Water and Ethanol Sorption Phenomena on Starch

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The sorption behavior of water and ethanol on starch material has been investigated in relation to the adsorptive separation of water from ethanol. The adsorption isotherms of water-starch, ethanol-starch and water-ethanol-starch were measured using a Cahn electrobalance. Careful examination of the many sorption isotherm models resulted in selection of Sircar's model and the potential theory to best represent the isotherm data of water-starch and ethanol-starch adsorption. Experimental results showed that ethanol as well as water can adsorb on starch. The adsorption rate of ethanol, however, is much slower than that of water. This suggests that the selective removal of water from ethanol vapor in a packed-bed adsorber is likely a rate-dependent, not an equilibrium-dependent, process.

Introduction

The removal of water from ethanol using a fixed-bed adsorber is a well-known process (Ladisch and Dyck, 1979; Ladisch and Tsao, 1982; Ladisch et al., 1984; Bienkowski et al., 1986; Lee and Ladisch, 1987). Compared to distillation, which required about 2.8×10^6 J/L of ethanol to break the azeotrope using benzene (Katzen et al., 1980), adsorption is energy-efficient with estimates of 5.6×10^5 J/L to arrive at 99.6% ethanol from a 95% solution using starch (Ladisch et al., 1984) and 2.0×10^6 J/L to go from 85% to 99.5% using cornmeal (Hassaballah and Hills, 1990). Starch containing adsorbents are now used in fermentation ethanol plants to remove water from alcohol in the production of fuel-grade ethanol. In this context, studies of sorption behavior and development of predictive equations for adsorption isotherms of water and ethanol on starch-containing materials are needed.

Water adsorption on many adsorbents has been related to the attraction between the water molecule and polar groups (mainly hydroxyl groups) in the absorbent. In zeolites, the silica/alumina ratio can be adjusted to give higher affinity for water and other polar molecules (Ruthven, 1984). For water-silica adsorption, 1 mole of hydroxyl group adsorbs 1 mole of water group at BET monolayer surface coverage (Gregg and Sing, 1982). For a water-biopolymer system, one molecule of water is adsorbed per polar group in protein (gelatin and collagen) at 50% relative humidity (Kleeberg and Luck, 1984). Researchers investigating such areas as drying phenomena, textile fibers, and food science have tried to find the water sorption isotherms on other biological materials as well. Generally, it is accepted that water sorption isotherms on hydrophilic polymers have a sigmoidal shape and are type II isotherms according to Brunauer's classification (Brunauer, 1945).

A similar relationship between polar interactions and adsorption is evident in starch-based materials. The typical composition of dry corn is 75% starch and 10% protein with the balance consisting of minor constituents including fats and sugars (Anderson, 1970). The starch fraction is a mixture of amylose, a linear polymer of D-glucose units joined by α-1,4 bonds, and amylopectin, a polymer of linear, 1,4 D-glucose chains linked at branch points by α-1,6-bonds (van den Berg, 1981). The polar attraction of water and the hydroxyl groups of the anhydrous glucose units is the main force for water adsorption on starch. The sorption isotherm of water-starch covering a wide range of relative humidity has been predicted previously by an empirical correlation which is based on the number of water molecules associated with each polar group (van Krevelen and Hoftijzer, 1976; van den Berg, 1981).

Although it has not been as widely studied as water adsorption, ethanol adsorption on starch materials has also been described previously in the literature. Bushuk and Winkler (1957) found that ethanol adsorption on wheat flour occurred at a much slower rate than the water adsorption at room temperature. Gupta and Bhatia (1969) measured the sorption isotherm of ethanol vapor on starch. They found that the BET equation represented the sorption data moderately well and that some irreversible adsorption of ethanol (about 2.5 g ethanol per 100 g starch) occurred. In gas chromatographic studies using starch material as an absorbent, the ethanol adsorption found was negligible after the adsorbent had been used for several cycles (Hong et al., 1982; Rebar et al., 1984). On the other hand, Robertson et al. (1983), Crawshaw and Hills (1990),

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and Hassaballah and Hills (1990) reported that some ethanol was adsorbed on starch materials under the conditions that resulted in high water loading.

In this work, the water-starch and the ethanol-starch adsorption isotherms, measured by a Cahn electrobalance, are presented with proper mathematical models that give equilibrium loadings of water and ethanol. The measurements were taken over a wide range of relative humidity, with emphasis on values of temperature near the adsorption condition for the removal of water from ethanol. This work extends a voluminous literature on water adsorption and desorption on whole corn for grain drying applications at temperatures below 60°C, and adds to results from several references that address sorption at 60 to 80°C as reviewed by Chen and Morey (1988).

It has been reported that more than 70 equations have been applied to represent the water sorption isotherm on starch materials (van den Berg and Bruin, 1981). This work identifies the proper selection of suitable adsorption isotherm equations to represent the data. The emphasis is on finding a model with a minimal number of adjustable parameters that can cover wide ranges of temperature as this is of considerable importance in defining the separation capabilities of starch used as a polysaccharide sorbent. Experimental data are also presented on the adsorption rates of ethanol and water on starch, which can explain the adsorptive separation of water from ethanol using the polysaccharide adsorbent at temperatures above 80°C.

Models previously applied to water adsorption on starch

A number of models have previously been applied to the adsorption of water on starch materials. Henderson (1952) developed an equation for the water-grain system, which was later modified by Day and Nelson (1965) and by Neuman et al. (1986). Neuman et al. (1986) successfully modeled the water adsorption on corn grits (i.e., ground corn) at temperatures between 70 and 100°C. The advantage of the Henderson and modified equations is their simplicity. Using three parameters, the equations successfully describe the water sorption behavior including the sigmoidal shape even at different temperatures. This model, however, is somewhat empirical since the physical significance of the parameters in this equation can be difficult to define.

