UNIVERSITY OF BIRMINGHAM

University of Birmingham
Research at Birmingham

Experimental vapour pressures of eight n-Alkanes (C$_{17}$, C$_{18}$, C$_{20}$, C$_{22}$, C$_{24}$, C$_{26}$, C$_{28}$ and C$_{31}$) at ambient temperatures

Alam, Salim; Nikolova, Irina; Singh, Ajit; MacKenzie, A. Robert; Harrison, Roy

Link to publication on Research at Birmingham portal

Accepted Manuscript

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, Roy M. Harrison
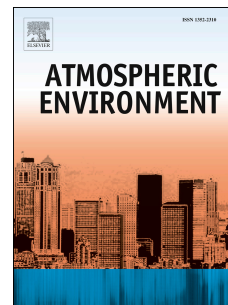
Please cite this article as: Alam, M.S., Nikolova, I., Singh, A., MacKenzie, A.R., Harrison, R.M., Experimental vapour pressures of eight n-alkanes (C$_{17}$, C$_{18}$, C$_{20}$, C$_{22}$, C$_{24}$, C$_{26}$, C$_{28}$ and C$_{31}$) measured at ambient temperatures, *Atmospheric Environment* (2019), doi: https://doi.org/10.1016/j.atmosenv.2019.06.025.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

1
2

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

6
7

Mohammed S. Alam[1], Irina Nikolova[1], Ajit Singh[1]
A.R. MacKenzie[2¥] and Roy M. Harrison[1*†]

[1] Division of Environmental Health and Risk Management
School of Geography, Earth and Environmental Sciences
University of Birmingham, Edgbaston, Birmingham B15 2TT
United Kingdom

[2] School of Geography, Earth and Environmental Sciences
University of Birmingham, Edgbaston, Birmingham B15 2TT
United Kingdom

[*] To whom correspondence should be addressed.
Tele: +44 121 414 3494; Fax: +44 121 414 3709; Email: r.m.harrison@bham.ac.uk

[†] Also at: Department of Environmental Sciences / Center of Excellence in Environmental Studies, King Abdulaziz University, PO Box 80203, Jeddah, 21589, Saudi Arabia

[¥] Also at: Birmingham Institute of Forest Research, University of Birmingham, B15 2TT

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 x 10^{-3} Pa for

40 C_{17}, to 1.7 $\pm$0.6 x 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

49

2

1. INTRODUCTION

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

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

3

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 Dp < 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 McFiggins, 2010). Since the measured thermodynamic property data are

4

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 C_{10} to C_{30} 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). C_{10} to C_{30} 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-C_{92}

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 (C_{17}, C_{18}, C_{20}, C_{22}, C_{24}, C_{26}, C_{28} and C_{31}) at close to ambient

5

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, C_{17}, C_{18}, C_{20}, C_{22}, C_{24}, C_{26}, C_{28} and C_{31} 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 C_7 to C_{40})

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 cm^3 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

6

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

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

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 K^{-1} mol^{-1}, *T* is temperature (K), *V*(*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-C_{31}

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×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-d_{42} and pentacosane-d_{52} (Sigma Aldrich, UK),

7

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,.

8

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 J K^{-1} 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-C$_{17}$ and n-C$_{18}$ alkanes in comparison to the literature, they are in

217   reasonable agreement (see Figure 1). Similarly, the vapour pressure of n-C$_{20}$ 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-C$_{22}$ and n-C$_{26}$ alkane vapour pressures when compared to the

221   estimation method of Compernolle 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-C$_{24}$ and n-C$_{28}$ 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-C$_{31}$ is in very good agreement with the estimation method of Compernolle 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 Mrydal 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 $C_{10} - C_{28}$ range, at temperatures between 323 and 588 K. Their data for n-C_{22} is in good agreement

249 with this study but there is less agreement for the less volatile n-alkanes (n-C_{24} and n-C_{28}). This is

250 due to the vapour pressures of the latter alkanes being measured at elevated temperatures (n-C_{24}:

251 453–588 K and n-C_{28}: 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.

