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A COMMENT ON THE DERIVATION

OF THE LANGMUIR ISOTHERM FOR THE

ADSORPTION KINETICS

by

Chris Frenzen

Technical Report For Period

February 1991 - April 1991

Approved for public release; distribution unlimited

Prepared for: Naval Postgraduate School
Monterey, CA 93943

91-01525

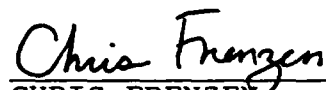NAVAL POSTGRADUATE SCHOOL
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REPORT DOCUMENTATION PAGE	Form Approved OMB No 0704-0188

1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b RESTRICTIVE MARKINGS

2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	Approved for public release; distribution unlimited

4 PERFORMING ORGANIZATION REPORT NUMBER(S)	5 MONITORING ORGANIZATION REPORT NUMBER(S)
NPS-MA-91-010	NPS-MA-91-010

6a NAME OF PERFORMING ORGANIZATION	6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION
Naval Postgraduate School	MA	Naval Postgraduate School

6c ADDRESS (City, State, and ZIP Code)	7b ADDRESS (City, State, and ZIP Code)
Monterey, CA 93943	Monterey, CA 93943

8a NAME OF FUNDING/SPONSORING ORGANIZATION	8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Naval Postgraduate School	MA	O&MN Direct Funding

8c ADDRESS (City, State, and ZIP Code)	10 SOURCE OF FUNDING NUMBERS			
Monterey, CA 93943	PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification) A Comment on the Derivation of the Langmuir Isotherm for the Adsorption Kinetics

12 PERSONAL AUTHOR(S)
Chris Frenzen

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Technical	FROM 02/91 TO 04/91	910401	12

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	ordinary differential equations

19 ABSTRACT

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20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED

22a NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE (Include Area Code)	22c OFFICE SYMBOL
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DD Form 1473, JUN 86   Previous editions are obsolete.   SECURITY CLASSIFICATION OF THIS PAGE

S/N 0102-LF-014-6603

A Comment on the Derivation of the Langmuir Isotherm for Adsorption Kinetics*

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Abstract

The justification for the use of the Langmuir isotherm, basically an equilibrium relation, to relate the subsurface concentration $C(t)$ at time t to the adsorbed surface concentration $\Gamma(t)$ depends, in many adsorption kinetics models, on the presence of two very different time scales. Though this was implicit in the recent derivation in [1], it was not specifically pointed out. The second 'long' time scale is particularly important because it governs the time evolution of $C(t)$, the subsurface concentration, and helps to determine when the Langmuir isotherm approximation is valid. Here the Langmuir isotherm is derived mathematically from the adsorption kinetics equations governing the surface concentration, the subsurface concentration *and* the bulk phase adjacent to the surface.

The dependence of Γ^∞, the equilibrium concentration of a surface-active component at an interface, and C^∞, the corresponding bulk phase concentration, are often related by the Langmuir isotherm (Langmuir [2]):

$$\Gamma^\infty = \frac{\gamma \hat{\Gamma} C^\infty}{1 + \gamma C^\infty} \tag{1}$$

In (1) $\hat{\Gamma}$ represents the saturated surface concentration while γ is a constant. Frequently the assumption is made that at any time t the adsorbed surface concentration $\Gamma(t)$ and the 'subsurface' concentration C(t) (ie., the concentration in a thin layer of bulk phase adjacent to the surface) are related by the equation

$$\Gamma(t) = \frac{\gamma \hat{\Gamma} C(t)}{1 + \gamma C(t)}; \tag{2}$$

see the references given in [1]. Equation (2) is often used as a boundary condition to determine the surface concentration from the subsurface concentration at time t. Some of the the inadequacies of making the intuitive assumption in (2) and the desirability of replacing it with a more fundamental description of the Langmuir isotherm have been discussed in [1]. We also note that in many time dependent problems it is important to establish how initial values of the surface and subsurface concentrations evolve over time to eventually satisfy (2). This time evolution can greatly affect surface tension. For example (see [3], p. 62), at the surface of ordinary tap water the surface tension immediately after formation of the surface is close to the value for pure water, but usually rapidly falls to something like half this value due to adsorbed contaminants.

