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Interaction of water vapor and compressible sugar

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Summary

The interaction of water vapor with Compressible Sugar NF (DiPac) has been characterized by studying the adsorption and desorption behavior of the solid, preconditioned by drying at 70°C in a vacuum oven. An unusual stepwise adsorption isotherm and extensive isothermal desorption hysteresis were evident for this material at 25°C. The temperature dependence of the adsorption process was used as the basis for a complete thermodynamic analysis: partial molal free energies, enthalpies and entropies of adsorption were calculated. Exothermic maxima in the isosteric heats of adsorption profile indicated discrete stages of surface hydration, thereby accounting for the stepwise nature of the isotherm. Strong interaction of water in the initial stages of adsorption, reflected by primary and secondary exothermic maxima of −74.0 kJ and −27.5 kJ per mole of water, suggested that this water was not released during isothermal desorption, thereby accounting for the hysteresis.

Introduction

The quantity and state of moisture present in a tableting excipient can profoundly influence the processing characteristics of a powder blend of which it is a component as well as the properties of the final dosage form itself. This is particularly important for a direct compression excipient because it generally represents most of the powder present in a formulation, and because it has been chosen to provide specific attributes such as flowability and compressibility, which may be moisture sensitive.

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Since there is usually no explicit drying step involved in the manufacture of tablets by direct compression, the quantity and state of moisture in the powder blend depend upon the sorption characteristics of the powders and their history of exposure to conditions of varying humidity and temperature. It is important to note that each material as received may contain moisture at a level significantly below or above the equilibrium moisture content, so both the kinetics and thermodynamics of sorption are important considerations.

The objective of this study is to characterize the interaction of water vapor and a particular direct compression excipient to provide the basis for subsequent investigation of the role of sorbed moisture in the processing of that excipient. Compressible Sugar NF was chosen as the excipient because it was suspected that the moisture content of this material was critical to its compressibility (Sheth et al., 1980).

Materials and Methods

Pretreatment of solid

Compressible Sugar NF (DiPac, Amstar) was used without further chemical purification. Two different methods were employed to remove moisture from 200–300 g samples of the powder distributed to a bed height of approximately 0.5 cm.

Method A — a conventional tray dryer (Colton Model 1018-E, Arthur Colton) maintained at 70 ± 0.5°C for 24 h.

Method B — a vacuum oven (Model 5831, National Appliance) maintained for 1 week at 70 ± 0.1°C without interruption.

In the latter, the Vacuum pump (Dist-O-Pump, Welsh Scientific) was operated continuously and a relatively constant pressure of 400 μm Hg, as determined by a McLeod gauge (Model A-185, Research and Development Glass Products), was achieved after 6 h.

In both cases the warm solid was placed in a desiccator containing P_2O_5 (ACS grade, Fisher Scientific) and allowed to cool to room temperature prior to use.

Water vapor sorption studies

Water vapor sorption was performed using 150 mm polypropylene desiccators (Nalgene Desiccator, Nalge), each containing 100 ml of a sulfuric acid solution, as controlled relative humidity (RH) chambers. Relative humidites varying from 9–72%, were established based upon concentrative relations at 25°C (Stokes and Robinson, 1949) and 20°C (Weast, 1978). The actual concentration of sulfuric acid for each humidistat solution was determined by titration with standardized sodium hydroxide solution on the final day of the study, i.e. after adsorption or desorption. Reagent grade concentrated H_2SO_4 (J.T. Baker Chemicals) and distilled water were used in the preparation of all humidity controlling solutions.

Appropriately conditioned samples of compressible sugar with an initial weight in the range of 2–4 g were distributed in 35 × 10 mm polystyrene petri dishes (Falcon 3001, Div. of Becton, Dickinson). Three dishes were placed in each relative humidity chamber and all chambers were placed in a controlled-temperature cabinet (Model 815 Low Temperature Incubator, Precision Scientific) where they were maintained at the desired temperature ±0.1°C for 14 days. The gain or loss of water was determined gravimetrically and all weighings were performed on an analytical balance whose sensitivity was 10^{-4} g (Mettler Instrument Corporation).

Adsorption studies were performed using material preconditioned by Method A or B. Desorption studies were performed using pretreated material (Method B) that had been subsequently exposed to 70% RH for 14 days. The actual initial moisture content of the powder in each study was determined by loss on drying (LOD) of a representative 2–4 g sample dried in the vacuum oven for 48 h at 70°C.

