28

Physical Property Data on Fluorinated Propanes and Butanes as CFC and HCFC Alternatives

Adolph L. Beyerlein, Darryl D. DesMarteau, and Sun Hee Hwang
Department of Chemistry, Clemson University,
Clemson, South Carolina 29634-1905,

N. Dean Smith,
Industrial Processes Branch (MD-62B),
EPA Air and Energy Engineering Research Laboratory,
Research Triangle Park, North Carolina 27711

Powell Joyner,
EPRI,
3412 Hillview Avenue
Palo Alto, California 94303

I. Introduction

The authors are investigating fluorinated propane derivatives as second generation alternatives for currently used CFC and HCFC chemicals. One fluorinated ether was also studied. These investigations have included both (i) synthesis and (ii) the measurement and estimation of their physical properties. In this paper we will describe only the results of the physical property investigations. A total of 22 compounds were investigated with boiling points ranging from -34.6°C to 76.7°C. The measured properties presented for these compounds include: melting point, boiling point, vapor pressure below the boiling point, heat of vaporization, critical properties (temperature, density and pressure), liquid densities, and liquid phase heat capacities. Measured vapor pressures are reported from below the boiling point up to the critical point for two of these compounds; E-125a (b.p.=-34.6°C and T_c= 80.7°C), and HFC-236ea (b.p.=6.5°C and T_c=141.1°C). For the readers convenience the chemical formula that corresponds to the ASHRAE number code is provided in Table 1A of the Appendix to this paper. Vapor pressures and liquid phase densities were also measured for CFC-12 in order to judge the accuracy of our experimental methods. The measured vapor pressures were also compared with vapor pressures estimated using modified corresponding states methods[1] to evaluate the accuracy of these estimation methods.

In the next section the experimental methods for the measurement of the physical properties are briefly described. The estimation of vapor pressure and vapor densities in the coexistence region from the measured critical properties and the boiling point is also discussed. Section III presents results and Section IV discusses the potential alternatives in terms of the measured and estimated physical properties.

II. Experimental Methods and Modified Corresponding States Estimation.

The compounds were synthesized to 99.5% purity and the vapor pressure was measured with a mercury isotensicope up to one 1 atmosphere to determine the boiling point. The melting point was determined as the thermocouple temperature at which a solidified ring of the compound disappeared from the surface of a sample tube. The critical temperature was measured by observing the disappearance of the meniscus in a sealed tube. The liquid density in the liquid-vapor coexistence region was determined by enclosing a weighed sample in 1.5 ml tube and measuring the displacement of the meniscus to within 0.05 mm from the bottom of the tube with a Gaertner cathetometer. The cathetometer readings are converted to volume by a calibration procedure with weighed amounts of water in the tube. The experiment is performed for four samples of differing weight, their weights ranging from about 0.4 g to 0.8 g. The four sample weights may be expressed in terms of the volume of liquid and vapor and their densities and these expressions are solved for the liquid and vapor densities. The law of rectilinear diameters was then used to obtain the critical density to within 2%. The accuracy of the vapor density obtained from these experiments is not reported since more accurate vapor densities can be calculated from the critical constants using modified corresponding states methods.

The vapor pressure above the boiling point was measured with a Baratron MKS 315 pressure sensor with a vacuum on its reference side. The pressure sensor is connected to a stainless steel sample cell immersed in a bath thermostatted to within ±0.1°C. The cell contained about 20 g of sample. Since the pressure sensor is external to the temperature bath both the sensor and its connection to the sample cell are heated to a temperature well above the critical temperature of the sample. The electronic readout via a MKS 272C power supply automatically compensates for the temperature effect on the pressure sensor.

