Water Sorption Properties of a Polysaccharide Adsorbent

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A flow method was used to determine equilibrium isotherms of the water–corn grit system in the temperature range of 345–373 K. A modified Henry equation was used to fit the experimental data. Calculated values of the heat of adsorption (10.8–14.6 kcal/g–mol) and surface area (170 m²/g) are similar to values previously reported based on data taken at lower temperatures. These data extend knowledge of the equilibrium behavior of water with respect to corn grits to the temperature range used for the selective adsorption of water from alcohol vapor by corn.

Introduction

The use of corn as an adsorbent for water in the dehydration of ethanol is known (Ladisch et al., 1984; Voloch et al., 1984) and is currently being used on an industrial scale. The separation is carried out at temperatures above the dew point of an ethanol–water mixture (353 K) at atmospheric pressure. The process takes place outside of the range of published isotherm data for water, although such data are needed for the mathematical modeling of the process.

The adsorption and desorption properties of water on cereal grains at temperatures below 323 K are known (Brusink and Winkler, 1957; Rodrigues-Arias et al., 1963; Chung and Pfoet, 1967a). These data were generated by placing the adsorbent in contact with vapors at different water partial pressures in a sealed, constant-temperature container for up to 6 days (Chung and Pfoet, 1967a). The water vapor pressure of the container was obtained by placing either saturated salt solutions or various concentrations of sulfuric acid solutions below the sample.

Our experimental data were obtained by passing a water-saturated gas stream through a column packed with the adsorbent until equilibrium was attained as determined by measuring total content in the effluent from the column. This approach had been used by Jury and Edwards (1971) to obtain the isotherms for the silica gel–water system and by Dupret and Guilhot (1974) for starch–alcohol–water at 298 K. Flow methods offer good control of the saturation pressure with the equilibrium being attained faster than in static methods.

Experimental Methods and Materials

Apparatus. Figure 1 shows a schematic diagram of the experimental apparatus. The carrier gas, nitrogen, was saturated with water by passing it through two gas washing bottles (Ace Glassware Co., Vineland, NJ) in series, each filled with deionized water. The carrier gas flow rate was controlled at 90 cm³/min (measured at a reference state of 21 °C and 1 atm) with a mass flow controller (Model 8240, Matheson Co., Joliet, IL). The gas washing bottles were submerged in a water bath (having a 40-L volume) which was kept at constant temperature with an immersion circulator (Model E2, Haake Co., Germany). The partial pressure of water in the vapor leaving the saturator was fixed by the temperature (measured within 0.2 K) and atmospheric pressure (measured by a mercury barometer, Prince, Southampton, PA). The measured atmospheric pressure and temperature were used to specify the water vapor concentration. This was checked by measuring the total water adsorbed on the corn adsorbent and the calcium sulfate as described below. The difference between the specified and measured values was generally less than ±3%. Different saturation levels were obtained by varying the temperature in the bath. In order to obtain saturation below room temperature, the water tank was cooled with a refrigeration unit. Saturation temperatures from 279 to 363 ± 0.2 K were obtained.

The nitrogen, saturated with water, was then heated and fed into the column. All the connections between the saturators and the column were traced with heating tapes in order to avoid condensation as well as to bring the gas to the desired equilibrium temperature.

The adsorbent was packed in a stainless steel column (0.5363 cm o.d. × 18 cm) which was kept at constant temperature by an electrical column heater (Hess Laboratory, Menlo Park, CA). The adsorbent was corn grits (Type 800, Gooch Mills, Lincoln, NE), with an average particle size of 0.106 cm (standard deviation of 0.048 cm). Two different columns were alternated throughout the experiments, with one being dried while the other was in use. Due to small differences in the column internal diameter, 5.761 g of grits (oven dry weight) was packed in one column and 5.758 g of another. The temperature at the column wall and in the gas washing bottles were monitored with thermocouples. The system absolute pressure (124 ± 4 kPa) was obtained by combining the readings from the mercury manometer (see Figure 1) and the mercury barometer.

A tube filled with indicating calcium sulfate (Drierite, W.A. Hammond Drierite Co., Xenia, OH) was weighed and then placed in the column outlet to adsorb any moisture present in the effluent stream. An analytical balance sensitive to ±10 μg (Sartorius, Model 2434, Westbury, NY), was used to determine weights. At the end of a run, the Drierite tube was again weighed. The difference in weights corresponded to the water adsorbed by the Drierite. Similarly, the weight gain due to water adsorption for the column packed with the corn was also determined. The combined weight gain of the calcium sulfate and the corn grits was consistent with the water content expected for a gas stream saturated with water at the indicated temperature and pressure. The use of calcium sulfate to gravimetrically determine the relative humidity of a gas stream has previously been reported by Nelson (1967).

