Vapor Pressure and Boiling Point of β-Ethoxypropionitrile

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β-Ethoxypropionitrile is prepared and the boiling point data for it are obtained at pressures ranging from 25 to 760 mmHg. The data are well fitted to the Calingaert–Davis equation.

β-Ethoxypropionitrile is an intermediate chemical in the synthesis of thiamine (vitamin B_1) and is prepared from acrylonitrile and ethyl alcohol. It boils at 171–173 °C at 760 mmHg. Its use as solvent is still unexplored because of its toxicity and high cost of production. The vapor pressure data are needed to facilitate its purification. In the present work, β-ethoxypropionitrile is prepared in the laboratory, and boiling points at various subatmospheric pressures are determined. The Calingaert–Davis equation fits the data well.

Experimental Section

(a) Preparation of β-Ethoxypropionitrile. Chemicals. Acrylonitrile (BDH, U.K.) and ethyl alcohol (95% w/w technical) are used without further purification. Sodium ethoxide, 16% w/w in absolute alcohol, is prepared and used.

Equipment. The all-glass experimental set up is shown in Figure 1. The temperature of the water bath is maintained at the desired level by heating with an electric coil heater (not shown in figure).

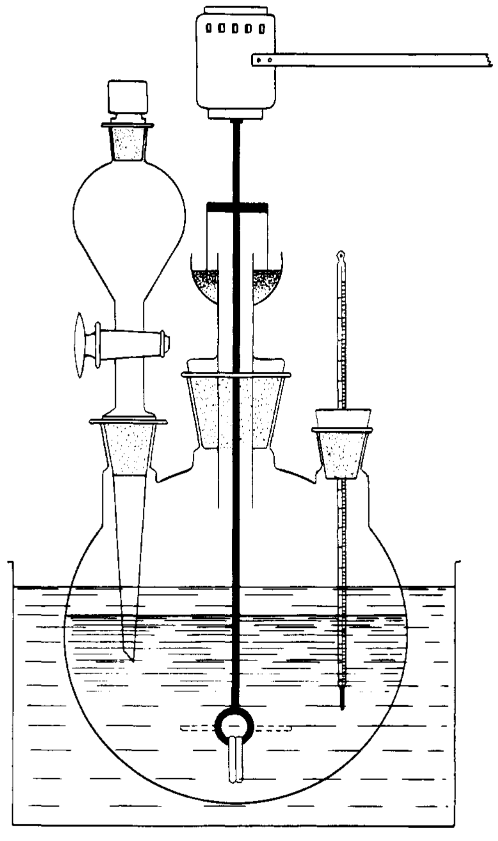

Figure 1. Experimental set up for the preparation of β-ethoxypropionitrile.

Procedure. Ethyl alcohol is taken in the three-necked flask and a small quantity of sodium ethoxide is added to it. The contents are heated to 35 °C agitating continuously. Then acrylonitrile is added from the dropping funnel in such a manner that the temperature of the reaction mixture does not rise beyond 40 °C so as to suppress the side reactions. The reaction of acrylonitrile with ethyl alcohol is as follows:

$$C_2H_5OH + CH_2CHCN \xrightarrow{\text{Na ethoxide}} C_2H_5OCH_2CH_2CN$$

The reaction mixture is well stirred for 30 min, and the contents of the flask are neutralized by the addition of acetic acid to bring the pH to 6–6.5. Then the volatiles (including water) other than ethoxypropionitrile are distilled off and pure fraction is collected between 171 and 174 °C at atmospheric pressure. Again it is redistilled and the fraction collected at 171.5–172 °C is used for determining the vapor pressure data. The physical properties of this fraction are given in Table I. The purity of the β-ethoxypropionitrile is determined by a chemical method as described below: 0.3–0.4 g of β-ethoxypropionitrile taken in a 500-ml round-bottom flask is refluxed with 15 ml of 75% w/w sulfuric acid for 3 h on water bath and then 100 ml of water followed by 70 ml of 30% w/v sodium hydroxide solution are added and mixed thoroughly. The ammonia produced during the hydrolysis of the nitrile is distilled off in a Kjeldahl apparatus into 50 ml of 0.2 N sulfuric acid for 45 min. The excess sulfuric acid is titrated with 0.1 N sodium hydroxide solution using methyl red indicator. The following formula is used to calculate the purity.

$$\underset{(\text{w/w})}{\%\ \text{nitrile}} = \{[(50 \times 2 \times \text{normality of sulfuric acid}) - (\text{titer value} \times \text{normality of sodium hydroxide})] \times 0.9913\}/\text{weight of the substance}$$

(b) Determination of Boiling Points at Various Pressures (below 760 mmHg). The boiling point data, for β-ethoxypropionitrile at various pressures ranging from 25 to 760 mmHg are obtained in a modified Swietoslawski ebulliometer. The ebulliometer is earlier standardized by measuring the vapor pressure–temperature data for tri-*n*-butyl phosphate (TBP), which excellently coincides with that of Evans et al. (*1*). The pressure in the ebulliometer is regulated by vacuum pump and a controlled leak of dry air into a surge reservoir. The pressure is read to the nearest 0.5 mm on a mercury manometer by means of a cathetometer. All the readings are taken at 28 ± 0.1 °C.

