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## Atmospheric gas–particle partitioning of E-EHMC and Z-EHMC estimated from their liquid vapour pressures at 298.15 K

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**Abstract:** The UVB filter E-ethylhexyl *p*-methoxycinnamate (E-EHMC) is extensively used as UV protectant in commercial products. Besides, it is well known that it photoisomerise into Z-EHMC. In this work,  $\Delta_{\text{vap}}H (T_m)$  and vapour pressure,  $P$  (Pa) at 298.15 K, of E-EHMC and Z-EHMC were estimated using an indirect experimental method developed in our laboratory named

effusion method under atmospheric pressure (EMAP). The atmospheric particle bound fraction ( $\Phi$ ) and the gas–particle partition coefficient ( $K_p$ ) for E-EHMC and Z-EHMC were derived from the vapour pressure,  $P$  (Pa) (298.15 K), estimated by EMAP methodology.

**Keywords:** vapour pressure; gas–particle partition coefficient; EMAP; particle-bound fraction.

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## 1 Introduction

In modern life, the natural or synthetic organic substances are used massively. They can be present in personal care products, surfactants and surfactant wastes, human and veterinary pharmaceuticals products, plasticisers and industrial additives but they could cause adverse ecological or human health effects when they are released into the environment. These substances have been called emergent contaminants (ECs) and they are being assessed in the environment. Mostly, their use is not currently regulated (Petrovic et al., 2003).

Among the ECs, the chemical UVB filters (290–320 nm) are organic molecules usually used as solar radiation protectant in commercial products like cosmetic, manufacture of plastic, pesticides, etc. The E-ethylhexyl *p*-methoxycinnamate (E-EHMC) is extensively used as chemical UVB filter (Gasparro et al., 1998). It is well known that its main solar radiation absorption mechanism is the fast photoisomerisation into the Z-EHMC isomer (Pattanaargson et al., 2004; Huong et al., 2007). In several analysed ecosystems, both substances have been found in similar concentrations (Balmer et al., 2005; Benedé et al., 2014).

The physical and chemical properties of commercial substances are required for EPA (US Environmental Protection Agency) and EC (European Community) registration (EPA US, 1996; OECD, 1993). The vapour pressure together with the aqueous solubility and the octanol/water partition coefficient data are used to characterise their performance in the commercial products. The volatility of these substances is decisive for assessing the level of spontaneous emissions during their production, applications and use of products, as well as for the estimation of their distribution in the environment. In the case of vapour pressure, the Knudsen effusion method is approved by the Organisation for Economic Cooperation and Development as discussed in the OECD vapour Pressure Curve Guideline 104 and the EPA Product Properties Test Guidelines OPPTS 830.7950 vapour pressure (EPA US, 1996; OECD, 1993). Nevertheless, there are other techniques such as gas chromatography (GC) headspace technique (Oxley et al., 2009), gas saturation (Spencer and Cilath, 1983; Sonnefeld et al., 1983), gas chromatographic retention time (GC-RT) methods (Bidleman, 1984; Wania et al., 2002), steam balance method (Murray et al., 1974; Oja and Suuberg, 1997) and theoretical estimations (Santos and Leal, 2012; Barley and McFiggans, 2010) are used to measure this property.

Once in the atmosphere, the ECs can be moved from the emitting sources to remote regions by long-range atmospheric transport. Nevertheless, their gas–particle partitioning govern the atmospheric fate of ECs because reaction with OH radicals, dry and wet deposition as well as the photolysis differ if the ECs are present in atmospheric gas, particle or both phases (Bidleman, 1988).

The adsorption onto the particle surface and absorption into the organic phase of aerosols are the main atmospheric partitioning mechanisms of the organic substances present in the atmosphere. They are intrinsically related with the volatility of each organic molecule. For instance, vapour pressure ( $P_L$ ) indicates the tendency of a chemical to volatilise from a liquid or solid phase and the octanol–air partition coefficient ( $K_{OA}$ ) describes the equilibrium partitioning of a chemical between pure organic solvent and the gas phase in contact. The subcooled liquid vapour pressure ( $P_L$ ) has been used as descriptor of both adsorptive and absorptive partitioning (Pankow, 1987) while the octanol–air partition coefficient ( $K_{oa}$ ) is a successful absorptive partitioning descriptor (Finizio et al., 1997; Harner and Bidleman, 1998).

The E-EHMC vapour pressure at 298.15 K was estimated in  $1.8 \times 10^{-3}$  Pa using online EPISuite-EPA (2016) but, the differences in the physico-chemical properties of each isomers are not contemplated in the theoretical methods currently developed (Parnis et al., 2015). Recently, using the experimental GC-RT methodology, Pegoraro et al. (2015) have reported a vapour pressure of  $(1.8 \pm 0.1) \times 10^{-4}$  Pa and  $(9.8 \pm 0.1) \times 10^{-4}$  Pa for E-EHMC and Z-EHMC, respectively.

The low vapour pressure at 298.15 K of the target molecules together with the modest volume of Z-EHMC obtained after the photosynthesis were the main motivations for the election of the indirect EMAP methodology to estimate the  $\Delta_{\text{vap}}H(T_m)$  and the vapour pressure,  $P$  (Pa) (298.15 K), of E-EHMC and Z-EHMC.

The aim of this study is to determine the vapour pressure of E-EHMC and Z-EHMC with the proposed EMAP method in order to estimate the gas–particle atmospheric partition of both emerging contaminants.