The BET equation (Brunauer et al., 1938) has been applied very widely to water adsorption on hydrophilic polymers including natural fibers, proteins, epoxy, and phenolic resin (summary by Barrie, 1968). The BET equation, however, tends to overpredict sorption equilibria in the high relative humidity region ($P/P_0 > 0.5$). The BET equation is more frequently used in determining the surface area for adsorption and is seldom used for correlating adsorption data (Yang, 1987). Based on water-corn isotherm data in the range $P/P_0 < 0.5$, Neuman et al. (1986) estimated the surface area for water adsorption on grits (average particle size of 1,050 μm) as 170 m^2/g corn grits. Surface areas for pure starch evaluated using the same approach (Morsi et al. 1967; Baghwan et al., 1972) were in the range of 260 m^2/g to 298 m^2/g.

To correct for the overprediction of the sorption amount at high relative humidities, the Guggenheim-Anderson-deBoer (GAB) theory (van den Berg, 1981) was developed to account for the difference in properties between a bulk liquid and a multilayer sorbed phase. This correlation seems to give a better fit for the water-starch system than the BET equation for a wider range of surface coverage, especially at higher relative humidity (Buleon et al., 1982; van den Berg, 1981). However, unless the heat of sorption on the first and following layers are known, the GAB model becomes a five-parameter equation, which must be fit to data using nonlinear parameter estimation methods.

Models considered in this work

Since one goal of the research was to obtain equilibrium relationships that could be extrapolated to a range outside of the experimental determinations, other models that have not been used to predict water sorption on starch were considered. Two of these, Sircar's (1985) model and the potential theory (Polanyi, 1914), appeared to have possibilities in terms of explaining the experimental results in a useful and physically meaningful manner. Sircar's model and the potential theory are briefly discussed here for the application to water-starch and ethanol-starch adsorption systems.

Sircar (1985) developed a three-parameter isotherm equation for nonporous adsorbents to compensate for the overprediction of the BET equation in the higher relative humidity region. The model assumes that a multilayer is formed at any value of relative humidity and that the surface area of each layer increases as the relative humidity increases. The equation is in the form,

$$\frac{v}{v_m} = \frac{C_1(P/P_0)[1 + (C_\infty - 1)(P/P_0)]}{(1 - P/P_0)[1 + (C_1 - 1)(P/P_0)]} \tag{1}$$

where

C_1 = temperature-dependent constant describing the adsorbate-surface interaction for the first layer

C_∞ = temperature-dependent constant describing the adsorbate-surface interaction for subsequent layers

As C_∞ approaches 1, the equation reduces to the BET model. When C_∞ approaches zero, Eq. 1 becomes a monolayer Langmuir-type equation.

Sircar's model has been used to describe ethanol, benzene, and cyclohexane adsorption on cabosil at 20°C (Sircar, 1985) and correctly predicts the sigmoidal shape of the isotherm. The results also indicate that it compensates for the overprediction of adsorption frequently exhibited in predictions by the BET equation in the higher relative humidity region. Sircar did not postulate the functional forms of C_1 and C_∞ in Eq. 1 in terms of the temperature, and the temperature dependence of the adsorption isotherm was not checked apparently. However, he suggested that C_1 and C_∞ indicate the strength of the isotherm: higher values of C_1 and C_∞ reflect a stronger adsorption. For an adsorbate-adsorbent system, the volume adsorbed in a monolayer v_m should remain constant, and the C_1 and C_∞ values would be expected to decrease as the temperature increases.

The potential theory was studied because it allows prediction of the equilibrium adsorption isotherm at different temperatures from a single correlation obtained from a few measurements. Polanyi (1914) defined the adsorption potential ϵ as the work done by the adsorption forces in bringing the molecules from the gas phase to the adsorbed film on the adsorbent surface. Thus, for 1 mole of an ideal gas,

$$\epsilon = \int_P^{P_0} V\,dP = RT \ln (P_0/P) \tag{2}$$

where
ϵ = adsorption potential
R = gas constant.

Since the adsorption potential represents the work of temperature-independent dispersion forces, mainly the van der Waal's force, ϵ is only a function of the volume of the adsorbed phase, and the function is independent of temperature. Thus,

$$\epsilon = f(N\,V_m) \tag{3}$$

where
N = number of moles of adsorbed phase
V_m = molar volume of adsorbate

Combining Eqs. 2 and 3 gives,

$$RT \ln (P_0/P) = f(N\,V_m) \tag{4}$$

Thus, for a given adsorbent-adsorbate system, a plot of $N \times V_m$ vs. $RT \ln (P/P_0)$ gives a unique temperature-independent relation. This relation makes it possible to predict the isotherm at other temperatures, once the isotherm for a given gas at one temperature is known, which is the main advantage of this model.

Dubinin (1960) proposed a functional form of this characteristic curve for two types of adsorbents, microporous materials (in which the adsorbate interacts with opposite walls in the pore) and materials with large pores (or no pores in which the adsorbate interacts with a single surface). The characteristic curve for a microporous material is,

$$W = W_0 \exp\left(-\kappa_1 \frac{\epsilon^2}{\beta^2}\right) \tag{5}$$

where
W = $N \cdot V_m$ = volume of adsorbed phase
W_0 = micropore volume
β = affinity coefficient characterizing the polarizability of the adsorbate
κ_1 = constant for an adsorbent

The adsorption potential can be eliminated:

$$\ln W = \ln W_0 - \frac{\kappa_1}{\beta^2} [RT \ln (P_0/P)]^2 \tag{6}$$

A plot of $\ln W$ vs. $[RT \ln (P_0/P)]^2$ should result in a straight line in this case with the intercept equal to $\ln W_0$.

