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A Full Analytical Solution for the Sorption−Desorption Kinetic Process Related to Langmuir Equilibrium Conditions

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A full analytical solution for the kinetics of an adsorption−desorption reaction is presented. The proposed solution is made by solving the differential equation which describes the accumulation rate of the sorbed complex, based on a site specific, single layer adsorption mechanism. Two important features of the presented solution are as follows: (a) Unlike previously presented analytical solutions, this equation does not impose any initial conditions and is also applicable for nonzero initial sorbed concentrations. Thus, the proposed equation might be used for modeling desorption as well as adsorption or as a part of a model that describes solute transport through an adsorptive medium in nonequilibrium conditions. (b) It converges with the Langmuir/Scatchard equations at infinite time (i.e., chemical equilibrium).

Introduction

The mathematical modeling of adsorption−desorption reactions in nonequilibrium conditions is of great importance in soil and water science as well as in life science fields. Whenever a prediction of the concentration of a solute moving through an adsorptive media is desired (for agricultural or environmental purposes, for example) and equilibrium conditions cannot be assumed, there is a need to mathematically model the rate of the adsorption−desorption process.[1−4] In life science, kinetic modeling of the binding of ligands to receptors on cell membranes[5] or to nucleic acids[6−7] might also have important implications. It should be mentioned that computer resources allow solving of the problem numerically, without the need for analytical solutions. The advantage of such a solution is that it allows an explanatory basis and, in addition, it might be easier to combine it as a subroutine into a complex flow model.

Conventional Equations. The inventory of kinetic equations was extensively reviewed by Sparks,[1] distinguishing between "mechanistic rate laws" and "apparent rate laws". While the former refers to rate laws which are based on theoretical reasoning and supposed to be related to the mechanism of the chemical reaction, the latter refers to empiric equations which are used to fit experimental data. Among the most widely used *apparent rate laws* are the pseudo-first-order[8] and the pseudo-second-order[9] kinetic equations (eqs 1 and 2, respectively), apparently due to their simplicity and great ability to fit to experimental data.

$$\frac{dC(t)}{dt} = k(C(t) - C_{eq}) \tag{1}$$

$$\frac{dC(t)}{dt} = k(C(t) - C_{eq})^2 \tag{2}$$

where $C(t)$ is the concentration at time t (M), C_{eq} is the equilibrium concentration (M), and k is the rate constant (s^{-1} and $M^{-1}\ s^{-1}$ for eqs 1 and 2, respectively).

Despite that, these equations are not related to the chemistry or to the physical properties of the adsorption reaction and should be therefore considered as empirical, rather than explanatory models.[10]

Because of their empiric nature, the coefficients derived from eqs 1 and 2 depend on the initial concentrations of the reaction[9,11] and therefore cannot be extrapolated and used for prediction of the kinetics of the reaction at different initial concentrations.[9,10]

Mechanistic Adsorption−Desorption Rate Laws. A reversible adsorption process in which a solute (A) reacts with an unoccupied binding site (B) to create a sorbed complex (C), as it is in most sorption processes, might be described as

$$A + B \leftrightarrow C \tag{3}$$

Thus, the accumulation rate of C should be a function of the rate of C formation, minus C disintegration to A and B by the reverse reaction. The most trivial way to describe the kinetics of such reaction would be an overall second-order kinetics equation for the formation of C and a first-order kinetics equation for the dissociation of C to A and B; thus, we may write

$$\frac{dC}{dt} = k_f[A][B] - k_b[C] \tag{4}$$

where dC/dt represents the accumulation rate of the sorbed complex ($M\ s^{-1}$) and k_f ($M^{-1}\ s^{-1}$) and k_b (s^{-1}) are the kinetic coefficients for sorption and desorption, respectively.