## 2 Experimental methodologies

### 2.1 Reactives

The E-EHMC (Merck, 99.5%), 1-octanol (Sigma-Aldrich, 99.8%), *n*-hexane (Sintorgan, 99.98%), dimethyl sulfoxide (Riedel de Haën, 99.50%), *N,N*-dimethylaniline (Riedel de Haën, 99.50%), 6:2 fluorotelomer alcohol (Sigma-Aldrich, 99.8%), ethylacetate (Biopack, 99.40%), ethanediol (Cicarelli, 98%), hexadecane (Cicarelli, 98%), di-butyl phthalate (Anedra, 99.5%) and triethanolamine (Merck, 98%) were used without further purification. Deionised water ( $18 \text{ M}\Omega \text{ cm}^{-1}$ ) was obtained from a Millipore.

Z-EHMC was synthesised by irradiation ( $\lambda = 254 \text{ nm}$ ) of a solution of the commercial E-EHMC in nitrile acetate. The pure Z-EHMC sample was laboriously isolated from the product mix using silica gel columns. Its purity was checked by HPLC-UV in our laboratory.

### 2.2 Instrumental

An analytical balance, an oven Dalvo Instrumentos BHR11 1320w with thermocouple including thermal digital controller from room temperature up to 501 K, a digital thermometer (253–473 K) and a chronometer were used in this work.

### 2.3 Cottrell's method

To determine  $\Delta_{\text{vap}}H(T_m)$  and vapour pressure at 298.15 K of E-EHMC, the Cottrell's reflux method was used as direct methodology (OECD, 1993). Initially, the sample was degassed and measured pressures were achieved with a vacuum pump. In all the essays, each experimental pressure and boiling temperature was measured with a mercury manometer and a digital thermometer, respectively. Approximately, 5 g of the E-EHMC was placed in a round-bottom flask boiler and connected to a refrigerant and a vacuum system, then, at a fixed and predetermined pressure, the substance was heated until it boiled and its temperature was registered.

### 2.4 Effusion method under atmospheric pressure

In this work, the indirect EMAP methodology will be used to estimate the  $\Delta_{\text{vap}}H(T_m)$  and the vapour pressure,  $P$  (Pa) (298.15 K), of E-EHMC and Z-EHMC, respectively.

The Knudsen and Langmuir's methods are based on the kinetics theory of gases from which they derived an expression for the slow isothermal effusion out of a small conical orifice in a cell. Effusion occurs when the diameter of the hole is smaller than the mean free path in the gas, so that no collisions occur when the molecules pass through the hole (Knudsen, 1909; Gokcen, 1965; Langmuir, 1913). Then, the mass loss by effusion through an orifice, in a given period of time, is directly proportional to the vapour pressure of a substance in equilibrium with its condensed phase inside the cell as is described in the Knudsen's equation (equation (1)):

$$P_k = \left( \frac{\Delta m}{tA_0} \right) \sqrt{\frac{2\pi RT}{M}}, \quad (1)$$

where  $P_k$  is the estimated vapour pressure (Pascal),  $\Delta_m$  is the mass loss by effusion (kg),  $t$  is the time remaining uncovered orifice (s),  $A_0$  is the orifice area ( $\text{m}^2$ ),  $R$  is the gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ ),  $T$  is the temperature (K) and  $M$  is the molecular weight ( $\text{kg mol}^{-1}$ ). Despite that this is a direct methodology, several corrections to this equation have been suggested to obtain accurate results (Clausing, 1932; Motzfeldt, 1955; Whitman, 1952).

In general, Knudsen's method allows measurement of low vapour pressures in the range of  $1-1 \times 10^{-6}$  Pa characteristic of the high molecular weight organic and inorganic compounds. Likewise, the kinetics theory of gases, initially developed for ideal gases, is also successful to describe real gases and liquids behaviour. In this methodology, it was assumed that:

- at each fix temperature, vapour pressure of the substance into the cell is constant during the effusion measurement
- the rate of molecules escaping through the orifice is equals to the rate at which molecules would strike an area of wall equal to the orifice area if the orifice were closed
- the diameter of the hole is smaller than the mean free path in the gas, so that no collisions occur as the molecules pass through the hole
- the liquid volume is much smaller than the gas one therefore it is neglected and the gas-phase behaviour can be treated as ideal.

Several experimental setups of Knudsen's cell consist in a vacuum box thermostatised coupled with an experimental device in order to sense the mass loss of the sample like a quartz microbalance, TGA or mass spectrometer (Gupta et al., 2008; Booth, 2009).

EMAP is an indirect methodology developed in this work in order to estimate the  $\Delta_{\text{vap}}H(T_m)$  and the vapour pressures at 298.15 K of the molecules under study, considering the same assumption above mentioned.

EMAP methodology uses the effusion process under environmental pressure conditions to determine an apparent vapour pressure,  $P_{\text{EMAP}}$  (Pa) (298.15 K) and vapourisation enthalpy,  $\Delta_{\text{vap}}H_{\text{EMAP}}(T_m)$ , of the organic substances under study. The mean of experimental measured temperatures is  $T_m$ . The original Knudsen's equation (equation 1), without further corrections, was used to estimate the experimental  $P_{\text{EMAP}}$  (Pa).

A well-known set of molecules, hereafter called standard substances, has been measured in the same conditions in order to calibrate this experimental system. As usual, the experimental vapourisation enthalpy,  $\Delta_{\text{vap}}H_{\text{EMAP}}(T_m)$ , as well as the extrapolated  $P_{\text{EMAP}}$  (Pa) (298.15 K) of the standard molecules will be correlated with their selected bibliographic data of  $\Delta_{\text{vap}}H_{\text{bib}}(T_m)$  and  $P_{\text{bib}}$  (Pa) (298.15 K), respectively.

