Determining the Heat of Sorption on Organic and Inorganic Powders using DVS

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Dynamic Vapour Sorption (DVS) allows a simple and accurate determination of the heat of sorption for a wide range of solid-vapour systems. This paper describes heat of sorption measurements on an alumina and a crystalline lactose sample using water and 1-butanol.

Introduction

Understanding the interaction between vapours and solid materials is important for a wide range of industries, including pharmaceuticals, foods, flavours, porous materials and catalysts. The heat of sorption for a particular vapour-solid system can yield significant information about the sorption mechanism. This application note describes a simple and accurate method to determine heats of sorption for various vapour-solid systems.

Theory

An adsorption isotherm describes the equilibrium vapour uptake as a function of vapour partial pressure. If isotherms are measured at different temperatures, it is possible to calculate the isoteric heat of sorption, via a Clausius-Clapeyron type equation [1]:

$$\left(\frac{\partial \ln p}{\partial T}\right)_\theta = -\frac{\Delta H_s}{RT^2} \tag{1}$$

where p is the partial pressure, T is temperature, R is the universal gas constant, and ΔH_s is the heat of sorption. ΔH_s values can be obtained if sorption isotherms are measured at different

temperatures and assuming the heat of sorption is exclusively exothermic and independent of temperature. With $d(1/T)/dT=-1/T^2$, equation (1) can be rearranged to:

$$\left(\frac{\partial \ln p}{\partial(1/T)}\right)_\theta = \frac{\Delta H_s}{R} \tag{2}$$

If the partial pressures (p_1 and p_2) at two temperatures (T_1 and T_2) and identical surface coverages are obtained, then the heat of sorption can be calculated directly via:

$$\Delta H_s = -R\frac{\ln\left(p_2/p_1\right)}{1/T_2 - 1/T_1} \tag{3}$$

Equation (3) can be used for any vapour-sorbate system over a wide range of temperatures.

Method

Dynamic Vapour Sorption (DVS) is a well-established method for the determination of vapour sorption isotherms. The DVS instrument used for these studies measures the uptake and loss of vapour gravimetrically using a SMS ultra-balance with a mass resolution of ±0.1 µg. The high mass resolution and excellent baseline stability allow the instrument to measure the

adsorption and desorption of very small amounts of probe molecule. The vapour partial pressure around the sample is controlled by mixing saturated and dry carrier gas streams using electronic mass flow controllers. The temperature is maintained constant ±0.1 °C, by enclosing the entire system in a temperature-controlled incubator.

α-lactose monohydrate was used as a model pharmaceutical excipient for these studies and γ-alumina sample was used as a model inorganic material.

The samples were placed into the DVS instrument where they were initially dried in a 200-sccm stream of dry air (< 0.1% relative humidity). Each sample was then exposed to a certain partial pressure profile. For the alumina experiments the RH was increased in 10% steps up to 90%. This profile was reversed for desorption. For the lactose experiments the RH (or relative concentration in the case of butanol) was increased in 1% steps up to 10% and then in 10% steps up to 90% with a final step of 5% up to 95%. Again, this profile was reversed for desorption. From the equilibrium uptakes at each partial pressure, the sorption isotherms were calculated. Isotherms were collected at two to three temperatures for each vapour-solute system. The isoteric heat of sorption was calculated for a series of coverages using the isotherms collected at two temperatures.