The liquid phase heat capacity was measured using a Perkin Elmer DSC-4 differential scanning calorimeter using sapphire reference standards. The samples were contained in stainless steel sample capsules of 75 microliter capacity with an O-ring seal. The sample capsules are manufactured by Perkin Elmer and the leakage during a calorimeter experiment is negligible. The capsules were filled using a microliter syringe in a cold room with a temperature below the boiling point of the sample (as low as -40°C). The DSC measurement was corrected for vapor volume and heat of vaporization effects due to changes in the relative sizes of the liquid and vapor phases. We kept the vapor volume at a minimum by using sample sizes of 60 mg or larger. For these samples sizes the corrections ranged from 1 to 6%.

In order to evaluate these compounds as refrigerants, vapor pressures and vapor densities are needed up to temperatures approaching the critical point. These were not measured but can be estimated from our measured critical constants and boiling point with modified corresponding states estimation methods.[1] The accuracy of these estimation methods was evaluated by comparisons of the estimated vapor pressures with the measured values obtained in this work for CFC-12, E-125a, and HFC-236ea. The modified corresponding states methods used for this evaluation is based on the following expression for the compressibility Z,

$$Z = \frac{P}{\rho RT} , \tag{1}$$

$$Z = Z^{(o)} + \omega Z^{(1)} , \tag{2}$$

$$Z^{(1)} = \frac{Z^{(R)} - Z^{(o)}}{\omega_R} \tag{3}$$

where ω is the Pitzer acentric factor for the system of interest and ω_R is the same factor for a reference fluid which was selected to be HFC-134a. The quantity ρ is the density, P is the pressure and T is the Kelvin temperature. The quantity $Z^{(o)}$ is the compressibility of a simple fluid which is defined to be the Benedict-Webb-Rubin equations with the simple fluid constants of Lee and Kesler.[2] The modified Benedict-Webb-Rubin equation of state with constants obtained by McLinden et. al.[3] was used to obtain the reference fluid compressibility $Z^{(R)}$. The acentric factor is calculated from the equations of Lee and Kesler,[2]

$$\omega = -\frac{\ln P_c + f^{(o)}(T_{br})}{f^{(1)}(T_{br})} , \tag{4}$$

where P_c is the critical pressure in units of atmospheres and,

$$f^{(o)}(T_r) = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln(T_r) + 0.16934 \, T_r^6 , \tag{5}$$

$$f^{(1)}(T_r) = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln(T_r) + 0.43577 \, T_r^6 . \tag{6}$$

The quantity $T_r (= T/T_c)$ is the reduced temperature and T_{br} is the reduced boiling point.

The procedure is to calculate $Z^{(o)}$ and $Z^{(1)}$ for the critical point (temperature, density and pressure in reduced units being unity) and then solving Equations (4) to (6) and the relation below,

$$Z_c = \frac{P_c}{\rho_c RT} = Z_c^{(o)} + \omega \, Z_c^{(1)} , \tag{7}$$

for the critical pressure and acentric factor using the measured value for the critical density ρ_c. The subscript c in Equation (7) refers to the critical point. The vapor pressure may then be evaluated from the following equation for a reduced temperature T_r,

$$\ln\left(\frac{P}{P_c}\right) = f^{(o)}(T_r) + \omega\, f^{(1)}(T_r) \quad . \qquad (8)$$

The vapor pressure and temperature are then converted to density using Equations (1) to (3).

III. Results and Discussion

The measured melting points, boiling points, critical parameters, heat of vaporization at the boiling point and the liquid phase heat capacity are given in Table 1. The critical pressures listed in the Table are measured values for E-125a, HFC-236ea, and HFC-227ea. For the remaining compounds the critical pressure was calculated from the measured critical temperature and critical density using modified corresponding states equations. The melting point and boiling point are accurate to within ±0.1°C and the critical temperature is accurate to within about ± 0.2°C. The critical density is accurate to within about 2% excepting for C-326d and HCFC-234da. For the latter compounds the measurements were obtained over a very limited temperature range and only approximate critical densities could be obtained by a rectilinear diameter extrapolation. The liquid phase heat capacity is accurate to within about 3%.