The following equation is postulated by the same author for large pore and nonporous sorbents:

$$W = W_0 \exp\left(-\kappa_2 \frac{\epsilon}{\beta}\right) \tag{7}$$

Similarly, from Eqs. 2 and 7,

$$\ln W = \ln W_0 - \frac{\kappa_2}{\beta} [RT \ln (P_0/P)] \tag{8}$$

Plotting $\ln W$ vs. $RT \ln (P_0/P)$ should thus give a straight line with the intercept being $\ln W_0$.

Potential theory has previously been used most frequently for describing adsorption of nonpolar molecules, although there are some examples of adsorption of polar molecules. Dubinin et al. (1966) found that the potential theory gave a good fit for the water adsorption on zeolite NaX at temperatures from 20°C to 280°C. Kuo et al. (1985) reported that the adsorption of ammonia on silica gel is in good agreement with the potential theory. Pedram and Hines (1983) successfully applied the potential theory to the water-silica gel adsorption.

Experimental Apparatus

Figure 1a is a simplified schematic diagram of the experimental apparatus used to measure the adsorption isotherm of water-starch. A stainless steel column (0.914 m long, 3.81 cm^3 OD), which was wrapped in heat tape (700 W, 115 V), was connected to a Cahn Electrobalance (Model No. 1000). An RTD probe (OMEGA, Model No. PRX-FR-100-E) was installed through the bottom of the column with its tip located close to the sample bucket containing the starch.

During water adsorption experiments, nitrogen gas (99.998% purity) was saturated by first passing through two 500-mL washing bottles maintained at a slightly elevated temperature in a water bath (Haake, Model No. 2). Excess moisture was removed via a knock-down drier in an oil bath (Haake Model No. F4391) maintained at the desired temperature (±1°C). This saturated nitrogen stream entered the column where it combined with a dry nitrogen stream (which also passed through the balancing unit to prevent moisture from entering the weighing mechanism). The flow rates of the nitrogen streams were regulated by two mass flow controllers (Matheson, Model No. 8240, rated at 100 mL/min full for the dry stream and 2 L/min for the wet stream). During a run, temperature in the adsorption chamber was constant. The relative humidity was also held constant until no further weight increases were evident. A typical run at 70°C is depicted in Figure 2. After equilibrium was achieved, the relative humidity was increased to the next desired value. The flow rate of the dry nitrogen was maintained between 25 and 100 mL/min, and the flow rate of the wet nitrogen was maintained at 10 to 500 mL/min. All the flow rates were based on room temperature. By adjusting flow rates of both streams (wet and dry) and controlling the temperature inside the knock-down drum, the adsorption chamber could be maintained at a specified relative humidity.

Stainless steel tubing (1/4 in. OD, 6.4 mm) is used to connect the water bath, oil bath, and the adsorption column. The tubing is covered with heat tape (Cole-Parmer, Model No. J-3122-12, 120 VAC) to keep the inside of the tubing warm. This prevents water loss due to condensation at the wall of the connecting tubing.

The water used in this work was purified through reverse osmosis followed by deionization. The starch used in this work is an A.C.S. reagent grade (supplied by Sigma Chemical Co.). The particle size of the starch was analyzed using a Zeiss (West Germany) IBAS 2000 image analysis system. The particle diameters range from 1.55 μm to 17.54 μm with the mean ranging from 6.79 μm to 8.91 μm (Long, 1988). Prior to an adsorption run, the starch was dried at 115°C for 24 to 36 hours at

