



# Thermochemical study of 2,4-, 2,6- and 3,4-dihydroxybenzoic acids in the liquid phase using a TG apparatus

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## ABSTRACT

The vapor pressures of the liquid 2,4-, 2,6- and 3,4-dihydroxybenzoic acids were determined by thermogravimetry (TG) under both isothermal and non-isothermal conditions, respectively. D.s.c. and isothermal measurements after a thermal treatment were used to verify that no appreciable decomposition process occurs in the three isomers investigated in the temperature range considered. From the temperature dependence of vapor pressure derived by the experimental data the molar enthalpies of vaporization  $\Delta_{\text{v}}^{\text{g}}H_{\text{m}}^{\circ}(T)$  were determined, respectively, at the middle ( $T$ ) of the respective temperature intervals. The melting temperatures and the molar enthalpies of fusion of these compounds were measured by d.s.c. The vapor pressures of these compounds in the solid state, measured by torsion-effusion technique, were compared with recently published data, while the corresponding molar sublimation enthalpies were determined. In order to validate the vapor pressure results determined by TG, the experimental vapor pressure data regarding solid ferrocene and 1,2-dihydroxybenzoic acid were successfully compared with literature values in the range 20–200 Pa. In addition, the experimental molar enthalpies of fusion were compared with those calculated by subtracting the molar vaporization enthalpies to the sublimation ones, both adjusted to their respective melting temperatures. Finally, the standard ( $p^{\circ} = 0.1$  MPa) molar enthalpies, entropies and Gibbs energies of sublimation, corrected at the reference temperature of 298.15 K, have been calculated using the estimated heat capacity differences between gas and liquid for vaporization experiments and the estimated heat capacity differences between gas and solid for sublimation experiments. From the averages of the  $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(298.15 \text{ K})$  values the following increasing-order of volatility can be established for these three isomers, on the basis of the occurrence of *intra*-molecular and *inter*-molecular hydrogen bonds: 2,6-dihydroxybenzoic acid < 2,4-dihydroxybenzoic acid < 3,4-dihydroxybenzoic acid.

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## 1. Introduction

Hydroxybenzoic acids have active bacteriostatic fragrant properties and are typically used in pharmaceutical and perfumery industry. Dihydroxybenzoic acids (DHBAs) are used as intermediates for pharmaceuticals (especially for those with antipyretic, analgesic and antirheumatism effects) and other in the synthesis of organic compounds (resins, polyesters, plasticizers, dyestuff, preservatives and rubber chemicals). The destructive metabolic property of oxygen containing benzoic acid derivatives such as 3,4-dihydroxybenzoic acid (catabolite of epinephrine and anticarcinogenic agent [1]) and 3,4-dimethoxybenzoic acid is used in the application for pharmaceuticals. DHBAs are also used as model matrices for ionization of peptides, proteins and carbohydrates in

the MALDI (matrix assisted laser desorption ionization mass spectroscopy) technique [2,3]. In the MALDI mechanism, the analyte incorporated into a matrix could undergo sublimation due to the fact that it is subjected to an intense laser pulse [3].

Thermogravimetry under both isothermal and non-isothermal conditions (denoted as NITG and ITG, respectively) shows many advantages in the determination of vapor pressure of pure substances over the more conventional procedures like Knudsen and torsion effusion methods (even if precision and accuracy is usually slightly lower): relatively small amount of substance, simplicity of the experimental set-up and short experimental times. Moreover, vapor pressures and sublimation/vaporization enthalpies determined by a dynamic TG unit using the Clausius–Clapeyron equation, enabled the authors to conclude that vaporization rate is commonly not significantly affected by the flow rate of the purge gas used [4]. Gupta et al. [5] demonstrated the reliability of TG to determine vapor pressure and enthalpy of vaporization of a drug, using the same procedure adopted in [4]. By contrast, some

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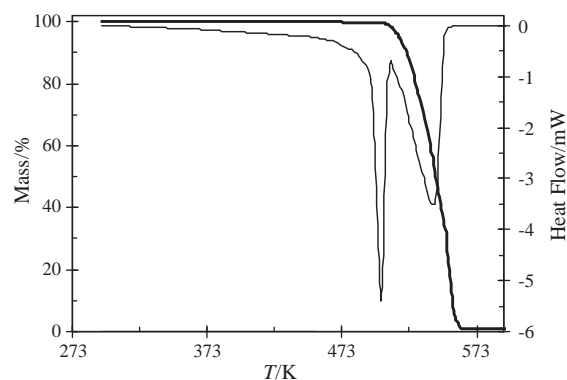
authors [6,7] proposed revised vaporization equations justified by the fact that the rate of vaporization is limited by diffusion. However, recently it was demonstrated that in some cases the influence of diffusion on the rate of mass loss recorded by a TG apparatus under a flowing inert gas conditions is negligible [8]. Recently, the sublimation enthalpies of the six *x,y*-dihydroxybenzoic acids were measured using thermogravimetry [3], but the accuracy of these measurements could be questionable, since no other techniques were used to compare these results. More recently, the sublimation vapor pressures of the six dihydroxybenzoic acids were obtained using the Knudsen effusion technique [9], while the standard molar enthalpies of formation in the crystalline state were determined from the enthalpies of combustion in oxygen at 298.15 K. By combining the standard molar sublimation enthalpies with the standard molar enthalpies of formation in the crystalline state, the corresponding standard molar enthalpies of formation in the gaseous state were calculated, but a clear correlation between the sublimation properties (i.e., enthalpy) of these materials and their performance as MALDI matrix is not found, also in this recent study [9]. However, no vapor pressure data are available in literature for these compounds in the liquid (molten) state, probably due to the high values of experimental temperature and to their possible decomposition. Therefore, the aim of the present paper, which extends our previous studies on compounds of pharmaceutical interest [8], pesticides [10] and dinitrobenzoic acids [11], is to verify that all the three isomers do not undergo decomposition in the liquid state, and subsequently to measure their vapor pressures in the liquid phase using a TG apparatus, and finally to determine the standard ( $p^\circ = 0.1$  MPa) molar enthalpies of vaporization,  $\Delta_1^g H_m^\circ(T)$ , at the mean temperature of the experiments, ( $T$ ).

The vapor pressures of the tested compounds were also measured in the solid state by torsion-effusion technique and compared with the recently published data [9], and the corresponding molar sublimation enthalpies were determined. In order to validate the vapor pressure results determined by TG the experimental molar enthalpies of fusion measured by d.s.c. were compared with those calculated by subtracting the molar vaporization enthalpies to the sublimation ones, both adjusted to their respective melting temperatures using the heat capacity differences between gas and liquid as well as the heat capacity differences between gas and solid,  $\Delta_1^g C_{p,m}^\circ$  and  $\Delta_{cr}^g C_{p,m}^\circ$ , respectively, estimated by applying a group additivity scheme taken from literature [12]. Finally, the standard ( $p^\circ = 0.1$  MPa) molar enthalpies, entropies and Gibbs energies of sublimation were also calculated at the reference temperature of 298.15 K.

