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Physical Properties of a Refrigerant Mixture of Monofluoromonochloromethane and Tetrafluorodichloroethane

JOSEPH V. SINKA
Specialty Chemicals Division, Allied Chemical Corp., Morristown, N. J. 07960

The physical properties presented describe the mixture of 55.1 wt. % monofluoromonochloromethane and tetrafluorodichloroethane, forming a minimum-boiling azeotrope at 291.2° K. The pressure-volume-temperature properties have been measured and correlated with the Martin-Hou equation of state. The vapor pressure and liquid densities were fitted to equations and the critical properties obtained.

THE MATERIALS, monofluoromonochloromethane (Refrigerant 31) and tetrafluorodichloroethane (Refrigerant 114), were obtained from commercial sources and purified by fractional distillation. The purity of each component, as determined by gas chromatography, was 99.9 mole % or better. The precautions in handling the mixture were described in a previous publication (*4*).

As previously (*4*), the term vapor pressure will be used to describe the pressure exerted by a vapor when a state of equilibrium has been reached between a liquid and its vapor. Obviously, this term is used in the general sense here, since the composition of the vapor and liquid are not exactly the same, except at the azeotropic state. However, every effort that was practical was taken to minimize the vapor space above the mixture and to obtain data at the bubble point.

The apparatus and techniques employed were discussed in detail in earlier papers (*1, 3, 4*). However, a few brief remarks are made.

The pressure-volume measurements were obtained on a constant-volume cell constructed of a 300-cc. high-pressure stainless steel cylinder. The sample was confined in the cell with a 5-cm. stainless steel diaphragm. The volume change due to the displacement of the diaphragm from the null point was negligible. Nitrogen was used as the pressure transfer media and the pressure was read on calibrated Heise gages, connected to the system, covering various ranges.

The critical temperature was determined by observation of the meniscus in a sealed glass tube, which was slowly heated and cooled in a stirred liquid bath. The average value of several observations was 415.2° ± 0.1° K.

Extrapolation of the near-critical isochor to the critical temperature determined the critical pressure. This gave a value of 749 ± 1 p.s.i.a.

The critical density was determined by a standard rectilinear diameter plot, using the liquid densities calculated from the liquid density equation and saturated vapor densities calculated from the equation of state. The value determined was 0.539 ± 0.001 gram per cc.

The temperature was measured with a platinum resistance thermometer calibrated by the U. S. National Bureau of Standards (° C. Int., 1948). The volume was determined by calibration with water and corrected for thermal expansion, using the coefficient of thermal expansion for stainless steel.

The liquid densities were determined by a float technique. The calibrated glass floats were corrected for thermal expansion and found accurate to 0.1% over the range covered. The floats were found incompressible in the given pressure range by checking their accuracies in known liquids.

The uncertainties in the input variables were determined during the calibration procedures to be 0.1% for volume, 0.01% for temperature, 0.2% for pressure, and 0.03% for weight of sample during repeated runs.

DATA

Tables I to III contain vapor pressure, liquid density, pressure-volume-temperature data, and correlating equations. The underlined digits are kept for consistency and may be omitted for hand calculations.

Table I. Vapor Pressure

$$\text{Log } P = A + B/T + CT + DT^2$$

where: P = p.s.i.a.
T = T° K.
A = $8.31265\underline{6}$
B = -0.147347×10^4
C = -0.771637×10^{-2}
D = 0.761974×10^{-5}

T°, K.	Pressure Obsd.	Pressure Calcd.	% Dev.
260.85	14.696	14.7764	−0.54
273.16	24.105	23.9460	0.65
291.00	45.162	44.5612	1.33
303.35	64.3	65.42	−1.74
323.18	113.0	113.61	−0.54
343.22	186.4	185.68	0.38
363.20	288.5	287.28	0.42
373.14	352.0	351.10	0.25
393.16	511.1	511.60	−0.09
403.16	609.9	610.10	−0.03
413.16	721.5	722.61	−0.15

Normal boiling point, calcd. = 260.71° K.

