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Kinetic and Thermodynamic Study on the Liquid Phase Adsorption by Starchy Materials in the Alcohol-Water System

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Abstract. Improving adsorptive processes demands a constant search for new adsorbents. In the case of alcohol-water separation, zeolites are widely used. The use of new adsorbents as a substitute for zeolites, mainly starch, has been proposed recently. This work is a thermodynamic and kinetic study of liquid phase adsorption of water from methanol, ethanol, propanol and butanol-water mixtures using starch as the adsorbent. The thermodynamic data were obtained by means of the static method at three different temperatures (25, 40 and 50°C), and were correlated by the Langmuir isotherm. The kinetic data were obtained in a finite liquid bath cell. The influence of temperature and molecular chain length of the alcohol on the capacity and adsorption rate were determined.

Keywords: alcohol, starch, adsorption

Introduction

One of the main problems related to the production of anhydridrous ethanol derived from fermentation is the high cost of separating ethanol from the fermentation broth. When distillation is used to dehydrate ethanol, 50% of the total energy is consumed. This frequently indicates a negative energy balance. An alternative to this process is the use of preferential adsorption of water, using specific adsorbents for this purpose, such as cellulose and starch, studied by Ladisch and Dyck (1979).

Numerous studies have proven that it is possible to use biomaterials for ethanol dehydration. Ladisch and Hong (1983) studied the separation of ethanol-water mixture, in the vapor phase, using starch (corn and potato), xylan, pure cellulose and corn residue. They concluded that these materials had the capacity of adsorbing water in the decreasing order: corn starch, corn residue, xylan and pure cellulose. They explained this fact due to concentration of amylopectin present in each studied materials, that is to say, the capacity of adsorption will be greater when the concentration of amylopectin be great. In other work, Robertson et al. (1983) used starch, at the ambient temperature, in adsorption of ethanol vapors and water simultaneously in a closed recirculating system. They found evidence of considerable ethanol adsorption under several different conditions.

Since 1989, the use of starch products to adsorb water, have been broadly studied to develop models for fitting experimental thermodynamic and kinetic data for this new adsorbent. Hills and Pirzada (1989) studied the adsorption of pure water vapor on starch using the air as a carrier gas. Thermodynamic data were obtained by varying the relative humidity of the air from 17 to 78% and measuring the weight gain of the adsorbent at equilibrium at 40°C. The isotherms show adsorption capacity on the order of 0.16 g of water/g of starch. They studied, also, the kinetics of the process and concluded that the saturation of the bed happens in around 2 hours, with the adsorbed amount being directly proportional to the concentration of water in the

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air. The maximum diffusivity value obtained was at the order of 14.10^{-13} m^2/s.

In a subsequent work, Hassaballah and Hills (1990) analyzed the influence of some parameters in the adsorption drying process of an ethanol-water mixture, in the vapor phase, with starch adsorbents. The following effects were examined: variation of particle size, water concentration and feed flow rate. Also the regeneration conditions of the bed on the quality of the final product and breakthrough times were investigated. They concluded that an ethanol concentration of 85% by weight in the feed produced a better product, where the final concentration was around 99.8% ethanol by weight.

Crawshaw and Hills (1990) studied adsorption on starch adsorbents to obtain the selectivity of such a material for ethanol and water. They determined that these materials adsorb more water than ethanol, using a feed ethanol concentration of 5% by weight at 90°C. The selectivity, according to these authors can be improved, increasing the amount of amylopectin present in the starch.

Crawshaw and Hills (1992) complemented the in previous work with on adsorption kinetics study. They determined the rates of adsorption for both components and subsequent desorption with warm feed. The form of the adsorption curve for the ethanol at 90°C, atmospheric pressure, and feed concentration below 90% ethanol by weight did not seem very usual, and fast initial uptake preceded temporary desorption and finally, slow readsorption until equilibrium was reached. For feed concentrations above 90% ethanol by weight, this temporary desorption was not observed.

Recently, two works stand out in the study of the adsorption on nonconventional adsorbents. In the first, Westgate and Ladisch (1993) studied the adsorption of present water in several organic solvents, such as organic acids, alcohol, cetones, ethers and aromatics, using starch adsorbents. They concluded that small apolar molecules, e.g., methanol and formic acid, will have smaller mass transfer rates and less strong interactions with the starch, due to their high polarity, and they are more difficult to separate from water than constituents with high molecular weight or low polarity.

