Diffusion controlled LHHW kinetics. Simultaneous determination of chemical kinetic and equilibrium adsorption constants by using the Weisz-Prater approach

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HIGHLIGHTS

- Diffusion-adsorption-reaction system with LHHW type kinetics was solved.
- The Thiele modulus and the dimensionless adsorption constant characterize the system.
- The Weisz-Prater parameter allows determining the kinetics and adsorption constants.
- The limit value of the Weisz-Prater parameter implying chemical control is not unique.
- Those "limit" values will increase with the dimensionless adsorption constant's value.

ARTICLE INFO

ABSTRACT

A method to simultaneously determine the chemical kinetics (kC_T) and Langmuir's adsorption equilibrium (K_L) constants in porous catalyst particles where chemical reactions following Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics (first order on the concentration of the adsorbed species) proceed under the existence of diffusion mass transfer limitations was proposed. Two parameters characterize this steady state diffusion-adsorption-reaction system: the well known Thiele modulus ϕ and the dimensionless adsorption equilibrium constant K, which is defined as the product between K_L and the fluid phase concentration of the reactant (C_f). It was shown that the non-linear adsorption equilibrium is the reason that, given ϕ, the larger the K, the flatter the concentration profile and, consequently, the volume average chemical reaction rate and the effectiveness factor are higher. Although the Weisz-Prater (W-P) criterion has been previously extended to non-linear kinetics to evaluate the relative magnitude of diffusion limitations inside porous catalyst particles, this method allows determining the kinetic and adsorption parameters by using the W-P parameter, as assessed from a few laboratory experiments. Differently from the classical W-P criterion (first order kinetics), a single value of W-P parameter below which the chemical control could be secured does not exist for LHHW kinetics. Those "limit" values depend on K and increase with it. The fact that ϕ is independent from C_f, while K certainly depends on it, makes it easier to simultaneously determine K_L and kC_T under reaction conditions. When K is small (e.g., lower than 0.1), the model converges to the solutions typical in textbooks, where linear adsorption equilibrium is taken into account, which under steady state conditions only allow estimating the kC_TK_L product, but not the individual constants.

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1. Introduction

Heterogeneously catalyzed chemical reactions require that the reacting species adsorb on surface active sites of the catalyst to further react and then the products desorb (Froment et al., 2011). It is very common to find that the adsorption-desorption steps are much faster than the chemical reaction, thus ensuring an adsorption equilibrium condition. Some typical examples of these situations can be found in reactions that obey a Langmuir-Hinshelwood-Hougen-Watson (LHHW; Langmuir, 1916; Hinshelwood, 1926; Hougen and Watson, 1943) type kinetics; for instance, in the methylcyclohexane dehydrogenation over Pt-Al$_2$O$_3$ (Sinfelt

Nomenclature

Symbols

A	identity of the reactant
C	concentration (gmol/m^3)
D	diffusivity in the particle (m^2/s)
E	enzyme concentration (kg/m^3)
g	function containing the concentration dependence in Eq. (17)
K	adsorption equilibrium constant (m^3/gmol for Langmuir's equilibrium or dimensionless for Henry's equilibrium)
k	chemical reaction, adsorption or desorption rate constant (1/s or m^3/s gmol for adsorption)
M	Thiele modulus, as used by Chu and Hougen (1962)
P	product
Q	concentration in the solid phase, adsorbed compound (gmol/m^3)
R	catalyst particle radius (m)
r	radial distance (m)
r	chemical reaction rate per unit volume (gmol/s m^3)
Sh	Sherwood number (dimensionless)
t	time (s)
V	volume (m^3) or vacant sites
W	catalyst mass (kg)
X	conversion (dimensionless)
$*$	adsorbed species
$\circ$	initial

Greek symbols

δ	density (kg/m^3)
ε	porosity (dimensionless)
ϕ	Thiele modulus (dimensionless)
φ	fractional coverage (dimensionless)
Γ	dimensionless chemical reaction rate per unit volume
η	effectiveness factor (dimensionless)
K	dimensionless Langmuir's adsorption equilibrium constant
θ	Weisz-Prater parameter (dimensionless)
ρ	dimensionless radial distance
ξ	dimensionless concentration in the particle

Subscripts

ads	adsorption
CAT	catalyst
des	desorption
eq	chemical equilibrium
f	fluid phase
G	generalized
H	refers to Henry's adsorption equilibrium
L	refers to Langmuir's adsorption equilibrium
M	modified
m	Michaelis-Menten
obs	observed
p	particle
s	solid phase
T	refers to total sites in the solid
V	refers to vacant adsorption sites

et al., 1960), the oxidation of nitric oxide over carbon catalysts (Chu and Hougen, 1962), or the esterification of acetic acid with ethanol over ion exchange resins (Bamunusingha et al., 2016). Moreover, it is very common in porous catalysts that the diffusion transport process of reactant and product molecules impose restrictions on their access to active sites and, consequently, the occurrence of concentration gradients, which will produce chemical reaction rate profiles (Chu and Hougen, 1962).

Once the kinetic expression for a given reaction is accepted, it is necessary to assess the corresponding kinetic and adsorption parameters. In general, the laboratory experiments aimed at determining those parameters are performed with as small as possible particle size in order to avoid the limitations imposed by the diffusion process of the reacting species in the catalyst pore system (Sherwood et al., 1975; Berty, 1999; Froment et al., 2011). The final objective is to induce conditions where diffusion mass transfer limitations do not exist and, consequently, the slowest step is the process of adsorption-reaction-desorption. It is also a common practice to perform the experiments under fluidynamics conditions that ensure the lack of mass transfer limitations outside the particles.

However, under certain circumstances, it is not always possible to reduce the particle size as much as needed and diffusion mass transfer limitations in the internal pore system of the catalyst particles rise. Another influencing issue is the pore size in catalysts which, in some cases such as zeolites, is in the range of molecular sizes. One of the consequences is the development of decreasing concentration profiles along the particles, which obviously influence the observed chemical reaction rates. In the absence of external mass transfer limitations, the effectiveness factor is defined to be the relationship between the volume averaged chemical reaction rate in the catalyst particle and the chemical reaction rate at the external surface of the particle (Thiele, 1939). Thus, the concept of effectiveness factor allows writing the reaction term in the reactor's mass balance as a function of the fluid phase concentrations (which are observable), thus greatly simplifying their design (Aris, 1975; Levenspiel, 1999; Fogler, 2006; Froment et al., 2011).