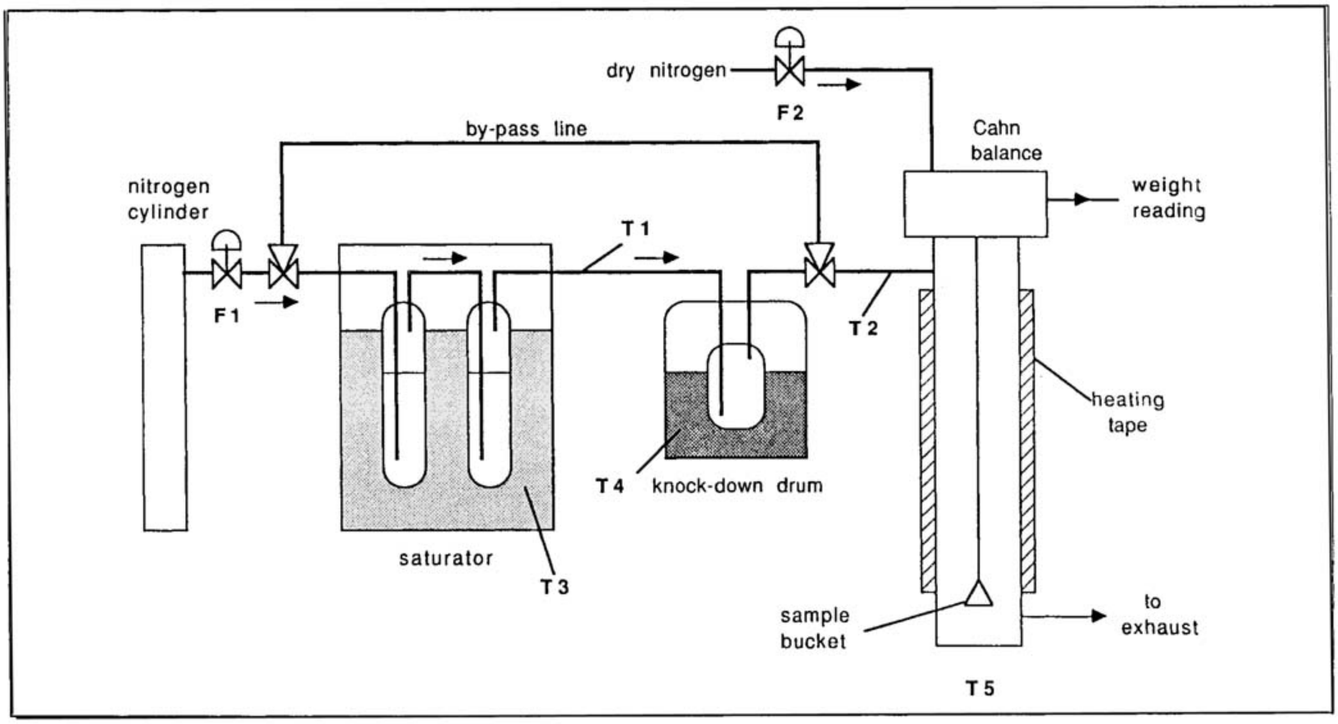

Figure 1a. Experimental apparatus.

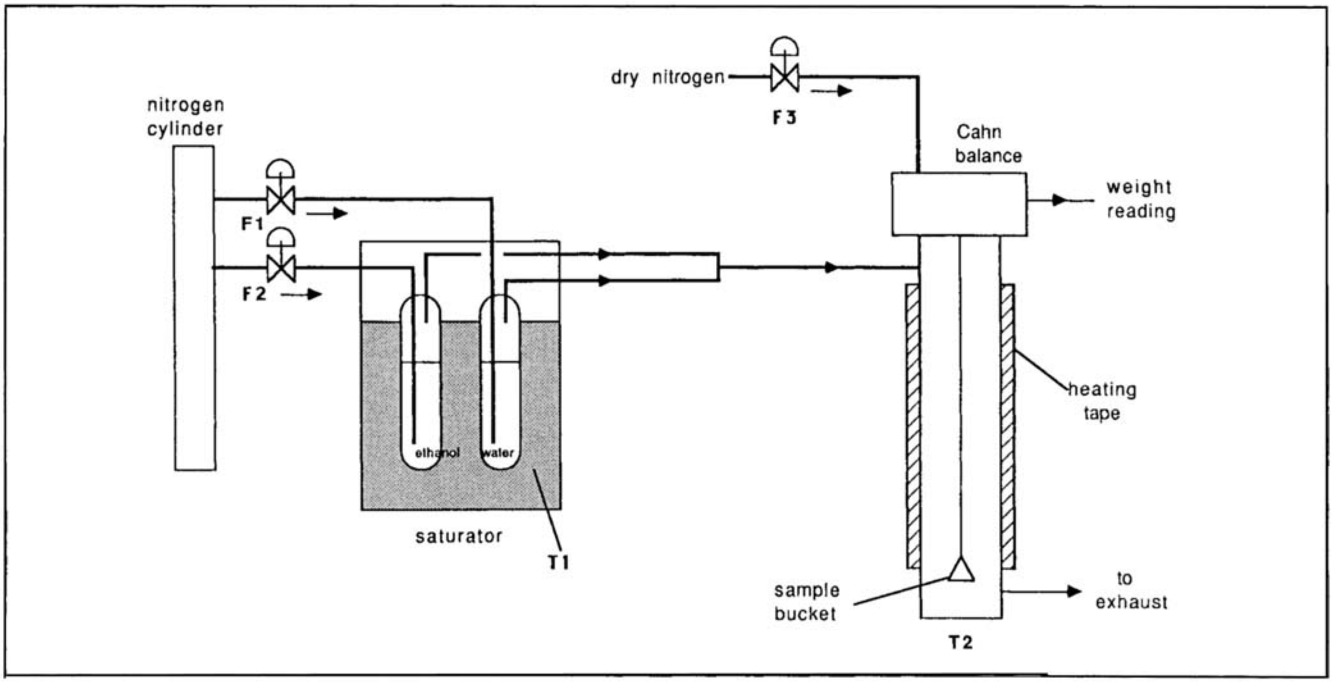

Figure 1b. Experimental apparatus to measure water-ethanol-starch isotherm.

atmospheric pressure with dry nitrogen. The adsorption isotherm was measured at relative humidities ranging from 0.05 to 0.9 and the temperatures ranging from 70°C to 115°C.

The temperature of the adsorption chamber (inside the stainless steel column) was controlled by a microprocessor-based computer (Texas Instruments, Programmable Controller, Model No. PM-550) which regulates the heat output of the tape surrounding the adsorption chamber. The control was sufficiently accurate to maintain the actual temperature inside the column (T5) within a range of ±0.1°C of the desired value. The same computer controlled the temperatures inside the tubing (*T*2), and monitored the values in the water bath (*T*3), oil bath (*T*4), and the tubing (*T*1). All the temperature probes were RTD's (OMEGA PRX-FR-100). The weight change of the sample (starch) was continuously measured at predetermined time intervals (from 30 seconds to 30 minutes), and the measured data were stored in the diskette or the hard disk by the same computer unit.

