Equilibrium Isotherms of Water and Ethanol Vapors on Starch Sorbents and Zeolite 3A

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An adsorption equilibrium apparatus (gravimetric method) was used to obtain the water vapor isotherms on zeolite 3A, potato starch, corn starch, cassava starch, and cellulose at room temperature. Experimental results show that at low relative pressure, $P/P^0 = 0.6$, the water−ethanol sorption ratio in potato starch was the highest at 64.2. The obtained sorption ratios from high to low are potato starch, cellulose, corn starch, cassava starch, and zeolite 3A. It was found that starch biosorbents are a better choice than zeolite 3A for the selective adsorption of water and ethanol. Several isotherm models—Langmuir, modified Brunauer−Emmett−Teller (mod-BET), Halsey, Smith, Henderson, Oswin, Ferro−Fintan, Guggenheium−Anderson−De Boer (GAB), or Peleg—were applied to fit the water and ethanol vapor equilibrium data obtained from this study. The accuracy of the models was evaluated by using the average relative deviation. The Langmuir model was better for the zeolite 3A adsorption system. The starch biosorbent isotherms were fitted well using the GAB, Ferro−Fintan, or Peleg models. The Peleg model with four parameters gave the best fit for the starch system, and the Smith model was good for the cellulose system.

Introduction

Ethanol dehydration using zeolite 3A sorbent is the industrial practice of today. However, the water vapor adsorption capacity of starch sorbents can be two times greater than zeolite.[1] Some starch sorbents will adsorb at most 50 % of their weight of water which can prevent formation of a gelatin mass and may retain their free-flowing granular state. But starch powders may have to be immobilized for handling and for recovery to reuse.

The need for an efficient method for dehydration of ethanol arises from the increasing demand for bioethanol as a renewable resource alternative to gasoline. Bioethanol with a moisture content less than 0.5 % (by weight) is blended with gasoline to make an alternative fuel called gasohol. Compared with unleaded gasoline, gasohol has a higher octane value and many other advantages. Bioethanol can replace the lead additive to lower the risk of explosion. With its higher oxygen content, bioethanol can increase the efficiency of combustion. Since bioethanol has a higher flash point and ignition point than gasoline, gasohol storage is safer than gasoline. It also reduces the release of CO by (20 to 30) % and CO_2 by about 25 % from the fuel. On the other hand, current engines may need to be modified when the fuel is a gasoline−bioethanol mixture.

Distillation is the traditional method to separate water from fermentation ethanol, which is (10 to 15) % (by weight) ethanol. The bottleneck here is the azeotrope, where the mixture is still only 95.6 % (by weight) ethanol. Since ethanol as a gasoline additive must be anhydrous alcohol with a moisture content less than 0.5 % (by weight), more separation is required. After distillation, the next step is a dehydration process. It is estimated that perhaps 50 % of the total energy consumption of an alcohol plant is used in the distillation and dehydration section.

There are recent reports[2,3] which describe membrane pervaporation for ethanol dehydration. Compared with distillation, membrane pervaporation saves energy, but this new method can be difficult to scale up for industrial-quantity production. Adsorption technologies[4,5] have also been reported to remove low levels of water from ethanol,[6−13] for example, dehydration with molecular sieves using zeolite 3A. The objective of this work is to compare selected biosorbents—potato starch, corn starch, cassava starch, and cellulose—with zeolite 3A in gas-phase and liquid-phase adsorption. These selected biosorbents require only moderate temperatures for regeneration and their adsorption characteristics to remove water from ethanol deserve more study. Several isotherm models—Langmuir, modifieed Brunauer−Emmett−Teller (mod-BET), Halsey, Smith, Henderson, Oswin, Ferro−Fintan, Guggenheium−Anderson−De Boer (GAB), or Peleg—were applied to fit the water and ethanol vapor equilibrium data obtained from this study.

Experimental System

Sorbents. The sorbents which were used in this experiment were commercial zeolite 3A, cassava starch, corn starch powder, potato starch and cellulose. The surface properties were measured with a BET sorptometer (Micromeritics ASAP 2000). Each sorbent was degassed at (373 ± 1) K under vacuum before nitrogen adsorption measurements were carried out at (77 ± 1) K. The specific surface area and total pore volume were calculated by the BET method. The physical characteristics and the suppliers of the adsorbents are listed in Table 1.

Sorbates. Ethanol (Echo, 99.5 %) and deionic water vapors were selected as the sorbates in this study.

