Vapor Pressures of Acetonitrile Determined by Comparative Ebulliometry

Michael B. Ewing* and Jesus C. Sanchez Ochoa

Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom

The vapor pressures of acetonitrile have been measured over the temperature and pressure range of 278 K and 4.3 kPa to 540 K and 4455 kPa. The upper limit exceeds the temperature at which decomposition of acetonitrile begins (about 536 K) so we were able to assess the effect of pyrolysis on the vapor pressures. Acetonitrile is strongly hygroscopic, and a comparison of results obtained with “wet” and “dry” samples allowed us to investigate in a similar way the effect of water as an impurity. The results have been correlated using generalized Wagner equations, a key feature of which is the use of the reversed reduced temperature $\tau = 1 - T/T_c$ where T_c is the critical temperature. The standard form with terms in τ, $\tau^{1.5}$, $\tau^{2.5}$, and τ^5 produced unacceptable systematic deviations; but the equation $\ln(p/p_c) = (T_c/T)(c_1\tau + c_{1.5}\tau^{1.5} + c_2\tau^2 + c_{2.5}\tau^{2.5} + c_{5.5}\tau^{5.5})$, where p_c is the critical pressure, fits our results from 291 K to 535 K with a standard deviation of 63×10^{-6} in ln p and significantly extends the range of correlation, toward both the triple and critical points, compared with work already in the literature. By extrapolation to T_c = 545.46 K, we obtain 4835 kPa for the critical pressure p_c and 167 Pa for the triple-point pressure at T^{s+l+g} = 229.35 K. An Antoine equation that describes the results below a pressure of 125 kPa with a standard deviation of 1.5 mK in the condensation temperature has also been obtained.

Introduction

Vapor pressures of pure substances can be measured accurately and rapidly using comparative ebulliometry.[1−5] The sample and a reference fluid are boiled, in separate ebulliometers, under a common pressure of gas such as helium or nitrogen, and the condensation temperatures T_s of the sample and T_r of the reference are measured. The common pressure is calculated from the known p, T behavior of the reference fluid as $p(T_r)$ to give a state point (p,T_s) for the sample. The method has many advantages: direct measurement of pressure is avoided, the fluids are degassed by boiling, and the ebulliometers act at heat pipes to provide high-performance thermostats. The corresponding disadvantages are the considerable demands on thermometry, the solubility of the buffer gas at high pressures, and thermal gradients due to pressure heads, although these are readily calculated and are invariably small compared to the gradients in a static apparatus. But the greatest advantage is speed of measurement; typically, a (p,T) point can be obtained in an hour compared with perhaps a day for a dew pressure in a static experiment.

Acetonitrile is an important organic solvent for polar materials, and its vapor pressure has been measured many times, although there are large discrepancies among the published values.

Measurement Section

Materials. The acetonitrile was HPLC-grade material supplied by B. D. H. Chemicals with a minimum purity of 99.9 mol % and a maximum water content of 0.02 mol %. We did not attempt to purify the material by distillation because this would have had little useful effect on the water content, which we anticipated would be the major purity problem. As shown below, water was indeed a serious impurity.

Burfield et al.[6,7] studied the effectiveness of various desiccants and drying regimes for organic solvents. Known amounts of tritiated water were added to rigorously dried solvents and the drying procedures were assessed by the residual water content obtained from the tritium activity. They found that most chemical desiccants were largely ineffective for acetonitrile, and only molecular sieves could produce “super dry” acetonitrile with mole fractions of H_2O less than 10^{-6}. Consequently, we have followed the recommendations of Burfield et al. using 3A molecular sieves, activated at a temperature of 525 K, and two-stage drying for periods of 7 days and at least 1 day, respectively.

Apparatus and Procedures. The sample ebulliometer was evacuated for 10 h, with heating to above 375 K, before loading the acetonitrile, while the ebulliometer was flushed with dry argon. A sample of volume 40 cm^3 was used for a series of measurements (identified as set A in Table 1) from low pressures up to 175 kPa, but a larger 205 cm^3 sample was required at higher reduced temperatures. This second series of measurements (set B in Table 1) was begun at atmospheric pressure, providing an overlap with those of set A and extended into the region of thermal decomposition. The acetonitrile was drawn from the same stock, but the samples were dried separately, and some contamination with water during transfer to the ebulliometer seems inevitable because acetonitrile is so highly hygroscopic.[6,7] In addition, a set of measurements was made between 354 K and 99 kPa and 431 K and 703 kPa with a sample, as supplied by B. D. H. Chemicals, to investigate the effect of water as an impurity.

