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A DSC/TGA method for determination of the heat of vaporization

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Abstract

A method for the instantaneous determination of the heat of vaporisation of liquids by simultaneous DSC/TGA is discussed. The method has been applied specifically to the evaporation of water from porous materials.

INTRODUCTION

Thermoanalytical techniques have been employed in the measurement of many basic thermodynamic quantities. The recent development of more advanced computer-controlled instrumentation has allowed increasingly more sophisticated experiments to be performed. Two widely used thermoanalytical techniques are differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

DSC measures the difference in the energy required to keep a sample and reference cell at the same temperature [1,2]. DSC allows for quantitative calorimetric measurements to be made. The measured power flux, $\mathrm{d}H/\mathrm{d}t$, is given by the relation

$$\mathrm{d}H/\mathrm{d}t = mC_\mathrm{p}\,\mathrm{d}T/\mathrm{d}t \quad (1)$$

where m is the sample mass, C_p the sample heat capacity, and $\mathrm{d}T/\mathrm{d}t$ the scan rate [2]. It is assumed in eqn. (1) that the mass remains constant over the course of the scan, i.e. that the sample is non-volatile or is confined appropriately within the sample cup.

Thermogravimetric analysis (TGA) records the sample mass as a function of time or temperature. If the sample is undergoing decomposition with formation of volatile products, or is evaporating, then the mass of the sample will vary over the course of a scan.

Recent advances in thermoanalytical instrumentation have made possible simultaneous measurements by DSC and TGA. Here, we exploit simulta-

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neous DSC/TGA as a method for measurement of the enthalpy of vaporization and/or enthalpy of desorption.

Simultaneous DSC/TGA allows for the measurement of the time or temperature dependence of both mass and energy flux. If the sample mass changes during the experiment, e.g., vaporization, chemical reaction, etc., an additional term is added to the equation for the measured instantaneous power flux

$$\mathrm{d}H/\mathrm{d}t = m(t)C_p(T)\ \mathrm{d}T/\mathrm{d}t + \mathrm{d}m/\mathrm{d}t\ \Delta H_v(T) \tag{2}$$

where $\mathrm{d}H/\mathrm{d}t$ is the measured instantaneous power flux, $m(t)$ is the sample mass at time t, $\mathrm{d}T/\mathrm{d}t$ is the scan rate, $\mathrm{d}m/\mathrm{d}t$ is the differential mass (DTG) and $\Delta H_v(T)$ is the enthalpy of transition (vaporization). All variables which are a function of temperature (e.g. C_p) may also be parameterized as a function of time.

Previous measurements of the enthalpy of vaporization of a liquid by DSC have been performed isothermally. After heating a sample to the desired temperature, a hole can be opened in the sample cup and the integral of the heat-flux amplitude recorded and used to calculate the enthalpy of vaporization [2]. The above experiment, while sometimes appropriate, does not allow for the rapid determination of the temperature dependence of the heat of vaporization or the enthalpy of desorption of a liquid from a matrix, nor does it allow for the determination of the heat of vaporization as a function of liquid content. We believe that the method described below will be most useful for studying the evaporation of solvents from various polymer matrices. Such information is not readily available for incorporation into engineering models.

Other investigators have used thermal analysis techniques to study water sorption/desorption from zeolites [3,4], silicates [5], titania [6], goethite [7], aluminas [4], and ion exchange resins [8]. However, none of the earlier studies has attempted to measure the heat of vaporization of a liquid from heterogeneous systems under dynamic conditions. Indeed, most of the other workers only employed a single thermal analysis technique to characterize the thermal event. Morishige et al. [6], however, used simultaneous DSC/TGA to analyze water adsorption on titania. Because high scan rates (20°C min^{-1}) were used in their experiments, it was not possible to determine the heat of desorption quantitatively, as the heat flux and mass outputs were not sufficiently coordinated with each other.

Here we discuss an apparently new thermal analysis method utilizing current advances in thermoanalytical instrumentation. The simultaneous measurement of DSC and TGA on this instrument to a precision of ± 10 W and ± 0.01 mg allows for calculation of the heat of vaporization (or desorption) in the scanning mode. Slow scan rates were used to minimize thermal lags in the system. To our knowledge, this is the first time such a measurement has been reported.

EXPERIMENTAL

Experiments were performed on a Setaram TG–DSC 111 with the aid of ASI Thermal Analysis Plus software (Astra Scientific International, San Jose, CA). Normal calibration procedures for DSC and TGA were followed.