The key to the validity of (2) lies in the presence of two very different time scales: t_p, the characteristic time defined by the rate constants for adsorption and desorption of subsurface surfactant into the surface, and t_s, the characteristic time defined by the rate constants for passage of subsurface surfactant into and out of the bulk phase. The letters p and s stand for presteady state and steady state respectively. When $t_p \ll t_s$ the relaxation in surface concentration for a given change in subsurface concentration is very rapid. The time scale t_s is particularly important because it controls the time evolution of C(t), something which could not be determined from the derivation given in [1]. The purpose of this letter is to extend the model given in [1] to take into account the passage of subsurface surfactant between the subsurface layer and the bulk phase, thereby deriving the Langmuir isotherm and conditions for its validity from an adsorption kinetics point of view.

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As in [1], let J^+ be the rate at which subsurface surfactant is adsorbed and J^- be the rate at which adsorbed surfactant is desorbed. Assuming no evaporation, we have

$$\frac{d}{dt}\Gamma = J^+ - J^-.$$

We assume, as in [1], that

$$J^+ = k_1 C(t)\left(1 - \frac{\Gamma(t)}{\hat{\Gamma}}\right), J^- = k_2\Gamma(t)$$

where k_1 and k_2 are rate constants. Consequently

$$\frac{d}{dt}\Gamma(t) = k_1 C(t)\left(1 - \frac{\Gamma(t)}{\hat{\Gamma}}\right) - k_2\Gamma(t). \tag{3}$$

Let K^+ be the rate at which bulk phase surfactant passes into the subsurface, and K^- the rate at which subsurface surfactant passes back into the bulk phase. Then

$$\frac{d}{dt}C(t) = J^- - J^+ + K^+ - K^-.$$

We will assume that if C^∞ is the equilibrium bulk phase concentration, then

$$K^+ - K^- = k_3(C^\infty - C(t))$$

for some rate constant k_3. Therefore

$$\frac{d}{dt}C(t) = -\left(k_1 C(t)\left(1 - \frac{\Gamma(t)}{\hat{\Gamma}}\right) - k_2\Gamma(t)\right) + k_3(C^\infty - C(t)). \tag{4}$$

It is equation (4), governing the time evolution of C(t), which was not present in [1]. As initial conditions to (3) and (4) we assume

$$\begin{aligned}\Gamma(0) &= \bar{\Gamma}\\ C(0) &= C^\infty.\end{aligned} \tag{5}$$

In many cases $\bar{\Gamma}$ may be zero, but it need not be.

To understand more fully (3), (4) and (5) we shall now nondimensionalize them by letting

$$\begin{aligned}\Gamma(t) &= C^\infty\Gamma^*(t^*)\\ C(t) &= C^\infty C^*(t^*)\\ t &= \frac{1}{k_3}t^*\end{aligned} \tag{6}$$

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where starred quantities are dimensionless. We have chosen $1/k_3$, the characteristic time for passage of subsurface surfactant into and out of the bulk phase, to nondimensionalize t. Thus $t = t_s t^*$ where $t_s = 1/k_3$. As in [1], we shall let $\rho = k_1/k_2$ and for purposes of discussion here we shall assume that ρ is an order one quantity. The other cases discussed in [1] can be easily adapted to this one.

By our assumption on ρ, $1/k_2$ is a characteristic time for adsorption and desorption into the surface, and we therefore let $t_p = 1/k_2$. Defining

$$\varepsilon = \frac{t_p}{t_s} = \frac{k_3}{k_2},$$

we shall assume that

$$\varepsilon \ll 1.$$

Physically this corresponds to assuming that the characteristic time scale t_p over which changes between the surface and subsurface concentrations occur is much shorter than the time scale t_s over which changes between the subsurface and bulk phase concentrations occur.

Inserting (6) into (3),(4) and (5) and *dropping the stars* for convenience, we find their dimensionless form to be

$$\varepsilon \frac{d}{dt} \Gamma(t) = \rho C(t) \left(1 - \frac{C^\infty}{\hat{\Gamma}} \Gamma(t) \right) - \Gamma(t) \tag{7}$$

$$\varepsilon \frac{d}{dt} C(t) = - \left(\rho C(t) \left(1 - \frac{C^\infty}{\hat{\Gamma}} \Gamma(t) \right) - \Gamma(t) \right) + \varepsilon(1 - C(t)) \tag{8}$$

$$\begin{aligned} \Gamma(0) &= \frac{\bar{\Gamma}}{C^\infty} \\ C(0) &= 1. \end{aligned} \tag{9}$$

