# A comparison of vapour pressure measurements of quinizarin and *leuco*-quinizarin via transpiration and thermogravimetry

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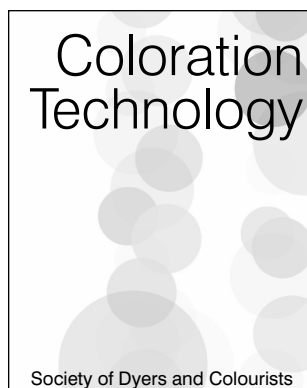
The vapour pressure of solids can be obtained using a number of methods, including the Knudsen effusion method, the Knudsen torque-effusion method and a transpiration method. Each method has benefits and disadvantages. Reported is a comparison of vapour pressure data for two compounds, quinizarin and *leuco*-quinizarin, using a transpiration method and a recently developed method based on thermogravimetry. Thermogravimetry provided vapour pressure–temperature dependence data for each compound with expediency and in agreement with the transpiration method.

Introduction

The pressure exerted by a solid or liquid at equilibrium with its own vapour phase is called the vapour pressure of that substance [1]. The vapour pressure of dyes can be used to provide data such as heat of vaporisation, heat of sublimation and rate of mass loss during a particular process or reaction [2–6]. Also, certain structure–property relationships can be obtained from vapour pressure measurements. For instance, heat of sublimation obtained from vapour pressure data can provide evidence of inter-molecular interactions, including hydrogen bonding and the effect of substituent groups on isomeric molecular properties. Thermodynamic and kinetic data of this kind are particularly valuable for designing molecules and modelling chemical processes such as those commonly used in textile applications, environmental chemistry and chemical synthesis.

In the case of textiles, experimental vapour pressure data can be employed to assist in the design of molecules for a number of applications. For example, in the case of transfer printing and the DuPont Thermosol dyeing process, a fibre is coloured via transition of the dye from the solid state to the gas phase, thereby facilitating gas-phase dyeing [7]. Although it might be advantageous for a dye to possess high vapour pressure for ease of transfer on to a substrate, the dye may subsequently re-volatilise during the lifetime of the product, resulting in a loss of dye from the dyed material [8]. Hence, for optimum properties, the dyestuff must be designed to exhibit a given vapour pressure over a limited energy (temperature) range.

A further example of the importance of vapour pressure is in the application of volatile ultraviolet (UV) absorbers that are commonly applied to polyester fibres and other plastics to provide UV protection. UV absorbers with high vapour pressure may not be suitable due to mass loss during the life of the UV-protected product.

More recently, dyes and other compounds have been applied to, and extracted from, fibres using supercritical (SC) fluid media. For environmental and economic reasons, a number of research groups worldwide are currently developing textile application methods using SC carbon dioxide [9–19]. Among the benefits of processing fibres using carbon dioxide in the supercritical state is abundance, low cost, non-flammability, recyclability, non-toxicity at low levels, and low critical temperature and pressure of carbon dioxide. The use of SC carbon dioxide technology in coloration gives renewed emphasis on the need for vapour pressure data of dyes, auxiliaries and dyestuff intermediates, since solute vapour pressure is a key factor in determining the solubility characteristics of solutes in SC fluids [15].

A model for predicting solubility of solutes in SC fluids has been proposed [20] based on the Redlich–Kwong equation of state and requires input parameters for the solvent or cosolvent, solute and processing conditions [21–23]. For the solute or cosolvent, properties required for the model include molar volume, critical temperature and pressure, molecular weight, boiling point and saturation vapour pressure. The predicted solubility in the SC fluid is obtained from Eqn 1:

$$y = P_V^{SAT} Q_V^{SAT} \exp\left[\frac{V^S}{RT}\left(P - P_V^{SAT}\right)\right] / Q_V P \qquad (1)$$

where y is the mole fraction solubility in the fluid phase, P_V^{SAT} is the saturated vapour pressure of the solid solute, Q_V^{SAT} is the fugacity coefficient at saturation pressure and takes into account non-ideality of the pure saturated vapour, V^S is the molar volume of the solid solute, Q_V is the vapour phase fugacity coefficient in the high-pressure gas mixture, R is the universal gas constant, T is the Kelvin temperature and P is the total pressure of the system [23].

