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Vapor Pressure of Heptane from the Triple Point to the Critical Point

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We have used a metal ebulliometer to make measurements of the vapor pressures of heptane. Measurements spanned the temperature range from 335 K to 503 K, and measured pressures ranged from 30 kPa to 1597 kPa. The sample purity was determined by chromatographic analysis, and the measured pressures were adjusted for the presence of the impurities found. The adjusted results were found to be in good agreement with the best available data from the literature, and a reliable vapor pressure curve could be established for temperatures up to the critical point (540.13 K). We have also used thermodynamic calculations and published thermal data to extend the vapor pressures down to the triple point (182.603 K). We estimate that our vapor pressure curve has an uncertainty of 0.2% to 0.3% in the vicinity of the triple point, decreasing to 0.03% to 0.05% in the range 300 K to 400 K, and increasing to about 0.1% at 500 K. The calculated critical pressure was found to be (2739.7 ± 2.5(1σ)) kPa.

Introduction

The thermophysical properties of heptane, a midrange alkane important to the fuel and petrochemical industries, have been the subject of study for many years. Its liquid-phase heat capacity is used as a standard in the field of calorimetry for temperatures up to 400 K. Its vapor pressure curve is also used as one of the standards in the evaluation of vapor pressure measurements by ebulliometry. It was recently used as a test fluid in an interlaboratory test study for the determination of the vapor pressure of liquids by ebulliometry (up to 400 K), sponsored by ASTM Committee E-37 On Thermal Measurements (Olson, 1996).

Many of the vapor pressure measurements reported in the literature were part of larger studies on a range of hydrocarbons or were auxiliary measurements in a phase equilibrium study. Some may have been affected by the presence of undetected impurities. Some of the data were probably considered adequate at the time they were measured, but they do not meet current standards of accuracy. As a result, various data sets in the literature are highly discordant at temperatures above about 425 K. We have remeasured the portion of the vapor pressure curve from 335 K to 503 K. In this work we will compare our results with some of the more recent measurements (Wisniewska et al., 1993; Zawisza and Vejrosta, 1982) and with older literature values which are recognized to be of high accuracy (Willingham et al., 1945). We also make a comparison with the recommended vapor pressure values of two organizations which are engaged in evaluating and correlating such data and with several other recent correlations. The present work includes measurements in the range 100 kPa to 200 kPa, for which literature data are very sparse. We present our estimates for the virial coefficients B and C calculated from a generalized model and use them in the calculation of the enthalpy of vaporization of heptane.

Experimental Section

The vapor pressures were measured in a metal comparative ebulliometer which has been described by Weber and Silva (1996). Only a brief description is given here.

Two identical boilers, with vapor-lift pumps and reflux condensers, were connected through a manifold which was filled with helium gas at a precisely controlled pressure (±20 Pa). Two liquid-nitrogen-cooled traps in the manifold prevented any possible cross-contamination between the boilers. A platinum resistance thermometer in each boiler measured the boiling temperature on the ITS-90 scale with a reproducibility of 5 mK to 7 mK. Temperatures were monitored continuously with a computer. Each boiler was surrounded by a temperature-controlled cylindrical shield. The temperature of the shield for the reference boiler varied from 210 K to 310 K, and it was controlled with liquid methanol circulated from a temperature-controlled bath. The shield for the boiler containing the heptane sample was required to vary between 320 K and 500 K. For temperatures up to 375 K it was controlled with an ethylene glycol/water solution which was circulated by a thermostated bath. For higher temperatures, it was fitted with resistive heating controlled by a simple commercial controller using a probe-type thermocouple sensor which was attached to the shield with thermally conducting cement. This arrangement controlled the shield with a tolerance of about ±1 K.

Approximately 50 cm^3 of liquid heptane was placed in one boiler, and a like amount of 1,1,1,2-tetrafluoroethane (HFC 134a), the reference fluid, was placed in the other. Electrical power was supplied to the boilers by means of capsule-type heaters mounted in re-entrant wells under the vapor-lift pumps. Insulation around the outside of the shields allowed operation over a wide temperature range. The apparatus can be operated at pressures to at least 3 MPa.