Experimentally, a glass tube with metallic crew cap with a 15 cm of longitude was used as effusion cell. The metallic crew cap has a conical orifice with a diameter of  $1.41 \pm 0.02$  mm in order to allow the scape of the molecules by effusion under atmospheric pressure condition. In this case, the diameter was measured with a digital Vernier scale.

An isothermal thermostatised chamber was used to carry out the experimental effusion process. This chamber consisted of an oven with variable temperature or a thermostatised chamber, according to the required working temperature. The temperature range used with each molecule lies between its boiling and fusion points, as can be seen in Table 1. The remaining mass into the cell was weighted on an analytical balance in

order to detect the scape of the molecules throughout the conical pinhole. The time was measured with a digital chronometer and all these experimental procedures were carried out under atmospheric pressure at sea level, considered constant for all the experiments.

**Table 1** Experimental EMAP and bibliographic data for standard molecules

<i>Compound</i>	$\Delta_{\text{vap}}H_{\text{bib}}$ (kJ mol <sup>-1</sup> ) <sup>I</sup>	$T_m$ (K) <sup>II</sup>	$T_b$ (K) <sup>III</sup>	$T_{\text{min}}-T_{\text{max}}$ (K) <sup>IV</sup>	$T_m$ (K) <sup>V</sup>	$t_{\text{max}}-t_{\text{min}}$ (h) <sup>VI</sup>	$\Delta_{\text{vap}}H_{\text{emap}}$ (kJ mol <sup>-1</sup> ) <sup>VII</sup>	$ \Delta E $ <sup>VIII</sup> (kJ mol <sup>-1</sup> )
n-Hexane C <sub>6</sub> H <sub>14</sub>	30.7 <sup>a</sup>	313 <sup>a</sup>	341.9 <sup>a</sup>	288–331	309	2.12–0.6	30.43 ± 0.30	0.27
Ethyl Acetate C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	34.6 <sup>a</sup>	313 <sup>a</sup>	350.2 <sup>a</sup>	294–349	319	1.2–0.5	34.96 ± 0.49	0.36
Water H <sub>2</sub> O	42.48 <sup>b</sup>	333 <sup>b</sup>	373 <sup>b</sup>	296–362	335	4.95–0.5	42.24 ± 0.52	0.24
FTOH 6:2 C <sub>8</sub> H <sub>5</sub> F <sub>13</sub> O	56.69 <sup>c</sup>	395 <sup>c</sup>	438 <sup>c</sup>	370–440	403	2.22–0.6	57.74 ± 0.87	1.05
Dimethyl Sulfoxide C <sub>2</sub> H <sub>6</sub> OS	48.6 <sup>a</sup>	392 <sup>a</sup>	464 <sup>a</sup>	382–453	419	2.22–0.6	52.56 ± 0.87	2.13
N,N–dimethyl– Benzenamine C <sub>8</sub> H <sub>11</sub> N	49.2 <sup>a</sup>	378 <sup>a</sup>	466 <sup>a</sup>	370–461	423	1.55–0.6	52.43 ± 0.80	1.52
1–Octanol C <sub>8</sub> H <sub>18</sub> O	58.3 <sup>d</sup>	433 <sup>d</sup>	468 <sup>d</sup>	411–464	437	1.45–0.55	69.24 ± 0.80	1.41
Ethandiol C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	57.3 <sup>e</sup>	436 <sup>e</sup>	470.5 <sup>e</sup>	381–466	427	76–0.93	64.00 ± 0.38	0.51
Hexadecane C <sub>16</sub> H <sub>34</sub>	65.7 <sup>f</sup>	455 <sup>f</sup>	560 <sup>f</sup>	442–493	468	2.9–1.1	63.97 ± 0.86	1.73
Dibutyl phthalate C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	78.48 <sup>g</sup>	460 <sup>g</sup>	613 <sup>g</sup>	433–488	461	22–2.7	78.16 ± 1.11	0.32
Triethanolamine C <sub>6</sub> H <sub>15</sub> NO <sub>3</sub>	87.6 <sup>h</sup>	470 <sup>h</sup>	608 <sup>h</sup>	443–497	470	15.3–1	89.36 ± 1.23	1.76

<sup>I</sup>Bibliographic enthalpy of vapourisation at  $T_m$  (K), <sup>II</sup>Bibliographic mean temperature, <sup>III</sup>Bibliographic boiling point, <sup>IV</sup>EMAP temperature range, <sup>V</sup>EMAP mean temperature, <sup>VI</sup> EMAP time range, <sup>VII</sup>EMAP enthalpy of vapourisation at  $T_m$  (K), <sup>VIII</sup>Absolute difference between EMAP and bibliographic enthalpies.

<sup>a</sup>Chickos and Acree (2003), <sup>b</sup>Sabbah et al. (1999), <sup>c</sup>Krusic et al. (2005), <sup>d</sup>Stephenson and Malanowski (1987), <sup>e</sup>Jones and Tamplin (1952), <sup>f</sup>Ubbelohde (1938), <sup>g</sup>Hammer and Lydersen (1957), <sup>h</sup>Dow (2003).

Initially, the tubes were individually weighted with each cap. Three of them were left empty for blank purpose. Each compound under study was measured by triplicate. Then, approximately 0.3 mL of the substance were incorporated in each tubes and then, they were individually weighted with their respective caps. Afterward, the pinholes were closed until use. With the same procedure, several standard substances were prepared in order to validate this experimental method.

