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Equilibrium and kinetic parameters of the adsorption of α-chymotrypsinogen A onto hydrophobic porous adsorbent particles

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Abstract

Adsorption equilibria and rate kinetics for the binding of α-chymotrypsinogen A onto hydrophobic porous adsorbent particles, have been investigated for three different temperatures. The results show that the amount of protein adsorbed increases as the temperature increases.

The values of the parameters that characterize the mechanisms of pore diffusion and adsorption were determined. The values of the pore diffusion coefficient and the values of the time constants for the mass transfer steps of pore diffusion and adsorption suggest that the pore diffusion mechanism in the porous structure of the adsorbent particles is rate limiting. An analysis of the results of the adsorption of α-chymotrypsinogen A suggests that the heat of adsorption is positive, and this would indicate that the adsorption of α-chymotrypsinogen A onto the hydrophobic adsorbent particles used in this work is entropically driven.

1. Introduction

The design, optimization, scale-up and control of affinity adsorption systems require that the mass transfer and adsorption mechanisms are quantified. The most commonly used mode of operation in affinity adsorption separations is the fixed bed mode with axial flow [1]. Batch (finite bath) adsorption systems could be appropriate where the fluid to be processed was of high viscosity or contains particulate material. It has been shown [1–7] that, for a given affinity adsorption system, the parameters that characterize the intraparticle mass transfer mechanisms in purely diffusive adsorbent particles (for affinity adsorption systems with perfusive particles, Refs. 8–14 should be consulted) as well as the adsorption mechanisms should be independent of the operational mode (e.g., batch, fixed bed, fluidized bed), and therefore, if these parameters are estimated by utilizing information obtained from finite bath experiments (batch experiments are easier to perform and analyze [1–7,15,16] than column experiments), then their values could characterize the mechanisms (intraparticle mass transfer and adsorption mechanisms) in other operational modes.

In this work, the dynamic and equilibrium

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behavior of the adsorption of α-chymotrypsinogen A onto the surface of the pores of SynChroprep Propyl HIC porous adsorbent particles is studied by performing finite bath experiments. Then the experimental dynamic and equilibrium adsorption data are used together with the predictions calculated from a mathematical model to obtain the values of the parameters that characterize the mechanisms of pore diffusion and adsorption in the adsorbent particles for α-chymotrypsinogen A.

2. Mathematical model

In this work, single-component adsorption is considered to occur in purely diffusive adsorbent particles (in purely diffusive adsorbent particles the intraparticle convective velocity [9] is taken to be equal to zero) suspended in the liquid of a finite bath, and the mass transfer and interaction steps are as follows: (i) the transport of adsorbate from the bulk fluid to the external surface of the adsorbent particle (film mass transfer); (ii) the transport of adsorbate within the porous adsorbent particle (intraparticle pore diffusion); (iii) the interaction between the adsorbate molecules and the active sites on the surface of the pores of the adsorbent particle (adsorption step). The porous adsorbent particles are suspended in the liquid of the finite bath by agitation so that the liquid has free access, and the bulk concentration of the adsorbate is taken to be uniform throughout the bath except in a thin film (film mass transfer resistance) of liquid surrounding each particle.

A differential mass balance for the adsorbate in the fluid phase of the finite bath gives

$$\frac{dC_d}{dt} = \left(\frac{1-\epsilon}{\epsilon}\right) \cdot \left(\frac{\alpha+1}{r_0}\right) \cdot K_f[C_p(t,r_0) - C_d] \quad (1)$$

Eq. 1 can be used for particles having geometry of slab, cylinder or sphere by putting $\alpha = 0$, 1 or 2, respectively. The initial condition of Eq. 1 is given by

$$C_d = C_{d0} \text{ at } t = 0 \quad (2)$$

The transport of the adsorbate in the adsorbent particle is considered to be governed by the diffusion [2,7] of the species in the pore fluid (pore diffusion) of the particle. The intraparticle (pore diffusion) transport mechanism is taken to be one-dimensional and in particles that have an axis of symmetry. It is understood that in the case of the slab and the cylinder, the particles are of infinite extent or alternatively one must artificially assume that the ends of a finite cylinder or edges of a finite slab are sealed in order to keep the problem one-dimensional. A differential material balance for the adsorbate in the adsorbent particle is given by

$$\frac{\partial(\epsilon_p C_p)}{\partial t} + \frac{\partial C_s}{\partial t} = \frac{1}{r^\alpha} \cdot \frac{\partial}{\partial r} \cdot \left(r^\alpha \epsilon_p D_p \cdot \frac{\partial C_p}{\partial r}\right) \quad (3)$$

