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# Vapor Pressure Characterization of Several Phenolics and Polyhydric Compounds by Knudsen Effusion Method

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The vapor pressures of anthracene, catechol, hydroquinone, caffeic acid, ferulic acid, gentisic acid, and myoinositol have been measured by an isothermal Knudsen effusion method. The vapor pressure correlations fit to the following linear equations: anthracene, ln($p$/Pa) = (31.886 ± 0.440) to (11496 ± 149) $T$/K (from 320 K to 354 K); catechol, ln($p$/Pa) = (31.05 ± 0.18) to (9618 ± 56) $T$/K (from 295 K to 310 K); hydroquinone, ln($p$/Pa) = (34.595 ± 0.455) to (12102 ± 150) $T$/K (from 327 K to 348 K); caffeic acid, ln($p$/Pa) = (45.122 ± 1.320) to (20466 ± 550) $T$/K (from 409 K to 424 K); ferulic acid, ln($p$/Pa) = (39.454 ± 0.402) to (15925 ± 153) $T$/K (from 369 K to 390 K); gentisic acid, ln($p$/Pa) = (36.297 ± 0.454) to (14184 ± 168) $T$/K (from 362 K to 379 K); and myoinositol, ln($p$/Pa) = (44.366 ± 0.702) to (20931 ± 315) $T$/K (from 438 K to 458 K). The sublimation enthalpies and entropies of these samples are calculated.

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## Introduction

Biomass pyrolysis is a complex process involving both physical and chemical processes. Under a rapid heating rate, the transport of pyrolysis tars from the substrate to the surrounding atmosphere may be controlled by internal and external mass transport. In coal pyrolysis, the tar vaporization step has been widely applied to describe this process.[1−4] Many of tar components are not very stable at high temperature, and the volatility characterization of biomass tars and tar-related compounds must be accomplished under relatively low temperature. The Knudsen effusion method[5,6] is one of the most widely applied techniques to determine the vapor pressures of compounds to as low as several millipascals. The standard Knudsen effusion method measures the mass loss of the test sample due to a low flow of vapor through a small orifice under isothermal conditions and is used to determine the vapor pressure of pure compounds. On the other hand, for the vapor pressures of complex mixtures exhibiting a wide range of volatility, a non-isothermal Knudsen effusion method was developed by Oja and Suuberg[7] to determine the volatilities of pyrolysis tars from cellulose,[7] coal,[8] and tobacco.[9]

The knowledge of vapor pressures of biomass tars and tar-related compounds is useful in modeling the process behavior in biomass pyrolysis. However, the vapor pressures of many tobacco tar-related compounds, especially those containing heteroatoms, are not available in the literature. As a part of the program on the study of the vaporization of biomass tars, the vapor pressures of some typical tobacco pyrolysis tar compounds including catechol, hydroquinone, and some of their precursors (such as caffeic acid, ferulic acid, gentisic acid, and myoinositol) have been determined by the standard isothermal Knudsen effusion method. The vapor pressures and sublimation enthalpies of catechol,[10−11] hydroquinone,[11−14] and myoinositol[15−17] have been characterized by other researchers. No such data are available in the literature for the rest of these organic acids.

**Table 1. Compounds Examined**

| compound | formula | formula weight | manufacturer | purity |
|---|---|---|---|---|
| anthracene | $C_{14}H_{10}$ | 178.23 | Fluka | 99.6 % [a] |
| caffeic acid | $C_9H_8O_4$ | 180.16 | Sigma | >99.0 % [b] |
| catechol | $C_6H_6O_2$ | 110.11 | Acros | >99.5 % [b] |
| ferulic acid | $C_{10}H_{10}O_4$ | 194.18 | Aldrich | >99.0 % [c] |
| gentisic acid | $C_7H_6O_4$ | 154.12 | Aldrich | 99.9 % [b] |
| hydroquinone | $C_6H_6O_2$ | 110.11 | Acros | >99.5 % [b] |
| myoinositol | $C_6H_{12}O_6$ | 180.16 | Aldrich | 99.4 % [a] |

[a] GC. [b] HPLC. [c] Thin-layer chromatography.

## Experimental Section

The samples of compounds tested in this work were commercially available and were used as received without further purification. The detailed descriptions of these samples are listed in Table 1.