In a second work, Carmo (1995) developed a thermodynamic and kinetic adsorption study of water in an ethanol-water mixture, in liquid phase, on "pellets" of manioc starch. It was concluded that the starch has affinity for the water in the presence of ethanol, with an adsorption capacity of around 15% by mass at 25°C. This capacity decreases as temperature increases. The adsorptive process kinetics depended on: temperature, interstitial velocity, and diameter of the particles. It was concluded that an increase in temperature caused an increase in the adsorption rates, though it decreased the capacity to retain water at equilibrium.

Table 1. Manioc Starch physical parameters.

Mean diameter (mm)	Tyler/Mesh (mm)	Mean mass (g)
2.19	2.00–2.38	0.0101
2.60	2.38–2.83	0.0131
3.09	2.83–3.36	0.0201
3.68	3.36–4.00	0.0302
Apparent density (g/ml)	Real density (g/ml)	Porosity pore diameter (μm)
1.157	1.558	0.257
		0.35

Materials and Methods

Manioc starch spherical pellets, commercially obtained in 500 g packages with diameters ranging from 2.00 to 4.00 mm, were used. They are constituted basically of amylopectin and amylose, have a hard structure, and do not swell in the experimental concentration range of the kinetic and thermodynamic study. Physical characterization of this material can be found in the work of Carmo and Gubulin (1995), and is summarized in Table 1.

The alcohol-water solutions were prepared at the required mass concentrations (concentration range from 0 to 50 wt% alcohol for the thermodynamic tests and at around 90 wt% alcohol for the kinetic tests) from methanol, ethanol, propanol and butanol (of the Synth) brand and distilled water, using a scale of 0.001 g accuracy. The commercial alcohol was treated with previously activated 3A zeolite (300°C for 24 h) in order to remove any remaining water.

For measuring the concentration of the fluid phase, a Reichert-Jung Auto Abbé refractometer with automatic calibration was used and data reproducibility at the order of 0.5% was obtained in this experimental concentration range.

Experimental Procedure

The equilibrium data were obtained by a static method, which consists at adding a specific amount, M_s, of treated thermally (105°C for 16 h) adsorbent (≅15 g), and a specific mass, M_f, of aqueous alcohol solution (≅50 g) with a well-known initial concentrations, W_b^o to a 125 ml flask. Several initial concentrations were used in order to obtain a wide range of isotherms at three different temperatures (25, 40 and 50°C). The flasks were maintained in a thermostatic bath with an accuracy of ±0.1°C, and gently shaken during approximately seven days, where after this the fluid phase concentration was measured and the final concentration, W_b, of the liquid was determined.

In order to obtain the amount of water adsorbed in the solid phase, a mass balance was used between the phases, where alcohol was considered to be the nonadsorbable component. This hypothesis agrees with the work of Rebar et al. (1984), where it was demonstrated that the chemical affinity of starch to water is much greater than alcohol. Equation (1) describes the mass balance, where at equilibrium $t \to \infty$, $W_b \to W_b^e$.

$$q_s = \frac{M_f}{M_s}\left[\frac{W_b^e - W_b^o}{W_b^e}\right] \tag{1}$$

To obtain kinetic data, the static method was again used. This method allows the accomplishment of experiments by immersion in a thermostatic system, with less variation of the liquid volume and little mechanical damage during the experiment, and with relative ease of operation, and control of the initial conditions and collection of samples.

The material used in the finite bath method, consists of:

I. Glass cell, where the adsorbent and the alcohol-water mixture are contacted;
II. Glass hypodermic syringe, to withdraw samples of the alcohol-water mixture, during the transient process of adsorption;
III. Agitator (in the glass cell), to increase the contact between the solution and the adsorbent, minimizing the formation of the external liquid film to the particle;
IV. Thermostatic bath, to the control the temperature.