Results and Discussion

A procedure for obtaining dry powder without perturbing the structure of the solid, and an accurate method of initial moisture content determination, are the fundamental requirements of any water vapor sorption study. Preliminary studies with compressible sugar indicated that vacuum drying at elevated temperature was necessary to prepare essentially dry powder; yet excessive exposure to conditions of high temperature and low pressure produced an obvious physical change in the powder as evidenced by a yellow discoloration. Presented in Fig. 1 are results obtained by pretreating different amounts of solid in the vacuum oven at 70°C for various uninterrupted periods of drying. It should be noted that an attempt to dry a single sample to constant weight by periodically pressurizing the chamber, allowing the sample to cool to room temperature. and weighing it led to an erroneously low LOD. Apparently an equilibrium state was reached where each subsequent drying period was spent removing moisture that had been adsorbed from the atmosphere during the weighing operation. Also, a sample of the material dried for 10 days under the described conditions showed a slightly greater LOD, but this duration of drying produced the visible yellow discoloration mentioned earlier.

As a result of this study, a one-week time period was selected for bulk pretreatment (Method B), although it was recognized that this procedure would not produce absolutely dry solid. To compensate for this fact, the moisture content of the bulk pretreated material was determined at the start of each study by placing an aliquot

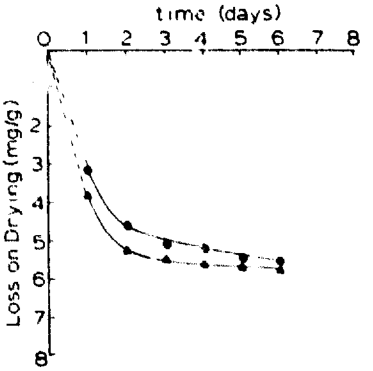

Fig. 1. Loss of drying of compressible sugar in a vacuum oven at 70°C. Key: ▲, 5 g sample; ●, 20 g sample. Time is in days of uninterrupted drying.

in the vacuum oven for an additional two days of drying. Since this moisture content reflects the state of the material at the beginning of the study, it is referred to as the 'initial moisture content', and it is represented as an ordinate intercept on subsequent plots. Pretreatment of bulk sample by Method A was used only for comparative purposes.

Adsorption results

The results of a long-term adsorption study using compressible sugar are presented in Fig. 2. Each line in this figure traces the average increase in weight of 3 samples stored in a controlled humidity chamber at 25°C. Generally, the variability between replicates was small; vertical bars representing ±1 standard deviation are included where this interval exceeds the size of the symbol. Two important features of the water-compressible sugar interaction are evident from this crude kinetic analysis.

(1) At all relative humidities, it appears that most of the water is adsorbed during an initial period of less than 14 days. Even the solid exposed to 66% RH adsorbed 95% of its final moisture level within the first 7 days. This region appears to involve the high energy interaction sites in the surface which were exposed by the stress of pretreatment.

(2) True equilibrium was not achieved at any relative humidity, even after 123 days of exposure. A nearly equivalent 'steady-state' of moisture gain was evident for all samples at all humidities.

The term steady-state is used here in reference to that region of each kinetic profile in Fig. 2 which is characterized by a constant rate of moisture gain. This

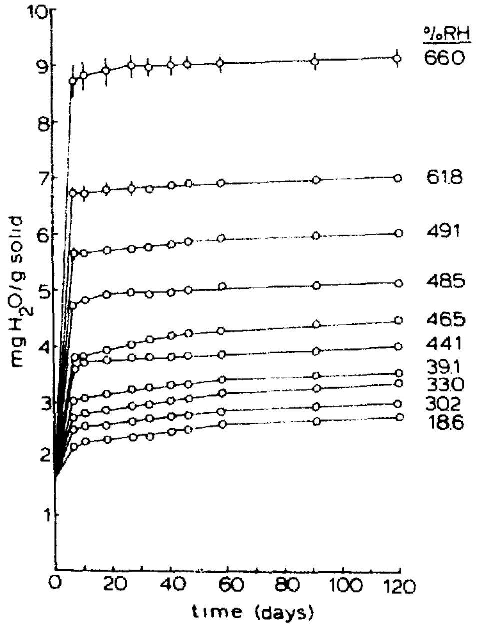

Fig. 2. Adsorption of water vapor by compressible sugar at various relative humidities (% RH) at 25°C after pretreatment by Method B. (Vertical bars represent ± standard deviation.)

region owes its existence to the fact that compressible sugar is a soluble material and that water is capable of diffusing into the solid. Compressible sugar can certainly not be considered an inert adsorbent for water; it appears that moisture sorption at each humidity would continue until a one-phase solid solution of water in sucrose existed.

An important implication of this observation is that it is not possible to perform an equilibrium sorption study in a reasonable length of time. However, it is also true that one will seldom be dealing with compressible sugar in its true equilibrium state. The compromise position taken in this analysis was to focus on the large magnitude effects of varying humidity, exemplified by the initial period of adsorption in Fig. 2.

Fig. 3 shows the effect of duration of exposure on the development of the adsorption isotherm. These isotherms were constructed from the data presented in Fig. 2 at 11 days and 123 days. Although there is an absolute difference of approximately 0.5 mg H_2O/g solid between these curves, the difference is constant across the entire relative humidity range and the unusual features of the isotherm are clearly defined in both cases. Consequently, a convenient 14-day exposure period was used in all subsequent work.