A Knudsen effusion thermogravimetric technique has been employed to measure the vapor pressures of these compounds. The fabrication process and dimensions of the sample holder, called the Knudsen cell, are shown in Figure 1. Approximately 10 mg of test sample was put into a cylindrical shaped cell, which was made from 0.0254 mm thick stainless steel foil and covered by a lid with a coaxial effusion orifice. The sample cell was then hermetically sealed by a mechanical press. The

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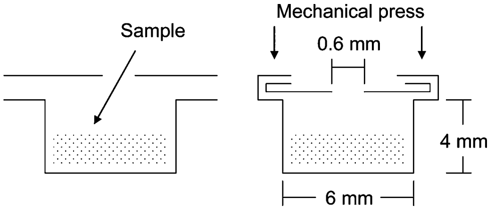

**Figure 1.** Schematic of the Knudsen effusion cell.

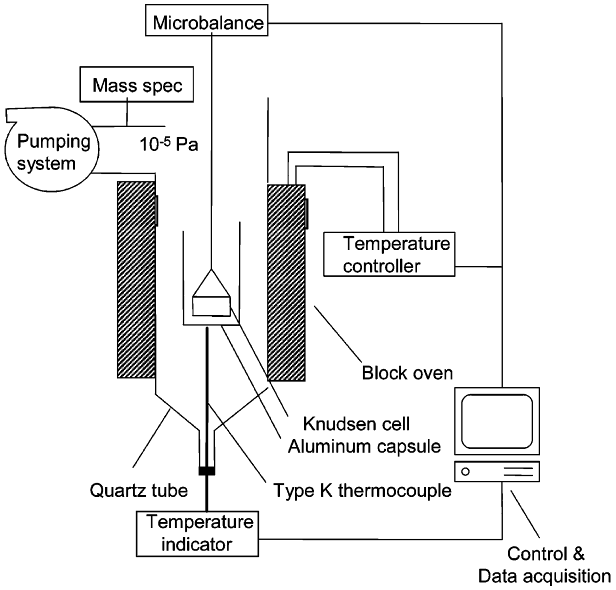

**Figure 2.** Schematic of the Knudsen effusion apparatus.

cell was hung on a Cahn 121 microbalance (Thermo Cahn, Madison, WI) with back pressure as low as $10^{-5}$ Pa maintained by a turbo pump and a mechanical pump. The schematic of the apparatus is shown in Figure 2. The aluminum capsule was painted black by using high temperature paint to enhance the radiative heat transfer. The temperature of the Knudsen cell was measured by a type K thermocouple, which was calibrated against several ASTM standard mercury thermometers within the temperature range from (40 to 200) °C. The temperature signal was monitored by an Omega DP470 temperature indicator with an uncertainty of 0.1 K. The temperature of the external block oven was precisely controlled by a LC6 programmed temperature controller (Julabo USA Inc., Allentown, PA). The sample mass loss and the corresponding temperature were simultaneously monitored over a temperature range. A QME 200 quadrupole mass spectrometer (Pfeiffer Vacuum, Nashua, NH) was used to monitor any possible thermal decomposition of the test samples in the vapor pressure measurement process.

Initially the orifices were made manually by a fine drill. The diameter of the hole was measured by an optical microscope. As Ribeiro Da Silva et al.[18] suggested, the ragged edges and the irregular shape of the holes are somehow unavoidable. Measuring the area of these holes not only is tedious but also increases the uncertainty of the test results. The real diameter of the orifice was different in each case, with deviation as high as 5 %. To improve the measurement accuracy, the orifices were made by a chemical etching technique (Fotofab Corp., Chicago, IL), with a diameter of (0.60 ± 0.0025) mm. The images of Knudsen holes made separately by these two methods are shown in Figure 3. It is clear that the hole made by the chemical etching technique is much better than the one made by mechanical drilling. The potential measurement error of the diameter of the orifice due to the thermal expansion is relatively small (less than 0.3 %) according to the current measurement conditions.

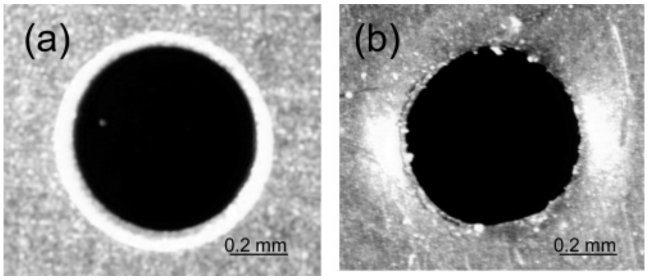

**Figure 3.** Microphotographs of Knudsen effusion holes: (a) made by chemical etching and (b) made by mechanical drilling.