Since the apparatus has been described in detail before,[2] only a brief description is given here. The sample and reference ebulliometers are connected through metal condensers (cooled with water) and traps (cooled with solid CO_2) to a common pressure line that has a 2 dm^3 ballast volume and appropriate gauges and valves that allow the apparatus to be evacuated and pressurized with dry

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* To whom correspondence should be addressed. E-mail: m.b.ewing@ucl.ac.uk.

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helium. The ebulliometers themselves were constructed from stainless steel tubing and had re-entrant thermometer wells, fitted with twin radiation shields, that provide a depth of immersion for long-stem platinum resistance thermometers of 32 cm in the sample ebulliometer and 45 cm in the reference. We have confirmed[2] experimentally that the temperature difference along the thermometer was attenuated by a factor of 10^6 for an immersion of only 15 cm. Band heaters (maximum power 140 W) were clamped to the lower 4 cm of the cylindrical boiler, and the ebulliometers were thermally insulated sufficiently well to support a temperature difference of about 200 K. However, no secondary heating was used and we relied instead on the exceptionally high thermal conductivity of the ebulliometer, acting as a heat pipe, to eliminate temperature gradients.

Thermometry is especially important in comparative ebulliometry because temperature is the only experimental physical quantity that is measured. The thermometers were calibrated on ITS-90 by N. P. L., and their resistance at the temperature of the triple point of water was checked regularly during the project. The pressure was calculated from the condensation temperature on the water using the correlation provided by Wagner[8] for the vapor pressure of water, and small corrections were applied for differences in the heads of helium and gaseous water or acetonitrile.

The measurements were always taken with increasing pressure to avoid the possibility of cross contamination between water and sample during depressurization. Similarly, the apparatus was always left under pressure during a break in the measurements. Up to 4 h were required to obtain the first point when the apparatus was initially at room temperature, but thereafter, equilibration was obtained within an hour following an increase in pressure.

Results and Discussion

Wagner[9] has developed a family of equations for correlating vapor pressures. The general form of the equation is

$$\ln(p/p_c) = (T_c/T) \sum_i c_i \tau^i \quad (1)$$

where T_c and p_c are the critical temperature and pressure and

$$\tau = 1 - T/T_c \quad (2)$$

is a reversed reduced temperature variable. The summation in eq 1 provides a bank of terms with integer and half-integer powers of τ from which the form of the correlating equation can be determined. In practice, terms in τ and $\tau^{1.5}$ are always present, and a standard form given by

$$\ln(p/p_c) = (T_c/T)(c_1\tau + c_{1.5}\tau^{1.5} + c_{2.5}\tau^{2.5} + c_5\tau^5) \quad (3)$$

has proved to be satisfactory for most results. An alternative standard form with terms in τ^3 and τ,[6] rather than $\tau^{2.5}$ and τ,[5] is also widely used. However, additional and alternative terms have been required when the data were particularly precise or extensive.[2,8−11]

Critical temperatures are readily determined (for example, by direct observation in a sealed tube), but critical pressures are much more challenging, and reliable experimental values are rare, especially for organic fluids. Equation 1 is readily modified by taking ln p, rather than $\ln(p/p_c)$, as the objective function in the regression analysis and treating ln p_c as an adjustable parameter. We have demonstrated[1] that Wagner equations are remarkably successful in extrapolating reliably to the critical pressure from surprisingly low reduced temperatures. Consequently, our preferred approach now is to combine our vapor pressures with literature critical temperatures to obtain the critical pressure p_c from the regression analysis. For acetonitrile, we have also obtained the triple-point pressure by extrapolation.