## 2. Experimental

### 2.1. Compounds

2,4-Dihydroxybenzoic acid (CAS No.: 89-86-1), 2,6-dihydroxybenzoic acid (CAS No.: 303-07-1) and 3,4-dihydroxybenzoic acid (CAS No.: 99-50-3) supplied by Sigma–Aldrich with a certified purity >0.95 mass fraction were purified by repeated sublimation under reduced pressure until purity >0.99 mole fraction, checked by d.s.c. using the fractional method [13]. In order to verify the possible occurrence of decomposition in the three isomers, their purity was checked once again after melting, subsequent cooling down to room temperature and heating up to the highest temperature investigated. The final purity was slightly lower than that measured before melting for 2,4- and 2,6-DHBA (>0.99 mole fraction), while that of 3,4-DHBA decreases to 0.978 mole fraction, probably due to a negligible fraction of decomposition. However, neither phase transition nor decomposition events were clearly evidenced between room and melting temperature, in disagreement



**Fig. 1.** Simultaneous TG/d.s.c. curves of 2,4-dihydroxybenzoic acid under a stream of pure inert gas atmosphere under a heating rate of  $33.3 \text{ mK s}^{-1}$ .

with what has been reported for these compounds in [9], where decomposition seems to occur during fusion (it is not clearly indicated how this process was detected) along with phase transitions at 405.0 K, 301.7 K and 404.2 K for 2,4-, 2,6- and 3,4-DHBA, respectively. Purity of benzoic acid (from Fluka), used to convert mass loss rates and torsion-effusion angles into vapor pressures, was found to be 0.994 mole fraction, while those of recommended reference compounds for melting temperature and enthalpy [14,15] (standard indium and tin supplied by Rheometric Scientific), were found to be >0.9999 mass fraction. As a consequence, all these calibrants were used without further purification. As a further confirmation of our findings, the TG/d.s.c. curves of 2,4-dihydroxybenzoic acid, reported in Fig. 1 as an example, showed the characteristic shapes of all compounds undergoing vaporization without decomposition after melting.

### 2.2. Thermogravimetry and torsion measurements of vapor pressures

Details of the TG (under isothermal (ITG) and non-isothermal (NITG) conditions) and d.s.c. measurements, along with the procedures adopted for temperature and heat flux calibrations, have been recently reported elsewhere [10].

The NITG and ITG experiments enable the vapor pressure  $p$  of a compound at a temperature  $T$  to be determined from its mass-loss rate ( $\Delta m/\Delta t$ ) using the Langmuir equation [16], which can be modified assuming the following form:

$$p = \frac{\Delta m}{\Delta t} \sqrt{\frac{T}{M}} \frac{\sqrt{2\pi R}}{S\alpha'} = \nu k_{cal} \quad (1)$$

where  $\nu = (\Delta m/\Delta t)(1/S)\sqrt{T/M}$ ,  $M$  is the molar mass of the compound,  $\alpha'$  is the vaporization constant equal to unity only for experiments in vacuo [17],  $S$  is the surface of the sample considered equal to the area of the bottom of the crucible,  $R$  is the gas constant,  $k_{cal} = (\sqrt{2\pi R}/\alpha')$  is the instrumental constant. The two  $k_{cal}$  values are derived for isothermal and nonisothermal methods by carrying out the NITG and ITG experiments under the same condition of the three dihydroxybenzoic acids examined on compounds whose vapor pressures for the same temperature intervals investigated are taken from literature [18] (i.e., liquid benzoic acid in this paper).

The torsion-effusion assembly, the operative conditions used in the present work and the procedure to determine the instrumental constants necessary to convert the torsion-effusion angle values to vapor pressures at each selected temperature have been described in detail elsewhere [19]. The relative atomic masses adopted in this study were those recommended by the IUPAC commission [20].

### 3. Results and discussion

#### 3.1. Calibration of the thermogravimetry and torsion-effusion assemblies

In order to verify if vaporization process occurring in a sample subjected to a TG measurement under an inert flowing gas atmosphere could be limited by diffusion, the mass loss rates of liquid benzoic acid calculated from NITG and ITG experiments were compared with the corresponding values predicted using the following equation proposed by Pieterse and Focke [6,21], according to a procedure described in detail in previous papers [8,10,11]. In order to convert the mass loss rates recorded during NITG and ITG experiments into vapor pressures, the vaporization of benzoic acid was considered, using the vapor pressure data collected from literature [18]. The corresponding  $\ln(k_{\text{cal}})$  values selected from NITG and ITG experiments, corresponding to the temperature intervals considered, are listed in a Supplementary Data File (Table S1), where a very narrow range of instrumental constants values were found (deviation of all the values around the mean values  $D$  is lower than  $\pm 0.08$ ). Before conversion of NITG and ITG mass loss rate data into vapor pressure values according to Eq. (1) by using a final mean value of  $\ln[k_{\text{cal}}/(\text{kg}^{0.5} \text{ s}^{-1} \text{ m K}^{-0.5} \text{ mol}^{-0.5})] = 12.47 \pm 0.01$  (the associated uncertainty is twice the standard deviation of the mean), a final test was made to check the internal consistency of vapor pressure measurements from both NITG and ITG experiments. The experimental vapor pressure values of two reference compounds (ferrocene and 1,2-dihydroxybenzoic acid, both in the solid state, were considered in this study) were compared with those taken from literature at the same temperatures [22,23]. A statistical analysis ( $t$ -test) was applied to decide if  $p_{\text{Exp}}$  and  $p_{\text{Lit}}$  values are equal by verifying, at a confidence level of 0.95, the validity of the following null hypotheses:  $H_0(\text{slope}) = 1$  and  $H_0(\text{intercept}) = 0$ . To this end, the experimental vs. literature vapor pressure plots for ferrocene and 1,2-dihydroxybenzoic acid were reported in Fig. S1 (Supplementary Data File), while the most important regression and  $t$ -test parameters were summarized in Table 1. The null hypotheses, related to both slope (expected value equal to 1) and intercept (expected value equal to 0), cannot be rejected at a confidence level of 0.95, since  $|((\text{slope} - 1)/\sigma_{\text{slope}})\sqrt{N - 2}| < t_{0.975}$  and  $|((\text{intercept} - 0)/\sigma_{\text{intercept}})\sqrt{N - 2}| < t_{0.975}$ , where  $N$  is the number of data fitted and  $\sigma$  are the standard deviations of slope and intercept [24]. The results of this  $t$ -test confirm that  $p_{\text{Exp}}$  and  $p_{\text{Lit}}$  values are equal (at least in the vapor pressure range investigated) and, therefore, that the final  $\ln(k_{\text{cal}})$  value can be used to convert both the NITG and ITG mass loss rate data into vapor pressure values in a limited temperature range.

As far as the calibration of the torsion-effusion assembly is concerned, its instrumental constant was determined in separate experiments by subliming high purity standard samples of benzoic acid using a pyrophillite cell having a hole with a 0.8 mm diameter, and a final value of  $\ln[k_{\text{cal}}/(\text{Pa degree}^{-1})] = -1.75 \pm 0.23$  was found.