**Table 2. Vapor Pressure Data of Anthracene**

| run 1 | | run 2 | | run 3 | |
|---|---|---|---|---|---|
| $T$/K | ln($p$/Pa) | $T$/K | ln($p$/Pa) | $T$/K | ln($p$/Pa) |
| 323.0 | −3.70 | 321.2 | −3.96 | 320.2 | −4.04 |
| 328.2 | −3.09 | 326.6 | −3.36 | 326.1 | −3.46 |
| 330.8 | −2.89 | 331.8 | −2.73 | 331.5 | −2.92 |
| 333.3 | −2.56 | 334.6 | −2.47 | 334.3 | −2.62 |
| 336.0 | −2.24 | 337.2 | −2.18 | 340.1 | −2.02 |
| 338.5 | −2.02 | 340.1 | −1.89 | 343.0 | −1.73 |
| 341.2 | −1.77 | 342.7 | −1.63 | 345.6 | −1.46 |
| 343.7 | −1.46 | 345.5 | −1.38 | 348.6 | −1.16 |
| 346.4 | −1.23 | 347.8 | −1.14 | 351.3 | −0.92 |
| 351.6 | −0.89 | 350.8 | −0.88 | 354.1 | −0.65 |

**Table 3. Vapor Pressure Data of Catechol**

| run 1 | | run 2 | | run 3 | |
|---|---|---|---|---|---|
| $T$/K | ln($p$/Pa) | $T$/K | ln($p$/Pa) | $T$/K | ln($p$/Pa) |
| 295.3 | −1.52 | 295.9 | −1.46 | 296.2 | −1.41 |
| 296.2 | −1.44 | 296.2 | −1.42 | 297.3 | −1.30 |
| 298.2 | −1.20 | 298.3 | −1.21 | 299.4 | −1.06 |
| 300.2 | −0.99 | 300.3 | −0.97 | 301.4 | −0.86 |
| 302.2 | −0.76 | 302.3 | −0.77 | 303.5 | −0.61 |
| 304.2 | −0.55 | 304.4 | −0.54 | 305.6 | −0.42 |
| 306.1 | −0.33 | 306.2 | −0.36 | 307.6 | −0.22 |
| 308.2 | −0.16 | 308.6 | −0.14 | 309.8 | −0.01 |

**Table 4. Vapor Pressure Data of Hydroquinone**

| run 1 | | run 2 | | run 3 | |
|---|---|---|---|---|---|
| $T$/K | ln($p$/Pa) | $T$/K | ln($p$/Pa) | $T$/K | ln($p$/Pa) |
| 322.8 | −2.89 | 322.8 | −2.91 | 322.8 | −2.97 |
| 324.9 | −2.60 | 324.8 | −2.72 | 324.9 | −2.67 |
| 326.9 | −2.36 | 326.9 | −2.44 | 326.9 | −2.47 |
| 328.9 | −2.18 | 329.0 | −2.22 | 329.0 | −2.25 |
| 331.1 | −1.95 | 331.0 | −1.98 | 331.0 | −1.98 |
| 333.1 | −1.73 | 333.2 | −1.76 | 333.2 | −1.78 |
| 335.2 | −1.46 | 335.2 | −1.53 | 335.2 | −1.55 |
| 337.3 | −1.29 | 337.3 | −1.33 | 337.2 | −1.34 |
| 339.2 | −1.04 | 339.4 | −1.08 | 339.4 | −1.10 |

At the beginning of each measurement, the temperature of the sample cell was raised until a noticeable weight loss rate was observed. Approximately 5 % by mass of the sample has evaporated before the measurement commenced in order to minimize the impact from impurities whose volatilities may be higher than that of the sample.

During the vapor pressure characterization of levoglucosan, Oja and Suuberg[19] reported that the phase change may cause a change in the slope of the vapor pressure curve of the material if it happens in the temperature range of vapor pressure measurement. The potential phase transition of the test samples in the temperature range of vapor pressure measurement was monitored by a PC 409C TG-DSC (Netzsch Instrument Inc., Burlington, MA) from room temperature to 15 °C higher than the highest temperature used in the vapor pressure measurement for the corresponding sample at a heating rate of 2 K·min$^{-1}$ in helium.

**Table 5. Temperature Dependence of the Vapor Pressures and Sublimation Enthalpies and Entropies Obtained in the Current Study and in the Literature: Anthracene, Catechol, Hydroquinone, Caffeic Acid, Ferulic Acid, Gentisic Acid and Myoinositol**

