Vapour pressures of selected organic compounds down to 1 mPa, using mass-loss Knudsen effusion method

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ABSTRACT

A recently developed Knudsen effusion apparatus was improved and used for measurements of vapour pressures of selected organic compounds. Calorimetric studies were conducted using a Calvet-type calorimeter, complementing the information obtained for the vapour pressures and facilitating the modelling and analysis of the data.

Vapour pressures of benzoic acid, a reference substance, were determined at temperatures between 269 K and 317 K, corresponding to a pressure range from 2 mPa to 1 Pa, extending the range of results available in the literature to lower pressures. Benzanthrone was studied between temperatures 360 K and 410 K (5 mPa–1 Pa) in order to test the apparatus at higher temperatures.

Values presented in the literature for the vapour pressure of solid *n*-octadecane, one of the most promising compounds to be used as "phase change material" for textile applications, were found inconsistent with the triple point of the substance. Sublimation pressures were measured for this compound between $T = 286$ K and 298 K (2–20 mPa) allowing the correction of the existing values. Finally, vapour pressures of diphenyl carbonate, a compound of high industrial relevance for its use in the production of polycarbonates, were determined from $T = 302$ K to 332 K (0.02–1 Pa).

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1. Introduction

Vapour pressure is one of the most important thermophysical properties in the chemical industry given its influence on separation processes [1]. Increasing demands for higher process efficiency require precise and accurate data. In the agrochemical industry, the vapour pressure of the active ingredient in the formulation determines its availability, and has a preponderant role in transport, distribution and faith of the compounds in the soil [2].

The vapour pressure of a substance is closely related with its evaporation rate, and is of high relevance in health and safety studies, regarding air quality in workplaces and in domestic environments, as vapour pressure determines to which extent a substance may be available for inhalation. Under the REACH program by the European Union (Registration, Evaluation, Authorization and Restriction of Chemical substances), which requires the characterization and testing of all the chemicals produced or commercialized in the European Union, substances are considered to be non-volatile if $p(293.15 \text{ K}) \leqslant 0.01$ Pa. In such cases, expensive inhalation tests are not required, saving considerable amounts of money and minimizing animal testing [3].

But the accurate determination of such low vapour pressures is not easy. One of the most common methods for the determination of vapour pressures under 1 Pa is the Knudsen effusion method [4–6]. In this work a mass-loss technique was used for pressure measurements down to around 1 mPa, well below the usual range of application of this technique, and in the range of interest for measurements performed regarding the REACH program. The Knudsen effusion apparatus was previously tested with the study of phenanthrene and anthracene [7]. In this work, we present results obtained with benzoic acid down to $T = 269$ K providing new data in pressure ranges for which no accurate data was available. Benzoic acid has been recommended as secondary standard for enthalpy of sublimation measurements [8], and as reference material for vapour pressure measurements [9]. Benzanthrone, for which several quality data sets exist in literature for a small pressure range, was also studied up to $T = 410$ K, in order to test the apparatus for higher temperatures and expand the range of data available.

In this work we also present the results obtained in the study of two industrially relevant compounds. With a melting point around $T = 301$ K (28 °C), *n*-octadecane is one of the most promising compounds to be used as phase change material (PCM). PCMs are materials which can absorb and release large quantity of latent heat during a phase change. Their application ranges from heat storage, cooling and refrigeration, to thermal comfort in clothes and buildings. Having a transition temperature close to the comfort

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temperature of the human body and an enthalpy of fusion higher than other PCMs with phase transitions in the same range of temperatures [10], *n*-octadacane has been the subject of many studies regarding application in clothes with built-in thermo-regulating properties [10–12], and in polyurethane foams for thermal insulation of buildings [10,13,14].

The vapour pressure of the PCM has an important role in the optimization of the processes through which the PCM is integrated in the fibres or into polyurethane foams. During a literature review, inconsistencies were found in the vapour pressure data available in the literature, including values recommended in a preeminent database. This served as a motivation for the study performed here.

Another compound of great interest for the polymer industry is diphenyl carbonate (DPC), which is used in combination with bisphenol A in the production of polycarbonates, being a key intermediate in the production process. It is also a product of the decomposition of polycarbonates. Traditionally, DPC is prepared through the reaction of phenol with phosgene, but the high demand for this compound, consequence of the growth in the polycarbonate market, motivated the chemical industry as well as oil companies to develop new, safer, more efficient and environmentally friendly production methods. The vapour pressure of DPC is relevant for a number of processes, from production to transport, and its use in the manufacturing of other products.