Apparatus and Procedure. Figure 1 shows the adsorption equilibrium apparatus used in this study.[14−16] The mass change during adsorption was measured by an electronic microbalance (Cahn C-33). The uncertainty of the microbalance was 0.1 μg. The pressure of this system was controlled from ($1.333 \cdot 10^2$ to

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Table 1. Physical Properties of the Adsorbents

adsorbent	supplier	BET surface area $m^2 \cdot g^{-1}$	pore volume $cm^3 \cdot g^{-1}$
zeolite 3A	Alfa Aesar	26.5935	0.0935
cassava starch	Ten-ii company	0.0454	0.0002
potato starch	ICE Biomedicals	0.0676	0.0010
corn starch powder	Sigma	0.0123	0.0004
cellulose	Sigma	0.0914	0.0023

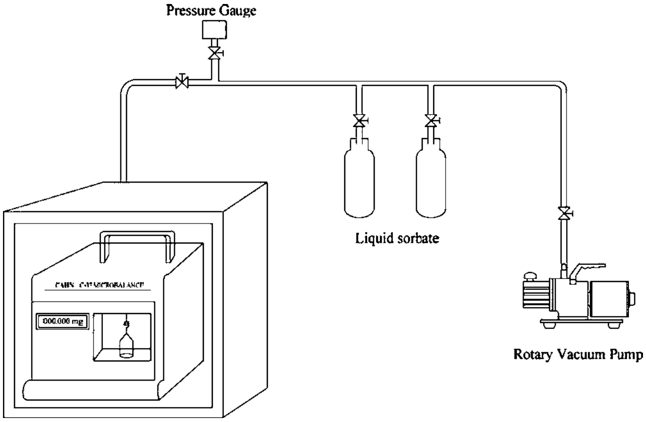

Figure 1. Static adsorption apparatus (gravimetric method) used in this work.

$3.999 \cdot 10^4$) Pa and measured with a pressure gauge (Cole Parmer U-68700, uncertainty ± 0.1333 Pa). The temperature of the microbalance compartment was maintained at 297 K, and the adsorption isotherms were plotted as the adsorption capacity (mg sorbate/g sorbent) versus relative pressure, P/P^0, where P is the operating pressure (Pa) and P^0 is the saturated vapor pressure of the liquid sorbate (Pa). After regeneration in a vacuum dryer (at 373 K for 24 h), about 50 mg of granular sorbent was placed on the pan of the microbalance. The liquid sorbate was then put into glass bottles in a constant temperature water bath (see Figure 1). Degassing (thawing then freezing) was repeated at least three times. To get the desired amount of volatile vapor into the adsorption chamber, the temperature of the water bath was varied. At equilibrium, the amount of sorbent and sorbate was recorded together with the equilibrium pressure of the adsorption system. The amount of sorbate vapor for adsorption was increased, and the system was allowed to come to equilibrium again for another reading.

In this study the microbalance gravimetric method was used to obtain the adsorption isotherms. This static adsorption apparatus is shown in Figure 1. Before each experiment, the adsorbent was placed in a vacuum oven for 24 h to remove impurities and moisture from the adsorbent. Then (10 to 15) mg of regenerated adsorbent particles were placed on the microbalance, and the weight was recorded. Vacuum was then switched on to reduce the system pressure to 2.666 Pa with the system temperature maintained at the room temperature of 297 K (24 °C). When the entering gas adsorbate reached the desired value for pressure, the valve was closed to start the adsorption of the gas onto the sorbent on the microbalance. Adsorption equilibrium was achieved when the microbalance reading remained constant. The weight reading shown on the microbalance was recorded together with the final system pressure. This process was repeated, and more adsorbate gas was added into the system until the final system pressure reached the saturated vapor pressure. The experimental data are presented as the equilibrium isotherm obtained by plotting the adsorption uptake versus the relative pressure P/P^0 of adsorbate gas.

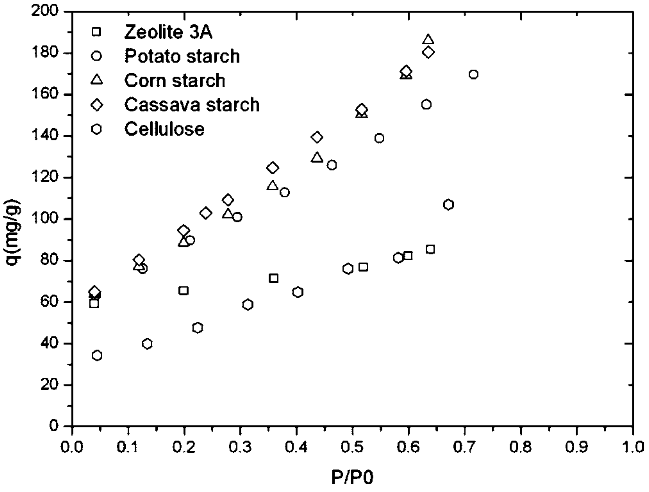

Figure 2. Water vapor equilibrium isotherms for selected sorbents (297 K).