Presented in Fig. 4 are adsorption isotherms for compressible sugar pretreated using Methods A and B. These data clearly demonstrate the impact of rigorous sample pretreatment. Method A only removes the physically adsorbed moisture from the surface of compressible sugar particles and the surface obtained from this moderate pretreatment is energetically homogeneous. The resultant adsorption data appears to correspond to a classical type II isotherm (Brunauer, 1942). The results in Fig. 4 show that the method of pretreatment not only influences total water content,

Fig. 3.

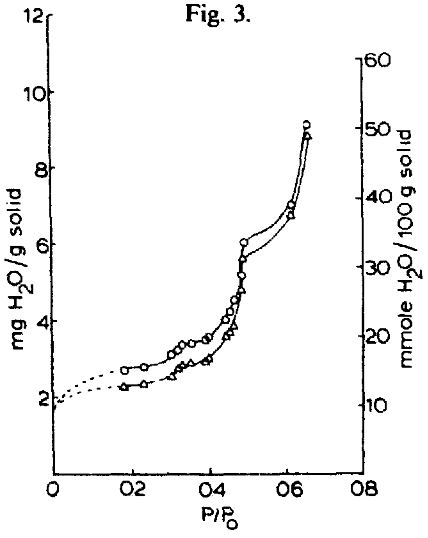

Fig. 4.

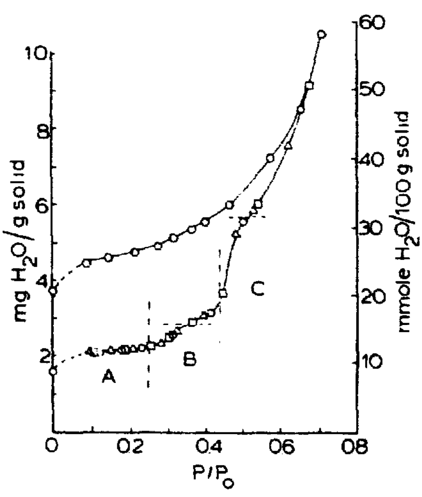

Fig. 3. Effect of time of exposure on the water vapor adsorption isotherm of compressible sugar at 25°C after pretreatment by Method B. Key: △, 11-day exposure period; ○, 123-day exposure period.

Fig. 4. Effect of pretreatment method on the 14-day water vapor adsorption isotherm of compressible sugar at 25°C. Key: ○, pretreatment Method : △, □, ○, represent the results of independent studies conducted using pretreatment Method B. Vertical lines divide the isotherm into 3 regions: A, B and C. Horizontal lines identify moisture contents which correspond to adsorbate condensations.

but it also affects the shape of the isotherm. As a consequence of vigorous drying, a stepwise isotherm results and the dehydration process exposes an energetically heterogeneous surface. The reproducibility of the experimental method is demonstrated by the inclusion of results from 3 independent studies.

There are several reasons why an energetically heterogeneous surface is consistent with the structure of compressible sugar. This direct compression excipient consists of particles which are aggregates of sucrose crystals. The surface region of these crystals includes some non-crystalline non-sucrose substances which are quite hygroscopic when dry (Tippens et al., 1965). Even if the small crystals were perfect, they would present different crystallographic faces which possess different adsorption energies (Brunauer, 1942; Adamson, 1976). Grinding of the aggregates in the last stages of processing also contributes to the heterogeneity. Fracture undoubtedly exposes a new surface which may be characterized by ridges, asperities, and other structural aberrations. On the other hand, particle–particle attrition may actually smooth out irregularities producing a portion of interface which is amorphous. Finally, some intra-aggregate spaces may provide regions for condensation at higher relative humidities. For surfaces which are in close proximity, the effect of capillarity would be profound given the adsorbent's capacity for hydrogen bonding.

An interpretation of the complex adsorption behavior in Fig. 4 is facilitated by separating the isotherm into 3 distinct regions. Region A is the result of adsorption of water vapor on specific high energy sites on the dehydrated surface. An increase in relative vapor pressure of the adsorptive (water) progressively fills the sites until they are exhausted. A capacity-limited process such as this could be explained by the Langmuir equation (Langmuir, 1918):

$$\frac{n}{n_m} = \frac{(aP/P_0)}{(1 + aP/P_0)} \tag{1}$$

where n is the amount adsorbed at relative vapor pressure P/P_0, n_m is the monolayer capacity and a is a constant (temperature dependent). This functional relationship was tested by using the low relative pressure data from the adsorption isotherm in Fig. 4, and the result is presented in Fig. 5. The good linearity up to $P/P_0 = 0.25$ (25% RH) supports the fact that the adsorbed water molecules are localized in specific sites. It also supports the contention that these are high energy sites because they appear to be saturated before further adsorption takes place. Above a relative vapor pressure of 0.25 Langmuir's theory fails.