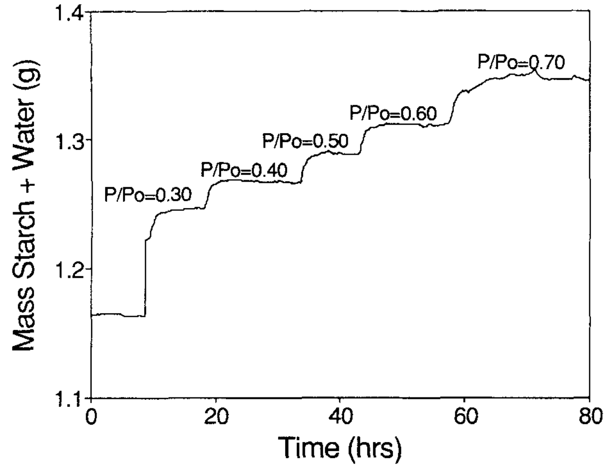

Figure 2. Typical water adsorption run ($T = 70°C$).

The same experimental setup and procedures were used for the ethanol-starch adsorption experiments. The ethanol was 200-proof USP-grade absolute ethanol (Midwest Grain Co., IL). Since the ethanol rapidly absorbs water from the air, precautions were taken to prevent water contamination in the system during both loading of ethanol into the saturator as well as during the experiment. Before loading, the saturator, consisting of testing bottles plus connecting lines, was first rinsed with the same ethanol used in the experiment and was then dried in an oven at 85°C for 24 hours. The saturator was purged with dry nitrogen and sealed at the inlet and outlet sides by three-way valves. Vacuum was applied to one end of the bottle and the absolute ethanol was drawn into the other end, minimizing contact with the air. After being filled, the saturator was quickly connected to the system that was also previously dried by purging nitrogen. The water content in the absolute ethanol was measured by the Karl-Fischer titration method using an Aquatest IV liquid water analyzer (Photovolt Co., NY). Typical water content in the freshly opened bottle of absolute ethanol is between 500 to 800 ppm by weight. The adsorption system (which includes the adsorption chamber, tubings, and the knock-down drum) was also dried previously by purging with nitrogen. The saturator was quickly connected to the system. Even with all of these precautions, the water content of the ethanol in the saturator was still about 0.1%.

The ethanol content in the vapor stream was analyzed using a standard gas chromatography setup (Shimadzu, Model No. GC-14A) and GC column (Haysep-D, Supelco Co.). The water content in the vapor phase was measured by condensing the vapor stream exiting the adsorption chamber. The condensate was analyzed for the water content using Aquatest IV. The typical water content was approximately 2,000 to 4,000 ppm by weight which is slightly higher than the water content in the ethanol inside the saturator. The ethanol-starch adsorption was evaluated for the relative humidities ranging from 0.2 to 0.5 and temperatures from 70°C to 100°C.

The experimental apparatus used in measuring the adsorption isotherm on starch when both ethanol and water vapors are present is shown in Fig. 1b. Two saturators were placed in the water bath, one for ethanol and the other for water. Two nitrogen streams ($F1$ and $F2$) passed through each saturator at predetermined flow rates. Both streams were saturated with either ethanol or water at the temperature, $T1$, and flowed directly into the adsorption chamber. Desired relative humidities of ethanol and water in the adsorption chamber could be obtained by adjusting flow rates of nitrogen ($F1$, $F2$, and $F3$) and by adjusting the temperature of the water bath ($T1$). The total weight gain was measured after equilibrium is reached.

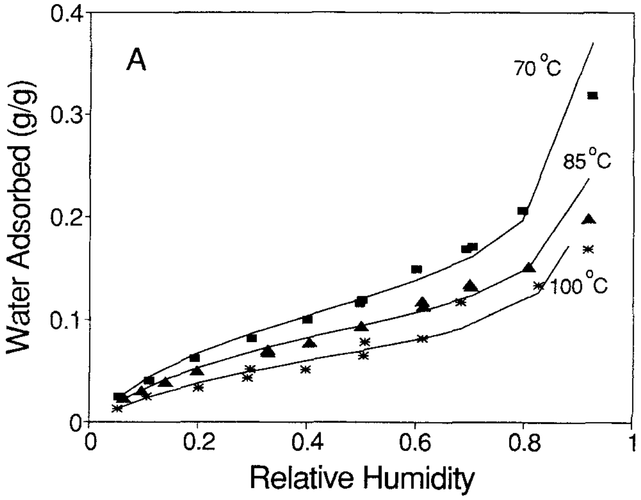

Figure 3a. Water-starch adsorption isotherms and Sircar's model predictions using constants from Sircar's method.

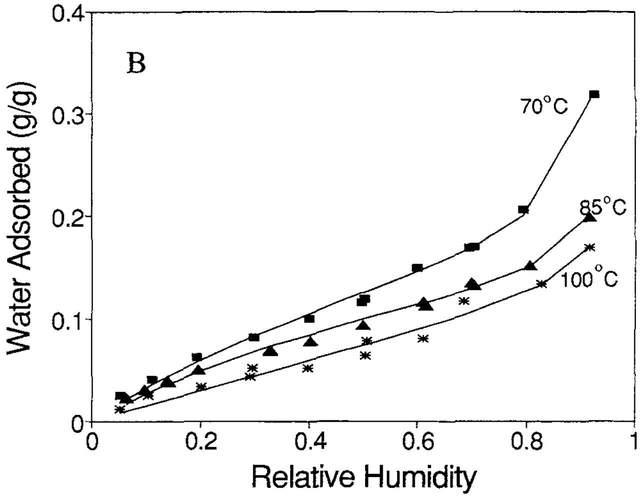

Figure 3b. Sircar's model predictions using constants from nonlinear parameter estimation.