10

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 Hanshow (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; Compernolle et al., 2011;

280 O'Meara et al., 2014). Myrdal and Yalkowsky, 1997 and Nannoolal et al. (2008) calculate vapour

11

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 Compernolle 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 (Compernolle 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

12

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 Compernolle 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

328

329 **CONFLICTS OF INTEREST**

330 There are no conflicts to declare.

REFERENCES

Alam, M.S., Liang, Z., Zeraati-Rezaei, S., Stark, C., Xu, H., MacKenzie, A.R., and Harrison, R.M., 2018. Mapping and quantifying isomer sets of hydrocarbons (≥C12) in diesel exhaust, lubricating oil and diesel fuel samples using GC×GC-ToFMS, Atmos. Meas. Tech., 11, 3047-3058.

Alam, M.S., Zeraati-Rezaei, S., Stark, C.P., Liang, Z., Xu, H., and Harrison, R.M., 2016. The characterisation of diesel exhaust particles – composition, size distribution and partitioning Faraday Discuss., 2016, 189, 69-84.

Atkins, P., De Paula, J., and Keeler, J., 2018. Atkins' Physical Chemistry, Oxford University Press.

Atkinson, R.W., Fuller, G.W., Anderson, H.R., Harrison, R.M., and Armstrong, B., 2010. Urban ambient particle metrics and health: a time-series analysis, Epidemiology, 21, 501-511.

Barley, M.H. and McFiggans, G., 2010. The critical assessment of vapour pressure estimation methods for use in modelling the formation of atmospheric organic aerosol, Atmos. Chem. Phys., 10, 749-767.

Bilde, M., Barsanti, K., Booth, M., Cappa, C.D., Donahue, N.M., Emanuelsson, E.U., McFiggans, G., Krieger, U.K., Marcolli, C., Topping, D., Ziemann, P., Barley, M., Clegg, S., Dennis-Smither, B., Hallquist, M., Hallquist, Å.M., Khlystov, A., Kulmala, M., Mogensen, D., Percival, C.J., Pope, F., Reid, J.P., Ribeiro da Silva, M.A.V, Rosenoern, T., Salo, K., Pia Soonsin, V., Yli-Juuti, T., Prisle, N.L., Pagels, J., Rarey, J., Zardini, A.A., and I. Riipinen, 2015. Vapor pressures and transition enthalpies of low-volatility organic molecules of atmospheric relevance: From dicarboxylic acids to complex mixtures, Chem. Rev., 2015, 115, 4115-4156.

Calvert, J.G., 1990. IUPAC Glossary of atmospheric chemistry terms, Pure Appl. Chem., 62, 11, 2167-2219.

Cappa, C.D., Lovejoy, E.R., and Ravishankara, A.R., 2007. Determination of evaporation rates and vapor pressures of very low volatility compounds: A study of the C-4-C-10 and C-12 dicarboxylic acids, J. Phys. Chem. A, 111, 3099-3109.

Chickos, J., and Hanshaw, W., 2004a. Vapor pressures and vaporization enthalpies of the n-alkanes from C21 to C30 at T = 298.15 K by correlation gas chromatography, J. Chem. Eng. Data, 49, 77-85.

Chickos, J., and Hanshaw, W., 2004b. Vapor pressures and vaporization enthalpies of the n-alkanes from C31 to C38 at T = 298.15 K by correlation gas chromatography, J. Chem. Eng. Data, 49, 620-630.

Chickos, J.S., and Lipkind, D., 2009. Hypothetical thermodynamic properties: vapor pressures and vaporization enthalpies of the even n-alkanes from C78 to C92 at T = 298.15 K by correlation gas chromatography, J. Chem. Eng. Data, , 53, 2432-2440.

Chirico, R.D., Nguyen, A., Steele, W., and Strube, M.M., 1989. Vapor Pressure of n -alkanes revisited. new high-precision vapor pressure data on n-decane, n-eicosane, and n-octacosane, J. Chem. Eng. Data, 34, 149-156.

