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Density of Deuterated Isobutyric Acid between 11 and 30 °C

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The density of 94%-deuterated isobutyric acid has been measured between 11 and 30 °C with an uncertainty of 3 × 10^{-5} g/cm³. The density as a function of temperature can be represented by the equation d_{94} (g/cm²) = 1.060866 − 0.001117t + 1.4 × $10^{-7}t^2$, where the temperature, t, is in degrees Celsius. The density of fully deuterated isobutyric acid is calculated to be d_{100} (g/cm³) = d_{94} + 0.0056 (±0.003).

I. Introduction

The density of 94%-deuterated isobutyric acid has been measured between 11 and 30 °C by means of a magnetic suspension densimeter with a calibration accuracy of 3 × 10^{-5} g/cm³ and a precision of 5 × 10^{-6}. There have been no previous reports of the density of deuterated isobutyric acid.

II. Experimental Methods

A. Sample Material. Isobutyric acid in which the hydrogen atoms (paraffinic as well as acidic) had been replaced by deuterium atoms was obtained from Merck, Sharp, and Dohme Canada, Ltd. The material was specified to be 98% deuterated, but mass spectrometric analysis indicated a deuteration of 94.1% ± 0.3%. The material was handled in a dry nitrogen atmosphere.

Table I. Density of 94%-Deuterated Isobutyric Acid as a Function of Temperature

temp, °C	density, g/cm³	temp, °C	density, g/cm³
11.393	1.048 160	25.792	1.032 159
16.918	1.042 010	30.077	1.027 400
21.472	1.036 943	30.459	1.026 972

B. Temperature Control and Measurement. The temperature of the sample was controlled to 0.001 °C by circulating water. The temperature was measured by a quartz thermometer which had been calibrated with respect to a platinum resistance thermometer on the International Practical Temperature Scale of 1968. Temperatures are thus accurate to 0.002 °C.

C. Density Measurement. The density of the deuterated isobutyric acid was measured by means of a magnetic suspension densimeter (*1*, *2*). In this instrument, a small quartz buoy containing a magnet is levitated in the sample by means of a solenoid and a feedback system. The square of the solenoid current required to support the buoy in the liquid sample is linearly related to the fluid density. The instrument was calibrated by suspending the buoy in liquids of known density. In this case, solutions of sucrose in water were used (*3*). The calibration had an uncertainty of 3 × 10^{-5} g/cm³, which would usually determine the accuracy of the measurements. For deuterated isobutyric acid, however, the lower limit on the accuracy was determined by the uncertainty in the extent of

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deuteration, as discussed below.

III. Results

Table I shows the measurements of density as a function of temperature. The following function describes the density of the 94.1%-deuterated isobutyric acid within a standard deviation of 5×10^{-6} g/cm^3

$$d_{94}\ (g/cm^3) = 1.060866 - 0.001117t + 1.4 \times 10^{-7}t^2$$

where the temperature t is in degrees Celsius.

By comparison with the density of hydrogenated, as opposed to deuterated, isobutyric acid (*4*, *5*), the density of fully deuterated isobutyric acid is calculated to be

$$d_{100}\ (g/cm^3) = d_{94} + 0.0056\ (\pm 0.003)$$

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Vapor Pressure of 2,4-Hexadiyne: Solid (0–21 °C) and Liquid (91–135 °C)

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2,4-Hexadiyne (or dimethyldiacetylene, DMDA) was purified by room temperature sublimation (x = 0.9985) and its vapor pressure measured at several temperatures in the solid and liquid ranges. For the solid between 0 and 21 °C, the Antoine equation, log (p/Torr) = 10.34167 − 2706.727/(t + 255.444), reproduces the data with an average fractional deviation of 4.2×10^{-4}; for the liquid between 91 and 135 °C, log (p/Torr) = 7.05185 − 1416.427/(t + 210.006), with an average fractional deviation of 4.7×10^{-4}. Cox equation constants are also given for the liquid data. The index of refraction of DMDA was compared with that of naphthalene at a temperature near 87 °C.

Introduction

Dimethyldiacetylene, DMDA, is an unusual substance, being an isomer of benzene, yet melting 60 deg higher, and boiling 50 deg higher. Its uncommon cohesion is surely a result of its geometry; apparently its structure allows for more efficient intermolecular attraction among neighbors. In spite of its fundamental interest as a model rodlike molecule, many of its physical properties remain unmeasured; this paper provides vapor pressure measurement in limited temperature ranges for both the solid and liquid phases, with an average precision of 0.04%.

Experimental Section

DMDA was purchased from Farchand Division, Chemsampco, Inc., and subjected to room temperature sublimation at a pressure of approximately 300 Torr, onto an ice-water cold finger. This procedure produced a satisfactory purity and recovered 85% of the starting material. It was found that slight yellowing of the white, needlelike crystals occurs upon standing in the dark for several weeks in the presence of air; measurements were always made on freshly prepared samples.

An estimate of the purity of the sublimed material was obtained by sealing a sample into a triple-point cell and measuring its cooling curve. The sample was melted in order to place it into the cell, and noticeable yellowing occurred in the process. In spite of this, repeat cooling curves provided consistent estimates of mole fraction impurity of 0.0015. It is believed that the starting material used for the vapor pressure measurements was at least as pure as that used in the cooling curve analysis.

Vapor pressure measurements on the solid (repeated after sequential degassings until reproducibility was obtained) were obtained with a Baratron capacitance manometer equipped with a 100-Torr head. No attempt was made to calibrate the head; a certificate of calibration was provided by the manufacturer, and it is likely that its accuracy exceeded the precision in the pressures reported herein. The temperature of the solid–vapor equilibrium was measured with a MINCO platinum resistance thermometer (PRT) calibrated against a Leeds and Northrup certified PRT. It is believed to be accurate to better than 0.01 °C. No evidence of decomposition was observed during these measurements. Those on the liquid were obtained by comparative ebulliometry with modified Ambrose boilers, as previously described (*1*, *2*). The temperature of the liquid–vapor equilibrium of DMDA was measured with a PRT calibrated and certified by Leeds and Northrup; that of the water was measured by the same kind of PRT, but calibrated against the first in our laboratory. A thermostated G-2 Mueller bridge was used to measure the resistance of the PRT's used in this study. The Chebyshev polynomial published by Ambrose and Sprake (*3*) was used to calculate the vapor pressure of water from its boiling temperature.

Because some decomposition was anticipated, two sets of measurements were made on sequential days, each one starting at about 90 °C and proceeding upward to about 130 °C, on the same sample. A pattern in the errors would indicate decomposition with time.

Refractive index measurements were made on an Abbe refractometer whose stage was fitted to accept circulating thermostat fluid. The thermometer attached to the stage read 87 °C, but it appeared likely that the surfaces of the prisms

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