Sample, blank and standard tubes, distributed in a metallic test-tube rack, were introduced into the isothermal thermostatised chamber with open pinholes, all together and for triplicate. Then, when the metallic test-tube rack with the tubes was placed into

the chamber, the measurement time began. The substances were maintained into the chamber for a time enough to assure that, at least, the less volatile compounds have a vapour pressure fluctuation below 10% according to the reproducibility of the method (see quality criteria section).

After the test time, the rack together with the tubes was removed from the chamber, the tube pinholes were closed and then, the rack was put into a dry chamber to avoid any eventual water condensation until they acquired room temperature and also for the samples transportation purpose. Then, they were weighted individually at room temperature with open orifice assuming that, during this procedure, the mass loss is below instrumental detection limit.

After this operation, all the tubes were closed again and they were ready for another essays at different temperatures. In the case of the thermically unstable substances, fresh sample was always used at each temperature. The reported vapour pressure error corresponds to the average of the triplicate data errors. With this methodology, it was possible to estimate the apparent vapour pressure,  $P_{EMAP}$  (Pa), for each substance and temperature, using equation (1).

(Note: this method is not valid for hygroscopic substances).

### 3 Results and discussions

A typical Clausius–Clapeyron’s linear plot of  $\ln(P)$  against  $1/T$  was obtained with the experimental data according to the expression

$$\ln(P) = -\frac{\Delta_{\text{vap}}H}{R} \left( \frac{1}{T} \right) + B, \quad (2)$$

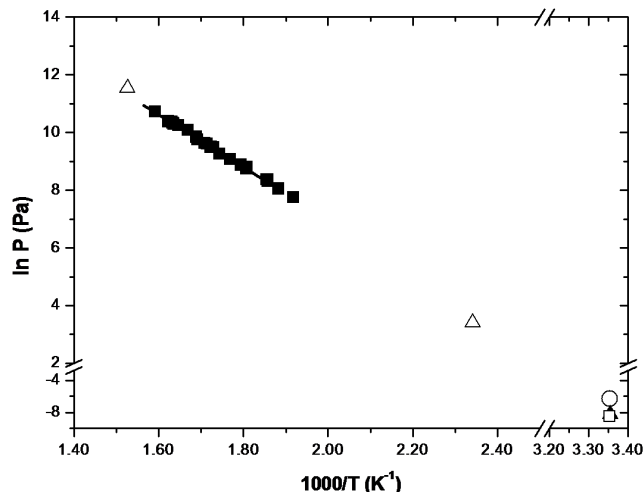
where  $P$  is the vapour pressure (Pascal),  $\Delta_{\text{vap}}H$  is the enthalpy of vapourisation ( $\text{kJ mol}^{-1}$ ),  $R$  is the universal gas constant ( $\text{kJ mol}^{-1} \text{K}^{-1}$ ),  $T$  is the absolute temperature (K) and  $B$  is a constant.

#### 3.1 Cottrell’s method

As can be seen in Figure 1, a linear behaviour was obtained in the range of temperature from 521 until 613 K, from three independent experiments. From the slope, it was derived a  $\Delta_{\text{vap}}H_m$  ( $\text{kJ mol}^{-1}$ ) =  $77.6 \pm 1.4$  for E-EHMC at  $T_m = 567$  K. On the other hand, Pegoraro et al. (2015) have estimated for E-EHMC a  $\Delta_{\text{vap}}H_{298.15} = 108.9 \pm 1.8 \text{ kJ mol}^{-1}$ , using GC-RT methodology.

Besides, the extrapolated vapour pressure of E-EHMC at 298.15 K was estimated in  $(3.4 \pm 0.3) \times 10^{-3}$  Pa that is almost a factor 2 bigger than  $1.8 \times 10^{-3}$  Pa previously estimated at the same temperature (EPISuite-EPA, 2016).

A boiling point of  $664 \pm 1$  K for E-EHMC was derived by the experimental data extrapolation which is in reasonable agreement with the boiling temperature of  $T_b = 653$  K suggested by the European Chemical Agency (ECHA) database. Also, it was included, in Figure 1, the vapour pressure of 30 Pa at 427 K from the same database (ECHA, 2016).

**Figure 1** Clausius-Clapeyron's plot for E-EHMC using Cottrell's method

The symbols are: ■, this work; ○, ref. (EPISuite-EPA, 2016); △, ref. ECHA. □ this work, extrapolated data (equation (3)). ▲ ref. Pegoraro et al. (2015). The equation of the line obtained by a linear regression is given by:  $y = (-9306 \pm 52) (K) x + (25.54 \pm 0.09)$   $R^2 = 0.999$ .

Nevertheless at higher temperatures, it occurs its thermal decomposition turning the sample into a brownish liquid. Therefore, this estimated boiling point for practical applications should be used carefully.

Since the linearity of Clausius-Clapeyron's equation can be reduced only to an enclosed range of temperature, new mathematic approaches have been developed to extend the range of extrapolation temperature accurately (Chickos and Hanshaw, 2004; Gobble et al., 2013).