The vapour pressure measurements were complemented with calorimetric studies of heat capacities and enthalpies of fusion, for a better analysis and determination of thermodynamic parameters.

2. Experimental

2.1. Vapour pressures

In the Knudsen effusion method, a compound is placed at the bottom of a cylindrical cell and its vapour is allowed to effuse through a small orifice of area A_0 located at the top of the cell, into an evacuated space. For a particular temperature, T, the vapour pressure can be calculated through equation (1), where M is the molar mass of the effusing vapour, m is the mass of effused compound during the effusion time t, R is the molar gas constant, and w_0 is the transmission probability factor, calculated through equation (2), where ℓ is the length of the effusion orifice and r its radius.

$$p = (m/w_0 A_0 t) \cdot (2\pi RT/M)^{1/2}, \qquad (1)$$

$$w_0 = [1 + (3\ell/8r)]^{-1}. \qquad (2)$$

A recently developed Knudsen effusion apparatus was used in this work. The characteristics of the apparatus as well as the experimental procedure have already been described in detail [7]. For the present work, improvements were made aiming at the measurement of lower pressures. Segments of the apparatus were redesigned, which together with the use of only stainless-steel parts and metal–metal ultra-high-vacuum connections, contribute to an ultimate vacuum during experiments below 3×10^{-6} Pa.

One of the main limitations of the mass-loss technique for the measurement of pressures below 0.1 Pa is the effusion time necessary to obtain a measurable mass loss. For such low pressures, more complex techniques such as mass spectroscopy or quartz crystal microbalance are normally applied. In the current apparatus however, this limitation is overcome by a fully automated operation, made possible by using a cold trap equipped with an electronic level sensor, and permanently connected to a 160 dm^3 liquid-nitrogen reservoir. Experiments can run longer, allowing effusion times up to 70 h or more. Since the calculation of the

vapour pressure does not depend exclusively on the mass loss, but rather of the effusion rate (mass/time), longer effusion times reduce the influence that eventual errors in the determination of the mass have on the results. Nevertheless, improvements to the apparatus previously described [7] were also made regarding this aspect, with a more precise analytical balance being used, a Mettler Toledo AT201 with a resolution of 0.01 mg.

2.2. Calorimetry

The measurement of enthalpies of fusion was performed using a commercial Calvet-type calorimeter Setaram C80. The calibration of the calorimeter was performed and is regularly verified using high-purity reference materials: indium (mass fraction > 0.99999), tin (mass fraction > 0.99999) and gallium (mass fraction > 0.999995).

The same calorimeter was used in the heat capacity determinations, using a temperature increment method. The validity of the method was first confirmed by the study of the heat capacity of solid benzoic acid, suggested as primary reference material for heat capacity measurements [8].

All calorimetric studies were performed in stainless steel cells, using around 0.5 g of substance. The temperatures and enthalpies of fusion were determined using heating rates of 0.008 K · s^{-1}.

2.3. Chemicals

A list of the compounds used in this work is given in table 1, together with the respective values of their mass fraction purity. All compounds were used as received, without further purification. In the measurements with benzoic acid, a high-purity sample was used, directly traceable to NIST SRM (National Institute of Standards, USA – Standard Reference Material) benzoic acid batch 350b.

3. Results and discussion

The areas, A_0, and transmission probability factors, w_0, of the effusion orifices used in the Knudsen effusion cells are given in table 2, while table 3 presents the results of the vapour pressure measurements performed in this work. These measurements were complemented by calorimetric studies of heat capacities, summarised in table 4, and by the determination of temperatures and enthalpies of fusion, presented in table 5 together with the average values of results available in the NIST database [15].

3.1. Benzoic acid and benzanthrone

The results for the two reference compounds are depicted in figure 1, together with values from literature for benzoic acid [16–33] and for benzanthrone [32–35].

TABLE 1
List of compounds used in this work and respective values of mass fraction purity.

Chemical name	CAS No.	Source	Mass fraction purity
Benzoic acid	65-85-0	Merck KGaA, Germany	0.9997[a]
Benzanthrone	82-05-3	ABCR GmbH, Germany	0.994
n-Octadecane	593-45-3	Aldrich Chemistry, Germany	0.995
Diphenyl carbonate	102-09-0	Aldrich Chemistry, Germany	0.998

[a] Directly traceable to NIST SRM (National Institute of Standards, USA – Standard Reference Material) benzoic acid batch 350b.