| | $T$ | $\ln(p/\mathrm{Pa}) = -A/(T/\mathrm{K}) + B$ | | $\Delta_{\mathrm{sub}}H$ | $\Delta_{\mathrm{sub}}S$ | |
|---|---|---|---|---|---|---|
| run | K | $A$ | $B$ | $\mathrm{kJ{\cdot}mol^{-1}}$ | $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$ | $R^2$ |
| Anthracene | | | | | | |
| run 1 | 323 to 352 | 11470 ± 251 | 31.860 ± 0.747 | 95.36 ± 2.09 | 264.89 ± 6.21 | 0.996 |
| run 2 | 321 to 351 | 11901 ± 89 | 33.115 ± 0.266 | 98.95 ± 0.74 | 275.32 ± 2.21 | 0.999 |
| run 3 | 320 to 354 | 11450 ± 106 | 31.676 ± 0.312 | 95.19 ± 0.88 | 263.36 ± 2.60 | 0.999 |
| all data | 320 to 354 | 11496 ± 149 | 31.886 ± 0.440 | 95.58 ± 1.24 | 265.10 ± 3.66 | 0.995 |
| Li et al.[23] | 348 to 368 | 12332 ± 229 | 34.199 ± 0.641 | 102.53 ± 1.90 | 284.33 | |
| Oja and Suuberg[19] | 318 to 363 | 12024 ± 337 | 33.281 | 100.00 | 276.7 | |
| Hansen and Eckert[25] | 313 to 363 | 12339 | 34.261 | 102.6 ± 2.6 | 284.85 | |
| Rordorf[26] | 318 to 373 | 11877 | 33.002 | 98.74 | 274.38 | |
| Catechol | | | | | | |
| run 1 | 295 to 308 | 9762 ± 113 | 31.54 ± 0.38 | 81.165 ± 0.943 | 262.18 ± 3.13 | 0.999 |
| run 2 | 296 to 309 | 10822 ± 83 | 34.88 ± 0.27 | 79.786 ± 0.484 | 257.53 ± 1.61 | 1.000 |
| run 3 | 296 to 310 | 10729 ± 68 | 34.60 ± 0.22 | 78.863 ± 0.707 | 254.58 ± 2.34 | 1.000 |
| all data | 295 to 310 | 9618 ± 56 | 31.05 ± 0.18 | 79.963 ± 0.462 | 258.18 ± 1.53 | 0.999 |
| Hydroquinone | | | | | | |
| run 1 | 323 to 339 | 12024 ± 183 | 34.404 ± 0.552 | 99.97 ± 1.52 | 286.03 ± 4.59 | 0.998 |
| run 2 | 323 to 339 | 12115 ± 101 | 34.623 ± 0.305 | 100.73 ± 0.84 | 287.85 ± 2.54 | 0.999 |
| run 3 | 324 to 339 | 12169 ± 153 | 34.770 ± 0.464 | 101.17 ± 0.28 | 289.08 ± 3.86 | 0.999 |
| all data | 325 to 339 | 12102 ± 150 | 34.595 ± 0.455 | 100.61 ± 1.25 | 287.62 ± 3.78 | 0.996 |
| Coolidge and Coolidge[12] | 324 to 345 | 13217 | 38.055 | 109.89 | 316.39 | |
| Bender et al.[13] | 341 to 400 | 12233 | 35.137 | 101.71 | 292.13 | |
| DeKruif et al.[14] | 330 to 351 | 12339 | 34.261 | 102.59 | 284.85 | |
| Caffeic Acid | | | | | | |
| run 1 | 409 to 424 | 20124 ± 630 | 44.306 ± 1.513 | 167.31 ± 5.24 | 368.36 ± 12.58 | 0.994 |
| run 2 | 411 to 423 | 20619 ± 1116 | 45.508 ± 2.677 | 171.43 ± 9.28 | 378.35 ± 22.26 | 0.986 |
| run 3 | 410 to 424 | 20726 ± 1226 | 45.722 ± 2.941 | 172.32 ± 10.19 | 380.13 ± 24.45 | 0.979 |
| all data | 409 to 424 | 20466 ± 550 | 45.122 ± 1.320 | 17016 ± 4.58 | 375.14 ± 10.98 | 0.985 |
| Ferulic Acid | | | | | | |
| run 1 | 369 to 390 | 16520 ± 257 | 41.015 ± 0.674 | 137.35 ± 2.13 | 341.00 ± 5.61 | 0.999 |
| run 2 | 369 to 390 | 15920 ± 251 | 39.438 ± 0.661 | 132.36 ± 2.09 | 327.89 ± 5.50 | 0.998 |
| run 3 | 369 to 390 | 15378 ± 184 | 38.018 ± 0.484 | 127.85 ± 1.53 | 316.08 ± 4.03 | 0.999 |
| all data | 369 to 390 | 15925 ± 153 | 39.454 ± 0.402 | 132.40 ± 1.27 | 328.02 ± 3.34 | 0.998 |
| Gentisic Acid | | | | | | |
| run 1 | 362 to 379 | 14047 ± 355 | 35.917 ± 0.958 | 116.78 ± 2.95 | 298.61 ± 7.97 | 0.996 |
| run 2 | 362 to 379 | 14186 ± 285 | 36.303 ± 0.770 | 117.95 ± 2.37 | 301.83 ± 6.40 | 0.997 |
| run 3 | 362 to 379 | 14325 ± 274 | 36.686 ± 0.739 | 119.10 ± 2.27 | 305.01 ± 6.15 | 0.997 |
| all data | 362 to 379 | 14184 ± 168 | 36.297 ± 0.454 | 117.93 ± 1.40 | 301.77 ± 3.77 | 0.997 |
| Myoinositol | | | | | | |
| run 1 | 439 to 457 | 21263 ± 303 | 45.056 ± 0.675 | 176.78 ± 2.52 | 374.60 ± 5.61 | 0.999 |
| run 2 | 440 to 458 | 20540 ± 124 | 43.507 ± 0.275 | 170.77 ± 1.03 | 361.72 ± 2.28 | 0.999 |
| run 3 | 438 to 457 | 20945 ± 460 | 44.431 ± 1.026 | 174.14 ± 3.83 | 369.40 ± 8.53 | 0.997 |
| all data | 438 to 458 | 20931 ± 315 | 44.366 ± 0.702 | 174.02 ± 2.62 | 368.86 ± 5.84 | 0.995 |
| Barone et al.[15] | 461 to 493 | 18614 ± 161 | 40.687 ± 0.576 | 154.76 ± 1.34 | 338.27 ± 4.79 | |
| De Wit et al.[16] | 448 to 472 | 20050 | 42.47 | 166.70 | 353.10 | |

