but approach those of the former. Heating for ten days at 110° caused partial decomposition; aqution required several minutes, and repeated evaporation of an acid free solution gave partial conversion to the *cis* form. The salt reacted with silver carbonate and with ammonium hydroxide (with and without charcoal catalysis) in the expected fashion. Hydrogen chloride dissolved in a mixture of alcohol and ether reacted with the carbonate salt to give the purple *cis* dichloro salt.

Tri-trimethylenediamine Cobaltic Chloride $[\text{Co}(\text{tn}_3)\text{Cl}_3]$.—All attempts to prepare this salt by the methods which

have commonly been used for synthesizing the corresponding ethylenediamine compound were unsuccessful. In some cases, it is true, the desired salt was formed, but always in poor yield. In the presence of charcoal, however, the synthesis of $[\text{Co}(\text{tn}_3)\text{Cl}_3]$ by aerial oxidation of mixtures of cobalt chloride and trimethylenediamine proceeded smoothly. It was found best to decrease the basicity of the solution by the addition of trimethylenediamine hydrochloride:

Twelve grams of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.05 mole), 13.2 g. of 85% trimethylenediamine (0.15 mole) and 7.4 g. of the amine hydrochloride (0.05 mole) were dissolved in 40 cc. of water. A gram of decolorizing charcoal was added, and a vigorous stream of air was bubbled through the solution for eighteen hours. The charcoal was removed by filtration and washed with 20 cc. of water in small portions. The combined filtrate and washings were poured into 200 cc. of alcohol. After purification, the pinkish yellow precipitate weighed 16.9 g., which is 87% of the calculated amount.

Anal. for chloride. Calcd. for $[\text{Co}(\text{tn}_3)\text{Cl}_3]$: Cl, 27.44. Found: Cl, 27.08, 27.37.

Tri-neopentanediamine Cobaltic Chloride, $[\text{Co}(\text{dan}_3)\text{Cl}_3]$.—This salt was prepared in the same way as the trimethylenediamine compound. The yield was 84% of the calculated amount. Because of its high solubility, the compound was difficult to purify completely. *Anal.* Calcd. for $[\text{Co}(\text{dan}_3)\text{Cl}_3]$: N, 17.8; Cl, 22.55. Found: N, 16.8; Cl, 22.16.

Trimethylenediamine Di-ethylenediamine Cobaltic Chloride $[\text{Co}(\text{en}_2\text{tn})\text{Cl}_3]$.—Four grams of acid-free *trans* $[\text{Co}(\text{en}_2\text{Cl}_2)\text{Cl}]$ (0.014 mole) and 2 g. of 85% trimethylenediamine (0.023 mole) were dissolved in 25 cc. of water. As the solution was evaporated on the steam cone, the color changed from green to orange. After cooling, alcohol was added to precipitate the brownish yellow luteo salt in 30% yield. In another experiment, in which decolorizing carbon was used as a catalyst, the reaction was complete within a few minutes at room temperature. The yield was more than 90%.

Anal. Calcd. for $[\text{Co}(\text{en}_2\text{tn})\text{Cl}_3]$: N, 23.37; C, 23.38; Cl, 29.58. Found: N, 22.45; C, 22.86; Cl, 29.36.

Neopentanediamine Trimethylenediamine Ethylenediamine Cobaltic Chloride, $[\text{Co}(\text{en}(\text{tn}(\text{dan})\text{Cl}_2)]$.—One and five-tenths grams of $[\text{Co}(\text{en}(\text{tnCl}_2)\text{Cl}]$ (0.005 mole) 0.6 g. of 95% neopentanediamine (0.0056 mole) and 0.5 g. of decolorizing carbon were ground together in 10 cc. of water for thirty minutes. The charcoal was removed, the washings were added to the main filtrate, and 100 cc. of alcohol and 60 cc. of ether were added. The pale pink precipitate which formed was recrystallized, dried at 110° and analyzed for chloride.

Anal. Calcd. for $[\text{Co}(\text{en}(\text{tn}(\text{dan})\text{Cl}_2)]$: Cl, 26.49. Found: Cl, 26.54.

Attempts to Introduce Hexamethylenediamine and Decamethylenediamine into Cobaltic Complexes.—Hexamethylenediamine and *cis* $[\text{Co}(\text{en}_2\text{Cl}_2)\text{Cl}]$ were brought together under a variety of conditions in water and in alcohol, both in the presence and in the absence of decolorizing carbon. For the most part, the amine failed to react. A small amount of a brownish yellow material was obtained in one experiment, but its failure to crystallize indicated that it was not a simple luteo salt.

Decamethylenediamine likewise showed little tendency to react. In one case a small amount of a yellow crystalline compound was obtained. Analysis showed this to be $[\text{Co}(\text{en}_3)\text{Cl}_3]$, formed by a disproportionation reaction, rather than $[\text{Co}(\text{en}_2\text{dn})\text{Cl}_3]$.

