Vapor Pressure of 2-(Difluoromethoxy)-1,1,1-trifluoroethane $CHF_2-O-CH_2CF_3$ (HFE-245)

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The vapor pressure of 2-(difluoromethoxy)-1,1,1-trifluoroethane, a candidate alternative refrigerant that is also known as HFE-245, has been measured. The vapor pressure was determined at temperatures between 261 K and 369 K by two ebulliometric techniques. The differences in these two methods arise from the method used to determine pressure. At $p < 200$ kPa, a comparative instrument was used and pressures were obtained from the temperature at which water boiled at the same pressure. At pressures up to 747 kPa, the pressures were measured directly. A correlation for the vapor pressure from 261 K to the critical temperature is provided. The comparative ebulliometric measurements have an expanded uncertainty ($k = 2$) of less than $0.0005 \cdot p$, while the direct ebulliometric measurements have an expanded uncertainty ($k = 2$) of $0.002 \cdot p$.

Introduction

We have published comparative ebulliometric measurements of the vapor pressure of nine compounds: 1,1,1,2-tetrafluoroethane (HFC-134a) by Goodwin et al. (1992a), chlorodifluoromethane (HCFC-22) by Goodwin et al. (1992a), 1,1-dichloro-1-fluoroethane (HCFC-141b) by Defibaugh et al. (1993) and Weber (1992), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123) by Goodwin et al. (1992b), difluoromethane (HFC-32) by Weber and Goodwin (1993), 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124) by Boyes and Weber (1994), pentafluoroethane (HFC-125) by Boyes and Weber (1995), and 1-chloro-1,1-difluoroethane (HCFC-142b) by Boyes and Weber (1995), and 1,1-difluoroethane (HFC-152a) by Silva and Weber (1993). In this paper we report vapor pressure measurements, by both direct and comparative ebulliometry for 2-(difluoromethoxy)-1,1,1-trifluoroethane (HFE-245) at pressures in the range 15 kPa to 747 kPa, corresponding to temperatures from 261 K to 369 K.

Throughout the remainder of the text 2-(difluoromethoxy)-1,1,1-trifluoroethane will be referred to, with refrigeration industry nomenclature described by Downing (1988), as HFE-245.

Experimental Section

Two ebulliometric techniques have been used for the measurements reported here. For pressures in the range 15 kPa to 202 kPa, we used a comparative ebulliometer to measure the condensing temperatures of the liquid under study and that of a reference liquid when both liquids were boiling at the same pressure. A second ebulliometer was used to measure the condensation temperatures of HFE-245 between 302 K and 369 K; in this apparatus the pressure was measured directly. Both apparatuses and procedures have been described elsewhere, by Goodwin et al. (1992a), Defibaugh et al. (1993), Defibaugh and Morrison (1996), Weber (1992), and Silva and Weber (1993), and only the important features are discussed here.

The comparative ebulliometer consisted of two glass boilers connected by a helium-filled manifold. One boiler contained HFE-245, while the other boiler contained a reference fluid. Water was selected as the reference fluid in the experiments discussed here. The pressure within the apparatus was determined from the known vapor pressure of water. Condensation temperatures of both fluids were determined on ITS-90 using two long-stem platinum resistance thermometers. The stability of the thermometers was checked in a triple-point-of-water cell prior to use. We estimate that the condensing temperatures could be measured with an expanded uncertainty ($k = 2$) of less than 5 mK. The pressure was controlled with a ballast volume of about 0.015 m^3 wrapped in fiber-glass insulation.

In the direct ebulliometer, condensation temperatures were measured with 100 Ω capsule platinum resistance thermometer, which, when calibrated against the standard long-stem thermometers discussed above, was found to have an expanded uncertainty ($k = 2$) of 0.06 K. Before measurements were initiated, the ebulliometer was evacuated at a temperature of about 300 K with a rotary vacuum pump until the pressure was below 1 Pa. The apparatus was then cooled to 273 K, and about 20 cm^3 of liquid sample was condensed into the boiler. Argon buffer gas was used to pressurize the fluid. Heat was applied to the boiler, and the temperatures indicated by three thermocouples located in the boiler were monitored. Measurements commenced when all three thermocouple temperatures were within 2 K of the value obtained from the platinum resistance thermometer used for the condensation measurements. Condensation temperatures and pressures were measured, the system pressure was raised, and the process was repeated.

