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Vapor Pressure of 1-Nitropropene

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The vapor pressure of 1-nitropropene is reported over the temperature range 28–100 °C. The measurements are for an experimentally obtained equilibrium mixture of cis–trans isomers. The vapor pressure equation was determined to be $\ln P = -(4.458 \times 10^3)(1/T) + 17.27$. The molar enthalpy of vaporization is 8.854 kcal/mol.

Introduction

In the course of the study of the thermal decomposition of nitroalkenes, it became necessary to measure the vapor pressure of 1-nitropropene over the temperature range of 28–100 °C. At the higher temperature limit 1-nitropropene begins to undergo thermal decomposition. The vapor pressure of 1-nitropropene has been previously reported by Redemann, Chaikin, and Fearing (1). Since the previous study did not report the method of synthesis employed, it is not clear whether the study dealt with a pure material or an equilibrium mixture of cis and trans isomers.

Experimental Section

A mixture of the cis and trans forms of 1-nitropropene was synthesized by dehydration of 1-nitro-2-propanol by using phthalic anhydride according to the procedure of Buckley and Scaife (2). The middle fraction boiling at 80 °C at 78 torr was collected. NMR spectra (Figure 1) showed the isomeric composition to be 32% cis form and 68% trans form. 1-Nitro-2-propanol was prepared by the aldol condensation of acet-aldehyde and nitromethane in 2-propanol by using a potassium fluoride catalyst (3). The middle fraction boiling at 77 °C at 7 torr was collected.

The vapor pressure was measured with an isoteniscope. The procedure is similar to that described by Weissberger (4) except that in our experiments we used the original method of Smith and Menzies (5) in which the U-tube was charged with the material whose vapor pressure was to be measured. Measurements were made on water to check the validity of the

Table I. Vapor Pressure Data for 1-Nitropropene

T, °C	P, torr	T, °C	P, torr	T, °C	P, torr
28.0	11.7	62.7	54.7	88.7	143.4
34.3	16.4	70.6	74.4	90.2	149.9
40.1	20.4	75.1	88.7	95.8	177.5
46.1	27.5	78.0	97.3	98.3	195.1
51.8	34.9	80.9	107.2	100.0	203.7
57.2	43.9	84.2	120.6		

method. Measurements made over a temperature range of 25–35 °C when averaged reproduced literature values (δ) to within 1%.

A sample was degassed in the isoteniscope by alternate freezing, pumping, and thawing 3 times in a liquid-nitrogen bath. The sample was then allowed to thermally equilibrate for 20 min in a heated, circulating silicone oil bath. The temperature of both the bath and the vapor in the isoteniscope were measured with thermocouples connected to a digital thermometer; bath and vapor pressures were within 0.3 °C during any set of measurements. Vapor pressure readings were made by different readings from an open-end mercury manometer.

Results and Discussion

The measured vapor pressures are shown in Table I. A least-squares fit to a Clapeyron equation yields (pressure in torr and T in kelvin)

$$\ln P = [(-4.458 \pm 0.02) \times 10^3](1/T) + (17.27 \pm 0.13)$$

The resulting molar enthalpy of vaporization is 8.854 ± 0.040 kcal/mol.

Since the isomeric sample composition in the previously reported study of the vapor pressure of 1-nitropropene is not known, comparison of our data with previously measured data is difficult. Using the values obtained in the vapor pressure equation, we predict the normal boiling point of the mixture to be 147 °C while Redemann and co-workers predict it to be 140 °C. Our experimental error is largest at the lower end of the vapor pressure scale. For example, our least-squares fit showed the largest residuals to be associated with the data points at the lower end of the vapor pressure scale. Since our method reproduces results for known materials, we have no