It is important to notice that eq 4 ignores transport limitations, and therefore it is only applicable when transport processes are very fast relative to the adsorption reaction.[11]

At chemical equilibrium the overall accumulation rate of the sorbed complex is zero (dC/dt ($t \rightarrow \infty$) = 0), and we can express the equilibrium constant of the reaction in eq 3 as

$$K_L = \frac{[C]}{[A][B]} = \frac{k_f}{k_b} \tag{5}$$

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The index $_L$ for the equilibrium constant indicates that when applying the appropriate mass balance for the concentrations of A and B (as will be shown), the equilibrium constant is actually the Langmuir or Scatchard coefficient.

Kuo and Lotse[12] presented an analytical solution for eq 4 by integrating it, using the initial condition of a "clean" sorbent ($C(0) = 0$); thus, when there is no sorbate initially adsorbed, this results in eq 6. Consequently, eq 6 is only applicable for adsorption processes that start with zero sorbed complex concentration. The solution presented in that study is

$$\ln\left(\frac{C - Y - X}{C + Y - X}\right) = 2Yk_f t + \ln\left(\frac{X + Y}{X - Y}\right) \quad (6)$$

where

$$Y = \left\{\frac{1}{4}\left(A_0 + B_0 + \frac{k_b}{k_f}\right)^2 - A_0 B_0\right\}^{1/2} \quad (6.1)$$

$$X = \frac{1}{2}\left(A_0 + B_0 + \frac{k_b}{k_f}\right) \quad (6.2)$$

A_0 is the initial solute concentration, B_0 is the initial binding sites concentration, and C is the sorbed complex concentration.

Thus, when the the initial solute and adsorption site concentration and the kinetic coefficients are known, eq 6 can be used to calculate the adsorbed complex concentration at any given time. Alternatively, fitting eq 6 to experimental data may be used to derive the kinetic coefficients.

This work aims to present an analytical solution to eq 4 which would also apply when a nonzero initial concentration of the sorbed complex exists.

Theory

Assumptions. Some of the assumptions needed for the kinetic model are actually identical to those employed for the Langmuir model:[13,14]

(1) Monolayer and site specific adsorption.

(2) All sites have the same adsorption energy.

In addition to the Langmuir assumptions we need to assume that:

(3) There are no solute concentration gradients due to electrostatic effects.[15] The solute should be homogenically dispersed, so we can assume that the concentration near the surface equals that of the bulk solution.

(4) No distinction is made between activity and concentration; therefore, we must assume that the ionic strength is low.

(5) Adsorption and desorption are the only rate-limiting processes; thus, transport of solutes in solution is very fast.

Solving Eq 4. We can examine the process presented in eq 3 from mass conservation considerations (i.e., the concentrations of A or B at any time must be equal to their initial concentrations minus the concentration adsorbed since $t = 0$). And since the concentration adsorbed equals that of the formed complex, which is its actual concentration minus the initial concentration ($C - C_0$), we can write

$$A = A_0 - (C - C_0) \quad (7)$$

$$B = B_0 - (C - C_0) \quad (8)$$

where A_0, B_0, and C_0 are the initial concentrations of A, B, and C, respectively.

Substituting the mass balance for A and B to eq 4 yields

$$\frac{dC}{dt} = k_f(A_0 - (C - C_0))(B_0 - (C - C_0)) - k_b(C) \quad (9)$$

Rearranging eq 9 yields a second-order differential equation for C in the general form of

$$\frac{dC}{dt} = aC^2 + bC + c \quad (10)$$

where

$$a = k_f \quad (10.1)$$

$$b = -k_f\left(A_0 + B_0 + 2C_0 + \frac{k_b}{k_f}\right) \quad (10.2)$$

$$c = k_f(A_0 + C_0)(B_0 + C_0) \quad (10.3)$$

With the use of Maple 7 software (Waterloo Maple, Inc., 1981−2001), an integrated solution for that differential equation is achieved (for detailed justification see Appendix A)

$$C(t) = -\frac{b}{2a} - \frac{1}{2}\frac{(e^{(b^2 - 4ac)^{1/2}\,(t+Z)} - 1)\dfrac{(b^2 - 4ac)^{1/2}}{a}}{e^{(b^2 - 4ac)^{1/2}\,(t+Z)} + 1} \quad (11)$$

with Z as an integration coefficient. If we define

$$X = \sqrt{b^2 - 4ac} \quad (12)$$

we can write eq 11 as

$$C(t) = -\frac{b}{2a} - \frac{(e^{X(t+Z)} - 1)X}{2a(e^{X(t+Z)} + 1)} \quad (13)$$