Standard deviation = 0.37 p.s.i.a.
Average per cent deviation = 0.56

Table II. Liquid Density

$$D = D_o + \sum_{i=1}^{i=4} A_i \left[(1 - T/T_c)^{1/3}\right]^i$$

where: D = gram per cc.
T = t° K.
T_c = 415.22° K.
D_o = 0.5391
A_1 = $0.56927\underline{2}$
A_2 = $0.14890\underline{2} \times 10^1$
A_3 = $-0.16483\underline{3} \times 10^1$
A_4 = $0.98890\underline{2}$

T°, K.	Density Obsd.	Density Calcd.	% Dev.
205.02	1.503	1.5032	−0.01
248.16	1.402	1.4014	0.03
287.43	1.300	1.3004	−0.03
322.32	1.199	1.1990	−0.00
351.50	1.099	1.0990	−0.00
375.22	0.998	0.9979	0.01
404.92	0.798	0.7980	−0.00

Standard deviation = 0.25×10^{-3}
Average per cent deviation = 0.015

Table III. Equation of State

$$P = \frac{RT}{V - b} + \frac{A_2 + B_2T + C_2e^{-KT/Tc}}{(V - b)^2} + \frac{A_3 + B_3T + C_3e^{-KT/Tc}}{(V - b)^3} + \frac{A_4}{(V - b)^4} + \frac{A_5 + B_5T + C_5e^{-KT/Tc}}{(V - b)^5}$$

The equation parameters are:

P = p.s.i.a.
V = cc. per gram
T = t° C. + 273.16
R = 0.1287070×10^2 cc., p.s.i.a./° K., gram
b = 0.3777405 cc. per gram
K = 0.5475×10^1
T_c = 415.22
A_2 = -0.2351595×10^5
B_2 = 0.2302919×10^2
C_2 = -0.3169159×10^6
A_3 = 0.3111256×10^5
B_3 = -0.2750807×10^2
C_3 = 0.5292572×10^6
A_4 = -0.1575132×10^5
A_5 = -0.3253440×10^4
B_5 = 0.2012582×10^2
C_5 = -0.1332969×10^6

Observed Data			Calculated Data	
Volume	Temperature	Pressure	Pressure	% deviation
18.9988	373.17	212.5	211.92	0.27
19.0397	413.18	245.0	244.10	0.36
19.0806	453.16	276.6	275.08	0.54
19.1165	488.25	304.0	301.65	0.77
19.1510	522.06	329.9	326.87	0.91
9.8407	393.16	380.0	378.94	0.27
9.8513	413.16	415.2	414.11	0.26
9.8619	433.16	449.5	448.31	0.26
9.8778	463.16	499.1	498.23	0.17
9.8936	493.16	548.0	546.94	0.19
9.9090	522.14	596.3	593.16	0.52
6.3068	403.17	521.0	522.44	−0.27
6.3170	433.16	613.8	613.11	0.11
6.3272	463.16	700.7	700.04	0.09
6.3373	493.16	784.0	784.36	−0.04
6.3472	522.16	864.3	864.07	0.02
4.9200	423.16	666.5	668.17	−0.25
4.9266	448.08	768.8	769.27	−0.06
4.9332	473.16	868.3	867.76	0.06
4.9450	517.96	1036.9	1038.05	−0.11
3.2305	423.16	780.0	782.20	−0.28
3.2323	433.16	854.5	852.52	0.23
3.2340	443.16	922.1	921.79	0.03
3.2375	463.16	1054.6	1057.59	−0.28
2.5049	423.16	821.2	823.21	−0.24
2.5063	433.16	919.6	918.97	0.06
2.5076	443.16	1014.6	1013.57	0.10
2.5084	449.16	1070.1	1069.82	0.02
1.9704	415.22	750.4	749.36	0.13
1.9708	418.16	787.0	786.66	0.04
1.9718	428.16	911.6	913.14	−0.16
1.9729	438.16	1041.6	1039.03	0.24
1.7917	418.16	793.2	791.05	0.27
1.7960	428.16	929.8	932.45	−0.28
1.7969	438.16	1074.3	1074.06	0.02