The vapour pressure of the solid solute is a key parameter in determining the accuracy of the model. Thus, it is

important that accurate vapour pressure values are obtained. The vapour pressure of solids can be predicted using several estimation methods [21]. However, not all of the methods provide precise and accurate data for a broad range of temperatures. Furthermore, estimation methods of vapour pressure commonly do not account for positional isomer effects, which can have a profound effect on the vapour pressure of a given compound. Hence, there is a need for a rapid and accurate method for determining the experimental vapour pressure of experimental compounds to assess their suitability for use in applications in which vapour pressure is a critical property, as is the case for predicting solubility in SC fluids.

Methods for determining vapour pressure

Several ways of measuring vapour pressure have been reported. However, not all methods provide precise and accurate data. Some techniques produce useful data over a particular temperature range, whereas other methods fail in the same range. The vapour pressures of disperse dyes, for example, are low, and measurements are commonly performed using the Knudsen effusion method, Knudsen's torque effusion or a transpiration method [23]. The Knudsen effusion method involves measurement of mass loss with temperature [24] whereas the Knudsen torsion-effusion method involves measurement of the electromagnetic current generated in the system [25].

A further technique used to measure vapour pressure is the gas flow or transpiration method. This technique utilises pure nitrogen gas as the carrier gas and requires measurement of the condensed vapour by spectrophotometric analysis using Dalton's Law [26]. This is given by Eqn 2:

$$P_v = \left[n_D / (n_C + n_D) \right] P \tag{2}$$

where P_v is the vapour pressure of the compound, n_D is the number of moles of compound in the saturated gas, n_C is the number of moles of nitrogen passing over the solid and P is atmospheric pressure [23]. For accurate and precise data to be obtained, the carrier gas must be completely saturated with vapour and the inert gas must not solubilise the sample.

Only limited published work on the determination of vapour pressure of selected disperse dyes and dyestuff intermediates is available. Furthermore, most of the vapour pressure data have been determined using slightly different experimental systems and data obtained for the same compound can vary depending on the type of system used. Shimizu et al. measured the vapour pressure and heat of sublimation for 10 anthraquinone derivatives, 12 mono-azo compounds and two other non-ionic compounds [23]. The apparatus used was based on a modified transpiration method. The apparatus consisted of a pre-heater connected to a vapour generator at constant temperature. The latter was used to hold the test compound. Nitrogen gas was passed through the vapour generator, which carried the saturated dye vapour through a vapour guide tube to a condenser. The amount of dye condensed was measured spectrophotometrically and the vapour pressure was calculated as described above. Heat of sublimation calculated for the test compounds showed that the enthalpy of

sublimation is dependent on the structural characteristics of the compounds. Strong dye–dye interactions such as intermolecular hydrogen bonding increased the heat of sublimation. On the other hand, the presence of intramolecular hydrogen bonding resulted in a minimal increase in the heat of sublimation.

Nishida et al. reported the use of the transpiration method to determine the vapour pressures of six non-ionic azo dyes [27]. The heats of sublimation (ΔH_s) of the test compounds were found to be higher than azobenzene, the reference compound. The difference in ΔH_s was attributed to the incorporation of polar substituents that contributed to increased intermolecular forces. The presence of electrophilic groups, such as nitrogen and chlorine, were believed to enhance the dipole moment of the molecules resulting in higher heats of sublimation. However, the presence of bulky substituents such as those present in CI Disperse Blue 165 (1) countered the effect of an electrophilic substituent, the net result depending on the overall structure of the dye molecule.