The pressure was controlled in the direct ebulliometer with an automatic controller. Pressures were measured with a quartz transducer, for which the manufacturer quoted a precision and accuracy of 0.01 kPa and 0.3 kPa

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Table 1. Vapor Pressures p^{l+g} at Temperatures T for HFE-245

T/K	p^{l+g}/kPa	T/K	p^{l+g}/kPa	T/K	p^{l+g}/kPa	T/K	p^{l+g}/kPa
Comparative Ebulliometry							
260.653	15.222	282.751	45.250	300.091	92.818	311.304	140.291
263.483	17.724	285.428	50.909	302.471	101.637	313.734	152.723
266.085	20.318	287.397	55.434	304.678	110.398	315.215	160.701
270.426	25.328	290.114	62.185	304.677	110.378	317.200	171.901
274.184	30.437	293.290	70.902	307.167	120.956	318.602	180.159
277.305	35.294	295.807	78.467	307.160	120.917	320.070	189.155
280.120	40.191	298.119	85.976	309.622	132.164	322.057	201.892
Direct Ebulliometer							
302.028	100.083	317.235	172.141	334.980	301.727	349.926	460.475
302.042	100.105	321.812	200.345	334.902	301.573	354.086	512.938
308.059	124.984	321.814	200.396	340.426	354.568	358.125	569.974
308.054	124.871	321.894	200.924	345.376	406.694	355.447	533.053
312.634	147.002	329.198	253.345	345.336	406.222	360.488	604.765
312.859	148.116	328.831	250.524	345.300	405.707	360.453	604.608
317.456	173.452	335.019	302.096	350.000	460.566	369.143	747.473
317.335	172.755						

respectively. When we compared this device with a standard dead weight pressure gauge, we found differences of less than 0.0004·p at pressures between 100 kPa and 750 kPa.

Sample Purity

The HFE-245 was obtained from the Halocarbon Products Corporation. (To describe materials and experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular product or equipment is necessarily the best available for the purpose.) Gas chromatographic analysis (with a thermal conductivity detector and a 3-m column packed with Carbopack and 5% Fluorcol as the stationary phase operating at 383 K) indicated the presence of air with a mole fraction of 0.0003 in the sample as supplied. The sample was degassed and dried with the following procedure. First, the gas-phase sample was dried by passing it slowly over grade 0.4-nm molecular sieve, previously baked, under vacuum, at 500 K for 48 h. The sample was collected down stream of the drier, where it was degassed by vacuum sublimation with liquid nitrogen-cooled finger. This process was repeated three times. The fluid used in these measurements had a minimum mole fraction purity of 0.9997.

For other fluids, we have used a Burnett apparatus to measure higher vapor pressures than attainable with the ebulliometers described above. The Burnett apparatus has gold-plated internal surfaces. We performed several tests of the compatibility of HFE-245 with gold, stainless steel, and copper in sealed, thick-walled borosilicate glass ampules. One ampule contained just HFE-245; four other ampules were prepared with HFE-245 and the following materials: copper filings, stainless steel filings, gold wire, and ground glass. Each ampule had a total volume of 5 cm^3 and was filled with between 0.4 cm^3 and 0.5 cm^3 of liquid HFE-245. The ampules were immersed in an oil bath at room temperature and then heated in steps of 10 K to 400 K. At 400 K three of the tubes failed. They were HFE-245 alone, HFE-245 + gold wire, and HFE-245 + ground glass. At 400 K, the vapor pressure of HFE-245 is about 1 MPa, a pressure at least a factor of 10 below that at which the glass ampules were rated for operation. The remaining two tubes with HFE-245 and either copper or stainless steel filings were left in the bath at 400 K for 1 week. The surviving tubes showed no obvious changes in appearance. Because of these unfavorable results, particularly with gold, we did not put the HFE-245 in the Burnett apparatus. In the absence of additional measurements, it is not possible to offer an explanation for these observations.