The initial and boundary conditions for Eq. 3 are

$$C_p = 0 \text{ at } t = 0,\ 0 \leq r \leq r_0 \quad (4)$$

$$C_s = 0 \text{ at } t = 0,\ 0 \leq r \leq r_0 \quad (5)$$

$$\epsilon_p D_p \cdot \left.\frac{\partial C_p}{\partial r}\right|_{r=r_0} = K_f[C_d - C_p(t,r_0)], \quad t > 0 \quad (6)$$

$$\left.\frac{\partial C_p}{\partial r}\right|_{r=0} = 0, \quad t > 0 \quad (7)$$

If restricted [1,5,7,13] pore diffusion occurs, then ϵ_p and D_p could vary with the loading of the adsorbate in the adsorbed phase, as shown by the restricted pore diffusion mathematical model of Petropoulos et al. [7]. If the effect of restricted pore diffusion on the mass flux of the adsorbate is not significant, then the values of ϵ_p and D_p may be considered to be constant [1,2,5,7].

It is apparent that Eq. 3 can be solved only if an appropriate expression for the term $\partial C_s/\partial t$ is available. This term represents the accumulation of the adsorbed species on the internal surface of the porous adsorbent particle, and it can be quantified if a mathematical expression could be constructed that would describe the mechanism of the adsorption of the adsorbate onto the active site on the surface of the pore. In this work, the interaction between unbound adsor-

bate A in the pore fluid and vacant active site S on the surface of the pore is considered to be of the form [1–3]

$$A + S \underset{k_2}{\overset{k_1}{\rightleftarrows}} AS \tag{8}$$

where AS represents the adsorbate–active site complex. Then assuming elementary interactions, the rate of the adsorption step may be described by the following second-order reversible interaction:

$$\frac{\partial C_s}{\partial t} = k_1 C_p (C_T - C_s) - k_2 C_s \tag{9}$$

The accumulation term, $\partial C_s/\partial t$, in Eq. 9 becomes equal to zero when adsorption equilibrium is established, and the following expression for the equilibrium isotherm is then obtained:

$$C_s = \frac{C_T K C_p}{1 + K C_p} \tag{10}$$

Eq. 10 represents the Langmuir equilibrium adsorption model where

$$K = K_0 \cdot \exp(-\Delta H/RT) \tag{11}$$

Eq. 11 is the Van 't Hoff equation and represents the temperature dependence of the equilibrium association constant, K ($K = k_1/k_2$); the parameter ΔH in Eq. 11 represents the heat of adsorption. It is worth mentioning that at equilibrium the value of C_p in Eq. 10 should be equal to the value of C_d.

It should be noted at this point that the adsorption mechanism presented in Eq. 8 and whose dynamic and equilibrium quantitative expressions are given by Eqs. 9 and 10, respectively, represents the simplest non-linear adsorption mechanism. Complex non-linear adsorption mechanisms that could account for other phenomena in biomolecule adsorption such as steric effects, conformational changes, multipoint adsorption, and lateral interactions have been presented by Liapis and co-workers [1,2,4,7], Norde [17], Lundstrom et al. [18], Yon [19], Mark et al. [20] and Myers [21]; the determination of the parameters that characterize the adsorption steps of complex non-linear adsorption mechanisms requires data from different complex experiments that are not yet well established and which are beyond the scope of the present work. In this work, the goal is to obtain values for the phenomenological parameters that characterize (a) pore diffusion of the adsorbate in the pore fluid and (b) adsorption of the adsorbate on the surface of the pores of the adsorbent particles, from simple, inexpensive, and easy-to-perform batch experiments and non-linear adsorption models which could provide appropriate approximate representations for the mechanisms of pore diffusion and adsorption and whose numerical solution could be obtained efficiently with a small amount of computational effort and without using a super-computer. The values of the phenomenological parameters of pore diffusion and adsorption obtained from the combination of simple batch adsorption experiments and non-linear adsorption models described in this work, could then be used to simulate, examine, and study the adsorption of the adsorbate in fixed bed, fluidized bed, periodic counter-current bed, and continuous counter-current bed chromatographic columns. This simulation approach could (a) reduce significantly the experimental effort, (b) provide useful information about the relative importance of the film mass transfer, pore diffusion, and adsorption mechanisms, (c) provide useful quantitative results for the rates of the mass transfer and adsorption mechanisms, and (d) could provide reasonable quantitative information about the adsorption efficiency of different modes of operation, and this would be useful in selecting the system and mode of operation that could be used in the scale-up process.

