



Hysteresis Effects in Vapour Sorption

Frank Thielmann, Surface Measurement Systems Ltd.

Hysteresis effects in vapour sorption on solid materials can have different causes. Four different mechanisms responsible for fundamental hysteresis effects are described and discussed in this paper. Although hysteresis can occur as a combination of different causes, misinterpretation occurs quite regularly in literature. For this reason it is important to analyse the hysteresis shape carefully.

Introduction

Sorption isotherms describe the amount of vapour adsorbed or desorbed at different equilibrium concentrations (partial pressures) in the gas phase. Generally one can distinguish between the *adsorption* isotherm (when the partial pressure is increased) and the *desorption* isotherm (when the partial pressure is decreased). In some cases adsorption and desorption isotherm don't coincide. The difference between them is called *hysteresis* or *hysteresis gap*.

There are various causes for hysteresis effects and those most relevant to vapour sorption will be explained in this paper by means of four typical examples.

Method

Example I: Capillary Condensation in Mesoporous Alumina

Isotherms can be divided into six different types based on the BDDT classification [1]. They are shown in Figure 1. A general discussion on isotherm types and adsorption mechanisms can be found in [9].

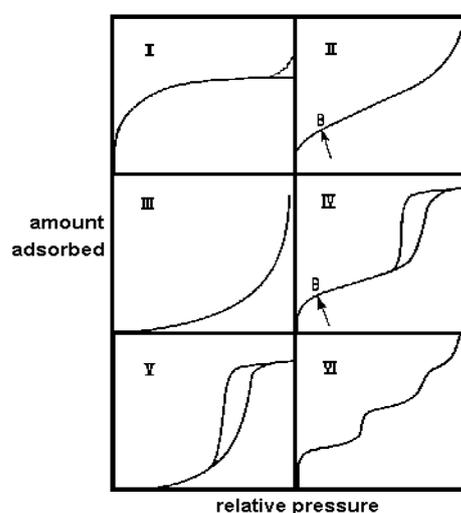


Figure 1. Isotherm types according to the BDDT classification.

Types IV and V show a characteristic hysteresis loop. The starting point of the hysteresis is typically just above the monolayer range (> 0.3 p/p₀) and the hysteresis disappears at very high partial pressures close to saturation. This kind of behaviour is associated with capillary condensation taking place in the mesopores structure [2]. According to the IUPAC classification [3] mesopores have a pore diameter between 2 and 50 nm. There are various explanations discussed in literature [4] why



adsorption and desorption out of mesopores occur at a different partial pressure (which is the reason for the hysteresis). However, it is important to notice that this is an equilibrium phenomenon.

Attempts have been made to correlate the shape of the hysteresis with the geometry of the pore structure and hysteresis loops have been classified in type A, B and E by de Boer [5]. This was later replaced by the H classification [4].

An example for a mesopores hysteresis is shown in Figure 2. The isotherm shape is type IV which is common for a non-polar vapour such as octane adsorbing on a rather polar surface.

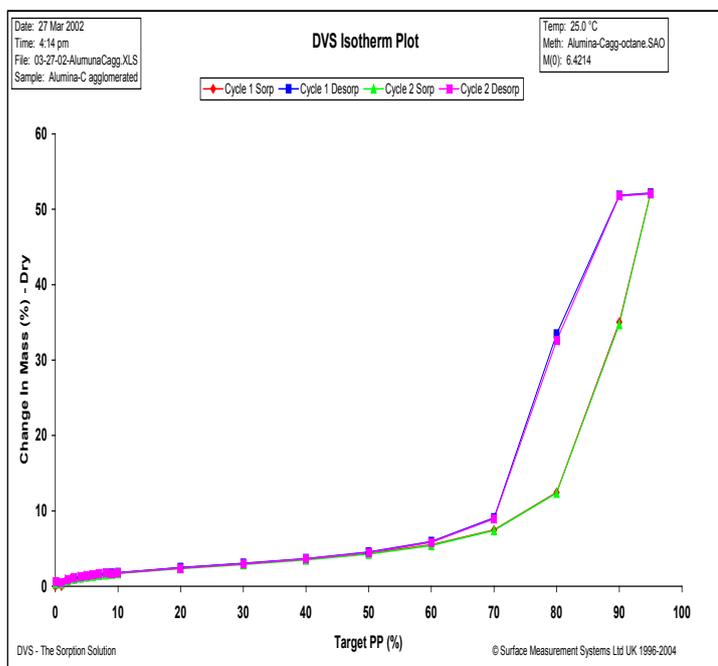


Figure 2. Adsorption- and desorption isotherms of octane on mesoporous alumina (first cycle in red and blue, second cycle in green and pink).

The alumina sample was produced by agglomeration of flame-hydrolysed γ -alumina (Alumina C, Degussa). Alumina C consists out of sub-micron particles and is non-porous. Due to the agglomeration in water and subsequent drying aggregation occurs and the mesoporosity is most likely due to the void spaces between adhering primary (nano-) particles. This agrees well with the observed H3 type hysteresis. The latter is typical for aggregates [4].