Then, the experimental values of E-EHMC vapour pressure versus  $1000/T$  ( $K^{-1}$ ), shown in Figure 1, were adjusted using a third-order polynomial, which allowed a good extrapolation for the temperature. This equation was then used to extrapolate the vapour pressure at  $T = 298.15$  K and to predict the normal boiling temperature.

$$\ln(P/P_0) = AT^{-3} + BT^{-2} + CT^{-1} + D. \quad (3)$$

The present E-EHMC experimental data give values of  $A = 3.03 \times 10^{-7}$  ( $K^3$ ),  $B = -5.72 \times 10^{-4}$  ( $K^2$ ),  $C = 3.85 \times 10^{-1}$  ( $K^1$ ) and  $D = -8.05 \times 10^1$  (adimensional) ( $R^2 = 0.999$ ), using equation (3). In this approach, a boiling point of E-EHMC of 659 K was obtained and is in better accordance with the  $T_b = 653$  K suggested by ECHA database (ECHA, 2016).

Also, equation (3) was used to extrapolate the vapour pressure,  $P$  (Pa) (298.15 K). A vapour pressure of  $(1.95 \pm 0.02) \times 10^{-4}$  Pa was obtained for E-EHMC isomer. This value is almost one order of magnitude lower than  $1.8 \times 10^{-3}$  Pa estimated previously at the same temperature (EPISuite-EPA, 2016) but it is in accordance, within experimental error, with  $(2.54 \pm 0.02) \times 10^{-4}$  Pa at 298.15 K estimated by Pegoraro et al. (2015).



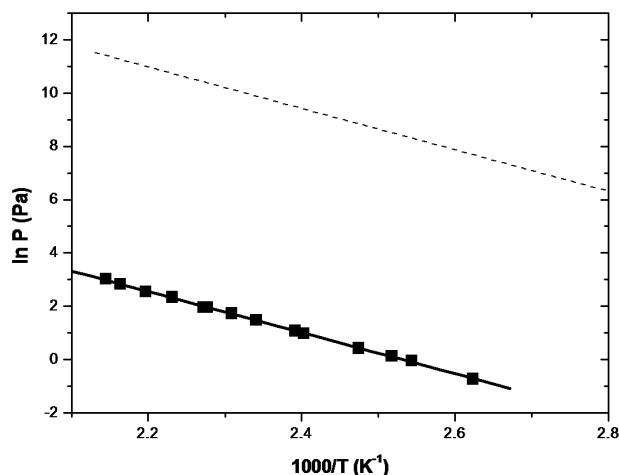
### 3.2 Effusion method under atmospheric pressure

#### 3.2.1 Estimation of the enthalpy of vapourisation

The EMAP method was used to measure the apparent vapour pressure,  $P_{\text{EMAP}}$  (Pa), of several liquid substances, using Knudsen's equation (equation (1)), following the experimental procedure above described. The  $P_{\text{EMAP}}$  (Pa) values were represented in a classic Clausius–Clapeyron's plot (equation (2)) in order to determine the experimental  $\Delta_{\text{vap}}H_m(T_m)$  for each substance.

In Figure 2, the bibliographic data together with the  $P_{\text{EMAP}}$  (Pa) for ethanediol vapour pressure were plotted using a typical Clausius–Clapeyron's graphic, as an example. As can be seen, similar slopes could be observed in the graphic using bibliographic and EMAP data from which can be derived the  $\Delta_{\text{vap}}H_m(T_m)$  value of the substance. Nevertheless, EMAP method cannot reproduce the real vapour pressure of the substance at each temperature since both lines are not coincident. Therefore, the EMAP is not an absolute methodology to determine vapour pressure. To provide an experimental validation of the EMAP methodology, a calibration curve was done. Thus, a careful selection of standard substances was made to provide a wide range of organic compounds with different functional groups and  $\Delta_{\text{vap}}H_m(T_m)$  to assure that any new substance can be included accurately within this calibration. The selected substances are liquid, in standard condition; the molecular weight range included mass from 18 to 362.03 g mol<sup>-1</sup> and boiling point from 341.9 to 613.0 K.

**Figure 2** Clausius–Clapeyron's plot for Ethanediol



Bibliographic (----) and EMAP (-■-) data.

A similar range of temperature for both, EMAP and bibliographic experimental values, was taken into account as selection criteria to choose the bibliographic  $\Delta_{\text{vap}}H_m(T_m)$ . The temperature and time range used in each EMAP experiment were also detailed in Table 1 together with the experimental  $\Delta_{\text{vap}}H_{\text{EMAP}}$  obtained at  $T_m$  (K) and the absolute difference between both sources of  $\Delta_{\text{vap}}H_m(T_m)$  data. Then, bibliographic against EMAP vapourisation enthalpies of the standard substances were correlated. A linear behaviour was obtained with an equation of  $\Delta_{\text{vap}}H_{\text{bib}}(T_m/\text{K}^{-1}) = 0.99 \Delta_{\text{vap}}H_{\text{EMAP}}(T_m/\text{K}^{-1})$  with a

$R^2 = 0.998$ . This defines the performance of this methodology to describe  $\Delta_{\text{vap}}H_m (T_m \text{ K}^{-1})$  for different substances, which, in turns, becomes a good tool to accurately determine this magnitude for an unknown substance. In the light of the above described, the experimental  $\Delta_{\text{vap}}H_{\text{EMAP}} (T_m \text{ K}^{-1})$ , within experimental error, can reproduce the  $\Delta_{\text{vap}}H_m (T_m)$  of a substance under study.

### 3.2.2 Estimation of the vapour pressure

Partitioning between the gas phase and environment condensed phase is an important process in determining the transport and fate of organic chemicals in the atmosphere as well as in others environmental compartments. The  $P$  (Pa) (298.15 K) is an environmental relevant data since it is a useful descriptor of the atmospheric transportation and distribution of the organic substances in the environment (Bidleman, 1988).