To derive the integration constant Z we can introduce as a boundary condition the initial concentration at $t = 0$ ($C(0) = C_0$) and get (for detailed justification see Appendix B)

$$Z = \frac{\ln\left(\dfrac{k_f A_0 + k_f B_0 + k_b + X}{-k_f A_0 - k_f B_0 - k_b + X}\right)}{X} \quad (14)$$

Substituting the integration constant Z into eq 13 yields (for detailed justification see Appendix B):

$$C(t) = \frac{1}{2}(A_0 + B_0) + C_0 + \frac{1}{2K_L} - \frac{(Ye^{tX} - 1)X}{2k_f(Ye^{tX} + 1)} \quad (15)$$

where

$$X = k_f\sqrt{-4(A_0 + C_0)(B_0 + C_0) + \left(A_0 + B_0 + 2C_0 + \frac{1}{K_L}\right)^2} \quad (15.1)$$

and

$$Y = \frac{k_f\left(A_0 + B_0 + \dfrac{1}{K_L}\right) + X}{-k_f\left(A_0 + B_0 + \dfrac{1}{K_L}\right) + X} \quad (15.2)$$

An important feature of eq 15 is that it converges with the Langmuir or Scatchard equations at chemical equilibrium. This can be tested by checking the limit of eq 15 when $t \rightarrow \infty$.

$$\lim_{t \to \infty} C(t) = \frac{1}{2}(A_0 + B_0) + C_0 + \frac{1}{2K_L} - \frac{(Ye^{X\infty} - 1)X}{2k_f(Ye^{X\infty} + 1)} \quad (16)$$

After some algebraic manipulations, substitution of the mass balance equation for A (eq 7), and recalling that at $t = 0$, the total concentration of sites (B_T) must equal the sum of occupied and unoccupied sites (C_0 and B_0, respectively), we can derive (for detailed justification see Appendix C)

$$C_\infty = \frac{AB_T K_L}{1 + K_L A} \quad (17)$$

where C_∞ is the equilibrium sorbed complex concentration [mol $\times$ kg^{-1}], A is the equilibrium solution concentration [M], B_T is the total adsorption sites concentration [mol kg^{-1}], and K_L is the Langmuir adsorption coefficient [M^{-1}].

Conclusions

Whenever possible, the use of mechanistic rate laws is preferred over the use of apparent rate laws because the former may give insights regarding the mechanisms of the adsorption−desorption processes.[1,11] Mechanistic models may be used for extrapolating the rate constants in order to predict reaction rates in different sorbent or adsorbate initial conditions. Such evaluation of virtual experiments must be based on a model which is physically rationalized, whereas empirical or semiempirical models cannot be used for such extrapolations.

Coefficients derived from mechanistic rate laws may also be used for describing reaction rates in a binary solute system in which two solutes compete on the same type of adsorption sites[16] or to describe the movement and breakthrough curve of a reactive solute in an adsorptive media in nonequilibrium conditions;[17] such predictions may be useful in soil science,[18] environmental applications,[4, 18−20] and even chromatography.[17]

Despite the advantages of mechanistic rate laws, they are not widely used even in cases when the quite restrictive theoretical assumptions needed to apply them may be valid. We ascribe that at least in part to the need to work with nonintegrated differential equations (as eq 9) and the substantial computer resources needed to fit such equations to experimental data.[7] In addition, analytical solutions may also be valuable in discerning the qualitative time behavior.[11] The analytical solution presented here might help in making the mechanistic rate law expressed in eq 4 more accessible for researchers, since integrated rate laws are easier to work with and require less computer resources.