In cases where the concentration of the chemical species in the particle external surface changes fast and the diffusion rates are slow as compared to the overall dynamics of the system, the accumulation term for the reactant in the particles cannot be considered negligible in the mass balances (Bidabehere et al., 2015, 2017). Consequently, the concentration profiles will differ from those predicted under the assumption of steady state concentration profiles. These situations can be adequately described with the concept of transient effectiveness factor (indeed all the effectiveness factors are transient, and limiting cases can be considered). It has been shown that for first order chemical reactions and linear adsorption equilibrium, the transient effectiveness factor depends not only on the Thiele modulus but also on the system's adsorption capacity, a fact that should be taken into account when kinetic experiments are designed. The Damköhler number deserves attention in flow reactors as well (Bidabehere et al., 2015).

When the chemical reaction obeys LHHW type kinetics, the adsorption of the involved species should be taken into account in the formulation of the effectiveness factor (Chu and Hougen, 1962) and the solution of the mass balance equations can be certainly complex when the source term in them is not linear. In those cases, numerical methods are needed to find the concentration profiles and consequent chemical reaction rate profiles, and the effectiveness factors should be expressed by means of approxima-

tions (Bischoff, 1965; Horvath and Engasser, 1973; Rajadhyaksha et al., 1976; Sundaram, 1982; Gottifredi and Gonzo, 2005a, 2005b, 2006; Boldrini et al., 2014). Similar issues do occur in reactions which are catalyzed by immobilized enzymes following Michaelis-Menten-type kinetics (Gottifredi and Gonzo, 2005a). Given the mathematical similarity between Michaelis-Menten and Langmuir-Hinshelwood-Hougen-Watson kinetics, their analysis are identical (Gottifredi and Gonzo, 2005a; Towler and Sinnott, 2013). Aris (1957, 1965), Petersen (1965), Bischoff (1965), Roberts et al. (1966), and Knudsen et al. (1966) showed that is possible to produce general expressions, in conceptual terms, for the effectiveness factor by means of an adequate definition of the Thiele modulus, covering various particle geometries and kinetics.

The very well known criterion by Weisz and Prater (1954) allows evaluating the relative importance of diffusion mass transfer limitations in porous catalyst particles, which can be directly determined in laboratory experiments, provided a number of parameters are known. The Weisz-Prater approach has been used to determine the pure, intrinsic kinetic constant, only in catalytic systems with first order kinetics and linear equilibrium adsorption. Although it has been used for the case of steady state concentration profiles (that is, the conventional approach (Weisz and Prater, 1954; Fogler, 2006; Froment et al., 2011)), it is also applicable to cases of transient concentration profiles (Bidabehere et al., 2017). Petersen (1965) and Bischoff (1965) extended the Weisz-Prater criterion to non-linear kinetics. However, no method has been developed which allows determining the kinetic and adsorption parameters that characterize these reacting systems from a few laboratory experiments.

It is the objective of this work to propose a method to determine simultaneously the chemical kinetic and equilibrium adsorption constants from experimental measurements, based on the Weisz-Prater approach, in catalyst particles where chemical reactions following LHHW kinetics proceed under the simultaneous existence of diffusion mass transfer limitations. Consequently, it is necessary to analyze soundly the effects of adsorption on the concentration and reaction rate profiles, as well as on the catalytic effectiveness factors.

2. Theory

2.1. System description

Gaseous phase reactant A is the only compound adsorbing on the surface of spherical porous catalyst particles with uniform size and irreversible reacts following a kinetics which is first order on the concentration of the adsorbed species. There only exists one type of catalytic sites, which are uniformly distributed throughout the particles, and the adsorption process proceeds on single sites and is not dissociative. The adsorption and desorption steps are very fast as compared to diffusion and chemical reaction rates, thus defining an adsorption equilibrium described by a Langmuir isotherm (Langmuir, 1916). The resistance to mass transfer in the film surrounding the particles is considered negligible and, then, the concentration in the outer surface of the particles is the same as that in the bulk of the fluid phase. It is also assumed that the concentration of reactant in the fluid phase evolves slowly as compared to the dynamics of the particles, thus allowing considering a steady state condition in the internal concentration profiles (Bidabehere et al., 2015). This is a condition usually assumed in modelling these systems (Levenspiel, 1999; Fogler, 2006; Froment et al., 2011). The system is isothermal, catalyst deactivation is neglected and diffusion follows a Fick's law-type mechanism, where the diffusivity in the particle (D) is constant and can

be evaluated from the tortuosity factor and the molecular and Knudsen diffusion coefficients (Satterfield, 1981).

2.2. Mass balance equations

The rate of the chemical reaction in the solid is

$$r_s = k_s Q. \tag{1}$$

Given a Langmuir adsorption equilibrium exists, the concentration of the adsorbed species (Q) can be related to the concentration of the diffusing species (C) (see Appendix A):

$$Q = C_T \left(\frac{K_L C}{1 + K_L C} \right) \tag{2}$$

where C_T is the total concentration of the active sites in the solid and K_L is the adsorption equilibrium constant of reactant A at the system temperature. Then the mass balance of the reactant in the particles, in the steady state, can be written as

$$\varepsilon_p D \nabla^2 C = (1 - \varepsilon_p) k_s C_T \left(\frac{K_L C}{1 + K_L C} \right) \tag{3}$$

and the boundary conditions are

$$\nabla C|_{r=0} = 0 \tag{4}$$

$$C|_{r=R} = C_f. \tag{5}$$

For spherical particles Eqs. (3)–(5) can be written in dimensionless terms as follows:

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{d\xi}{d\rho} \right) = \phi^2 \left(\frac{\xi}{1 + K\xi} \right) \tag{6}$$

$$\left. \frac{d\xi}{d\rho} \right|_{\rho=0} = 0 \tag{7}$$

$$\xi|_{\rho=1} = 1 \tag{8}$$

where

$$\xi = \frac{C}{C_f}, \quad \rho = \frac{r}{R}, \quad K = K_L C_f, \quad \phi = R\sqrt{\frac{k C_T K_L}{D}}, \quad k = k_s \frac{(1 - \varepsilon_p)}{\varepsilon_p}. \tag{9}$$

It should be noted that two parameters characterize this catalytic system: the well known Thiele modulus ϕ and the dimensionless adsorption equilibrium constant K. The dimensionless adsorption equilibrium constant represents the relationship between the number of covered and still free (vacant) adsorption sites that would be reached in the case concentration gradients in the particles do not exist, that is, $Q|_{r=R}$ and $C_V|_{r=R}$ (see Appendix A, Eq. (A.11)).