Example II: Hydration of Nedocromil Sodium

Hydrates and solvates show a very characteristic hysteresis gap which sometimes even resembles mesopores hysteresis, however, for entirely different reasons. Figure 3 shows the water sorption isotherm of nedocromil sodium (monohydrate). It can exist as a stoichiometric mono- and trihydrate as well as a heptahemihydrate

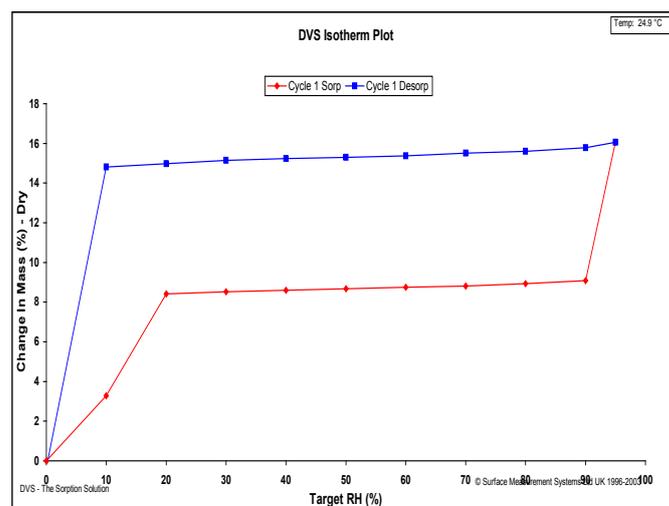


Figure 3. Water adsorption (red) and desorption (blue) isotherms on nedocromil sodium at 25 °C.

After initial drying (not shown) the sample exists as monohydrate. At 20% RH the sample exists as a trihydrate and converts at 90% to the higher hydrate. During desorption this species remains stable through the 10% RH step and returns straight to the monohydrate when the partial pressure is reduced to 0% RH [6].

The hysteresis is due to the fact the stoichiometric hydrate remains nearly unchanged (extremely small adsorption or desorption of water) until the transformation point (phase change) is reached. Although the cause of hydrate/solvate hysteresis is different this is again an equilibrium effect.

Example III: Bulk Absorption in Starch

An entirely different kind of hysteresis is observed when water sorption isotherms of organic, non-rigid solids are considered. A good example are water sorption isotherms on starch. The adsorption and desorption is shown in Figure 4.

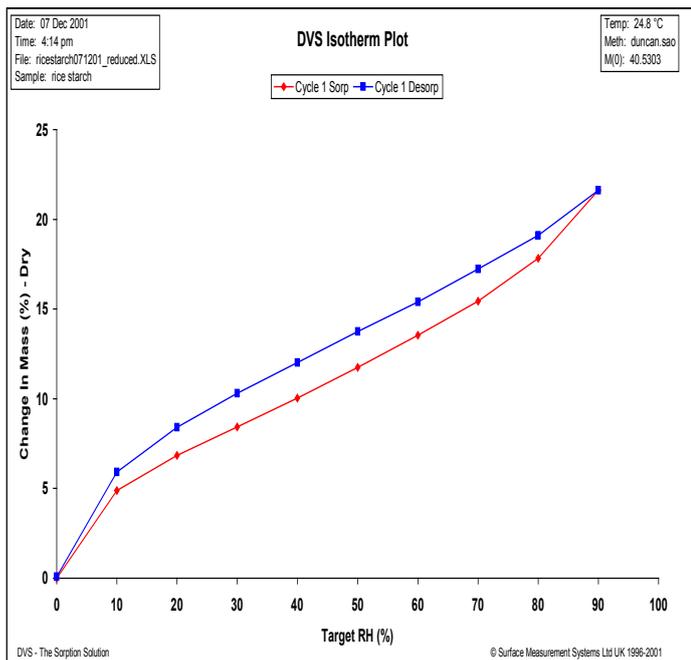


Figure 4. Water adsorption (red) and desorption (blue) isotherms on rice starch at 25 °C.

This is a typical hysteresis shape for many pharmaceutical and food materials. An obvious characteristic is that the gap remains over the entire partial pressure range. This is very different from a mesoporous system as described in example I where the hysteresis loop opens/closes in the monolayer range. For these kinds of materials capillary condensation might occur but is hardly ever the only reason for hysteresis (if at all). Classical mesoporosity predominately exists in rigid materials which is not the case here.

The observed hysteresis in starch is also different from simple hydrate/solvate formation as described for example II. Unlike in a hydrate, water uptake occurs continuously here. However, this does not exclude the possibility of hydration *in combination* with other effects.

Organic, partially amorphous polymers are structurally rather complex. For this reason an interpretation of hysteresis effects is not straight forward. Apart from the previously discussed effects there can be other causes for hysteresis. (Partially) amorphous materials tend to exhibit a considerable bulk *absorption* of water. However, this is a slow, diffusion controlled process and therefore non-equilibrium regime. This can be proved by the fact that the uptake is often

directly proportional to the temperature while equilibrium surface adsorption decreases with temperature [7]. In some cases bulk absorption is accompanied by swelling effects.