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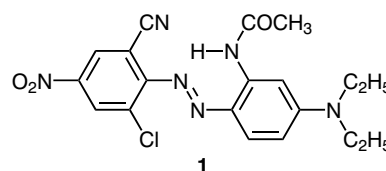
Nishida et al. also studied vapour pressures and heats of sublimation of 13 disperse dyes using another form of transpiration method [28,29]. Here also the effect of dipole moment and intermolecular interactions in molecules on vapour pressure was found to be significant. Vapour pressures of some vat dyes have also been reported [30].

Thermogravimetric method

Price et al. have described a method for the measurement of vapour pressure, heats of sublimation and vaporisation by thermogravimetry [31–35]. The vapour pressures of CI Disperse Yellow 54 (2) and CI Disperse Red 60 (3) have been studied by this method in addition to work on UV absorbers and plasticisers.


2   3
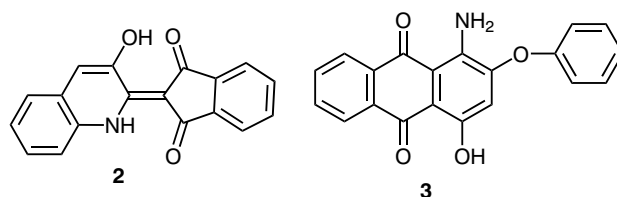
Other workers have adopted the same method to study fragrances and pharmaceuticals [36–43]. A thermobalance was used to measure the rate of mass loss per unit area of the dyes. Vapour pressure plots were generated using the Langmuir (or Hertz–Knudsen) equation shown in Eqn 3:

$$dm/dt = P_v \alpha \left(M/2\pi RT \right)^{1/2} \tag{3}$$

where, dm/dt is the rate of mass loss per unit area, P_v is the vapour pressure, M is the molecular weight of the effusing vapour, R is the universal gas constant, T is the Kelvin temperature and α is the vaporisation coefficient.

The vaporisation coefficient was determined by calibrating the equipment with substances of known vapour pressure. Data such as heats of sublimation and/or vaporisation were obtained directly from the data, whereas the melting point and heat of fusion were found indirectly.

One of the drawbacks to the transpiration and Knudsen methods is that they are time consuming and highly susceptible to variability. Thermogravimetry, however, potentially provides a method of obtaining vapour pressure data in a short period of time. To date, little direct comparison between the thermogravimetric method and another method for vapour pressure determination has been conducted. The purpose of the present paper, therefore, is to compare thermogravimetry and a transpiration method using identical materials. Two pure anthraquinone-based compounds were employed, quinizarin (1,4-dihydroxy-anthraquinone) (**4**) and *leuco*-quinizarin (2,3-dihydro-9,10-dihydroxy-1,4-anthracenedione) (**5**). These two compounds are used in the synthesis of some disperse dyes and are of interest to the authors as dyestuff intermediates with potential to be employed in the synthesis of anthraquinone-based dyes using SC carbon dioxide as the reaction medium. Hence, adequate solubility in the medium is critical and accurate prediction of solubilities at various temperatures and pressures is desirable. The development of a rapid and accurate method for vapour pressure measurement of dyes and dyestuff intermediates is therefore important.

4   **5**
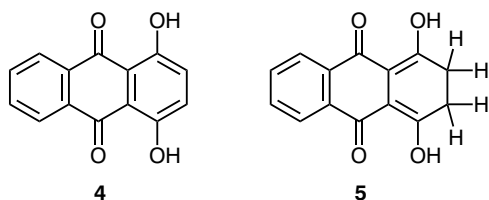
Experimental

Materials
Quinizarin and *leuco*-quinizarin were purchased from Aldrich Chemicals, Milwaukee, USA. Analytical grade isobutanol and acetone was purchased from Fisher Scientific, Fairlawn, NJ, USA. Re-sublimed benzoic acid (> 99.99%) was purchased from Aldrich Chemicals, UK. Dry, oxygen-free nitrogen was purchased from National Specialty Chemicals, Durham, NC, USA.

