Vapor Pressure Relations for the Seven Pentadienes

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Experimental values of vapor pressure for the seven isomeric pentadienes were measured in the range 2 to 25 mm. of Hg by means of the inclined-piston deadweight gage. For 3-methyl-1,2-butadiene, additional measurements were made by comparative ebulliometry over the range 150 to 906 mm. of Hg. Correlations of the present results with selected literature values are given in terms of Cox equations.

THERMODYNAMIC studies of hydrocarbons which are in or are related to petroleum are in progress at the Bureau of Mines Bartlesville Petroleum Research Center as part of American Petroleum Institute Research Project 62. This paper summarizes the experimental measurements of vapor pressure that were determined for pentadienes and correlates these results with previous measurements reported by Forziati, Camin, and Rossini (*4*).

MATERIAL

The samples were API research grade, purified and made available by the American Petroleum Institute Research Project 58B at Carnegie-Mellon University. Purities of the compounds were determined from freezing temperatures *vs.* fraction melted data obtained during low-temperature calorimetric measurements conducted by the Petroleum Thermodynamics Group, Bureau of Mines Bartlesville Petroleum Research Center.

EXPERIMENTAL METHODS

Static Measurements. An inclined-piston manometer, described by Douslin and McCullough (*2*) and Douslin and Osborn (*3*), was used for low-pressure measurements below room temperature. Briefly, the method consists of balancing the known weight, W, of a free piston declined from the horizontal by a measured angle, θ, against the pressure exerted by the vapor of the sample placed in a thermostated bath. From the acceleration of gravity, and the weight, area, and angle of declination of the piston, the vapor pressure was calculated directly as a primary quantity.

$$P_{\text{mm. of Hg}} = (g/g_{\text{std}})(W \sin \theta)/A \qquad (1)$$

Corrections were applied, when significant, for the vapor head between piston face and the surface of the liquid.

Ebulliometric Measurements. The comparative ebulliometric method described by Waddington *et al.* (*10*) and more recently by Osborn and Douslin (*7*) was used only for 3-methyl-1,2-butadiene in the range 149 to 906 mm. of Hg. In this method the boiling temperature of the sample is compared directly with the boiling temperature of standard water under the same pressure of a helium gas blanket. Pressure is then determined by reference to the International Steam Tables (*6, 8*). Temperatures were measured with a precision of 0.001° on the International Temperature Scale [T, °K. = t, °C. (Int., 1948) + 273.15] (*9*) by using a 25-ohm platinum resistance thermometer that had been calibrated by the National Bureau of Standards and checked at the triple-point temperature of a certified benzoic acid cell.

RESULTS

Observed values of the vapor pressure in the low-temperature, low-pressure ranges, as shown in Table I, made with the inclined-piston manometer, complement the results of Forziati, Camin, and Rossini (*4*) which are nearly all above room temperature. For 3-methyl-1,2-butadiene,

Table I. Experimental Vapor Pressures of Pentadienes by Inclined-Piston Manometer

	Pressure, Mm. of Hg						
t, °C.	1,2-Pentadiene	1, *cis*-3-Pentadiene	1, *trans*-3-Pentadiene	1,4-Pentadiene	2,3-Pentadiene	3-Methyl-1,2-butadiene	2-Methyl-1,3-butadiene
−60.010	2.442	2.623	3.134	8.036	1.847	3.151	. . .
−57.598	3.008	3.234	3.833	9.684	2.292	3.841	6.322
−55.186	3.683	3.951	4.660	11.623	2.819	4.688	7.627
−52.770	4.487	4.792	5.642	13.887	3.449	5.680	9.160
−50.351	5.440	5.808	6.807	16.508	4.208	6.856	10.951
−47.930	6.574	7.006	8.169	19.540	5.098	8.237	13.039
−45.507	7.897	8.393	9.757	23.043	6.159	9.861	15.453
−43.083	9.440	10.013	11.614	27.083	7.402	11.749	18.248
−40.656	11.230	11.912	13.763	. . .	8.869	13.951	21.452
−38.227	13.311	14.104	16.246	. . .	10.563	16.481	25.119
−35.797	15.701	16.627	19.096	. . .	12.539	19.401	. . .
−33.364	18.474	19.515	22.364	. . .	14.829	22.756	. . .
−30.929	21.641	22.844	26.092	. . .	17.459	26.581	. . .
−28.493	25.258	. . .	. . .	. . .	20.486	. . .	. . .
−26.054	. . .	. . .	. . .	. . .	23.949	. . .	. . .