Region B can be thought of as adsorption taking place on a new surface where specific high energy interaction sites have been saturated. In the early stages of region B, it is likely that adsorbed water molecules start to form clusters around the higher energy sites of the hydrated surface. As relative humidity increases, the clusters grow and a lateral adsorbate condensation eventually occurs. Completion of this layer on the hydrated surface appears at about a relative vapor pressure of 0.33, which corresponds to a moisture content of approximately 2.8 mg of H_2O/g solid. At this point, no attempt will be made to explain the character of this layer, except to note that it is not the type of condensed monolayer with two-dimensional

Fig. 5.

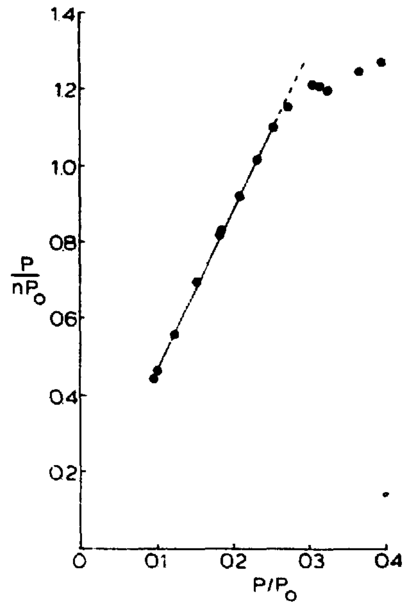

Fig. 6.

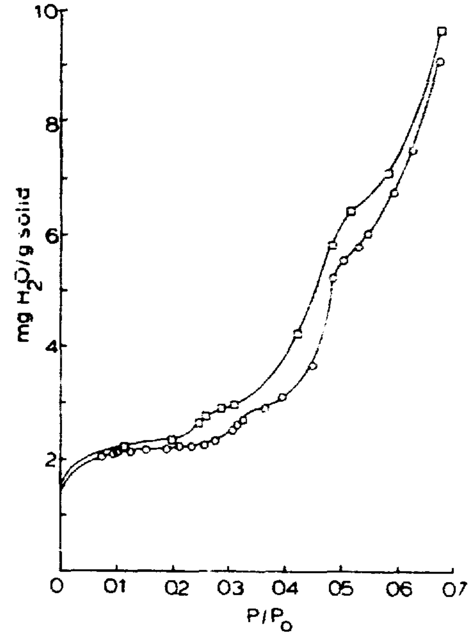

Fig. 5. Langmuir plot of the 14-day water vapor adsorption of compressible sugar at 25°C after pretreatment by Method B. (Solid line represents the results of a linear regression analysis of the data $P/P_0 < 0.25$).

Fig. 6. Effect of temperature on the 14-day water vapor adsorption isotherm for compressible sugar at 19.8°C (□) and 25.0°C (○) after pretreatment by Method B.

mobility associated with the inert surface. This region is followed by a steep rise in vapor uptake characteristic of multimolecular adsorption.

Region C in this unusual adsorption isotherm once again shows a condensation, this time at a moisture content of 5.4 mg H_2O/g solid, approximately twice that associated with the first condensation. The evidence does not support the concept of capillary condensation, or condensation in the intra-aggregate spaces as an explanation for this behavior, but instead seems to indicate that the influence of the solid extends over more than one condensed layer. There are experimental data which suggest that a sucrose molecule in solution is associated with from 2 water molecules (dilute solution) to 9 water molecules (concentrated solution) (Chattoraj and Moulik, 1975), so that the hypothesis of a distinct second condensed layer is not unreasonable. This extension of influence beyond the first layer also gains credence when the effect of moderate pretreatment is viewed in Fig. 4. As evidenced by adsorption, pretreatment Method A removes most of the higher layers of adsorbed moisture but has little effect on the first and second layers.

At higher relative vapor pressure, condensation in the intra-granular spaces undoubtedly occurs. Region C terminates when the adsorbent dissolves in the adsorbate. The relative humidity of a saturated solution of sucrose is equivalent to 77.41% at 25°C (Whittier and Gould, 1930).

Adsorption thermodynamics

In an effort to substantiate the qualitative tenets of this description of the adsorption isotherm, a limited thermodynamic evaluation of the adsorption process was undertaken. The effect of a small temperature change on the course of adsorption is presented in Fig. 6.

Before proceeding with the analysis, two aspects of the procedure need to be addressed. First, as discussed previously, the system is not at equilibrium, yet relationships of equilibrium thermodynamics will be used. Obviously, the extent of adsorption will be underestimated and so will the related integral thermodynamic quantities. The 14-day data were chosen because the details of the adsorption isotherm had clearly developed and because it was a convenient experimental period. The thermodynamic quantities calculated from these data present a pattern consistent with the adsorption process even if they are not exact.

