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Vapor Pressure of Pentafluorodimethyl Ether

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Vapor pressures of pentafluorodimethyl ether (E125) have been measured from (228 to 331) K using two ebulliometers. Experimental pressures ranged from (65 to 2024) kPa. Thermodynamic calculations were used to estimate pressures down to 140 K (16.5 Pa), and a vapor pressure curve is given which is valid from 140 K to the critical point (354.49 K). The normal boiling temperature was determned to be 238.06 K. The enthalpy of vaporization has been calculated from (140 to 300) K.

Introduction

An ever-widening range of compounds is being surveyed in the search for useful substitutes for the chlorofluorocarbons as refrigerants, foam-blowing agents, and cleaning agents. Fluorinated ethers form one possible group of replacements. However, their thermophysical properties have not been extensively studied. We present here the vapor pressure curve of pentafluorodimethyl ether (known to the refrigeration industry as E125) over a wide range of temperature. This work is part of a larger effort in our laboratory to provide thermophysical properties for this fluid, which is being considered as a possible substitute, either as a pure fluid or as a component of a binary mixture, for R22 or for the azeotrope R502.

We are aware of only two other recent research efforts on E125 (Wang et al., 1991; and Salvi-Narkhede et al., 1992), and we compared our results with their results where possible.

Experimental Section

The vapor pressures were measured in two metal ebulliometers. One was a single-boiler type which utilized a pressure gauge and which measured the condensing temperature of the fluid. A platinum resistance thermometer measured temperature with an uncertainty of approximately ±0.025 K, and a resonating-quartz type pressure gauge measured pressure with an uncertainty of about ±0.2 kPa. This device was used in the temperature range (299 to 331) K (ITS-90) at pressures from (900 to 2024) kPa. A total reflux condenser at the top of the boiler prevented the sample from escaping. The results are given in Table 1. This apparatus will be described more fully in a future paper.

The other apparatus was a comparative ebulliometer which has been described by Weber and Silva (1996). Briefly, two identical boilers with condensers were interconnected through a manifold. The boilers utilized vapor-lift pumps; thus, they measured boiling temperatures. Two platinum resistance thermometers measured the relative temperatures with an uncertainty of approximately ±0.010 K. A reference fluid, 1,1,1,2-tetrafluoroethane (R134a), was placed in one (the reference) boiler. Its boiling temperature was used to determine the system pressure with an estimated uncertainty of about ±0.03% (Goodwin et al., 1992). Measurements with this apparatus were made in the range (228 to 326) K at pressures from (65 to 1799) kPa. The results are given in Table 2.

Table 1. Vapor Pressure Data for E125 from the Single-Boiler Apparatus

T/K	*P*/kPa	*T*/K	*P*/kPa
299.083	900.2	317.308	1450.4
300.020	924.0	317.316	1450.3
300.060	925.2	318.692	1500.4
301.036	950.2	319.328	1524.2
302.933	1000.2	320.044	1550.3
303.833	1025.2	321.353	1600.4
304.752	1050.3	321.962	1624.2
306.488	1100.2	322.637	1650.3
307.331	1125.2	323.233	1674.2
308.182	1150.3	323.885	1700.4
309.823	1200.3	325.082	1749.2
311.397	1250.3	326.870	1824.2
312.945	1300.3	327.459	1849.3
314.437	1350.3	329.174	1924.2
315.893	1400.3	331.380	2024.2
315.900	1400.3		

Table 2. Vapor Pressure Data for E125 from the Comparative Ebulliometer

T/K	*P*/kPa	*T*/K	*P*/kPa
228.924	64.94	258.500	240.14
230.395	69.96	260.650	260.56
231.781	74.96	262.601	280.26
233.078	79.90	264.456	300.02
234.323	84.89	268.874	351.26
235.516	89.89	272.691	400.65
236.660	94.90	276.163	450.07
237.752	99.89	279.845	507.21
238.804	104.88	282.375	549.73
239.813	109.83	282.456	551.05
239.819	109.89	285.239	600.85
241.178	116.84	287.817	650.07
242.655	124.87	290.366	701.36
243.550	129.90	292.675	750.54
244.414	134.87	295.058	803.90
245.238	139.83	299.079	900.23
246.899	150.21	302.983	1001.76
248.428	160.23	309.829	1200.37
251.272	180.28	315.893	1399.90
253.876	200.35	321.373	1601.00
256.266	220.19	326.297	1799.40
258.497	240.09		

Results

A total of 31 pressure−temperature pairs were obtained with the single-boiler apparatus, and 45 pressure−temperature pairs were obtained with the comparative ebulliometer. Two of the latter pairs were deleted because they deviated from the vapor pressure curve by 3 times the standard deviation of the fit.

