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The Composition of the Azeotropes Acetaldehyde — Ethyl Ether, Propylene Oxide — Ethyl Ether and Ethylene Glycol — Diethylene Glycol Monoethyl Ether

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The compositions of three azeotropes with minimum boiling points have been investigated. The azeotrope, acetaldehyde-ethyl ether, boils at 18.9° C at 760 mm Hg and contains 76.5 per cent by weight of acetaldehyde. The azeotrope, propylene oxide-ethyl ether, boils at 32.6° C at the same pressure and contains 49.6 % propylene oxide. At 36 mm Hg the azeotrope, ethylene glycol-diethylene glycol monoethyl ether, boils at 108.5° C and consists of 26.6 % ethylene glycol and 73.4 % diethylene glycol monoethyl ether.

When working on ethylene oxide and products therefrom, mixtures were found which contained the components of the azeotropes mentioned in the heading. The first two azeotropic compositions do not seem to have been published before. The third one has earlier been investigated at 760 mm Hg [1].

EXPERIMENTAL

Distillation apparatus. A Podbielniak Hyper-Cal apparatus, Cat. No. HC-701-A, Series "D", has been used for all distillations. A 25 mm I.D. × 36″ long Heli-Grid packed column was used. All distillations were carried out with a reflux ratio of 200 : 1.

Analyses. Mixtures of acetaldehyde and ethyl ether were analysed by a spectrophotometric method. A suitable amount of the sample was diluted with ethyl ether to 100 ml volume and the extinction of this solution was measured in a Beckman Spectrophotometer, model DU, with light path of the sample holder 1.00 cm. By means of the molar extinction coefficient at 288 mμ of pure acetaldehyde in ethyl ether, which was found to be 17.3 $l \cdot mole^{-1} \cdot cm^{-1}$, the content of acetaldehyde in the sample could be calculated using Lambert-Beer's law.

Mixtures of propylene oxide and ethyl ether were analysed by determining the propylene oxide content using a method given by Lubatti for ethylene oxide [2].

Mixtures of ethylene glycol and diethylene glycol monoethyl ether (the latter henceforth called ethyl diglycol) were analysed by determining the ethylene glycol content using a method given by Pohle, Mehlenbacher and Cook [3]. This method is based on the Malaprade potassium periodate oxidation method [4].

Starting materials. Pure acetaldehyde was prepared by fractional distillation of technical acetaldehyde.

Pure ethyl ether was prepared by drying usual laboratory ethyl ether first with anhydrous calcium chloride and then with metallic sodium. The dry ether was fractionated.

Pure propylene oxide was prepared by fractionation of a technical propylene oxide.

In the experiment for obtaining the azeotrope, ethylene glycol-ethyl diglycol, chemicals of technical quality were used.

AZEOTROPES

In order to obtain the azeotrope of acetaldehyde and ethyl ether a mixture of 75 % acetaldehyde and 25 % ethyl ether was distilled. (All compositions in this paper are given in per cent by weight). The main fraction was analysed to contain 76.5% acetaldehyde. The boiling point of this fraction was measured by boiling it slowly under reflux in a Claisen flask and the temperature was read on a thermometer graduated to 0.1° C. The boiling point of pure acetaldehyde was determined in the same way on the same occasion. The temperature of the boiling azeotrope was 19.9° C and that of the pure acetaldehyde 21.4° C. The boiling point of acetaldehyde is given as 20.4° C at atmospheric pressure [5]. The boiling point of the azeotrope would thus be 18.9° C.

To obtain the azeotrope, propylene oxide — ethyl ether, a mixture of 50% of the former substance and 50 % of the latter was fractionated. The main fraction contained 49.6 % propylene oxide. The boiling point of the fraction was measured in the way described above and was found to be 2.0° C lower than that of pure ethyl ether. The boiling point of ethyl ether is given as 34.6° C [6] and thus the boiling point of the azeotrope would be 32.6° C at 760 mm Hg. The same method gave the boiling point of propylene oxide as 34.2° C whereas the published value is 33.9° C at atmospheric pressure [7].

To obtain the azeotrope, ethylene glycol — ethyl diglycol, a mixture of 50 % technical ethylene glycol and 50 % technical ethyl diglycol was fractionated at 36 mm Hg. The main fraction was redistilled under the same conditions. After the first fractionation the main fraction contained 26.5 % ethylene glycol and, after the second one, 26.6 %. The temperature was measured with an iron-constantan thermocouple, which was calibrated against a standardised thermometer. The thermocouple E.M.F. was measured with a potentiometer from Leeds & Northrup Co. In this way the boiling point of the azeotrope was determined to be 108.5° C at 36 mm Hg.

This azeotrope is reported [1] to boil at 195.0° C at 760 mm Hg and to contain 29.5 % ethylene glycol under those conditions.

The following correlation between vapour pressure and temperature of ethylene glycol is given [8]:

$$\log p = 7.8808 - \frac{1\,957}{193.8 + t}$$

where p is the pressure in mm Hg and t the temperature in ° C. From this equation the boiling point of pure ethylene glycol is calculated to be 115.6° C at 36 mm Hg.

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