An important feature of eq 15 is that at infinite time (i.e., chemical equilibrium) it converges with the Langmuir/Scatchard equations (Appendix C). Since the Langmuir coefficient K_L (which reflects the equilibrium conditions and the ratio between kinetic coefficients) and the total concentration of adsorption sites ($B_0 + C_0$) may be derived from relatively simple equilibrium batch adsorption experiments, only one of the fitted parameters of the kinetic coefficients for the kinetic experiment are left, assuming that the initial concentrations of the adsorbent A, the sorbate B, and the complex C are known. It is important to mention that eq 15 is not exclusively applicable for adsorption−desorption processes but to any chemical process that follows eq 3 in a closed system.

Appendix

A. **Justification of the Differential Equation Solution.** To minimize algebraic errors, the following mathematical terms were compared to those obtained by using Maple 7 software (Waterloo Maple, Inc., 1981−2001).

As shown before, for brevity we substitute

$$X = \sqrt{b^2 - 4ac} \quad (12)$$

into eq 11, yielding

$$C(t) = -\frac{b}{2a} - \frac{(e^{X(t+Z)} - 1)X}{2a(e^{X(t+Z)} + 1)} \quad (13)$$

By differentiating eq 13 by time we get

$$\frac{dC(t)}{dt} =$$
$$-\frac{X}{2a}\left(\frac{Xe^{X(t+Z)} \times (e^{X(t+Z)} + 1) - Xe^{X(t+Z)} \times (e^{X(t+Z)} - 1)}{(e^{X(t+Z)} + 1)^2}\right) \quad (13.1)$$

which can be rearranged to

$$\frac{dC(t)}{dt} = \frac{-X^2 e^{X(t+Z)}}{a(e^{X(t+Z)} + 1)^2} \quad (13.2)$$

To prove that eq 13.2 complies with the initial differential equation that describes the kinetics of the process (eq 10), we can introduce the integrated equation (eq 13) into eq 10

$$\frac{dC(t)}{dt} = a\left(-\frac{b}{2a} - \frac{(e^{X(t+Z)} - 1)X}{2a(e^{X(t+Z)} + 1)}\right)^2 +$$
$$b\left(-\frac{b}{2a} - \frac{(e^{X(t+Z)} - 1)X}{2a(e^{X(t+Z)} + 1)}\right) + c \quad (13.3)$$

And after simplifying the right-hand side we obtain

$$\frac{dC(t)}{dt} = \frac{(e^{X(t+Z)} - 1)^2 X^2}{4a(e^{X(t+Z)} + 1)^2} - \frac{b^2}{4a} + c \quad (13.4)$$

Rearranging eq 12 to $c = (b^2 - X^2)/4a$ and introducing it to eq 13.4 yields

$$\frac{dC(t)}{dt} = \frac{(e^{X(t+Z)} - 1)^2 X^2}{4a(e^{X(t+Z)} + 1)^2} - \frac{b^2}{4a} + \frac{b^2 - X^2}{4a} \quad (13.5)$$

which can be simplified to

$$\frac{dC(t)}{dt} = \frac{-X^2 e^{X(t+Z)}}{a(e^{X(t+Z)} + 1)^2} \quad (13.6)$$

Thus, the same term is obtained by both differentiating the integrated equation (eq 13.2) and substituting the integrated equation into the original differential equation (eq 10).