Table 1. Vapor Pressures p of Acetonitrile at Temperature T with Deviations $\Delta \ln p$ from the Wagner Equation (6)

T/K	p/kPa	$10^2\ \Delta\ln p$	T/K	p/kPa	$10^2\ \Delta\ln p$
Set A (Not in Regression)				Set B	
277.922	4.323	0.0214	354.550	100.745	−0.0085
278.625	4.490	0.0346	360.942	122.631	−0.0079
281.567	5.247	0.0382	371.739	168.122	−0.0057
285.376	6.385	0.0361	378.815	204.592	−0.0037
287.667	7.165	0.0350	384.111	235.792	0.0007
Set A (in Regression)			394.294	306.279	0.0038
290.647	8.296	0.0032	405.236	399.500	0.0056
292.746	9.182	0.0058	415.213	502.665	0.0090
295.784	10.604	0.0073	423.683	605.601	0.0043
300.824	13.366	−0.0114	431.124	708.993	0.0029
303.811	15.271	−0.0118	437.302	804.861	0.0015
309.636	19.639	−0.0150	443.496	910.819	−0.0001
315.433	24.972	−0.0023	449.596	1025.474	−0.0021
321.118	31.311	0.0073	455.736	1151.968	−0.0004
325.022	36.387	0.0117	461.874	1290.201	−0.0024
331.275	45.907	0.0109	468.370	1450.280	−0.0016
336.413	55.169	0.0054	474.052	1602.627	−0.0021
341.179	65.072	0.0064	479.154	1749.838	−0.0019
345.575	75.440	0.0067	484.769	1923.878	−0.0019
349.328	85.311	0.0039	490.370	2110.770	−0.0006
352.879	95.589	0.0047	495.752	2303.512	−0.0009
354.665	101.120	0.0025	501.480	2523.662	−0.0007
357.556	110.614	−0.0028	506.921	2747.952	0.0007
361.612	125.129	−0.0083	512.610	2999.224	0.0046
368.966	155.329	−0.0071	518.008	3254.077	0.0011
373.170	175.036	−0.0098	523.151	3512.890	0.0007
			527.790	3760.372	0.0012
			532.079	4001.463	−0.0007
			535.032	4174.613	−0.0022

Here we use Wagner equations to assess the internal consistency of our two sets of results, separately and combined. Trejo and McLure[12] reviewed the critical properties of acetonitrile, and we have adopted their experimental value, which, adjusted to ITS-90, is $T_c = (545.46 \pm 0.3)$ K.

Table 1 lists the vapor pressures of acetonitrile obtained with two samples that were dried separately. The 25 results in set A cover the range 278 K and 4.3 kPa to 373 K and 175 kPa and those in set B the range 355 K and 101 kPa to 535 K and 4175 kPa. The first five points of set A at temperatures $277.9 < T/\mathrm{K} < 288$ are discussed below but were not used for the final regression analyses.

The 29 results of set B for the larger sample were correlated by the equation

$$\ln(p/\mathrm{kPa}) = \ln(p_c/\mathrm{kPa}) + (T_c/T)(c_1\tau + c_{1.5}\tau^{1.5} + c_2\tau^2 + c_3\tau^3) \quad (4)$$

where $T_c = 545.46$ K, $p_c = 4836.3$ kPa, $c_1 = -7.601380$, $c_{1.5} = 0.074994$, $c_2 = 2.323761$, and $c_3 = -3.640424$, with standard deviations σ of 13×10^{-6} in ln p and 0.7 mK in the condensation temperature T. By contrast, the standard form of the Wagner eq 3 gave a comparatively poor fit to the same data with standard deviations $\sigma(\ln p) = 141 \times 10^{-6}$ and $\sigma(T) = 8.1$ mK and large systematic deviations. Such a comparison illustrates the difficulties of correlating vapor pressures and suggests that our results happen to be well conditioned to the form of eq 4. Nevertheless, such a high level of internal consistency for the results is most

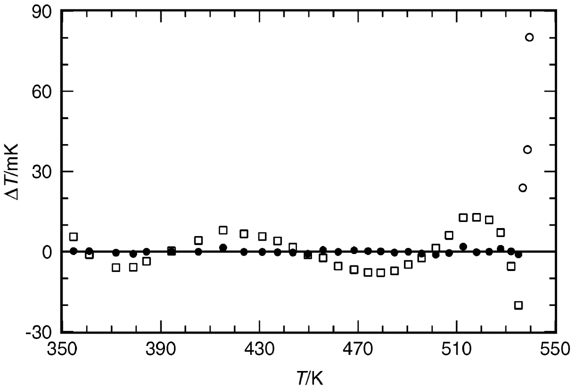

Figure 1. Deviations ΔT of condensation temperatures of acetonitrile from Wagner equations with four terms in τ: ●, deviations of set B from eq 4; ○, deviations of decomposing sample from eq 4; □, deviations of set B from standard form eq 3.

