

Experimental vapour pressures of eight n-Alkanes (C₁₇, C₁₈, C₂₀, C₂₂, C₂₄, C₂₆, C₂₈ and C₃₁) at ambient temperatures

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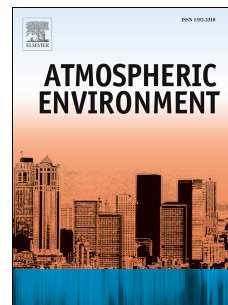
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Experimental vapour pressures of eight n-alkanes (C₁₇, C₁₈, C₂₀, C₂₂, C₂₄, C₂₆, C₂₈ and C₃₁) measured at ambient temperatures

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Experimental Vapour Pressures of Eight n-Alkanes (C₁₇, C₁₈, C₂₀, C₂₂, C₂₄, C₂₆, C₂₈ and C₃₁) Measured at Ambient Temperatures

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37 **ABSTRACT**

38 We present direct room-temperature vapour pressure measurements for eight semi-volatile n-
39 alkanes of atmospheric importance. Measured vapour pressures range from $8.4 \pm 1.6 \times 10^{-3}$ Pa for
40 C_{17} , to $1.7 \pm 0.6 \times 10^{-8}$ Pa for C_{31} . The new measurements for C_{17} - C_{18} are in reasonable agreement
41 but at the lower end of values in the literature; the new measurements for C_{28} and C_{31} are one-to-
42 two orders of magnitude higher than most literature values, but six orders of magnitude higher than
43 the lowest values in the literature. Our measurements are suitable for atmospheric aerosol
44 modelling and interpretation of environmental measurements, interpolated in carbon number where
45 necessary, and extrapolated over temperatures relevant to the atmospheric boundary layer using the
46 Clausius-Clapeyron equation with literature values of the enthalpy of vaporisation.

47
48 **Keywords:** Physico-chemical properties; vapour pressure; n-alkanes

49

50 **1. INTRODUCTION**

51 The equilibrium saturation vapour pressure (henceforth vapour pressure, p) of a compound is an
52 intrinsic physical property related to its molar entropy and molar volume, and which plays a crucial
53 role in determining a compound's transport behaviour in industrial, environmental, or biological
54 media. Vapour pressure is defined as the pressure exerted by a pure substance, at a given
55 temperature, in a system containing only the vapour and condensed phase (liquid or solid) of the
56 substance at equilibrium (Calvert, 1990). The vapour pressure of a substance is highly dependent
57 upon temperature through the Clapeyron and Clausius-Clapeyron equations (e.g. Atkins et al. 2018),
58 and varies for different compounds of the same molecular mass due to molecular interactions (inter-
59 and intramolecular in the condensed, and intramolecular in the vapour phase). For a substance to be
60 in phase equilibrium, it must be in chemical, thermal and mechanical equilibrium (Bilde et al.,
61 2015).

62
63 Many compounds of environmental interest - e.g., sulphuric acid, persistent organic pollutants, and
64 (our focus in the current study) organic compounds derived from crude-oil fractionation — have
65 small but environmentally important vapour pressures, the accurate measurement of which poses a
66 significant experimental challenge, particularly for semi-volatile (1 to 10^{-6} Pa at room temperature)
67 and 'non-volatile' ($p < 10^{-6}$ Pa) organic compounds. Given the exponential increase in the number of
68 unique isomers possible as a function of carbon atoms in an organic molecule, the number of
69 organic compounds in an atmospheric sample could be in the range of 10^3 - 10^4 (Goldstein and
70 Galbally, 2007). Comparing these relative numbers with the experimental saturation vapour
71 pressure literature available for atmospherically relevant organic molecules, it is evident that very
72 limited data are available for low volatility and polyfunctional molecules, largely due to
73 measurement challenges (Barley and McFiggins, 2010; Compernelle et al., 2011; Bilde et al.,
74 2015). There are, however, well established experimental methods that provide good results at low
75 pressures; for example the transpiration (Verevkin et al., 2000) and the Knudsen effusion techniques

76 (Dekruif and Vanginkel, 1077; Hallquist et al., 1997). Vapour pressure measurements have been
77 conducted at ambient temperatures for few organic compounds using different techniques based
78 upon the rate of evaporation of a compound under well controlled conditions (Razzouk et al., 2009;
79 Cappa et al., 2007; Koponen et al., 2007). The majority of studies however, estimate p from
80 experiments performed at high temperatures (Sawaya et al., 2006; O'Meara et al., 2014 and refs
81 within), with subsequent extrapolation to ambient temperatures.