Note that *all* dependent and independent variables in (7), (8) and (9) are dimensionless $O(1)$ quantities. The system (7),(8),(9) is a singular perturbation problem, characterized by the presence in (7) and (8) of a small parameter multiplying the highest derivatives. We cannot let $\varepsilon \to 0$ and still hope to satisfy the initial conditions in (9). The resolution of this problem is found in the existence of a 'boundary layer' in time where $\Gamma(t)$ and $C(t)$ change so rapidly that one cannot neglect the derivative terms in (7) and (8). This

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region corresponds, as we shall see, to the rapid relaxation of the surface and subsurface concentrations from their initial values. After this rapid relaxation, or pre-steady state period, the surface concentration $\Gamma(t)$ is in steady state with respect to the instantaneous value of the subsurface concentration C(t). This yields the Langmuir isotherm given in (2).

Away from the region of rapid transition,ie.,in the steady state, we look for the so-called 'outer' solutions in the form of asymptotic expansions in ε:

$$\Gamma^{outer}(t) = \Gamma_0(t) + \varepsilon\Gamma_1(t) + \ldots, C^{outer}(t) = C_0(t) + \varepsilon C_1(t) + \ldots. \quad (10)$$

Substituting (10) into (7) and (8) then yields to $O(\varepsilon^0)$:

$$\rho C_0(t)\left(1 - \frac{C^\infty}{\hat{\Gamma}}\Gamma_0(t)\right) - \Gamma_0(t) = 0,$$

or

$$\Gamma_0(t) = \frac{\hat{\Gamma}\rho C_0(t)}{\hat{\Gamma} + \rho C^\infty C_0(t)}. \quad (11)$$

This is, of course, the dimensionless Langmuir isotherm given in (2) with $\gamma = \rho/\hat{\Gamma}$. The $O(\varepsilon^0)$ surface concentration $\Gamma_0(t)$ is in steady state with the instantaneous value of the $O(\varepsilon^0)$ subsurface concentration $C_0(t)$.However (11) yields no information about the time dependence of $C_0(t)$, and we cannot possibly satisfy the initial conditions in (9).To discover the former, we add (7) and (8) together and find, after cancelling a common factor of ε, that to $O(\varepsilon^0)$,

$$\frac{d}{dt}\left(\Gamma_0(t) + C_0(t)\right) = 1 - C_0(t).$$

This coupled with (11) then leads to the following single differential equation for $C_0(t)$:

$$\frac{d}{dt}C_0(t) = \frac{1 - C_0(t)}{1 + \dfrac{\hat{\Gamma}^2\rho}{\left(\hat{\Gamma} + \rho C^\infty C_0(t)\right)^2}}. \quad (12)$$

Since C(t) is a concentration, we will always require $C_0(0) \geq 0$. We should not necessarily require $C_0(0) = 1$, however. We are discussing the outer solution, and rapid changes may already have taken place in $\Gamma(t)$ and C(t) making them differ from their initial values. We will shortly discover how to choose $C_0(0)$ by 'matching' it with the rapidly varying or 'inner'

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boundary layer solution. $C_0(t) \equiv 1$ is a solution to (12) and it is not hard to see that when $C_0(0) \geq 0$ all solutions of (12) tend to one as $t \to \infty$. For example, if $0 \leq C_0(0) < 1$, (12) implies that

$$0 \leq \frac{\frac{d}{dt}C_0(t)}{1 - C_0(t)} < 1,$$

so that

$$C_0(0) \leq C_0(t) \leq 1 - e^{-t}(1 - C_0(0)) \tag{13}$$

for all $t \geq 0$. Using (12) and (13) we then find that

$$\frac{d}{dt}C_0(t) \geq \frac{1 - C_0(t)}{1 + \dfrac{\hat{\Gamma}^2 \rho}{\left(\hat{\Gamma} + \rho C^\infty C_0(0)\right)^2}},$$

and integrating this inequality gives

$$1 - C_0(t) \leq (1 - C_0(0))e^{-\lambda_1 t}, \tag{14}$$

where

$$\lambda_1 = \frac{1}{1 + \dfrac{\hat{\Gamma}^2 \rho}{\left(\hat{\Gamma} + \rho C^\infty C_0(0)\right)^2}}.$$

Combining (13) and (14) together then gives

$$(1 - C_0(0))e^{-t} \leq 1 - C_0(t) \leq (1 - C_0(0))e^{-\lambda_1 t} \tag{15}$$

if $0 \leq C_0(0) < 1$. In the same way, if $C_0(0) > 1$ we find that

$$(C_0(0) - 1)e^{-t} \leq C_0(t) - 1 \leq (C_0(0) - 1)e^{-\lambda_2 t} \tag{16}$$

where

$$\lambda_2 = \frac{1}{1 + \dfrac{\hat{\Gamma}^2 \rho}{\left(\hat{\Gamma} + \rho C^\infty\right)^2}}.$$