Methods
General
Quinizarin and *leuco*-quinizarin were recrystallised twice from isobutanol. Elemental analysis was performed at Atlantic Microlabs, Norcross, GA, USA. Melting points were obtained using a MeltTemp apparatus and were uncorrected.

Spectrophotometric analysis
A Varian Cary 3E UV–Vis spectrophotometer, interfaced to a computer with Win UV Bio software, was used for spectrophotometric analysis. Calibration curves were obtained for each compound at the maximum wavelength (λ_{max}) in acetone (λ_{max} of **4** = 478 nm; λ_{max} of **5** = 376 nm).

Differential scanning calorimetry
A Perkin-Elmer DSC 7 Differential Scanning Calorimeter (DSC) was used. The instrument was calibrated for temperature and heat flow response using the melting temperature and heat of fusion of pure tin. Due to the possibility of sublimation of the test materials under high temperatures, standard non-volatile aluminium sample pans were replaced with pressure resistant stainless steel pans, which resist pressure up to 32 atm. Data analysis was carried out using Pyris version 3.5 software.

Transpiration method
An apparatus was designed and built for vapour pressure measurements. The apparatus consisted of a 2.54×91.0 cm cylindrical copper tube into which was inserted a 1.27 cm $\times$ 30.5 cm copper tube. The inner tube was sealed at one end with a 6.6×10^{-3} cm wire mesh filter and connected to a copper sample collection tube via a union fitting. A type K thermocouple probe was inserted at the outlet of the sample tube. The test compound was coated onto 0.5 mm glass beads, which were loaded into the inner tube, and the tube capped with glass wool to insure close packing. Nitrogen gas was passed over the test compound at constant flow rate and temperature. Constant temperature was achieved by pre-heating the gas using a Fisher High Temperature Bath model 160 pre-heater. The flow rate of the gas was controlled by a two-way pressure regulator connected to a micro valve. The outer tube of the transpiration apparatus was heated to a constant temperature via a heating tape controlled by an Omega CN 76000 microprocessor temperature controller (90.0–170.0 °C). The temperature was controlled in the system to an accuracy of ± 0.2 °C. The entire system was insulated and vapour generated in the heated tube was carried to the condenser assembly by the nitrogen gas. The condensed vapour on the temperature probe and the sample collection tube was measured spectrophotometrically by dissolution in acetone.

Approximately 0.45 g of the test compound was coated onto approximately 13.5 g of glass beads by dissolving the compound in acetone and allowing slow evaporation of the solvent while in contact with the beads. The coated beads were then placed in the inner copper tube of the transpiration apparatus. The pre-heater was set at approximately the same temperature as the set temperature of the transpiration apparatus. Nitrogen gas was slowly released and the flow set to the desired rate using the flow meter. The experimental temperature was set and allowed to equilibrate to within ± 0.2 °C of the set temperature. After a specific running time (at least 12 h), heating was discontinued and nitrogen flow ceased. The inner tube was removed from the outer tube, and the condensed vapour in the condenser assembly was dissolved in acetone. The acetone solution was then diluted to a known volume and absorbance at λ_{max} of the test compound was measured spectrophotometrically. The concentration and moles of the test compound in solution was calculated from a previously prepared calibration curve of the test compound. The total mass of nitrogen that had flowed over the test compound was calculated from the experimental run time, flow rate and density of nitrogen at the set temperature. The vapour pressure of the test compound was calculated using Dalton's law. The procedure was repeated in triplicate at each temperature.

Thermogravimetric method

Measurements were carried out on a TA Instruments TGA 2950 thermobalance with a water-cooled vertical furnace. The temperature of the thermobalance was first calibrated using indium, tin, bismuth and lead [44] and the magnitude and linearity of the balance response was checked with standard milligram masses. Samples were placed in tared aluminium DSC sample pans with internal diameter 12.5 mm. The pan was filled completely with material, which was then melted so that a known sample surface area was obtained. A thermocouple was placed as close as possible to the surface of the sample to accurately record its temperature without interfering with the operation of the balance.