82
83 Ultrafine particles (UFP, with particle diameter $D_p < 100$ nm) in the urban atmosphere are
84 dominated by particles composed of semi-volatile organic compounds (SVOC) (Harrison et al.,
85 2011; Kumar et al., 2014). Accumulating evidence indicates that UFP are toxic and have potentially
86 harmful effects on human health (Atkinson et al., 2010). In order to understand and model the
87 atmospheric behaviour of SVOC, it is necessary to specify their chemical composition, their phase
88 partitioning and the size distribution of the particulate fraction, and the vapour pressures of the
89 constituent molecules (Harrison et al., 2019; Nikolova et al., 2018). Diesel exhaust vapour and
90 particulate phases consist of SVOC in the range $C_{12} - C_{34}$ (Alam et al., 2016). Many of these SVOC
91 in UFP have solid-liquid phase transitions at temperatures well above room temperature but are
92 usually regarded as being present in UFP as super-cooled liquid mixtures. Thus, vapour pressures,
93 at atmospherically relevant temperatures (i.e., approximately 240-310K for the near-surface
94 atmosphere), are of fundamental importance for developing atmospheric and thermodynamic
95 models (Clegg et al., 2008). For unstudied compounds (usually those without industrial
96 applications), numerous vapour pressure estimation techniques are available in the literature, based,
97 for example, on structure-activity relationships. For compounds with industrial applications,
98 experimental data for vapour pressures and thermodynamic quantities may exist but at much higher
99 temperatures than found in the atmosphere (Barley and McFiggans, 2010). Vapour pressure
100 estimation and extrapolation methods have recently been reviewed (Bilde et al., 2015; O'Meara et
101 al., 2014; Barley and McFiggans, 2010). Since the measured thermodynamic property data are

102 scarce and mostly unavailable for atmospherically relevant compounds, these estimation methods
103 are widely used as an approximation.

104 n-Alkanes are important constituents of the atmosphere, arising from both anthropogenic and
105 biogenic sources (Dunmore et al., 2015; Harrad et al., 2003; Sartin et al., 2002; Fraser et al., 1997).
106 Compounds from C₁₀ to C₃₀ partition between the vapour and condensed phases, and hence
107 influence concentrations of airborne particulate matter (Fujitani et al., 2012; Lipsky and Robinson,
108 2006). C₁₀ to C₃₀ n-alkanes are important components of vehicle emissions, deriving from both
109 diesel fuel and lubricating oil (Sakurai et al., 2003; Karjalainen et al., 2016; Alam et al., 2016).
110 Prediction of the atmospheric behaviour of diesel exhaust particles requires knowledge of the
111 physico-chemical properties of their chemical constituents, of which n-alkanes are among the most
112 abundant (Harrison et al., 2016; Alam et al., 2018).

113

114 The majority of literature values of vapour pressure of the n-alkanes were estimated from
115 extrapolation of vapour pressures measured at higher temperatures (Chirico et al., 1989; Morgan
116 and Kobayashi, 1994; Sawaya et al., 2006; Razzouk et al. 2009). Very few studies have measured
117 vapour pressures of n-alkanes at 298 K (Chickos and Hanshaw, 2004a; Chickos and Hanshaw,
118 2004b) and more recently extended measurements (and estimations) for n-alkanes up to n-C₉₂
119 (Chickos et al., 2009). Although variability amongst reported vapour pressures is relatively small
120 for the more volatile compounds, literature values for the lower volatility compounds can vary by
121 more than five orders of magnitude for a single compound (see Figure 3 of Nikolova et al., 2018
122 and cf. Figure 1, below). With such a large range of extrapolated vapour pressures for a given
123 compound, the behaviour of atmospheric models will depend greatly on which set of vapour
124 pressures is adopted (Nikolova et al., 2018).

125

126 In this study, the transpiration method is adopted to make new measurements of vapour pressures of
127 eight low volatility n-alkanes (C₁₇, C₁₈, C₂₀, C₂₂, C₂₄, C₂₆, C₂₈ and C₃₁) at close to ambient

128 temperatures. In the transpiration method, a stream of nitrogen is slowly passed over the headspace
129 above the pure n-alkane, picking up and transferring any material which is then trapped by a sorbent
130 and analysed using comprehensive gas chromatography time-of-flight mass spectrometry. The
131 vapour pressure is then calculated based on the mass of the compound transferred by the nitrogen
132 gas stream (Verevkin et al., 2000).

133

134 **2. EXPERIMENTAL**

135 **2.1 Experimental Setup**

136 The experimental methodology was adopted from Verevkin et al. (2000) and is briefly described
137 here. Individual n-alkane standards, C₁₇, C₁₈, C₂₀, C₂₂, C₂₄, C₂₆, C₂₈ and C₃₁ were purchased from
138 Sigma Aldrich, UK (purity >99%). Approximately 0.5 g of the individual n-alkane was dissolved in
139 dichloromethane (DCM, purity ≥99.9%; VWR International Ltd, UK) and ultrasonicated for 180
140 min at 298 K. The n-alkane was then coated onto 1 mm diameter glass beads; microscopy revealed
141 the liquid coating to be present as a super-cooled liquid. Super-cooled liquid has a higher saturation
142 vapour pressure than the more thermodynamically stable, but presumably kinetically hindered,
143 crystalline solid. The coated beads were packed into a U-tube of length 20 cm and inner diameter
144 0.5 cm, and kept at a constant temperature of 298(±2)K, using a dry bath/block heater. A gentle flow
145 of nitrogen (CP grade (N5.2) BOC, purity 99.9992%) was passed through the U-tube, such that
146 contact time with the coated beads was long enough to allow the vapour to equilibrate with the pure
147 liquid phase, after which the saturated vapour was stripped out of the nitrogen gas flow in a
148 stainless steel thermal adsorption tube. Adsorption tubes (designed to collect SVOC from C₇ to C₄₀)
149 were packed with 1 cm quartz wool, 300 mg Carbograph 2TD 40/60 (Markes International Ltd,
150 UK), and were analysed using 2-dimensional Gas Chromatography Time of Flight Mass
151 Spectrometry (GC×GC-ToFMS). The optimum flow rate of nitrogen used in these experiments was
152 between 15.6 – 31.2 cm³ min⁻¹, in order to not be too slow, thus avoiding transportation of material
153 from the U-tube due to diffusion, and not too fast, to ensure saturation of the nitrogen flow with the

154 n-alkane (Verevkin et al. 2000). Assuming that the saturated nitrogen flow was subject to Dalton's
155 law of partial pressures, the vapour pressure, p was calculated by assuming the validity of the ideal
156 gas law (eq 1).