The highest temperature employed in the Knudsen effusion technique was at least 20 °C lower than the reported melting points of the test samples in order to minimize the possible thermal decomposition during the vapor pressure measurements. The thermal stability of caffeic acid, ferulic acid, gentisic acid, and myoinositol was further examined. A 20 mg sample was placed inside a ceramic crucible with a cover and held at the highest temperature of the vapor pressure measurement for 3 h in the TG-DSC under an atmospheric pressure and flowing helium. The purity of the residues and the original samples were compared using proton nuclear magnetic resonance spectroscopy ($^1$H NMR) by a Varian Unity 400 spectrometer (Varian Inc., Palo Alto, CA). Only caffeic, ferulic, and gentisic acids were examined by high-performance liquid chromatography (Agilent series 1100 model HPLC with a diode array UV detector at 326 nm wavelength) on a Waters Symmetry $C_{18}$ analytical column (3.9 mm i.d. × 150 mm, 5 mm particles). The mobile phase consisted of methanol/water/acetic acid (5:94:1, v/v/v, eluent A) and methanol/acetic acid (99:1, v/v, eluent B). The gradient elution profile was as follows: 5 % B for 5 min, linearly increased to 35 % B in 5 min, further to 100 % B in 2 min, and finally held for 5 min. The flow rate was set to 1.4 mL/min, and the total run time was 15 min.

After 3 h holding at the highest experimental temperature of the vapor pressure measurement in the TG, the mass losses of caffeic acid, ferulic acid, gentisic acid, and myoinositol were less than 1 % of the initial mass. HPLC analysis also showed the change in purity levels of the heated samples was less than 0.5 %. The NMR spectra of the heated samples did not show any sign of decomposition. Accordingly, the thermal decomposition of the tested samples under the current temperature range is negligible.

## Results and Discussion

A simplified Knudsen effusion equation can be used to describe the correlation between the vapor pressure of the test sample inside the cell and other physical and chemical parameters:[5,20]

$$p_0 = \frac{m}{tA_0W_0}\left(\frac{2\pi RT}{M}\right)^{0.5} \tag{1}$$

where $p_0$ is the vapor pressure near the orifice, $m$ is the mass loss of the sample through the orifice during time $t$, $A_0$ is the area of the orifice, $R$ is the gas constant, $T$ is the absolute temperature of the sample, $M$ is the molecular weight of the sample, and $W_0$ is the Clausing factor and can be expressed as

$$W_0 = \frac{1}{1 + \frac{3L}{8r}} \tag{2}$$

where $L$ and $r$ are the thickness of the cell cover and the radius of the orifice, respectively.

Due to the continuous sample loss through the orifice, the vapor pressure inside the cell is not maintained under a real equilibrium condition, which will lead to $p_0$ being less than the equilibrium vapor pressure ($p_s$) in a completely airtight system. A correlation derived by Whitman[21] and Motzfeldt[22] can be used to correct the deviation from the equilibrium vapor pressure as

$$p_s = p_0\left(1 + \frac{W_0A_0}{A_s}\left(\frac{1}{\alpha} + \frac{1}{W} - 2\right)\right) \tag{3}$$

where $A_s$ is the cross section of the sample cell; α is the vaporization coefficient of the test material; and $W$ is the shape factor of the sample cell, which can be expressed as the ratio of the radius to the height of the sample cell.