Results and Discussion

The equilibrium adsorption isotherm of water on pure starch was measured at 70, 85, 100 and 115°C with the relative humidity between 0.05 and 0.9. A number of equilibrium evaluations were duplicated, in many cases using different starch samples. At lower temperatures, the water adsorbed varied by less than 5%. At 100°C, the values exhibited greater variability with deviations of up to about 15% for different starch samples. The isotherms determined for 70, 85 and 100°C are shown in Fig. 3a. Due to experimental limitations, the relative humidity at 115°C was limited to 0.4. The sorption capacity at

Table 1. Parameters for Water-Starch Adsorption Isotherm: Sircar's Method vs. Nonlinear Parameter Estimation

Sircar's Method				Nonlinear Parameter Estimation			
Temp. (°C)	v_m	C_1	C_∞	Temp. (°C)	v_m	C_1	C_∞
70	0.1295	4.002	0.1595	70	0.1727	2.068	0.0777
85	0.1067	3.824	0.1185	85	0.1404	2.121	0.0456
100	0.0758	3.788	0.1605	100	0.1362	1.123	0.0325

115°C is very close to the sorption capacity at 100°C in this relative humidity range, thus the data points are not shown in Fig. 3a.

Sircar's model for water sorption

Sircar's model (Eq. 1) was applied to the data in Fig. 3a. Initially parameters were estimated by the method described by Sircar (1985). C_1 and v_m were evaluated from a linearized plot at relative humidities below 0.35 where the effect of C_∞ is small. The value of C_∞ was then determined by a best fit of the data using the values of C_1 and v_m. The value of v_m, which represents the monolayer adsorption and was expected to be constant, decreases with increasing temperature (Table 1). Table 1 also shows that, with the exception of C_∞ at 100°C, the values of C_1 and C_∞ decrease with increasing temperature as expected. This result is somewhat deceptive, however, since small changes in v_m could completely reverse this trend with little effect on the overall fit of the data. The model gave a satisfactory fit of the data at low relative humidities, but exhibited some deviation at the highest relative humidities (Figure 3a).

We tried an alternate approach of evaluating the constants C_1, C_∞, and v_m by a nonlinear parameter estimation method (NLIN in SAS IBM 3090) and obtained a better fit of the data at high relative humidities (Figure 3b). However, the data at low relative humidity were consistently underestimated. The values of C_1, C_∞, and v_m again decreased with increasing temperature, but differed substantially in magnitude from those evaluated by Sircar's method (Table 1).

The two primary assumptions in Sircar's model are that the adsorbate-surface interaction energy is constant after the first layer ($C_2 = C_3 = C_\infty$), and the number of adsorption sites is constant. For the strong water-starch polar interactions, it seems unlikely that the interaction energy is constant for different layers. If this is the case, the model would still predict adsorption at low relative humidities (at which a monolayer is formed) reasonably well, but would show deviations at high relative humidities since C_∞ is not really constant. Thus, it seems that Sircar's method for parameter estimation yields more meaningful values for C_1 and v_m than the nonlinear method.

The lack of a constant value for v_m was at first puzzling. Further analysis suggested that the swelling of starch, which occurs as water is sorbed, results in the breaking of inter- and intramolecular hydrogen bonds, and the exposure of additional sorption sites. This effect would be particularly pronounced at lower temperatures where a relatively high water loading may, in turn, promote an increase in available sites. Consequently, v_m should increase with decreasing temperature. The assumption that the number of adsorption sites remains constant over a range of temperatures would therefore not be applicable in this case.

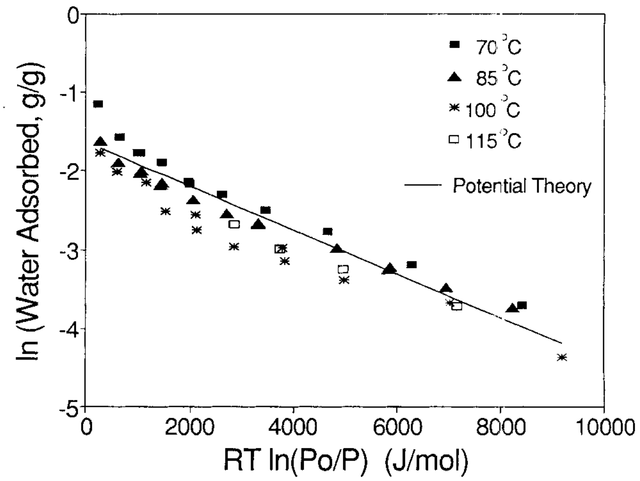

Figure 4. Dubinin's model for large-pore sorbents applied to water-starch adsorption.

Potential theory for water sorption

The potential theory was also applied to water-starch adsorption. Dubinin's theory for small-pore adsorbents exhibited poor agreement between the model prediction and actual data, particularly at high relative humidities (results not shown). The large-pore theory (Eq. 8) gave the fit to all the data shown in Figure 4. (Note that the density of the adsorbed phase is assumed constant.) If the isotherms are fit by the potential theory individually, the values of the slope, κ_2/β, were found to be similar (Table 2), while the intercept decreased as temperature increased. The corresponding limiting volume for adsorption decreased from 0.234 to 0.127 cm^3/g as the temperature increases from 70 to 115°C (an adsorbate density of 0.998 g/mL was assumed). This follows the same trend as the decrease in v_m in Sircar's model and, like the change in v_m, is probably a result of changes in the starch structure with changes in temperature.