157

$$p = \frac{mRT}{V(\text{total})MW} \approx \frac{mRT}{V(N_2)MW}$$

158

(eq1)

159

160 Where p is the vapour pressure (Pa), m is the mass of the measured n-alkane (g), R is 8.3144598 J
161 $\text{K}^{-1} \text{mol}^{-1}$, T is temperature (K), $V(\text{total})$ is the total volume of gas sampled, which is closely
162 approximated by $V(N_2)$, the calculated volume of N_2 (m^3) and MW is the molar mass (g mol^{-1}). The
163 vapour pressure, p , was calculated from the mass of the n-alkane collected on the adsorption tube
164 after the sampling time period. Each experiment was repeated five times with the exception of n-C₃₁
165 (completed four times) as the time taken for this experiment was >10 days. Blanks were also
166 sampled and all were below detection limit.

167

168 2.2 Analytical Instrumentation

169 Adsorption tubes were desorbed using thermal desorption (Unity 2, Markes International Ltd, UK)
170 and subsequently analysed using a gas chromatograph (GC, 7890A, Agilent Technologies, USA)
171 equipped with a Zoex ZX2 modulator (Houston, USA). The first dimension was equipped with a
172 non-polar capillary column (SGE DBX5; 30 m, 0.25 mm ID, 0.25 μm – 5% phenyl
173 polysilphenylene-siloxane), and the second dimension was equipped with a mid-polar capillary
174 column (SGE DBX50; 4.0 m, 0.1 mm ID, 0.1 μm – 50% phenyl polysilphenylene-siloxane). The
175 GC \times GC was interfaced with a BenchTOF-Select, time-of-flight mass spectrometer (Markes
176 International Ltd, UK) with a scan speed of 50 Hz and mass range 35 – 600 m/z. All data produced
177 was processed using GC Image v2.5 (Zoex Corporation, USA). The adsorption tubes were spiked
178 with 1 ng of deuterated internal standards, eicosane-d₄₂ and pentacosane-d₅₂ (Sigma Aldrich, UK),

179 for quantification and desorbed onto the cold trap at 380°C for 15 min (trap held at 20°C). The trap
180 was then purged onto the first dimension column at 380°C and held for 3 min. The initial
181 temperature of the primary oven was 80°C and then increased by 2.5°C min⁻¹ to 320°C and held for
182 5 min. The initial temperature of the secondary oven was 80°C and was increased by 2.5°C min⁻¹ to
183 150°C and then increased by 3.0°C min⁻¹ to 330°C and held for 8 min. Helium was used as the
184 carrier gas at a constant flow rate of 0.8 L min⁻¹.

185

186 Compounds were identified based on the NIST mass spectral library, known retention times and in
187 conjunction with authentic standards. The quantification for n-alkanes was performed by the linear
188 regression method using seven-point calibration curves established between the authentic
189 standards/internal standard concentration ratios. The calibration curves for all n-alkanes were highly
190 linear ($r^2 > 0.99$).

191

192 3. RESULTS AND DISCUSSION

193 The observed experimental vapour pressures are presented in Table 1, and illustrate the repeatability
194 of the transpiration technique for measuring individual vapour pressures of n-alkanes. Due to the
195 slight deviation in the temperature (296 – 300 K), the observed vapour pressures were adjusted to
196 298 K for each compound using the Clausius-Clapeyron equation, integrated assuming the enthalpy
197 of vaporisation is independent of temperature over the range of the temperature correction (eq 2).

198

$$p_{298K} = \frac{p_i}{\exp\left(\frac{\Delta H_{vap}}{R}\right)\left(\frac{1}{298} - \frac{1}{T_i}\right)}$$

199

(eq 2)

200

201 Where p_{298K} is the vapour pressure at 298 K, p_i is the measured vapour pressure of n-alkane (i) at
202 observed T (K), ΔH_{vap} is the enthalpy of vaporisation (obtained from Chickos and Hanshaw,.

203 2004a), or calculated using $\Delta H_{vap} = -3.82(\pm 0.03) \ln p_i + 70.0(\pm 0.2)$ adopted from Goss and
204 Schwarzenbach (1999), R is the universal gas constant ($8.3144598 \text{ J K}^{-1} \text{ mol}^{-1}$) and T_i is the
205 measured temperature during the experiment for specific n-alkane (i).

206 The ΔH_{vap} is a function of temperature and is not constant. Therefore, extrapolation of vapour
207 pressures to higher temperatures or extrapolation from higher temperature data for a given
208 compound to ambient temperatures leads to significant uncertainty. Unlike the majority of
209 previously published literature (discussed herein), the experimental vapour pressures presented in
210 Table 1 are made close to ambient temperatures (296 – 300 K) for all compounds and so the
211 Clausius-Clapeyron equation can be used to adjust the presented vapour pressures to 298 K.