According to the Knudsen cell dimension shown in Figure 1, $W$ is 0.75. In eq 3, if the vaporization coefficient α is close to 1, $p_s$ approximately equals $1.005p_0$. Since the difference between $p_s$ and $p_0$ is much smaller than the experimental error during the measurement, the vapor pressure calculated by eq 1 is used as the saturated vapor pressure of the test samples in the current study.

The sublimation enthalpy and sublimation entropy of test substances can be derived by the Clausius−Clapeyron equation:

$$\ln p_s = -\frac{A}{T} + B \tag{4}$$

where $A$ is $\Delta_{sub}H/R$ and $B$ is $\Delta_{sub}S/R$. These values were calculated by treating the experimental data using the method of least squares. The sublimation enthalpy and entropy obtained from eq 4 are the mean values in the experimental temperature range.

On the basis of the experimental results of DSC, there was no phase transition phenomenon observed for any compounds of interest within the test temperature range. Considering the relatively small impact of pressure on solid-phase transition, the potential influence of the crystalline phase transition in the present study is negligible. As expected, no significant thermal decomposition has been found from the mass spectra of the samples in the vapor pressure measurement process since the highest temperature was at least 20 °C lower than the reported melting point for each sample.

The experimental results of anthracene, catechol, and hydroquinone are listed in Table 2 through Table 4. The constants $A$ and $B$ in the Clausius−Clapeyron equation were derived by using a linear least squares curve-fitting routine to calculate the linear correlation between ln($p$/Pa) and $T$/K. The results are listed in Table 5. Both the vapor pressures and the sublimation enthalpies of anthracene measured in the current study are in good agreement with data in the literature.[23−26] The reliability of the current test method for vapor pressure characterization has been established.

**Table 6. Vapor Pressure Data of Caffeic Acid**

| run 1 | | run 2 | | run 3 | |
|---|---|---|---|---|---|
| $T$/K | ln($p$/Pa) | $T$/K | ln($p$/Pa) | $T$/K | ln($p$/Pa) |
| 409.3 | −4.90 | 411.0 | −4.62 | 409.9 | −4.72 |
| 411.5 | −4.56 | 413.0 | −4.51 | 412.1 | −4.71 |
| 413.4 | −4.33 | 415.0 | −4.10 | 413.9 | −4.37 |
| 415.5 | −4.18 | 417.1 | −3.91 | 416.0 | −4.13 |
| 417.6 | −3.87 | 419.1 | −3.75 | 418.1 | −3.80 |
| 419.7 | −3.67 | 421.3 | −3.48 | 420.1 | −3.67 |
| 421.4 | −3.39 | 423.3 | −3.15 | 422.2 | −3.27 |
| 423.7 | −3.22 | | | 424.2 | −3.18 |

**Table 7. Vapor Pressure Data of Ferulic Acid**

| run 1 | | run 2 | | run 3 | |
|---|---|---|---|---|---|
| $T$/K | ln($p$/Pa) | $T$/K | ln($p$/Pa) | $T$/K | ln($p$/Pa) |
| 369.1 | −3.79 | 368.7 | −3.70 | 369.2 | −3.60 |
| 373.2 | −3.26 | 373.0 | −3.25 | 373.3 | −3.20 |
| 377.2 | −2.74 | 375.2 | −3.03 | 375.3 | −2.95 |
| 381.3 | −2.26 | 377.2 | −2.82 | 377.4 | −2.74 |
| 383.6 | −2.04 | 379.4 | −2.51 | 379.3 | −2.53 |
| 385.4 | −1.86 | 381.4 | −2.28 | 381.6 | −2.30 |
| 387.7 | −1.63 | 383.2 | −2.09 | 383.4 | −2.12 |
| 389.5 | −1.42 | 385.6 | −1.81 | 385.7 | −1.82 |
| | | 387.5 | −1.63 | 387.5 | −1.67 |
| | | 389.8 | −1.45 | 389.8 | −1.42 |