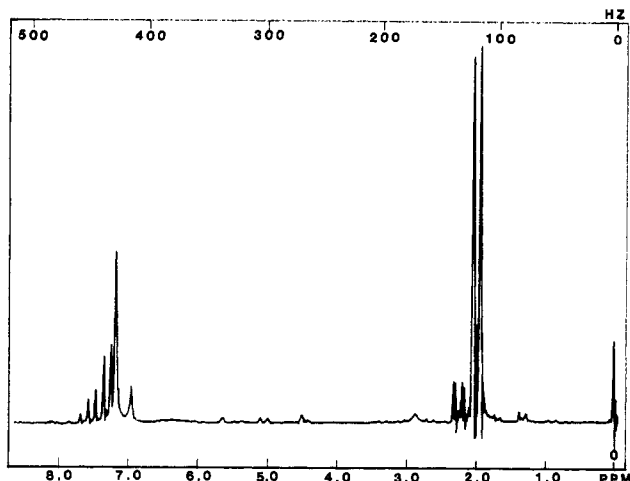


Figure 1. NMR spectrum of 1-nitropropene.

reason to suspect that our measurements for the titled material contain any errors above and beyond those associated with the measurement process. We must attribute the difference between our results and those published previously to the fact that the two studies might possibly represent different mixtures of isomers. We know that the composition of the isomeric mixture is temperature dependent. Two samples distilled and collected

at different temperatures will have slightly different compositions. For example, our calculated slope in the vapor pressure equation corresponds to a value of 1935.7 when phrased in terms of logarithms to the base 10, a deviation of 390 parts in 2306 or 17% from the previously reported value of 2306. This deviation is well outside of our experimental error.

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Registry No. 1-Nitropropene, 3156-70-5.

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Virial Coefficients of Ethanol from 373.07 to 473.15 K

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Pressure, volume, and temperature were measured for the ethanol system at temperatures of 373.07, 388.17, 398.15, 400.81, 423.15, 448.15, and 473.15 K. The apparatus was a Kay-type PVT tube, in which the sample was compressed by a mercury piston. From the PVT data, second virial coefficients were computed. The apparatus and the calculational procedure were checked with both toluene and tetramethylsilane systems in order to verify the results reported herein. Our second virial coefficients and those from the literature were compared with predictions from the Tsonopoulos correlation. In the course of this investigation, the critical point of ethanol was checked, as well as the normal boiling point.

Introduction

Ethanol is an interesting compound as part of a binary system because of its high acentric factor, 0.644 (1), and the many nonideal systems formed (2). This investigation was undertaken in the hopes of preparing mixtures of ethanol with various members of the dimethylsiloxane series for measurements of mixture second virial coefficients. However, our apparatus was found to be unsuitable because of the difficulty of loading a mixture of known composition into our cell with a vacuum line where the molecular weight of one or both of the compounds is small and the compound is a liquid at room temperature. Therefore, this effort was abandoned, and this note reports the ethanol data obtained.

Dymond and Smith (3) present very few data for the second virial coefficients of ethanol, as compared to other compounds. There have been only three previous investigations (4-6), and their data range from 313.15 to 399.4 K. As usual, there is much scatter; in the neighborhood of 333 K, values reported are -1.285 (5), -1.522 (6), and -1.988 (4) m³ kmol⁻¹.

Experimental Section

Materials. Ethanol was obtained as absolute 200 proof spectrometric grade from AAPER Alcohol and Chemical Co., Louisville, KY 40214. It was dried over activated silica gel.

Apparatus. Our PVT apparatus was developed by Kay (7) and has been reported upon in a recent series of papers (8, 9). Briefly, a sample of pure ethanol was loaded from a vacuum line into the experimental tube, which is composed of two precision-bore glass tubes of differing diameters. The volume of this tube was determined by mercury weighings. The ethanol sample was confined by mercury in the experimental tube, which was attached via a compressor block to a pressure measuring system. The tube temperature was maintained constant by condensing vapors inside a vapor jacket; the temperature was measured by a thermocouple. Details of the experimental procedure, the calculational procedure, and the apparatus are well documented in the literature, and the interested reader is referred to the most recent references (10, 11).

Results and Discussion

This section discusses in turn the measurements of the normal boiling point of ethanol, critical point, and the PV iso-

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