The initial condition of Eq. 9 is given by Eq. 5. Eqs. 1, 3 and 9 could now be solved simultaneously (assuming that the values of C_{d0}, ϵ, ϵ_p, r_0, K_f, k_1, k_2, C_T and D_p are known) in order to obtain the dynamic behavior of C_d, C_p and C_s. In this work, the values of C_{d0}, ϵ, ϵ_p and r_0 are known. The value of the film mass transfer coefficient, K_f, of the adsorbate in Eqs. 1 and 6, is calculated from the following expression [22]:

$$K_f = \frac{2D_{mf}}{d_p} + 0.31 \cdot \left[\frac{(\Delta\rho)\mu g}{\rho^2}\right]^{1/3} \cdot \left(\frac{\mu}{\rho D_{mf}}\right)^{-2/3} \quad (12)$$

The values of C_T and K ($=k_1/k_2$) are obtained from the experimental equilibrium adsorption data; and the values of k_1 and D_p (the parameter k_2 in Eq. 9 is replaced by k_1/K) are obtained by matching the dynamic predictions of the theoretical model with the experimental data (the variation of C_d with time, t) obtained from the batch experiments. Then the value of k_2 is obtained from the values of k_1 and K since $k_2 = k_1/K$. The parameters D_p, k_1 and k_2 characterize the mechanisms of pore diffusion and adsorption, and their values should be independent [1–7] of the operational mode (e.g., batch, fixed bed, periodic counter-current bed, fluidized bed).

Eqs. 1, 3 and 9 were solved by using the numerical method described in Refs. 2, 4 and 13.

3. Experimental

3.1. Materials

The adsorbent particles are SynChroprep Propyl HIC Lot No. 1853, and were purchased from SynChrom, Lafayette, IN, USA. These adsorbent particles are spherical, and are formed from macroporous silica to which a polyamide layer containing a propyl hydrophobic ligand is covalently bonded. The diameter of the adsorbent particles is 15 μm and their density is 0.5 g/ml, as reported by SynChrom. The void fraction (porosity), ϵ_p, of the adsorbent particles is 0.55 [23,24], while the mean pore diameter of the pores of the particle (porous silica) before the polyamide layer is put on, is between 279 and 299 Å [24]. It is important to note at this point that the mean pore diameter of the adsorbent particles should be lower because when the polyamide layer is put on the diameter of the pores should become smaller; furthermore, the pore connectivity [7] of the pores of the porous particles could be changed when the polyamide layer is put on the surface of the pores of the porous particles. The pore-size distribution, mean pore diameter, and pore connectivity of the pores of the porous adsorbent particles were requested [24] but could not be provided by SynChrom.

The protein α-chymotrypsinogen A was purchased from Sigma, St. Louis, MO, USA. The molecular mass and the isoelectric point of α-chymotrypsinogen A are 25 000 daltons and 9.1, respectively [25].

The filters used were Durapore (polyvinylidine difluoride) membrane filters with a pore size of 5.0 μm. The filter holders were Swinnex, 13 mm disk filter holders, and the filters were trimmed in order to fit in the filter holders. The filters and the filter holders were purchased from Millipore, Bedford, MA, USA.

3.2. Methods

α-Chymotrypsinogen A was dissolved in 0.1 M phosphate buffer containing 1.8 M ammonium sulfate. To a 100-ml beaker, 50 ml of buffer containing protein was added, a stirring bar was placed in the beaker, the beaker was covered with Parafilm, and set on top of a submersible magnetic stirrer in a constant-temperature water bath. The solution was stirred at 1200 rpm for 0.5 h while the solution reached thermal equilibrium.