There are models in the literature trying to take some of these different influences into account. The most well-known approach for modelling hysteresis is that of Young and Nelson [8]. This theory divides moisture sorption in three basic mechanisms: surface adsorption, multilayer adsorption (or any kind of condensation effect in general) and bulk absorption. It provides equations to fit these contributions separately. Figure 5 shows the results for starch. The data have been analysed using the SMS Isotherm Analysis Suite v1.1

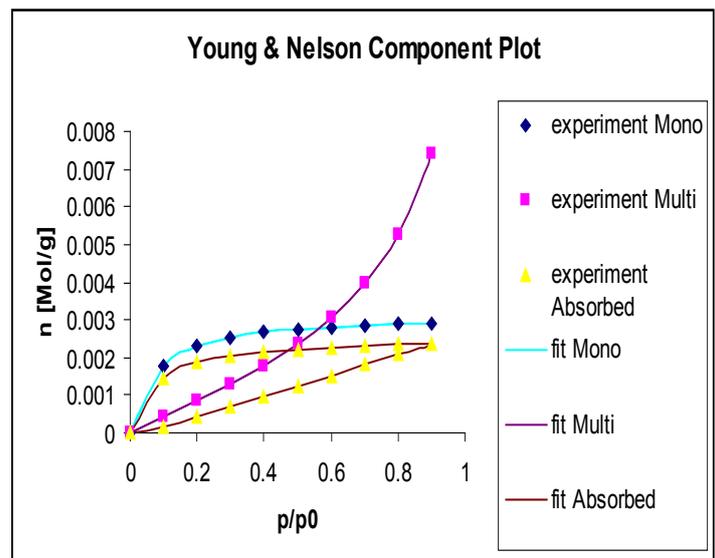


Figure 5. Young & Nelson fits for the different contributions to water sorption on rice starch: monolayer formation (blue), condensation (pink) and bulk absorption (yellow). The resulting total adsorption constants yielded the following: $A=0.0029$ Mol/g, $B=0.0026$ Mol/g and $E=0.072$.

Example IV: Irreversible Adsorption of Water on a Drug Compound

Water (and other polar solvents) can sometimes induce morphology changes (glass transition, recrystallisation etc.) in organic materials. This could result in an open hysteresis. An example of a proprietary drug salt form is shown in Figure 6. Morphology changes during the adsorption stage mean that the material from which the desorption occurs is different to the starting material where adsorption took place.

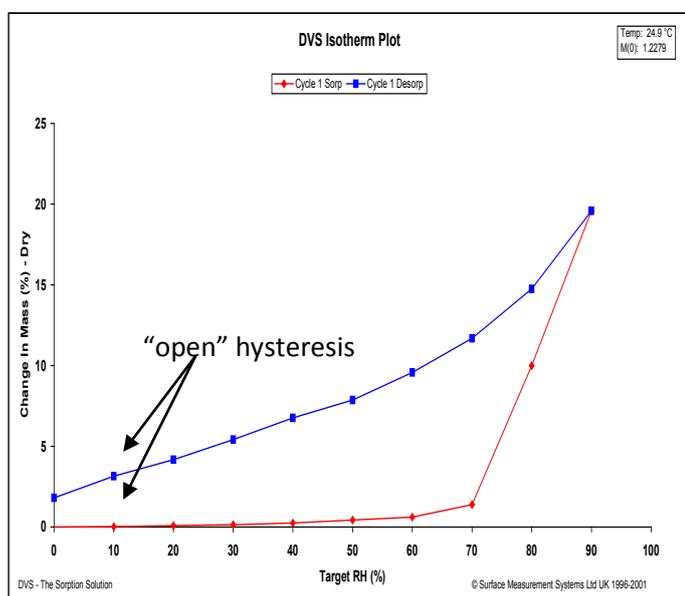


Figure 6. Water adsorption (red) and desorption (blue) isotherms on a drug salt form at 25 °C.

Another cause for open hysteresis is chemisorption of the probe molecule on the surface. This can be either a kinetic effect (sometimes called “reversible” chemisorption) or an irreversible adsorption. An example for the latter would be an amine vapour adsorbing on a catalyst surface. A good example for “reversible” chemisorption is a microporous system

(with pores smaller than 2 nm). Due to its enhanced adsorption potential desorption from micropores is very slow and often not completed on the time scale of a standard experiment. For this reason an open hysteresis loop is observed although the process is fundamentally fully reversible [2].

Conclusion

Hysteresis of sorption isotherms can have various causes. Some of the fundamental mechanisms include capillary condensation, hydrate formation, bulk sorption, morphology changes and chemisorption. In some cases combination of these effects can occur.

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Head Office:
Surface Measurement Systems, Ltd
5 Wharfside, Rosemont Road
London HA0 4PE, UK
Tel: +44 (0)20 8795 9400
Fax: +44 (0)20 8795 9401
Email: science@surfacemeasurementsystems.com

United States Office:
Surface Measurement Systems, Ltd, NA
2125 28th Street SW, Suite I
Allentown PA, 18103, USA
Tel: +1 610 798 8299
Fax: +1 610 798 0334