The evaporation of pure liquids (water and methanol) and the evaporation of water from porous substrates have both been investigated.

Water used in this study was distilled before use. All other materials were used as received.

For samples containing water, scans were run from 25 to 125°C; for samples containing methanol, scans were run from 15 to 75°C. For aqueous samples, the scan rate was varied from 0.25 to 5°C min^{-1}. The specific scan rates were 0.25, 0.5, 1, 3, and 5°C min^{-1}. Only the two slowest scan rates are useful for accurate experiments. The atmosphere surrounding the samples was dry nitrogen.

Two separate runs were made during each calorimetric experiment. First, the empty sample cup was measured against the reference cup. Next, an appropriate evaporating sample was run versus an empty cup. The blank run was subtracted from the sample run in order to obtain the absolute instantaneous heat flux values ($\mathrm{d}H/\mathrm{d}t$) required for the subsequent calculations. If a sample contains a relatively small amount of liquid which is evaporated from a porous matrix, it may be appropriate to subtract the power resulting from comparison of the sample with the dry matrix. In this way the contribution resulting from the heat capacity of the dry matrix to the heat flux can be eliminated. This latter approach assumes that the heat capacity of the matrix material is not a function of hydration.

RESULTS AND DISCUSSION

For the dynamic determination of the heat of vaporization (desorption) using the Setaram DSC/TGA, eqn. (2) is used to model the evaporation process. This equation is used to analyze each data set. A twenty-point sliding average or a Savitsky–Golay smoothing algorithm were employed to reduce the noise in the data.

The data are exported for analysis from the thermal analysis software. The following variables are used in the calculation of the heat of vaporization of the water: elapsed time, temperature, power, mass of sample, and $\mathrm{d}m/\mathrm{d}t$. The first four quantities are measured and recorded continuously during the course of the experiment; the last quantity is calculated later. An example of the exported raw data is shown in Fig. 1.

The nominal scan rate is used in eqn. (2) in order to determine the heat of vaporization. In order to test the validity of using the nominal scan rate, we calculated the instantaneous scan rate using the measured temperature and elapsed time. Our analysis showed that the actual scan rate was no more

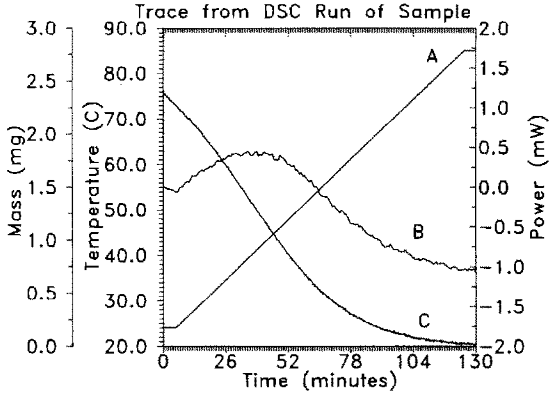

Fig. 1. Sample plot of raw data from a sample run. Curve A, temperature; curve B, power; curve C, mass.

than ±2% from the nominal scan rate. Because the recorded data are averaged over several data points, temporary deviations from the nominal scan rate produced no effect on the final results.

Figure 2 compares the temperature dependence of the actual heat of vaporization with the value determined by the method at a scan rate of 0.5°C min^{-1}. The experimental data in Fig. 2 have been corrected by applying a factor of 1.02, a characteristic peculiar to our calorimeter, and a correction due to scan rate as described below and in Fig. 3.

The temperature dependence of the heat of vaporization of water is found to be a function of scan rate. Figure 3 shows a plot of the heat of vaporization of water measured at 75°C as a function of scan rate. A 2%

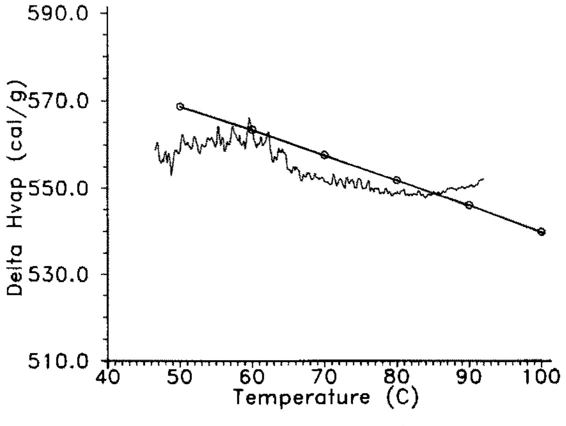

Fig. 2. Plot of the temperature dependence of the heat of vaporization of water. The circles represent the literature values of the heat of vaporization, and the solid, jagged line represents the data measured at a scan rate of 0.5°C min^{-1} corrected for calorimetric and scan rate effects. The line through the circles represents a least-squares fit to the literature values.