In the batch experiments with α-chymotrypsinogen A, 0.1 g of adsorbent particles were added. Samples of 0.8 ml were removed from the continuously stirred suspension at various time intervals. The concentration of α-chymotrypsinogen A was measured at 5, 10 and 20 min and every 20 min thereafter until there was no further change in protein concentration in two consecutive samples.

Since adsorbent particles were suspended in the removed sample, the sample was filtered through a Millipore filter into a cuvette with a volume of 0.9 ml and a light path of 1 cm before being read at 280 nm in an Hitachi U-2000 spectrophotometer; the duration of this filtration is less than 10 s. After the reading was made, the solution was returned to the finite bath (the

beaker with the protein solution and the adsorbent particles).

Protein solutions with initial concentrations of about 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 mg/ml were used at three different buffered pH values (5.0, 7.0 and 9.0) and three different temperatures (15, 25 and 35°C). Forty-five different solutions in duplicate were run [26]. Both dynamic (unsteady-state) and equilibrium adsorption data were measured [26].

4. Results and discussion

In Fig. 1 the equilibrium experimental and theoretical results of the adsorption of α-chymotrypsinogen A onto SynChroprep Propyl HIC porous adsorbent particles are presented for pH 5.0 and three different temperatures (15, 25 and 35°C); the theoretical results were obtained by using Eq. 10. The error in the values of C_s in Fig. 1 is ± 0.5 kg/m^3 particle, and this is a relatively small error if one considers the magnitude of the values of C_s in Fig. 1. The correlation coefficient between the experimental and theoretical data in Fig. 1 is about 0.9978, and this indicates that the correlation is good. In Table 1, the values of the parameters C_T and K of Eq. 10 that provided the best fit between the experimental and theoretical equilibrium data shown in Fig. 1, are presented. Experimental and theoretical equilibrium data for pH values of 7.0 and 9.0 are reported in Ref. [26].

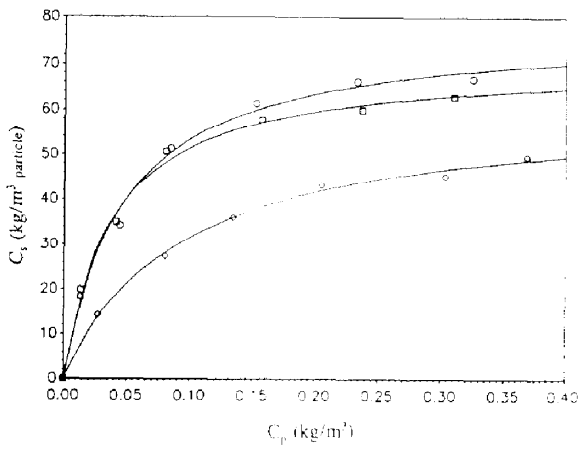

Fig. 1. Equilibrium adsorption isotherms for α-chymotrypsinogen A; pH 5.0. ◇ = Experimental results at 15°C; □ = experimental results at 25°C; ○ = experimental results at 35°C; lines = theoretical results.

Table 1
Values of the parameters C_T and K of Eq. 10 for α-chymotrypsinogen A; pH 5.0

Temperature (°C)	C_T (kg/m^3 particle)	K (m^3/kg)
15	60.95	10.82
25	70.71	26.77
35	78.22	21.52

While there is no clear trend in the values of the equilibrium association constant, K, presented in Table 1, the value of the apparent maximum capacity C_T increases as the temperature is increased from 15 to 35°C. This increase in the value of C_T with temperature could be caused by swelling of the polyamide layer containing the propyl hydrophobic ligand, making more binding sites available in the interior of the porous adsorbent particles; it should be mentioned at this point that we were told [24] that it is possible for the polyamide layer (containing the propyl hydrophobic ligand) to swell. The increase in the value of C_T could also be due to deviations from the Langmuir-type equilibrium behavior in which every binding site is equivalent. However, the experimental data in Fig. 1 are, for practical purposes, quantitatively described satisfactorily by Eq. 10. It is worth mentioning at this point that the overall free energy change ΔG ($\Delta G = \Delta H - T\Delta S$) associated with the adsorption of α-chymotrypsinogen A, could have a rather complex temperature dependence since hydrophobic interactions are largely entropic [27,28] in nature, while electrostatic interactions contribute to the enthalpy. The results in Fig. 1 show that the amount of protein adsorbed at equilibrium increases as the temperature increases.