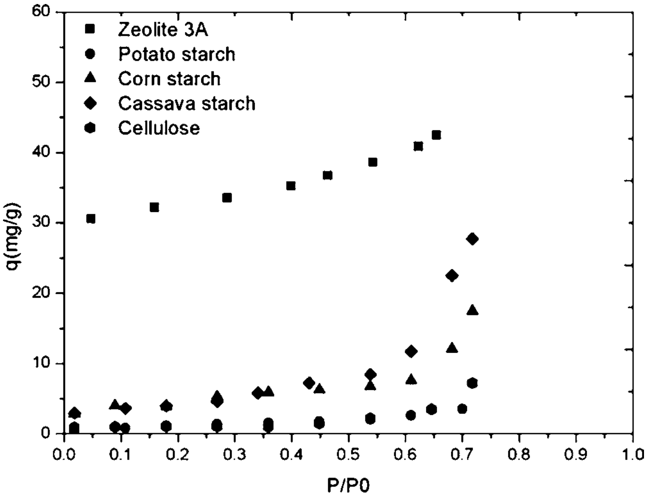

Figure 3. Ethanol vapor equilibrium isotherms for selected sorbents (297 K).

Results and Discussion

Equilibrium Isotherms. The starch sorbents and zeolite 3A are two different types of sorbents based on their material nature and surface properties in Table 1. Since zeolite 3A has been widely used in the ethanol dehydration process in industry, any new sorbent for ethanol dehydration should be compared with the adsorption uptake of zeolite 3A. Zeolite 3A (mean pore size 0.38 nm) is known to be a good sorbent for water vapor. As shown in Figures 2 and 3, for a relative pressure of $P/P^0 \sim 0.7$, water vapor adsorption on zeolite 3A was 82.1 $mg \cdot g^{-1}$, and ethanol adsorption was 40.9 $mg \cdot g^{-1}$.

The starch adsorbent is (70 to 80) % amylopectin which is a compact, highly branched molecule with up to a million glucose residues. The glucose units in the spiral side chain bundles have OH^- groups that can hydrogen bond with water or ethanol molecules. Amylopectin exhibits selective adsorption for H_2O (critical diameter 0.28 nm) and C_2H_5OH (critical diameter 0.44 nm) because ethanol is a bigger molecule and encounters steric hindrance in forming hydrogen bonds and thus has lower adsorption. Because of the smaller molecular size of water, it can more easily get into the 3-D branching structure of amylopectin. More extensive hydrogen bonds can be formed by the interaction of water and amylopectin than by the interaction of ethanol and amylopectin. As shown in the

Table 2. Water−Ethanol Adsorption Ratio at Relative Pressure $P/P^0 = 0.6$

adsorbent	water mg water/g adsorbent	ethanol mg ethanol/g adsorbent	adsorption ratio mg water/mg ethanol
zeolite 3A	82.1	40.9	2.0
potato starch	167.6	2.6	64.2
corn starch	169.2	7.6	22.3
cassava starch	171.3	11.7	14.6
cellulose	81.3	3.5	23.2

Table 3. Regression Constants and Mean Relative Deviation of Selected Adsorption Models for Water Vapor Adsorption Data in This Work (297 K)

model	constants	zeolite 3A	potato starch	corn starch	cassava starch	cellulose
GAB	X_0	3.364	0.086	0.078	0.09	0.041
	C	834.249	105.07	87.581	59.455	82.51
	K	0.397	0.765	0.919	0.77	0.916
	E(%)	3.4	2.37	1.78	2.55	4.1
Peleg	K_1	10	0.156	0.231	0.158	0.173
	K_2	103.148	0.109	0.108	0.091	0.074
	n_1	0.001	1.976	2.236	1.346	3.754
	n_2	0.001	0.140	0.166	0.119	0.27
	E(%)	46.3	1.41	1.02	0.50	4.71
Ferro−Fontan	γ	259.202	0.013	0.013	0.069	0.002
	α	292.044	1.092	0.918	1.49	0.875
	r	90.623	0.486	0.508	0.7	0.47
	E(%)	15.5	1.74	1.03	0.94	3.36
Henderson	A	11.426	200.233	71.376	122.802	238.126
	B	0.016	2.922	2.434	2.697	2.299
	E(%)	0.9	6.26	7.42	4.07	8.13
Oswin	A	9.9	0.141	0.148	0.145	0.078
	B	0.004	0.273	0.337	0.296	0.351
	E(%)	7.1	4.24	5.28	2.34	6.12
Halsey	A	0.505	0.923	2.913	1.465	0.964
	B	0.102	2.3	1.774	2.102	1.756
	E(%)	0.1	1.72	1.34	2.49	3.52
mod-BET	X_0	0.01	0.096	0.107	0.102	0.056
	C	0.729	48.632	20.795	29.032	18.768
	E(%)	2.5	3.49	7.37	4.09	8.01
Smith	A	3.298	0.072	0.061	0.069	0.031
	B	−2.631	−0.214	−0.282	−0.24	−0.149
	E(%)	1.2	2.78	1.18	3.77	2.58
Langmuir	q_m	0.08	0.218	0.26	0.239	0.0157
	K_L	2.421	0.192	0.112	0.143	0.096
	E(%)	6.58	14.38	14.59	11.39	15.49