212

213 3.1 Comparison with Published Data

214 Figure 1 illustrates the absolute difference of \log_{10} saturation vapour pressure between literature
215 data and measurements made in our lab. Although, the vapour pressure data presented in this study
216 are amongst the lowest for n-C₁₇ and n-C₁₈ alkanes in comparison to the literature, they are in
217 reasonable agreement (see Figure 1). Similarly, the vapour pressure of n-C₂₀ alkane is lower than the
218 selected literature, but in excellent agreement with the estimation methods of Nannoolal et al.
219 (2008) and Myrdal and Yalkowsky (1997) when using the boiling point of Joback and Reid (1997).
220 There is very good agreement for n-C₂₂ and n-C₂₆ alkane vapour pressures when compared to the
221 estimation method of Compernelle et al. (2008) and the experimentally determined pressures of
222 Goss and Schwarzenbach (1999), Chickos and Hanshaw (2004a) and Morgan and Kobayashi
223 (1994). For n-C₂₄ and n-C₂₈ alkanes, the experimental saturation vapour pressures are higher than
224 the saturation vapour pressures among the selected literature and these two compounds do not well
225 fit the linear trend seen in Figure 2. Their measured vapour pressures were, however, very
226 repeatable (Table 1) and we have no reason to doubt the quality of the data. The saturation vapour
227 pressure of n-C₃₁ is in very good agreement with the estimation method of Compernelle et al.
228 (2001) and the experimentally determined pressure reported by Chickos and Hanshaw (2004b), but

229 are relatively much higher than those estimated by Kudchadker and Zwolinski (1966), Nannoolal et
230 al. (2008) and Myrdal and Yalkowsky (1997); the latter two studies using the boiling point of
231 Joback and Reid (1987).

232 Kudchadker and Zwolinski (1966) report some of the lowest vapour pressures among the selected
233 literature (see Figure 1). They use an extrapolation of existing experimental data (measured by the
234 chemical and petroleum industries, at unreported but presumably much higher temperatures) for n-
235 alkanes based on Antoine constants and the Kreglewski-Zwolinski correlation. The extrapolation
236 capabilities of the Antoine equation are limited; particularly for low pressures and near the triple
237 point, and it is usually utilised over a limited temperature range. Extrapolation of vapour pressure
238 data using the Antoine equation should be avoided when temperature intervals for correlation
239 exceed 50 K (Ruzicka and Majer, 1996). Their vapour pressures however, are in good agreement
240 with those estimated by Nannoolal et al. (2008) and Myrdal and Yalkowsky (1997) when using the
241 boiling point of Joback and Reid (1987). Ruzicka and Majer (1996) investigated four types of
242 empirical relationships frequently used for correlation of vapour pressure data, including Antoine,
243 Wagner, Quasi-polynomial and Cox equations. They demonstrated that the use of different types of
244 correlation equations can considerably affect the results of the extrapolation, and indicated that the
245 Antoine equation revealed the poorest performance, which is related to over-fitting of the vapour
246 pressure data; a typical effect observed when using simple extrapolations with too many parameters.
247 Morgan and Kobayashi (1994) reported direct vapour pressure measurements of ten n-alkanes in the
248 C₁₀ – C₂₈ range, at temperatures between 323 and 588 K. Their data for n-C₂₂ is in good agreement
249 with this study but there is less agreement for the less volatile n-alkanes (n-C₂₄ and n-C₂₈). This is
250 due to the vapour pressures of the latter alkanes being measured at elevated temperatures (n-C₂₄:
251 453–588 K and n-C₂₈: 483–588 K). Vapour pressure data measured at the conditions of interest (298
252 K) have lower uncertainty than data that are extrapolated from significantly larger temperatures.
253 The authors discuss that the accuracy of low pressure direct measurements can be affected by the
254 inadequacy of the experimental method, phenomenological effects, and thermal decomposition.

255 Vapour pressure data can also be affected by small impurities within the pure n-alkane, particularly
256 for the less volatile hydrocarbons, or vapours that may interfere with the measurements (e.g.
257 impurities present in the carrier gas). Thermal decomposition is known to limit the accuracy of
258 critical property measurements such as the critical pressure, critical temperature, melting and
259 boiling points (Morgan and Kobayashi,1991). The study also used the Wagner vapour pressure
260 equation to extrapolate between mid-pressure range data towards low reduced temperatures which
261 limits the flexibility of the relationship in low-pressure extrapolations. Many studies have identified
262 the Cox equation as the most reliable for extrapolation towards low temperatures as they offer the
263 possibility of changing both the number of parameters and the reference temperature and pressure
264 (Ruzicka and Majer, 1996). It is, therefore, not surprising that the reported vapour pressures in
265 Chirico et al. (1989), Chickos and Hanshaw (2004a) and Ruzicka and Majer (1993) are very
266 similar, and in excellent agreement, particularly for the low molecular weight n-alkanes.

267

268 As the chain length of the n-alkanes increases, the intermolecular van der Waals forces increase, up
269 until a chain length at which the sample can be vaporised only through rupture of the C-C bonds
270 (Morgan and Kobayashi, 1991). This occurs typically close to C_{100} , where samples will have a
271 melting point but no longer have a triple point. Most of the estimation methods reported in the
272 literature require a normal boiling point that is used to extrapolate down to atmospherically relevant
273 temperatures (Barley and McFiggans, 2010). Due to the high boiling point, small errors in the slope
274 can produce substantial differences in the predicted vapour pressure, particularly for the low
275 molecular weight compounds.