For a typical kinetic mass transfer test, alcohol-water solutions were prepared with a given mass M_f (≅75 g) with an initial concentration W_b^o (≅10 wt% water) and placed in a sealed thermostatic cell. As soon as the system reached thermal equilibrium, a device at the cap was removed from the cell and, at time $t = 0$, a mass of thermally treated adsorbent M_s (≅25 g) was introduced into the cell as quickly as possible. The system was then sealed and, at regular time intervals, liquid samples were taken through a rubber septum with a long hypodermic needle. The sample concentration was measured by means of refractometry. The concentration of the adsorbed phase was obtained by a simple mass balance, which considered alcohol as the nonadsorbable component, according Eq. (2).

$$q_{(t)} = \frac{M_f}{M_s}\left[\frac{W_{b(t)} - W_b^o}{W_{b(t)}}\right] \tag{2}$$

where $q_{(t)}$ is the concentration of the adsorbed phase (g/gads), at the instant t and $W_{b(t)}$ is the concentration of alcohol on solution, at the instant t. It fits to stand out that the alcohol used for the kinetic experiments were the methanol, ethanol, propanol and butanol.

Results and Discussion

Equilibrium Data and Thermodynamic Model

The obtained isotherms, which relate the concentrations on liquid and solid phases at the temperatures of 25, 40 and 50°C, can be seen in Figs. 1–4, respectively to the methanol, ethanol, propanol and butanol.

From the isotherms it can be noted that there is a decrease of adsorption capacity (represented by horizontal plateau) with temperature increases. This is because of the increase in the molecular vibratory energy, which at higher temperatures favors a smaller number of adsorbed molecules at the equilibrium. Due to the exothermic character of the adsorption process, an

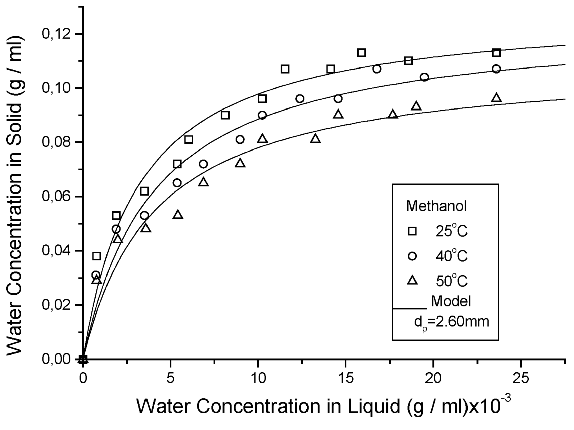

Figure 1. Adsorption isotherms to the methanol-water/starch system.

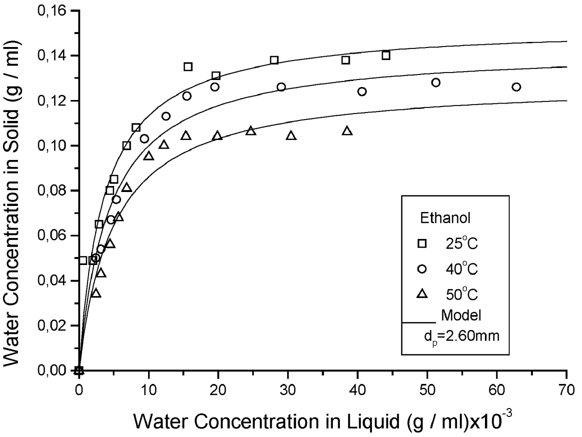

Figure 2. Adsorption isotherms to the ethanol-water/starch system.

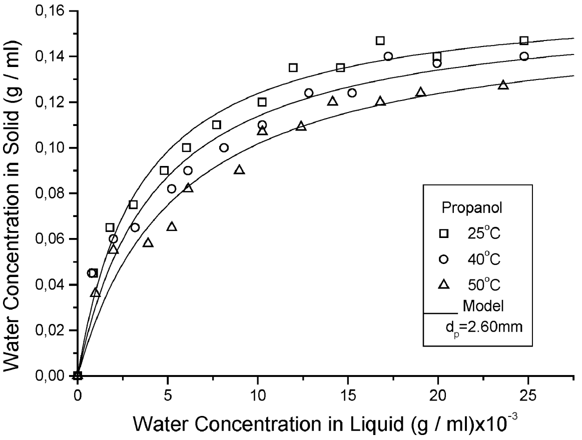

Figure 3. Adsorption isotherms to the propanol-water/starch system.