Clegg, S.L., Kleeman, M.J., Griffin, R.J., and Seinfeld, J.H., 2008. Effects of uncertainties in the thermodynamic properties of aerosol components in an air quality model - Part 2: Predictions of the vapour pressures of organic compounds, Atmos. Chem. Phys., 8, 1087-1103.

Compernolle, S., Ceulemans, K., and Muller, J.-F., 2011). Evaporation: a new vapour pressure estimation method for organic molecules including non-additivity and intramolecular interactions, Atmos. Chem. Phys., 11, 9431-9450.

Dekruif, C.G., and Vanginkel, C.H.D., 1977. Torsion-weighing effusion vapor-pressure measurements on organic-compounds, J. Chem. Thermodyn., 9, 725-730.

Dunmore, RE., Hopkins, J.R., Lidster, R.T., Lee, J.D., Evans, M.J., Rickard, A.R., Lewis, A.C, and Hamilton, J.F., 2015. Diesel-related hydrocarbons can dominate gas phase reactive carbon in megacities, Atmos. Chem. Phys., 15, 9983-9996.

Fraser, M.P., Cass, G.R., Simoneit, B.R.T., and Rasmussen, R.A., 1997. Air quality model evaluation data for organics. 4. C2-C36 non- aromatic hydrocarbons, Environ. Sci. Technol., 31, 2356-2367.

Fujitani, Y., Saitoh, K., Fushimi, A., Takahashi, K., Hasegawa, S., Tanabe, K., Kobayashi, S., Furuyama, A., Hirano, S., and Takami, A.: 2012. Effect of isothermal dilution on emission factors of organic carbon and n-alkanes in the particle and gas phases of diesel exhaust, Atmos. Environ., 59, 389-397.

Goldstein, A. H., and Galbally, I.E., 2007. Known and unexplored organic constituents in the Earth's atmomsphere, Environ. Sci. Technol., 41, 1514-1521.

Goss, K.-U., and Scharzenbach, R.P., 1999. Empirical prediction of heats of vaporization and heats of adsorption of organic compounds, Environ. Sci. Technol., 33, 3390-3393.

Hallquist, M., Wangberg, I., and Ljungstrom, E., 1997. Atmospheric fate of carbonyl oxidation products originating from alpha-pinene and Delta(3)-carene: Determination of rate of reaction with OH and NO_3 radicals, UV absorption cross sections, and vapor pressures, Environ. Sci. Technol., 31, 3166-3172.

Harrad, S., Hassoun, S., Callen Romero, M.S., and Harrison. R.M., 2003. Characterisation and source attribution of the semi-volatile organic content of atmospheric particles and associate vapour phase in Birmingham, UK, Atmos. Environ., 37, 4985-4991.

Harrison, R.M., Beddows, D.C.S., Alam, M.S., Singh, A., Brean, J., Xu, R., Kotthaus, S., and Grimmond, S., 2019. Interpretation of particle number size distributions measured across an urban area during the FASTER Campaign, Atmos. Chem. Phys., 19, 39-55.

Harrison, R.M., Jones, A.M., Beddows, D.C.S., Dall'Osto, M., and Nikolova, I., 2016. Evaporation of traffic-generated nanoparticles during advection from source, Atmos. Environ. 125 1-7.

Harrison, R.M., Beddows, D.S., and Dall'Osto, M., 2011. PMF analysis of wide-range particle size spectra collected on a major highway, Environ. Sci. Technol., 45, 5522-5528.

Joback, K., and Reid, R., 1987. Estimation of Pure-component properties from group-contributions, Chem. Eng. Commun., 57, 233-243.