Standard error = 0.18
Average per cent deviation = 0.23

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Pressure-Volume-Temperature Relationship for a Mixture of Monochlorotrifluoromethane and Trifluoromethane

The pressure-volume-temperature properties of a 50-50 mole % mixture of monochlorotrifluoromethane and trifluoromethane in the ranges of 14.7 to 74.8 atm., 1.6 to 19.1 cc. per gram, and 298° to 492° K. were correlated, using the Martin-Hou equation of state. Vapor pressures and saturated liquid densities were determined to near the critical temperature (292.6° K.) from 203° and 229.8° K., respectively.

JOSEPH V. SINKA, ELI ROSENTHAL, and RONALD P. DIXON
Specialty Chemicals Division, Buffalo Research Laboratory, Allied Chemical Corp., Buffalo, N. Y.

IN A PROGRAM to supply accurate and reliable data on refrigerants, the authors measured the pressure-volume-temperature properties, vapor pressure, and liquid densities of Refrigerant 503. This refrigerant (*1*), which has a composition of 50-50 mole % trifluoromethane and monochlorotrifluoromethane, forms a minimum-boiling azeotrope at −87.85° C., 1 atm. No published equations correlating the above properties are presently available.

EXPERIMENTAL

Sample Preparation. Each component of the mixture was purified to 99.9 mole % or better, as indicated by gas chromatographic analysis. The bulk mixture being above the critical temperature at 23° C., no segregation problems were encountered upon sampling.

Due to the low freezing point of the mixture, special precautions were taken in degassing the sample to avoid pumping off any refrigerant. During the vapor pressure measurements, the degassing cycles were repeated until reproducible pressure readings were observed.

Temperature Measurements. All temperature measurements were made by a calibrated platinum resistance thermometer (degrees Centigrade, Int. 1948) whose resistance was measured by a Leeds and Northrup Speedomax high-precision resistance recording bridge. Periodically, the accuracy of the recorder was checked with the ice point resistance of the thermometer. The absolute temperature scale is defined as 0° C. = 273.15° K.

Pressure Measurements. All pressure measurements were taken with the *PVT* apparatus described in an earlier paper (*5*).

Vapor Pressure. The term vapor pressure is used here in the general sense, since the composition of the azeotrope does not remain invariant with changes in temperature (*5*). However, accurate vapor pressure data of this mixture can be obtained by taking measurements at the bubble point.

For the vapor pressure measurements, the sample cell was filled to a point which enabled measurement of several data points at close to the bubble point pressure. The data covered the temperature range from 203° to 283° K. (Table I) and is represented by the following equation.

$$\mathrm{Log}_{10}P_{(\mathrm{atm})} = A + B/T + CT + DT^2 \qquad (1)$$

where T is ° K. = 273.15 + t° C.

The constants for Equation 1 are shown in Table I.

This equation has a standard per cent deviation of 0.10 for the experimental data. Extra significant figures have been kept for consistency in computation.

Liquid Density. The saturated liquid densities were determined by a float technique which has been described in detail in an earlier paper (*5*). The data covered the temperature range from 229.8° to 284.2° K.

The equation used to correlate the saturated liquid densities was that of Martin and Hou (*3*).

$$d = d_0 + \sum_{i=1}^{4} A_i\left[\left(1 - \frac{T}{T_c}\right)^{1/3}\right]^i \qquad (2)$$

The constants for Equation 2 and the experimental data are shown in Table II.

***PVT* Measurements.** The range which was covered by the *PVT* data (Table III) is from 298° to 492° K., 1.6 to 19.1 cc. per gram, 14.7 to 75.0 atm. The data, consisting of eight isochors, were fitted with a Martin-Hou equation