For each molecule, the  $P$  (Pa) (298.15 K) can be obtained by direct measure, extrapolation of the Clausius–Clapeyron’s plot or correlating bibliographic with experimental data. For substances with low vapour pressure, the first procedure can result experimentally unavailable.

Depending on the molecules, the extrapolation procedures could be biased since the linearity of Clausius–Clapeyron’s equation can be reduced only to an enclosed range of temperature. A good practice to reduce this inconvenience is to correlate the bibliographic with experimental  $P$  (Pa) at a determined temperature, in this case, 298.15 K.

Table 2 collects the experimental data of the standard molecules used in the correlation graphic of  $\ln(P_{\text{bib}}/\text{Pa})$  against  $\ln(P_{\text{EMAP}}/\text{Pa})$  at 298.15 K, that are depicted in Figure 3. The equation of the line obtained by a linear regression is given by:

$$\ln(P_{\text{bib}}/\text{Pa}) = (1.319 \pm 0.028) \ln(P_{\text{EMAP}}/\text{Pa}) + (11.54 \pm 0.26) \quad R^2 = 0.9973. \quad (4)$$

Then, the unknown vapour pressure at 298.15 K of any substance under study can be obtained from its experimental value of  $P_{\text{EMAP}}$  at 298.15 K using the correlation curve (Figure 3, equation (4)). The corrected value was called  $P_{\text{corr}}$  (Pa) at 298.15 K (see Table 2).

### 3.3 Quality criteria

There are quality criteria for repeatability and reproducibility of the Knudsen effusion method that has been established by the OECD for vapour pressure studies (OECD, 1993). They estimated the repeatability of vapour pressure values must be between a range of RSD (relative standard deviation) of 5–20%. On the one hand, the repeatability is the variation in the vapour pressure obtained when the same procedure is used several times while measuring the same sample at a given temperature. The repeatability for the EMAP vapour pressure measurements at each temperature lies into a range of RSD of 0.5–15% and this is clearly compatible with the OECD criteria.

On the other hand, reproducibility is the average of the vapour pressure at a given temperature when measuring the same sample at different times using the same procedure. The estimated reproducibility by OECD for the Knudsen effusion method is up to 50%. Several essays were carried out in order to determine the reproducibility of the vapour pressure obtained by EMAP when the effusion time changes.

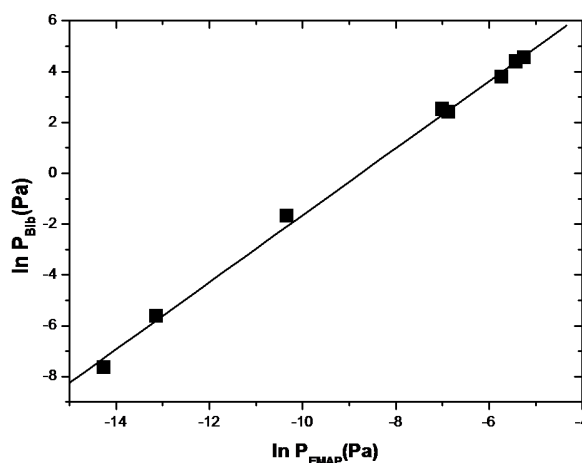
**Table 2** Experimental vapor pressure values of standard and target molecules

Compound	$\ln(P_{EMAP}/Pa)$ at $T_m$	$\ln(P_{corr}/Pa)$ at 298.15 K <sup>f</sup>	$\ln(P_{bib}/Pa)$ at 298.15 K
N,N-dimethyl- Benzenamine	-5.245	-	4.238 <sup>a</sup>
Dimethyl Sulfoxide	-5.412	-	4.378 <sup>b</sup>
FTOH 6:2	-5.723	-	3.784 <sup>c</sup>
Ethanediol	-6.999	-	2.509 <sup>d</sup>
1-Octanol	-6.863	-	2.398 <sup>e</sup>
Hexadecane	-10.328	-	-1.68 <sup>f</sup>
Dibutylphthalate	-13.129	-	-5.627 <sup>g</sup>
Triethanolamine	-14.255	-	-7.642 <sup>h</sup>
Z-EHMC	-12.590	-5.07±0.10 <sup>i</sup>	-
E-EHMC	-14.889	-8.10±0.16 <sup>i</sup>	-

<sup>a</sup>Stephenson and Malanowski (1987), <sup>b</sup>Fulem et al, (2011), <sup>c</sup> Krusic et al, (2005),

<sup>d</sup>Verevkin (2004), <sup>e</sup>Nasirzadeh et al, (2006) <sup>f</sup>Goss et al, (1999), <sup>g</sup>Stales et al, (1997),

<sup>h</sup>Daubert and Danner (1989), <sup>i</sup>This work.