Measurements were made under helium (flow rate: 90 ml min^{-1} into the furnace and 10 ml min^{-1} though the balance assembly). Experiments were carried out on continuous heating at 1 °C min^{-1} and the rate of mass loss could be resolved down to *ca.* 25 mg min^{-1} m^{-2} under such conditions.

Results and Discussion

The molecular design of anthraquinone-based dyes and intermediates for use in SC carbon dioxide requires knowledge of the effects of substituents (auxochromes) present on the anthraquinone moiety on solubility properties in this fluid. Substituents commonly used in anthraquinone-based dyes include hydroxy, chloro, nitro, and primary and secondary amino groups. Primary and secondary amino groups have been studied previously [45–47]. However, little research has been dedicated to the analysis of dyes and dyestuff intermediates based on hydroxy anthraquinones for use in SC carbon dioxide.

Quinizarin and *leuco*-quinizarin are compounds commonly used in condensation reactions for the synthesis of anthraquinone dyes. The synthesis of dyes in SC carbon dioxide using these intermediates is under study in our laboratory. Hence, prediction of the solubility properties in SC carbon dioxide of these two compounds is of particular interest, since the ability to predict solubilities of dyes and dyestuff intermediates would facilitate rapid selection of candidates for experimental study using this medium. An accurate and expedient method for the measurement of vapour pressure is an important factor in predicting SC carbon dioxide solubility.

Compounds **4** and **5** were recrystallised from isobutanol and analysed by elemental analysis: **4**, theory: C, 69.94; H, 3.33%; found: C, 69.82; H, 3.36%; and **5**, theory: C, 69.35; H, 4.13%; found: C, 69.46; H, 4.23%. The λ_{max} for **4** and **5** were 7611 and 13 439 dm^3 mol^{-1} cm^{-1}, respectively. Visual observation of the melting temperature of each compound using a Melt Temp apparatus gave melting points for quinizarin and *leuco*-quinizarin of 198–199 and 154–156 °C, respectively, and by DSC analysis the melting points obtained were 200.91 and 155.81 °C; where required these data were used in the thermodynamic calculations. The λ_{max} for **4** and **5** was 7600 and 13 400 dm^3 mol^{-1} cm^{-1}, respectively.

Transpiration vapour pressure method

Theory

For each test compound, the Clausius–Clapeyron equation was used to determine the heat and entropy of sublimation. For a solid, the Clausius–Clapeyron equation takes the form shown in Eqn 4:

$$\mathrm{d}(\ln P)/\mathrm{d}T = \Delta H_s/RT^2 \qquad (4)$$

where, ΔH_s is the heat of sublimation, R is the universal gas constant, T is the Kelvin temperature and P is the vapour pressure of the solid at that temperature [30].

Eqn 5 gives the heat of sublimation for a range of temperatures, where ΔC_p is the difference in heat capacities between the gaseous and solid phases at constant pressure:

$$\Delta H_{sub}(T) = \Delta H_{sub}(T_m) + \int_T^{T_m} \Delta C_p(T)\mathrm{d}T \qquad (5)$$

However over a narrow temperature range, ΔC_p can be assumed to be independent of temperature [48]. Thus, ΔH_s can be assumed to be constant [24] and the Clausius–Clapeyron equation can thus be re-written as Eqn 6:

$$\log P = -A/T + B \qquad (6)$$

where, $A = \Delta H_s/2.303R$, $B = \Delta S_s/2.303R$ and P is expressed in Pa, R in J K^{-1} mol^{-1}, and ΔS_s is the entropy of sublimation in J mol^{-1} K^{-1} [18].

Therefore, the logarithm of vapour pressure for each compound was plotted against the reciprocal of Kelvin temperature, and the heat and entropy of sublimation for **4** and **5** were determined. The heat of vaporisation was also deduced using Eqn 7 (heat of fusion was obtained from the DSC analysis):

$$\Delta H_{sub} = \Delta H_{vap} + \Delta H_{fus} \qquad (7)$$

Procedure

It was necessary to determine the experimental time and gas flow rate that would ensure repeatability, accuracy and, in the case of flow rate, equilibrium of vapour in the carrier gas. Too high a flow may yield lower vapour pressure values due to incomplete saturation of the vapour in the carrier gas.