276

277 **3.2 Use by Atmospheric Science Community**

278 A number of estimation methods to calculate vapour pressures have been used in the atmospheric
279 science community (Myrdal and Yalkowsky, 1997; Nannoolal et al., 2008; Compennolle et al., 2011;
280 O'Meara et al., 2014). Myrdal and Yalkowsky, 1997 and Nannoolal et al. (2008) calculate vapour

281 pressures using the temperature boiling points of Joback and Reid (1987), Stein and Brown (1994)
282 and Nannoolal et al (2004). For example UmanSysProp
283 (<http://umansysprop.seaes.manchester.ac.uk>) is an online web-based facility for the prediction of
284 properties of individual organic compounds (including sub-cooled liquid vapour pressure) using
285 specific functional groups ((Topping et al., 2016). Under standard atmosphere conditions, the
286 methods of Myrdal and Yalkowsky (1997) and Nannoolal et al. (2008) using Joback and Reid
287 (1987) boiling points produce the lowest vapour pressures for the n-alkanes studied in comparison
288 to the same methods but using the boiling point of Stein and Brown (1994), see Figure 2. The
289 discrepancy is more evident for $n > 20$, where the deviations of the sub-cooled vapour pressure
290 become very large. Many studies have reported that the method of Joback and Reid (1987) tends to
291 over-predict the boiling points of the compounds measured in this study, and hence underestimates
292 the slope of the vapour pressure curve (Clegg et al., 2008; Barley and McFiggans, 2010;
293 Compennolle et al., 2011). On the other hand, the estimation of vapour pressure by Myrdal and
294 Yalkowsky (1997) using the boiling point of Nannoolal et al. (2004) tends to overestimate vapour
295 pressures (2010). Figure 2 illustrates the substantial range of estimated (and measured) vapour
296 pressures for the studied n-alkanes. The disagreement between estimated vapour pressures of the
297 same compound at high molecular weight (over 9 orders of magnitude) illustrates the need to
298 directly measure vapour pressures at the conditions of interest, and show the difficulties in
299 accurately extrapolating and predicting data at ambient temperatures. This is further discussed in
300 Nikolova et al. (2018).

301

302 A new vapour pressure estimation method ('EVAPORATION') for zero-, mono- and poly-
303 functional groups has recently been published (Compennolle et al., 2011). Although this method is
304 particularly developed for oxidised biogenic molecules, it has been reported to produce accurate
305 (O'Meara et al., 2014). O'Meara et al. (2014) in their assessment of vapour pressure estimates have
306 compared the vapour pressure error of organic compounds based on seven methods, including

307 EVAPORATION. They show that the error in the vapour pressure among the 90 organic compounds
308 is relatively small for the EVAPORATION method (running close to zero).

309

310 Overall, the technique described in this study gave repeatable measurements and vapour pressures
311 intermediate between the highest and lowest values available from the literature, suggesting that the
312 literature data were subject to random error, exacerbated by the large temperature extrapolation,
313 rather than systematic bias. For atmospheric aerosol modelling and interpretation of environmental
314 measurements we recommend direct use of our data, interpolated in carbon number where
315 necessary, and extrapolated over temperatures relevant to the atmospheric boundary layer using
316 equation (2), above. Of the existing parameterisations, we have used Compernelle et al. (2011) as
317 base case in a recent modelling study (Nikolova et al., 2018) because it follows our direct
318 measurements reasonably well.

319

320 **DATA ACCESSIBILITY**

321 Data supporting this publication are openly available from the UBIRA eData repository at
322 <https://doi.org/10.25500/eData.bham.00000292>

323

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328

329 **CONFLICTS OF INTEREST**

330 There are no conflicts to declare.

331

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508 **TABLES LEGENDS**

509 **Table 1:** Saturation vapour pressure measurements for eight n-alkanes at ambient temperatures
510 (K). Vapour pressures at 298K were calculated using (eq2) and the average vapour
511 pressures reported with 1σ standard errors including error propagation through equation
512 2 of the main text. Vapour pressures at 298K were calculated with the use of ΔH_v^a
513 (experimental: Chickos and Hanshaw (2004a)) and ΔH_v^b (calculated: Goss and
514 Schwarzenbach, 1999).
515

516 **FIGURE LEGENDS**

517 **Figure 1:** Absolute error of \log_{10} saturation vapour pressure between literature and our study. The
518 n-alkanes are detailed in the legend. Abbreviations in the x-axis are as follows:
519 (subscript 'e' denotes experimental studies): KU – Kudchadker and Zwolinski (1996),
520 CHR – Chirico et al. (1989), MO – Morgan and Kobayashi (1994), RU – Ruzicka and
521 Majer (1993), GO – Goss and Schwarzenbach (1999), CH1 – Chickos and Hanshaw
522 (2004a), CH2 – Chickos and Hanshaw (2004b), N – Nannoolal et al. (2008), MY –
523 Myrdal and Yalkowsky (1997), CO – Compernelle et al.(2011). Abbreviations in
524 parenthesis point to the boiling point method, as follows: (JR) – Joback and Reid
525 (1987), (SB) – Stein and Brown (1994), (N) – Nannoolal et al. (2004).
526