The second point relates to the lack of data in the lower relative vapor pressure region, i.e. $P/P_0 < 0.1$. This is a very important region of the isotherm, but it is not possible to explore this region using the experimental method employed in this study. To complete the initial portion of the isotherms, an extrapolation was used employing the following empirical relationship:

$$\frac{P}{P_0(n - n_i)} = b + m(P/P_0) \tag{2}$$

where P/P_0 is the relative vapor pressure, n is the total water content, n_i is the initial water content, b and m are temperature-dependent constants. This approach has been utilized by Wu and Copeland (1961) and Hollenbeck et al. (1977). The extrapolated data and selected values from the smooth curves of Fig. 6 are presented in Table 1, along with the parameters of Eqn. 2 calculated by least-squares regression, for each temperature. Eqn. 2 is analogous to the Langmuir equation and in using it we assume that there are no discontinuities in the extrapolated region.

Given these limitations, standard free energy relations (Copeland and Young, 1961) were used to calculate the following adsorption thermodynamic properties:

$$\overline{\Delta G}_2 = RT\ln(P/P_0) \tag{3}$$

$$n_1\overline{\Delta G}_1 = RT\int_0^{P/P_0} n_2 \, d\ln(P/P_0) \tag{4}$$

$$G = n_1\overline{\Delta G}_1 + n_2\overline{\Delta G}_2 \tag{5}$$

where $\overline{\Delta G}_2$ and $\overline{\Delta G}_1$ are the relative partial molal free energy changes of the adsorbate and adsorbent, respectively; n_2 and n_1 are the number of moles of adsorbate and adsorbent, respectively; and where ΔG is the integral free energy change associated with the adsorption process.

Fig. 7 presents the relative partial molal free energy changes of the adsorbate

TABLE 1

SMOOTHED ADSORPTION DATA AT 25.0°C AND 19.8°C

n_2 (mmole 100 g)	P/P_0		n_2 (mmole/ 100 g)	P/P_0	
	19.8°C	25.0°C		19.8°C	25.0°C
10.0	0.015[a]	0.017[b]	27	0.448	0.478
10.5	0.025[a]	0.027[b]	28	0.455	0.481
11.0	0.037[a]	0.042[b]	29	0.461	0.483
11.5	0.057[a]	0.070[b]	30	0.469	0.485
12	0.085[a]	0.145	31	0.475	0.502
13	0.190	0.275	32	0.482	0.523
14	0.228	0.303	33	0.490	0.540
15	0.250	0.320	34	0.496	0.556
16	0.283	0.353	35	0.503	0.569
17	0.23	0.394	36	0.518	0.580
18	0.346	0.417	36	0.550	0.590
19	0.365	0.431	38	0.567	0.598
20	0.382	0.442	39	0.578	0.605
21	0.395	0.451	40	0.586	0.611
22	0.406	0.457	42	0.600	0.624
23	0.416	0.463	44	0.613	0.635
24	0.425	0.467	46	0.627	0.646
25	0.433	0.471	48	0.640	0.657
26	0.441	0.475	50	0.653	0.667

[a] Extrapolated according to linear Eqn. 2. Regression results: slope = 0.198, intercept = 1.05×10^{-2}, $r = 0.9996$.

[b] Extrapolated according to linear Eqn. 2. Regression results: slope = 0.219, intercept = 1.13×10^{-2}, $r = 0.9950$.

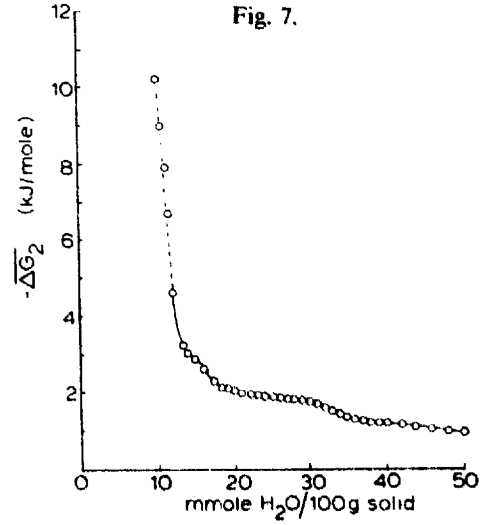

Fig. 7.

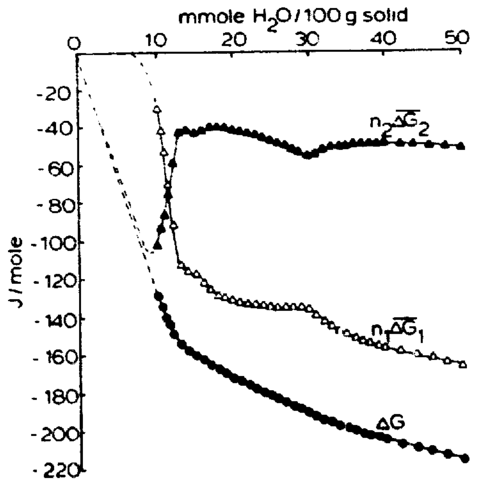

Fig. 8.