The measure liquid density, ρ_l, in the coexistence region has been given an analytic representation using least squares methods and the following relations,

$$\rho_l = A - Bt - Ct^2 \, . \qquad (9)$$

where t is the centigrade temperature. The values for the empirical constants (A,B,C) are presented in Tables 1A of the Appendix to this paper. The constants yield density in Kg/m^3.

The liquid densities were also measured for CFC-12 to check the accuracy of our measurement and estimation methods. The measured liquid densities and calculated vapor densities are compared with the available literature values[4] in Table 2. The measured liquid densities are within 1% of the literature values. The vapor densities which are obtained by the modified corresponding states methods are within about 3% of

Table 1

Boiling point, melting point, critical properties, heat vaporization at the boiling point and liquid phase heat capacity for HCFC's which are potential alternatives for currently used refrigerants and blowing agents.

Compound Code	T_b(°C)	T_{melt} (°C)	ΔH_{vap} Kj/mol	T_c(°C)	P_c (KPa)	ρ_c Kg/m^3	C_p(liq.) (40°C) (Kj/Kg)
E-125a	-34.6	-156.1	21.81	80.7	3253	584	1.306
HFC-236ea	6.5	-146.1	27.00	141.1	3533	579	1.292
HFC-245fa	15.3	-102.1	28.05	157.5	3644	533	1.328
HFC-227ea	-15.2	-127.1	22.73	103.5	2943	603	1.241
HFC-236fa	-1.1	-94.2	25.62	130.6	3177	556	1.365
HCFC-225da	50.8	-130.3	27.29	206.2	3006	589	1.093
HCFC-226da	14.1	-119.6	24.45	158.5	3024	591	1.220
C-326d	38.1	-94.8	28.77	196.9	(2950)	(558)	1.184
HCFC-243da	76.7	-71.6	32.65	251.9	3496	514	1.248
HCFC-226ea	17.6	-134.0	26.33	158.3	2947	584	1.194
HCFC-234da	70.1	-98.0	31.64	242.5	(3353)	(552)	1.180
HCFC-225ba	51.9	-132.6	29.45	212.9	3074	586	1.088
HFC-227ca	-16.3	-140.3	23.69	106.3	2874	594	1.252
HFC-245cb	-18.3	-81.1	23.65	108.5	3113	499	1.459
HFC-245ca	24.96	-73.4	29.05	178.4	3855	529	1.446
HFC-236cb	-1.44	-105.4	25.29	130.1	3118	545	1.469
HFC-235ca	28.1	-85.0	27.75	170.3	3044	541	1.228
HFC-254cb	-0.78	-121.1	24.82	146.1	3753	467	1.573
HCFC-244ca	54.8	-101.8	31.27	221.0	- - -	- - -	- - -
HFC-347ccd	15.1	-124.9	25.87	144.2	2572	532	1.359
HFC-329ccb	- - -	-122.3	- - -	140.2	- - -	- - -	- - -
HFC-338eeea	25.4	-91.5	29.68	148.6	- - -	- - -	- - -

the literature values. The measured critical density for CFC-12 (567 Kg/m^3), which is obtained by extrapolation of density data ranging from temperatures 20°C to 85°C, is within 2% of the literature value (558 Kg/m^3).

In order to evaluate the accuracy of the corresponding states estimation methods the vapor pressures of CFC-12, E-125a, and HFC-236ea were measured. In Table 3 our measured vapor pressures for CFC-12 are compared with the literature values and with those estimated by modified corresponding states methods. In Table 4 we make the same comparisons for the ether compound, E-125a. Our measured vapor pressures for CFC-12 are within 1% of the literature values which is excellent agreement. In the case of E-125a our measured values are within 2% of the values obtained by van Hook et. al.[5] The vapor pressures estimated by modified corresponding states methods are within 4% of the measured values. Similar good agreement is obtained between our measured and estimated vapor pressures for HFC-236ea. We have found that there may be

Table 2

Comparison of measured liquid densities and modified corresponding states vapor densities with literature values for CFC-12.

