



Vapor Sorption Characterization of Hydrates

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INTRODUCTION

Materials can interact with water vapor (humidity) in several different ways, including surface adsorption (where typically smaller amounts of water are loosely held on the surface), chemisorption, bulk absorption into the internal structure, and chemical reaction. Hydrates are formed when water is incorporated into the lattice structure of solids. Hydrates generally are stoichiometric (i.e., the amount of water adsorbed corresponds to a specific number of moles of water). Because many hydrates are only stable under specific temperature and humidity conditions, the formation of hydrates or the dehydration of hydrated materials must be evaluated under a variety of conditions.

EXPERIMENTAL

Vapor sorption (VS) of hydrates is accomplished by stepping the humidity up and down over a broad range (0-90 %RH) multiple times. This process allows the presence of multiple hydrated forms, the reversibility of hydration-dehydration, as well as humidity-induced amorphous to crystalline structural changes to be identified.

RESULTS AND DISCUSSION

Nedocromil sodium is known to exist in mono-, tri-, and heptahemi-hydrate forms. The starting material for the VS results shown in Figure 1 is the monohydrate. As the humidity is increased to 20 %RH, the dried material gains 8 %. No further weight gains occur as humidity is increased until the humidity exceeds 90 %RH, when a second weight change occurs. If the humidity is then decreased, no change occurs until exposure below 10 %RH returns the material to its original state. Using the equation: Hydrate Stoichiometry (number of waters of hydration) = $[(\% \text{ Weight Change} \times \text{Molecular Weight of the Material}) / (100 \% \times \text{Molecular Weight of Water})]$, the two weight changes correlate well with those expected for conversion to the trihydrate at 20 %RH, conversion of the trihydrate to the heptahemi-hydrate above 90 %RH, and then conversion directly back to the monohydrate below 10 %RH. The conversion between the three hydrates is reversible and is repeatable on subsequent humidity cycles.

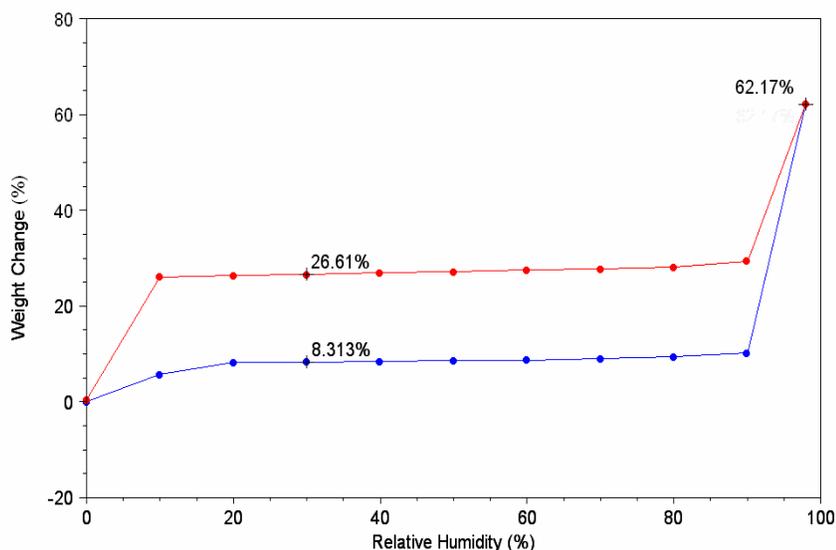


Figure 1. Reversible Conversion Between Hydrates

Figure 2 and 3 illustrate a material (diphenylhydantoin), where previous “humidity history” affects the VS adsorption/desorption profile obtained. In both VS experiments, the material is stepped from 10 %RH to 90 %RH and then back down to a low humidity before again raising the humidity to 90 %RH. In the first experiment, however, the lowest humidity used is 5 %RH, while in the second experiment it is 0 %RH. Initial exposure to 90 %RH results in a weight gain consistent with formation of a tetrahydrate (4 waters of hydration). Decreasing the humidity to 20 %RH converts the tetrahydrate to the monohydrate. The monohydrate is stable down to 5 %RH. However, if the humidity is lowered to 0 %RH, the anhydrous form is obtained. Figure 2 shows that the monohydrate once formed is stable up to about 40 %RH. Moreover, Figure 3 shows that this material has three different forms (anhydrous, monohydrate, tetrahydrate), which are stable (once formed by previous “humidity history”) in the 20-40 % humidity range.