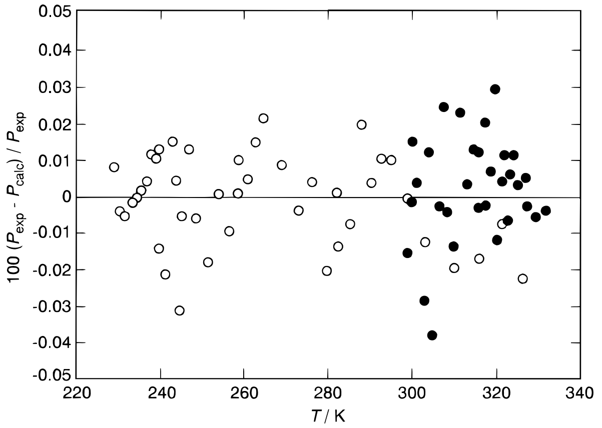

Figure 1. Relative deviations of the data from eq. 1: ○, comparative ebulliometer; ●, single-boiler ebulliometer.

Table 3. Purity analysis of the E125 Sample

$x \times 10^2$	K^a
0.025	12
0.004	1
0.010	2

[a] K is the distribution coefficient.

The data were represented with a Wagner-type vapor pressure equation

$$\ln(P/P_c) = (T_c/T)(a_1\tau + a_2\tau^{1.5} + a_3\tau^{2.5} + a_4\tau^5) \qquad (1)$$

with $\tau = 1 - T/T_c$, $a_1 = -7.656\,35$, $a_2 = 1.865\,45$, $a_3 = -2.798\,96$, $a_4 = -3.390\,15$, and $P_c = 3350.8$ kPa. The critical temperature, $T_c = 354.49$ K, was taken from Schmidt et al. (1996). The temperature of the normal boiling point was found to be 238.06 K. The standard relative deviation of the fit was 0.014% in pressure. The relative deviations are shown in Figure 1. The figure shows that there is very good agreement between the two data sets in the region of overlap; the systematic difference is about 0.01%. We used eq 1 to calculate the Pitzer acentric factor, $\omega = 0.326$.

Sample Purity

The sample of E125 was quite pure as received from the supplier. Duplicate gas chromatograms of both phases in the supply cylinder revealed three impurities present in very low concentrations. The results of the analysis are shown in Table 3. Here, K, the distribution coefficient, $= y/x$, is the mole fraction of the impurity in the vapor phase divided by that of the liquid phase. In addition, there was a small amount of air in the E125 sample. Air does not affect ebulliometric measurements since it does not condense in the condenser; therefore, it is not returned to the boiler. Weber and Silva (1994) showed how dilute impurities affect ebulliometric measurements. For boiling temperature measurements (comparative ebulliometer) the relative error in pressure is $\delta P/P = (K_2 - 1)x_2$, while for the condensing temperature measurements (single boiler), $\delta P/P = K_2(K_2 - 1)x_2$ (Note, this equation was given incorrectly in Weber and Silva (1994)). These equations indicate that an impurity with a K value of 12 would cause appreciable errors. However, this impurity would be very volatile, and an approximate calculation shows that it probably would not liquefy in the condensers (which operated at (180 to 193) K), and thus it would be ejected from the boilers much the same as air. The relatively good agreement between the different ebulliometers in the region where the data overlap strongly supports this conclusion. The third listed impurity may be the source of the very small systematic differences seen in Figure 1.

The present results also offer an answer to a related question which has concerned ebulliometrists for some time; namely, what is the effect of the solubility of the pressurizing gas in the fluid of interest? Ebulliometry was originally designed for low-pressure measurements. In the case of higher pressure measurements, such as the results presented here, the increased solubility of the gas (with a very large K value) could cause appreciable errors. The equations given in the previous paragraph show that the two ebulliometers would be affected differently by any dissolved gas. In the present measurements the comparative ebulliometer used helium gas for the pressurizing agent while the single-boiler apparatus used argon. The excellent agreement between the two devices at pressures from (900 to 1799) kPa indicates that solubilities of these two gases have not caused errors. In the condenser there is a gas–liquid interface between the pressurizing gas and the condensing test fluid. Any gas which dissolves at this interface re-evaporates almost immediately as the condensed liquid flows back into the boiler. Thus, it does not take part in the phase equilibrium conditions in the boiler.