2.3. Effectiveness factor

As already mentioned, provided there is no resistance to mass transfer in the film surrounding the particles, the effectiveness factor is the relationship between the volume averaged chemical reaction rate in the catalyst particle ($\bar{r}$) and the chemical reaction rate corresponding to the conditions observed in the fluid phase, which are coincident to those in the external particle surface ($r = R$) (Thiele, 1939)

$$\eta = \frac{\bar{r}}{r|_{r=R}} = \frac{\left(\frac{1}{V_p} \right) \int_{V_p} k C_T \left(\frac{K_L C}{1 + K_L C} \right) dV}{k C_T \left(\frac{K_L C_f}{1 + K_L C_f} \right)}. \tag{10}$$

If the dimensionless variables are used in Eq. (10), then

$$\eta = 3(1 + K) \int_0^1 \left(\frac{\xi}{1 + K\xi} \right) \rho^2 d\rho \qquad (11)$$

where the concentration profile in the particle, $\xi = \xi(\phi, K, \rho)$, can be obtained from the solution of Eqs. (6)–(8), provided the parameters ϕ and K are known.

3. Results and discussion

3.1. Concentration and chemical reaction rate profiles in the catalyst particles

Fig. 1 shows the dimensionless concentration profiles for two different values of the dimensionless adsorption equilibrium constant K, at various Thiele moduli ϕ. The profiles represent the numerical solution of the set of Eqs. (6)–(8). As expected, given the diffusion restrictions in the pore system, the reactant concentration decreases steadily along the radial distance, the minimum values being observed at the center of the particle.

As it is well known from conventional approaches, where the effect of the non-linear adsorption is not considered, for a given K value, the higher the Thiele modulus, the steeper the concentration drop. Moreover, for a certain ϕ, the larger the K, the less pronounced the concentration profiles. This is the effect of the non-linear dependence of the kinetic expression on the concentration of the diffusing species (C), as it will be shown later (see Fig. 2).

A simple exercise with Eqs. (1), (2) and (9) shows that the normalized reaction rate Γ is

$$\Gamma = \frac{r}{r|_{r=R}} = (1 + K) \left(\frac{\xi}{1 + K\xi} \right). \qquad (12)$$

This equation allows observing how Γ depends on ξ for different values of K. Fig. 2 clearly shows that at very low values of K, for example less than 0.1, the Γ-ξ relationship follows approximately a straight line with slope 1. This corresponds to the particular cases of diffusion-reaction analysis in porous particles, first order kinetics, isothermal situation where adsorption is not considered (Levenspiel, 1999; Fogler, 2006; Froment et al., 2011), or when the adsorption equilibrium follows a linear, Henry's law-type behavior (Whitaker, 1986; Bidabehere et al., 2015, 2017). Moreover, in those cases, the steady state effectiveness factor only depends on the Thiele modulus and the kinetic constant can be determined
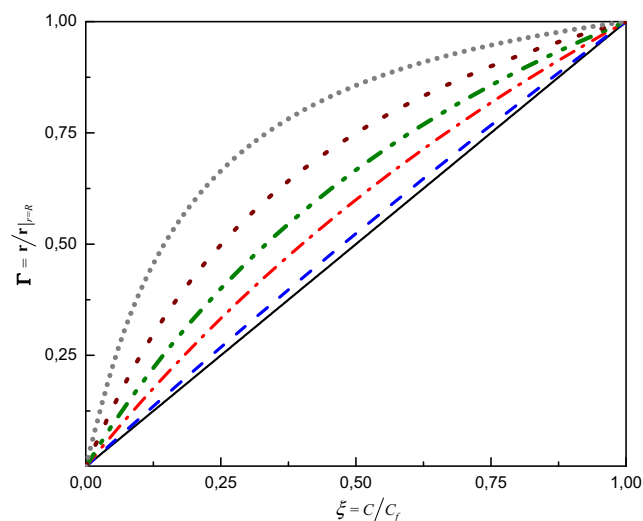

Fig. 2. Dimensionless chemical reaction rate (Γ) as a function of dimensionless reactant concentration (ξ). Lines: $K \to 0$ (solid), $K = 0.1$ (dash), 0.5 (dash dot), 1 (dash dot dot), 2 (dot), 5 (short dot).

from experimental observations by means of the well known Weisz-Prater approach (Weisz and Prater, 1954; Fogler, 2006; Bidabehere et al., 2017). If the adsorption equilibrium is linear, then, the Thiele modulus includes the Henry adsorption constant, $K_H = K_L C_T$

$$\phi = R\sqrt{\frac{kK_H}{D}}. \qquad (13)$$

But if the adsorption equilibrium is not linear (e.g. it follows a Langmuir-type process, Eq. (2)), provided K is not negligible, it can be seen in Fig. 2 that Γ is higher than the prediction by the models ignoring adsorption, or with linear adsorption equilibrium. Moreover, at every ξ, the larger the K, the more important the difference.