15

434 Karjalainen, P., Ntziachristos, L., Murtonen, T., Wihersaari, H., Simonen, P., Myllari, F., Nylund,
435 N.-O., Keskinen, J., and Ronkko, T.: 2016. Heavy duty diesel exhaust particles during engine
436 motoring formed by lube oil consumption, Environ. Sci. Technol., 50 12504-12511.
437
438 Koponen, I.K., Riipinen, I., Hienola, A., Kulmala, M., and Bilde, M., 2007. Thermodynamic
439 properties of malonic, succinic, and glutaric acids: Evaporation rates and saturation vapor pressures,
440 Environ. Sci. Technol., 41, 3926-3933.
441
442 Kudchadker, A.P., and Zwolinski, B.J., 1966. Vapor pressures and boiling points of normal alkanes,
443 C21 to C100, J. Chem. Eng. Data, 11, 11, 253-255.
444
445 Kumar, P., Morawska, L., Birmili, W., Paasonen, P., Hu, M., Kulmala, M., Harrison, R. M.,
446 Norford, L., and Britter, R., 2014. Ultrafine particles in cities, Environ. Intl., 66, 1-10.
447
448 Lipsky, E.M., and Robinson, A.L.. 2006. Effects of dilution on fine particle mass and partitioning
449 of semivolatile organics in diesel exhaust and wood smoke, Environ. Sci. Technol., 40, 155-162.
450
451 Morgan, D.L., and Kobayashi, R., 1991. Triple point corresponding states in long-chain n-alkanes,
452 Fluid Phase Equilibr., 63: 317-327.
453
454 Morgan, D.L., and Kobayashi, R., 1994. Direct vapor pressure measurements of ten n-alkanes in
455 the C1-C28 range, Fluid Phase Equilibr., 97, 21, l-242.
456
457 Myrdal, P.B., and Yalkowsky, S.H., 1997. Estimating pure component vapor pressures of complex
458 organic molecules, Ind. Eng. Chem. Res., 36, 2494-2499.
459
460 Nannoolal, Y., Rarey, J., Ramjugernath, D., and Cordes, W., 2004. Estimation of pure component
461 properties: Part 1. Estimation of the normal boiling point of non-electrolyte organic compounds via
462 group contributions and group interactions, Fluid Phase Equilibr., 226, 45-63.
463
464 Nannoolal, Y., Rarey, J., and Ramjugernath, D., 2008. Estimation of pure component properties:
465 Part 3. Estimation of the vapor pressure of non-electrolyte organic compounds via group
466 contributions and group interactions, Fluid Phase Equilibr., 269, 117-133.
467
468 Nikolova, I., Cai, X., Alam, M.S., Zeraati-Rezaei, S., Zhong, J., MacKenzie, A.R., and Harrison,
469 R.M., 2018. The influence of particle composition upon the evolution of urban ultrafine diesel
470 particles on the neighbourhood scale, Atmos. Chem. Phys., 18, 17143-17155.
471
472 O'Meara, A.M., Booth, A.M., Barley, M.H., Topping D., and McFiggans G., 2014. An assessment
473 of vapour pressure estimation methods, Phys. Chem. Chem. Phys., 16, 19453-19469.
474
475 Razzouk, A., Naccoul, R.A., Mokbel, I., Saab, J., and Jose, J., 2009. Vapor and sublimation
476 pressures of three normal alkanes: C20, C24, and C28, Chem. Eng. Data, 54, 1214-1219.
477
478 Ruzicka, K., and Majer V., 1993. Simultaneous treatment of vapor pressures and related thermal
479 data between the triple and normal boiling temperatures for n-alkanes C5-C20, J. Phys., Chem. Ref.
480 Data, 23,1-39.
481
482 Ruzicka, K., and Majer, V., 1996. Simple and controlled extrapolation of vapor pressures toward the
483 triple point, AIChE J., 42, 1723-1740.
484
485