527

528 **Figure 2.** Vapour pressure data for selected n-alkanes at 298 K. Abbreviations in the legend are as
529 follows: (subscript 'e' denotes experimental studies): KU – Kudchadker and Zwolinski
530 (1996), CHR – Chirico et al. (1989), MO – Morgan and Kobayashi (1994), RU –
531 Ruzicka and Majer (1993), GO – Goss and Schwarzenbach (1999), CH1 – Chickos and
532 Hanshaw (2004a), CH2 – Chickos and Hanshaw (2004b), N – Nannoolal et al. (2008),
533 MY – Myrdal and Yalkowsky (1997), CO – Compernelle et al.(2011), EPI Suite – U.S.
534 Environmental Protection Agency calculator. Abbreviations in parenthesis point to the
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 538 (eq2) and the average vapour pressures reported with 1 σ standard errors including error propagation through equation 2 of the main text. Vapour
 539 pressures at 298K were calculated with the use of ΔH_v^a (experimental: Chickos and Hanshaw(2004a)) and ΔH_v^b (calculated: Goss and Schwarzenbach,
 540 1999).
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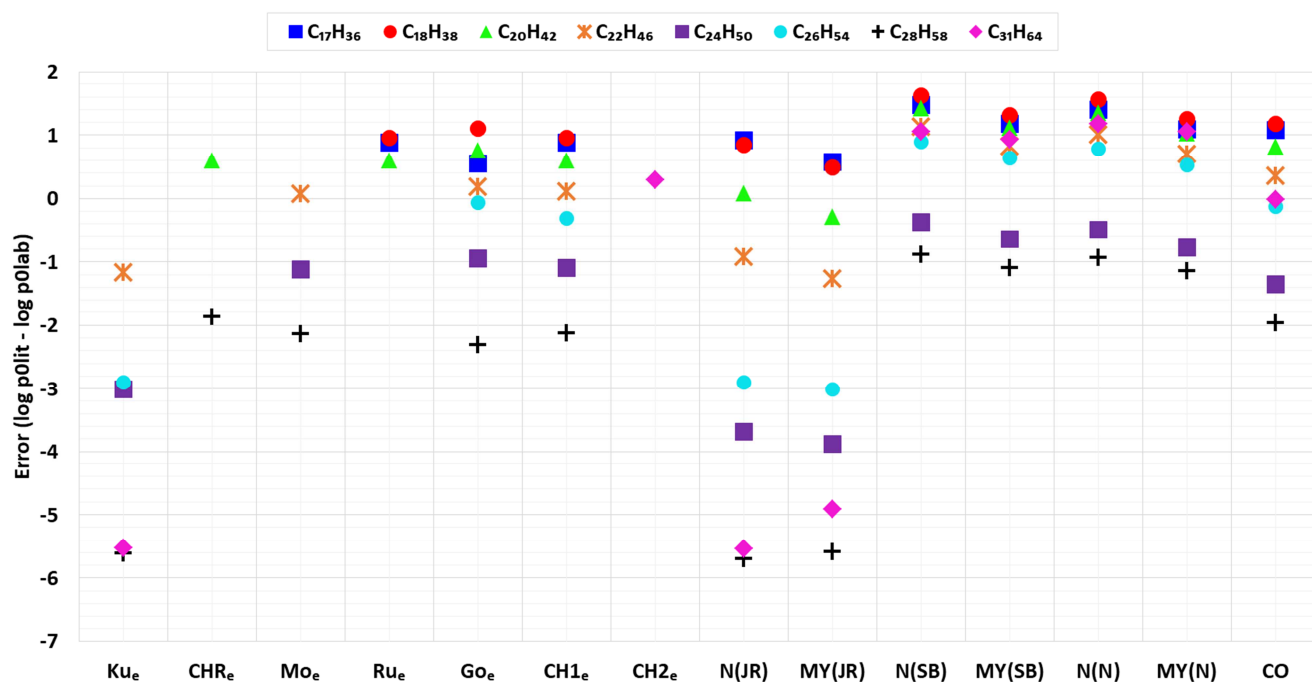
n-C₁₇ Alkane				n-C₁₈ Alkane			
ΔH_v^a (KJ/mol)		ΔH_v^b (KJ/mol)		ΔH_v^a (KJ/mol)		ΔH_v^b (KJ/mol)	
86.3 (± 1.2)		88.86 (± 0.28)		91.1 (± 1.3)		93.02 (± 0.29)	
At 298 K				At 298 K			
Vapour Pressure, p / Pa (10^{-3})				Vapour Pressure, p / Pa (10^{-3})			
297.5	5.30	5.62	5.63	300.0	2.78	2.18	2.17
296.0	6.06	7.66	7.72	299.0	2.13	1.89	1.88
296.5	8.36	9.97	10.02	298.5	2.59	2.43	2.43
297.0	8.89	9.99	10.03	298.5	2.53	2.38	2.38
296.5	7.23	8.63	8.67	297.0	1.87	2.12	2.12
298	8.37 (± 1.63)	8.41 (± 1.64)		298	2.20 (± 0.20)	2.20 (± 0.20)	
n-C₂₀ Alkane				n-C₂₂ Alkane			
ΔH_v^a (KJ/mol)		ΔH_v^b (KJ/mol)		ΔH_v^a (KJ/mol)		ΔH_v^b (KJ/mol)	
101.9 (± 1.4)		99.21 (± 0.32)		111.9 (± 2.7)		103.25 (± 0.34)	
At 298 K				At 298 K			
Vapour Pressure, p / Pa (10^{-4})				Vapour Pressure, p / Pa (10^{-4})			
297.0	6.48	7.44	7.42	298.0	0.75	0.75	0.75
297.0	2.50	2.87	2.86	298.0	1.61	1.61	1.61
297.0	5.29	6.08	6.06	298.0	2.49	2.49	2.49
298.5	4.52	4.22	4.23	298.5	2.07	1.92	1.93
298.0	5.49	5.49	5.49	298.5	1.71	1.59	1.60
298	5.22 (± 1.57)	5.21 (± 1.56)		298	1.67 (± 0.56)	1.67 (± 0.57)	
n-C₂₄ Alkane				n-C₂₆ Alkane			
ΔH_v^a (KJ/mol)		ΔH_v^b (KJ/mol)		ΔH_v^a (KJ/mol)		ΔH_v^b (KJ/mol)	
121.9 (± 2.8)		101.63 (± 0.32)		131.7 (± 3.2)		115.58 (± 0.39)	
At 298 K				At 298 K			
Vapour Pressure, p / Pa (10^{-4})				Vapour Pressure, p / Pa (10^{-6})			
297.0	1.81	2.14	2.08	298.0	4.05	4.05	4.05
297.0	2.23	2.63	2.56	299.0	6.15	5.15	5.26
297.0	2.86	3.38	3.29	299.0	5.85	4.90	5.01
297.0	2.74	3.24	3.15	299.0	8.29	6.94	7.09

