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

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

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

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

Literature Cited

(1) Greer, S. C.; Moldover, M. R.; Hocken, R. *Rev. Sci. Instrum.* **1974**, *45*, 1462–1463.
(2) Greer, S. C. *Phys. Rev. A* **1976**, *14*, 1770–1780.
(3) Zunder, K.; Seiler, W.; Bunnagel, R. *Zucker* **1974**, *27*, 642–647.
(4) Khosla, M. P.; Widom, B. *J. Colloid Interface Sci.* **1980**, *76*, 375–392.
(5) Woermann, D.; Sarholz, W. *Ber. Bunsenges. Phys. Chem.* **1965**, *69*, 319–326.

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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, $\log(p/\text{Torr}) = 10.34167 - 2706.727/(t + 255.444)$, reproduces the data with an average fractional deviation of 4.2×10^{-4}; for the liquid between 91 and 135 °C, $\log(p/\text{Torr}) = 7.05185 - 1416.427/(t + 210.006)$, 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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Table I. Vapor Pressure of Solid 2,4-Hexadiyne[a]

t/°C	p/Torr	t/°C	p/Torr
0.00	0.5566	16.24	2.392
8.45	1.215	21.22	3.617
13.04	1.822		

[a] Antoine equation: $\log(p/\text{Torr}) = 10.34167 - 2706.727/(255.444 + t)$.

Table II. Vapor Pressure of Liquid 2,4-Hexadiyne[a]

t/°C	p/Torr	t_{water}/°C	t/°C	p/Torr	t_{water}/°C
91.991	229.98	69.615	103.832	344.93	79.267
98.925	293.52	75.350	112.047	450.86	85.995
107.526	390.17	82.327	116.678	520.55	89.729
119.026	559.37	91.631	121.785	607.09	93.824
124.557	658.92	96.049	129.032	749.03	99.593
130.706	785.82	100.939	135.444	895.34	104.658
95.303	259.03	72.384			

[a] Antoine equation: $\log(p/\text{Torr}) = 7.051846 - 1416.427/(210.006 + t)$. Cox equation: $\log(p/\text{atm}) = A'(1 - 402.688/T)$, where $\log A' = 0.830531 - 4.61921 \times 10^{-4}\,T + 3.07146 \times 10^{-7}T^2$.

were somewhat lower in temperature. Because of this uncertainty, we also measured the index of refraction of a very pure sample of naphthalene, obtained from Ambrose of NPL for use as a vapor pressure standard, under identical conditions.

Results

Results of the vapor pressure measurements are presented in Tables I and II, along with constants of appropriate correlating functions. There is definite curvature in ln p with $1/T$ for the solid, in spite of the narrow range of temperatures studied.

Data for the liquid include the temperature of the boiling water in equilibrium under the same helium pressure as the sample. The points are numbered chronologically, the first six measured on one day, and the last eight on the next. The sample was allowed to cool to room temperature overnight. Yellowing of the sample occurred on both days, and there is a trend in the deviations of the observed pressures from those produced by the correlating equations. It appears that a slight lowering of the pressure occurred over time, with the first day's data generally higher than, and the second day's lower than, the calculated values. No attempt was made to take this trend into account in the present work. The eighth point, being more than 3.5 standard deviations from its calculated value, was omitted in fitting equations to the data.

The indices of refraction of DMDA and naphthalene at a temperature near 87 °C are, respectively, 1.4760 and 1.5924.

Discussion

Cleveland et al. (*4*) report 129.51 ± 0.03 °C as the boiling point of DMDA, compared with the presently observed value, 129.54 °C. If the pressure were indeed dropping slightly with time, our value would be expected to be somewhat high.

The enthalpy of sublimation at 25 °C, under the assumption of vapor ideality, is 14.00 kcal/mol; extrapolation of the Cox equation under the same assumption provides 10.15 kcal/mol as the enthalpy of vaporization at 25 °C. Thus, the enthalpy of fusion would be 3.85 kcal/mol. Cleveland et al. (*4*) state that when heptane was used to depress the freezing point of DMDA, the lowering corresponded to 0.60 ± 0.03 °C/mol % impurity. Using the present value for enthalpy of fusion, and a melting point of 338.2 K, we calculate a freezing point depression constant of 0.590 °C/mol % impurity, in good agreement with the experimentally determined value.

The rodlike structure of DMDA might lead one to expect an elevated value for its Trouton's Rule constant; it is 22.63 cal/(mol K). This is a real effect, and is evidence for some degree of ordering in the liquid.

The triple point of the sample of DMDA used in the cooling curve analysis ($x = 0.9985$) was 64.87 °C; that of an absolutely pure sample would be 64.96 by this analysis, following Rossini (*5*). Cleveland and co-workers (*4*) report an "ultimate freezing point" of 65.08 °C; the difference (0.12 °C) is a real one, but may be partially accounted for by the effect of reduced pressure in lowering the triple point relative to the freezing point.

If we equate the expressions for solid and liquid vapor pressures we obtain the value 66.1 °C for the triple point. When the extent of extrapolation is considered, this is surprisingly close to the correct value. The vapor pressure at 64.96 °C calculated from the Cox equation is 79.9 Torr.

Registry No. DMDA, 2809-69-0.

Literature Cited

(1) Ambrose, D. *J. Sci. Instrum.* **1968**, 41.
(2) Meyer, E. F.; Hotz, R. D. *J. Chem. Eng. Data* **1973**, *18*, 359.
(3) Ambrose, D.; Sprake, C. H. S. *J. Chem. Thermodyn.* **1972**, 603.
(4) Cleveland, F. F.; Greenlee, K. W.; Bell, E. L. *J. Chem. Phys.* **1950**, *18*, 355.
(5) Rossini, F. D. *Chemical Thermodynamics*; Wiley: New York, 1950; pp 454–8.

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FTIR Measurements of Solubilities of Anthracene in Supercritical CO_2

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The solubility of anthracene in carbon dioxide was measured at temperatures from 20 to 95 °C and at pressures up to 1200 bar. Anthracene concentrations were determined from the absorption in the IR region of anthracene C–H stretching vibrations. The results are compared with known literature data on solubilities of anthracene in CO_2. In addition, the observed frequency shift is discussed in terms of intermolecular interactions.

Introduction

During the past few years solvent extraction with supercritical fluids has become an important technological process. It has been used in decaffeinating coffee beans (*1*), regenerating activated carbon (*2*), deasphalting petroleum (*3*), separating organic chemicals from water (*4*), separating of a mixture of aromatic isomers (*5*), and in many other processes (*6*). In these extraction processes the effectiveness of the solvent is

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