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We note that (12) can be solved implicitly by separation of variables, but we find that (15) and (16) supply more information. Equations (15) and (16) imply that all solutions of (12) with $C_0(0) \geq 0$ tend to one as $t \to \infty$, at a rate controlled by the characteristic time $t_s = 1/k_3$. In dimensional notation recall that this means that the $O(\varepsilon^0)$ outer solution $C^\infty C_0(t)$ tends to C^∞ as $t \to \infty$, and hence from (11) that the $O(\varepsilon^0)$ outer solution $C^\infty \Gamma_0(t)$ (in dimensional notation) tends to

$$\frac{\hat{\Gamma} \rho C^\infty}{\hat{\Gamma} + \rho C^\infty}$$

as $t \to \infty$. This is precisely the form of the Langmuir isotherm given in (1) with γ set equal to $\rho / \hat{\Gamma}$.

What about the 'inner' or boundary layer solution in which $\dfrac{d\Gamma}{dt}$ and $\dfrac{dC}{dt}$ change rapidly? To see this rapid change we introduce a 'stretched' dimensionless time $\tilde{t}$ defined by $\tilde{t} = \dfrac{t}{\varepsilon}$. Since $\dfrac{d}{d\tilde{t}} = \varepsilon \dfrac{d}{dt}$, when derivatives with respect to $\tilde{t}$ are $O(1)$, derivatives with respect to t are $O\left(\dfrac{1}{\varepsilon}\right)$ and rapid changes are occurring. Note that $\tilde{t} = k_2 t_d = t_d/t_p$ where t_d denotes dimensional time. Hence $\tilde{t}$ measures dimensionless time at a rate characteristic of the rapid processes of adsorption and desorption into the surface.

Using $\tilde{t}$ instead of t in (7) then gives

$$\frac{d}{d\tilde{t}} \Gamma(\tilde{t}) = \rho C(\tilde{t}) \left(1 - \frac{C^\infty}{\hat{\Gamma}} \Gamma(\tilde{t})\right) - \Gamma(\tilde{t}) \qquad (17)$$

$$\frac{d}{d\tilde{t}} C(\tilde{t}) = -\left(\rho C(\tilde{t}) \left(1 - \frac{C^\infty}{\hat{\Gamma}} \Gamma(\tilde{t})\right) - \Gamma(\tilde{t})\right) + \varepsilon(1 - C(\tilde{t})). \qquad (18)$$

These are the differential equations for the 'inner' or boundary layer solution describing rapid changes in Γ and C. Again we look for solutions in the form of asymptotic series in ε:

$$\Gamma^{inner}(\tilde{t}) = \tilde{\Gamma}_0(\tilde{t}) + \varepsilon \tilde{\Gamma}_1(\tilde{t}) + \dots$$

$$C^{inner}(\tilde{t}) = \tilde{C}_0(\tilde{t}) + \varepsilon \tilde{C}_1(\tilde{t}) + \dots.$$

Substituting these into (17) and (18) and using the initial conditions in (9), we find the $O(\varepsilon^0)$ 'inner' problem to be

$$\frac{d}{d\hat{t}}\tilde{\Gamma}_0(\hat{t}) = \rho\tilde{C}_0(\hat{t})\left(1 - \frac{C^\infty}{\hat{\Gamma}}\tilde{\Gamma}_0(\hat{t})\right) - \tilde{\Gamma}_0(\hat{t}) \tag{19}$$

$$\frac{d}{d\hat{t}}\tilde{C}_0(t) = -\left(\rho\tilde{C}_0(\hat{t})\left(1 - \frac{C^\infty}{\hat{\Gamma}}\tilde{\Gamma}_0(\hat{t})\right) - \tilde{\Gamma}_0(\hat{t})\right) \tag{20}$$

$$\tilde{\Gamma}_0(0) = \frac{\bar{\Gamma}}{C^\infty}, \tilde{C}_0(0) = 1. \tag{21}$$