Table 2. Parameters in Dubinin's Model Applied to Water-Starch and Ethanol-Starch Adsorption

	Water		
Temp.	κ_2/β	Intercept	*Wo* (mL/g)
70	0.000280	−1.45	0.234
85	0.000251	−1.76	0.172
100	0.000268	−1.97	0.139
115	0.000234	−2.07	0.127
Overall	0.000277	−1.64	0.194

	Ethanol		
	κ_2/β	Intercept	*Wo* (mL/g)
Total Ethanol	0.000167	−2.20	0.142
Reversible Ethanol	0.000287	−2.36	0.121

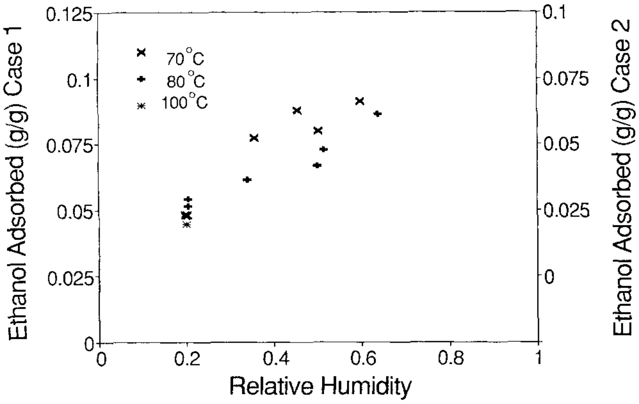

Figure 5. Ethanol-starch adsorption isotherms.

Case 1 assumes no prior adsorption of ethanol. Case 2 assumes irreversible adsorption of 2.5 g per 100 g starch.

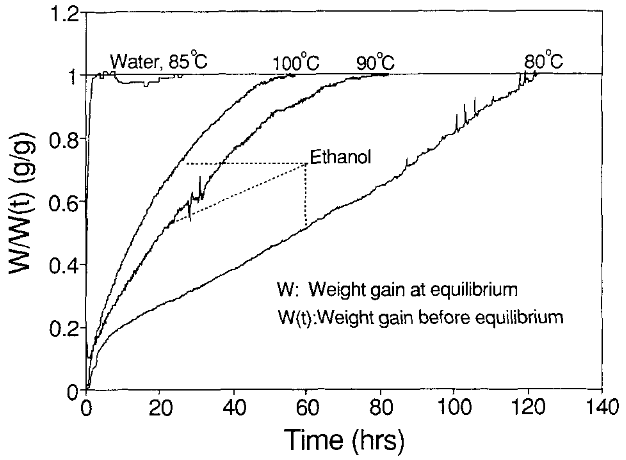

Figure 6. Time course of water-starch and ethanol-starch adsorptions at a relative humidity of 0.2.

Ethanol-starch adsorption

Ethanol sorption on starch required much longer periods than water to achieve equilibrium, particularly at the lower temperatures. The rigorous measurement of ethanol loading was further complicated by the presence of 0.08% to 0.3% by weight (0.2% to 0.8% by volume) water, despite very stringent and careful control of experimental conditions. This small amount of water originated from the ethanol in the saturator and gave a weight gain on the starch which was 5% to 10% of the total (ethanol + water). Consequently, the water content in the vapor phase was measured at the end of each adsorption experiment. The weight gain which would be due to the adsorption of water, estimated using the potential theory, was subtracted from the total weight gain. Finally, some irreversible ethanol adsorption (2-2.5 g ethanol/100 g dry starch) on starch was observed. Consequently, adsorption is shown based on two cases: (1) the pure dry weight of starch, that is, initial dry weight before the first adsorption; and (2) the initial dry weight of starch plus an additional weight of irreversibly adsorbed ethanol at 2.5 g per 100 g dry starch. Case 2 is of practical significance since the regeneration condition in an industrial cornmeal adsorber probably cannot remove this ethanol.

Duplicate evaluations of equilibrium weight gain at 80°C (relative humidity of 0.2) and 90°C (relative humidity of 0.2 and 0.5) exhibited less than 10% deviation with the 80°C runs at high humidities subject to a higher degree of variability (Figure 5). The total ethanol adsorbed (case 1) ranges from 80% to 90% of the equilibrium amount of water adsorbed on starch at similar relative humidity and temperature. The ethanol, which reversibly adsorbs (case 2) at equilibrium, ranges from 40% to 50% of the adsorption amount of water at similar conditions.

Since the potential theory for large pores agreed reasonably with the water adsorption results, it was applied to data for the total of reversibly and irreversibly sorbed ethanol. The slope and intercept were 0.000167 and −2.20, respectively. (The density of the adsorbed phase was assumed to be 0.798 g/mL.) For reversibly sorbed ethanol, the slope and intercept were 0.000287 and −2.36, respectively. The intercepts for the irreversibly and reversibly sorbed ethanol correspond to available pore volumes of 0.12 and 0.14 mL/g of starch. These values are lower than volumes of 0.139 to 0.172 at 100 and 85°C for water, and may reflect a lower extent of swelling for ethanol on starch compared to water.

The large extent of ethanol adsorption at equilibrium was surprising, since operational conditions in a packed-bed adsorber and elution profiles from GC columns packed with corn or starch and operated at 40 to 90°C gave excellent separation of water from ethanol and only a small apparent adsorption of ethanol (Hong et al., 1982; Rebar et al., 1984). More recently, Hassaballah and Hills (1990) and Crawshaw and Hills (1990) have reported operating conditions at which significant ethanol adsorption occurs. The long run times of the latter experiments suggest that residence time could be a factor, and would be consistent with reports of significant ethanol and methanol adsorption at 27°C on wheat starch after long periods (Bushuk and Winkler, 1957).