Temp (°C)	Liquid Density (Kg/m^3)			Vapor Density (Kg/m^3)		
	This Work	Literature	% Dev	Corresponding states	Literature	% Dev
20	1313.	1326.4	-0.98	32.6	31.55	3.23
25	1301.	1308.7	-0.62	37.3	36.13	3.32
30	1286.	1290.6	-0.37	42.6	41.22	3.36
35	1269.	1272.1	-0.25	48.5	46.90	3.40
40	1250.	1253.4	-0.25	55.0	53.27	3.33
45	1230.	1234.3	-0.39	62.3	60.50	2.96
50	1207.	1214.9	-0.66	70.3	68.51	2.58

Table 3

Comparison of measured and modified corresponding states vapor pressures with literature values for CFC-12.

Temp (°C)	Measured (KPa)	Literature (KPa)	Percent Dev.	Corresponding States(KPa)	Percent Dev.
17.1	525.3	522.9	0.45	522.3	0.57
25.5	665.5	660.7	0.71	659.3	0.93
33.1	810.8	806.7	0.50	803.7	0.88
43.8	1056.8	1051.8	0.47	1044.7	1.15
45.0	1091.6	1082.9	0.79	1075.7	1.46
50.3	1234.9	1223.0	0.96	1215.8	1.55
55.9	1394.9	1388.1	0.49	1378.5	1.18
59.9	1524.9	1515.1	0.64	1504.0	1.37
64.9	1695.9	- - - -	- - -	1671.9	1.41
70.3	1894.2	- - - -	- - -	1867.6	1.40
75.4	2099.5	- - - -	- - -	2071.3	1.34
79.9	2287.8	- - - -	- - -	2262.1	1.12
84.8	2510.1	- - - -	- - -	2484.6	1.02
89.8	2741.1	- - - -	- - -	2722.3	0.69
93.4	2919.8	- - - -	- - -	2915.9	0.13

larger differences of the order of 9% between measured and estimated vapor pressures for HFC-227ea, indicating modified corresponding states methods are less accurate for this compound. However our vapor pressure measurement work on HFC-227ea is still preliminary and we do report any values in this paper. The overall agreement between measured vapor pressures and those from estimation methods is very good demonstrating that modified corresponding states method is reliable for obtaining PVT properties of HCFC's.

Table 4

Measured vapor pressures for E-125a compared with measured values of van Hook et. al. and vapor pressures estimated by modified corresponding states methods.

Temp (^oC)	Measured (KPa)	Van Hook et al. (KPa)	% Dev. from Van Hook	Corres. States (KPa)	% Dev. Meas. & C. States
5.4	499.9	491.49	1.68	482.47	3.49
10.1	580.6	572.16	1.45	560.37	3.48
14.8	668.9	661.87	1.05	645.10	3.55
20.0	776.6	772.38	0.54	754.00	2.91
24.8	889.3	885.62	0.41	863.93	2.85
30.4	1034.2	1032.37	0.18	1008.32	2.50
34.7	1159.9	1156.52	0.29	1129.72	2.60
40.0	1326.6	1324.30	0.17	1295.38	2.35
45.3	1508.5	1509.58	-0.07	1478.08	2.02
50.4	1703.2	1705.77	-0.15	1670.92	1.90
54.9	1880.8	1894.64	-0.74	1858.42	1.19
59.9	2100.5	2123.22	-1.08	2084.52	0.76
65.9	2393.1	2425.86	-1.36	2383.00	0.42
70.0	2610.1	2752.04	-1.61	2607.72	0.09
74.8	2892.1	2938.61	-1.61	2891.90	0.01
78.0	3087.1	3143.68	-1.83	3098.10	-0.35
80.0	3203.1	3277.90	-2.34	3228.90	-0.81
T_c=80.6		3326.10	-2.20		
T_c=80.7	3252.8			3242.2	0.33