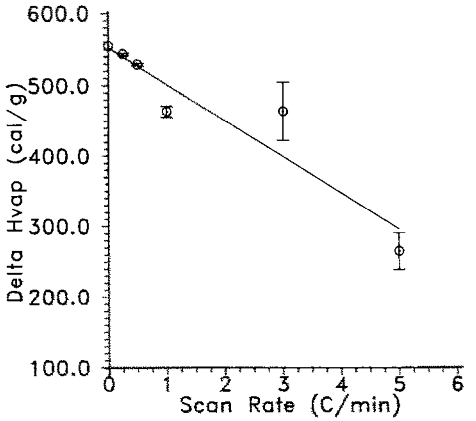

Fig. 3. Plot of the measured heat of vaporization of water versus scan-rate at 75 ° C. The heat of vaporization at 0°C min^{-1} is the literature value of the heat of vaporization of water at this temperature. The line is a least-squares fit to the data at 0.25, 0.5, 1, 3, and 5°C min^{-1}.

power correction has been applied to the data shown in Fig. 2 to account for the systematic calorimetric error discussed above. The value plotted at 0°C min^{-1} scan rate is the literature value of the heat of vaporization determined by other methods. In order to determine the heat of vaporization within a few percent, the calorimeter should be operated at a scan rate which is slow enough to avoid a significant lag between the power and mass measurements which may be due to different response times of the calorimetric and mass signals, as well as to thermal and mass transport effects within the calorimetric zone of the instrument. The line drawn through the data points is a least-squares fit of the measured points. Notice that extrapolation to 0°C min^{-1} yields approximately the literature value of the heat of vaporization. Therefore, if great accuracy in the determination of the enthalpy of vaporization of a liquid is desired, extrapolation to zero scan-rate is indicated. This step ensures that the measured responses reflect "equilibrium".

Figure 4 shows the mass dependence of the measured heat of vaporization of water. The data shown in this plot were all taken at a scan rate of 0.5°C min^{-1} and measured at 65°C. The data here are corrected using an independently determined calorimetric constant. Notice that as the total sample mass decreases, the value of the heat of vaporization approaches the true value. The line shown is the least-squares fit through the data points for sample masses of 14.7 and 45.8 mg.

Analysis of Figs. 3 and 4 suggest that the absolute accuracy of the measurement of the enthalpy of vaporization (desorption) using the method described here can be maximized by using small sample sizes and by extrapolating the data to zero scan-rate. The number and type of measurements completed using the DSC/TGA method described here would depend on the relative accuracy required and the amount of sample available

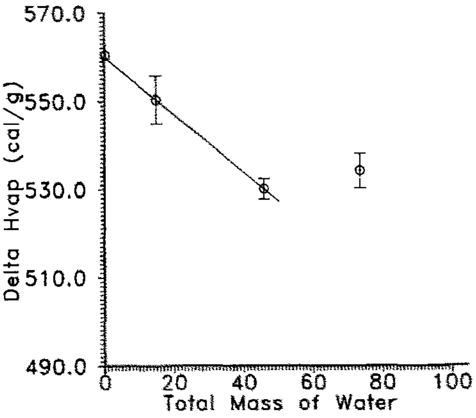

Fig. 4. Plot of the measured heat of vaporization of water versus mass of sample at 65°C. The heat of vaporization at zero mass is the literature value of the heat of vaporization of water at this temperature. The line is a least-squares fit to the data at 14.7 and 45.8 mg.

for analysis. Inaccuracies in the determination of the heat of evaporation presumably arise from transport of molecules outside the calorimetric zone and are related to lags in the calorimeter response.