Table II. Experimental Vapor Pressures of 3-Methyl-1,2-butadiene

(Ebulliometric results)

t, °C.	Pressure, Mm. Hg	t, °C.	Pressure, Mm. Hg
+0.578	149.41	25.454	433.56
5.479	187.57	30.543	525.86
10.416	233.72	35.671	633.99
15.391	289.13	40.837	760.00
20.404	355.22	46.042	906.06

Table III. Sample Purity and Constants of Cox Vapor Pressure Equation

Compound	Purity, Mole %	ϕ^a	a_0	a_1	a_2	a_3	a_4
1,2-Pentadiene	99.92 ± 0.04	318.006	2.938157	-3.430984×10^{-2}	1.998474×10^{-4}	-5.217635×10^{-7}	5.100650×10^{-10}
1, *cis*-3-Pentadiene	99.91 ± 0.04	317.218	2.152901	-2.164099×10^{-2}	1.233365×10^{-4}	-3.174349×10^{-7}	3.066138×10^{-10}
1,*trans*-3-Pentadiene	99.90 ± 0.02	315.182	0.821528	-7.73513×10^{-4}	8.95173×10^{-7}	...	...
1,4-Pentadiene	99.98 ± 0.01	299.117	0.812446	-7.52279×10^{-4}	8.34048×10^{-7}	...	...
2,3-Pentadiene	99.88 ± 0.02	321.415	0.840659	-7.95992×10^{-4}	8.89607×10^{-7}	...	...
3-Methyl-1,2-butadiene	99.98 ± 0.005	313.987	0.830404	-8.01748×10^{-4}	9.42462×10^{-7}	...	...
2–Methyl-1,3-butadiene	99.83 ± 0.08	307.217	0.820543	-8.31178×10^{-4}	10.32622×10^{-7}	...	...

[a] ϕ Normal boiling point in °K.

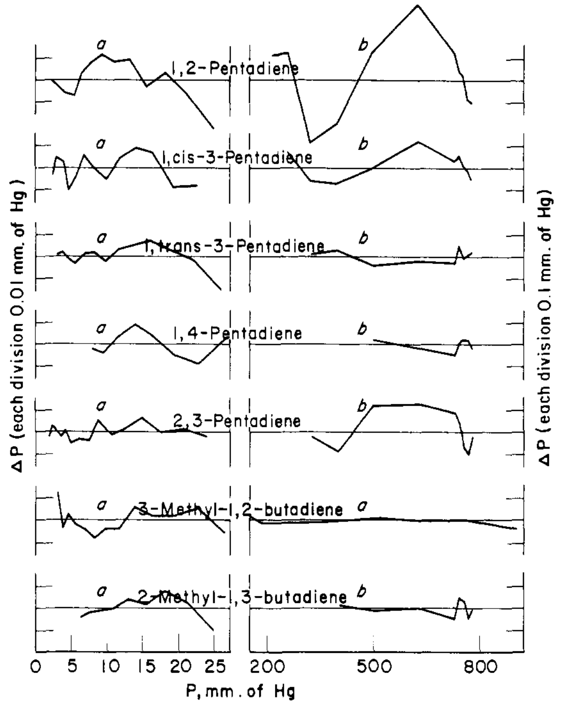

Figure 1. Deviations of experimental points from Cox equations, Table III

a. Present results

b. Forziati, Camin, and Rossini (*4*)

vapor pressures were also measured in the comparative ebulliometric range (Table II), because this compound was not included in the work by Forziati *et al.* The combined data were correlated with the Cox (*1*) equation

$$\log P\ (\text{atm.}) = A\ (1 - \phi/T) \qquad (2)$$

where

$$\log A = \sum_{i=0}^{m} a_i T^i\ (m = 2 \text{ or } 4)$$

in which the derived parameters ϕ and a_i are summarized, as shown in Table III. Equation 2, in the form

$$\log \frac{\log P}{1 - \phi/T} = \sum_{i=0}^{m} a_i T^i \qquad (3)$$

was fitted to the experimental points with assigned weighting factors $[P_i \ln P_i/\sigma_i]^2$. For the present series the estimated uncertainty, σ_i, in the measured pressure was made proportional to pressure according to the relation $\sigma_i = 1 \times 10^{-6} + 2 \times 10^{-5} P_i$ (atm.).

Because of the large pressure range of the combined data, the exactness of the Cox correlations cannot be interpreted meaningfully by values of the standard deviations. Instead, a deviation plot (Figure 1) with the abscissa sectioned into two major pressure ranges was used. Each range has a separately scaled ordinate for observed minus calculated pressures which show percentage deviations of about the same order of magnitude. This behavior of the values obtained from the Cox equations suggests that the equations are also valid in the intermediate pressure range between 25 and 250 mm. of Hg, and possibly as far as one-half unit on the logarithmic pressure scale beyond the upper and lower limits of the experimental ranges. Very few data, other than those of Forziati *et al.* (*4*), are available for comparison with present results. For 1,4-pentadiene, the values reported by Lamb and Roper (*5*) from 1.60 to 572.7 mm. of Hg were compared with values obtained with the Cox equation and found to be higher over the entire range. The percentage differences varied from 2.5 at the lowest pressure to 0.5 at the highest pressure, with somewhat smaller values at intermediate pressures.

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RECEIVED for review November 25, 1968. Accepted December 26, 1968. Contribution 160, Thermodynamics Laboratory, Bartlesville Petroleum Research Center, Bureau of Mines, U.S. Department of the Interior, Bartlesville, Okla. 74003. Support provided equally by the American Petroleum Institute Research Project 62 and the Bartlesville Petroleum Research Center, Bureau of Mines, U.S. Department of the Interior, Bartlesville, Okla.