To determine the range of gas flow rate to be used for accurate vapour pressure measurements, the vapour pressure of **4** at 100 °C was determined with a run time of 18 h with varying nitrogen flow rate [15]. Constant vapour pressure values were obtained in the range 43–75 ml min^{-1}; the flow fluctuated significantly below 35 ml min^{-1}. The flow rate range compares well with the flow rates used for disperse dyes by other workers. Nishida *et al.* used approximately 25–55 ml min^{-1} [28] and Shimizu *et al.* used 20–40 ml min^{-1} [23]. Using the optimum flow rate range, vapour pressure measurements were made as a function of time. Constant vapour pressure measurements were obtained for run times between 12 and 24 h.

Using the above conditions vapour pressure measurements were determined for compounds **4** and **5** from 90–120 °C at 10 °C intervals and the results are shown in Figure 1. The reproducibility of the data was good, with the average scatter of the vapour pressure being reproducible up to ± 4.5% [15]. As expected, a graph of logarithm of vapour pressure versus the inverse of the absolute temperature yields a straight line as shown in Figure 2. Selected thermodynamic data for compounds **4** and **5** are shown in Table 1.

Thermogravimetric vapour pressure method

Theory

Analysis of the thermogravimetric data is based on the Langmuir equation (Eqn 3) for evaporation *in vacuo* [49]. Usually, α, the vaporisation coefficient, is assumed to be unity. However, in the case of a material volatilising into a
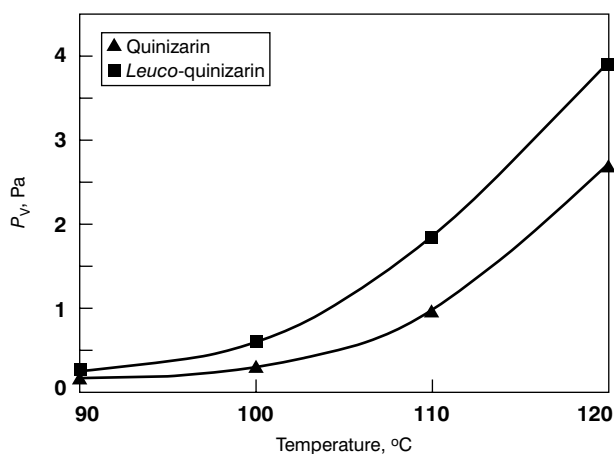

Figure 1 Plot of vapour pressure versus temperature for compounds **4** and **5**
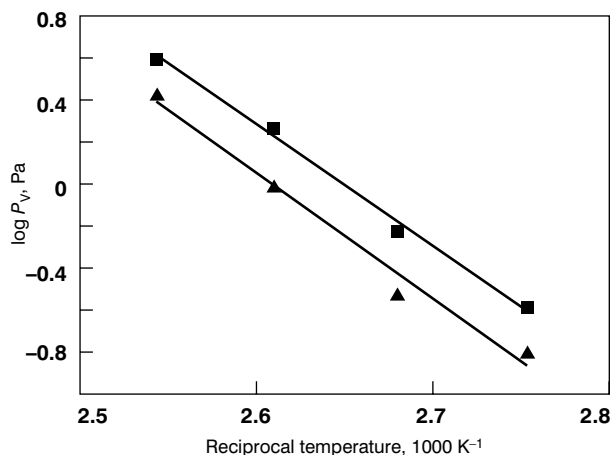

Figure 2 Logarithm of vapour pressure versus reciprocal of temperature for compounds **4** and **5**

flowing gas stream at 1 atm rather than a vacuum this assumption is no longer valid. Furthermore, from the point of view of the kinetic theory of gases, this equation is proper when the vapour near the surface does not move macroscopically, and when the state of vapour is described by a Maxwell function. In the current configuration, the sample is contained in an open pan and these conditions cannot be satisfied. In order to accommodate these effects, Eqn 3 can be rearranged to give Eqn 8:

$$p = kv \qquad (8)$$

$$\text{where} \quad v \text{ is } \frac{dm}{dt}\sqrt{T/M}$$

where k can be evaluated by calibration with substances of known vapour pressure [31].