Fig. 7. Relative partial molal free energy (ΔG_2) of adsorbed water on compressible sugar after 14 days at 25°C.

Fig. 8. Integral free energy of adsorption (ΔG) and relative partial molal free energy contributions of adsorbate ($n_2\overline{\Delta G}_2$) and adsorbent ($n_1\overline{\Delta G}_1$) for the water–compressible sugar system at 25°C.

($\overline{\Delta G_2}$) at 25.0°C. The plot was constructed by substituting the adsorption data from Table 1 into Eqn. 3. The relative partial molal free energy of the adsorbate reflects the difference between adsorption of 1 mole of water vapor on the solid surface and on water, i.e. liquid water is the reference state. As expected, the drier the solid the greater the magnitude of this quantity, with the negative sign indicating that adsorption is spontaneous. There are two inflection points in the otherwise monotonous curve: 15.5 and 30 mmole H_2O/100 g solid. These points coincide with completion of first and second layers as theorized in the preceding analysis of the isotherm. The contribution of the adsorbate to the overall free energy change of the adsorption process, as reflected in Eqn. 5, is given by the product $n_2\overline{\Delta G_2}$. This quantity has been calculated and included in Fig. 8.

While the thermodynamic quantities of the adsorbate are very important, they do not exclusively characterize the adsorption process unless the adsorbent is inert. The contribution of the adsorbent to the overall free energy change of adsorption may be determined indirectly from Eqn. 4, a form of the Gibbs-Duhem relationship. This quantity was evaluated graphically, using the trapezoidal rule (Hollenbeck, 1977), and is also included in Fig. 8 along with the integral free energy change calculated from Eqn. 5.

The integral free energy function appears deceptively smooth, emphasizing the point that the partial molal quantities are much more informative. In that regard, it would be desirable to consider the relative partial molal free energy changes of the adsorbent, $\overline{\Delta G_1}$, but unfortunately it is not possible to separate this term from the product $n_1\overline{\Delta G_1}$. The quantity n_1 refers to the number of moles of adsorbent in the 'surface region' which participate to some extent in the adsorption process. Even if pure sucrose were the adsorbent, and the molecular weight were known, it would be impossible to determine the layers of sucrose molecules actually involved in the adsorption process and therefore it is not possible to determine n_1. Also n_1 is not constant for a give amount of adsorbent, but varies with n_2.

The temperature dependence of the adsorption process was used to compute isosteric heats of adsorption:

$$\overline{\Delta H_2} = \left[\frac{\delta\left(\dfrac{\overline{\Delta G_2}}{\Delta T}\right)}{\delta\left(\dfrac{1}{T}\right)} \right]_{n_1, n_2} \tag{6}$$

$$\Delta H = \left[\frac{\delta\left(\dfrac{\Delta G}{\Delta T}\right)}{\delta\left(\dfrac{1}{T}\right)} \right]_{n_1, n_2} \tag{7}$$

where $\overline{\Delta H_2}$ is the relative partial molal enthalpy of adsorbed water on compressible sugar, and where ΔH reflects the total enthalpy change for the process. The enthalpy analysis is completed by recognizing that:

$$n_1\overline{\Delta H}_1 = \Delta H - n_2\overline{\Delta H}_2 \qquad (8)$$

The relative partial molal enthalpy functions are presented in Fig. 9. Three exothermic maxima in the adsorbate function occur at the following coordinates:

(i) 12 moles H_2O/100 g solid, $\overline{\Delta H}_2 = -74$ KJ/mole;
(ii) 17 moles H_2O/100 g solid, $\overline{\Delta H}_2 = -27.5$ KJ/mole;
(iii) 35 moles H_2O/100 g solid, $\overline{\Delta H}_2 = -17$ KJ/mole.

Note that each maximum occurs within one of the regions described previously.

To complete the thermodynamic analysis, relative partial molal entropy functions were determined and are presented in Fig. 10.

Because of the inability to determine the relative partial molal thermodynamic properties of the adsorbent, it is not possible to compare the adsorbate and adsorbent on a molar basis. Therefore, the effect of adsorption on the state of the components in this study will be assessed by comparing partitioned quantities (e.g. $n_2\overline{\Delta G}_2$ and $n_1\overline{\Delta G}_1$) with the adsorption isotherm in Fig. 4.

Region A of the adsorption isotherm includes adsorbate levels up to 12 mmoles H_2O/100 g compressible sugar. Actual data are not available for the initial portion, but it is clear that from 10 to 12 mmoles adsorbate per 100 g adsorbent, there is a dramatic change in the character of both the adsorbate and adsorbent. The behavior for the adsorbate is not unexpected, since the most dramatic change in character will occur when the solid is dry.

The first exothermic maximum in Fig. 9 can be assigned to the fixation of water

Fig. 9.