The vapor pressure of HFC 134a, the reference fluid in this work, has been reported by Goodwin et al. (1992), and the temperature in that boiler was used to determine the

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system pressure. From previous results with this apparatus and from propagation of uncertainty studies, we estimate that the overall uncertainty of our experimental vapor pressures reported here is 0.03% to 0.05% (1σ) of the pressure for temperatures up to about 400 K, and it increases to about 0.1% at 500 K.

Samples

The samples came from two shipments from the same supplier, and they were reported to be from the same batch of heptane. Both had a claimed nominal mole fraction purity of 0.993. Two loadings of the apparatus were made from the first shipment, and they were labeled samples 1 and 2. Sample 3 was loaded from the second shipment, which was received two years later. Because this purity level was considered to be marginal for making high accuracy measurements, the composition of all the samples was carefully monitored with a gas chromatograph, and corrections were made for the impurities found. We confirmed the analysis of the supplier. Four unidentified impurities were found in the first shipment. We used the sample without further purification, and we adjusted the results for the presence of the impurities. This adjustment was made with the relationship given by Weber and Defibaugh (1998)

$$\delta P/P = \sum_i (K_i - 1)x_i/\Delta Z_{\mathrm{lv}} \tag{1}$$

where ΔZ_{lv} is the compressibility factor difference between the saturated vapor and liquid sample and $K_i = y_i/x_i$, with x_i and y_i being the mole fractions of impurity i in the liquid and vapor phases, respectively. The K_i values were determined by measuring the compositions of both phases in the sample cylinder. All x_i values were assumed to be proportional to the peak areas of the chromatogram. K_i and ΔZ_{lv} are functions of temperature. For K_i we used the relationship

$$K_i = \exp[a_i(T_c/T)\tau^{\beta}] \tag{2}$$

which is an approximation of the expression given by Japas and Levelt-Sengers (1989). Here, $\tau = (T_c - T)/T_c$, and the critical exponent β was taken to have the practical wide-range value 0.35. The coefficients a_i for the impurities were determined from the chromatographic analysis at ambient temperature.

To calculate the compressibility factor of the saturated vapor, we made use of the estimated virial coefficients given by Weber (1995). For the liquid phase, we calculated $Z_1(T)$ from the estimated temperature variation of the density of the saturated liquid using

$$\rho_1 = \rho_c + b\tau^{\beta} \tag{3}$$

where $\rho_c = 2.315\ \mathrm{mol{\cdot}dm^{-3}}$, $T_c = 540.13$ K, and $b = 5.92\ \mathrm{mol{\cdot}dm^{-3}}$, on the basis of the data for heptane given by Reid, Prausnitz, and Poling (1987). We also made a small correction for the fact that x_i is a function of P and therefore of T.

Prior to the loading of sample 1, the apparatus was evacuated and flushed several times with heptane gas. However, when sample 1 was reanalyzed after the measurements, it was found to contain a very small amount of an additional, relatively volatile impurity. This impurity could only be a contaminant picked up from the apparatus itself. It was assumed to be a remnant of the previous contents of the apparatus, a highly fluorinated butane. We therefore took its value for K to be equal to the ratio of the two vapor pressures at ambient temperature and calculated its a value in eq 2 from this information. Sample 2 did not contain this contaminant, and we assumed that the boiler was completely purged by the first sample. Prior to the loading of sample 3, at a much later date, the apparatus was filled with a "dummy" sample of heptane which was discarded after the boiler had been operated for about 1 h. No further contamination was found. Analysis of the second shipment (sample 3) indicated an impurity "fingerprint" similar to that of the first shipment, but it also showed the presence of small amounts of three additional impurities, including one of high relative volatility. These may have been introduced during the transfer of the sample to a shipping container.