In this work, benzoic acid was employed to calibrate the apparatus using the vapour pressure data of De Kruif and Blok [50]. At the melting temperature, Eqn 7 can be used to calculate the heat of fusion. Below the melting temperature the heat of sublimation is given according to modified version of Kirchoff's law (Eqn 6). Combining Eqn 6 with Eqn 8 gives Eqn 9:

$$\ln v = \mathrm{B}' - \frac{\Delta H}{RT} \qquad (9)$$

where B′ is a new constant. Thus, the heats of vaporisation and sublimation can be found directly from the rate of mass loss obtained by thermogravimetry providing the molecular weight of the vaporising species is known [31].

In cases where the material is insufficiently volatile in the solid state, measurements can be made by this technique using an approximation for the vapour pressure in this region by taking into account the material's melting temperature and heat of fusion measured by DSC and extrapolating the data according to Eqn 10 [31,33]:

$$p(T) = p(T_{\mathrm{m}})\exp\left\{\frac{-\Delta H_{\mathrm{sub}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{m}}}\right)\right\} \qquad (10)$$

where $p(T_{\mathrm{m}})$ is the vapour pressure at the melting temperature, obtained by extrapolation of the vapour pressure data in the melt, and ΔH_{sub} is the heat of sublimation from Eqn 7.

Procedure

Variations in gas flow rate or heating rate did not appear to affect the rate of mass loss [43]. Doubling the free surface area of the sample (by using two cups) doubled the absolute rate of mass loss. Observation of the rate of mass loss at a

Table 1 Selected thermodynamic data for compounds **4** and **5**

Compound	Temp. (°C)	A	B	ΔH_{sub} (kJ mol⁻¹)	ΔS_{sub} (J mol⁻¹ K⁻¹)	ΔH_{vap} (J mol⁻¹)	ΔH_{fus} (kJ mol⁻¹)
4	90	6020	15.71	115.49	205.41	98.65	16.85
5	90	5782	15.31	110.64	197.17	95.64	15.01

constant temperature confirmed that the process followed zero order kinetics (i.e. dm/dt was constant [51]) and served to check that the free surface area was not changing significantly or that thermal degradation of the sample was not occurring.

A calibration curve was constructed using benzoic acid as a reference compound and using vapour pressure data from the literature [50,53,54]. Representative calibration curves have been published elsewhere [31,34,36,37,43]. Once calibrated, vapour pressure data of other compounds can be obtained. To test the method, this approach was undertaken using compounds in which accurate vapour pressure data is known via other methods. For example, the thermogravimetric data was in good agreement with literature data using dioctyl phthalate [34]. However, no comparison between the thermogravimetric method and a transpiration method to obtain vapour pressure data for anthraquinone-based compounds has been reported.

Comparison of the transpiration and thermogravimetric methods

The temperature range used for the transpiration method was 90–140 °C, while sufficient volatility to conduct the thermogravimetric-based experiments was achieved at temperatures greater than 200 °C. The data can be conveniently com-pared, however, by calculating the vapour pressure across the entire temperature range using Eqns 9 and 10 and data obtained by DSC. Figures 3 and 4 show graphs of experi-mental vapour pressure versus temperature for compounds **4** and **5**, respectively, using the two techniques as well as the vapour pressure calculated using Eqn 10.