As the non-linearity in the source term of the mass balance (right hand side in Eq. (6)) can influence strongly the concentration profiles in the catalyst particles, it will, consequently, impact on the efficiency of the particle to catalyze a given reaction (i.e., its effectiveness factor η). It can be deduced from Fig. 2 that, for a certain K value, the relative difference between the dimensionless chemical reaction rates predicted by the model including
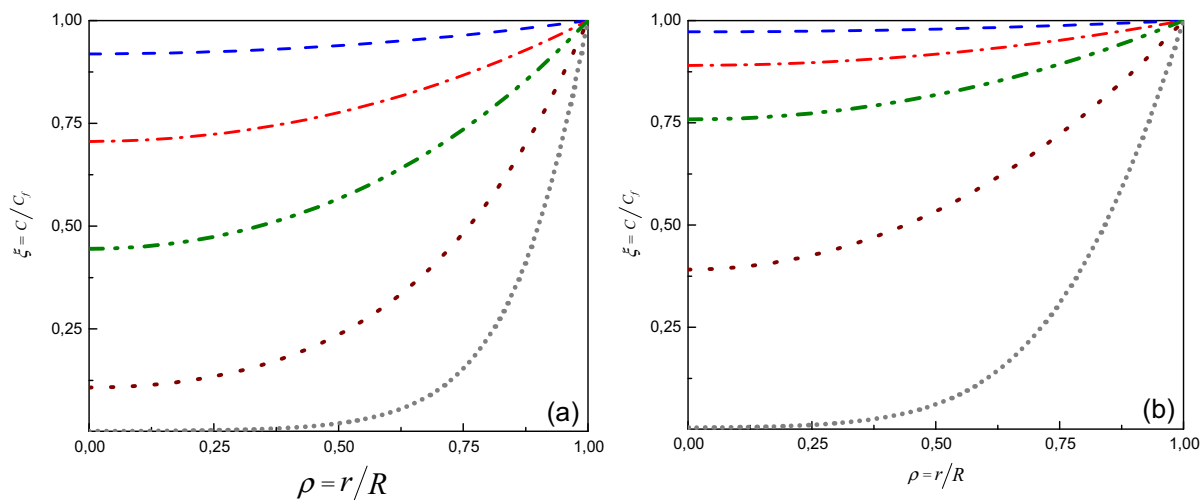

Fig. 1. Dimensionless reactant concentration profiles in the particles. (a) K = 1; (b), K = 5. Lines: ϕ = 1 (dash), 2 (dash dot), 3 (dash dot dot), 5 (dot), 10 (short dot).

adsorption (non-linear kinetics) and that from the model ignoring it (linear kinetics) increases as long as the local dimensionless concentration decreases. Then, the effects of the non-linear chemical kinetics will be more noticeable at low dimensionless concentration, particularly if K is large. These facts can be easily observed in the comparison between Fig. 3a and b, where the dimensionless chemical reaction rate profiles are shown for the same set of parameters used in Fig. 1, which indicate that, for the same ϕ, the larger the K, the flatter the profiles. In turn, this suggests a better utilization of the available active sites is done in that case.

3.2. Catalytic effectiveness

In linear adsorption and kinetic systems, the dimensionless reaction rate profiles along the particles do not depend on the fluid phase concentration (Aris, 1975; Levenspiel, 1999; Fogler, 2006; Froment et al., 2011). However, for the LHHW kinetics, they depends both on ϕ and K (see Fig. 3) and, considering the definition of the latter (K = $K_L C_f$), they consequently depend on C_f. Thus, according to Eq. (11) it is expected that the effectiveness factor also depends on the observed concentration in the fluid phase (C_f) through K. It should be noted that K_L is an intrinsic property of the system, while C_f is an experimental parameter. Fig. 4 shows the effectiveness factor (η) represented, conventionally, as a function of the Thiele modulus (ϕ), considering different K values according to Eq. (11).

It can be seen that if K is very low, the relationship between η and ϕ is essentially the typical one (no adsorption or linear adsorption considered),

$$\eta = (3/\phi^2)(\phi \coth(\phi) - 1). \qquad (14)$$

If the non-linear adsorption of the reactant is taken into account, the shape of the $\eta - \phi$ relationship is similar. Nevertheless the higher the K, the more efficient the performance of the catalyst particles, particularly if ϕ is larger than 1. This is consistent with the previous observations about the lower impact of diffusion restrictions on the concentration profiles at larger K values (profiles become flatter along the particle, see Fig. 1). Consequently, the volume average chemical reaction rates and the effectiveness factors are higher.

It is important to note that both K = $K_L C_f$ and $\phi = R\sqrt{kC_T K_L/D}$ depend on K_L and, then, different values of this constant will produce changes on the two parameters characterizing the system
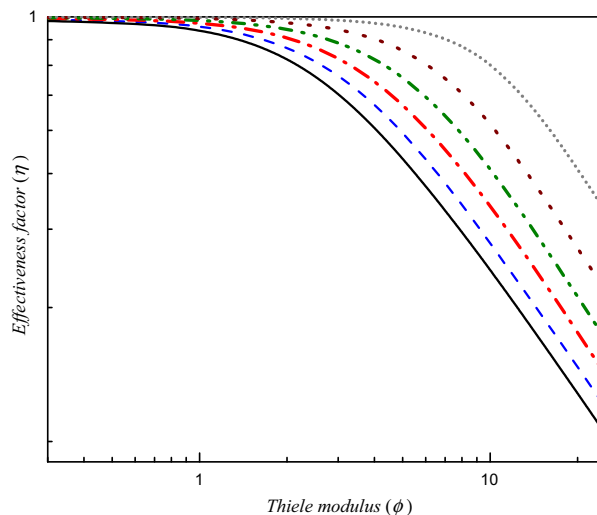

Fig. 4. Effectiveness factors (η) as a function of the Thiele modulus (ϕ). Lines: K $\to$ 0 (solid), K = 0.1 (dash), 0.5 (dash dot), 1 (dash dot dot), 2 (dot), 5 (short dot).

model: the higher the K_L, the lower the effectiveness factor. This behavior was also observed by Chu and Hougen (1962), who represented the effectiveness factor as a function of $M = R\sqrt{k/D}$, using K_L as a parameter for given values of C_f. However, when a given catalyst is considered at a certain temperature, R, kC_T, K_L and D will be constant and, in this case, Fig. 4 shows that the higher the concentration of reactant in the fluid phase (C_f), the higher the effectiveness of the catalyst particles. A similar behavior was shown by Rajadhyaksha et al. (1976) in their studies of effectiveness factors in LHHW type and general order kinetics.