#### 3.2. Experimental vapor pressure measurements above the liquid and solid phases and related thermodynamic functions

The experimental  $p/T$  values determined from the NITG and ITG methods are given for each separate run in the Supplementary Data File (Tables S2 and S3, respectively). The relative deviations of experimental vapor pressures ( $p_{\text{Exp}}$ ) derived from NITG and ITG from those calculated using the Clausius–Clapeyron-based regression equation ( $p_{\text{Calc}}$ ) are also given in Tables S2 and S3 of the Supplementary Data File, respectively. The corresponding vaporization mass loss rates so determined, were converted into the corresponding vapor pressures using the mean  $k_{\text{cal}}$  value.

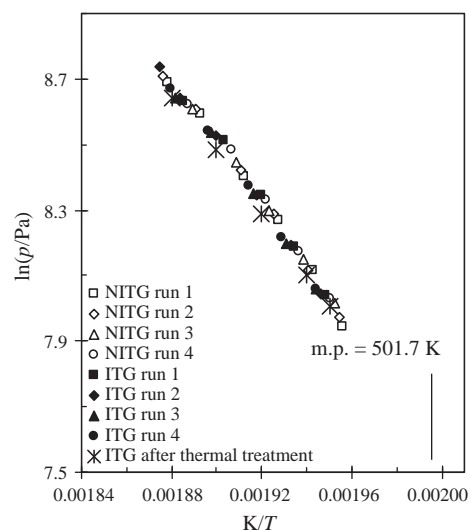


Fig. 2. Experimental vapor pressures of liquid 2,4-dihydroxybenzoic acid.

The Clausius–Clapeyron plots for the  $\ln(p/\text{Pa})$  vs.  $T^{-1}$  experimental NITG and ITG data points concerning liquid 2,4-, 2,6- and 3,4-dihydroxybenzoic acids are presented in Figs. 2, 3 and 4, respectively. In order to confirm a substantial stability of these three isomers in the liquid state, further ITG experiments were performed. After a thermal treatment in which the three isomers were heated at constant heating rate up to their melting temperatures, then cooled at room temperature (without using liquid nitrogen) and subsequently heated (at constant heating rate) up to given constant temperatures within their experimental temperature ranges. The corresponding  $\ln(p/\text{Pa})$  vs.  $T^{-1}$  data (five data points) for 2,4-, 2,6- and 3,4-DHBA, also reported in Figs. 2, 3 and 4 respectively, for comparison purpose, agree satisfactorily with those determined without the thermal treatment, thus confirming that no significant amount of decomposition was found for the three isomers.

Tables 2–4 present the detailed parameters of Clausius–Clapeyron equation derived from least-square treatment of the experimental  $p/T$  NITG and ITG data and the standard molar enthalpies of vaporization at the mean temperature of the

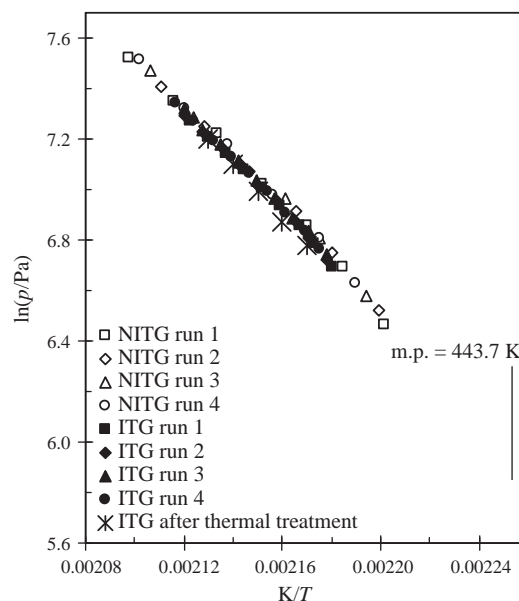


Fig. 3. Experimental vapor pressures of liquid 2,6-dihydroxybenzoic acid.

**Table 1**

Comparison of experimental and literature vapor pressure values to check the internal consistency of vapor pressure data derived by NITG and ITG experiments. Statistical analysis is applied to decide if  $p_{\text{Exp}}$  and  $p_{\text{Lit}}$  values are equal at a confidence level of 0.95.

| Parameters for statistical analysis                         |   |  |
|---|---|--|
| <i>Ferrocene</i> ( <i>cr</i> ) <sup>a</sup>                 |   |  |
| Mean regression equation <sup>b</sup>                       | $p_{\text{Exp}}/\text{Pa} = (0.99 \pm 0.01) \cdot p_{\text{Lit}}/\text{Pa} + (0.4 \pm 1.2)$ | $p_{\text{Exp}}/\text{Pa} = (1.01 \pm 0.01) \cdot p_{\text{Lit}}/\text{Pa} + (-1.2 \pm 1.2)$ |
| Range of linearity (Pa)                                     | 21–180  | 21–180   |
| $R^2$   | 0.9992  | 0.9993   |
| Confidence level (CL)                                       | 0.95  | 0.95   |
| Confidence interval; confidence limits of the slope         | 0.03; (0.96–1.02)   | 0.03; (0.98–1.04)  |
| Confidence interval; confidence limits of the intercept     | 3.1; (-2.7 to 3.5)  | 3.0; (-3.3 to 2.7)   |
| $t_{0.975}$ ( $n-2$ ) value; ( $n=7$ ) <sup>c</sup>         | 2.57  | 2.57   |
| Significance test of the slope <sup>d</sup>                 | $ -0.782  < 2.57$ ( $H_0$ cannot be rejected at CL=0.95)                                    | $ 1.138  < 2.57$ ( $H_0$ cannot be rejected at CL=0.95)                                      |
| Significance test of the intercept <sup>e</sup>             | $0.346  < 2.57$ ( $H_0$ cannot be rejected at CL=0.95)                                      | $ -0.995  < 2.57$ ( $H_0$ cannot be rejected at CL=0.95)                                     |
| <i>1,2-Dihydroxybenzoic acid</i> ( <i>cr</i> ) <sup>f</sup> |   |  |
| Mean regression equation <sup>b</sup>                       | $p_{\text{Exp}}/\text{Pa} = (1.00 \pm 0.01) \cdot p_{\text{Lit}}/\text{Pa} + (0.1 \pm 1.1)$ | $p_{\text{Exp}}/\text{Pa} = (1.00 \pm 0.01) \cdot p_{\text{Lit}}/\text{Pa} + (-0.3 \pm 1.2)$ |
| Range of linearity (Pa)                                     | 25–166  | 25–166   |
| $R^2$   | 0.9992  | 0.9990   |
| Confidence level (CL)                                       | 0.95  | 0.95   |
| Confidence interval; confidence limits of the slope         | 0.03; (0.97–1.03)   | 0.03; (0.98–1.04)  |
| Confidence interval; confidence limits of the intercept     | 2.6; (-2.6 to 2.7)  | 3.0; (-3.3 to 2.7)   |
| $t_{0.975}$ ( $n-2$ ) value; ( $n=8$ ) <sup>c</sup>         | 2.45  | 2.45   |
| Significance test of the slope <sup>d</sup>                 | $ -0.310  < 2.45$ ( $H_0$ cannot be rejected at CL=0.95)                                    | $ 0.584  < 2.45$ ( $H_0$ cannot be rejected at CL=0.95)                                      |
| Significance test of the intercept <sup>e</sup>             | $ 0.052  < 2.45$ ( $H_0$ cannot be rejected at CL=0.95)                                     | $ -0.275  < 2.45$ ( $H_0$ cannot be rejected at CL=0.95)                                     |

<sup>a</sup> Literature data are taken from [22].