To illustrate the application of the method, the heat of vaporization of methanol was also determined using the above method. As illustrated in Fig. 5, the agreement between the literature values for the heat of vaporization of methanol and the measured values in this study is excellent. The error bars in the plot are the standard deviation of 10 measurements. This is a further

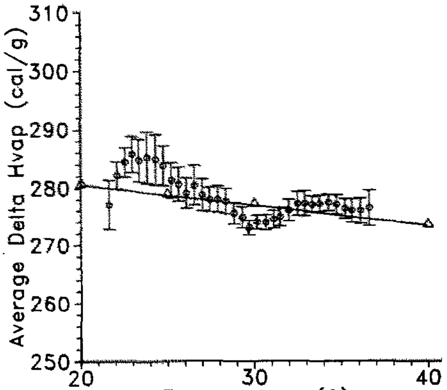

Fig. 5. Plot of the temperature dependence of the heat of vaporization of methanol. The circles represent the measured values of the heat of vaporization at a scan rate of 0.5°C min^{-1}. The error bars are the standard deviation of 10 independent measurements. The triangles represent the literature values for the heat of vaporization of methanol. The line is a least-squares fit to the literature data.

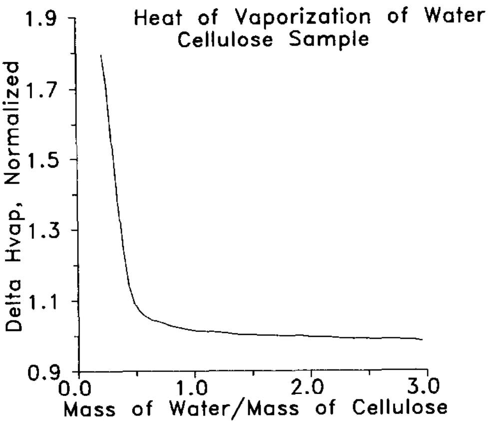

Fig. 6. Plot of the normalized heat of vaporization of water from a cellulose sample as a function of water content. The normalized heat of vaporization is the ratio of the measured heat of vaporization to the heat of vaporization of bulk water.

indication of the utility of this method for determination of the temperature dependence of the heat of vaporization of pure liquids.

The work on the heat of vaporization of pure water was used as a basis to examine the heat of vaporization/desorption of water in porous matrices. What effect, if any, does the surface of the matrix have on the heat of vaporization of water? A number of samples containing approximately 5–15 wt.% cellulose were examined using this method. Figure 6 illustrates the heat of vaporization from one of the cellulose samples as a function of water content. Most of the water had a heat of vaporization equal to that of bulk water as determined earlier in this study. However, approximately 10% of the water had an anomalously large heat of vaporization. The water evaporating with an anomalously high enthalpy of vaporization must reflect water which is either desorbing directly from the surface of the matrix material or which is modified structurally by propinquity to the surface of the material. For a discussion of the properties of interfacial water see ref. 9.

Figure 7 shows the heat of vaporization of water from 242 Å silica pores as a function of water content. The enthalpy of vaporization of water from this sample is similar to the results for the cellulose samples. Because the surface area of this silica sample was known, we were able to calculate the amount of water that would be equivalent to monolayer desorption from the silica surface. Our calculations indicate that between three and five layers of water molecules have an anomalously high heat of vaporization. This supports other work suggesting that propinquity to a surface modifies the structure of water. Logically, the water molecules closest to the surface would be affected the most as indeed is indicated by the data.

Evaporation processes are important to a number of technologies. Therefore, studies of the evaporation of liquids near surfaces are important to

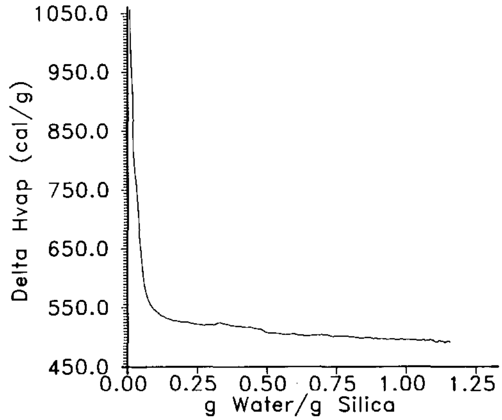

Fig. 7. Plot of the heat of vaporization of water from 242 Å silica pores as a function of water content.

many engineering calculations. Furthermore, the properties of water in confined spaces remains an area of active research interest. Commonly used engineering models do not account for the higher heat of vaporization of water near the surface of the substrate. Higher heats of vaporization may result from direct desorption of water molecules to the surface or from modified interfacial water structure.

CONCLUSION

A method to determine the heat of vaporization (desorption) of liquids using DSC/TGA is discussed. The method appears to be useful in studies of evaporation and desorption of liquids from porous matrices.

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