Extrapolation to Lower Pressures

Due to the temperature limitations of the apparatus, we were not able to measure vapor pressures below 228 K for E125. Salvi-Narkhede et al. (1992) have reported the triple point temperature to be in the range (116 to 117) K. It would be useful to have estimates of the vapor pressures at temperatures below 228 K, where the vapor pressure is 65 kPa. This is possible through standard thermodynamic calculations. The general technique has been used many times; however, we will give our version here in order to illustrate the value of several estimation methods. The calculation requires certain thermodynamic properties, the most important of which are ideal-gas heat capacity, C_p^o, the liquid-phase heat capacity, $C_{p,L}$, an equation of state for the gas phase, and the liquid-phase molar volume, v_L. Some of these quantities have not been measured for E125; therefore, estimates are required. Hurly (1995) has recently measured the ideal-gas heat capacity in the range (250 to 400) K, but the liquid-phase heat capacity has not been reported. Defibaugh (1995) and Salvi-Narkhede et al. (1992) measured v_L. The gas-phase equation of state has not been reliably determined; therefore, we used the method of Weber (1994) to estimate the virial coefficients, B and C. This method requires a value for the dipole moment, μ, which also must be estimated. From the information that $\mu = 1.3$ D for dimethyl ether, and $\mu = 0.5$ D for perfluorodimethyl ether, we estimated that for E125, $\mu \simeq 0.7$ D. This value would indicate that E125 is only slightly polar.

The thermodynamic calculation is based on the identity that, at any temperature, $\Delta_{vap}H = T\Delta_{vap}S$. The calculation starts with a reference temperature, T_0, where the vapor pressure has been accurately determined to be P_0. We arbitrarily set the thermodynamic properties of the saturated liquid; $H_L = S_L = 0$ at T_0. Then the ideal-gas properties H_0^o and S_0^o (at T_0 and $P_1 = 101.325$ kPa) are used as adjustable parameters which are varied to give the correct values of (dP_σ/dT) and P_0, respectively. Then, from thermodynamics, we can calculate the enthalpy at any temperature for each phase on the saturation boundary. The difference between these two quantities is the enthalpy of vaporization, which may be expressed as

$$\Delta_{\mathrm{vap}}H = H_0^{\circ} - \int_{T_0}^{T}(C_{P,\mathrm{L}} - C_P^{\circ})\,\mathrm{d}T + \delta H(T) - v_{\mathrm{L}}(P_{\sigma} - P_0) \tag{2}$$

Similarly, for the entropy

$$\Delta_{\mathrm{vap}}S = S_0^{\circ} - \int_{T_0}^{T}(C_{P,\mathrm{L}} - C_P^{\circ})/T\,\mathrm{d}T + \delta S(T) \tag{3}$$

where

$$\delta H(T) = H(T,P_{\sigma}) - H^{\circ}(T,P_1) \tag{4a}$$

$$\delta S(T) = S(T,P_{\sigma}) - S^{\circ}(T,P_1). \tag{4b}$$

Equations 4a,b are calculated with the aid of the virial coefficients from standard thermodynamic formulas. Equation 4b contains an ideal-gas term which is very sensitive to the calculated value of the vapor pressure. That term is the most important one in determining P_{σ}. Equations 2 and 3 make use of the approximation that $C_{P,\mathrm{L}} \cong C_{\sigma}$, the heat capacity of the saturated liquid. This approximation is quite good at low reduced temperatures but becomes less accurate with increasing temperature. The solution is iterative since P_{σ} and v_{G} must be found by successive approximations, but the convergence is rapid. The liquid volume, v_{L}, was taken to be a constant, 0.1 L·mol^{-1}, which is sufficiently accurate for the small correction term in eq 2. This formulation is limited to regions where the virial coefficients provide a sufficiently accurate equation of state, but they have been found to be adequate for pressures to at least 2000 kPa.