adsorption isotherms of starch in Figures 2 and 3, the selectivity of starch for water and ethanol was significant.

The relative separation of ethanol and water by starch adsorbents was better compared to zeolite 3A (see Table 2). At a low relative pressure of adsorbate, water vapor adsorption in starch was more than in zeolite 3A. When the relative pressure $P/P^0 = 0.6$, the water vapor adsorption on starch ((167.6 to 171.3) $\text{mg}\cdot\text{g}^{-1}$) was twice that in zeolite 3A (82.1 $\text{mg}\cdot\text{g}^{-1}$). Because of the 3-D steric obstacle presented by the highly branched amylopectin molecule, ethanol adsorption on starch was mostly below 20 $\text{mg}\cdot\text{g}^{-1}$, while ethanol adsorption on zeolite 3A was 40.9 $\text{mg}\cdot\text{g}^{-1}$. Potato starch had the highest water−ethanol sorption ratio at 64.2.

The mechanism of adsorption for cellulose and starch is similar. Cellulose consists of linear extended polysaccharides with up to several thousand glucose units. It has a more crystalline structure than starch due to extensive hydrogen bonds within and between individual polysaccharide chains. Cellulose also has OH^- in the glucose units to hydrogen bond with water and ethanol. Figure 2 shows that water vapor adsorption in starch was better than cellulose.

Isotherm Modeling for Equilibrium Data. The isotherm models that were used to fit the data are Langmuir, mod-BET, Halsey, Smith, Henderson, Oswin, Ferro−Fintan, GAB, and Peleg. A nonlinear least-squares regression was used to determine the model parameters. The mean relative deviation (D) value was calculated to evaluate the goodness of fit of the various isotherm models,

$$D = \frac{1}{N}\sum_{\text{i}=1}^{n}\left|\frac{m_\text{i} - m_\text{pi}}{m_\text{i}}\right|\cdot 100\ \%$$

where D = mean relative deviation (%), N = number of experimental data, m_i = experimental data, and m_pi = calculated values from model.

The Langmuir model is often used to describe monolayer adsorption. As shown in Table 3, the Langmuir model regression in the case of zeolite 3A had the lowest mean relative deviation. Therefore, the equilibrium gas adsorption theory from the Langmuir model was more suitable for water vapor adsorption in zeolite 3A. As for starch and cellulose, the Langmuir model may not be applicable.

Several isotherm models are mentioned in the literature:[7,17−20] two-parameter models (such as mod-BET, Halsey, Smith, Henderson, and Oswin), three-parameter models (such as Ferro−Fintan and GAB), and a four-parameter model (Peleg). These models were used to fit the experimental data of starch and cellulose for water vapor sorption, and the results are also given in Table 3. On the basis of the values of the mean relative deviation, the use of the Halsey, Smith, GAB, Ferro−Fintan, and Peleg models to describe starch adsorption appear to be appropriate. The four-parameter Peleg model gave the lowest mean relative deviation. Previous work[7] has shown that the Halsey and Smith model can give accurate correlations for the starch adsorbents used in the present work. However, the Henderson, Halsey, mod-BET, and Smith models to describe zeolite 3A adsorption also appear to be appropriate.

The important variable in the Halsey model is temperature. In an earlier study,[11] the isotherm regression for potato starch had mean relative deviations which decreased from (68.7 to 36.3) % when the temperature is lowered from (60 to 30) °C. The temperature in this work was 24 °C, and the Halsey model showed a good regression fit. In the Smith model, the relevant relative pressure range is from 0.35 to 0.9. The relative pressure in this work is within this range, and so the Smith model showed a good regression fit too.