**Table 8. Vapor Pressure Data of Gentisic Acid**

| run 1 | | run 2 | | run 3 | |
|---|---|---|---|---|---|
| $T$/K | ln($p$/Pa) | $T$/K | ln($p$/Pa) | $T$/K | ln($p$/Pa) |
| 362.0 | −2.90 | 362.0 | −2.88 | 361.8 | −2.95 |
| 364.0 | −2.64 | 364.1 | −2.68 | 363.9 | −2.67 |
| 366.2 | −2.46 | 366.1 | −2.45 | 365.7 | −2.46 |
| 368.2 | −2.26 | 368.2 | −2.21 | 368.2 | −2.21 |
| 370.3 | −1.97 | 370.2 | −2.01 | 370.0 | −2.00 |
| 372.4 | −1.84 | 372.3 | −1.82 | 372.3 | −1.80 |
| 374.6 | −1.51 | 374.5 | −1.52 | 374.4 | −1.52 |
| 376.7 | −1.39 | 376.5 | −1.36 | 376.4 | −1.40 |
| 378.7 | −1.21 | 378.6 | −1.22 | 378.6 | −1.18 |

**Table 9. Vapor Pressure Data of Myoinositol**

| run 1 | | run 2 | | run 3 | |
|---|---|---|---|---|---|
| $T$/K | ln($p$/Pa) | $T$/K | ln($p$/Pa) | $T$/K | ln($p$/Pa) |
| 439.1 | −3.37 | 440.2 | −3.16 | 438.3 | −3.40 |
| 442.1 | −3.06 | 443.9 | −2.77 | 442.7 | −2.84 |
| 445.2 | −2.68 | 445.3 | −2.62 | 444.7 | −2.63 |
| 447.1 | −2.51 | 448.7 | −2.26 | 446.6 | −2.43 |
| 450.4 | −2.13 | 450.4 | −2.09 | 448.9 | −2.28 |
| 452.2 | −1.98 | 453.9 | −1.73 | 450.8 | −2.02 |
| 455.4 | −1.61 | 456.4 | −1.51 | 452.9 | −1.85 |
| 457.4 | −1.46 | 458.1 | −1.34 | 454.8 | −1.61 |
| | | | | 456.5 | −1.44 |

By using the same method, the vapor pressures of caffeic acid, ferulic acid, gentisic acid, and myoinositol were calculated and are shown in Table 6 through Table 9. Temperature dependency of the vapor pressures and sublimation enthalpies and entropies are summarized in Table 5. The linear correlation between ln($p$/Pa) and $T$/K shown in Figure 4 through Figure 7 confirms that the sublimation enthalpies can be assumed as constants in the temperature range studied. $\Delta_{sub}H$ of myoinositol measured by Barone et al.[15] is (154.7 ± 1.4) kJ·mol$^{-1}$ from 461 K to 493 K. The values reported by De Wit et al.[16] and Costa et al.[17] are 168.0 kJ·mol$^{-1}$ at 462 K and (167 ± 2) kJ·mol$^{-1}$ at 474.15 K, respectively. In the current study, $\Delta_{sub}H$ of myoinositol is (174.02 ± 2.62) kJ·mol$^{-1}$ from 438 K to 458 K, close to the values of the latter two but significantly higher than that of the former.