3.3. The Weisz-Prater approach in LHHW type kinetics

Laboratory reactors with different configurations can be used to determine chemical reaction rates as a function of concentration in the fluid phase (Berty, 1999; Froment et al., 2011), these being "observed" rates (r_{obs}), which are also the volume averaged reaction rates in the particle ($\bar{r}$). As already shown in the previous section, the effectiveness factor is not only a function of the ϕ but also of K and, consequently, of C_f. Then, from Eq. (10)
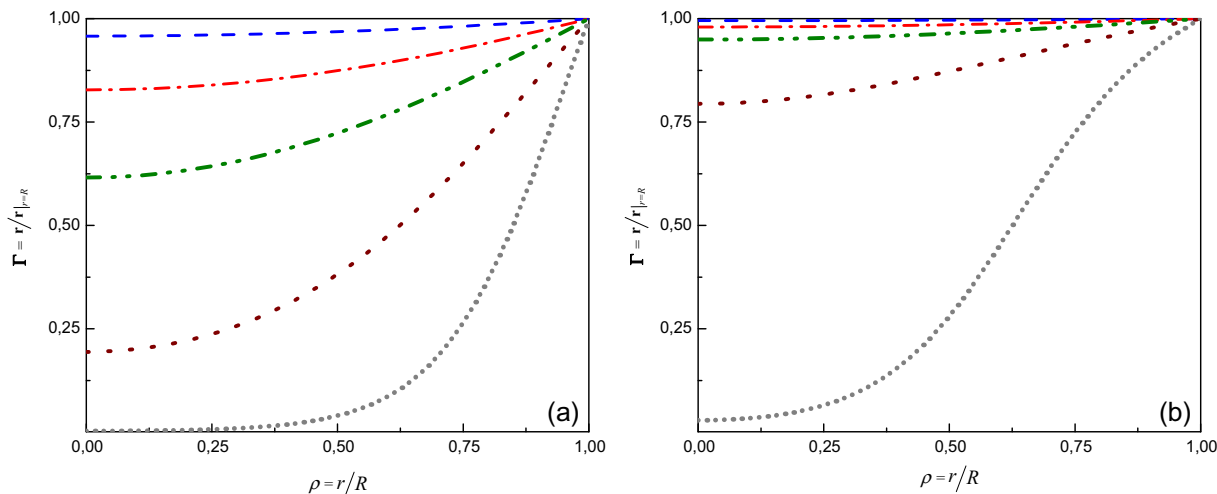

Fig. 3. Dimensionless chemical reaction rates (Γ) as a function of position in the catalyst particles (ρ). (a) K = 1, (b) K = 5. Lines: ϕ = 1 (dash), 2 (dash dot), 3 (dash dot dot), 5 (dot), 10 (short dot).

$$r_{obs} = \eta k C_T \left(\frac{K_L C_f}{1 + K_L C_f} \right) \qquad (15)$$

but, since η is a complex function of K and ϕ, Eq. (15) cannot be used directly to determine kC_T and K_L by data fitting.

The Weisz-Prater parameter has been extensively used to evaluate the relative magnitude of diffusion limitations inside porous catalyst particles by means of the so-called Weisz-Prater criterion (Weisz and Prater, 1954; Levenspiel, 1999; Fogler, 2006; Froment et al., 2011) and to determine pure, intrinsic kinetic constants in systems where those limitations exist (Fogler, 2006; Bidabehere et al., 2017). Even though the concepts of "Weisz-Prater parameter" and "Weisz-Prater criterion" have been used indistinctly, it is necessary to be aware of the differences between them.

The Weisz-Prater parameter (also known as Wagner-Weisz-Wheeler modulus (Levenspiel, 1999)) is defined as the relationship between the observed chemical reaction rate and a characteristic rate of diffusion mass transport (Weisz and Prater, 1954; Fogler, 2006),

$$\theta = \frac{R^2}{D C_f} (r_{obs}). \qquad (16)$$

It should be noted that Eq. (16) corresponds to a dimensionless group, which contains experimentally observable amounts and, most importantly, it is independent from the kinetic expression. The classic criterion by Weisz and Prater states that, only in the case of first order kinetics, if the Weisz-Prater parameter calculated from Eq. (16) is much smaller than one, then the diffusion limitations inside the catalyst particles are negligible. That statement is valid when the concentration profiles inside the particles are either at the steady state (Weisz and Prater, 1954; Fogler, 2006; Froment et al., 2011) or under transient conditions (Bidabehere et al., 2017). Petersen (1965) and Bischoff (1967) introduced the concept of generalized Weisz-Prater parameter

$$\theta_G = \frac{(r_{Aobs}) R^2}{2 \int_{C_{eq}}^{C_f} D(C) g(C) dC} g(C_f), \qquad (17)$$

which can be applied to different types of kinetic expressions and also in the case the diffusion coefficient changes with the concentration. For the system being considered in this work $g(C) = C/(1 + K_L C)$, $C_{eq} = 0$ and the diffusion coefficient is constant. The generalized Weisz-Prater criterion, states that if $\theta_G << 1$, then the intra-particle diffusion limitations can be neglected.

For the kinetic expression considered here (i.e., LHHW type kinetics), if Eq. (15) is used in Eq. (16), then

$$\theta = \frac{\eta R^2 k C_T}{D C_f} \left(\frac{K_L C_f}{1 + K_L C_f} \right) \qquad (18)$$

or (see Eq. (9))

$$\theta = \eta \phi^2 \left(\frac{1}{1 + K} \right), \qquad (19)$$

η being given by Eq. (11).

It can be seen in Eq. (16) that, provided R and D are known, the Weisz-Prater parameter can be calculated from experimental observations. Eq. (19) shows that, for the system described by Eqs. (6)–(8), θ depends both on ϕ and K and, consequently, on C_f (see Eq. (9)). Fig. 5 shows the Weisz-Prater parameter (θ), calculated from Eq. (19), as a function of K for different values of ϕ. The shaded area in Fig. 5 corresponds to situations where diffusion limitations inside the catalyst particles can be neglected, that is, $\eta > 0.95$. In those cases, then,

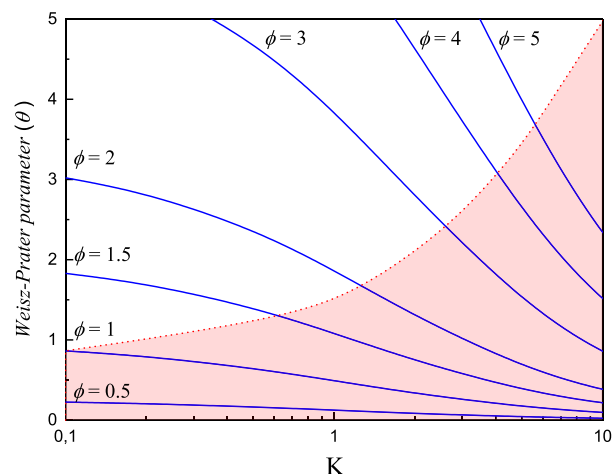$$r_{obs} \cong r|_{r=R} = k C_T \left(\frac{K_L C_f}{1 + K_L C_f} \right) \qquad (20)$$