Results

Water sorption isotherms at 25 and 60 °C were collected on an alumina sample (see Figure 1). Above 70% RH the water uptakes are lower at 60 °C, compared to the 25 °C results. The lower surface coverages at 60 °C are expected for a surface adsorption mechanism. Both isotherms show a mixed Type II/III behaviour, indicated by the low initial adsorption and substantial uptake at higher RH.
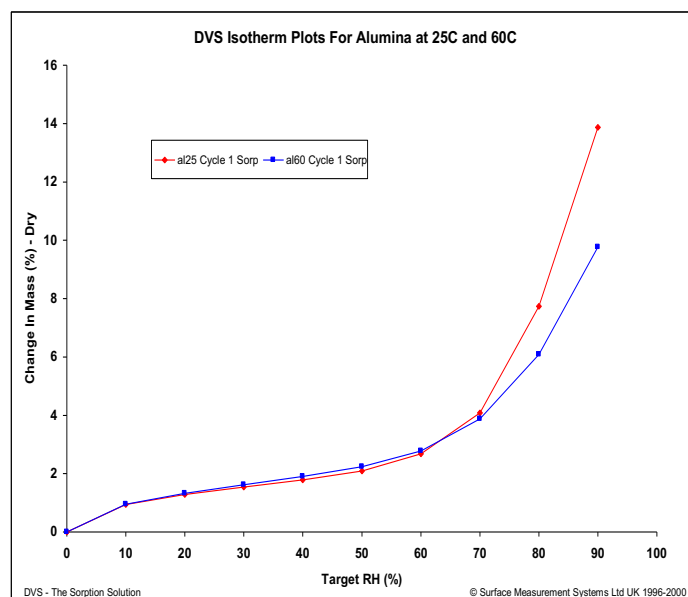

Figure 1. Water sorption isotherms on alumina at 25 °C (red) and 60 °C (blue).

The heat of sorption was calculated at 5 different water surface coverages (see Table 1). As Table 1 indicates, the heat of sorption is fairly similar for all surface coverages considered. Heat of sorption values have not been calculated from low surface coverages since the isotherms are nearly identical at this stage and no accurate calculation would be possible. The heat of vaporisation for water at 25 °C is 43.99 kJ/mol [2]. This agrees favourably with the average heat of sorption, indicating that the water molecules in the vapour phase are interacting mostly with water, not the alumina surface (condensation mechanism). These results agree with the strong Type III contribution of the adsorption isotherm.

Table 1. Water heat of sorption values over a range of surface coverages on alumina from isotherms at 25 and 60 °C

Change in mass (%)	Heat of sorption (kJ/mol)
5.86	-44.7
6.83	-44.8
7.81	-44.8
8.79	-45.0
9.76	-45.3

Water sorption isotherms were collected on crystalline α-lactose monohydrate at 25, 35,

and 45 °C (see Figure 2). All three isotherms show a Type III sorption mechanism, where water forms clusters on the surface rather than a monolayer. Below 80% RH, there is virtually no change in the moisture uptakes at the three temperatures. At high relative humidity values, the lactose is able to sorb more water at lower temperatures, which is typical for surface adsorption.
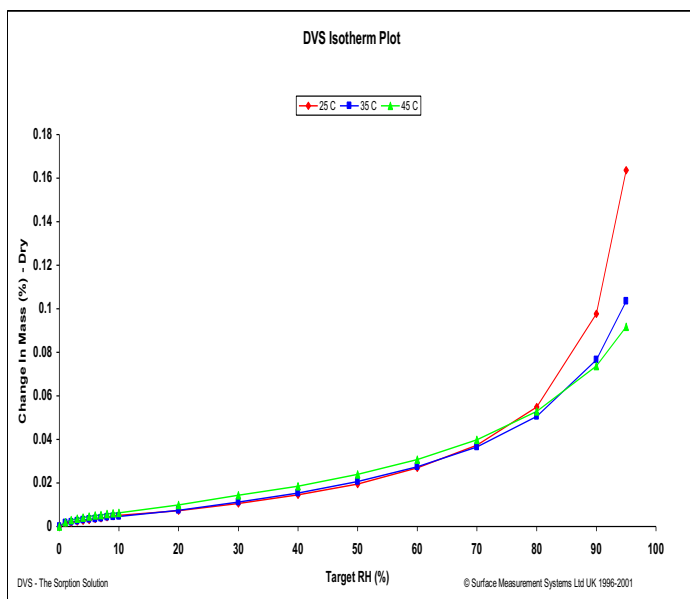

Figure 2. Water sorption isotherms on α-lactose monohydrate at 25 °C (red), 35 °C (blue), and 45 °C (green).