Adding (19) to (20) and applying (21), we conclude that

$$\tilde{\Gamma}_0(\hat{t}) + \tilde{C}_0(\hat{t}) = B \tag{22}$$

where the constant B is defined by

$$B = 1 + \frac{\bar{\Gamma}}{C^\infty}. \tag{23}$$

Thus, on the boundary layer time scale $\hat{t}$, the sum of the surface and sub-surface concentrations is conserved. Using (22) to eliminate $\tilde{C}_0(\hat{t})$ from (19) then gives

$$\frac{d}{d\hat{t}}\tilde{\Gamma}_0(\hat{t}) = \rho\frac{C^\infty}{\hat{\Gamma}}\left(\tilde{\Gamma}_0(\hat{t}) - \tilde{\Gamma}_1\right)\left(\tilde{\Gamma}_0(\hat{t}) - \tilde{\Gamma}_2\right) \tag{24}$$

where

$$\tilde{\Gamma}_1 = \frac{\frac{\hat{\Gamma}}{C^\infty}(1 + \frac{1}{\rho}) + B + \sqrt{\left(\frac{\hat{\Gamma}}{C^\infty}(1 + \frac{1}{\rho}) + B\right)^2 - \frac{4B\hat{\Gamma}}{C^\infty}}}{2}$$

$$\tag{25}$$

$$\tilde{\Gamma}_2 = \frac{\frac{\hat{\Gamma}}{C^\infty}(1 + \frac{1}{\rho}) + B - \sqrt{\left(\frac{\hat{\Gamma}}{C^\infty}(1 + \frac{1}{\rho}) + B\right)^2 - \frac{4B\hat{\Gamma}}{C^\infty}}}{2}.$$

Both $\tilde{\Gamma}_1$ and $\tilde{\Gamma}_2$ are real and positive, and since

$$\left(\frac{\hat{\Gamma}}{C^\infty}(1 + \frac{1}{\rho}) + B\right)^2 - \frac{4B\hat{\Gamma}}{C^\infty} \geq \left(\frac{\hat{\Gamma}}{C^\infty}(1 + \frac{1}{\rho}) - B\right)^2,$$

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we find from (25) that

$$\tilde{\Gamma}_1 \geq \frac{\frac{\hat{\Gamma}}{C^\infty}(1 + \frac{1}{\rho}) + B + \left|\frac{\hat{\Gamma}}{C^\infty}(1 + \frac{1}{\rho}) - B\right|}{2}$$

$$\tilde{\Gamma}_2 \leq \frac{\frac{\hat{\Gamma}}{C^\infty}(1 + \frac{1}{\rho}) + B - \left|\frac{\hat{\Gamma}}{C^\infty}(1 + \frac{1}{\rho}) - B\right|}{2}.$$

(26)

It follows from (26) that

$$\tilde{\Gamma}_1 \geq B$$

$$\tilde{\Gamma}_2 \leq B.$$

(27)

Note that $\tilde{\Gamma}_1$ and $\tilde{\Gamma}_2$ are equilibrium solutions of (24). If $\tilde{\Gamma}_0(0) \neq \tilde{\Gamma}_1$ and $\tilde{\Gamma}_0(0) \neq \tilde{\Gamma}_2$, (24) may be solved using the initial condition

$$\tilde{\Gamma}_0(0) = B - 1$$

from (21) and (23) to yield

$$\tilde{\Gamma}_0(\tilde{t}) = \frac{\tilde{\Gamma}_1 - \tilde{\Gamma}_2 Z_0 e^{\alpha \tilde{t}}}{1 - Z_0 e^{\alpha \tilde{t}}}$$

(28)

where $\alpha > 0$ is given by

$$\alpha = \rho \frac{C^\infty}{\hat{\Gamma}} \sqrt{\left(\frac{\hat{\Gamma}}{C^\infty}(1 + \frac{1}{\rho}) + B\right)^2 - \frac{4B\hat{\Gamma}}{C^\infty}}$$

and

$$Z_0 = \frac{\tilde{\Gamma}_0(0) - \tilde{\Gamma}_1}{\tilde{\Gamma}_0(0) - \tilde{\Gamma}_2} = \frac{B - 1 - \tilde{\Gamma}_1}{B - 1 - \tilde{\Gamma}_2}.$$

(29)

From (28) and (29), $\tilde{\Gamma}_0(\tilde{t})$ blows up in finite time if and only if $0 < Z_0 < 1$, or if and only if $\tilde{\Gamma}_1 < B - 1$. By (27), however, this can never happen.