297.0	2.81	3.32	3.23	298.0	8.02	8.02	8.02
298		2.94 (± 0.48)	2.86 (± 0.47)	298	0.00	5.81 (± 1.45)	5.89 (± 1.45)
n-C₂₈ Alkane				n-C₃₁ Alkane			
		ΔH_v^a (KJ/mol)	ΔH_v^b (KJ/mol)			ΔH_v^a (KJ/mol)	ΔH_v^b (KJ/mol)
		141.9 (± 4.9)	108.66 (± 0.36)			157.3 (± 1.2)	139.00 (± 0.48)
At 298 K				At 298 K			
Vapour Pressure, p / Pa (10^{-5})				Vapour Pressure, p / Pa (10^{-8})			
298.0	4.75	4.75	4.75	297.0	0.76	0.94	0.91
297.5	4.75	5.23	5.12	296.5	0.93	1.29	1.24
297.5	3.55	3.90	3.82	298.0	2.37	2.37	2.37
297.5	3.10	3.41	3.34	297.5	1.88	2.09	2.06
297.5	3.47	3.82	3.74				
298		4.23 (± 0.67)	4.15 (± 0.67)	298		1.67 (± 0.58)	1.65 (± 0.59)

542 Footnote:
543 Column 1 - Temperature of each experiment
544 Column 2 - Vapour Pressure calculated at that temperature (in Column 1), using eq 1.
545 Column 3 - Vapour pressures at 298K using ΔH_v^a and Clausius-Clapeyron equation (eq 2). ΔH_v^a determined experimentally by Chickos and Hanshaw³⁴ (which are almost identical to
546 the literature recommendations).
547 Column 4 - Vapour pressures at 298K using ΔH_v^b and Clausius-Clapeyron equation (eq 2). ΔH_v^b determined by using the simple equation in the manuscript text (Goss and
548 Schwarzenbach³⁷.
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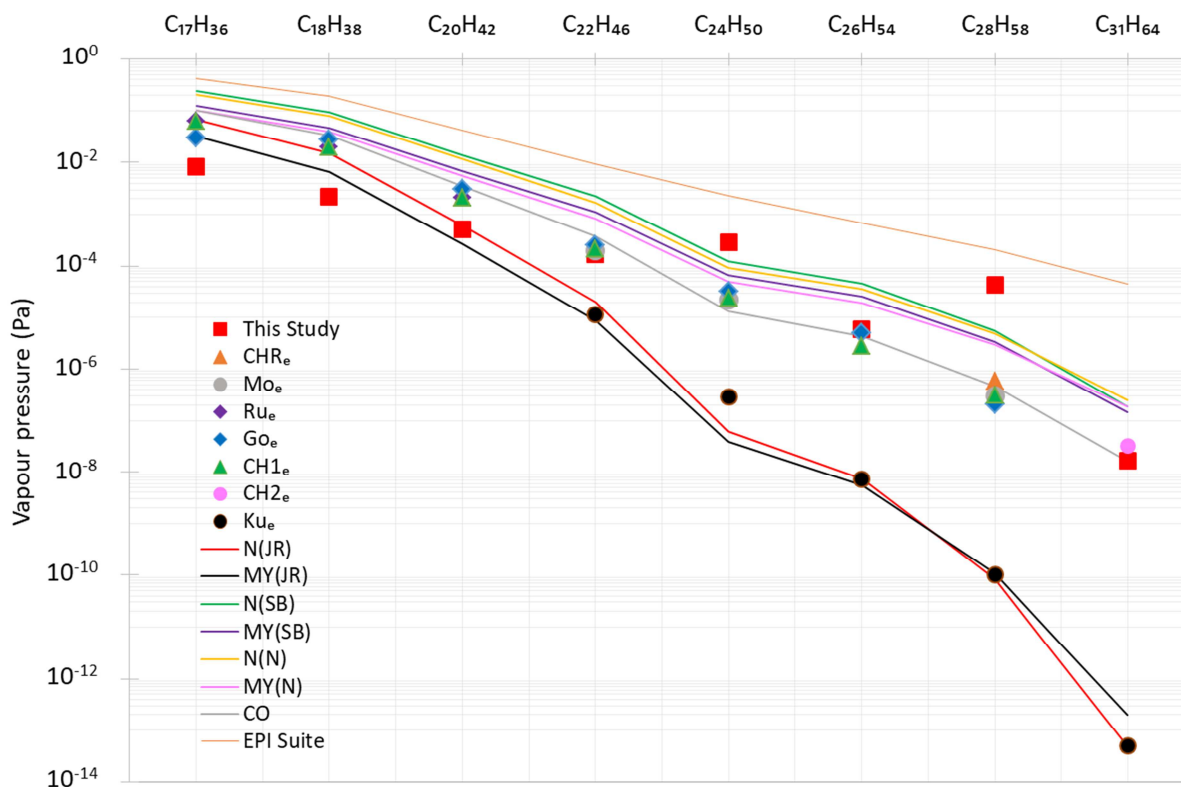