The vapor pressure measurements for E-125 and HFC-236ea have been given a compact analytic representation by fitting them to equations of the same form as those used by Lee and Kesler.[2] For E-125a this equation is,

$$\text{Ln}\ (P) = 19.0070 - \frac{11.16979}{T_r} - 5.58846\ \ln(T_r) + 0.25004\ (T_r)^6\ , \qquad (10)$$

and for HFC-236ea we have the following equation,

$$\text{Ln}(P) = 19.32756 - \frac{11.58641}{T_r} - 6.24181\ \ln(T_r) + 0.42877\ (T_r)^6 , \quad (11)$$

Other data that is needed to evaluate chemical alternatives as refrigerants are the vapor phase heat capacities. We did not measure these properties. However we have estimated the ideal gas heat capacities with good reliability using the extensive database of Benson et. al.[6]

V. Summary and Conclusions

By examining the range of boiling points and critical temperatures, we observe a number of compounds that are potential alternatives for currently used CFC's and HCFC's. However no fluorinated propane derivative with as low boiling point as CFC-12 (-29.8°C) or HFC-134a (-26.5°C) has been synthesized. After some searching HFC-245cb was synthesized with a boiling point of -18.3°C, which is the lowest boiling point fluorinated propane synthesized thus far. Its critical temperature of 108.5°C compares well with the critical temperatures of CFC-12 (112°C) and HFC-134a (101.1°C) and one might conclude that HFC-245cb may be an alternative for CFC-12 and HFC-134a for some applications. Other fluorinated propanes which may have similar applications as HFC-245cb are HFC-227ca (b.p. = -16.3°C, T_c=106.3°C) and HFC-227ea (b.p. = -15.2°C and T_c =103.5°C). The ether compound E-125 (b.p.=-34.6°C) may also be considered a potential alternative; however its low critical temperature of 80.7°C means it is only marginally suitable for air conditioning applications.

The compound HFC-245ca with a boiling point of 24.96°C and a critical temperature of 178.4°C is a very probable alternative for CFC-11 (b.p.=23.8°C and T_c=198°C). The compound, HFC-245ca, is particularly desirable because it contains no chlorine and potentially has a low atmospheric lifetime. Its thermal conductivity estimated by the Roy and Thodos method[7,8] is 8.96 x 10^{-3} W/(M-°K), which is comparable to that for CFC-11 and should make it as suitable a blowing agent as CFC-11 in the maufacture of foam insulation. The compounds HFC-236ea (b.p. = 6.5°C and T_c=141°C), HFC-236cb (b.p.=-1.44°C and T_c=130.1°C), HFC-254cb (b.p.=-0.78 and T_c=146.1°C), and HFC-236fa (b.p.=-1.1°C and T_c= 130.6°C) are potential alternatives for CFC-114 (b.p.=3.77 and T_c=145.7°C). Other compounds listed in Table 1 with boiling points between -18°C and 35°C have potential applications as blowing agents. Higher boiling point compounds most likely applications are as solvents or heat transfer fluids. The cyclic butane which contains one chlorine potentially has higher solvent power than most of the other alternatives with a similar low chlorine content. Another desirable trait C-326d is that the strained cyclic structure implies a low atmospheric lifetime.