486 Sartin, J., Halsall, C.J., Robertson, L.A., Gonard, R.G., MacKenzie, A.R., Berresheim, H., and
487 Hewitt, C.N., 2002. Temporal patterns, sources, and sinks of C8-C16 hydrocarbons in the
488 atmosphere of mace Head, Ireland, J. Geophys. Res., 107, D19, 8099, doi:10.1029/2000JD000232.
489
490 Sakurai, H., Tobias, H., Park, K., Zarling, D., Docherty, K.S., Kittelson, D.B., McMurry, P.H., and
491 Ziemann, P.J., 2003. On-line measurements of diesel nanoparticle composition and volatility,
492 Atmos. Environ., 37, 1199-1210.
493
494 Sawaya, T., Mokbel, I., Ainous, N., Rauzy, E., Berro, C., and Jose, J., 2006. Experimental vapour
495 pressures of six n-alkanes (C21, C23, C25, C27, C29, C30) in the temperature range between 350 K
496 and 460 K, J. Chem. Eng. Data, 51, 854-858.
497
498 Stein, S.E., and Brown, R.L., 1994. Estimation of normal boiling points from group contributions, J.
499 Chem. Inf. Comp. Sci., 34, 581-587.
500
501 Topping, D., Barley, M., Bane, M.K., Higham, N., Aumont, B., Dingle, N., and McFiggans, G.,
502 2016. UManSysProp v1.0: an online and open-source facility for molecular property prediction and
503 atmospheric aerosol calculations, Geosci. Model Dev., 9, 899-914.
504
505 Verevkin, S.P., Wandschneider, D., and Heintz, A., 2000. Determination of vaporization enthalpies
506 of selected linear and branched C-7, C-8, C-9, C-11, and C-12 monoolefin hydrocarbons from
507 transpiration and correlation gas-chromatography methods, J. Chem. Eng. Data, 45, 618-625.

17

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 – Compernolle 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 – Compernolle et al.(2011), EPI Suite – U.S.
534 Environmental Protection Agency calculator. Abbreviations in parenthesis point to the
535 boiling point method, as follows: (JR) – Joback and Reid (1987), (SB) – Stein and
536 Brown (1994), (N) – Nannoolal et al. (2004).

18

537   **Table 1.** Saturation vapour pressure measurements for eight n-alkanes at ambient temperatures (K). Vapour pressures at 298K were calculated using
538   (eq2) and the average vapour pressures reported with 1σ 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).
541

n-C_{17} Alkane				n-C_{18} 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-C_{20} Alkane				n-C_{22} 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-C_{24} Alkane				n-C_{26} 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

19

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-C_{28} Alkane			n-C_{31} 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)**

Footnote:
Column 1 - Temperature of each experiment
Column 2 - Vapour Pressure calculated at that temperature (in Column 1), using eq 1.
Column 3 - Vapour pressures at 298K using ΔH_v^a and Clausius-Clapeyron equation (eq 2). ΔH_v^a determined experimentally by Chickos and Hanshaw[34] (which are almost identical to the literature recommendations).
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 Schwarzenbach[37].