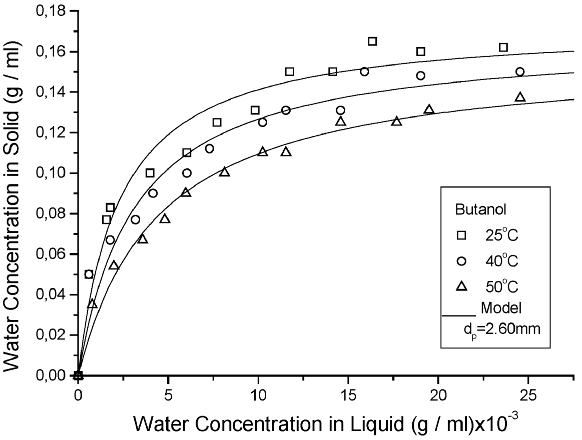

Figure 4. Adsorption isotherms to the butanol-water/starch system.

increase in temperature dislocates the equilibrium towards the region unfavorable to adsorption. A physical model was used to correlate the equilibrium data in this temperature range. The model is represented by the Langmuir isotherm, defined by Eq. (3).

$$\frac{q_s}{q_\infty} = \frac{KC_i}{1 + KC_i} \tag{3}$$

where q_∞ is the maximum adsorption capacity at the operation temperature (g/ml), C_i is the water concentration on liquid (g/ml) and K is the constant of Langmuir.

The parameters of this equation were related with temperature via a computer program, using an nonlinear parameter estimation routine. Tables 2–5 show the

Table 2. Langmuir Parameters obtained to methanol.

Temperature (K)	q_∞ (g/ml)	K (ml/g)
298	0.129	0.309
313	0.124	0.244
323	0.110	0.241

Table 3. Langmuir Parameters obtained to ethanol.

Temperature (K)	q_∞ (g/ml)	K (ml/g)
298	0.153	0.278
313	0.143	0.229
323	0.128	0.203

Table 4. Langmuir Parameters obtained to propanol.

Temperature (K)	q_∞ (g/ml)	K (ml/g)
298	0.166	0.289
313	0.163	0.230
323	0.158	0.180

Table 5. Langmuir Parameters obtained to butanol.

Temperature (K)	q_∞ (g/ml)	K (ml/g)
298	0.173	0.435
313	0.166	0.316
323	0.158	0.223

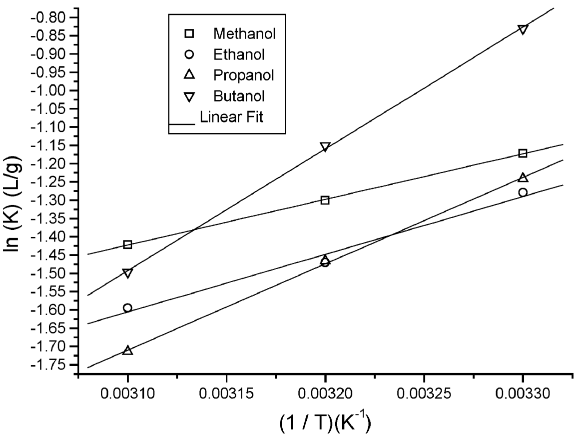

Figure 5. Langmuir Parameter as temperature function.

results, respectively, for methanol, ethanol, propanol, and butanol.

From these relations the parameter K was fitted as a function of temperature within the range 298–323 K through the van't Hoff equation represented in Fig. 5 and described by Eq. (4). The values of heat of sorption are illustrated in Table 6. Since adsorption is exothermic (ΔH is negative), K must decrease with increasing temperature.

$$K = K_o \exp\left(\frac{-\Delta H}{RT}\right) \tag{4}$$

It is interesting to compare the alcohol equilibrium curves at the same temperature, in order to obtain the influence of the molecular chain size of the alcohol on the adsorption capacities. The results of the adsorption thermodynamic study for the systems methanol-water, ethanol-water, propanol-water, and butanol-water on the starch, at the same temperature, indicate that an increase of the alcohol chain length leads to an increase of maximum adsorption capacity. This happens due to the decreasing polarity of the alcohol, which reduces the competition between the water and the alcohol in relation to adsorption by the starch. This can be observed for all alcohols studied and for all of the adsorption temperatures. That indicates that the presence of amylopectin in the starch is mainly responsible for the water adsorption, in contrast with the amylose, which is a linear and apolar molecule. The values of obtained sorption heat were also consistent with this hypothesis.

