yield, 87.6%. Hydrolysis with potassium hydroxide gave a 92.6% yield of the bromovanillin. Repeated crystallization from alcohol gave colorless needles; m. p., 178°.

Anal. Subs., 0.1987: AgBr, 0.1621. Calcd. for $C_8H_7O_3Br$: Br, 34.63. Found: 34.72.

Each of these products was further identified by the study of several of its derivatives, as shown in Table I.

Summary

1. Two new monobromovanillin substitution products have been prepared and their structures established.
2. A dibromovanillin has been obtained and the halogen atoms oriented.
3. The study of these compounds will be continued in this Laboratory.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

RECIPROCAL SOLUBILITY OF THE NORMAL PROPYL ETHERS OF 1,2-PROPYLENE GLYCOL AND WATER. CLOSED SOLUBILITY CURVES. II

BY HENRY L. COX, WILLIAM L. NELSON AND LEONARD H. CRETCHER

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In a discussion of concentration-temperature curves for partially miscible liquids, Findlay[1] has stated that the general form of solubility curve for all pairs of liquids may be ellipsoidal. While there are as yet insufficient data to prove the correctness of this view, considerable evidence in its favor has been presented by various investigators, notably Rothmund,[2] who found a tendency toward the formation of closed solubility curves in the systems β-collidine–water, methylethyl ketone–water at low pressure and diethylketone–water. The system ether–water investigated by Klobbie,[3] Hill,[4] and others may be classified among the systems exhibiting a similar tendency. In this case it is true that the upper consolute temperature lies above the critical point of one of the components and that the lower consolute temperature lies below the point at which a solid phase appears. The fact that the portions of these curves experimentally determinable are concave with respect to a common center is strongly indicative, however, of a closed solubility curve.[5]

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[1] Findlay, "The Phase Rule," Longmans, Green and Co., London, **1923**, 5th ed., p. 82.

[2] Rothmund, *Z. physik. Chem.*, **26**, 433, 492 (1898).

[3] Klobbie, *ibid.*, **24**, 615 (1897).

[4] Hill, THIS JOURNAL, **45**, 1143 (1923).

[5] It is true that Hill's data for the solubility of water in ether show that this part of the curve is substantially a straight line. It may be pointed out, however, that only a very small portion of the complete curve was determined.

Another system, hydrogen chloride–water, as investigated by Rupert,[6] is of particular interest in this connection. In this system the consolute points are also undeterminable.

The influence of pressure and the presence of a third component have been discussed by Timmermans,[7] Frankforter and Cohen,[8] Snell,[9] Dolgolenko,[10] and others, who have found numerous examples of systems possessing lower, and sometimes also upper consolute temperatures.

The data obtained by the authors are presented as further evidence in substantiation of Findlay's view.

In a recent paper from this Laboratory,[11] it was reported that three series of ethers had been found to possess, in binary mixture with water, properties of solubility similar to those of the system nicotine–water. The series so reported were bis(β-alkoxy)ethyl ether, ethylene-glycol mono-alkyl ether and ethylene-glycol dialkyl ether. Complete solubility data for the mono *n*-butyl and *iso*butyl ethers of ethylene glycol were determined.

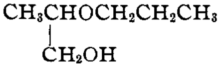
In continuing the work on closed solubility curves, the authors have prepared the two *n*-propyl ethers of 1,2-propylene glycol and have determined the solubility data for these substances with water.

Experimental Part

Preparation of the Ethers.—The method used to prepare the ethers was as follows: 2200 cc. of *n*-propyl alcohol and 500 cc. of 1,2-propylene oxide were heated in an autoclave for six hours at a temperature ranging between 180° and 205°. The pressure remained at about 200 lb. (90.8 kg.) throughout the run. The autoclave was then cooled, and the contents removed and distilled. Three hundred and twelve g. of product was obtained; b. p., 147–153°. The higher- and lower-boiling fractions were discarded. It was not possible to obtain a constant-boiling fraction by repeated refractionation of this material.

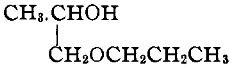
An examination of the structural formula of 1,2-propylene oxide indicates that on reaction with *n*-propyl alcohol two isomeric alcohol-ethers may be formed: one containing a primary alcohol group resulting from the addition of the propoxyl radical to carbon atom 2 of the oxide, and another containing a secondary alcohol group resulting from the addition of the propoxyl radical to carbon atom 1.

The compounds are represented by Formulas I and II.



$$\begin{array}{l}CH_3CHOCH_2CH_2CH_3\\ \quad\mid\\ \quad CH_2OH\end{array}$$

I



$$\begin{array}{l}CH_3.CHOH\\ \quad\;\mid\\ \quad\; CH_2OCH_2CH_2CH_3\end{array}$$

II

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[6] Rupert, This Journal, **31**, 851 (1909).

[7] Timmermans, *Z. physik. Chem.*, **58**, 129 (1907).

[8] Frankforter and Cohen, This Journal, **36**, 1128 (1914).

[9] Snell, *J. Phys. Chem.*, **2**, 482 (1898).

[10] Dolgolenko, *Z. physik. Chem.*, **62**, 499 (1908).

[11] Cox and Cretcher, This Journal, **48**, 451 (1926).

Separation of the Ethers.—It was shown by Stephan[12] that primary and secondary alcohols can be separated by boiling in benzene solution with phthalic anhydride. At the boiling point of this solution the primary alcohol is rapidly esterified; the secondary very slowly.