Table I. Analysis of β-Ethoxypropionitrile

Purity w/w	Refractive index η_D	Specific (20/20) gravity
99.8%	1.4065 at 20 °C	0.9072

Table II. Boiling Point Data of β-Ethoxypropionitrile

Sl no.	P, mmHg	Boiling point °C Exptl	Boiling point °C Calcd	d(deviation)[a] in %
1	25	75.1	77.5	+3.2
2	30	81.0	81.4	+0.49
3	40	88.2	87.7	−0.57
4	50	93.5	92.9	−0.64
5	60	97.4	97.2	−0.21
6	70	102.5	100.9	−1.56
7	80	103.7	104.2	+0.48
8	90	106.5	107.2	+0.66
9	100	109.4	109.9	+0.46
10	200	128.6	128.9	+0.23
11	300	141.1	141.0	−0.07
12	400	150.7	150.1	−0.40
13	500	158.5	157.4	−0.69
14	600	164.6	163.7	−0.55
15	760	171.7	172.1	+0.23

[a] (Calculated − experimental)/experimental × 100. Average deviation = 0.696%.

Results

The experimental results are fitted to the Calingaert–Davis equation using the method of least squares. The constants A and B of the Calingaert–Davis equation are found to be 7.6998 and 1937.5, respectively. The equation is as follows:

$$\log P = 7.6998 - (1937.5/(230 + t))$$

where P = pressure in mmHg and t = boiling point, °C.

The calculated values from the above equation are compared with the experimental values (Table II), and the average deviation is found to be 0.696%.

Literature Cited

(1) Evans, D. P., Davies, W., Jones, W. J., *J. Chem. Soc.*, 1310 (1930).

(2) Hala, E., Pick, J., Fried, V., Vilim, O., "Vapor Liquid Equilibrium", 2d English ed, Translated by G. Standart, Pergaman Press, London, 1967, pp 240, 254.

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Experimental Pressure–Volume–Temperature Relations for Saturated and Compressed Fluid Ethane

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In this paper we present the results of high precision experimental PVT measurements in compressed fluid ethane. The PVT measurements were performed on 22 nearly isochoric samples of ethane whose nominal densities ranged from 0.03 to 0.57 g cm^{-3}. In addition to these isochoric measurements, saturated vapor pressures have been measured at temperatures ranging from 214 to 305 K. Saturated liquid densities, thought to be accurate to within a few tenths of one percent, have been obtained from the intersection of the equation of state used to smooth the experimental isochoric data and the vapor pressure curve. The accuracy of the data is estimated to be within 0.2% except in the very neighborhood of the critical point.

There have been three major experimental investigations of pressure–volume–temperature relationships for compressed fluid ethane. The earliest study was performed by Reamer et al. (*7*) in 1944 and covered the temperature range of 310–510 K, with pressures ranging from 5 to 70 MPa (1 MPa = 9.869 233 atm = 145.0377 psia = 10 bar). Later, Michels et al. (*6*) published PVT measurements in the range of 273–423 K and 1.5–22 MPa. More recently, Douslin and Harrison (*3*) have reported comprehensive high precision measurements in the temperature range of 248–623 K with pressures ranging from 1.2 to 41 MPa. Even though these investigations cover a considerable portion of the PVT surface for ethane (see Figure 1), the low temperature, high density fluid remains uninvestigated.

In an attempt to correct this situation, the PVT relationship for 22 nearly isochoric samples of fluid ethane has been measured. These measurements range in density from 0.03 to 0.57 g cm^{-3} with temperatures ranging from 157 to 340 K at pressures to 70 MPa. Pressure measurements for the saturated vapor over the temperature range of 214–305 K are also reported and graphically compared to the results of other authors. Finally, saturated liquid densities have been obtained from the intersection of the function used to smooth the experimental PVT data and the vapor pressure curve.

Experimental Section

The experimental apparatus and procedure have been described in detail elsewhere (*9, 11*). Briefly, however, the stainless steel isochoric chamber was charged with ethane to a predetermined pressure, the mass of the charge being determined by differential weighings. The zero pressure volume of the system had been previously determined as a function of temperature by making a series of Burnett (*1*) type expansions into a reference chamber of known volume. The actual volume of the system at a given temperature and pressure was then calculated by correcting for the pressure distortion of the isochoric chamber (*8*). The uncertainty in the system volume obtained in this manner was estimated to be less than 0.025%.

Temperatures were measured on the IPTS-1948 using a platinum resistance thermometer which had been calibrated by the manufacturer. (This calibration was traceable to a calibration by the National Bureau of Standards.) These temperatures were then converted to the IPTS-1969 using the tables found in ref 2. The temperature of the system was controlled to within ±0.002

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