The heat of sorption was calculated at various surface coverages from 25 to 35 °C and 35 to 45 °C (see Table 2). Over the entire coverage range, the heat of sorption values are higher when measured from 25 to 35 °C compared to the values measured from 35 to 45 °C. As in the alumina results, the heat of sorption values agree favourably with the heat of vaporisation of water (43.99 kJ/mol) at higher coverages.

Table 2. Water heat of sorption values over a range of surface coverages on α-lactose monohydrate from isotherms at 25 and 35 °C and isotherms at 35 and 45 °C.

Change in mass (%)	Heat of sorption (kJ/mol) (25 and 35 °C)	Heat of sorption (kJ/mol) (35 and 45 °C)
0.06	-46.1	-43.3
0.07	-47.3	-44.2
0.08	-47.9	-44.5
0.09	-47.4	-45.2

Figure 3 shows n-butanol sorption isotherms on α-lactose monohydrate at 25 (red) and 35 °C (blue). Both isotherms indicate a Type II sorption mechanism, where the vapour forms a monolayer, followed by multilayer sorption. This isotherm shape is in contrast to water on α-lactose monohydrate (see Figure 2), where a Type III isotherm results. The change in isotherm shape shows a clear shift in the sorption mechanism from water to n-butanol. Water is highly polar, so the water-water interactions dominate on α-lactose monohydrate, forming island or clusters at low coverages. n-butanol is significantly less polar, so the interaction with the lactose surface dominates at low coverages, leading to monolayer formation.
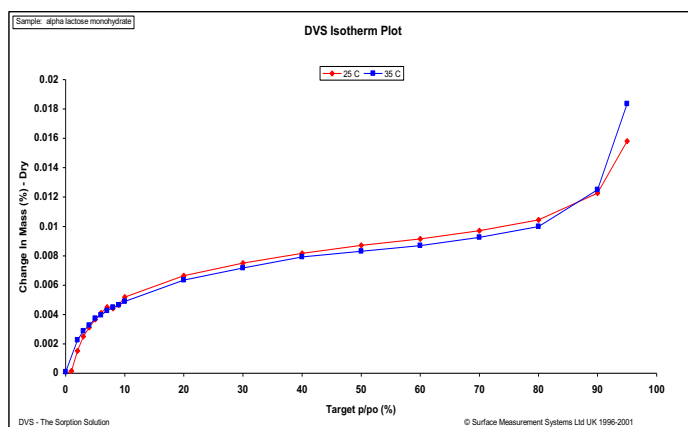

Figure 3. n-butanol sorption isotherms on α-lactose monohydrate at 25 °C (red) and 35 °C (blue).

The heat of sorption results over a range of n-butanol uptakes are displayed in Table 3. The

heat of sorption values decrease with increasing coverage. The heat of vaporisation for n-butanol is 52.35 kJ/mol at 25.0 °C [2]. At low surface coverages, the n-butanol surface interactions dominate, leading to the higher heat of sorption values. At high surface coverages, the butanol-butanol interactions dominate and the heat of sorption values decrease and approaches the heat of vaporisation for n-butanol.

Table 3. n-butanol heat of sorption values over a range of surface coverages on alpha-lactose monohydrate from isotherms at 25 and 35 °C.

Change in mass (%)	Heat of sorption (kJ/mol) (25 and 35 °C)
0.0055	-60.0
0.0073	-58.7
0.0091	-57.7
0.0110	-48.3
0.0128	-46.8

Conclusion

Heat of sorption values were readily measured on organic and inorganic surfaces using water and organic vapours. This technique can be applied to a wide range of vapour-solid systems. The heat of sorption values can give import information on the vapour sorption mechanisms.

Acknowledgement:

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References

[1] Atkins, P.W., Physical Chemistry, 6th Edition. W.H. Freeman and Company: New York (1998).

[2] Lide, D.R., editor, Handbook of Chemistry and Physics, 80th Edition CRC Press: New York (2000).