<sup>b</sup> Slope and intercept values with their standard deviations.

<sup>c</sup>  $n$  = number of points fitted to the regression line.

<sup>d</sup>  $H_0(\text{slope}) = 1$ ,  $H_1(\text{slope}) \neq 1$ : if  $H_0$  cannot be rejected at CL=0.95, thus regression slope is 1.

<sup>e</sup>  $H_0(\text{intercept}) = 0$ ,  $H_1(\text{intercept}) \neq 0$ : if  $H_0$  cannot be rejected at CL=0.95, thus regression intercept is 0.

<sup>f</sup> Literature data are taken from [23].

**Table 2**

Regression parameters of  $\ln(p/\text{Pa}) = a - b/(KT)$  equation, average temperature ( $\langle T_{\text{TG}} \rangle$ ) and corresponding pressure ( $p(T = \langle T_{\text{TG}} \rangle)$ ) as well as vaporization enthalpies and entropies at  $\langle T_{\text{TG}} \rangle$  and  $p(T = \langle T_{\text{TG}} \rangle)$  for 2,4-dihydroxybenzoic acid.

| Technique | $N^a$   | $\Delta T$ (K) | $\langle T \rangle$ (K) | $a$              | $b$ (K)          | $p(T = \langle T_{\text{TG}} \rangle)$ (Pa) | $\Delta_1^{\text{g}}H_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle)^b$ (kJ mol <sup>-1</sup> ) | $\Delta_1^{\text{g}}S_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle, p(T = \langle T_{\text{TG}} \rangle))^c$ (J K <sup>-1</sup> mol <sup>-1</sup> ) |
|-----------|---------|----------------|-------------------------|------------------|------------------|---|--|---|
| NITG      | 6       | 511.2–532.5    | 521.9                   | $26.53 \pm 0.74$ | $9486 \pm 385$   |   |  |   |
|           | 6       | 511.7–533.0    | 522.4                   | $26.63 \pm 0.61$ | $9538 \pm 318$   |   |  |   |
|           | 5       | 512.2–529.4    | 520.8                   | $26.49 \pm 0.40$ | $9461 \pm 207$   |   |  |   |
|           | 5       | 512.7–529.9    | 521.3                   | $26.57 \pm 0.90$ | $9500 \pm 466$   |   |  |   |
|           | 5       | 513.3–530.4    | 521.9                   | $26.58 \pm 1.00$ | $9504 \pm 523$   |   |  |   |
| ITG       | 6       | 513.8–533.5    | 523.7                   | $26.58 \pm 0.58$ | $9517 \pm 301$   |   |  |   |
|           | 6       | 514.3–534.0    | 524.2                   | $26.48 \pm 0.55$ | $9467 \pm 289$   |   |  |   |
|           | 5       | 514.3–532.0    | 523.2                   | $26.50 \pm 0.62$ | $9479 \pm 325$   |   |  |   |
|           | Average | 44             | 511–534                 | 522              | $26.55 \pm 0.67$ | $9495 \pm 350$                              | $4325 \pm 50$  | $79 \pm 4$  |

<sup>a</sup>  $N$  = number of experiments for each run.

<sup>b</sup>  $\Delta_1^{\text{g}}H_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle) = b \times R$ , where  $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ .

<sup>c</sup>  $\Delta_1^{\text{g}}S_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle, p(T = \langle T_{\text{TG}} \rangle)) = (a - \ln p^{\circ}) \times R$ , where  $p^{\circ} = 0.1 \text{ MPa}$ .

experiments,  $\langle T_{\text{TG}} \rangle$ , along with the associated errors (standard deviations). No remarkable differences were found in Tables 2–4 between the regression parameters of the Clausius–Clapeyron equations obtained by weighing slopes and intercepts proportionally to the experimental points derived from NITG and ITG experiments (indicated as average results) and those derived

by analyzing all the experimental points (global results, not reported herein). The equilibrium pressure related to this temperature,  $p(\langle T_{\text{TG}} \rangle)$ , and the entropies of vaporization at equilibrium conditions are also given in Tables 2–4.

The experimental  $p/T$  values determined by the torsion-effusion method above the three solid dihydrobenzoic acids tested, along

**Table 3**

Regression parameters of  $\ln(p/\text{Pa}) = a - b/(KT)$  equation, average temperature ( $\langle T_{\text{TG}} \rangle$ ) and corresponding pressure ( $p(T = \langle T_{\text{TG}} \rangle)$ ) as well as vaporization enthalpies and entropies at  $\langle T_{\text{TG}} \rangle$  and  $p(T = \langle T_{\text{TG}} \rangle)$  for 2,6-dihydroxybenzoic acid.

| Technique | $N^a$ | $\Delta T$ (K) | $\langle T \rangle$ (K) | $a$              | $b$ (K)        | $p(T = \langle T_{\text{TG}} \rangle)$ (Pa) | $\Delta_1^{\text{g}}H_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle)^b$ (kJ mol <sup>-1</sup> ) | $\Delta_1^{\text{g}}S_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle, p(T = \langle T_{\text{TG}} \rangle))^c$ (J K <sup>-1</sup> mol <sup>-1</sup> ) |
|-----------|-------|----------------|-------------------------|------------------|----------------|---|--|---|
| NITG      | 7     | 454.2–476.7    | 465.4                   | $28.34 \pm 0.74$ | $9915 \pm 344$ |   |  |   |
|           | 6     | 454.7–473.7    | 464.2                   | $28.30 \pm 0.66$ | $9890 \pm 305$ |   |  |   |
|           | 6     | 455.7–474.8    | 465.3                   | $28.21 \pm 0.64$ | $9847 \pm 297$ |   |  |   |
|           | 6     | 456.7–475.7    | 466.2                   | $28.36 \pm 0.55$ | $9915 \pm 255$ |   |  |   |
| ITG       | 9     | 460.9–473.4    | 467.1                   | $28.32 \pm 0.37$ | $9955 \pm 242$ |   |  |   |
|           | 9     | 461.3–473.8    | 467.5                   | $28.20 \pm 0.42$ | $9901 \pm 192$ |   |  |   |
|           | 9     | 461.7–474.2    | 468.0                   | $28.11 \pm 0.41$ | $9858 \pm 162$ |   |  |   |
|           | 9     | 462.0–474.7    | 468.4                   | $28.09 \pm 0.30$ | $9848 \pm 122$ |   |  |   |
| Average   | 61    | 454–477        | 465                     | $28.23 \pm 0.49$ | $9891 \pm 230$ | $1129 \pm 15$                               | $82 \pm 3$   | $139 \pm 5$   |

<sup>a</sup>  $N$  = number of experiments for each run.

<sup>b</sup>  $\Delta_1^{\text{g}}H_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle) = b \times R$ , where  $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ .

<sup>c</sup>  $\Delta_1^{\text{g}}S_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle, p(T = \langle T_{\text{TG}} \rangle)) = (a - \ln p^{\circ}) \times R$ , where  $p^{\circ} = 0.1 \text{ MPa}$ .