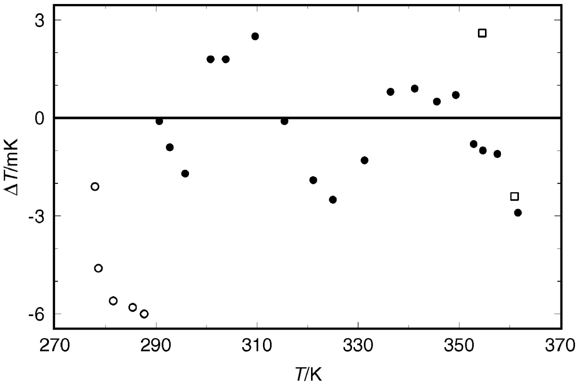

Figure 2. Deviations ΔT of condensation temperatures of acetonitrile from the Antoine eq 5: ●, set A for $T > 290.5$ K; ○, set A for $T < 290.5$ K; □, set B.

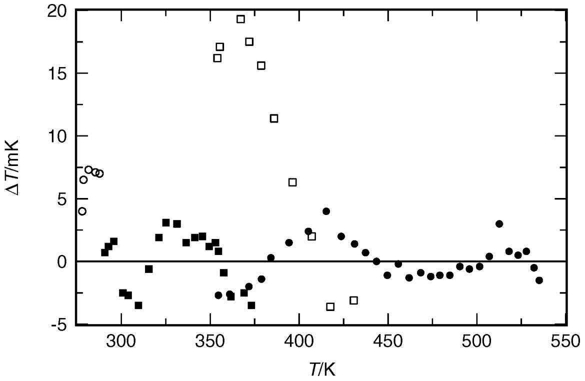

Figure 3. Deviations ΔT of condensation temperatures of acetonitrile from the final eq 6: ■, set A for $T > 290.5$ K; ●, set B; ○, set A for $T < 290.5$ K; □, "wet" sample.

pleasing considering that our estimated precision in the condensation temperatures of acetonitrile and water was 1 mK.

Three further measurements, not listed in Table 1, were made with this sample at higher temperatures, but these results are clearly affected by decomposition. If the first of these points is included in the regression, then the critical pressure so obtained increases by 1.6 kPa and standard deviations deteriorate significantly to $\sigma(\ln\, p) = 54 \times 10^{-6}$ and $\sigma(T) = 3.7$ mK. By contrast, if the final point (535.032 K, 4174.613 kPa) listed in Table 1 is omitted, then there is no change to the standard deviations and the calculated critical pressure increases by only 0.2 kPa. These results suggest that the thermal decomposition begins at a temperature between 535.0 and 536.8 K, which is just slightly higher than the 523 K value reported by Kratzke and Müller[13] as the greatest temperature at which they could work and avoid decomposition. Figure 1 shows the deviations from eq 4 of the results obtained with sample B, and the abrupt onset of decomposition is clear. Deviations of these data from the standard Wagner eq 3 are also plotted to show the comparatively large and systematic sinusoidal deviations.

The results obtained at lower pressures with sample A are not of such high quality as those in set B, but nevertheless a Wagner equation with terms in $\ln p_c$, τ, $\tau^{3/2}$, and τ^2 fits the data of set A at temperatures above 290 K with standard deviations of $\sigma(\ln\, p) = 49 \times 10^{-6}$ and $\sigma(T) = 1.2$ mK. This equation has one fewer term in τ than is usual for a Wagner equation and the value of the critical pressure obtained was ridiculously high, but no further terms were significant in the regression. An Antoine equation is much more convenient for routine calculations at low pressures and

$$\ln(p/\mathrm{kPa}) = 14.7340 - 3268.53/(T/\mathrm{K} - 31.615) \quad (5)$$

fits the results for set A over the temperature range 290 K to 362 K (or 8 kPa to 125 kPa in pressure) with standard deviations of $\sigma(\ln\, p) = 61 \times 10^{-6}$ and $\sigma(T) = 1.5$ mK.