Table 6. Heat of sorption values.

Alcohol	$-\Delta H$ (kcal/g-mol)
Methanol	2.481
Ethanol	3.138
Propanol	4.697
Butanol	6.623

Kinetic Data and Mathematical Model

The kinetic results are presented by means of uptake rate curves, relating the amount of water adsorbed by the solid or the dimensionless concentration on the adsorbed phase (ψ) for each time. Parameters like temperature and molecular chain of the alcohol were related to the adsorption rates.

A version of the pore diffusion model was applied with the diffusion resistance concentrated in the macropores. That model satisfactorily represented the experimental data, making it possible to estimate the diffusivities for several temperatures. The pore and bath mass balance was represented by Eqs. (5) and (6), respectively.

$$\frac{\partial C_i}{\partial t}\left[(1-\varepsilon_p)\frac{\partial q_s}{\partial C_i}+\varepsilon_p\right] = \varepsilon_p \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_p \frac{\partial C_i}{\partial r}\right) \tag{5}$$

$$\frac{\partial C_{b,i}}{\partial t} = \left[-\frac{(1-\varepsilon)}{\varepsilon}\frac{3}{R_p}\varepsilon_p D_p \frac{\partial C_i}{\partial r}\right]_{r=R_p} \tag{6}$$

The Eqs. (5) and (6) may be solved through the boundary conditions represented by Eqs. (7)–(9):

$$\text{at } t = 0 \quad C_i = C_{io} \quad \text{and} \quad C_{b,i} = C_{b,io} \tag{7}$$

$$\text{at } r = 0 \quad \frac{\partial C_i}{\partial r} = 0 \tag{8}$$

$$\text{at } r = R_p \quad C_i = C_{b,i}(t) \tag{9}$$

The solution of the foregoing partial differential equations (Eqs. (5) to (9)) was accomplished through discretization on space domains, using orthogonal Jacobi polynomials. The system of equations gives, for each instant a value of concentration in pellet and the value of concentration on solid surface, at function of adjustable kinetic data. Effective diffusivities were obtained through the relation between the experimental and predicted concentrations. The resulting sets of ordinary differential equations are solved in time with a marching procedure, i.e., subroutine DASSL (Petzold, 1989). Tests indicate that five internal collocation points are sufficient to provide a precise answer.

The objective function is, in this case one-dimensional, because the experiments are isothermal and the results were uni-modal.

A Tortuosity factor was calculated for all kinetics experiments through Eq. (10).

$$\tau = \frac{D_m}{D_p} \tag{10}$$

where D_p is pore diffusivity obtained from kinetic study, D_m is molecular diffusivity of water in alcohol, obtained by the Wilke and Chang correlation presented by Perry and Green (1984) and given by Eq. (11).

$$D_m = 7.4 \cdot 10^{-8} \frac{(\phi M_B)^{0.5} T}{\eta_B V_A^{0.6}} \tag{11}$$

Its terms are represented by molecular weight of solvent in g/mole, M, absolute temperature in Kelvin, K, viscosity of solvent in cP, η, molar volume of solute at its normal boiling temperature in cm^3/Mol, V, and a dimensionless association factor for the solvent, ϕ, for which recommended values are 1.9 if solvent is methanol, 1.5 for ethanol, and 1.0 for unassociated solvents like propanol and butanol. The molar volume of water at its normal boiling temperature was obtained by Tyn and Calus correlation, presented by Perry and Green (1984) and given by Eq. (12).

$$V_b = 0.285 V_c^{1.048} \tag{12}$$

where V_c is the critical molar volume.