Results

The vapor pressure HFE-245 has been determined in the range 15 kPa to 747 kPa, which corresponds to boiling temperatures from 261 K to 369 K. For the comparative measurements, water was used as a reference fluid. The pressure was calculated from the temperatures at which the water boiled with an equation reported by Goodwin et al. (1992). The direct measurements start at a temperature of 302 K, and the comparative measurements end at 322 K; therefore, both instruments have some overlap in temperature.

In Table 1 we list the 57 values of the vapor pressure determined at each of the experimental temperatures. Small corrections have been applied to account for the fluid head in each ebulliometer; for our comparative ebulliometry, we calculated a static head correction factor of 1.000 174.

Analysis and Discussion

The vapor pressures, listed in Table 1, were used to determine the coefficients in the vapor pressure equation of the type recommended by Wagner (1977). In this regression analysis, each observation was weighted. The comparative results were weighted by $\Delta p/p$ obtained from

$$\Delta p/p = \left\{\left(\frac{\delta p}{p}\right)^2 + \left(\frac{\delta T}{p}\right)^2\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)^2\right\}^{1/2} \qquad (1)$$

where $\delta T \approx 1.4 \times 10^{-3}$ K and $\delta p = 3$ Pa, a conservative estimate of the uncertainty in the vapor pressure of water. The direct ebulliometric results were weighted by (170 Pa)/p, where 170 Pa is an estimate of the uncertainty in the pressure measurement. The vapor pressure p^{l+g} of HFE-245 was adequately accommodated by

$$\ln(p^{l+g}/\mathrm{kPa}) = 8.022\,436\,1 + (-6.044\,838\,4\cdot\tau - 2.314\,101\,2\cdot\tau^{1.5} + 0.971\,281\,11\cdot\tau^{2.5} - 8.968\,287\,5\cdot\tau^{5})/T_r \quad (2)$$

where $T_r = T/T_c$, $\tau = (1 - T_r)$, and $T_c = (443.99_2 \pm 0.02)$ K obtained from refractive index measurements by Schmidt

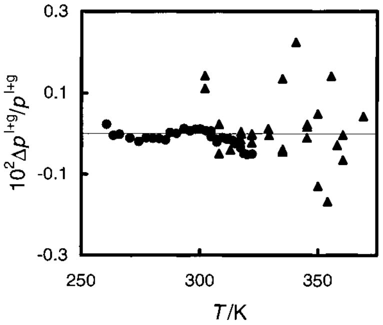

Figure 1. Fractional deviations $\Delta p^{l+g} = p(\text{exptl}) - p(\text{calcd})$ of the experimental vapor pressures from eq 2 for HFE-245. ●, This work, comparative ebulliometer; ▲, this work, direct ebulliometer.

(1994). The root-mean-squared standard deviation of eq 2 is 0.18% and has a standard uncertainty of $0.0004\langle p\rangle$. Equation 2 is of the form preferred by Ambrose (1986) for the representation of vapor pressure for most substances. The magnitude and sign of the coefficient of τ is within the range $-(7.5 \pm 1.5)$ expected by Ambrose (1986). Our values of the vapor pressure p^{l+g} are shown in Figure 1 as deviations from our smoothing eq 2. The comparative and direct ebulliometric measurements are in excellent agreement in the overlapping temperature range with differences of less than $1.5 \times 10^{-3} \cdot p^{l+g}$, well within the uncertainty assigned to the quartz pressure transducer. To our knowledge, there are no other determinations of p^{l+g} for HFE-245 reported in the literature with which to compare our results or extend our data to higher temperatures.

Assuming a critical temperature of $(443.99_2 \pm 0.02)$ K reported by Schmidt (1994), and extrapolating eq 2 about 75 K (equivalent to about 2.3 MPa) above the highest experimental results, provides a critical pressure of (3048 ± 22) kPa, where the uncertainty is the statistical ($k = 2$) value obtained from the regression. Had we adopted the alternative powers for τ of 1, 1.5, 3, and 6 in the regression analysis to obtain eq 2, then the estimated critical pressure would have been higher by 62 kPa. This difference should be taken as a plausible upper bound on the uncertainty in the critical pressure.

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