It follows from (28) and the above remarks that, whatever $\tilde{\Gamma}_0(0)$ is, all solutions $\tilde{\Gamma}_0(\tilde{t}) \to \tilde{\Gamma}_2$ as $\tilde{t} \to \infty$. Hence, from (22), $\tilde{C}_0(\tilde{t}) \to B - \tilde{\Gamma}_2$ as $\tilde{t} \to \infty$. Note that as $\varepsilon \to 0, \tilde{t} \to \infty$ when t differs from 0 by an O(1) amount.

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We shall now 'match' the inner and outer solutions together for both the $O(\varepsilon^0)$ surface and subsurface concentrations by requiring that the limit of the inner solution, as $\hat{t} \to \infty$, 'matches' or is equal to the limit of the outer solution as $t \to 0$. This implies that

$$\lim_{t \to 0} \Gamma_0(t) = \lim_{\hat{t} \to \infty} \hat{\Gamma}_0(\hat{t}), \lim_{t \to 0} C_0(t) = \lim_{\hat{t} \to \infty} \tilde{C}_0(\hat{t})$$

or , using (11) and (28)

$$\Gamma_0(0) = \frac{\hat{\Gamma}\rho C_0(0)}{\hat{\Gamma} + \rho C^\infty C_0(0)} = \tilde{\Gamma}_2, C_0(0) = B - \tilde{\Gamma}_2. \tag{30}$$

From (27), $C_0(0) \geq 0$, and we see that the matching conditions in (30) determine initial conditions for the outer solutions $\Gamma_0(t), C_0(t)$.

The final step is to form the 'composite' or uniformly valid solution by adding the $O(\varepsilon^0)$ inner and outer solutions together and subtracting the common parts as given in (30). This yields

$$\Gamma(t) = \Gamma_0(t) + \hat{\Gamma}_0(\hat{t}) - \tilde{\Gamma}_2 + O(\varepsilon), C(t) = C_0(t) + \tilde{C}_0(\hat{t}) - (B - \tilde{\Gamma}_2) + O(\varepsilon). \tag{31}$$

Recalling that $\hat{t} = \frac{t}{\varepsilon}$, we can write (31) as

$$\Gamma(t) = \Gamma_0(t) + \hat{\Gamma}_0\left(\frac{t}{\varepsilon}\right) - \tilde{\Gamma}_2 + O(\varepsilon), C(t) = C_0(t) + \tilde{C}_0\left(\frac{t}{\varepsilon}\right) - (B - \tilde{\Gamma}_2) + O(\varepsilon). \tag{32}$$

From (32) we see that the solutions for $\Gamma(t)$ and $C(t)$ each consist of an outer solution plus a boundary layer 'correction'. Equation (32) gives the uniformly valid composite solution to $O(\varepsilon)$ for the dimensionless system given by (7), (8) and (9).

Initially, by (21) and (30), $\Gamma_0(0) = \tilde{\Gamma}_2$ and $\tilde{\Gamma}_0(0) = B - 1 = \bar{\Gamma}/C^\infty$. Then as t increases $\hat{\Gamma}_0(\hat{t})$ rapidly approaches $\tilde{\Gamma}_2$.This domain of rapid change is the pre-steady state. After the pre-steady state the steady state begins. In this regime $\hat{\Gamma}_0(\hat{t}) \approx \tilde{\Gamma}_2$ and, to $O(\varepsilon)$, $\Gamma(t) = \Gamma_0(t)$, where the outer solution $\Gamma_0(t)$ is given by (11), with $C_0(t)$ satisfying (12). By (15) and (16) the outer (dimensionless) solution $C_0(t)$ tends to one for long times at a rate controlled by t_s.This means that $\Gamma(t)$ tends (in dimensional form) to the expression in (1) with $\gamma = \rho/\bar{\Gamma}$. We note that by using results in [4] we can prove that the composite solution in (30) is a uniformly valid solution to $O(\varepsilon)$ of the system

given in (7), (8) and(9). The reader can find further information on solution methods for problems of this type in [5] and [6].

To conclude, the validity of the derivation of the Langmuir isotherm given here depends on the presence of two different time scales t_p and t_s, with $t_p/t_s = \varepsilon \ll 1$. These time scales characterize the pre-steady and steady state time scales respectively. It is after the relatively short pre-steady state period that the $O(\varepsilon^0)$ surface concentration $\Gamma_0(t)$ is in steady state with the instantaneous value of $C_0(t)$, the $O(\varepsilon^0)$ surface concentration, yielding the (dimensionless) Langmuir isotherm given in (11).

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