The temperature is of great interest for kinetic adsorption processes, as its influence on diffusion is very significant. In Figs. 6–9, respectively, for methanol, ethanol, propanol and butanol, it is shown that the adsorption rate increases with increase of temperature. At the interval of 40 minutes, the adsorbent attained approximately 95% of saturation at 50°C, while at the same interval the adsorbent attained only around 80% at 25°C, to methanol. At the interval of 30 minutes, the adsorbent attained approximately 100% saturation at 50°C, while at the same interval the adsorbent attained only around 80% at 25°C, to ethanol. This occurs due to an increase in the degree of molecular agitation, facilitating the adsorption rates.

It is interesting to compare the alcohol kinetic curves for the same temperature, in order to observe the influence of the chain size of the alcohol in relation to the diffusivity. The results of the adsorption kinetic study for the systems methanol-water, ethanol-water,

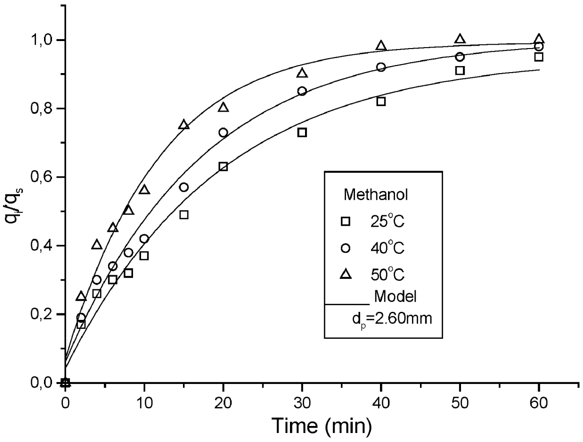

Figure 6. Uptake rate curves for several temperatures to the methanol-water system.

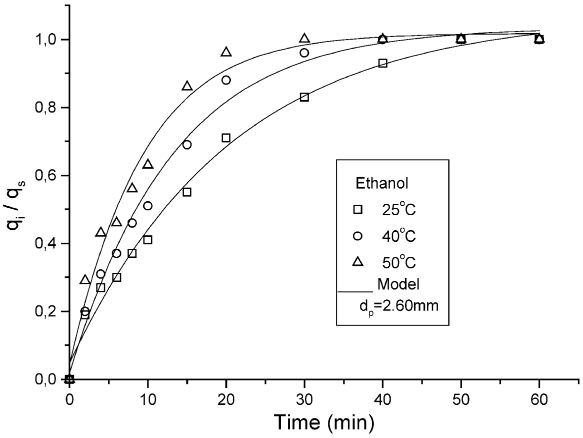

Figure 7. Uptake rate curves for several temperatures to the ethanol-water system.

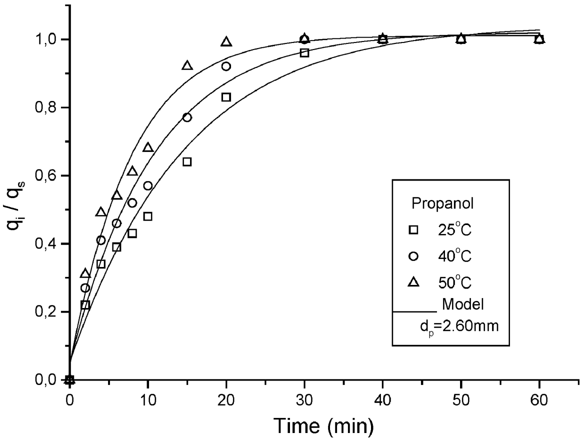

Figure 8. Uptake rate curves for several temperatures to the propanol-water system.

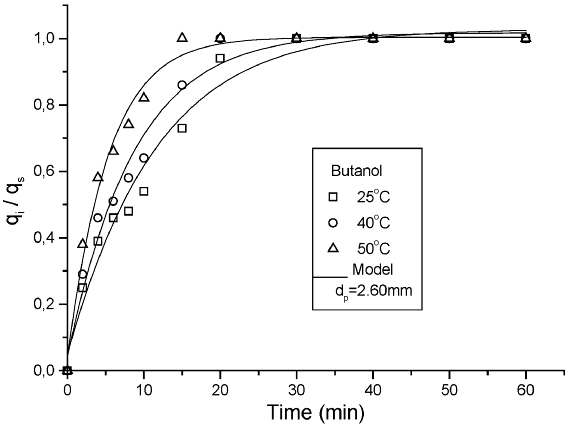

Figure 9. Uptake rate curves for several temperatures to the butanol-water system.