The three models—Peleg, Halsey, and Smith—were able to describe the water vapor isotherms of starch adsorbents. For cellulose, the Smith model gave the best result for water vapor sorption. As shown in Table 3, its mean relative deviation is 2.58, which was the lowest among the models considered in this study. The other models (Halsey, GAB, Ferro−Fintan, and Peleg) can also fit the adsorption behavior of cellulose adsorbents with mean relative deviations within (3 to 5) %. The three remaining models—Henderson, Oswin, and mod-BET—did not give satisfactory regression results for starch and cellulose.

Since the equilibrium isotherm data of ethanol vapor adsorption on different sorbents were also recorded in this study, the regression constants and mean relative deviation of selected adsorption models (as shown in Table 4) for the ethanol vapor adsorption isotherm data were obtained through the model regression. On the basis of the values of the mean relative deviation, the use of the Halsey, Smith, GAB, Ferro−Fintan, and Henderson models to describe starch adsorption appear to be appropriate. However, the Oswin, Henderson, Smith, and Langmuir models to describe zeolite 3A adsorption also appear to be appropriate.

Table 4. Regression Constants and Mean Relative Deviation of Selected Adsorption Models for Ethanol Vapor Adsorption Data in This Work (297 K)

model	constants	zeolite 3A	potato starch	corn starch	cassava starch	cellulose
GAB	X_0	1.178	0.03	0.112	0.103	0.286
	C	83.78	65.779	8.712	60.085	0.106
	K	0.286	1.039	1.087	1.224	0.995
	E(%)	2.7	0.5	2.7	0.9	0.3
Peleg	K_1	0.388	0.309	0.463	1.079	0.018
	K_2	1.661	0.215	0.156	0.101	0.001
	n_1	0.477	0.045	0.656	1.104	95.49
	n_2	1.381	0.119	1.181	0.189	105.633
	E(%)	128.3	8	5.6	18.6	1.3
Ferro−Fontan	γ	0.362	0.354	0.019	0.016	0.007
	α	27.115	1.223	0.983	0.846	7.094
	r	0.006	37.069	0.016	0.013	0.001
	E(%)	5.9	2	2.5	1.6	2.5
Henderson	A	1.114	0.863	0.768	0.542	6.728
	B	1.235	159.291	13.888	11.735	1.347
	E(%)	3.2	2.6	4.5	10.2	0.8
Oswin	A	0.229	0.005	0.047	0.113	0.006
	B	0.022	116.819	17.408	7.413	160.802
	E(%)	0.4	1.6	4.9	4.8	0.4
Halsey	A	270.882	1.574	1.681	2.592	20.954
	B	2.052	0.016	0.001	0.001	1.507
	E(%)	158.6	0.9	2.5	6.2	0.5
mod-BET	X_0	0.073	0.014	0.644	5.453	9.654
	C	26.297	0.43	0.022	0.004	0.001
	E(%)	15.8	6.1	4	6.1	0.5
Smith	A	0.973	0.017	0.061	0.281	0.131
	B	−0.473	−0.162	−0.646	−0.091	0.178
	E(%)	2.8	2.6	3.3	77.4	8.9
Langmuir	q_m	1.185	84.162	2.866	16.839	33.539
	K_L	61.601	0.002	0.208	0.05	0.006
	E(%)	3.4	8	5.9	19.1	1.3

Conclusion

The results of gas-phase adsorption studies in this work show that for water vapor adsorption starch is better than zeolite 3A and cellulose. For liquid-phase adsorption, the results show that starch has competitive adsorption capacities compared to zeolite 3A, although zeolite 3A may be preferable in this case because starch sorbents may need to be immobilized for handling and reuse.

In gas-phase adsorption, ethanol adsorption using starch was $< 12\ \mathrm{mg \cdot g^{-1}}$, whereas water adsorption in these starch adsorbents was $\sim 170\ \mathrm{mg \cdot g^{-1}}$. Compared with zeolite 3A, starch adsorbents are the better choice for the selective adsorption of water and ethanol. Potato starch might have the best water−alcohol selective separation in the gas phase with a ratio of 64.2 at 24 °C.

In the regression evaluation of isotherm models for water vapor sorption, it was clear that the Langmuir model was suitable for the equilibrium isotherm of zeolite 3A; the GAB, Ferro−Fontan, and Peleg models had good regression results for the starch adsorbents, and the Peleg model had the best regression result for starch adsorbents in this work. For cellulose, the Smith model gave the best regression result.

The selected biosorbents in this study are granular powders. The handling and physical stability for their reuse is not as good as zeolite 3A particles. The immobilization of starch adsorbents will be investigated in future work.

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