**Table 4**  
Regression parameters of  $\ln(p/\text{Pa}) = a - b(K/T)$  equation, average temperature ( $\langle T_{\text{TG}} \rangle$ ) and corresponding pressure ( $p(T = \langle T_{\text{TG}} \rangle)$ ) as well as vaporization enthalpies and entropies at ( $T_{\text{TG}}$ ) and  $p(T = \langle T_{\text{TG}} \rangle)$  for 3,4-dihydroxybenzoic acid.

| Technique | $N^a$ | $\Delta T$ (K) | $\langle T \rangle$ (K) | $a$          | $b$ (K)     | $p(T = \langle T_{\text{TG}} \rangle)$ (Pa) | $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle)^b$ (kJ mol <sup>-1</sup> ) | $\Delta_{\text{f}}^{\text{g}}S_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle, p(T = \langle T_{\text{TG}} \rangle))^c$ (J K <sup>-1</sup> mol <sup>-1</sup> ) |
|-----------|-------|----------------|-------------------------|--------------|-------------|---|---|--|
| NITG      | 11    | 485.8–505.7    | 495.8                   | 32.55 ± 0.90 | 12540 ± 448 |   |   |  |
|           | 11    | 485.2–505.0    | 495.1                   | 32.51 ± 0.92 | 12502 ± 457 |   |   |  |
|           | 10    | 486.6–504.7    | 495.8                   | 32.55 ± 0.83 | 12539 ± 409 |   |   |  |
|           | 10    | 486.2–504.1    | 495.2                   | 32.60 ± 0.91 | 12542 ± 451 |   |   |  |
| ITG       | 10    | 488.4–502.0    | 495.2                   | 33.61 ± 0.57 | 13042 ± 283 |   |   |  |
|           | 10    | 488.8–502.4    | 495.6                   | 33.30 ± 0.85 | 12891 ± 421 |   |   |  |
|           | 10    | 489.2–502.8    | 496.0                   | 32.88 ± 0.78 | 12681 ± 388 |   |   |  |
|           | 9     | 489.6–501.6    | 495.6                   | 32.47 ± 0.60 | 12480 ± 299 |   |   |  |
| Average   | 81    | 485–505        | 495                     | 32.81 ± 0.80 | 12651 ± 400 | 1445 ± 170                                  | 105 ± 4   | 177 ± 4  |

<sup>a</sup>  $N$  = number of experiments for each run.

<sup>b</sup>  $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle) = b \times R$ , where  $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ .

<sup>c</sup>  $\Delta_{\text{f}}^{\text{g}}S_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle, p(T = \langle T_{\text{TG}} \rangle)) = (a - \ln p^{\circ}) \times R$ , where  $p^{\circ} = 0.1 \text{ MPa}$ .

**Table 5**  
Regression parameters of  $\ln(p/\text{Pa}) = a - b(K/T)$  equation, average temperature ( $\langle T_{\text{te}} \rangle$ ) and corresponding pressure ( $p(T = \langle T_{\text{te}} \rangle)$ ) as well as sublimation enthalpies and entropies at ( $T_{\text{te}}$ ) and  $p(T = \langle T_{\text{te}} \rangle)$  derived by torsion-effusion measurements for all the compounds examined.

| Compound                       | $N^a$ | $\Delta T$ (K) | $\langle T \rangle$ (K) | $a$          | $b$ (K)     | $p(T = \langle T_{\text{te}} \rangle)$ (Pa) | $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T_{\text{te}} \rangle)^b$ (kJ mol <sup>-1</sup> ) | $\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^{\circ}(\langle T_{\text{te}} \rangle, p(T = \langle T_{\text{te}} \rangle))^c$ (J K <sup>-1</sup> mol <sup>-1</sup> ) |
|--------------------------------|-------|----------------|-------------------------|--------------|-------------|---|--|---|
| 2,4-Dihydroxybenzoic acid (cr) | 21    | 364.2–390.1    | 377.0                   | 36.91 ± 0.33 | 14445 ± 124 | 0.25 ± 0.02                                 | 120 ± 1  | 211 ± 4   |
| 2,6-Dihydroxybenzoic acid (cr) | 24    | 346.0–369.0    | 357.5                   | 35.58 ± 0.21 | 13118 ± 77  | 0.33 ± 0.02                                 | 109 ± 1  | 200 ± 3   |
| 3,4-Dihydroxybenzoic acid (cr) | 21    | 381.8–408.9    | 395.5                   | 39.98 ± 0.22 | 16356 ± 86  | 0.25 ± 0.02                                 | 136 ± 1  | 237 ± 3   |

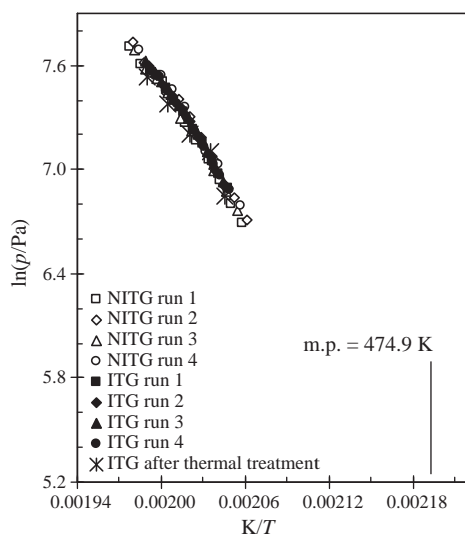
<sup>a</sup>  $N$  = number of experiments for each run.

<sup>b</sup>  $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T_{\text{te}} \rangle) = b \times R$ , where  $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ .

<sup>c</sup>  $\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^{\circ}(\langle T_{\text{te}} \rangle, p(T = \langle T_{\text{te}} \rangle)) = (a - \ln p^{\circ}) \times R$ , where  $p^{\circ} = 0.1 \text{ MPa}$ .

with the relative deviations of experimental vapor pressures ( $p_{\text{Exp}}$ ), are listed in Table S4 of the Supplementary Data File. The Clausius–Clapeyron plots for the  $\ln(p/\text{Pa})$  vs.  $T^{-1}$  experimental torsion-effusion data points concerning 2,4- and 3,4-dihydroxybenzoic acids are presented in Fig. 5 and compared with those reported in a recent paper for these compounds [9]. Good agreement was found between the present and the literature results. The regression parameters of the corresponding Clausius–Clapeyron equations, the equilibrium pressure related to this temperature,  $p(\langle T_{\text{te}} \rangle)$ , and the enthalpies and entropies of sublimation at equilibrium conditions ( $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T_{\text{te}} \rangle)$ ) and  $\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^{\circ}(\langle T_{\text{te}} \rangle, p(T = \langle T_{\text{te}} \rangle))$ , respectively are reported in Table 5.