552

553 **Figure 1.** Absolute error of \log_{10} saturation vapour pressure between literature and our study. The n-
 554 alkanes are detailed in the legend. Abbreviations in the x-axis are as follows: (subscript 'e' denotes
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 556 Morgan and Kobayashi (1994), RU – Ruzicka and Majer (1993), GO – Goss and Schwarzenbach
 557 (1999), CH1 – Chickos and Hanshaw (2004a), CH2 – Chickos and Hanshaw (2004b), N –
 558 Nannoolal et al. (2008), MY – Myrdal and Yalkowsky (1997), CO – Compernelle et al.(2011).
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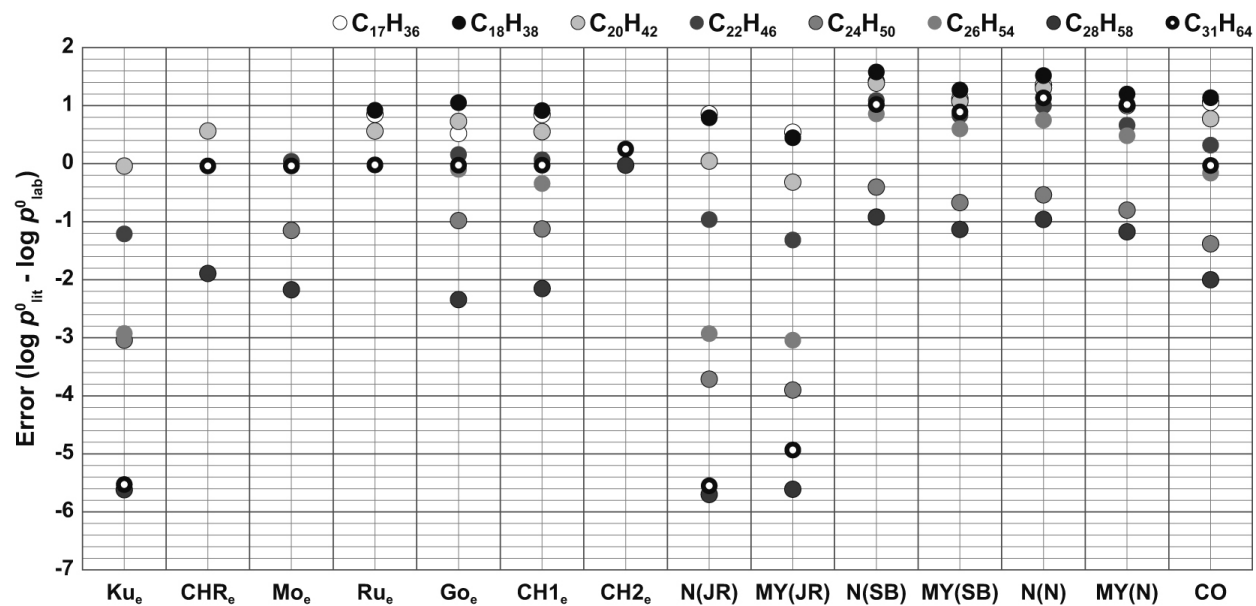


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566

567 **Figure 2.** Vapour pressure data for selected n-alkanes at 298 K. Abbreviations in the legend are as
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 569 CHR – Chirico et al. (1989), MO – Morgan and Kobayashi (1994), RU – Ruzicka and Majer
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 571 Chickos and Hanshaw (2004b), N – Nannoolal et al. (2008), MY – Myrdal and Yalkowsky (1997),
 572 CO – Compennolle et al.(2011), EPI Suite – U.S. Environmental Protection Agency calculator.
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 575



Experimental Vapour Pressures of Eight n-Alkanes (C_{17} , C_{18} , C_{20} , C_{22} , C_{24} , C_{26} , C_{28} and C_{31}) Measured at Ambient Temperatures

Mohammed S. Alam, Irina Nikolova, Ajit Singh, A.R. MacKenzie and Roy M. Harrison

HIGHLIGHTS

- High MW alkanes are semi-volatile and vapour pressure is an important property
- Reported individual vapour pressures range over up to 8 orders of magnitude
- New measurements are made at tropospheric ambient temperatures