Figure 2 shows the deviations from the Antoine eq 5 of the results from sample A and those from sample B in an overlapping temperature range. It was difficult to achieve smooth boiling of the water for the five results at very low pressures (4.3 to 7.2 kPa) because the ebulliometers, originally designed for high pressures, were not fitted with bubble caps.[33] These five data have not been included in any of the regression analyses because they fell short of the quality of the other results, but they are plotted in Figures 2−6 to show that the deviations from the smoothing equations are very small compared with those for the literature data.

Although the results obtained with samples A and B individually are internally consistent at a very high level and span only 3.7 mK at the normal boiling temperature, it has been rather difficult to combine the two data sets in a way that does justice to their individual merits. Nevertheless, the Wagner equation given by

$$\ln(p/\mathrm{kPa}) = \ln(p_c/\mathrm{kPa}) + (T_c/T)(c_1\tau + c_{1.5}\tau^{1.5} + c_2\tau^2 + c_{2.5}\tau^{2.5} + c_{5.5}\tau^{5.5}) \quad (6)$$

with $T_c = 545.46$ K and its 5 terms in τ, fits the combined data sets with standard deviations $\sigma(\ln\, p) = 63 \times 10^{-6}$ and $\sigma(T) = 2.0$ mK. The regression coefficients in eq 6 were $p_c = 4835.3$ kPa, $c_1 = -7.542771$, $c_{1.5} = -0.549679$, $c_2 = 4.958924$, $c_{2.5} = -5.030732$, and $c_{5.5} = -1.699257$. Figure 3 compares our experimental results with eq 6 as deviations ΔT in condensation temperature; such a deviation plot is especially useful for ebulliometric measurements because the uncertainty in boiling temperature should be approximately constant unlike plots of Δp or $\Delta \ln p$.

At low temperatures, there are systematic sinusoidal deviations, with extremes of about 3.5 mK, but above 425 K, or 600 kPa in pressure, eq 6 gives an excellent representation of the data and extrapolates smoothly to a critical pressure of (4835 ± 0.7) kPa. The quoted uncertainty in p_c is the standard deviation from the regression to eq 6, but if account is taken of the uncertainty of ±0.3 K given by Trejo and McLure for their measurement

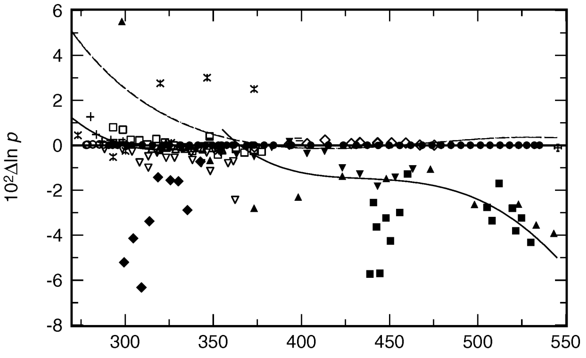

Figure 4. Fractional deviations $\Delta\ln p = \Delta p/p$ of the vapor pressure of acetonitrile from eq 6: ●, this work included in the regression; ○, this work excluded from the regression; +, Trejo et al.[12] critical point; ◇, Kratzke et al.;[13] ■, Mousa;[14] ▲, Francesconi et al.;[15] +, Putnam et al.;[16] ▽, Dojcansky;[17] △, Meyer;[18] ◆, Hall et al.;[19] □, Heim;[20] ▼, Warowny;[22] ×, DiElsi et al.;[25] |, Wilson;[26] −, Smith et al.;[17−31] *, Owens;[32] solid line, Dykyj et al.;[21] dot-dashed line, Yaws;[23] dashed line, DIPPR Project.[24]

of T_c, then the error in p_c increases to ±18 kPa. The agreement between our calculated value of p_c and Trejo's and McLure's direct observation of (4.83 ± 0.02) MPa is excellent. Although the sinusoidal deviations indicate that eq 6 is not perfect, the close agreement in the overlapping region between the results obtained with the two samples is very pleasing, and indeed, a standard deviation of 2.0 mK and a maximum deviation of 4 mK over such a wide temperature range is excellent compared with the literature that is discussed below. We also made measurements with a sample that was not dried over molecular sieves to assess the possible affect of water as an impurity. As Figure 3 shows, the condensation temperature is elevated by about 16 mK near atmospheric pressure but this is reduced to −3 mK at a pressure of 700 kPa.