Appendix B. Derivation and Substitution of the Integration Constant. To derive the "integration constant" Z, we introduce to eq 13 as a boundary condition the initial concentration of complexes at $t = 0$, $C = C_0$, yielding

$$C_0 = -\frac{b}{2a} - \frac{(e^{XZ} - 1)X}{2a(e^{XZ} + 1)} \tag{13.7}$$

And by elaborating on Z the following is obtained

$$Z = \frac{\ln\left(\dfrac{-2aC_0 - b + X}{2aC_0 + b + X}\right)}{X} \tag{13.8}$$

By substituting the expressions for the terms a and b (eqs 10.1 and 10.2, respectively), we get

$$Z = \frac{\ln\left(\dfrac{K_fA_0 + K_fB_0 + K_b + X}{-K_fA_0 - K_fB_0 - K_b + X}\right)}{X} \tag{14}$$

The introduction of the integration constant into eq 13 might be done by elaborating on eq 14 and defining Y as

$$Y = e^{XZ} = \frac{-2aC_0 - b + X}{2aC_0 + b + X} \tag{14.1}$$

Substituting again expressions for a and b to eq 14.2 yields

$$Y = \frac{k_f\left(A_0 + B_0 + \dfrac{1}{K_L}\right) + X}{-k_f\left(A_0 + B_0 + \dfrac{1}{K_L}\right) + X} \tag{14.2}$$

By introducing the definition of Y (eq 14.2) to eq 13 we obtain

$$C(t) = -\frac{b}{2a} - \frac{(Ye^{Xt} - 1)X}{2a(Ye^{Xt} + 1)} \tag{14.3}$$

Equation 15 is finally obtained by substituting the terms a and b (eqs 10.1 and 10.2, respectively), knowing the ratio between the two kinetic coefficients (eq 5)

$$C(t) = \frac{1}{2}(A_0 + B_0) + C_0 + \frac{1}{2K_L} - \frac{(Ye^{tX} - 1)X}{2k_f(Ye^{tX} + 1)} \tag{15}$$

Appendix C. Behavior of Eq 15 at Equilibrium Conditions ($t \rightarrow \infty$). After a long period of time the reaction will reach equilibrium. Thus,

$$\lim_{t \to \infty} C(t) = \frac{1}{2}(A_0 + B_0) + C_0 + \frac{1}{2K_L} - \frac{(Ye^{X\infty} - 1)X}{2k_f(Ye^{X\infty} + 1)} \tag{16}$$

Applying l'Hopital's law to eq 14.3 would yield

$$C_\infty = -\frac{b}{2a} - \frac{\dfrac{d(Ye^{Xt} - 1)X}{dt}}{\dfrac{d(2a(Ye^{Xt} + 1))}{dt}} \tag{16.1}$$

Rearranging eq 16.1 yields

$$C_\infty = -\frac{b}{2a} - X \tag{16.2}$$

And by elaborating the term for X (eq 12), we acquire

$$C_\infty = -\frac{b + \sqrt{b^2 - 4ac}}{2a} \tag{16.3}$$

This expression is actually the root equation for eq 10; thus, its solution must yield the equilibrium concentration C_{eq}. This means that there is no more change in the concentrations for all participants; thus, the accumulation *rate* is zero (i.e., equilibrium).

Now we can write eq 10 at equilibrium (zero accumulation rate)

$$\frac{dC(t)}{dt} = aC_\infty{}^2 + bC_\infty + c = 0 \tag{10.1}$$

Substituting the appropriate terms for a, b, and c yields

$$k_fC_\infty^2 - k_f\left(A_0 + B_0 + 2C_0 + \frac{k_b}{k_f}\right)C_\infty +$$
$$k_f(A_0 + C_0)(B_0 + C_0) = 0 \tag{10.2}$$

Since the sum of C_0 (initial "occupied" sites) and B_0 (initial "unoccupied" sites at time zero) must equal the total concentration of adsorption sites (B_T) and using the relation between the kinetic coefficients from eq 5, we get

$$C_\infty^2 - \left(A + C_\infty + B_T + \frac{1}{K_L}\right)C_\infty + (A + C_\infty)B_T = 0 \tag{10.3}$$

yielding

$$C_\infty = \frac{AB_TK_L}{1 + K_LA} \tag{17}$$

Equation 17 represents the concentration at infinite time (equilibrium) and is as a matter of fact identical to the one given by the Langmuir/Scatchard equation.

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