550
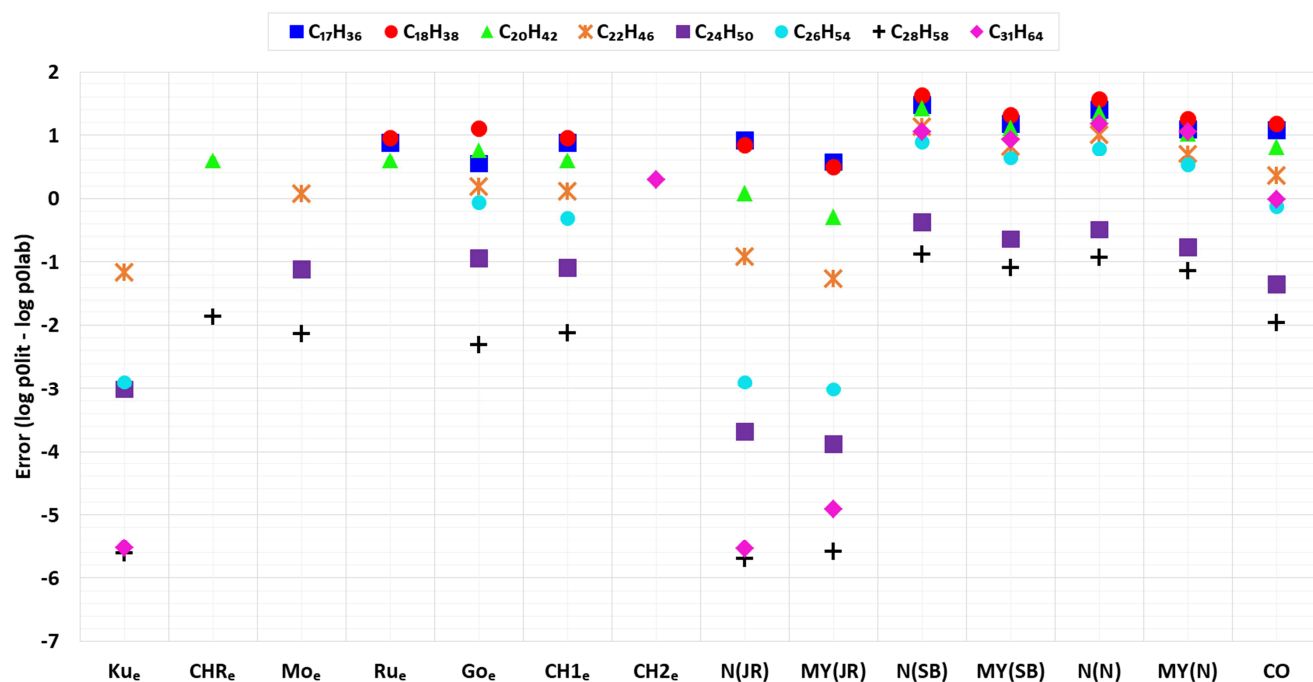
551

552

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

561

562

563
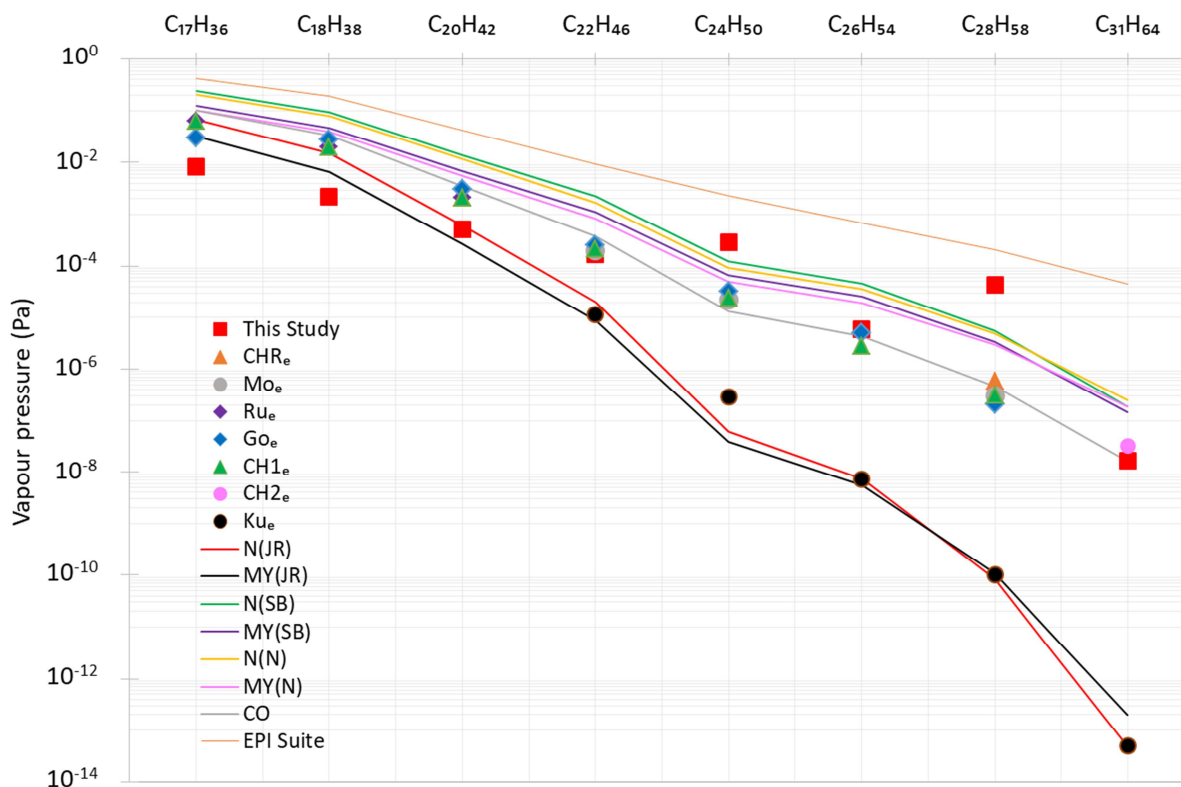
564
565
566
567 **Figure 2**. Vapour pressure data for selected n-alkanes at 298 K. Abbreviations in the legend are as
568 follows: (subscript 'e' denotes experimental studies): KU – Kudchadker and Zwolinski (1996),
569 CHR – Chirico et al. (1989), MO – Morgan and Kobayashi (1994), RU – Ruzicka and Majer
570 (1993), GO – Goss and Schwarzenbach (1999), CH1 – Chickos and Hanshaw (2004a), CH2 –