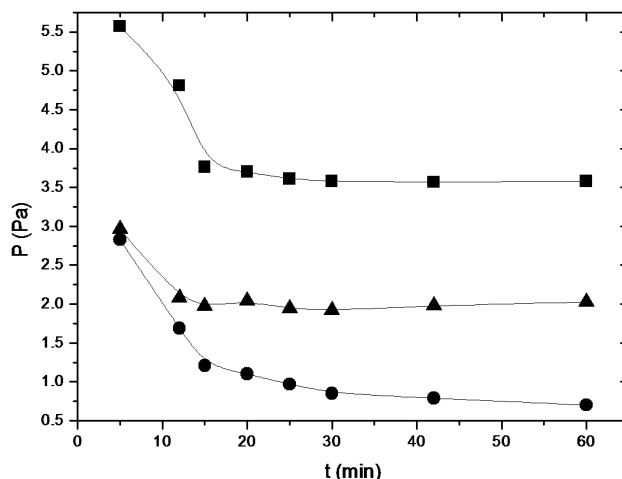
**Figure 3** Data correlation of vapor pressure at 298.15 K between bibliographic ( $\ln P_{bib}$ ) and experimental values obtained by the EMAP method ( $\ln P_{EMAP}$ )

The EMAP effusion results for hexane, ethyl acetate and water at 343.15 K are collected in Figure 4. As can be seen, they showed similar behaviour arising to a plateau where the fluctuation of the vapour pressure values are less than 2.5% and, within experimental error, turn to the essays independent of the time of measurement. This time is directly dependant of each substance and the temperature of each essay therefore it must be determined experimentally. In this methodology, it was used in all the cases measurement time bigger than 25 min.

The incidence of a low mass loss, temperature inhomogeneities together with the presence of air into the sample could be the main reasons to the upper limit of pressure at short time of measurement ( $t < 25$  min). Also, the temperature stability into the

thermostatic chamber plays the most important role to obtain experimental results with lower RSD.

**Figure 4** EMAP vapor pressure against effusion time at 343.15 K for Hexane (-■-), EthylAcetate (-▲-), Water (-●-)



Reproducible vapour pressures were obtained over a wide range of mass loss. In the set of experiments, each measurement for triplicate implies a range of average mass loss of approximately 30 mg. Within experimental error, the impurities in the original sample do not seem to have a relevant incidence in the experimental estimations.

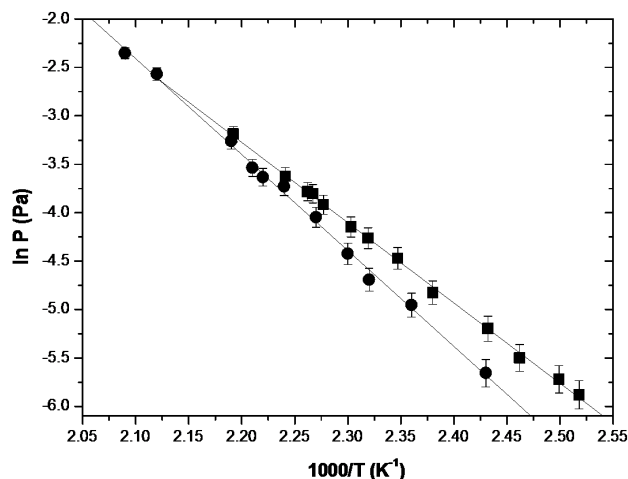
### 3.4 Vapourisation of *E*-EHMC and *Z*-EHMC

EMAP was used to determine the vapour pressure of liquid samples of *E*-EHMC and *Z*-EHMC esters. To check the correct development of the method, ethanediol was used as external standard in all these measurements, due to a similar behaviour with the samples. Blank, samples and standard all for triplicate were introduced into the chamber following all the steps described in Experimental Methodologies section. Fresh samples were always used at each temperature.

As can be seen in Figure 5, a linear behaviour for *E*-EHMC and *Z*-EHMC was obtained, in the measured temperature range. In Table 3, the linear regression values for the measured substances with EMAP methodology were collected.

According to Clausius–Clapeyron equation, the thermodynamic parameter obtained for *E*-EHMC sample was  $\Delta_{\text{vap}}H (T_m = 445) = 82.8 \pm 1.3 \text{ kJ mol}^{-1}$  and for *Z*-EHMC, a  $\Delta_{\text{vap}}H (T_m = 427) = 67.1 \pm 1.4 \text{ kJ mol}^{-1}$  was estimated.

EMAP estimates a  $P_{298.15 \text{ K}}$  of  $(3.04 \pm 0.06) \times 10^{-4} \text{ Pa}$  for *E*-EHMC that is in the same order of magnitude of  $(1.8 \pm 0.1) \times 10^{-4}$  and  $(1.95 \pm 0.02) \times 10^{-4} \text{ Pa}$  obtained by Pegoraro et al. (2015) and, in this work, by Contrell's method, respectively. But is almost one order of magnitude lower than  $1.8 \times 10^{-3} \text{ Pa}$  estimated previously (EPISuite-EPA, 2016).

**Figure 5** Clausius-Clapeyron plot for E-EHMC and Z-EHMC using EMAP method. E-EHMC (●) and Z-EHMC (■)**Table 3** Clausius-Clapeyron linear regression values of the substances under study

Compound	$\Delta_{\text{vap}}H/R$ (K)	Intercept	$R^2$
n-Hexane	$-3662 \pm 36$	$12.77 \pm 0.12$	0.998
Ethyl Acetate	$-4207 \pm 59$	$13.98 \pm 0.19$	0.998
Water	$-5082 \pm 62$	$15.64 \pm 19$	0.998
N,N-dimethyl-Benzenamine	$-6105 \pm 93$	$15.23 \pm 0.22$	0.998
Dimethyl Sulfoxide	$-6104 \pm 96$	$17.12 \pm 0.10$	0.998
FTOH 6:2	$-6948 \pm 104$	$17.58 \pm 0.26$	0.999
Ethanodiol	$-7675 \pm 46$	$18.74 \pm 0.11$	0.999
1-Octanol	$-7185 \pm 97$	$17.24 \pm 0.22$	0.999
Hexadecane	$-7698 \pm 103$	$15.49 \pm 0.22$	0.998
Dibutylphthalate	$-9406 \pm 133$	$18.42 \pm 0.29$	0.998
Triethanolamine	$-10753 \pm 148$	$21.81 \pm 0.32$	0.998
Z-EHMC	$-8072 \pm 169$	$14.48 \pm 0.39$	0.996
E-EHMC	$-9961 \pm 157$	$18.52 \pm 0.35$	0.998