The standard molar enthalpies of sublimation at 298.15 K,  $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K})$ , have been determined from the experimental

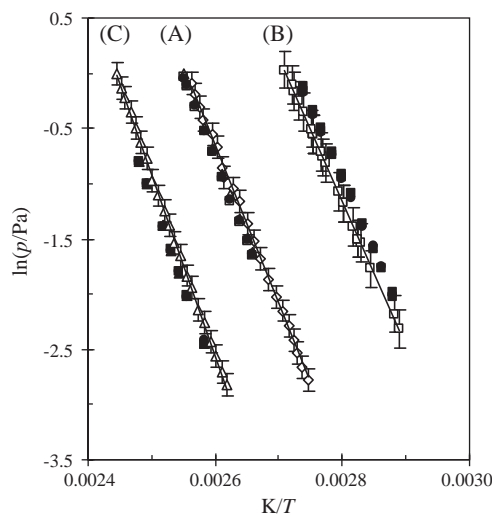


**Fig. 4.** Experimental vapor pressures of liquid 3,4-dihydroxybenzoic acid.

$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T_{\text{te}} \rangle)$  data derived by the torsion-effusion method (using the heat capacity differences of both solid and gaseous phases at constant pressure):

$$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K})/(\text{kJ mol}^{-1}) = \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(\langle T_{\text{te}} \rangle) - \Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^{\circ}(298.15 \text{ K} - \langle T_{\text{te}} \rangle) \quad (2)$$

where  $\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^{\circ}(\text{kJ mol}^{-1} \text{ K}^{-1}) = [0.00075 + 0.00015C_{\text{p,m}}(\text{cr})_{\text{estd}}(298.15 \text{ K})]$  is derived by Chickos et al. on the bases of statistical results [25] and  $C_{\text{p,m}}(\text{cr})_{\text{estd}}(298.15 \text{ K}) = (178 \pm 21) \text{ J mol}^{-1} \text{ K}^{-1}$  is estimated using a group additivity approach [12] and  $\langle T_{\text{te}} \rangle$  is the mean absolute temperature of the torsion-effusion experiments. The uncertainty associated to the



**Fig. 5.** Experimental torsion-effusion vapor pressures of solid compounds investigated in this study (white symbols) and comparison with those taken from literature [9] (black symbols). Error bars are estimated from the uncertainties in the determination of the corresponding rates of mass vaporized. (A) 2,4-dihydroxybenzoic acid; (B) 2,6-dihydroxybenzoic acid; (C) 3,4-dihydroxybenzoic acid.

**Table 6**

The experimental melting temperatures (from the onset of the d.s.c. melting peaks), the logarithm of the triple-point vapor pressures, the molar enthalpies and entropies of fusion, along with the molar enthalpies of fusion, measured and calculated at  $T = T_{\text{fus}}$ , where the estimated heat capacities  $C_{p,m}^{\circ}(\text{cr})_{\text{estd}}$  and  $C_{p,m}^{\circ}(\text{l})_{\text{estd}}$  at 298.15 K are  $178 \pm 21$  and  $305 \pm 36 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively, for all the compounds tested.

| Compound                  | $T_{\text{fus}}$ (K) | Comparison of parameters for the test of consistency of vapor pressure |                            |   |                   | $\Delta_{\text{cr}}^{\text{l}}S_{\text{m}}^{\circ}(\text{J K}^{-1} \text{ mol}^{-1})$ |
|---------------------------|----------------------|--|----------------------------|---|-------------------|---|
|                           |                      | $\ln(p(T = T_{\text{fus}}))(\text{Pa})^{\text{a}}$                     |                            | $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}})(\text{kJ mol}^{-1})$ |                   |   |
|                           |                      | Calc. from te <sup>b</sup>   | Calc. from TG <sup>c</sup> | Exp <sup>d</sup>  | Calc <sup>e</sup> |   |
| 2,4-Dihydroxybenzoic acid | 501.7                | $8.1 \pm 0.3$  | $7.6 \pm 0.7$              | $31 \pm 1$  | $36 \pm 2$        | $62 \pm 4$  |
| 2,6-Dihydroxybenzoic acid | 443.7                | $6.0 \pm 0.2$  | $5.9 \pm 0.5$              | $25 \pm 1$  | $25 \pm 3$        | $56 \pm 4$  |
| 3,4-Dihydroxybenzoic acid | 474.9                | $5.5 \pm 0.2$  | $6.2 \pm 0.8$              | $34 \pm 1$  | $31 \pm 6$        | $72 \pm 4$  |

<sup>a</sup> The associated errors were estimated equal to those of the intercepts (*a*) of the corresponding vapor pressure equations (Tables 2–5), from which the triple-point vapor pressures were calculated.

<sup>b</sup> Calculated at  $T = T_{\text{fus}}$  from vapor pressure equations obtained from torsion-effusion (te) measurements in Table 5.

<sup>c</sup> Calculated at  $T = T_{\text{fus}}$  from vapor pressure equations obtained from average values of NITG and ITG (TG) measurements in Tables 2–4.

<sup>d</sup> Determined directly from d.s.c. measurements, where the associated uncertainties are estimated taking into account the errors on the evaluation of both temperature and heat flux.

<sup>e</sup> Calculated using Eq. (5), where the associated uncertainties are standard deviations.

<sup>f</sup> Calculated using the enthalpies of fusion obtained from d.s.c. experiments. The associated uncertainties are estimated from those of the corresponding experimental  $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}})$  values.

value of  $C_{p,m}(\text{cr})_{\text{estd}}$  (298.15 K) are comparable to that assigned by Chickos et al. in [25]. A fair agreement is found between the molar enthalpy of sublimation of the isomer 2,4-DHBA determined in this study and adjusted at the middle of the experimental temperature range ( $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(393 \text{ K}) = 120.6 \text{ kJ mol}^{-1}$ ) and the corresponding literature data reported in [3] ( $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(393 \text{ K}) = 126 \pm 6 \text{ kJ mol}^{-1}$ ).

The experimental melting temperatures and enthalpies obtained from d.s.c. measurements are presented in Table 6 along with the standard molar enthalpies and entropies of sublimation (vaporization) calculated at the mean temperature of the torsion and TG experiments (being the latter denoted as  $\langle T_{\text{TG}} \rangle$ ). The errors associated to the melting enthalpies and entropies reported in Table 6 were the standard deviations. The enthalpies of sublimation derived from torsion experiments (calculated at  $T = \langle T_{\text{te}} \rangle$ ) and the enthalpies of vaporization derived from NITG and ITG experiments (calculated at  $T = \langle T_{\text{TG}} \rangle$ ) were adjusted at  $T_{\text{fus}}$  using the following Eqs. (3) and (4):

$$\begin{aligned} \text{torsion experiments: } & \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}})/(\text{kJ mol}^{-1}) \\ & = \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(\langle T_{\text{te}} \rangle) - \Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ}(T_{\text{fus}} - \langle T_{\text{te}} \rangle) \end{aligned} \quad (3)$$

$$\begin{aligned} \text{NITG and ITG experiments: } & \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}})/(\text{kJ mol}^{-1}) \\ & = \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle) - \Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ}(T_{\text{fus}} - \langle T_{\text{TG}} \rangle) \end{aligned} \quad (4)$$

where  $\Delta_{\text{cr}}^{\text{l}}C_{p,m}^{\circ}(\text{kJ mol}^{-1} \text{ K}^{-1}) = [0.01058 + 0.00026C_{p,m}(\text{l})_{\text{estd}}(298.15 \text{ K})]$  is derived by Chickos et al. [25] and  $C_{p,m}(\text{l})_{\text{estd}}(298.15 \text{ K}) = (305 \pm 36) \text{ J mol}^{-1} \text{ K}^{-1}$  is estimated according to a group additivity approach [12]. The uncertainty associated to the value of  $C_{p,m}(\text{l})_{\text{estd}}(298.15 \text{ K})$  are comparable to that assigned by Chickos in [25].