571 Chickos and Hanshaw (2004b), N – Nannoolal et al. (2008), MY – Myrdal and Yalkowsky (1997),
572 CO – Compernolle et al.(2011), EPI Suite – U.S. Environmental Protection Agency calculator.
573 Abbreviations in parenthesis point to the boiling point method, as follows: (JR) – Joback and Reid
574 (1987), (SB) – Stein and Brown (1994), (N) – Nannoolal et al. (2004).
575
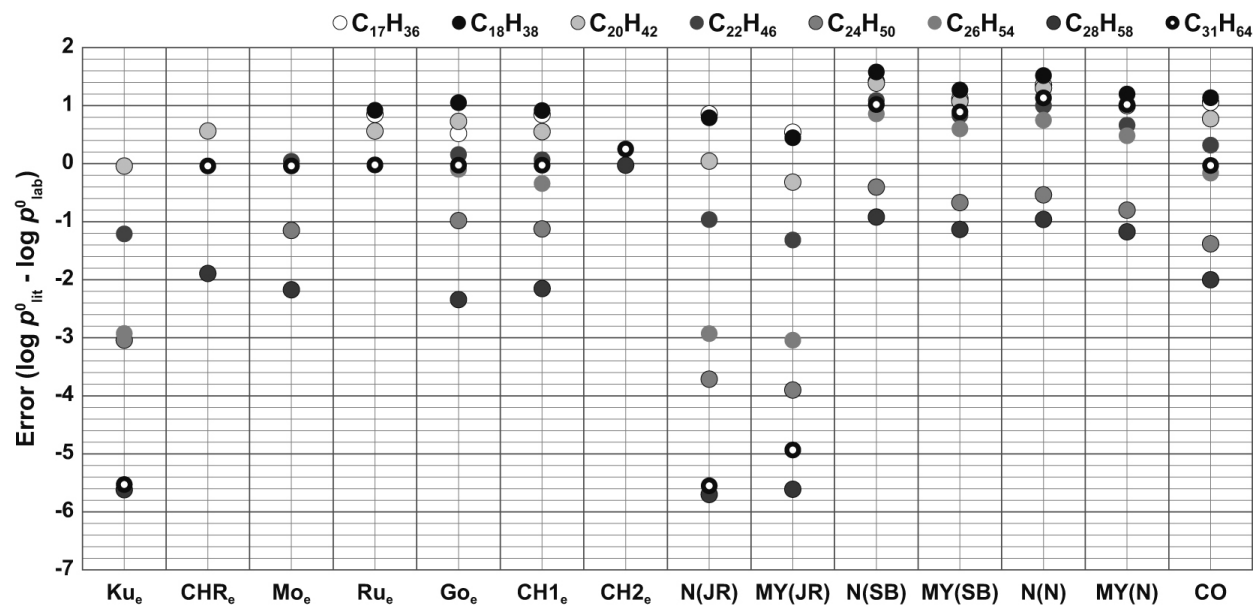
Experimental Vapour Pressures of Eight n-Alkanes (C$_{17}$, C$_{18}$, C$_{20}$, C$_{22}$, C$_{24}$, C$_{26}$, C$_{28}$ and C$_{31}$) Measured at Ambient Temperatures

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