Table 1. List of Impurities in the Samples and Their Effect on Measured Pressure at Ambient Temperature, According To Eq 1

	i	K_i	$100x_i$	$100\delta P/P$
	Samples 1 and 2			
	1[a]	22	0.014	0.30
	2	2.23	0.089	0.11
	3	1.15	0.42	0.06
	4	1.25	0.11	0.03
	5	1.10	0.062	0.01
Total Sample 1			0.69	0.51
Sample 2			0.68	0.21
	Sample 3			
	1	24	0.0056	0.13
	2	3.0	0.095	0.19
	3	1.39	0.39	0.15
	4	1.20	0.035	0.01
	5	1.30	0.10	0.03
	6	1.14	0.063	0.01
	7	1.49	0.023	0.01
total			0.71	0.53

[a] Sample 1 only.

Thus, we have made measurements on three samples, each of which had a slightly different composition. Table 1 shows how much these impurities would affect the measurements at ambient temperature. From eqs 1 and 2 we see that the error decreases with increasing temperature; the measurements began at 335 K. The reference sample of HFC 134a was also analyzed with the chromatograph, and we found no impurities which would significantly alter its vapor pressure.

Results and Comparisons

Measurements were made in the temperature range 335 K to 503 K. Pressures varied from 30 kPa to 1597 kPa. The data, adjusted for the impurities, are presented in Table 2.

We used thermodynamically calculated vapor pressures to extend our results downward in temperature to the triple point, 182.607 K (Zabransky and Ruzicka, 1994). These calculations require that $\Delta_{\mathrm{vap}}H = T\Delta_{\mathrm{vap}}S$ at the saturation boundary and follow the method given by more detail by Weber and Defibaugh (1996a). The thermophysical properties required are the heat capacity of the saturated liquid C_{sat}, taken from the correlation of Zabransky and Ruzicka (1994), the ideal gas heat capacity C_p°, taken from Ruzicka and Majer (1994), the estimated gas-phase virial coefficients B and C, from Weber (1995), and the molar volume of the saturated liquid, estimated from eq 3. A reference point is required, and we chose $T_{\mathrm{ref}} = 300$ K and $P_{\mathrm{ref}} = 6.6887$ kPa. The method requires that we arbitrarily set the liquid-phase properties, $H_L = S_L = 0$, at the reference

Table 2. Experimental Vapor Pressures for Heptane

T/K	P/kPa	T/K	P/kPa
	Sample 1		
355.899	62.503	377.268	119.434
359.210	69.482	380.130	129.452
363.492	79.475	382.836	139.321
367.376	89.500	386.617	154.371
370.925	99.446	390.085	169.321
374.219	109.546	394.397	189.252
	Sample 2		
335.188	30.303	367.733	90.423
339.317	35.308	371.255	100.423
342.996	40.310	374.510	110.415
349.358	50.269	377.544	120.394
352.183	55.286	380.390	130.382
354.804	60.285	383.069	140.381
357.252	65.269	386.826	155.364
359.559	70.277	390.313	170.377
363.894	80.452	394.609	190.385
	Sample 3		
370.976	99.663	485.187	1197.453
377.313	119.622	494.803	1397.634
386.648	154.596	503.406	1597.746
394.456	189.524	371.053	99.892
405.552	249.362	377.370	119.831
413.342	299.287	386.679	154.725
426.329	399.188	394.479	189.654
437.014	498.990	446.250	598.999
446.242	598.909	349.117	49.894
454.344	698.824	354.595	59.933
461.598	798.663	359.379	69.884
468.219	898.495	363.639	79.836
468.213	898.465	367.504	89.789
474.303	998.379	371.044	99.723
479.935	1098.265		

temperature. The ideal gas enthalpy and entropy at the reference temperature are then chosen to give the correct value for the vapor pressure and its temperature derivative. We used the values $H° = 36\,545.78$ J·mol^{-1} and $S° = 99.16616$ J·mol^{-1}·K^{-1} (at a pressure of 101.325 kPa). The pressure at the triple point was calculated to be 17.4×10^{-5} kPa.