Assuming that we had such a mixture, 130 g. of the product boiling between 147° and 153° was mixed with 260 g. of dry benzene and 163 g. of phthalic anhydride, and gently boiled under a reflux condenser for one hour. The solution was then cooled in ice to separate as much of the excess of phthalic anhydride as possible. The latter was removed by filtration. The flask was then placed in a water-bath, and the material subjected to vacuum distillation. The temperature of the bath was gradually raised to 85°, and as much distillate collected as possible at this temperature. This distillate, consisting for the most part of benzene and the secondary alcohol, was separated by repeated distillation.

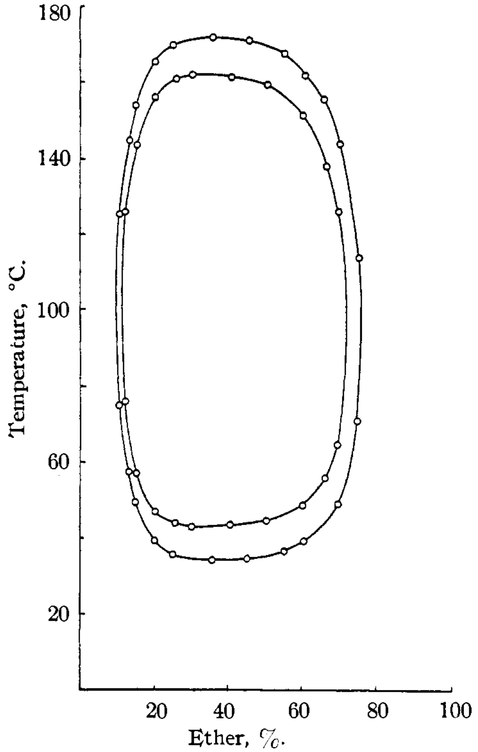

Fig. 1.—Solubility of propylene glycol-*n*-propyl ethers in water. The outer curve is that of 1-propoxy-propane-2-ol; the inner, that of 2-propoxy-propane-1-ol.

The secondary alcohol, 1-propoxy-propane-2-ol, thus prepared, boiled at 148.5–149°, at 730 mm.; d_4^{20}, 0.8886.

Calcd. for $C_6H_{14}O_2$: C, 60.97; H, 11.94. Found: C, 60.83; H, 12.10.

The residue from the vacuum distillation described above was filtered to remove phthalic anhydride; the filtrate was made alkaline with sodium carbonate and extracted with ether to remove any secondary alcohol that might have been present. The solution was then allowed to stand at room temperature for one hour to decompose any unchanged phthalic anhydride. On acidifying with hydrochloric acid, the phthalate was precipitated as a heavy oil. This was extracted with chloroform, and the chloroform solution dried over sodium sulfate to remove the phthalic acid.[13]

After removing the phthalic acid and sodium sulfate by filtration, and the chloroform by distillation in a vacuum, the phthalate was saponified by heating on a water-bath for one hour with an excess of aqueous sodium hydroxide. After cooling, the alcohol-ether was extracted with ethyl ether, the solution dried, the ether removed and the product purified by fractional distillation.

2-Propoxy-propane-1-ol boils at 150.5–151°, at 730 mm.; d_4^{20}, 0.8925.

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[12] Stephan, *J. prakt. Chem.*, [2] **60**, 248 (1899).

[13] Levene and Mikeska, *J. Biol. Chem.*, **65**, 507 (1925).

Calcd. for $C_6H_{14}O_2$: C, 60.97; H, 11.94. Found: C, 60.84; H, 12.04.

The Solubility Data.—The method of procedure was the same as that described in a previous paper.[14] The data are recorded in Table I and Fig. 1.

TABLE I

SOLUBILITY OF THE ISOMERIC *n*-PROPYL ETHERS OF 1,2-PROPYLENE GLYCOL IN WATER

1-Propoxy-propane-2-ol			2-Propoxy-propane-1-ol		
Ether, % by wt.	Lower soln., temp., °C.	Upper soln., temp., °C.	Ether, % by wt.	Lower soln., temp., °C.	Upper soln., temp., °C.
10.7	75.0	125.5	12.1	76.0	126.0
13.1	57.7	145.0	14.9	57.2	143.5
14.9	49.8	154.0	20.0	47.2	156.0
20.0	39.5	165.5	25.4	43.8	161.0
24.8	35.9	170.0	30.0	42.8	162.0
35.5	34.5	171.7	40.5	43.4	161.5
45.2	35.0	171.2	50.3	44.7	159.5
55.0	36.6	168.0	60.0	48.7	151.5
60.4	39.3	162.0	66.2	56.0	138.0
65.2	42.7	155.5	69.3	64.7	126.0
69.7	49.3	144.0	..	..	...
74.7	71.0	114.0	..	..	...

Summary

The isomeric *n*-propyl ethers of 1,2-propylene glycol have been prepared. Solubility data for these ethers and water have been determined.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE IRREVERSIBLE REDUCTION OF ORGANIC COMPOUNDS

IV. THE APPARENT REDUCTION POTENTIAL OF UNSATURATED CARBONYL COMPOUNDS

BY JAMES B. CONANT AND ROBERT E. LUTZ

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In a preliminary paper published a few years ago[1] we outlined a convenient and rapid method of studying the *irreversible* reduction of organic compounds. By an electrochemical device, it was possible to decide what reversible reducing agents of a graded series would reduce a given compound. It was found that with the compound studied, the oxidation-reduction potential of the reagent appeared to be the governing factor. The method has since been applied to the study of the irreversible reduction of a variety of compounds, particularly in aqueous solution.[2] In this paper we shall report the results of a further study of unsaturated

[14] Ref. 11, p. 452.

[1] Conant and Lutz, THIS JOURNAL, **45**, 1047 (1923).

[2] Conant and Pratt, *ibid.*, **48**, 2468 (1926).