

A SECOND GENERATION TWIN DOUBLE MICROCALORIMETER

Measurements of sorption isotherms, heats of sorption and sorption kinetics

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Abstract

A calorimetric method for the study of solid-vapor interactions is described. In one calorimetric chamber a vapor evaporates; in a second calorimetric chamber the vapor is absorbed by a sample. The two chambers are connected by a tube and form part of a double twin microcalorimeter. As vapor is sorbed by the sample the vapor pressure in the sorption chamber will increase from a low value to near saturation. The flow rate of the vapor is governed by diffusion through the tube between the vessels. From the thermal power measured in the vaporization calorimeter it is possible to evaluate the sorption isotherm, and using information from both calorimeters the heat of sorption may be calculated as a function of equilibrium vapor pressure. By conducting experiments with different sized samples it is also possible to study the kinetics of the sorption process. The paper describes some recent improvements of the technique and gives examples of its use.

Keywords: enthalpies, heats of sorption, sorption isotherms, microcalorimetry

Introduction

Solid-vapor interactions are of significant importance in many fields of science and technology: sorption of water vapor may initiate biological or nonbiological degradation processes in wood, foodstuffs and pharmaceuticals; solvent vapor sorption may cause a weakening of polymeric materials; drying agents protect products from the air humidity. It is therefore a common practice to study solid-vapor interactions. Usually only the sorbed amount of vapor on a material is measured as a function of the vapor pressure (the sorption isotherm). Studies of heat (enthalpy) of sorption are not as common. Here we present a method that determines these two properties simultaneously.

In the present paper we give a short description of the technique, report on the design of a new sorption vessel, and discuss results of some measurements. The reader is referred to our previous paper [1] for a detailed description of the design of the twin double microcalorimeter.

Method

The central part of the double sorption microcalorimeter is a calorimetric vessel with two chambers connected by a tube. A finely divided dry sample is placed in the sorption chamber and a vapor forming liquid is placed in the vaporization chamber (Fig. 1a). Vapor is allowed to diffuse freely from the liquid to the sample (Fig. 1b). Each chamber is placed in a heat conduction microcalorimeter that measures the thermal powers of the vaporization and sorption processes, respectively (Fig. 1c).

For a measurement a dry sample is placed in the sorption chamber and the vessel is lowered into the calorimeter. After thermal equilibrium has been reached, the measurement starts by the injection of the liquid into the vaporization chamber (Fig. 1a). During a measurement the vapor content of the sample will increase as it absorbs vapor, and the diffusive flow of vapor will decrease as the difference in vapor pressure between the two chambers decrease. From the measurements of the thermal powers in the vaporization and sorption chambers, respectively, it is possible to evaluate both the sorption isotherm of the sample and the enthalpy of sorption as a function of vapor pressure [1].

Compared to the description given in [1], the following changes should be noted:

- The sample is in the top chamber and the liquid in the vaporization chamber.
- A measurement is started by an injection of liquid into the vaporization chamber.
- Only two teflon seals are needed to seal the vessel.

Let us denote the thermal powers of vaporization and sorption P_v and P_s (W), respectively, and the specific heat of vaporization of the liquid $\Delta_v h$ (J g⁻¹). As the rate of sorption is low, the system can at any time be considered to be in a steady-state condition with the rate of vaporization equal to the rate of sorption:

$$F = \frac{P_v}{\Delta_v h} = \frac{P_s}{\Delta_s h} \quad (1)$$

Here, F is the diffusive flow of the vapor (g s⁻¹) and $\Delta_s h$ (J (g vapor)⁻¹) is the specific enthalpy of sorption of the vapor on the sample. Note that P_v , P_s and F are functions of time.

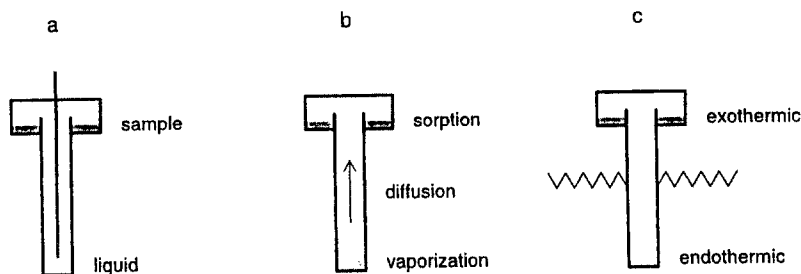


Fig. 1 Schematic descriptions of the principles of the present technique. a) Charging of vessel. b) Diffusion of vapor in the vessel. c) Calorimetric measurements. The two calorimeters should be thermally separated (zig-zag line)

The diffusion is assumed to be governed by Fick's law. With p and p_{sat} (Pa) equal to the vapor pressure at the sample and the saturation vapor pressure (at the liquid surface), respectively, this law may be written:

$$F = -K(p_{\text{sat}} - p) \quad (2)$$

Here, K (g (s Pa)^{-1}) is a constant that relates the vapor pressure difference to the diffusive flow. This vapor dependent constant is evaluated from calibration measurements.