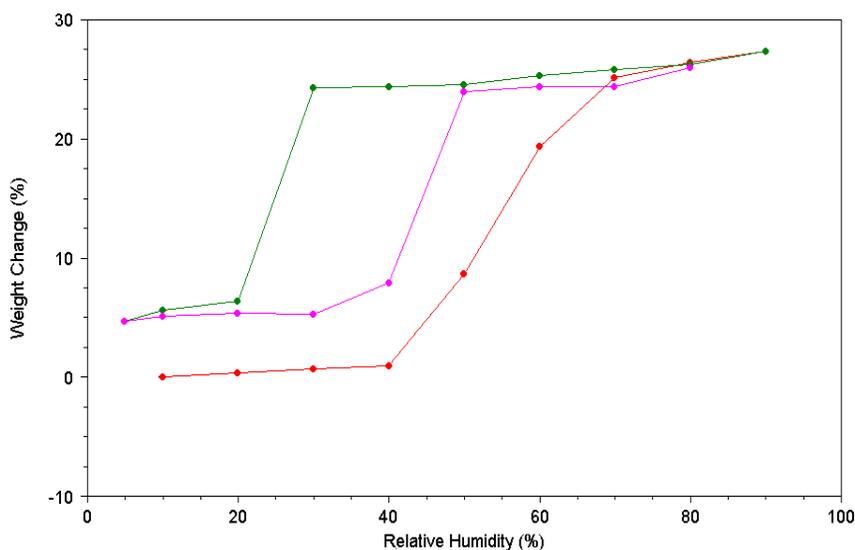


Figure 2. Diphenylhydantoin Exposure to 0 %RH

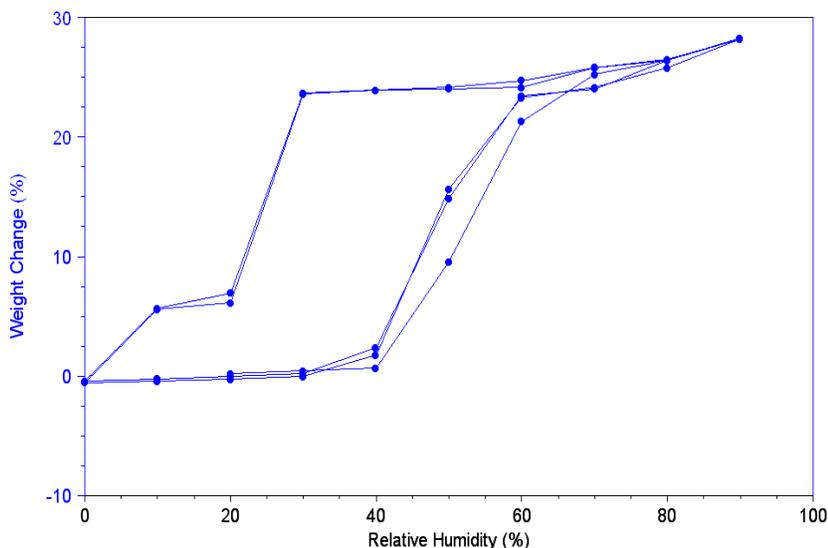


Figure 3. Diphenylhydantoin Exposed to 0 %RH

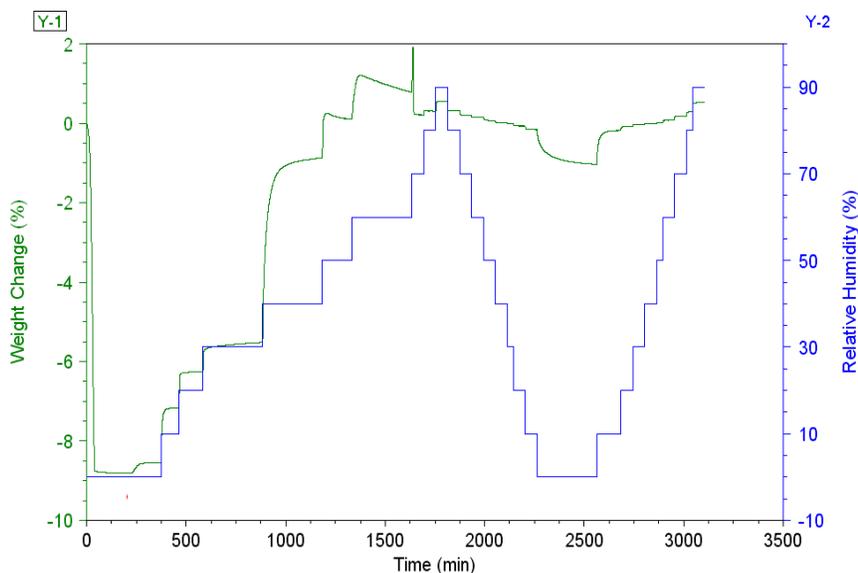


Figure 4. Naloxone Hydrochloride VS Experimental Profile

Figures 4 and 5 are the raw VS experimental profile and derived sorption profile for naloxone hydrochloride. On initial drying at 0 %RH and 60 °C, the material loses about 9 % of its original weight. This total weight loss indicates that the initial material is a dihydrate. In subsequent humidity exposure at 25 °C, normal stepped weight gains are observed as the humidity is increased from 10-50 %RH. The total weight gained over that humidity range corresponds to the 9 % lost during initial drying. At 60 %RH (and even more dramatically at 70 %RH), the material initially gains weight, but with time most of that weight gain decays away. That type of behavior is typical of a water-induced recrystallization where water acts as a plasticizer lowering the glass transition of an