Use of both the second and third virial coefficients allowed the calculations to be extended to higher temperatures and pressures. However, at pressures above approximately 750 kPa the uncertainties increase rapidly unless the available thermophysical property data are uncommonly accurate. For example, at 520 K ($P = 2048$ kPa) a 1% error in the second virial coefficient B leads to a 0.7% error in the calculated value of the vapor pressure. We have compared our estimated values for B with experimental values from Millat et al. (1994) and with older values taken from the compilation of Dymond and Smith (1980). In general the experimental data produced somewhat larger negative values for B (1.5% to 3%), although some were smaller. The experimental values all had rather large estimated uncertainties, on the order of ±20 cm^3/mol. Generalized expressions for estimating B cannot be expected to have errors better than 1% to 2%. Below, we will also consider the case where our estimated B was 1% larger in magnitude. Uncertainties in our representations for ρ_1 and for C_{sat} would contribute smaller errors, about 0.2% at 520 K.

Our results, those of Willingham et al. (converted to the ITS-90 temperature scale), and calculated values at 20 K intervals below 300 K were fit with the equation

$$\ln(P/P_c) = (c_1\tau + c_2\tau^{1.5} + c_3\tau^{2.5} + c_4\tau^5)/T_r \qquad (4)$$

where $T_r = T/T_c$, $T_c = 540.13$ K, $P_c = (2739.7 \pm 2.5(1\sigma))$ kPa, $c_1 = -7.900\,007\,23$, $c_2 = 2.169\,775\,74$, $c_3 = -3.143\,500\,07$, and $c_4 = -3.325\,930\,87$. We gave equal weighting to all the data. We also made use of measurements of T_c and P_c by Brunner (1988), who reported the values (540.13 ± 0.05) K (converted to the ITS-90 scale) and (2734 ± 5) kPa, respectively. The latter was used as a single datum. This point and the calculated values received somewhat lower weight, corresponding to their uncertainty. The standard relative deviation of the fit was 0.03% in pressure. Deviations of the data from eq 4 are shown in Figure 1. We see that in the region of overlap, 335 K to 372 K, there is excellent agreement between our data and those of Willingham et al. and also between the data sets on our three samples. This agreement indicates that eqs 1 and 2 and our analysis have successfully accounted for the effects of the impurities. Willingham et al. gave their sample purity as 0.9988, determined from freezing point depression studies. Also shown in Figure 1 is the reasonable agreement with the recent data sets of Wisniewska et al. (1993) and of Zawisza and Vejrosta (1982) at higher temperatures. The value of the Pitzer acentric factor was found to be 0.350.

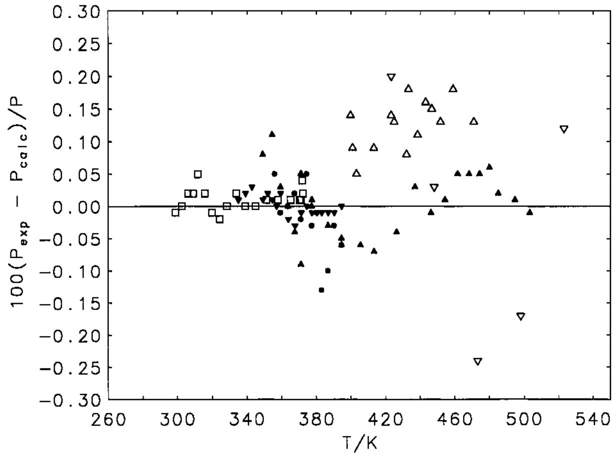

Figure 1. Deviation of the vapor pressure data from eq 4: (■) Willingham et al.; this research, (●) sample 1, (▼) sample 2, (▲) sample 3; (△) Wisniewska et al.; (▽) Zawisza and Vejrosta.