Summary

A study has been made of the coordinating tendencies of trimethylenediamine, neopentanediamine (2,2-dimethyltrimethylenediamine), hexamethylenediamine and decamethylenediamine. The latter two failed to coordinate with cobaltic

(22) Werner, *Helv. Chim. Acta*, 1, 10 (1918).

ion. The other two formed compounds which have been compared with those of ethylenediamine.

The dichloro salts $[\text{Co tn}_2\text{Cl}_2]\text{Cl}$ and $[\text{Co dan}_2\text{Cl}_2]\text{Cl}$, which could be obtained only in the *trans* form, are more soluble in water and alcohol than is the analogous ethylenediamine compound. They react with water almost instantly. The mixed salt $[\text{Co en tnCl}_2]\text{Cl}$ is intermediate in properties between $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ and $[\text{Co tn}_2\text{Cl}_2]\text{Cl}$.

The luteo type salts $[\text{Co tn}_3]\text{Cl}_3$, $[\text{Co dan}_3]\text{Cl}_3$ and $[\text{Co en tn dan}]\text{Cl}_3$ are much more soluble in water than is $[\text{Co en}_3]\text{Cl}_3$. Unlike most luteo cobaltic salts, they are pink in the solid state.

The mixed salt $[\text{Co en tn dan}]\text{Cl}_3$ is the first coordination compound which has been prepared having molecules of three different diamines attached to a single metallic ion.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Ternary System: *t*-Butyl Alcohol, Benzene and Water at 25°

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A number of investigations^{2,3,4,5,6} have been made of ternary systems involving an alcohol, benzene and water with the purpose of increasing our knowledge of solubility and distribution behavior. The system *t*-butyl alcohol, benzene and water, is also of interest because of some of the unique properties of the alcohol. It has the highest molecular weight of the monohydroxy saturated alcohols which are completely miscible with water at 25°. The other butyl alcohols have definitely higher dielectric constants, each about 18, while *t*-butyl alcohol has a dielectric constant of 11.8 and yet it is the only butyl alcohol completely miscible with water at 25°.

Measurements were made of the specific gravities and relative viscosities of saturated solutions throughout the complete range of concentration. Thus a calculation of the changes in volume and fluidity resulting from the mixing of these liquids was possible. As in previous investigations refractive indexes of saturated solutions were measured in order to provide a means of quickly analyzing the conjugate solutions formed when insufficient alcohol was present to bring about homogeneity of the liquid phases.

Materials

The *t*-butyl alcohol was obtained from Eastman Kodak Company. It was recrystallized several times with constant shaking. The final, constant, values of freezing point, specific gravity and refractive index for the alcohol used in this study are recorded in Table I. Evidence of a second crystalline form of this alcohol with a freezing point of 25.0° was obtained several times during the purification. This has been observed by other workers^{7,8} although they do not indicate the freezing points of the two forms.

(1) Present address: Eastman Kodak Company, Rochester, New York.

(2) Washburn, Haizda and Vold, *THIS JOURNAL*, **53**, 3237 (1931).

(3) Washburn and Strandkov, *J. Phys. Chem.*, **48**, 241 (1944).

(4) Albery and Washburn, *ibid.*, **49**, 4 (1945).

(5) Barbaudy, *Compt. rend.*, **182**, 1279 (1926).

(6) Olsen and Washburn, *THIS JOURNAL*, **57**, 303 (1935).

(7) Atkins, *J. Chem. Soc.*, **99**, 10 (1911).

(8) Getman, *THIS JOURNAL*, **62**, 2179 (1940).

Benzene of reagent quality from Coleman and Bell was dried with sodium and slowly distilled. The middle fraction was slowly recrystallized several times until the constants listed in Table I were obtained.

Redistilled water was used.

TABLE I

| Material | Specific gravity, d_{25}^4 | Refractive index, n_{25}^D | Freezing point, °C. |
|-------------------------|------------------------------|------------------------------|---------------------|
| <i>t</i> -Butyl alcohol | 0.78043 | 1.38483 | 25.66 |
| Benzene | .87366 | 1.49807 | 5.53 |

Procedure and Results

The ternary solubility curve was determined by titrating to the appearance of a second phase in a method similar to that described previously.^{2,3,4} The titrations were carried out in 50 ml. volumetric flasks which were mounted in a mechanical shaker in a constant temperature bath. The temperature of the bath was controlled to $\pm 0.04^\circ$. The capillary-tipped pipets from which water was added as the titrant were coated with bakelite lacquer, so that very small drops (about 5 mg.) could be added. When benzene was added as the titrant, untreated droppers were used which produced drops weighing around 4 mg. Titrations were handled so that less than 50 mg. of the titrant was added dropwise, thereby lessening evaporation losses. An hour of shaking after the addition of the last drop was considered sufficient in all cases for complete saturation.

The measurements of specific gravities and relative viscosities were made on the same solutions but a different series of titrations was carried out to provide solutions for the refractive indexes. The measurements were made immediately after each of the titrations. An Abbe refractometer was used in determining the refractive indexes. Glass-stoppered, capillary-stemmed pycnometers having a capacity of 5 ml. were used in the determinations of the specific gravities. Viscosity measurements were made by the use of two ordinary Ostwald viscometers. These values are recorded in Tables II and III. An immersion re-