Fig. 5. Weisz-Prater parameter (θ) as a function of the dimensionless adsorption equilibrium constant (K) at different values of the Thiele modulus (ϕ). Shaded area indicates the region where diffusion limitations inside the catalyst particles are negligible.

and the experimental values of r_{obs} as function of C_f could be used in Eq. (20) to determine the parameters (kC_T) and K_L. The classical criterion to disregard the effects of diffusion limitations ($\eta > 0.95$) for first order reactions is $\theta < 0.75$. Nevertheless, as it can be seen in Fig. 5 for non-linear systems, a single value of θ does not exist below which the chemical control could be assured. Those "limit" values will depend on K and will increase with it (see Fig. 5). The non-uniqueness of the "limit" θ is an expected behavior according to the extended Weisz-Prater criterion by Petersen (1965) and Bischoff (1967), who used a generalized Weisz-Prater modulus in order to determine if diffusion limitations exist in systems where the reaction kinetics is not first order. Differently from Eq. (16), the generalized Weisz-Prater modulus, given by Eq. (17), includes a complex expression containing the concentration dependence of the reaction kinetics, together with equilibrium adsorption constant (K_L), which is unknown. Thus, Eq. (16) is useful from the practical standpoint, since the right hand side only contains quantities which are directly observable.

3.4. Determination of intrinsic kinetic and adsorption equilibrium constants under the existence of diffusion limitations

The Weisz-Prater parameter (θ), which only contains experimentally observable amounts, could be linked to another groups of variables such as kC_T, K_L and C_f in a convenient form and, then, both kC_T and K_L could be evaluated by means of simple algebraic equations.

A modified Thiele modulus can be defined as

$$\phi_M = \frac{\phi}{\sqrt{1 + K}} = R \sqrt{\frac{k C_T K_L}{D (1 + K_L C_f)}}. \qquad (21)$$

If the effectiveness factor is plotted against this modified Thiele modulus, with K as a parameter, the curves are essentially the same in the whole range of ϕ_M. This is coincident with the generalization proposed by Bischoff (1965). It is to be noted that the definitions of the generalized Thiele modulus by Bischoff (ϕ_G) and the modified Thiele modulus (ϕ_M) differ, even though their numerical values are very similar for every K. Unlike ϕ_G, ϕ_M is defined by a simple algebraic equation. Moreover, it does not require to know the concentration at the center of the finite particles and to calculate integral expressions (Bischoff, 1965, 1967).

From Eqs. (19) and (21),

$$\theta = \eta \phi_M^2, \tag{22}$$

where both η and ϕ_M depend on the parameters characterizing the system (that is, ϕ and K). The relationship between the modified Thiele modulus (ϕ_M) and the Weisz-Prater parameter (θ), for different values of K, is shown in Fig. 6.

The solid line in Fig. 6 corresponds to the case of K → 0 (diffusion-reaction without adsorption) or linear adsorption equilibrium. In that case, both η (see Eq. (14)) and θ will only depend on ϕ (Fogler, 2006)

$$\theta = 3(\phi \coth(\phi) - 1). \tag{23}$$

It can be seen in Fig. 6 that the dependence between θ and ϕ_M is essentially the same, independently from the value of the parameter K. Then, such dependence could be expressed by an algebraic equation, which is analogous to Eq. (23)

$$\theta \cong 3(\phi_M \coth(\phi_M) - 1). \tag{24}$$

The fact that ϕ is independent from the fluid phase concentration (C_f), while K certainly depends on it (see Eq. (9)), makes it easier to simultaneously determine K_L and kC_T under reaction conditions. If experiments are performed for a given catalyst (that is, R, D, K_L and kC_T are the ones corresponding to that given system) to determine the reaction rates (r_{obs}) at different reactant concentrations in the fluid phase (C_f), Eq. (16) can be used to assess the corresponding values of the Weisz-Prater parameter. A priori, only a pair of experiments are necessary; for example using C_{f1} and C_{f2} to yield θ_1 and θ_2. Then, by means of the relationship shown in Fig. 6 (or by means of Eq. (24)), the corresponding values of the modified Thiele moduli (ϕ_{M1} and ϕ_{M2}) can be found. From Eq. (21) it is easy to see that

$$\frac{\phi_{M2}^2}{\phi_{M1}^2} = \frac{\phi^2/(1+K_2)}{\phi^2/(1+K_1)} = \frac{1+K_L C_{f1}}{1+K_L C_{f2}}. \tag{25}$$

Note that the Thiele modulus ($\phi = R\sqrt{kC_T K_L/D}$) is the same for both experiments; then, the only unknown in Eq. (25) is K_L. It can be observed in Eq. (21) that

$$\phi^2 = \phi_{M1}^2(1 + K_L C_{f1}) = \frac{R^2 K_L}{D} kC_T \tag{26}$$

where kC_T is the only unknown.