Once the values of the equilibrium parameters K and C_T have been determined, then the values of the kinetic parameters D_p, k_1 and k_2 that characterize the mechanisms of pore diffusion

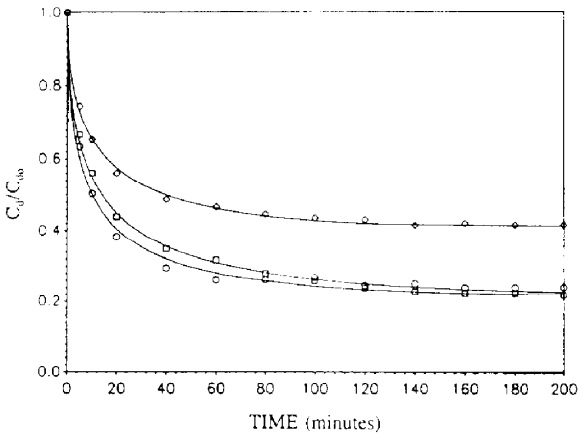

Fig. 2. Dynamic finite bath adsorption of α-chymotrypsinogen A; pH 5.0. ◇ = Experimental results at 15°C and C_{d0} = 0.19 kg/m^3; □ = experimental results at 25°C and C_{d0} = 0.19 kg/m^3; ○ = experimental results at 35°C and C_{d0} = 0.18 kg/m^3; lines = theoretical results.

and adsorption could be determined. The kinetic parameter k_2 in Eq. 9 is replaced by the term k_1/K, and thus, Eq. 9 takes the following form:

$$\frac{\partial C_s}{\partial t} = k_1 C_p (C_T - C_s) - (k_1/K) C_s \qquad (13)$$

The values of the kinetic parameters D_p and k_1 are determined by matching the dynamic experimental adsorption data obtained from batch experiments with the theoretical predictions obtained from the solution of the mathematical model presented in Eqs. 1–7 and 13. The value of the kinetic parameter k_2 is then calculated from the expression $k_2 = k_1/K$. The value of the film mass transfer coefficient K_f in Eqs. 1 and 6 is calculated from the expression in Eq. 12. In this work, the values of the parameters ϵ_p, r_0 and ϵ are as follows: $\epsilon_p = 0.55$ [23,24]; $r_0 = 7.5 \cdot 10^{-6}$ m; $\epsilon = 0.996$. The values of the temperature, T, and the initial concentration, C_{d0}, of the adsorbate in the finite bath are reported in the caption of Fig. 2.

In Fig. 2 the dynamic (batch) experimental and theoretical results of the adsorption of α-chymotrypsinogen A onto SynChroprep Propyl HIC porous adsorbent particles are presented for pH 5.0 and three different temperatures (15, 25 and 35°C). The experimental error in determining the ratio C_d/C_{d0} in Fig. 2 is ± 0.01. The correlation coefficient between the experimental and theoretical results in Fig. 2 is about 0.9989, and this indicates that the correlation is good. Experimental and theoretical dynamic adsorption data for pH values of 7.0 and 9.0 are reported in Ref. [26]. In Table 2, the values of the kinetic parameters D_p and k_1 that provided the best fit between the batch experimental and theoretical adsorption data shown in Fig. 2, are presented. Also in Table 2, the value of K_f, in Eqs. 1 and 6 of the mathematical model, calculated from Eq. 12 is presented, as well as the value of k_2 calculated from the expression $k_2 = k_1/K$. The values of the free molecular diffusion coefficient, D_{mf}, calculated from Eq. 8 in Ref. [29], are also presented in Table 2, so that their values can be compared with the values of the pore diffusion coefficient, D_p. Furthermore, in Table 2 the time constants for (a) pore diffusion, $(r_0)^2/D_p$, (b) interaction (adsorption) between adsorbate molecules and active sites, $1/(k_1 C_{d0})$,