In order to make a further test for the internal consistency of vapor pressure measurements a comparison was made between the triple-point vapor pressures (calculated at  $T = T_{\text{fus}}$ ) determined from the vapor pressure equations obtained from torsion-effusion measurements (Table 5) and those derived by the average values of NITG and ITG (TG) measurements (Tables 2–4). In Table 6 it can be observed that the extrapolated triple-point vapor pressures of 2,6-DHBA are practically coincident, while those of 2,4- and 3,4-DHBA agree satisfactorily within the uncertainties, which are estimated taking into account the errors associated to the intercepts (*a*) of the corresponding vapor pressure equations (Tables 2–5), from which the triple-point vapor pressures were calculated. Furthermore, using the sublimation and vaporization enthalpies extrapolated at  $T_{\text{fus}}$  using Eqs. (3) and (4), the corresponding enthalpies of fusion

$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}})$  were calculated from Eq. (5)

$$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}})/(\text{kJ mol}^{-1}) = \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(T_{\text{fus}}) - \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}}) \quad (5)$$

and compared in Table 6 with those determined from the d.s.c. curves with the view to test the internal consistency of both sublimation and vaporization enthalpies, obtained from torsion-effusion and TG experiments, respectively. A very good agreement is observed between experimental and calculated enthalpies of fusion for 2,6-dihydroxybenzoic isomer, while a slight difference (3 and 5 kJ mol<sup>-1</sup>) is found for the other two isomers, probably due to their longer way of extrapolation of the vaporization enthalpy (from  $T = \langle T_{\text{TG}} \rangle$  to  $T_{\text{fus}}$ ) as well as that of sublimation enthalpy (from  $T_{\text{fus}}$  to the reference temperature of 298.15 K). In brief, as far as vapor pressure and enthalpy are concerned, these tests of consistency can be considered positive, thus confirming the validity of all the methods employed.

The standard molar enthalpies of sublimation at 298.15 K,  $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(298.15 \text{ K})$ , have been also determined from the  $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle)$  values, derived by the NITG and ITG experiments, and the  $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}})$  values, obtained from d.s.c. measurements, according to the following Eq. (6):

$$\begin{aligned} \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(298.15 \text{ K})/(\text{kJ mol}^{-1}) & = \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle) + \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}}) \\ & - \Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ}(298.15 \text{ K} - T_{\text{fus}}) - \Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ}(T_{\text{fus}} - \langle T_{\text{TG}} \rangle) \end{aligned} \quad (6)$$

Furthermore, the standard ( $p^{\circ} = 0.1 \text{ MPa}$ ) molar entropies of sublimation adjusted at 298.15 K ( $\Delta_{\text{cr}}^{\text{l}}S_{\text{m}}^{\circ}(298.15 \text{ K})$ ) have been obtained from the torsion data using the following Eq. (7):

$$\begin{aligned} \Delta_{\text{cr}}^{\text{l}}S_{\text{m}}^{\circ}(298.15 \text{ K})/(\text{J mol}^{-1} \text{ K}^{-1}) & = \Delta_{\text{cr}}^{\text{l}}S_{\text{m}}^{\circ}(\langle T_{\text{te}} \rangle) \\ & - \Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ} \ln(298.15 \text{ K}/\langle T_{\text{te}} \rangle) \end{aligned} \quad (7)$$

while for the NITG and ITG data the following Eq. (8):

$$\begin{aligned} \Delta_{\text{cr}}^{\text{l}}S_{\text{m}}^{\circ}(298.15 \text{ K})/(\text{J mol}^{-1} \text{ K}^{-1}) & = \Delta_{\text{cr}}^{\text{l}}S_{\text{m}}^{\circ}(\langle T_{\text{TG}} \rangle) + \Delta_{\text{cr}}^{\text{l}}S_{\text{m}}^{\circ} \\ & - \Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ} \ln(298.15 \text{ K}/T_{\text{fus}}) - \Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ} \ln(T_{\text{fus}}/\langle T_{\text{TG}} \rangle) \end{aligned} \quad (8)$$

The uncertainties associated to the values of  $\Delta_{\text{cr}}^{\text{l}}S_{\text{m}}^{\circ}(298.15 \text{ K})$  were obtained taking into account the uncertainties assigned to the values of  $\Delta_{\text{cr}}^{\text{l}}S_{\text{m}}^{\circ}(T)$  and that of  $\Delta_{\text{cr}}^{\text{g}}C_{p,m}^{\circ}$ .

Finally, the standard ( $p^{\circ} = 0.1 \text{ MPa}$ ) molar Gibbs energies at 298.15 K ( $\Delta_{\text{cr}}^{\text{l}}G_{\text{m}}^{\circ}(298.15 \text{ K})$ ) have been calculated using the following Eq. (9):

$$\begin{aligned} \Delta_{\text{cr}}^{\text{l}}G_{\text{m}}^{\circ}(298.15 \text{ K})/(\text{kJ mol}^{-1}) & = \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(298.15 \text{ K}) \\ & - 298.15 \Delta_{\text{cr}}^{\text{l}}S_{\text{m}}^{\circ}(298.15 \text{ K}) \end{aligned} \quad (9)$$

**Table 7**The standard ( $p^\circ = 0.1$  MPa) molar enthalpies of sublimation, along with entropies and Gibbs energies of sublimation adjusted at  $T = 298.15$  K.

| Compound                  | Technique            | $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15\text{ K})$ (kJ mol <sup>-1</sup> ) | $\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^{\circ}(298.15\text{ K})$ (J K <sup>-1</sup> mol <sup>-1</sup> ) | $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(298.15\text{ K})$ (kJ mol <sup>-1</sup> ) |
|---------------------------|----------------------|--|---|--|
| 2,4-Dihydroxybenzoic acid | Torsion <sup>a</sup> | 122 ± 2  | 218 ± 5   | 57 ± 4   |
|                           | TG <sup>b</sup>      | 117 ± 7  | 204 ± 9   | 56 ± 5   |
|                           | Knudsen [9]          | 126.4 ± 0.8  | 227 ± 3   | 58.62 ± 0.16   |
| 2,6-Dihydroxybenzoic acid | Torsion <sup>a</sup> | 111 ± 2  | 205 ± 4   | 50 ± 3   |
|                           | TG <sup>b</sup>      | 113 ± 5  | 210 ± 8   | 50 ± 5   |
|                           | Knudsen [9]          | 109.1 ± 1.0  | 202 ± 3   | 48.78 ± 0.16   |
| 3,4-Dihydroxybenzoic acid | Torsion <sup>a</sup> | 139 ± 2  | 244 ± 7   | 66 ± 4   |
|                           | TG <sup>b</sup>      | 146 ± 7  | 263 ± 10  | 67 ± 6   |
|                           | Knudsen [9]          | 135.1 ± 1.2  | 234 ± 3   | 65.41 ± 0.30   |

<sup>a</sup>  $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15\text{ K})$  values have been determined from the experimental  $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(T_{\text{te}})$  data using Eq. (2).<sup>b</sup>  $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15\text{ K})$  values have been determined from the experimental  $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(T_{\text{TC}})$  data using Eq. (6), where  $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(T_{\text{fus}})$  values are obtained from d.s.c. measurements,  $\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^{\circ}$  and  $\Delta_{\text{f}}^{\text{g}}C_{\text{p,m}}^{\circ}$  values are calculated from the corresponding  $C_{\text{p,m}}(\text{cr})_{\text{estd}}$  and  $C_{\text{p,m}}(\text{l})_{\text{estd}}$ , estimated according to a group additivity approach [12].