The vapor pressures of acetonitrile have been measured many times, and the results are summarized in Figure 4 as fractional deviations, $\Delta\ln p = \Delta p/p$, from eq 6. Inconsistencies in the vapor pressures of organic compounds are not uncommon, but it is immediately clear that the results for acetonitrile are exceptionally scattered. Below the normal boiling temperature (354 K), the majority of the results are within 1% of our work, but results obtained by Hall and Baldt[19] are lower by up to almost 7%, while those obtained by Owens et al.[32] are too high by about 3%. Near room temperature, Francesconi et al.[15] lies above our equation by almost 6% (to give a total span of more than 12% in the literature data) but is lower by between 1 and 4% above 350 K. Mousa[14] also lies 4% below our work near the critical state but by 6% at 440 K.

The comparison with the literature is shown in Figure 5 on a more sensitive scale to reduce the congestion, but this discards the results of Mousa,[14] Francesconi et al.,[15] and Hall and Baldt,[19] none of which is discussed further. The remaining results at pressures above 200 kPa are those of Kratze and Müller,[13] Warowny,[22] and the critical point.[12] The excellent agreement with Trejo and McLure[12] at the critical point was noted above. The 14 vapor pressures reported by Kratze and Müller[13] in the temperature range 353−475 K are in good agreement with our work and have a root-mean-square (rms) deviation of 0.024% from eq 6, which is significantly less than their estimated accuracy of 0.1%. The work of Warowny,[22] which extends to 463 K or 1.3 MPa, lies below us (except for one pressure), but the deviation is only 0.7% on average.

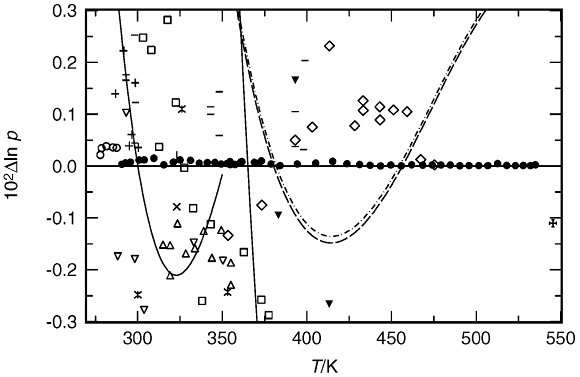

Figure 5. Fractional deviations $\Delta\ln p = \Delta p/p$ of the vapor pressure of acetonitrile from eq 6: ●, this work included in the regression; ○, this work excluded from the regression; +, Trejo et al.[12] critical point; ◇, Kratzke et al.;[13] +, Putnam et al.;[16] ▽, Dojcansky;[17] △, Meyer;[18] □, Heim;[20] ▼, Warowny;[22] ×, DiElsi et al.;[25] |,Wilson;[26] −, Smith et al.;[17−31] *, Owens;[32] solid line, Dykyj et al.;[21] dot-dashed line, Yaws;[23] dashed line, DIPPR Project.[24]

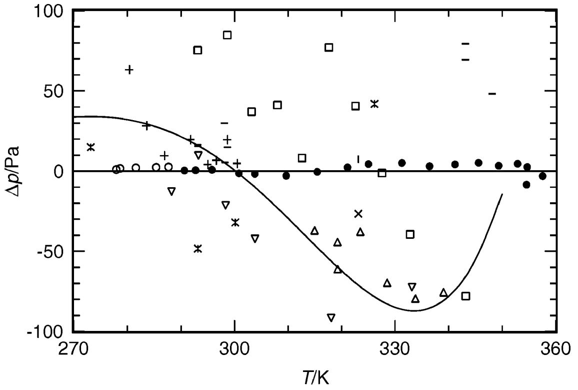

Figure 6. Deviations Δp of the vapor pressure of acetonitrile from eq 6: ●, this work included in the regression; ○, this work excluded from the regression; +, Putnam et al.;[16] ▽, Dojcansky;[17] △, Meyer et al.;[18] □, Heim;[20] ×, DiElsi et al.;[25] |, Wilson;[26] −, Smith et al.;[17−31] *, Owens;[32] solid line, Dykyj et al.[21]