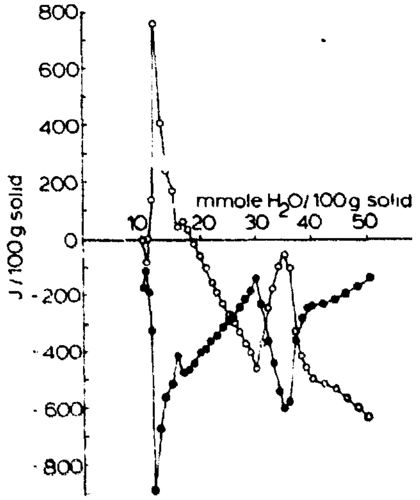

Fig. 10.

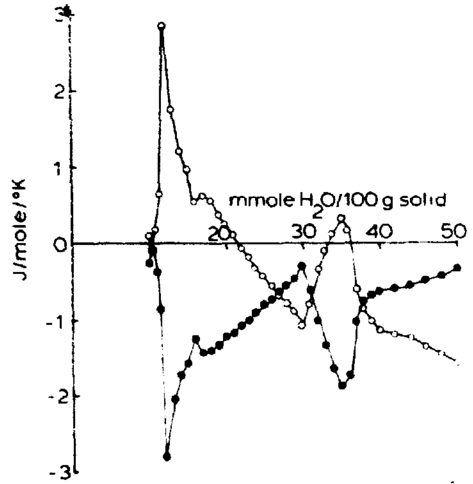

Fig. 9. Relative partial ' .l enthalpy contributions of adsorbate $(n_2\overline{\Delta H}_2)$ and adsorbent $(n_1\overline{\Delta H}_1)$ for the water–compressible sugar system at 25°C.

Fig. 10. Relative partial molal entropy contributions of adsorbate $(n_2\overline{\Delta S}_2)$ and adsorbent $(n_2\overline{\Delta S}_1)$ for the water–compressible sugar system at 25°C.

on specific sites. The relative partial molal enthalpy valve approaches that associated with irreversible chemisorption on oxides (Texter et al., 1978). Unlike the interaction with oxides, the initial adsorption of water on sucrose is not a chemical reaction and the enthalpy associated with this process must come from the formation of hydrogen bonds. The value of -74 KJ/mole indicates that 3 or 4 hydrogen bonds may be formed per water molecule.

Accompanying the adsorption of water in this region is a substantial change in the character of the adsorbent and certainly the assumption of inertness cannot be justified. This perturbation of the solid becomes significant after the specific adsorption sites have been saturated. In the region from 10–12 mmoles H_2O/100 g solid, it is suggested that the surface region is actually restructured into a hydrated form which then serves as a new surface for subsequent adsorption.

Region B of the isotherm, extending from 12 to 21 mmoles H_20/100 g solid reflects this further adsorption. Here, the adsorbate free energy function shows a minimum at approximately 15 mmoles H_2O/100 g solid corresponding to completion of a film on the restructured surface. The value of $\overline{\Delta H_2}$ at the second maximum in Fig. 9 is significantly decreased, although still substantial. Apparently each water molecule adsorbed at this stage forms two or more hydrogen bonds with the hydrated surface.

Region C is quite similar to region B, in terms of the thermodynamic quantities of adsorbate and adsorbent. After completion of the first layer there appears to be another build-up and condensation of the adsorbate to form a second layer. This phase change occurs at approximately 30 mmoles H_20/100 g solid, twice the value of the first phase change. The final maximum at an adsorbate content of 35 mmoles H_2O/100 g solid is still within the range referred to by Texter et al. (1978) as 'quasi-chemisorption'. The decrease in magnitude reflects the fact that the adsorbate is now involved in more lateral interactions.

Regions B and C of the isotherms are similar in that they reflect condensations of adsorbate. With regard to the adsorbate, in each region, the absolute value of the function $n_2\overline{\Delta H_2}$ decreases to a point and then suddenly increases rapidly. These increases, at 16–18 and 30–35 mmoles water H_2O/100 g solid, reflect the latent heat related per mole as a consequence of condensation. After condensation, the absolute value of the function once again decreases as adsorption takes place on the condensed layer. After each condensation the character of the surface region changes and a solid solution consisting of at least two components seems to be formed.

This point is demonstrated by the function $n_1\overline{\Delta H_1}$, which also shows discontinuities at the adsorbate levels associated with condensation. Also the function $n_1\overline{\Delta H_1}$ becomes negative above a value of 18.5 mmoles H_2O/100 g solid indicating that more energy is released as a consequence of hydration than is required to disrupt the adsorbent. These factors support the concept of stepwise surface hydration analogous to the formation of crystalline hydrates involving different fixed amounts of water.