In the case of Z-EHMC, a  $P_{298.15\text{ K}} = (6.3 \pm 0.5) \times 10^{-3}$  Pa was estimated using EMAP and is, in almost a factor 7, bigger than the  $(9.8 \pm 0.1) \times 10^{-4}$  Pa reported by Pegoraro et al. (2015). However, Z-EHMC is more volatile than E-EHMC in both experiments but, in this work, Z-EHMC is a factor 21 more volatile.

As can be observed, EMAP methodology can distinguish, within experimental error, the different vapourisation behaviour of each isomer.

### 3.5 Estimating gas–particle partition coefficient from vapour pressure

The distribution of an airborne particle-associated compounds between the gas phase and the surface of the airborne particles is described by an equilibrium constant referred to as the gas–particle partition coefficient,  $K_p$  (Pankow, 1987):

$$K_p = \frac{F \times TSP^{-1}}{C_g}, \quad (5)$$

where  $F$  is the equilibrium particle-phase concentration of the compound (mass/volume) and  $C_g$  is the equilibrium gas-phase concentration of the compound (mass/volume). TSP is the total suspended particles (mass/volume) and the ratio ‘F/TSP’ ( $C_{\text{Particle}}$ ) is the fractional concentration of a given organic compound on airborne particles.

It is well known that the logarithm of  $K_p$  correlates with the log of the saturation vapour pressure of the pure subcooled liquid,  $P_L^0$  (Pankow and Bidleman, 1991; Pankow, 1994). A experimental relationship between  $K_p$  and  $P_L$  has been reported by Naumova et al. (2003) and is showed in equation (6).

$$\text{Log } K_p = -0.860 \log P_L - 4.67. \quad (6)$$

Table 4 collects the obtained values of  $K_p$  (E-EHMC) and  $K_p$  (Z-EHMC) using the vapour pressure estimated by EMAP method into equation (6) and being in good agreement with the results previously reported by Pegoraro et al. (2015) (see Table 4).

**Table 4** Vapour pressure, gas-particle partition coefficient ( $K_p$ ) and particle bond-fraction ( $\Phi$ %) of Z-EHMC and E-EHMC esters

	$\ln PL$		$\log K_p (PL)$		$\Phi$ %	
Z-EHMC	-5.07 <sup>a</sup>	-6.99 <sup>b</sup>	-2.77 <sup>a</sup>	-2.06 <sup>b</sup>	4 <sup>a</sup>	16.43 <sup>b</sup>
E-EHMC	-8.10 <sup>a</sup>	-8.63 <sup>b</sup>	-1.65 <sup>a</sup>	-1.44 <sup>b</sup>	32 <sup>a</sup>	41.31 <sup>b</sup>

<sup>a</sup>This work, <sup>b</sup>Pegoraro et al. (2015).

### 3.6 Particle bound fraction

In the atmosphere, semi-volatile organic compounds (SVOCs) are present in the gas phase and attached to particles. The experimental value of the particle-bound fraction,  $\Phi$  (%), of each compound can be determined using the following equation:

$$\Phi = \frac{c_p}{c_G + c_p} = \frac{K_p \text{ TSP}}{1 + K_p \text{ TSP}}, \quad (7)$$

where  $C_p$  ( $\text{ng } \mu\text{g}^{-1}$  of particles) is the concentration of the compound on particles,  $C_G$  ( $\text{ng m}^{-3}$ ) is the concentration of the compound in the gas phase while  $K_p$  and TSP are in unit of  $\text{m}^3 \mu\text{g}^{-1}$  and  $\mu\text{g}_{\text{aerosol}} \text{m}^{-3}$  of air, respectively. TSP values can vary depending on the monitoring site. Lohmann and Lammel (2004) estimate TSP values of 55, 22, 14 and  $7.7 \mu\text{g}_{\text{aerosol}} \text{m}^{-3}$  of air, for urban, suburban, background, and remote site, respectively.

The models predict that E-EHMC will be more strongly adsorbed to the particulate matter than Z-EHMC one ( $\Phi_{\text{E-EHMC}} = 32 \pm 17\%$  and  $\Phi_{\text{Z-EHMC}} = 4 \pm 3\%$ ) and are, within experimental error, in good agreement with Pegoraro et al. (2015) results (see Table 4).

## 4 Conclusion

EMAP is an indirect methodology capable of providing accurate vapour pressures at 298.15 K for organic compounds if the method is properly calibrated. It reproduces the  $\Delta_{\text{vap}}H_m(T_m)$ . This is an inexpensive, quick and robust methodology to estimate thermodynamic properties of vapourisation for liquid organic substances. The blank, standard and sample tubes could be in the thermostatic chamber simultaneously, hence these facts reduce notably the experimental times. In addition, this method can be performed with small amounts of sample due to its iterative procedure and the low mass lost in each experiment. This technique was applied to determine a wide range of vapour pressures from  $10^{-3}$  to  $10^4$  Pa. Also, atmospheric gas–particle partitioning of the organic substances can be derived in good agreement with other methodologies well established.

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