Vapor Pressures and Densities of 2,3-Dimethyl-2-butene and 3,3-Dimethyl-1-butene

ARMEN BAGHDOYAN, JANA MALIK, and VOJTECH FRIED[1]
Brooklyn College of the City University of New York, Brooklyn, N.Y. 11210

The vapor pressures and densities of 2,3-dimethyl-2-butene and 3,3-dimethyl-1-butene were determined experimentally at different temperatures. The constants of the Antoine equation are: 6.93075, −1205.663, and 224.460 for 2,3-dimethyl-2-butene; and 6.75953, −1053.517, and 230.336 for 3,3-dimethyl-1-butene, respectively. The density equations are: $d^t = 0.70827 - 0.90023 \times 10^{-3}(t - 20) - 0.72335 \times 10^{-6}(t - 20)^2$ for 2,3-dimethyl-2-butene and $d^t = 0.65291 - 0.10064 \times 10^{-2}(t - 20) - 0.21039 \times 10^{-6}(t - 20)^2$ for 3,3-dimethyl-1-butene, respectively.

The literature dealing with the vapor pressures and densities of organic compounds is very extensive (*1, 2, 4, 6, 7*). However, not enough data are available for some of the olefinic hydrocarbons. Since the solution of a certain theoretical problem, statistical mechanics of solutions of isomers, required the knowledge of the vapor pressures and densities of 2,3-dimethyl-2-butene and 3,3-dimethyl-1-butene in a wide range of temperature, we have determined them experimentally.

EXPERIMENTAL

Aldrich chemicals of highest purity were used without further purification since gas chromatographic analysis failed to show any significant impurities. The small difference between the boiling point and condensation temperature, 0.002° C, at a pressure of 1 atm also indicated that the samples did not contain sufficient impurities of different volatility to have any significant effect on the vapor pressure measurements. Experimentally found densities (gram cc^{-1}) and boiling points (° C) were in good agreement with the literature values: 2,3-dimethyl-2-butene, d^{25} = 0.70375 (0.7034); t_{nbp} = 73.24 (73.21 − 73.24); 3,3-dimethyl-1-butene, d^{25} = 0.64787 (0.64786); t_{nbp} = 41.28 (41.24) (*1, 2, 6, 7*).

The vapor pressures were measured by a dynamic method using two ebulliometers connected in parallel to the pressure controlling system (*3*). One of the ebulliometers contained deionized and twice distilled water, and the other contained the substance under study. From the boiling point of water, the corresponding pressure in the system was determined (*6*), with an accuracy better than 0.1 mm Hg. The boiling points of water and the hydrocarbons respectively, were measured with a 25-ohm platinum resistance thermometer (Leeds and Northrup) in a Mueller bridge circuit (Leeds

[1] To whom correspondence should be addressed.

Table I. Densities of 2,3-Dimethyl-2-butene and 3,3-Dimethyl-1-butene at Different Temperatures

2,3-Dimethyl-2-butene			3,3-Dimethyl-1-butene		
Temp, ° C	d^t_{exp}, gram cc^{-1}	d^t_{calcd}, gram cc^{-1}	Temp, ° C	d^t_{exp}, gram cc^{-1}	d^t_{calcd}, gram cc^{-1}
20.00	0.7083	0.70827	20.00	0.6529	0.65291
25.00	0.7037	0.70375	25.00	0.6479	0.64787
30.00	0.6992	0.69919	30.00	0.6428	0.64282
40.00	0.6900	0.68997	40.00	0.6327	0.63270
50.00	0.6806	0.68061			

Table II. Vapor Pressures of 2,3-Dimethyl-2-butene and 3,3-Dimethyl-1-butene at Different Temperatures

2,3-Dimethyl-2-butene			3,3-Dimethyl-1-butene		
Temp, ° C	po_{exp}, mm Hg	po_{calcd}, mm Hg	Temp, ° C	po_{exp}, mm Hg	po_{calcd} mm. Hg
73.85	774.68	774.67	41.51	766.17	765.71
71.66	723.23	723.14	41.46	764.81	764.60
69.16	667.80	667.57	38.45	692.04	691.87
66.51	612.75	612.52	35.12	617.99	617.77
63.89	561.74	561.70	32.66	567.25	567.21
61.07	510.80	510.68	29.77	511.97	511.89
56.91	458.22	458.02	26.88	461.08	460.96
54.64	408.46	408.29	24.18	416.94	417.13
51.57	365.52	365.48	21.19	372.50	372.45
47.46	313.90	313.90	17.64	324.29	324.43
43.33	268.22	268.19	13.62	276.16	276.10
38.57	222.31	222.36	9.71	234.81	234.79
34.19	185.88	185.96	4.39	186.63	186.74
28.50	146.03	146.05	0.48	156.65	156.74
26.13	131.56	131.65	−4.14	126.43	126.49
21.87	108.65	108.70	−9.46	97.72	97.69
16.33	83.88	83.87			

Table III. The Constants of the Antoine Equation and of the Density Equation

Substance	Constants of the Antoine equation			Constants of the density equation		
	A	B	C	a	b	c
2,3-Dimethyl-2-butene	6.93075	−1205.663	224.460	0.70827	-0.90023×10^{-5}	-0.72335×10^{-6}
3,3-Dimethyl-1-butene	6.75953	−1053.517	230.336	0.65291	-0.10064×10^{-2}	-0.21039×10^{-5}

and Northrup) with an accuracy better than 0.01° C. The platinum resistance thermometer was calibrated by the National Bureau of Standards.

Single-stem pycnometers of about 10.0-cc capacity, calibrated with deionized, twice distilled water, were used for density measurements.

RESULTS AND DISCUSSION

The experimental data are given in Tables I and II. The vapor pressures and densities were fitted by least-squares method to an Antoine equation [$\log P = A + B/(t + C)$] and to an equation of the form $d^t = a + b(t - 20) + c(t - 20)^2$, respectively. The constants of these equations are seen in Table III.

As evident from Tables I and II, the data calculated from these equations are in excellent agreement with the experimentally found values. The maximum percent deviation and the standard deviation in the vapor pressures and densities are 0.06 ± 0.17 mm Hg and 0.007 ± 0.00003 gram cc^{-1} for 3,3-dimethyl-1-butene and 0.07 ± 0.12 mm Hg and 0.002 ± 0.00002 gram cc^{-1} for 2,3-dimethyl-2-butene, respectively.

The experimental results also agree very well with the excellent data measured by Camin and Rossini (*1*). However, the Antoine equations, as well as the density equation, given in this paper are applicable in a wider temperature range.

LITERATURE CITED

(1) Camin, D. L., Rossini, F. D., *J. Phys. Chem.*, **60**, 1446 (1956).
(2) Dreisbach, R. R., "Advanc. Chem. Ser.," 15, 22, 29, American Chemical Society, Washington, D. C., 1955, 1959, 1961.
(3) Hala, E., Pick, J., Fried, V., Vilim, O., "Vapor-Liquid Equilibrium," p 227, Pergamon, London, 1958.
(4) Jordan, T., "Vapor Pressure of Organic Compounds," Interscience, New York, 1954.
(5) Osborne, N. S., Stimson, H. F., Ginnings, D. C., *J. Res. Natl. Bur. Std.*, **23**, 261 (1939).
(6) "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Thermodynamics Research Center, Texas A and M University, College Station, Tex., 1966.
(7) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, N. Y. 1950.

RECEIVED for review July 13, 1970. Accepted October 27, 1970. This investigation was supported in part by Undergraduate Science Education Program Grants GY-7540, National Science Foundation.