The relative vapor pressure a is taken as a measure of the activity of the vapor:

$$a = \frac{p}{p_{\text{sat}}} \quad (3)$$

The combination of Eqs (1–3) gives

$$a = 1 - \frac{P_v}{K\Delta_v h p_{\text{sat}}} \quad (4)$$

The relative vapor content c of the sample at time t is obtained as an integral of the flow of vapor from the start of the measurement. This may be expressed as:

$$c = \frac{1}{m\Delta_v h_0} \int_0^t P_v dt \quad (5)$$

Here, the relative vapor content is defined as the ratio of the mass of the sorbed vapor m_v (g) and the mass of the dry sample m (g):

$$c = \frac{m_v}{m} \quad (6)$$

The relative vapor content as a function of the relative activity is the sorption isotherm. For sorption of water vapor relative vapor pressure and relative activity are called moisture content and relative humidity, respectively.

Finally the heat of sorption is obtained as:

$$\Delta_s h = \Delta_v h \frac{P_s}{P_v} \quad (7)$$

The absolute thermal powers P_v and P_s decrease continuously during a measurement of a simple sorption isotherm as the vapor content of the sample is being scanned from low to high values. At any time during a measurement values of a , c and $\Delta_s h$ may be evaluated, and thus nearly continuous functions of these properties may be derived.

In the present technique it is assumed that the sorption processes take place at essentially equilibrium conditions. This assumption is justified in most cases as the rate of sorption is low during a measurement, see e.g. the measurements on cotton fibers reported in [1]. Typically a measurement takes 1–3 days.

We believe that the method outlined above, i.e. to calculate sorption isotherms and sorption enthalpies as a function of the vapor state, is new. However, an arrangement with two calorimetric vessels connected by a tube was used by Calvet [2] for the measurement of heats of sorption.

Measurements

We have tested the method with measurements on various solid-vapor systems. Here we present results from three such systems:

Sorption isotherms

Measurements of sorption isotherms is of importance for the characterization of food stuffs, building materials, textiles and other materials whose properties and durability depend on their vapor content. Figure 2 shows the sorption isotherm of water vapor on an acetylated wheat straw pulp. Measurements of sorption isotherms and heats of sorption on pulps before and after various treatments will give information on how the materials have changed by the treatments.

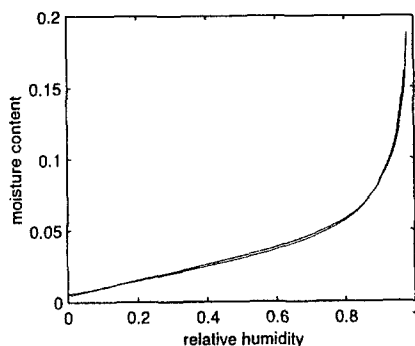


Fig. 2 Results from two measurements of the water vapor sorption isotherm of acetylated wheat straw pulp. The samples have dry masses of 11 and 24 mg, respectively

Critical vapor activity

Critical vapor activity is defined as the lowest relative vapor activity when (usually) unwanted processes start in a material. The concept may be used for different types of processes: sorption, crystallization, mould growth etc. Here we give an example of water vapor sorption on ampicillin sodium salt (ICI Biomedical Inc.), a pharmaceutical compound. Figure 3 shows the sorption isotherm and Fig. 4 shows the heat of sorption. It is clearly seen that the Ampicillin does not absorb any vapor below $a=0.5$. In the range $a=0.5-0.7$, three steps of sorption may be seen that presumably corresponds to three different hydrates with different critical relative humidities. Above this range the ampicillin is dissolved in the water. The heat of sorption peaks seen in Fig. 4 corresponds to the three steps seen in Fig. 3. The present results, which are reproducible, do not agree with previous sorption measure-

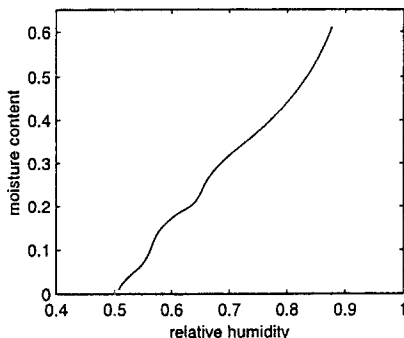


Fig. 3 Result from a measurement of the vapor sorption isotherm of 29 mg of sodium Ampicillin, cf. Fig. 4

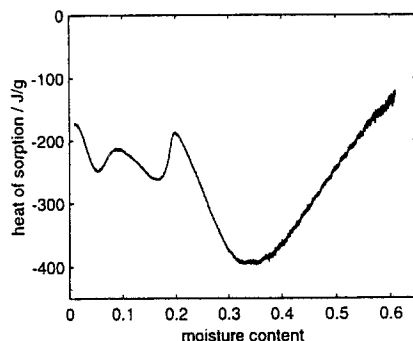


Fig. 4 The measured heats of sorption of water vapor on 29 mg of sodium Ampicillin, cf. Fig. 3. Zero on the y-axis is the enthalpy of liquid water. This should be seen as a qualitative result only, as the accuracy of the heat of sorption measurements are unknown

ments on sodium ampicillin by another calorimetric method [3]. However, it is not known if identical substances were used in these two investigations.

