Simultaneous Determination of Ethylene and 1,2-Propylene Glycols

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Ethylene and 1,2-propylene glycols can be determined simultaneously by periodate oxidation to formaldehyde and acetaldehyde which are determined polarographically after a simple distillation. The method is applicable to the analysis of mixtures of formaldehyde and acetaldehyde as well as to the determination of other substances which form these aldehydes on treatment. The principal limitation of the method is that there must not be formed any other volatile substances polarographically reducible under the same conditions as the aldehvdes.

LTHOUGH several methods for the quantitative deter-A mination of glycols have been described in the literature, little attention has been given to their determination in mixtures of each other. Those methods that have been used involve tedious and time-consuming procedures. It seemed desirable, therefore, to obtain a simple and rapid method for quantitatively determining the amounts of ethylene and 1,2-propylene glycols in the presence of one another.

The method described in this paper consists essentially of oxidizing the glycol mixture with periodic acid to give formaldehyde and acetaldehyde according to the following equations:

$$CH_{2}OH.CH_{2}OH + HIO_{4} \longrightarrow 2HCHO + HIO_{3} + H_{2}O$$

$$CH_{3}.CHOH.CH_{2}OH + HIO_{4} \longrightarrow HCHO + CH_{3}.CHO + HIO_{3} + H_{2}O$$

The resulting aldehydes are then determined polarographically.

From an examination of the equations of the reaction, it is seen that the acetaldehyde content gives a measure of the propylene glycol concentration. The ethylene glycol can be estimated by deducting the formaldehyde produced by the oxidation of propylene glycol from the total amount of formaldehyde found in the mixture.

Johnson (5) determined 2,3-butylene glycol by oxidizing it with potassium periodate in an acid medium to give acetaldehyde. This was distilled into a standard bisulfite solution to form the bisulfite addition product, which was subsequently determined by titration of the bound bisulfite with standard iodine solution. Hoepe and Treadwell (3) described a method utilizing the Malaprade reaction for the determination of glycerol, ethylene glycol, and 1,2-propylene glycol in mixtures. The resulting formic acid, total aldehyde, and formaldehyde were determined titrimetrically on aliquots of the oxidized solution. Mixtures of formaldehyde and acetaldehyde were determined by Ionescu and Slusanschi (4) using dimedon (dimethyldihydroresorcinol) as a precipitant, and noting the length of time required for the crystals to appear.

Boyd and Bambach (1) described a polarographic method for the determination of formaldehyde as a step in the procedure for the determination of serine in protein hydrolyzates. The method consisted of treating the hydrolyzate with periodic acid, quantitatively separating the resulting formaldehyde by distillation, and determining it polarographically using $0.05\ N$ potassium hydroxide in 0.1 N potassium chloride as the supporting electrolyte solution. The effect of the presence of other aldehydes such as acrolein, acetaldehyde, and propionaldehyde on the determination of formaldehyde was investigated by Whitnack and Moshier (6). They found that the most satisfactory results are obtained in 0.1 N lithium hydroxide containing 0.01 N lithium chloride at constant temperature and constant pH without the removal of dissolved oxygen.

EXPERIMENTAL

The procedure for the polarographic determination of formaldehyde in the presence of acetaldehyde as previously described by Whitnack and Moshier was followed in this study. A solution consisting of 0.1 N lithium hydroxide in 0.01 N lithium chloride was used as the supporting electrolyte medium. It was not necessary to add a maximum suppressor, inasmuch as no maximum was found to occur under the conditions used.

Preliminary studies revealed that the formaldehyde wave appeared at -1.45 to -1.58 volts (dropping mercury electrode vs. pool) and the acetaldehyde wave appeared at -1.65 to -1.85volts under the conditions of pH, concentration range, and capillary used. In the actual determination, it was found necessary only to determine the galvanometer readings at a point be-fore the appearance of the formaldehyde wave, -1.400 volts, at the height of the formaldehyde wave, -1.610 volts, and at the height of the acetaldehyde wave, -1.890 volts. These are the only points required for the quantitative determination of the aldehyde content of the mixture resulting from the oxidation of the glycols.

It was found that the height of the acetaldehyde wave decreased markedly (approximately 15% after 1 hour) when al-lowed to stand in contact with the alkaline electrolyte solution. The formaldehyde on the other hand was only slightly affected (approximately 5% decrease after 1 hour). For this reason, and also because of the volatilization of the acetaldehyde while in the polarographic cell, all determinations were made after standing in contact with the base solution in the cell for the same length of time (5 to 10 minutes).

MATERIALS AND APPARATUS

GLYCOLS. Pure ethylene glycol (Coleman and Bell Co.) and redistilled 1,2-propylene glycol (Eastman Kodak Co.) were used. The refractive indices and the specific gravities of the glycols checked the values reported in the literature.