Procedures. A run was started by bringing the water bath containing the gas saturators and the adsorption column to the desired temperature. Gas was passed...
through the saturators and then brought to column temperature. When the system had reached steady state, the saturated gas was allowed to flow through the column. The adsorption was carried out for 22–24 h, based on preliminary experiments which indicated that saturation of the corn grits was attained within this time period. The amount of water adsorbed by the grits was determined by weighing the column on the analytical balance. After each run, the column was regenerated by passing nitrogen through it at a flow rate of 200 cm³/min and a temperature of 363 K for 24 h. Completion of desorption was verified by weighing the column. As in adsorption, when the column no longer changed, the completion of this step was indicated.

Note that when the nitrogen was saturated with anhydrous ethanol instead of water, no weight increase of the corn was observed, even at temperatures as low as 318 K. This observation is consistent with the data of Hong et al. (1985), which also showed that corn grits do not adsorb ethanol to a significant extent at the conditions used here.

Development of a Modified Henderson’s Equilibrium Equation. There have been a number of attempts to obtain a general isotherm for the water-grain system (Chung and Pfoert, 1977a; b, Henderson, 1995; Strohman and Yoeger, 1997). The BET equation for a type II isotherm (Brunauer et al., 1938) describes the equilibrium moisture up to relative humidities of 50% at 293–323 K (Bhushuk and Winkler, 1957; Hall and Rodriguez-Arias, 1958). The volume of the monolayer, \( V_m \), may be considered temperature independent within a 30–50 K temperature range (Brunauer, 1945). The BET equation is

\[
P^* = \frac{1}{V_m C} \left[ C + 1 - \frac{B^*}{P} \right]
\]

where \( P^* \) designates the equilibrium partial pressure of water and \( P \) is the vapor pressure of pure water. The second parameter, \( C \), is a weak function of temperature for water adsorption on grain since the heat of adsorption is close to the heat of condensation in this case (Bhushuk and Winkler, 1957). Equation 1 is used later in this work to determine \( V_m \) and internal surface area. In order to fit the data with a smooth curve, a modified form of the empirical Henderson’s equation, which included temperature as a parameter, was used instead as discussed below. This equation (eq 3) was also used to obtain isotherms from which differential heats of adsorption were obtained by using eq 10 below.

Henderson (1995) developed an isotherm for water–grain systems of the form

\[
1 - (P/P^*) = \exp(-KTM^*)
\]

where \( M \) is g of water/100 g of adsorbent. Both \( K \) and \( n \) were assumed to be temperature independent. Hall and Rodriguez-Arias (1958) reported that, in the range of 275–333 K, \( n \) varied by 10% while \( K \) varied by 450%. In order to account for the temperature dependence of the parameters, Day and Nelson (1972) proposed that \( K \) and \( n \) should be expressed as

\[
K = \alpha T^n
\]

(3)

Initial fitting of our experimental data using eq 2 gave satisfactory results. The parameter \( n \) did not vary significantly with temperature while \( K \) was strongly temperature dependent. Thus, we modified eq 2 by assuming that \( n \) is temperature independent while \( K \) can be expressed by an Arrhenius-type function of temperature. The modified Henderson’s equation becomes

\[
\ln (1 - p/P^*) = \frac{-K_T^*}{RT} \left( -E/RT \right) (M^*) \]

Use of eq 5 allowed all of the experimental points obtained at different temperatures to be fitted with one correlation.

Results and Discussion

Adsorption Isotherm. Tables I–III give the experimental results obtained. Overall, 37 runs were carried out, including duplicate runs. All the data points were fitted with a nonlinear regression program to the modified Henderson’s eq 5, which was rearranged to give

\[
X = 0.01M = 0.01 \left[ \frac{-\ln (1 - (p/p^*)^n)}{K_T \exp(-E/RT)} \right]^1/n
\]

where \( X \) is g of water/g of adsorbent. A good fit was obtained, and the values of the constants were

\[
K_T = 0.00053473 \text{ K}^{-2}
\]

(7)

\[
E = 1.594 \text{ kcal/g-mol}
\]

(8)

\[
n = 1.856
\]

(9)

Figure 2 shows a plot of the isotherms calculated via eq 6–9 (solid lines) compared to the experimental points. Two
Figure 2. Adsorption isotherms for water-corn grits at 323-373 K. The data from 343 to 373 K were used to determine the constants in eq 5. The curve at 323 K was obtained by extrapolation of eq 5.