Data from the transpiration method are in good agreement with data obtained from thermogravimetry for both compounds. The heats of sublimation calculated using thermogravimetry were 92.9 and 94.1 kJ mol^{-1} for com-pounds **4** and **5**, respectively, which is lower than the transpiration method (Table 1). The heats of sublimation for compound **4** using the transpiration method agreed well with values reported previously using a similar transpiration method [23]. Thus, the lower values obtained by thermogravimetry might be a consequence of the
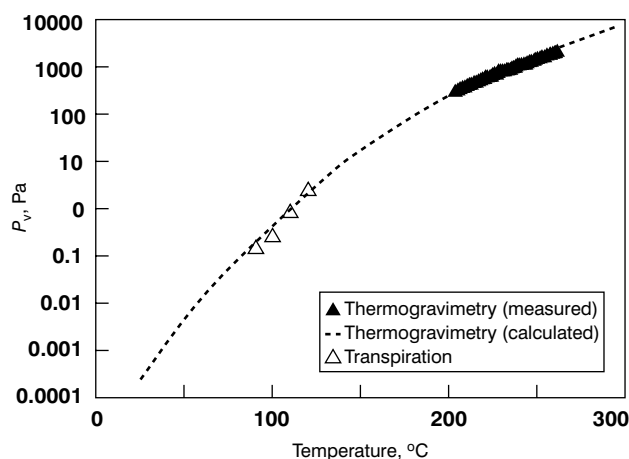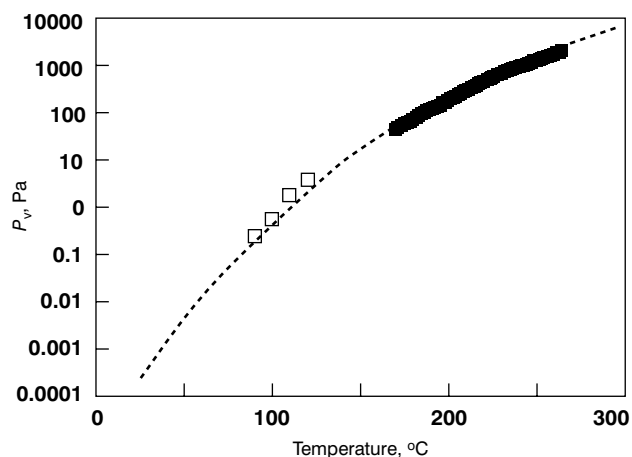
Figure 4 Comparison of vapour pressure versus temperature for **5** using thermogravimetry and the transpiration method

estimation method since the heats of sublimation were obtained by adding the heats of fusion from DSC and the heats of vaporisation from thermogravimetry. The major errors in this calculation arise from the uncertainty in the heats of fusion of compounds **4** and **5** arising from ill-defined melting peaks and the consequential difficulty in assigning an appropriate baseline for the integration of the heat flow. Furthermore, in order to compare between the two methods, the heats of sublimation should be corrected to the same temperature (usually 298.15 K), but in this instance the unreliability of the heat of fusion and arbitrary nature of the correction yields little improvement [34].

Vapour pressure results for the two compounds show that thermogravimetry is a viable alternative to the transpir-ation method. This would result in elimination of long and tedious runs required for the transpiration technique (*ca.* 20 h per vapour pressure value), since thermogravimetry is capable of rapid measurements of vapour pressure data both in solid and liquid phases of the compound. Vapour pressure data was obtained from the thermobalance at the data collection rate of the instrument (in this case 15 points per degree rise in temperature). An estimated number of over thirteen hundred data values were obtained for the temperature range of 170–250 °C under 2 h. It is likely that the thermogravimetric method would be suitable for the majority of non-ionic dyes.

Conclusions

It has been shown that it is possible to obtain vapour pressure data by thermogravimetry that compares well to a conventional transpiration method for two anthraquinone-based compounds. Once a calibration graph was establish-ed for the equipment, vapour pressure data was obtained very rapidly compared with the transpiration method, which takes many hours to obtain a single vapour pressure value at a given temperature.

Figure 3 Comparison of vapour pressure versus temperature for **4** using thermogravimetry and the transpiration method

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