ALDEHYDES. A stock standard solution of formaldehyde (0.795 mg. per ml.) was prepared from commercial formalin and standardized by the hydrogen peroxide method. A stock standard solution of acetaldehyde (0.470 mg. per ml.) was prepared by weighing a sample of pure acetaldehyde in an ampoule and diluting to a definite volume with distilled water; the acetaldehyde was purified by distillation through an efficient distillation column.

PERIODIC ACID. An approximately 0.5 N solution was pre-pared by dissolving 11 grams of periodic acid (The G. Frederick Smith Chemical Co.) in distilled water and diluting to 100 ml. The solution was stored in a dark glass-stoppered bottle. BASE SOLUTION. This consisted of a 1 N lithium hydroxide

solution in 0.1 N lithium chloride.

POLAROGRAPH. The Fisher Elecdropode was used in this work and all measurements were made at one tenth of the galvanometer sensitivity. The polarographic cell was a water-jacketed cell of about 35-ml. capacity connected in series through a small circulating pump with a constant-temperature bath thermostatically controlled at $\pm 0.2^{\circ}$ C.

DISTILLING APPARATUS. A simple distilling apparatus was used consisting of a semimicro 100-ml. Kjeldahl flask, a spray trap, a vertical condenser about 30 cm. in length, and a water bath for cooling the receiver.

PROCEDURE

PERIODIC ACID OXIDATION. An aqueous solution of the glycol mixture containing approximately 5 to 20 mg, of each of the glycols is pipetted into a 100-ml. Kieldahl flask, and approximately 3 ml. of the periodic acid solution are added, with sufficient water to bring the total volume to about 60 ml. A few glass beads are introduced into the flask to prevent bumping.

The Kjeldahl flask is placed in an upright position and connected to the distilling unit. A deep receiver flask—e.g., a Pyrex test tube, 45 × 190 mm.—containing 75 ml. of distilled water is used to absorb the aldehydes and to cover the end of the condenser to a height of several centimeters. In order to minimize any loss of acetaldehyde due to volatilization, the receiver is placed in an ice-water bath and kept cold throughout the course of the distillation.

The contents of the reaction flask are heated, gently at first, and the solution is distilled over at a rate of 3 to 4 ml. per minute until about 5 ml. remain in the Kjeldahl flask. Near the end of the distillation, the receiver flask is lowered so that the end of the condenser no longer extends below the surface of the liquid in the receiver. After the distillation is complete, the end of the condenser is rinsed with distilled water. The distillate is then quantitatively transferred to a 250-ml. volumetric flask, care being taken not to exceed a total volume of 225 ml. The aldehyde solution can be kept in this manner until ready for the polarographic measurements.

POLAROGRAPHIC ANALYSIS. Immediately prior to the polaro-graphic determination of the aldehydes, 25 ml. of the 1 N lithium hydroxide solution in 0.1 N lithium chloride are added to the distillate in the volumetric flask and the contents are diluted to the mark. In this way, the resulting solution has a concentration of 0.1 N lithium hydroxide in 0.01 N lithium chloride.

This practice seemed most advisable, since condensation of aldehydes is rapid in the presence of strong alkalies. By adding the base solution to the aldehyde mixture in the manner pro-posed, the time of contact of the aldehydes with the lithium hydroxide is reduced to a minimum.

The polarographic cell and electrodes are rinsed several times with the solution to be analyzed. A sample of the solution is then placed in the cell and allowed to come to constant temperature. After a definite length of time has elapsed from the moment of the addition of the supporting electrolyte solution, the galvanometer deflections at applied voltages of -1.890, -1.610, and -1.400 volts are read. The height of the acetaldehyde wave is the difference in the galvanometer reading between the first and second points; the height of the formaldehyde wave is the difference between the second and third points.

These wave heights are then compared to the values obtained from a 250-ml. solution prepared from the standard aldehyde solutions. The concentrations of formaldehyde and acetalde-hyde in the latter solution should be approximately the same as those in the sample solution polarographed, though in the latter case it is not necessary to submit the aldehydes to a periodic acid oxidation or distillation, since there is no change in concentration as a result of such treatment.

CALCULATIONS

1,2-PROPYLENE GLYCOL.

Weight in sample, mg. =
$$W_p = \frac{H_a}{H_s} \times V \times C_s \times \frac{76}{44}$$

$$= \frac{1.727 \times V \times H_a \times C_s}{H_s}$$

where $C_{\bullet} = \text{mg.}$ of acetaldehyde per ml. of stock standard solution

- Vvolume in ml. of stock standard acetaldehyde solution taken
- Ha acetaldehyde wave height from periodic acid oxidation of glycol mixture
- H_{\bullet} = acetaldehyde wave height of standard

Per cent by weight = $\frac{100 W_p}{S}$

where S = weight of sample in mg.