The standard ( $p^\circ = 0.1$  MPa) molar enthalpies and entropies of sublimation, obtained from torsion-effusion data using Eqs. (2) and (7) and from NITG and ITG using Eqs. (6) and (8), along with the Gibbs energies of sublimation at  $T = 298.15$  K (Eq. (9)) were given in Table 7 for all the compounds examined.

The standard molar enthalpies and entropies obtained by vapor pressure data determined using torsion-effusion are in good agreement with those obtained by thermogravimetry data especially for the 2,6-isomer, while some slight differences were observed for both 2,4- and 3,4-dihydroxybenzoic acids. On the other hand, comparison with literature values determined by Price et al. [3] is difficult because the sublimation enthalpy data were reported without any information about the experimental temperature range used. On the other hand, the standard molar Gibbs energies of sublimation derived by both methods showed an excellent agreement for all compounds studied. Furthermore, these values are in good agreement with those found in literature [9]: the percentage of relative deviation of  $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(298.15\text{ K})$  values calculated in the present study from those taken from literature do not exceed 5%, which correspond to about 2–3 kJ mol<sup>-1</sup>. On the basis of the averages of the  $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(298.15\text{ K})$  values (Table 7) the following increasing-order of volatility can be established for these three isomers:

2, 6-dihydroxybenzoic acid < 2, 4-dihydroxybenzoic acid  
< 3, 4-dihydroxybenzoic acid

A possible explanation can be provided on the basis of the occurrence of *intra*-molecular and *inter*-molecular hydrogen bonds. The 2,6-isomer exhibits two *intra*-molecular hydrogen bonds due to the presence of two OH groups in *ortho*-position with respect to the carboxylic group, while in the 2,4- and 3,4-isomers, only one *intra*-molecular bond can take place. This type of interaction avoids the occurrence of *inter*-molecular hydrogen bond, thus demonstrating the validity of the order proposed for the volatility scale.

#### 4. Conclusions

In the present paper the vaporization (and sublimation) vapor pressures and the standard molar enthalpies entropies and Gibbs energies of sublimation of three dihydroxybenzoic acids were determined using thermal analysis (thermogravimetry under non-isothermal and isothermal conditions coupled with d.s.c.) and torsion-effusion. A substantial agreement among NITG-ITG and torsion-effusion results was found, as it can be demonstrated by the good agreement between the enthalpies of fusion determined by d.s.c. and those calculated using the difference between sublimation and vaporization enthalpies calculated at  $T = T_{\text{fus}}$ , derived

by torsion-effusion and NITG/ITG data, respectively. In addition, the averages of the  $\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(298.15\text{ K})$  values enabled us to assess a volatility scale of the three isomers in the solid state on the basis of the number of *inter*-molecular hydrogen bonds they can form.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2011.01.001.

#### References

- [1] H. Babich, A. Sedletcaia, B. Kenigsberg, *Pharmacol. Toxicol.* 91 (5) (2002) 245–253.
- [2] (a) K. Strupat, M. Karas, F. Hillenkamp, *Int. J. Mass Spectrom. Ion Processes* 111 (1991) 89–102;  
(b) K. Strupat, J. Kampmeier, V. Horneffer, *Int. J. Mass Spectrom. Ion Processes* 169–170 (1997) 43–50.
- [3] D.M. Price, S. Bashir, P.R. Derrick, *Thermochim. Acta* 327 (1999) 167–171.
- [4] D.M. Price, *Thermochim. Acta* 367–368 (2001) 253–262.
- [5] P.K. Gupta, K.G. Ganesan, P.K. Gutch, L. Manral, D.K. Dubey, *J. Chem. Eng. Data* 53 (2008) 841–845.
- [6] N. Pieterse, W.W. Focke, *Thermochim. Acta* 406 (2003) 191–198.
- [7] R. Barontini, V. Cozzani, *Thermochim. Acta* 460 (2007) 15–21.
- [8] S. Vecchio, M. Tomassetti, *Fluid Phase Equilib.* 279 (2009) 64–72.
- [9] M.J.S. Monte, M.V. Gonçalves, M.D.M.C. Ribeiro da Silva, *J. Chem. Eng. Data* 55 (6) (2010) 2246–2251.
- [10] S. Vecchio, *Thermochim. Acta* 499 (2010) 27–33 (and references contained therein).
- [11] S. Vecchio, B. Brunetti, *J. Chem. Thermodyn.* 41 (2009) 880–887.
- [12] J.S. Chickos, D.G. Hesse, J.F.A. Liebman, *Struct. Chem.* 4 (1993) 261–269.
- [13] C. Plato, A.R. Glasgow Jr., *Anal. Chem.* 41 (1969) 330–336.
- [14] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley, D.D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements*, American Society for Metals, Metals Park, OH, 1973.
- [15] R. Sabbah, A. Xu-wu, J.S. Chickos, M.L. Planas Leitão, M.V. Roux, L.A. Torres, *Thermochim. Acta* 331 (1999) 93–204.
- [16] I. Langmuir, *Phys. Rev.* 2 (1913) 329–342.
- [17] H.A. Jones, I. Langmuir, G.M.J. Mackay, *Phys. Rev.* 30 (1927) 201–214.
- [18] R.M. Stephenson, S. Malanowski, *Handbook of the Thermodynamics of Organic Compounds*, Elsevier, New York, 1987, pp. 225–226.
- [19] B. Brunetti, V. Piacente, P. Scardala, *J. Chem. Eng. Data* 52 (2007) 24–29.
- [20] M.E. Wieser, M. Bergluna, *Pure Appl. Chem.* 81 (2009) 2131–2156.
- [21] W.W. Focke, *J. Therm. Anal. Calorim.* 74 (2003) 1107–1118.
- [22] V.N. Emel'yanenko, S.P. Verevkin, O.V. Krol, R.M. Varushchenko, N.V. Che-lovskaya, *J. Chem. Thermodyn.* 39 (2007) 594–601.
- [23] S.P. Verevkin, S.A. Kozlova, *Thermochim. Acta* 471 (2008) 33–42.
- [24] E.L. Bauer, *A Statistical Manual for Chemists*, second ed., Academic Press, New York & London, 1971, pp. 30–31.
- [25] J.S. Chickos, S. Hosseini, D.G. Hesse, J.F.A. Liebman, *Struct. Chem.* 4 (1993) 271–278.