Results from Carrara and Rubiolo (1994, 1996), who studied the hydrolysis of lactose by using *Kluyveromyces fragilis* β-galactosidase immobilized on chitosan beads, can be used to
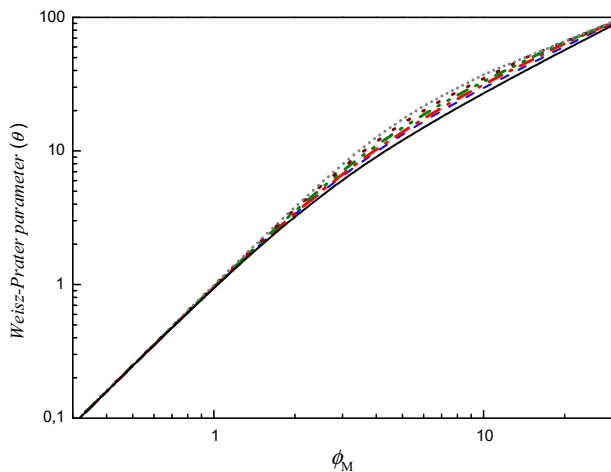

Fig. 6. Dependence between Weisz-Prater parameter (θ) and modified Thiele modulus (ϕ_M). Lines: K → 0 (solid), K = 0.1 (dash), 0.5 (dash dot), 1 (dash dot dot), 2 (dot), 5 (short dot).

exemplify the method. Those authors assumed that a Michaelis-Menten-type kinetics (without product inhibition) was applicable, which is widely recognized as having a complete mathematical similarity with LHHW type kinetics (Levenspiel, 1999; Gottifredi and Gonzo, 2005a; Froment et al., 2011; Towler and Sinnott, 2013). In those cases, the observed rate of reaction per volume of catalyst ($r_{obs}[gmol/(sm_{CAT}^3)]$) can be described in terms of the observed concentration of substrate in the fluid phase (C_f) by

$$r_{obs} = \eta \left(\frac{k_2 E^O C_f}{K_m + C_f} \right). \tag{27}$$

where $k_2[gmol_{substrate}/(skg_{proteine})]$ is the rate constant for the reaction of the enzyme-substrate (ES) complex to give product, $E^O[kg_{proteine}/m_{CAT}^3]$ is the initial enzyme concentration and $K_m[gmol/m^3]$ is known as the Michaelis-Menten constant (Froment et al., 2011). It is easy to see that an analogy between constants can be established to be

$$K_L \equiv 1/K_m \tag{28}$$

and

$$kC_T \equiv k_2 E^O \tag{29}$$

which would make Eqs. (27) and (15) to be identical.

The experiments were performed in a well-stirred batch reactor with W_{CAT}/V_f = 1.5 g immobilized enzyme/15 mL of substrate solution, without significant external mass transfer resistance (Sh > 20); catalysts particles had average diameter $d = 2R = 2.2 \ 10^{-3}$ m and a density of δ_{CAT} = 1102 kg/m³. Table 1 shows the values of conversion as a function of time observed by Carrara and Rubiolo (1996) after an initial enzyme concentration of 0.967 mg protein/mL and an initial lactose concentration of 15.0%. The values of observed reaction rates (r_{obs}) in Table 1 were calculated using a mass balance for the substrate in a well-stirred batch reactor with constant volume

$$-V_f \frac{dC_f}{dt} = \frac{W_{CAT}}{\delta_{CAT}} r_{obs}, \tag{30}$$

and the corresponding Weisz-Prater parameters (θ) were assessed by means of Eq. (16) using a value of diffusivity in the particles (D = 6.8 10^{-10} m²/s) taken from Bassi et al. (1987). Once the values of θ were known, they were used in Eq. (24) in order to calculate the corresponding modified Thiele modulus (ϕ_M).

Table 2 shows the calculation of both K_L and kC_T from various experimental points using Eqs. (25) and (26). Different pairs of points C_{f_1} and C_{f_2} were used in Eq. (25), the point at $t = 5$ min (i.e., C_{f_1} = 390.4 gmol/m³) being chosen as a reference. With ϕ_{M_1} and ϕ_{M_2} corresponding values (see Table 1), Eq. (25) can used to determine the value of K_L; furthermore, the value of kC_T was found by means of Eq. (26).

Even though a few experiments are needed to simultaneously determine kC_T and K_L, it would be convenient to perform some trial experiments to accomplish K = $K_L C_f$ to be in the 0.1–10 range, so as to improve parametric sensibility. If K << 0.1 the denominator in Eq. (2) is very close to one and the adsorption equilibrium can be adequately described by a linear relationship according to the Henry's law ($Q = K_L C_T C = K_H C$). In this limiting case, once the Weisz-Prater parameter is experimentally determined according to Eq. (16), the Thiele modulus (ϕ) can be calculated by means of Eq. (23), and the product kK_H can be assessed now from Eq. (13). Nevertheless, the parameters k and K_H cannot be individually determined when the steady state was assumed. On the other hand, provided K is very large, it is easy to see in Eq. (21) that $\phi_M^2 \to \phi^2/K_L C_f$ and K_L would cancel in Eq. (25), thus making it not possible to assess K_L by means of that equation. Moreover, C_f

Table 1
Application of the method to experimental results. Hydrolysis of lactose by β-galactosidase immobilized on chitosan beads. Data from Carrara and Rubiolo (1996).

Time	Lactose conversion	Fluid phase lactose concentration	Observed rate of reaction	Weisz-Prater parameter	Modified Thiele modulus
t	X	C_f	r_{obs}	θ	ϕ_M
(min)	(%)	(gmol / m^3)	(gmol/s m^3)	(dimensionless)	(dimensionless)
5	11	390.4	1.772	9.08	3.69
10	22	342.1	1.611	8.38	3.79
15	32	298.2	1.289	7.69	3.56
20	40	263.2	1.289	8.72	3.90
25	48	228.1	1.128	8.80	3.93
30	55	197.4	0.967	8.72	3.90
40	67	144.7	0.725	8.91	3.97
50	76	105.3	0.564	9.53	4.18

Table 2
Values of parameters K_L and kC_T. Hydrolysis of lactose by β-galactosidase immobilized on chitosan beads. Data from Carrara and Rubiolo (1996).

C_{f_2}	$K_L \times 10^3$	kC_T
(gmol/m^3)	(m^3/gmol)	(gmol/s m^3)
263.2	1.244	9.131
228.1	1.030	10.407
197.4	0.703	13.854
144.7	0.707	13.793
105.3	1.102	9.919
Mean value	0.957	11.421
Standard deviation	0.243	2.241

in the experiments should ensure that r_{obs}/C_f is not constant; otherwise, Eq. (16) will show identical values of the Weisz-Prater parameter and $\phi_{M1} = \phi_{M2}$, thus leading Eq. (25) to be inconsistent.