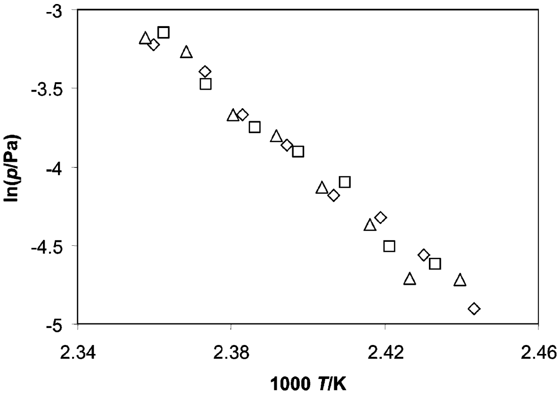

**Figure 4.** Plot of vapor pressure data for caffeic acid: ◇, run 1; □, run 2; Δ, run 3.

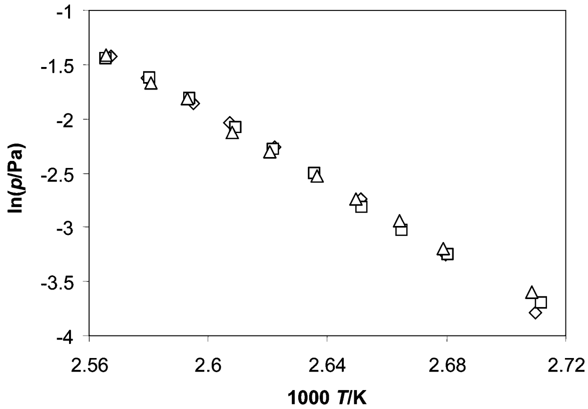

**Figure 5.** Plot of vapor pressure data for ferulic acid: ◇, run 1; □, run 2; Δ, run 3.

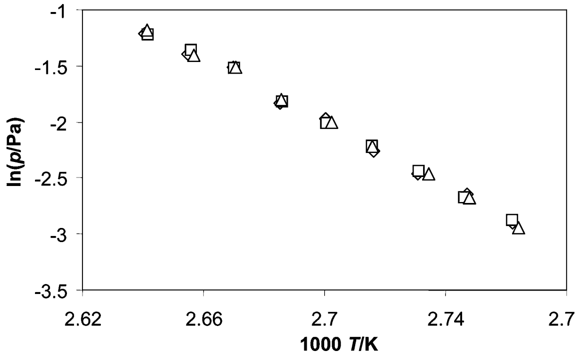

**Figure 6.** Plot of vapor pressure data for gentisic acid: ◇, run 1; □, run 2; Δ, run 3.

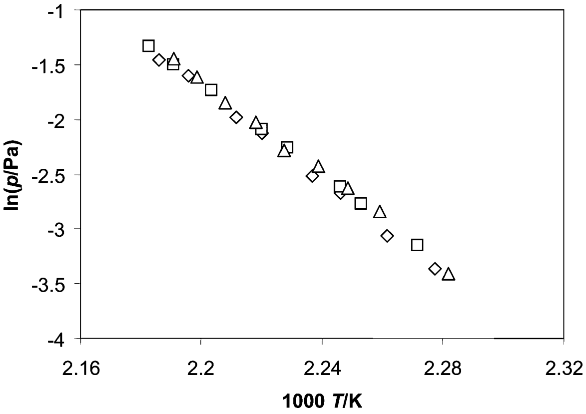

**Figure 7.** Plot of vapor pressure data for myoinositol: ◇, run 1; □, run 2; Δ, run 3.

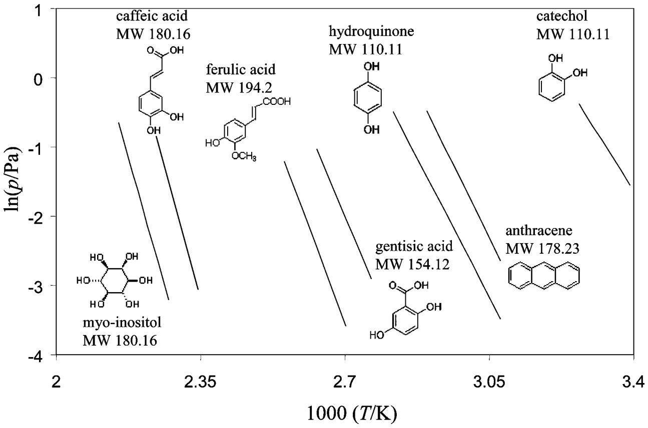

**Figure 8.** Comparison of the vapor pressures of anthracene, catechol, hydroquinone, caffeic acid, ferulic acid, gentisic acid, and myoinositol.

The vapor pressures of seven test samples are summarized in Figure 8. The effects of molecular properties and intermolecular interactions on the vapor pressure are quite complex. In general, higher molecular weight means stronger intermolecular forces caused by orientation (dipole−dipole), induction (dipole−induced dipole), and dispersion (induced dipole−induced dipole) among molecules. This tends to decrease the volatility of the compound. But when heteroatoms are present, especially oxygen and nitrogen, which can form hydrogen bonding, the influences of these dipole−dipole forces and dispersion forces on vapor pressures are weakened. Hydroquinone has the smallest molecular weight (MW = 110.11) among the studied compounds, but its volatility is even lower than that of anthracene (MW = 178.23). Each hydroquinone molecule has two hydroxyl groups that can form intermolecular hydrogen bonds, imparting a higher physical stability ascompared with that of anthracene. Consequently, it is not surprising to find that myoinositol has the lowest volatility among these compounds, considering the significant intermolecular interaction offered by six hydroxyl groups for each molecule. The role of intermolecular hydrogen bonds on the vapor pressure in the solid state has been discussed by other researchers[19,27−28] for hydroxyl and carboxylic functional groups. Brunetti et al.[27] measured the vapor pressure of some methyl derivatives of uracil and found that the vapor pressure of the uracil is significantly lower than that of 1,3-dimethyluracil, because uracil can form a three-dimensional pattern of intermolecular hydrogen bonds in the solid state and 1,3-dimethyluracil cannot form conventional hydrogen bonds. The position of the functional groups will also contribute to the volatility of the compound. For instance, the molecular weight and the number of functional groups of hydroquinone and catechol are identical. However, comparing with hydroquinone the two hydroxyl groups of catechol tend to form intramolecular rather than intermolecular hydrogen bonds because of their close proximity on the benzene ring. Therefore, the volatility of catechol is higher than that of hydroquinone. The actual vapor pressure of the compound is determined by the sum of all these effects.

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