Table 2
Values of the kinetic parameters for α-chymotrypsinogen A; pH 5.0

Temperature (°C)	K_f (m/s)	D_{mf} (m^2/s)	D_p (m^2/s)	D_p/D_{mf}	k_1 (m^3/kg·s)	k_2 (s^{-1})	r_0^2/D_p (s)	d_p^2/D_p (s)	$1/k_1 C_{d0}$ (s)	$1/k_2$ (s)
15	$5.48 \cdot 10^{-5}$	$7.22 \cdot 10^{-11}$	$8.70 \cdot 10^{-13}$	$1.20 \cdot 10^{-2}$	13.38	1.24	64.516	258.065	0.387	0.806
25	$6.12 \cdot 10^{-5}$	$8.93 \cdot 10^{-11}$	$9.77 \cdot 10^{-13}$	$1.09 \cdot 10^{-2}$	9.07	0.34	57.471	229.885	0.583	2.941
35	$7.18 \cdot 10^{-5}$	$1.22 \cdot 10^{-10}$	$1.29 \cdot 10^{-12}$	$1.06 \cdot 10^{-2}$	1.70	0.08	43.668	174.672	3.214	12.50

and (c) desorption of adsorbed adsorbate molecules, $1/k_2$, are presented. Some researchers might recommend that the time constant for pore diffusion might be estimated [30] from the approximate expression $(1/30)(d_p^2/D_p)$. However, the work of Knox and Scott [30] from which the approximate expression $(1/30)(d_p^2/D_p)$ might be inferred, is based on the linear Van Deemter theory for liquid chromatography which concerns itself with linear adsorption isotherms. But in the work presented in this paper, the mathematical model and the adsorption isotherm are nonlinear, and thus, the expression $(1/30)(d_p^2/D_p)$ would not be applicable. Some researchers consider the term d_p^2/D_p to represent the time constant for pore diffusion, and for this reason the values of the term d_p^2/D_p have been included in Table 2; it should be noted at this point that the majority of investigators consider the term r_0^2/D_p to represent the time constant of pore diffusion in purely diffusive adsorbent particles (the adsorbent particles of this work are considered to be purely diffusive because the intraparticle fluid velocity is considered to be equal to zero).

The dynamic experimental data in Fig. 2 are, for practical purposes, described satisfactorily by the dynamic theoretical results obtained from the solution of the batch adsorption model represented by Eqns. 1–7 and 13. The dynamic data in Fig. 2 indicate that the amount of adsorbed adsorbate increases as the temperature increases.

The data in Table 2 show that the values of the pore diffusion coefficient are about two orders of magnitude smaller than the values of the free molecular diffusion coefficient. Also, by comparing the values of the time constants r_0^2/D_p, $1/(k_1 C_{d0})$, and $1/k_2$ in Table 2, it can be observed that the time constant for pore diffusion is many times larger than the time constants of the adsorption and desorption steps. Furthermore, the time constant for desorption is larger than the time constant for adsorption. The results in Table 2 suggest that the adsorption step occurs significantly faster than the desorption step, while the slowest mechanism of the overall adsorption process is the mass transfer step of the adsorbate in the pores of the porous adsorbent particles. Thus, the rate-limiting step for the adsorption of α-chymotrypsinogen A onto the hydrophobic porous adsorbent particles employed in this work, is the pore diffusion step. This finding and the values of the ratio D_p/D_{mf} in Table 2 suggest that when the polyamide layer containing the propyl hydrophobic ligand is put on the surface of the pores of the porous silica, it has an important effect on the pore-size distribution, mean pore radius, and pore connectivity [1,7] of the resulting porous structure of the adsorbent particles. Furthermore, the adsorption of α-chymotrypsinogen A on the surface of the pores of the adsorbent particles could alter [1,7] the pore-size distribution, mean pore radius, and pore connectivity of the porous structure of the adsorbent particles as the adsorption process is proceeding and the loading of adsorbed adsorbate is increasing.