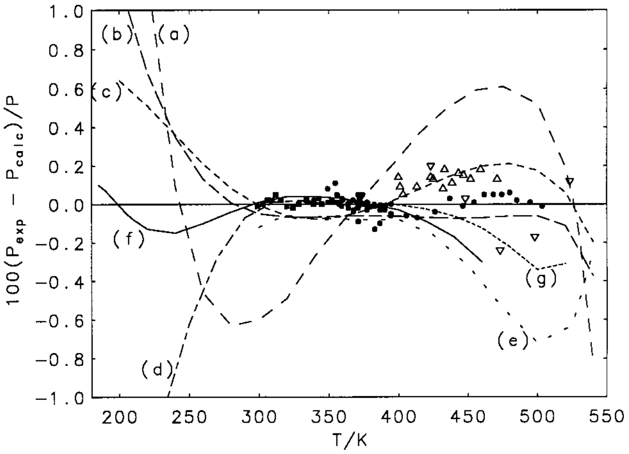

Figure 2. Deviation of other vapor pressure curves from eq 4: (a) DIPPR; (b) Poling; (c) Ambrose and Walton; (d) Ruzcika and Majer; (e) DECHEMA; (f) thermodynamic calculation; (g) thermodynamic calculation with $B \rightarrow 1.01B$.

Shown in Figure 2 are the deviations of vapor pressure curves from several other sources. All of the curves agree within about 0.1% between 280 K and 420 K except the recommended values from DIPPR (Daubert, 1990). The recommended values from DECHEMA (Stephan and Hild-

Table 3. Vapor Pressures of Heptane from Eq 4, Estimated Virial Coefficients, and Enthalpies of Vaporization

T/K	P/kPa	10^3B $\mathrm{dm^3 \cdot mol^{-1}}$	10^3C $(\mathrm{dm^3 \cdot mol^{-1}})^2$	$10^{-3}\Delta_{\mathrm{vap}}H$ $(\mathrm{kJ \cdot mol^{-1}})$
200	2.128×10^{-3}	−9453		43.08
220	2.164×10^{-2}	−6483		41.63
240	0.1401	−4784		40.26
260	0.6466	−3713		38.94
280	2.301	−2986		37.68
300	6.691	−2465		36.47
320	16.585	−2075		35.23
340	36.190	−1774		33.97
360	71.248	−1535		32.65
380	128.986	−1342	−290	31.24
400	217.970	−1183	−94	29.71
420	347.954	−1050	12	28.03
440	529.799	−938	68	26.16
460	775.565	−842	95	24.03
480	1098.92	−760	107	21.51
500	1515.11	−688	110	18.34
520	2048.46	−625	109	13.57

wein, 1987) show larger negative deviations at higher temperatures but converge at the critical point. The curves of Poling (1996) and of Ambrose and Walton (1989) agree better. The various curves all diverge at the lowest temperatures. Both Poling and Ruzicka and Majer used thermodynamically calculated vapor pressures, and we cannot explain the large relative differences.

In Figure 2 the increasing uncertainty of the thermodynamic calculation of vapor pressure becomes apparent at temperatures above 450 K. Also shown in the figure is the location the calculated curve would have if we increased the magnitude of B by 1%. This latter curve agrees much better with the data at temperatures above 420 K. This technique might have some promise for determining small errors in B in cases where the necessary thermal data are available.

We have calculated the enthalpy of vaporization $\Delta_{\mathrm{vap}}H$ of heptane by two methods. First, starting with the vapor pressure calculated via eq 4, we used the thermal data, the virial coefficients, and the reference point values to calculate $\Delta_{\mathrm{vap}}H$ at each temperature. The second method made use of the Clapeyron equation. The two methods for calculating $\Delta_{\mathrm{vap}}H$ agreed to within 0.1% between 260 K and 400 K. The difference increased to 0.3% at the triple point, and it increased to 0.6% at 500 K. The averages of the two values, along with values used for the virial coefficients, are shown in Table 3.

Conclusions

We have measured the vapor pressure of heptane between 335 K and 503 K, near the upper temperature limit of our apparatus. Our data, after correction for the detected impurities, agreed very well with the best published data in the region of overlap. We have presented a recommended vapor pressure curve for heptane from the triple point to the critical point. At temperatures above 400 K our new data should help resolve the large discrepancies found in the literature.

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