From the average values given in Table 2, the resulting value of Thiele modulus is $\phi = 4.41$. Moreover, the dimensionless adsorption equilibrium constant K $= K_L C_f$ varies in the range of 0.075–0.420. As it can be seen in Fig. 6, if $3.5 < \phi_M < 4.2$ (see the values in Table 1), all the curves for K < 0.5 are essentially coincident. This behavior justifies the use of Eq. (24) (or the solid line in Fig. 6) to obtain the value of ϕ_M as a function of θ. The accuracy of the method is given by that of the calculation of the Weisz-Prater parameter, $\theta = (R^2/D)(r_{obs}/C_f)$, from experimental observations, since both constants are calculated from this dimensionless group by means of algebraic equations.

Fig. 7 shows the experimental conversion as a function of time observed by Carrara and Rubiolo (1996) and the simulation from
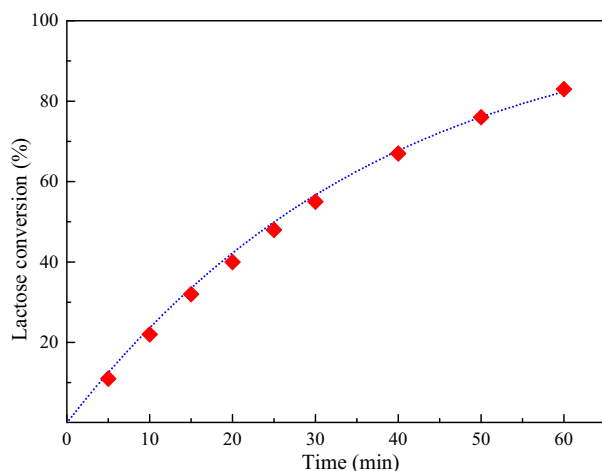

Fig. 7. Conversion of lactose as a function of time. (Diamonds: experimental points; short dot: simulated values for $kC_T = 11.421$ gmol/s m^3, $K_L = 9.57 \cdot 10^{-4}$ m^3/gmol, $D = 6.8 \cdot 10^{-10}$ m^2/s, $R = 1.1 \cdot 10^{-3}$ m, $\delta_{CAT} = 1102$ kg/m^3, and $W_{CAT}/V_f = 1.5$ g immobilized enzyme/15 mL of substrate solution).

Eq. (30), where the apparent rate of reaction is given by Eq. (15) and the parameters K_L and kC_T are the average values in Table 2.

4. Conclusions

The steady state diffusion-adsorption-reaction system in spherical porous catalytic particles where chemical reactions follow Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics can be described in terms of two parameters: the well known Thiele modulus (ϕ) and the dimensionless adsorption equilibrium constant K, which is defined as the product between the Langmuir's equilibrium constant (K_L) and the fluid phase concentration of the reactant (C_f). It was shown that for a certain ϕ value, the larger the K, the less pronounced the concentration profiles. As a consequence of the non-linearity in the source term of the mass balance, the volume average chemical reaction rates and, consequently, the effectiveness factors (η), will increase with the value of K, thus indicating a more efficient performance of the catalyst particles, particularly when ϕ is larger than 1.

Differently from first order kinetics, a single value of the Weisz-Prater parameter does not exist below which the chemical control could be assured in chemical reactions which follow LHHW kinetics. Those "limit" values depend on K and increase with it.

After the definition of the modified Thiele modulus ϕ_M, it can be observed an essentially unique relationship between η and ϕ_M, regardless the value of K. The same behavior was noticed for the relationship between θ and ϕ_M. This uniqueness allows the simultaneous determination of kinetic constants and adsorption parameters under reaction conditions, by means of the Weisz-Prater approach after a very low number of experiments.

The method proposed here was successfully applied to experimental results previously reported.

Appendix A

The reactive system is

$$A + V \overset{K_L}{\Longleftrightarrow} A* \overset{k_s}{\rightarrow} P + V. \tag{A.1}$$

The total concentration of catalytic sites is

$$C_T = Q + C_V. \tag{A.2}$$

The mass balance for the adsorbed species in the solid surface is

$$\frac{dQ}{dt} = k_{ads}CC_V - k_{des}Q - k_sQ. \tag{A.3}$$

If a pseudo-steady state is assumed in the solid ($dQ/dt = 0$), an equilibrium between the adsorbed ($A*$) and unadsorbed (A) species and the vacant sites in the solid (V) exists at every moment.

$$Q = \left(\frac{k_{ads}}{k_{des} + k_s}\right) C C_V. \tag{A.4}$$

Since it was assumed that the adsorption-desorption steps are much faster than the chemical reaction ($k_{ads} >> k_s$ and $k_{des} >> k_s$), Eq. (A.4) reduces to

$$Q = K_L C C_V, \tag{A.5}$$

where the adsorption equilibrium constant of reactant A, K_L, is

$$K_L = \frac{k_{ads}}{k_{des}} = \frac{Q}{C C_V}. \tag{A.6}$$

If Eqs. (A.2) and (A.5) are combined, the "adsorption equilibrium isotherm" is obtained

$$Q = C_T \left(\frac{K_L C}{1 + K_L C}\right). \tag{2}$$

It should be noted that, when diffusion-adsorption-reaction phenomena exist, the concentration of reactant inside the particle depends on the position ($C = C_{(r)}$); thus

$$Q_{(r)} = C_T \left(\frac{K_L C_{(r)}}{1 + K_L C_{(r)}}\right). \tag{A.7}$$

The fractional coverage (φ) represents the fraction of active sites which are covered. When there is a concentration profile along the particle, the local fractional coverage is

$$\varphi_{(r)} = \frac{Q_{(r)}}{C_T} = \left(\frac{K_L C_{(r)}}{1 + K_L C_{(r)}}\right) \tag{A.8}$$

from which it is straightforward to observe that

$$K_L C_{(r)} = \frac{\varphi_{(r)}}{1 - \varphi_{(r)}}. \tag{A.9}$$

The right hand side in Eq. (A.9) represents the local relationship between the concentrations of covered and still free active sites.

Particularly, at the external boundary of the particle ($r = R$), where ($C_{(R)} = C_f$)

$$K = K_L C_f = \frac{\varphi_{(R)}}{1 - \varphi_{(R)}}. \tag{A.10}$$

from which

$$K = \frac{Q|_{r=R}}{C_V|_{r=R}}. \tag{A.11}$$

Thus, the dimensionless adsorption equilibrium constant (K) represents the relationship between the number of covered and still free (vacant) adsorption sites that would be reached in the case that concentration gradients in the particles do not exist.

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