Ethanol uptake by the starch could, in part, be explained by sorption of the alcohol onto water. Under similar conditions, water is much more rapidly absorbed onto the starch than ethanol (Figure 6). The water-starch adsorption equilibrium at 80°C is attained in 3 to 4 hours, while the ethanol equilibrium loading requires at least 120 hours at a similar temperature, 85°C. However, prior adsorption of water would not be a major factor when previously dried starch is contacted

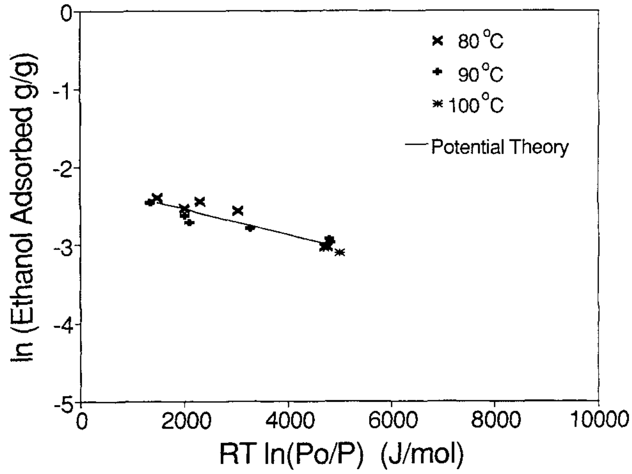

Figure 7. Dubinin's model for large pore sorbents applied to total ethanol-starch adsorption.

Table 3. Water-Ethanol-Starch Adsorption Isotherm at 90°C

Relative Humidity of Water	Relative Humidity of Ethanol	Ethanol + Water Adsorbed*	Water (A) Adsorbed (Calculated)**	Ethanol (B) Adsorbed (Calculated)†	(A) + (B)
0.109	0.2	0.0603	0.0305	0.0227	0.0532
0.113	0.273	0.0631	0.0313	0.0299	0.0612
0.118	0.296	0.063	0.0325	0.0321	0.0646
0.087	0.373	0.0607	0.0251	0.0395	0.0646

*Reversibly adsorbed; based on dry weight of starch in case 2.

**Based on Dubinin's equation for water-starch isotherm (Eq. 8) and overall water adsorption constants in Table 2.

†Based on Dubinin's equation for ethanol-starch isotherm (Eq. 8) and the constants for reversible adsorption of ethanol in Table 2.

with nearly anhydrous ethanol, as was the case for Figures 5 and 7. Consequently, ethanol adsorption can occur directly onto starch.

The rate of ethanol sorption decreases with decreasing temperature (Figure 6), and is consistent with Bushuk and Winkler's (1957) suggestion that a slower adsorption rate on wheat starch may reflect the slower diffusion rate of the ethanol relative to water. However, the diffusivities of water and ethanol through nitrogen differ only by a factor of 2 (0.305 cm^2/s for water and 0.168 cm^2/s for ethanol at 85°C based on Bird et al., 1960). We hypothesize that the interaction of starch with the adsorbate must also be a strong factor. This phenomenon suggests that the adsorptive separation of water from ethanol achieved with polysaccharide adsorbents is kinetically-controlled and that the separation in an adsorption column may be due to the much faster adsorption rate of the water vapor on starch as compared to ethanol vapor.

The measured extent of adsorption, when both water and ethanol vapors are present together (Table 3), is similar to the sum of the single-component loadings calculated from Eq. 8 and the appropriate constants given in Table 2. This indicates that there are enough adsorption sites for both water and ethanol molecules to adsorb at the low relative humidities studied. Hence, differences in adsorption rates are again indicated to be a factor.

Conclusions

Starch, which is the major constituent of corn, is considered responsible mainly for the water adsorption of corn. Previous studies have indicated hydroxyl groups in starch are the primary sites for the water molecule adsorption and found some qualitative relationships between the number of molecules of water adsorbed per hydroxyl group. In many cases, including biopolymers and nonorganic adsorbents, approximately 1 molecule of water is adsorbed per hydroxyl group for conditions where BET monolayer surface coverage occurs.

Among many models that could be applied to the water-starch and the water-grain adsorption isotherms, we have found that the recently developed Sircar's model accurately represented the water-starch adsorption isotherm data covering three different temperatures. The estimates for the parameters, however, are not completely consistent with the original assump-assumptions or expected trends. The potential theory (Dubinin's equation for large-pore sorbents) also accurately predicted water adsorption at a number of temperatures if the limiting volume of adsorbed phase is allowed to vary with temperature. The potential theory was also able to describe ethanol-starch sorption equilibria.

The observed rate of ethanol adsorption on starch was much slower than that of water. Two different stages were observed during the course of water-ethanol-starch adsorption: the first stage corresponds to water adsorption, while the second stage corresponds to ethanol adsorption. Hence, the water-ethanol separation may reflect a two-stage adsorption process. In the first stage, the total adsorbate on the surface quickly increases mainly due to water adsorption, while in the second stage, adsorption continues but at a much slower rate mainly due to ethanol uptake. The relationships between the properties of starch and rates of adsorption and the potential effects on ethanol dehydration are being investigated further.

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Notation

C_1 = constant in Sircar's model, dimensionless
C_∞ = constant in Sircar's model, dimensionless
N = number of moles of adsorbed phase, dimensionless
P = partial pressure of water at temperature T, atm
P_0 = vapor pressure of water at temperature T, atm
R = gas constant, J/mol·K
T = temperature, K
v = amount adsorbed in volume, cm^3/g
v_m = constant, monolayer amount adsorbed in volume, cm^3/g
V_m = liquid molar volume of adsorbate, cm^3/mol
W = $N \times V_m$ = volume of adsorbed phase, cm^3/g
W_0 = limiting volume of adsorbed phase, cm^3/g

Greek letters

β = affinity coefficient characterizing polarizability of the adsorbate, dimensionless
ϵ = adsorption potential, J/mol
κ_1 = constant in D-R model for large-pore sorbents, $(J/mol)^{-2}$
κ_2 = constant in D-R model for small-pore sorbents, $(J/mol)^{-1}$

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