Drying agents

The sorption properties of drying agents are of special importance to characterize. It is of interest to know both their absorption capacity (maximal c , Eq. (6)) and at which activity they absorb a vapor (a , Eq. (3)). Figure 5 shows the thermal powers measured in an experiment when 5 Å molecular sieves (Union Carbide) absorb ethanol vapor. It is seen that P_v is constant for more than 3 h, indicating that during this time the absorption process continues at constant rate. The maximum capacity (c_{\max}) of the molecular sieves may be found as:

$$c_{\max} = \frac{P_v \Delta t}{\Delta_v h m} \quad (8)$$

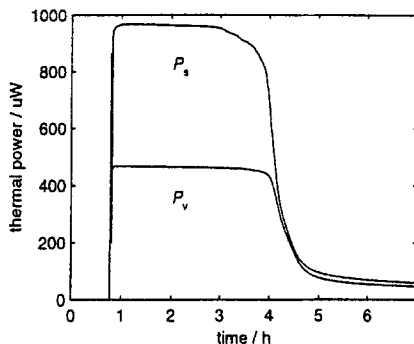


Fig. 5 Absolute values of the thermal powers measured during an experiment with ethanol vapor sorption on 86 mg of a 5 Å molecular sieve. Bottom curve is vaporization and top curve is sorption

Here, Δt is the time period P_v is held constant by the drying agent; $c_{\max}=0.1$ for the present case. With Eq. (7) it is found that the enthalpy of sorption is approximately twice that of the vaporization as P_s is approximately twice that of P_v .

Discussion

The examples given above illustrate some of the uses of the present technique. Some other uses and possible developments are briefly discussed below:

- As seen in Eqs (5) and (6), P_s is not used in the calculation of the sorption isotherm. It is thus possible to use the present vessel in an ordinary microcalorimeter with one measurement site and evaluate sorption isotherms solely from the result of a determination of P_v . However, the vessel must be constructed so that the thermal power of the sorption process in the sorption chamber will not disturb the measurement of P_v .
- By use of an efficient absorbent as the experimental sample, the diffusion coefficient of a vapor may be measured at different temperatures, atmospheric compositions and total pressures. The constant K in Eq. (2) may be expressed as:

$$K = kD_p \quad (9)$$

Here, k (m) is a new constant which does not depend on the vapor used, and D_p (g (s m Pa)^{-1}) is the diffusion coefficient of the vapor in the atmosphere of the vessel. The constant k may be determined from measurements with one vapor and used with Eqs (1–2) and (9) to evaluate D_p from a measurement with another vapor whose p_{sat} and $\Delta_v h$ are known.

- Desorption measurement may be made by charging the vessel with a wet sample in the sorption chamber and a drying agent in the vaporization chamber. As a wet sample contains some free (excess) liquid it will take some time for the diffusion process to remove this until the relative activity of the sample starts to decrease

from $a=1$. There will thus be time for the instrument to equilibrate before the interesting part of the measurement will begin.

- For any material the measurement-time is proportional to the size of the sample. By performing measurements with samples of different sizes or in vessels with different K values (Eq. (2)) it is therefore possible to make observations related to the kinetics of the sorption process. If samples of different size give the same result (sorption isotherm) the sorption is not influenced by the rate of sorption.

Some practical problems with the technique should be pointed out:

- The measurements should be performed with low enough value of dc/dt to allow the system to be at (near) equilibrium conditions. There are three possible reasons why this may not be the case:

1. The sorption is too rapid as the measurement is performed with a sample which is too small in relation to its sorption capacity.

2. The internal diffusion in the samples limit the rate of absorption because the sample is not enough finely divided.

3. The sample has time-dependent ('non-Fickian') sorption properties [4].

- Thermal cross-talk between the units for vaporization and sorption is a problem which has to be eliminated in the design of the double calorimeter or be compensated for. In our instrument about 0.6% of the heat evolved in one of the calorimeters is measured by the other calorimeter.

- Heat of surface adsorption within the calorimetric vessel may give a problem both because it influences P_v and P_s , and because the surface adsorbed vapor will be included in the value evaluated for F . Correction procedures or careful design is needed, otherwise measurements can only be performed on samples with high sorption capacity for which the vessel surface adsorption will be insignificant.

- A correction procedure for the increase of the amount of vapor in the vessel during a measurement has to be used for small samples for which this increase makes a significant contribution to F .

- At the start of a measurement with a dry sample the vapor pressure is zero within the whole vessel. When liquid is injected into the vaporization chamber it will take a few minutes for the vapor pressure gradient to be established. This initial phase of a measurement is reproducible and does not depend on the sample (as long as this is dry). A correction procedure for the build-up of the vapor gradient in the vessel at the start of a measurement should be used.

Conclusions

The present technique to study solid-vapor interactions has been shown to be powerful and versatile. Continued development is in progress at our laboratories.

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