Figure 3. Isotetera for water-corn grits system calculated by using eq 6. Runs carried out at 323 K give a first indication that eq 5 can be extrapolated. The experimental data agreed well with the predicted values as shown in Figure 2.

Heat of Adsorption. The differential heat of adsorption was calculated by plotting isotherms. The data were generated by using eq 6 to calculate values of $p^*$ and $P$, as indicated in Figure 3. The differential heat of adsorption, $-H$, can then be calculated via eq 10 from Treybal (1968)

$$-H = -\gamma \left( \frac{P}{p^*} \right) \left( \frac{dp^*}{dP} \right)$$

where the slopes of the isotherms lines in Figure 3 represent $dp^*/dP$.

Figure 4 shows the plot of the differential heats of adsorption predicted by eq 10 at 343, 353, and 373 K as a function of temperature (343-373 K) and initial water loading of corn grits.

Figure 4. Calculated differential heats of adsorption of water on corn grits as a function of temperature (343-373 K) and initial water loading of corn grits.

Figure 5. Replot of BET equation for estimating surface area (per Brunauer et al., 1938; Pedram and Hines, 1983). This surface area and the monolayer capacity of the adsorbent can be estimated from the adsorption isotherm data by using the BET isotherm which is given by eq 1 (Brunauer et al., 1938). Pic of $p^*/V(P - p^*)$ vs. $p^*/P$ yield straight lines up to a relative pressure of 0.4, as may be shown in Figure 5. The nonlinear nature of the line at $p^*/P > 0.4$ indicates that only a finite number of layers of water are adsorbed at equilibrium (Hall and Rodriguez-Arias, 1968). The surface area was calculated by using eq 1 and Figure 5. A similar technique was used by Pedram and Hines (1983) to estimate the surface area for the adsorption of water on silica gel.

We determined a value of 0.0481 cm$^3$ of water/g of corn for the monolayer capacity of corn grits. Using a value of $10.6 \times 10^{-18}$ cm$^2$ for the cross-sectional area of a water
molecule (Pedram and Hines, 1983; Gupta and Bhatia, 1969), we estimated the surface are for adsorption to be 170 m²/g of corn grits. This estimate is comparable to the values of 210 m²/g reported for starch (Gupta and Bhatia, 1969) and 263 m²/g for shelled corn (Hall and Rodriguez-Abas, 1968), which were also obtained by using water adsorption data.

Conclusions

Corn grits adsorb water in the range of 323-373 K. Experimental adsorption data were fitted to a modified Henderson's equilibrium equation. The equation was modified by assuming that one of its parameters, n, was temperature independent. The second parameter, K, was found to have an Arrhenius-type dependence on temperature. The modified equation may be useful for extrapolations to lower temperatures as well. The calculated heats of adsorption (10.6-14.6 kcal/g-mol) are close to the latent heats of condensation (9.7-10 kcal/g-mol), thus indicating a physical adsorption phenomenon.

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Nomenclature

\[ a = \text{constant in eq 3} \]
\[ b = \text{constant in eq 4} \]
\[ C = \text{constant in the BET eq 1, dimensionless} \]
\[ d = \text{constant in eq 3} \]
\[ e = \text{constant in eq 4} \]
\[ E = \text{constant characteristic energy, kcal/g-mol} \]
\[ H = \text{heat of adsorption, kcal/g-mol} \]
\[ K_v = \text{constant in eq 2, kcal/mol} \]

\[ K_v = \text{preexponential constant in eq 5, kcal/mol} \]
\[ N_v = \text{moisture (dry basis), g of water/100 g of adsorbent} \]
\[ n = \text{constant in eq 2, dimensionless} \]
\[ P = \text{partial pressure of water, kPa} \]
\[ P = \text{vapor pressure of water, kPa} \]
\[ R = \text{gas constant, kcal/(g-mol K)} \]
\[ T = \text{absolute temperature, K} \]
\[ V = \text{volume of adsorbate adsorbed, cm³ of liquid water/g of adsorbent} \]
\[ V_{mo} = \text{volume of the monolayer, cm³ of liquid water/g of adsorbent} \]
\[ X = \text{mass of adsorbate adsorbed, g of water/g of adsorbent} \]
\[ \gamma = \text{latent heat of condensation, kcal/g-mol} \]


Literature Cited


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