Fractional deviations $\Delta\ln p = \Delta p/p$ are rather severe at low pressures, so Figure 6 gives the deviations in terms of pressure. Results obtained by Putnam et al.[16] are consistently above our measurements, but the average deviation is only 19 Pa, while the work of Meyer et al.[18] is consistently low by up to 96 Pa. The vapor pressures obtained by Dojcansky et al.[17] are also lower than eq 6 except for one pressure, while the work of Heim et al.[20] cuts across our results with a rms deviation of 60 Pa. Our five results below 8 kPa, which we excluded from the regression because the experimental condensation temperatures were unstable, are also included in Figure 6; the deviations Δp are in the range 0.9−2.5 Pa, which, when compared to the literature data, indicates the exacting criteria we have applied to our measurements.

Several correlations have been proposed for the vapor pressures of acetonitrile and their deviations from eq 6 are also plotted in Figures 4 to 6. The Antoine equation, for temperatures up to the normal boiling temperature, obtained by TRC and recommended recently in a volume by Landolt−Börnstein[21] is based on the work of Putnam[16] and Meyer[18] as Figures 5 and 6 show. However, they also recommend an Antoine equation between the normal boiling temperature and 530 K, which is much less successful. It gives pressures 700 Pa higher than the low-pressure version at the normal boiling temperature (see Figure 5), but thereafter the calculated pressures are progressively too low, following Francesconi et al.,[15] Mousa,[14] and the highest pressure of Warowny[22] (see Figure 4), reaching −3.9% at 530 K. Although these deviations are less than the equation's estimated reliability of 5%, an Antoine equation is not really appropriate[33] for fitting vapor pressures above a reduced temperature of about 0.75. The correlations proposed by Yaws[23] and by DIPPR[24] use the same form of equation and have some identical parameters. Consequently, the calculated pressures are very similar and are virtually coincident on the scale of Figure 4. These two equations relied on Kratzke and Müller[13] above atmospheric pressures as Figures 4 and 5 show but are drawn too high by Owens et al.[32] below 350 K; deviations from eq 6 are too large to be included in Figure 6, but do appear in Figures 4 and 5.

Extrapolation downward is a severe test of a vapor pressure equation, and Wagner equations are, perhaps, especially susceptible because the reversed-temperature variable τ increases at lower temperatures. Frenkel et al.[34] have investigated extrapolation with the standard forms of the Wagner equation and showed that negative values of $\mathrm{d}p/\mathrm{d}T$, which lead to negative enthalpies of vaporization, may occur. Putnam et al.[16] report a triple point at $T^{\mathrm{s+l+g}} = 229.349$ K but not the corresponding pressure. DIPPR[24] uses the $T^{\mathrm{s+l+g}}$ of Putnam et al. and calculates the triple-point pressure as $p^{\mathrm{s+l+g}} = 187$ Pa. From eq 6, we obtain 229.349 K and 167 Pa for the triple point; $\mathrm{d}p/\mathrm{d}T$ decreases smoothly and is positive at all stages of the extrapolation over 60 K.

Although the combination of results obtained with two samples that evidently differed somewhat in their water content lead to a difference of 3.7 mK at the normal boiling temperature and to small systematic deviations from eq 6, such imperfections are very slight compared with the scatter of the data in the literature and the difference of 16 mK that we observed with a sample that had not been dried. At temperatures above 425 K, the measurements presented here resolve the large discrepancies that existed in the literature, and we conclude that eq 6 is by far the most reliable equation for the vapor pressure of acetonitrile. In particular, it extrapolates smoothly to both the triple point and the critical point, and the calculated vapor pressures at the extremes of the liquid regime are in excellent agreement with the best estimates in the literature.

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