ETHYLENE GLYCOL.

Weight in sample, mg. =
$$W_{\bullet} = \frac{1.033 \times V \times H_f \times C_{s'}}{H_{\bullet'}} - 0.408 W_{p}$$

where $W_p = \text{mg. of } 1,2$ -propylene glycol in sample

- = mg. of formaldehyde per ml. of stock standard solution
- volume in ml. of stock standard formaldehyde solution taken
- = formaldehyde wave height from periodic acid oxidation of glycol mixture
- $H_{s}' =$ formaldehyde wave length of standard

Per cent by weight = $\frac{100 W_{\bullet}}{S}$

where S = weight of sample in mg.

DISCUSSION

The values obtained at three different temperatures indicates that, within the range of 20° to 30° C., the height of the formaldehyde wave increases approximately 6.5% for each 1° C. rise in temperature. This is in agreement with the observation of Boyd and Bambach (1). The acetaldehyde wave height, however, increases only approximately 1.5 to 2.0% per degree rise in temperature, which is the same as that found by Elving and Rutner (2).

The data obtained in these studies indicate that, under the conditions used, there is a linear relationship between the height of the wave and the corresponding aldehyde content of the solution resulting from the action of periodic acid on the glycol mixture.

Using synthetic mixtures of the pure glycols an average precision and accuracy of better than 1.5% was obtained for propylene glycol and 2.2% for the ethylene glycol.

It is important that any material capable of being oxidized by periodic acid to give formaldehyde or acetaldehyde be absent. This includes such substances as α -amino alcohols, hydroxyamino acids (serine and threenine), and polyalcohols (glucose and other sugars). Monohydroxy alcohols, in general, such as methanol or ethanol do not affect the determination.

The polarographic method described need not necessarily be limited to the determination of mixtures of glycols but can also be successfully applied to the determination of formaldehyde and acetaldehyde in mixtures and to the determination of substances which form these aldehydes on oxidation-e.g., a mixture containing 1,2-propylene glycol and glycerol. The real limitation of the technique described-oxidation to formaldehyde and acetaldehyde, separation of the aldehydes, and polarographic measurement of the aldehyde content-is that there be absent and not produced any volatile substances polarographically reducible in the same potential range as the aldehydes under the conditions used.

Representative data on the analysis of mixtures of ethylene glycol and 1,2-propylene glycol in the manner described are given in Table I.

Table I. Simultaneous Determination of Ethylene Glycol and 1,2-Propylene Glycol in Synthetic Mixtures

Ethylene Glycol			Propylene Glycol		
$\frac{\text{Present}}{Mg.}$	Found Mg.	Error %	$\frac{\text{Present}}{Mg.}$	Found Mg.	Error %
4.31 4.31 8.62 8.62 10.94 10.94 10.94 10.94 10.94 10.94 10.94 10.94 10.94 16.41 16.41	$\begin{array}{r} \textbf{4.28} \\ \textbf{4.53} \\ \textbf{4.34} \\ \textbf{8.95} \\ \textbf{8.55} \\ \textbf{8.25} \\ \textbf{10.66} \\ \textbf{10.98} \\ \textbf{10.98} \\ \textbf{10.98} \\ \textbf{10.60} \\ \textbf{15.93} \\ \textbf{17.34} \end{array}$	$\begin{array}{c} -0.7 \\ +5.17 \\ +2.8 \\ -4.3 \\ +2.53 \\ -2.53 \\ +0.4 \\ +3.1 \\ -2.53 \\ +2.53 \\ -2.53 \\ +2.53 \\ +3.1 \\ -2.53 \\ +3.1 \\ -2.53 \\ +3.2 \\ +3.2 \\ -2.5 \\ $	$\begin{array}{c} \textbf{8.26}\\ \textbf{16.52}\\ \textbf{16.52}\\ \textbf{16.52}\\ \textbf{16.52}\\ \textbf{16.52}\\ \textbf{16.52}\\ \textbf{15.16}\\ \textbf{15.16}\\ \textbf{15.16}\\ \textbf{15.16}\\ \textbf{15.16}\\ \textbf{15.16}\\ \textbf{15.16}\\ \textbf{15.16}\\ \textbf{15.16}\\ \textbf{22.74} \end{array}$	8 18 16 50 16 72 16 43 16 71 17 02 15 38 15 52 15 26 15 18 22 55 14 91 23 02	$\begin{array}{c} -1.6\\ -0.1\\ +1.3\\ -0.2\\ +1.1\\ +2.8\\ \\ \\ +1.4\\ +0.7\\ +0.7\\ -1.1\\ -1.6\\ +1.1\\ \\ \\ \\ \\ +1.3\end{array}$
AV.		#2.2			≡ 1.3

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