amorphous material until it corresponds with the temperature of the experiment and spontaneous rearrangement (recrystallization) occurs to the material's more stable form. At 70 %RH and above, the weight change is minimal as would be expected for a crystalline material. Weight changes with subsequent decreasing humidity and on the second increasing humidity profile remain small indicating that the crystalline structure once formed is stable at 25 °C even at 0 %RH. The sorption plot (Figure 5) shows this behavior more clearly. These VS results suggest that the material initially is a crystalline dihydrate. On exposure to more "strenuous" drying conditions (0 %RH and 60 °C), the waters of hydration are lost, and the material becomes amorphous. On subsequent exposure to humidity the material rehydrates and forms its more stable crystalline form. The crystalline dihydrate remains stable at 25 °C regardless of humidity conditions.

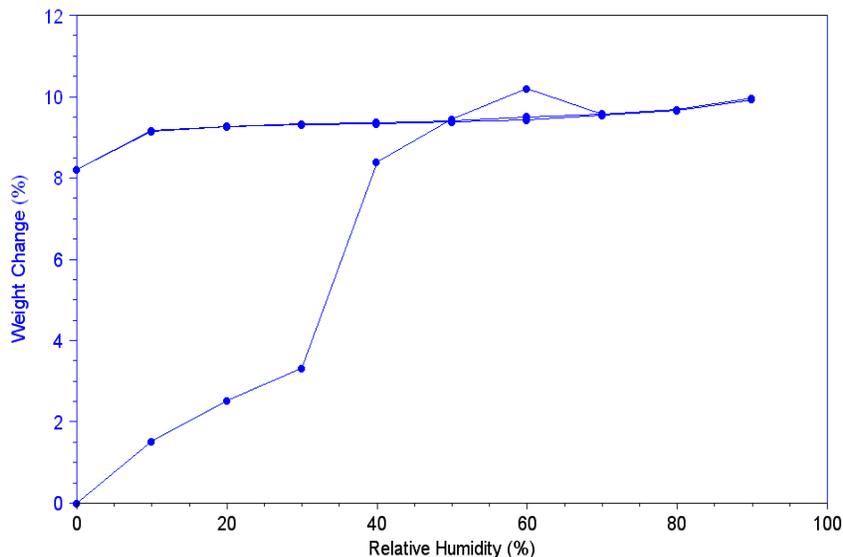


Figure 5. Naloxone Hydrochloride VS Sorption Profile

SUMMARY

Vapor sorption provides a convenient method for determining the presence of hydration/dehydration in solids. The adsorption/desorption profiles obtained are considerably different than those obtained for other water-induced phenomena, and hence can be readily identified.

KEY WORDS

Vapor Sorption, VS, Hydrates

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