propanol-water, and butanol-water on the starch, at the same temperature indicate that an increase of chain length of the alcohol leads to an increase in the uptake rate. This happens due to the decrease of alcohol polarity, causing a decrease of competition between the water and alcohol in relation to the starch. This can be observed for all of the alcohols studied and for all temperature. That indicates that amylopectin in the starch is mainly responsible for adsorption of wate, in contrast with the amylose, which is a linear and apolar molecule.

The values of diffusivities predicted by the model, in the alcohol-water system, for several temperatures and tortuosity factors are in the Table 7. Those values show that the temperature and the chain length of the alcohol had a pronounced effect on diffusivity values, favoring the kinetics process in virtue of an increase in molecular agitation and decrease on alcohol polarity.

Table 7. Diffusivity and tortosity values to the experimental kinetic runs.

Alcohol	Temperature (K)	Diffusivity $(\mathrm{cm}^2/\mathrm{s}) \cdot 10^6$	Tortuosity factor
Methanol	298	1.09	21.1
	313	1.60	17.0
	323	2.56	17.3
Ethanol	298	1.20	10.3
	313	1.80	9.11
	323	2.79	9.18
Propanol	298	1.37	4.66
	313	2.01	4.69
	323	2.96	4.09
Butanol	298	1.50	3.58
	313	2.16	3.81
	323	3.26	3.28

Table 8. Capacity and diffusivity between starch and zeolite to ethanol-water separation.

Adsorbent	Temperature (K)	Capacity (g/ml)	Diffusivity $(\mathrm{cm}^2/\mathrm{s}) \cdot 10^6$
Starch	298	0.153	1.20
	313	0.143	1.80
	323	0.128	2.79
Zeolite	298	0.289	4.42
	313	0.259	6.58
	323	0.219	10.2

The thermodynamic and kinetic data for the starch were compared with a conventional adsorbent, such as commercial 3A zeolite, obtained by Azevedo (1992) under the same conditions as for ethanol-water separation. Table 8 compared the capacity and diffusivity for the two adsorbents and shows that zeolite exhibits a higher uptake rate and capacity than does the starch for the same temperature range studied.

Conclusions

Thermodynamic results confirm the starch affinity for water in the presence of alcohol. In terms of adsorption capacity, manioc starch adsorbs water at a proportion of 15% of its dry mass at 25°C. The chain length of the alcohol also influences the adsorption capacity. It was verified that this capacity increases as alcohol polarity decreases.

The thermodynamic model represented by the Langmuir isotherm was in satisfactory accordance with the equilibrium data within the temperature range applied on this work.

The kinetic data, obtained in a finite liquid bath cell, were represented by means of uptake rate curves. The adsorption kinetic process depended of the parameters like temperature and chain length of the alcohol. Effective diffusivities predicted by the model for several temperatures showed that the temperature and the molecular chain of the alcohol have a very important influence on the kinetics process due to an increase in molecular agitation and a decrease in the alcohol polarity.

Nomenclature

C_i	Liquid phase concentration at time t (g/ml)
D	Diffusivity (cm^2/s)
d_p	Particle diameter (cm)
K	Langmuir constant (ml/g)
M_f	Mass of liquid (g)
M_s	Adsorbent mass (g)
q_i	Adsorbed phase concentration after specific time interval (g/ml)
q_s	Mono layer capacity (g/ml)
q_∞	Adsorbed phase concentration at equilibrium (g/ml)
R_p	Particle radius (cm)
W_b^e	Mass fraction of alcohol in solution at equilibrium, weight % alcohol
W_b^o	Initial mass fraction of alcohol in solution, weight % alcohol
W_b	Mass fraction of alcohol in solution after specific time interval, weight % alcohol
ρ_a	Water density (g/ml)
ρ_p	Adsorbent apparent density (g/ml)
ρ_s	Adsorbent real density (g/ml)
ε	Bath porosity
ε_p	Adsorbent porosity
$-\Delta H$	Heat of sorption (kcal/g-mol)

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