References

1. R. C. Reid, J. M. Prausnitz and Bruce E. Poling, The Properties of Gases and Liquids, 4th ed., (McGraw-Hill, New York, 1984).
2. B. I. Lee and M. G. Kesler, AIChE. J., 21, 510 (l975).
3. M. O. McLinden, J. S. Gallager, L. A. Weber, G. Morrison, D. Ward, A. R. H. Goodwin, M. R. Moldover, J. W. Schmidt, H. B. Chae, T. J. Bruno, J. F. Ely, M. L. Huber, "Measurement and Formulation of the Thermodynamic Properties of Refrigerants 134a (1,1,1,2-Tetrafluoroethane) and 123 (1,1-Dichloro-2,2,2-Trifluoroethane), ASHRAE Transactions, 95(2),263 (l989)
4. Handbook of Chemistry and Physics, Ed. R. C. Weast and M. J. Astle, 60th ed.,(CRC Press, Inc. Boca Raton, Fl., 1980).
5. Bao-Hai Wang, James L. Adcock, Shyam B. Mathur, and W. Alexander Van Hook, "Vapor Pressures, Liquid Molar Volumes, Vapor Nonideality, and Critical Properties of some Fluorinated Ethers ($CF_3OCF_2OCF_3$, $CF_3CF_2OCF_2H$, cyclo-$CF_2CF_2CF_2$-, CF_3OCF_2H, and CF_3OCH_3), and of CCl_3F and CF_2ClH", J. Chemical Thermodynamics, 23, 699 (1991).
6. S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O' Neal, A. S. Rodgers, R. Shaw, and R. Walsh, Chem. Rev. 69, 279 (1969).
7. D. Roy and G. Thodos, Ind. Eng. Chem., Fundam., 7, 529 (l968).
8. D. Roy and G. Thodos, Ind. Eng. Chem., Fundam., 9, 71 (l970).

Appendix

Table 1A

The coefficients for the mathematical representation of liquid density given by Equation (9). The last column gives the temperature range over which the measured data were obtained.

Compound Code	Formula	A	B	10^3C	Range (°C)
E-125a	CF_3OCF_2H	1389.0	3.847	2.660	9 to 61
HFC-236ea	CF_3CHFCF_2H	1467.4	2.941	6.252	1 to 95
HFC-245fa	$CF_3CH_2CF_2H$	1357.1	1.072	16.42	11 to 85
HFC-227ea	CF_3CHFCF_3	1501.6	3.274	17.64	2 to 65
HFC-236fa	$CF_3CH_2CF_3$	1447.4	2.728	13.54	0 to 98
HCFC-225da	$CF_3CHClCF_2Cl$	1583.3	1.420	10.13	24 to 103
HCFC-226da	$CF_3CHClCF_3$	1464.4	0.840	21.42	25 to 90
C-326d	cyclic-$(CF_2)_3CHCl$	- - -	- - -	- - -	- - -
HCFC-243da	$CF_3CHClCH_2Cl$	1471.5	1.745	3.956	24 to 93
HCFC-226ea	CF_3CHFCF_2Cl	1496.2	1.954	11.74	25 to 121
HCFC-234da	$CF_3CHClCFHCl$	- - -	- - -	- - -	- - -
HCFC-225ba	$CF_3CFClCFHCl$	1569.4	-0.335	26.97	24 to 97
HFC-227ca	$CF_3CF_2CF_2H$	1475.9	2.950	20.66	25 to 86
HFC-245cb	$CF_3CF_2CH_3$	1237.6	1.849	24.32	23 to 82
HFC-245ca	$HCF_2CF_2CH_2F$	1371.4	1.153	11.14	22 to 140
HFC-236cb	$CF_3CF_2CH_2F$	1344.8	-0.601	37.26	35 to 100
HFC-235ca	$CF_3CF_2CH_2Cl$	1515.4	4.013	4.456	46 to 95
HFC-254cb	$CF_2HCF_2CH_3$	1187.7	-0.369	27.70	23 to 110.
HCFC-244ca	$CF_2HCF_2CH_2Cl$	- - -	- - -	- - -	- - -
HFC-347ccd	$CF_3CF_2CF_2CH_3$	1337.2	1.575	11.21	22 to 112
HFC-329ccb	$CF_3CF_2CF_2CF_2H$	- - -	- - -	- - -	- - -
HFC-338eea	$CF_3CFHCFHCF_3$	- - -	- - -	- - -	- - -