The liquid-phase heat capacity is unknown. Therefore, to implement eqs 2 and 3, we used the Bondi/Rowlinson corresponding states correlation, given correctly by Reid et al. (1987), to estimate the integrands

$$(C_{P,\mathrm{L}} - C_P^{\circ})/R = 1.45 + 0.45\,(1 - T_{\mathrm{r}})^{-1} + 0.25\omega[17.11 + 25.2(1 - T_{\mathrm{r}})^{0.333}T_{\mathrm{r}}^{-1} + 1.742(1 - T_{\mathrm{r}})^{-1}] \tag{5}$$

This estimating function has been arrived at by correlation of data on a wide variety of substances, including ethyl ether. Still, it could have a rather large uncertainty; however, the effect of any uncertainties is somewhat attenuated since it appears in both eqs 2 and 3 in the same way.

For the reference point we used $T_0 = 240$ K and $P_0 = 110.75$ kPa. When the above technique was implemented, the adjustable parameters were found to be $H_0^{\circ} = 21\,017.6$ J·mol^{-1} and $S_0^{\circ} = 87.942$ J·(mol·K)$^{-1}$. The resulting calculated vapor pressures are given at 20 K intervals in Table 4 where they are compared with an extrapolation of eq 1. It can be seen from the table that the difference between these two independent methods is remarkably small; the difference is 0.14% or less except for the lowest temperature, 140 K, where the difference increases to 0.48%. At that point eq 1 has been extrapolated 88 K to a reduced temperature of 0.4, and the pressure is smaller than the lowest experimental value by a factor of 4000. Although eq 1 has an appropriate limiting form at low temperatures, it has generally not been considered good for long extrapolations. These results suggest that, if it has been fit to very precise data over a wide temperature range, it can be so extrapolated. At the highest temperatures the effects of some of the approximations increase the difference to 0.20%. However, the comparison in that range is only given for illustrative purposes since the calculation is not needed there. The comparisons between 220 K and 300 K indicate that eq 5 can be used successfully at low temperatures in the calculation of P_{σ}, where the expected accuracy should be about 0.1%.

Table 4. Comparison of Thermodynamically Estimated Vapor Pressures with Those from Eq 1 and Saturated Vapor Volumes, v_{G}, and Enthalpies of Vaporization, $\Delta_{\mathrm{vap}}H$

T/K	P(eqs 2−5)/kPa	P(eq 1)/kPa	v_{G}/(L·mol^{-1})	$\Delta_{\mathrm{vap}}H$/(J·mol^{-1})
140	0.01658	0.01650	70185	27 029
160	0.2823	0.2819	4710	25 709
180	2.3049	2.3019	647.6	24 461
200	11.459	11.445	153.4	23 242
220	40.314	40.290	44.37	22 006
240	110.75	110.79	17.191	20 695
260	253.98	254.24	7.806	19 248
280	509.19	509.84	3.953	17 581
300	921.6	923.5	2.147	15 568

From the comparisons given above, we consider eq 1 to be sufficiently accurate for the calculation of thermophysical properties over the whole temperature range from 140 K to the critical point. The corresponding molar volumes of the saturated vapor and the enthalpies of vaporization are also given.

Comparisons

The literature on the thermophysical properties of E125 is meager. We have compared only with the recent report of Salvi-Narkhede et al., who reported vapor pressure measurements on a series of fluorinated ethers. The agreement between their results for pentafluorodimethyl ether and our vapor pressures is very poor. They reported vapor pressures in the range (240 to 313) K, and their pressures are consistently (15 to 25) kPa higher than the values given here. Since they reported using a sensitive pressure gauge, it is possible that their sample contained a volatile impurity. It follows that their reported normal boiling temperature is 2.8 K lower than the one given here. Similarly, their critical temperature is about 1 K lower than the one measured by Schmidt et al. Their reported saturated vapor density at 303.12 K is about 15% higher than the value calculated with our vapor pressure curve and virial coefficients.

Conclusions

These results add considerably to the sparse body of information on the properties of E125. Two independent methods have been used to extrapolate our experimental results to much lower temperatures and pressures. The high level of agreement between the two appears to justify the approximations made. The vapor pressure equation given here and the techniques used above allow calculation of all the gas-phase thermodynamic properties as well as the enthalpies of vaporization and liquid-phase heat capacities. These techniques should be useful for E125 from 140 K to about 320 K, and the vapor pressure equation is reliable up to the critical point, 354.49 K.

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