The entropy functions in Fig. 10 are consistent with the preceding discussion. It is, however, important to note that there are regions of the adsorption process where the relative partial molal entropy of the adsorbent ($\overline{\Delta S_1}$) is actually negative. The explanation for this behavior relates to the standard state of the adsorbent, or more correctly the standard state of the adsorbent molecules in the surface region. These molecules are part of the solid, but they are not part of the bulk solid. The decrease in entropy for the adsorbent is not the result of stronger bonding, but instead a transition from restriction in two dimensions to restriction in all 3 dimensions. In the hydrated surface region, the adsorbent molecules are part of a solid solution and they are completely surrounded by water and/or other adsorbent molecules.

Desorption

Isothermal desorption of water from compressible sugar was also studied by placing wet solid in the various relative humidity chambers at 25°C. The initial moisture content of the wet compressible sugar was found to be 9.31 mg H_2O/g solid. The kinetic results of desorption are presented in Fig. 11. The desorption results at all relative vapor pressures show that sample weights decrease monotonically to a reasonably constant level. These pseudo-equilibrium results are presented as a desorption isotherm in Fig. 12. For comparative purposes the adsorption isotherm from Fig. 4 has also been included.

Obviously there is remarkable hysteresis in this sorption system. Given the difficulties encountered in drying compressible sugar, this behavior was not unexpected. When elevated temperature is required to dry a sample, simple desorption at room temperature cannot be expected to produce the same extent of moisture loss. As a general rule, isothermal desorption hysteresis is inevitable in any system whose dehydration requires elevated temperature.

Fig. 11.

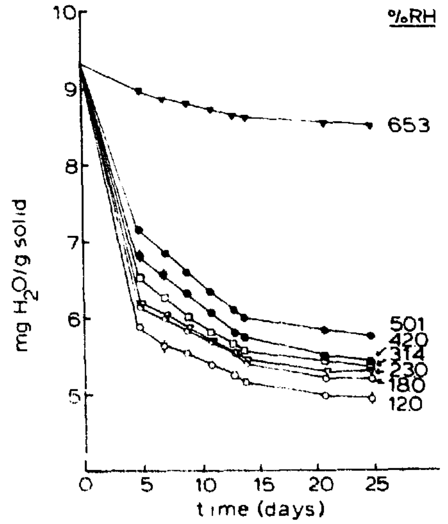

Fig. 12.

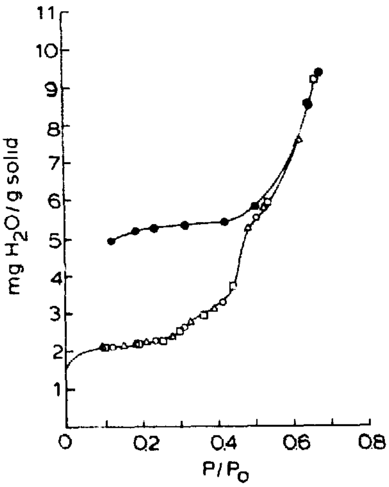

Fig. 11. Desorption of water from compressible sugar at various relative humidities at 25°C. (Initial moisture content = 9.31 mg H_2O/g solid; vertical bars represent ± 1 standard deviation).

Fig. 12. Water vapor adsorption–desorption isotherm for compressible sugar at 25°C. Key: △, □, ○, represent independent 14-day adsorption results after pretreatment by method B; ●, represents 25-day desorption results from solid with an initial moisture content of 9.31 mg H_2O/g solid.

The kinetic results in Fig. 2 show that adsorption equilibrium was not achieved. As mentioned earlier, the solid will continue to sorb moisture as long as the adsorbate diffuses into the solid. Let us consider the adsorption in the constant rate period at 20% RH, for example. If we assume that this sample would continue to adsorb moisture at the same rate, it would take over 41 years to reach the moisture content of 5.25 mg H_2O/g solid which corresponds to the level presented at this humidity in the desorption study. This result suggests that the adsorbate has undergone a substantive change, such as formation of a surface hydrate, even if that change is associated with a non-equilibrium position. The desorption isotherm levels off at a moisture content of approximately 5.2 mg/g of solid, which corresponds closely to that associated with the second layer condensation discussed previously. This level extends to quite low relative vapor pressures where the hysteresis is pronounced.

The desorption branch in Fig. 12 is quite similar to the adsorption isotherm for compressible sugar pretreated by Method A (Fig. 4). This observation supports the contention that a reversible surface hydration is involved and that drying by Method B produces no significant chemical change in the solid surface region.

The results of this work show that the moisture content of compressible sugar is indeed a complicated function of its history: time, temperature, pressure and relative humidity are all significant independent variables. To meet compendial standards (N.F. XV, 1980) compressible sugar must have a loss on drying at 105°C after 4 h at atmospheric pressure of from 0.30% to 1.0% of its weight. Assuming that all the weight loss is water, this corresponds to a moisture content range of approximately 3–10 mg H_2O/g solid. Needless to say, this is not a very restrictive standard and users of compressible sugar concerned with the potential effects of moisture should closely monitor the moisture content of their material.

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