The values of the parameters k_1 and k_2 for α-chymotrypsinogen A in Table 2 decrease as the temperature is increased; furthermore, the value of k_1 is about an order of magnitude larger than the value of k_2. If the forward and reverse interaction rate constants k_1 and k_2 for the adsorption of α-chymotrypsinogen A are described by an Arrhenius expression,

$$k_1 = k_{10} \cdot \exp(-E_1/RT) \tag{14}$$

$$k_2 = k_{20} \cdot \exp(-E_2/RT) \tag{15}$$

then, by using the values of k_1 and k_2 in Table 2, one obtains the following values for the pre-exponential factors k_{10} and k_{20}, and the activation energies E_1 and E_2: $k_{10} = 3.09 \cdot 10^{-13}$ m^3/kg · s, $k_{20} = 5.72 \cdot 10^{-19}$ s^{-1}, $E_1 = -18.09$ kcal/mol and $E_2 = -24.18$ kcal/mol (1 cal = 4.184 J). From these data the parameters $K_0 = k_{10}/k_{20}$ and $\Delta H = E_1 - E_2$ in Eq. 11 can be calculated, and their values are as follows: $K_0 = 5.40 \cdot 10^5$ m^3/kg and $\Delta H - 6.09$ kcal/mol. Thus, the adsorption of α-chymotrypsinogen A onto the adsorbent particles used in this work appears to be endothermic, since $\Delta H > 0$. Furthermore, the fact that $\Delta H > 0$, whereas the adsorption proceeds spontaneously ($\Delta G < 0$; $\Delta G = \Delta H -$

$T\Delta S$), indicates that an increase of entropy must be the driving force behind the adsorption of α-chymotrypsinogen A onto the adsorbent particles considered in this work.

5. Conclusions and remarks

The equilibrium and rate kinetics of the adsorption of α-chymotrypsinogen A onto hydrophobic porous adsorbent particles was studied experimentally and theoretically for three different temperatures. The results show that the amount of adsorbed protein increases as the temperature increases.

The calculated values for the pore diffusion coefficient and for the time constants of the mass transfer steps of pore diffusion, adsorption, and desorption, suggest that the rate-limiting step for the adsorption of α-chymotrypsinogen A onto the hydrophobic porous adsorbent particles employed in this work, is the pore diffusion step. The heat of adsorption for the α-chymotrypsinogen A system was found to be positive, and this would indicate that the adsorption of α-chymotrypsinogen A onto the hydrophobic adsorbent particles used in this work, is entropically driven.

The values of the parameters that characterize the mechanisms of pore diffusion and adsorption, determined in this work from information obtained from finite bath adsorption experiments and the mathematical model, could be used to characterize the same mechanisms when adsorption of α-chymotrypsinogen A occurs in a fixed bed, in a periodic counter-current bed, in a continuous counter-current bed, or in a fluidized bed.

Symbols

A molecule of adsorbate
AS adsorbate-active site complex
C_d concentration of adsorbate in the bulk fluid phase of finite bath, kg/m^3
C_{d0} initial concentration of adsorbate in bulk fluid phase of finite bath, kg/m^3
C_p concentration of adsorbate in pore fluid, kg/m^3
C_s concentration of adsorbate in adsorbed phase, kg/m^3 particle
C_T apparent maximum concentration of adsorbate in adsorbed phase, kg/m^3 particle
D_{mf} free molecular diffusion coefficient of adsorbate, m^2/s
D_p pore diffusion coefficient of adsorbate (in adsorbent particle), m^2/s
d_p mean diameter of the adsorbent particles ($d_p = 2r_0$), m
E_1 activation energy, kcal/mol
E_2 activation energy, kcal/mol
g standard acceleration of free fall, 9.80665 m/s^2
K equilibrium association constant ($K = k_1/k_2$), m^3/kg
K_f film mass transfer coefficient of adsorbate, m/s
K_0 pre-exponential factor in the Van 't Hoff equation, m^3/kg
k_1 forward interaction rate constant in reaction 8, $m^3/kg \cdot s$
k_{10} pre-exponential factor in Eq. 14, $m^3/kg \cdot s$
k_2 reverse interaction rate constant in reaction 8, s^{-1}
k_{20} pre-exponential factor in Eq. 15, s^{-1}
r radial distance in adsorbent particle, m
r_0 radius of adsorbent particle
R universal gas constant
S vacant active site
t time, s
T temperature, K

Greek letters

α form factor; 0, 1 and 2 for slab, cylinder and sphere, respectively
ΔG Gibbs free energy
ΔH heat of adsorption, kcal/mol of adsorbate
ΔS entropy
$\Delta\rho$ density difference between the particulate and continuous phases, kg/m^3
ϵ void fraction in finite bath
ϵ_p void fraction in porous adsorbent particle
μ viscosity of liquid solution, $kg/m \cdot s$
ρ density of liquid solution, kg/m^3

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