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On the solution of the diffusion problems in adsorption kinetics

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Every creation of a fresh interface between a solution of a surface-active substance and solid, liquid, or gas leads to the well known change of the boundary tension with time. From a thermodynamical viewpoint these time effects are due to the tendency of the system to reduce its free energy to a minimum value at equilibrium. The mechanism of this phenomenon is connected with a concentration change in the region immediately near the surface, caused by adsorption of solute molecules on it. This concentration gradient provokes a diffusion flow from the bulk to the surface.

Very often the time necessary to establish the equilibrium is entirely due to diffusion transport. In other cases some additional obstacles may occur. Usually they are regarded to the existence of different kinds of energy barriers (electrostatic, steric etc.) between solved and adsorbed states.

The description of the diffusion part of the process is usually based on a solution of Fick's second law

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 C}{\partial t^2} \qquad [1]$$

under certain boundary conditions. This solution is "tacked together" with the surface which is not present explicitly in the diffusion problem by means of an additional condition:

$$D \left(\frac{\partial c}{\partial x} \right)_{x=0} = \frac{dM}{dt} . \qquad [2]$$

One can easily integrate eq. [2] and find $M(t)$.

Using this approach, *Langmuir* and *Schäfer* (1) have determined the change of the adsorbed amount with time, but their result is only right for the earliest stage of the process. The derivation is based on a solution of eq. [1] under the boundary condition $c(o, t) = o$, which is fulfilled during a short time interval after the creation of a fresh interface.

The next important step was made by *Ward* and *Tordai* (2), who had used the more general solution of eq. [1] under the boundary condition $c(o, t) = \Phi(t)$*. Therefore they had found an expression which is valid for $o < t < t_{eq}$:

$$M(t) = 2 C_0 \left(\frac{D}{\pi} \right)^{\frac{1}{2}} t^{\frac{1}{2}}$$
$$- \left(\frac{D}{\pi} \right)^{\frac{1}{2}} \int_0^t \frac{\Phi(\tau)}{(t - \tau)^{\frac{1}{2}}} \, d\tau . \qquad [3]$$

The same case ($c(o, t) = \Phi(t)$) had been treated by *Baret* (3), who carried out the diffusion flow at the interface $D \left(\frac{\partial c}{\partial x} \right)_{x=0}$ by means of a direct differentiation of $c(x, t)$. In (2), an expansion of $c(x, t)$ in a MacLaurin series proceeds this step.

By use of Laplace transformation *Hansen* (4) had solved the problem under given flow at $x = o$. Thus eq. [2] participates as a boundary condition of eq. [1] and the solution gives an expression for $M(t)$ more directly. In the same

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*) $\Phi(t)$ is an unknown function of time, called by the authors "subsurface concentration".

article *Hansen* had derived a formula for the subsurface concentration, emphasizing its important role in connecting the bulk and surface behaviours:

$$C(o, t) = C_0 - \frac{1}{(\pi D)^{\frac{1}{2}}} \int_0^t \frac{M'(\tau)}{(t - \tau)^{\frac{1}{2}}} d\tau . \quad [4]$$

In several papers especially devoted to diffusion limited adsorption kinetics *Delahay* and *Fike* (5), *Sutherland* (6), and *Hansen* (7) have avoided the use of any analytical expression for the subsurface concentration by means of appropiate adsorption isotherms. Unfortunately the application of the final expressions is limited by the hypothesis of instantaneous equilibrium between subsurface and surface.

Further in (3) *Baret* proposed to solve a system of two equations; the first – representing the diffusion transport from the bulk to the subsurface and the second – describing the mechanism of adsorption-desorption exchange in an explicite manner. For example he has used for the second one a first order reaction equation which describes the transition between solved and adsorbed states under nonequilibrium conditions. It gives the net rate of adsorption as a sum of adsorption and desorption rates:

$$\frac{dM}{dt} = Va - Vd$$

$$= A \cdot C(o,t)[M_\infty - M(t)] - B \cdot M(t) . \quad [5]$$

Solving the diffusion problem under the same boundary conditions as *Hansen* in (4), *Baret* (3) has found another expression for the subsurface concentration:

$$C(o,t) = Co + \frac{1}{2(\pi D)^{\frac{1}{2}}} \int_0^t \frac{M(\tau)}{(t - \tau)^{\frac{1}{2}}} d\tau . \quad [6]$$

After its substitution in eq. [5] he has got an equation for the net rate time dependence, which describes the most general case of adsorption kinetics- when $\dfrac{dM}{dt}$ depends simultaneously on the diffusion transport from the bulk to the subsurface and on the overcoming

of the energy barrier between solved and adsorbed states:

$$\frac{dM}{dt} = A \cdot C_0 \cdot [M_\infty - M(t)] - B \cdot M(t)$$

$$- \frac{A}{(\pi D)^{\frac{1}{2}}} \int_0^t \frac{M(t) - M_\infty}{(t - \tau)^{\frac{1}{2}}} M(\tau) d\tau . \quad [7]$$

The last formula is of principle importance, since it enables to calculate the kinetic constants A and B for a given system by use of a numerical solution. In such a manner, we would be able to evaluate the adsorption and desorption energy barriers and to understand their nature and origin.

Other similar general expressions can be derived by substitution of $c(o,t)$ in equations of the same type as eq. [5]. They may take into account another mechanism of adsorption-desorption exchange; for instance to involve the role of the interaction between adsorbed molecules, localized or nonlocalized adsorption etc. (9, 10).

The lack of correspondence between eq. [4] and eq. [6], however should result in different expressions for the net rate of adsorption. That is why we need to remove this contradiction and to make out, which of these formulas is the correct one. On the other hand, in spite of the fact that one and the same final formula for $M(t)$ is obtained in three different papers, there are some unclear points in Ward and Tordai's (2) and Baret's (3) derivations.

The considered solutions, as far as obtaining the distribution $c(x,t)$ is concerned, are more or less trivial. Tacking the bulk together with the surface however, demands to find the functions $c(o,t)$ and $\left(\dfrac{\partial c}{\partial x}\right)_{x=0}$. This limiting transition is the most complicated step and as we will show further, it gives rise to errors or inaccuracies when applied incorrectly.

A physical picture of this process of reaching adsorption equilibrium (see for instance (2)) shows that the subsurface concentration and the diffusion flow at $x = o$ should have finite values in the interval $o < t < t_{eq} \cdot c(o,t)$ initially has to reduce its value by reason of the "emptyness" of the freshly formed surface and therefore an easy adsorption on it. From this moment, which is initial for the diffusion

transport since it corresponds to the creation of the initial concentration gradient, $c(o,t)$ begins to increase reaching the value of bulk concentration at equilibrium. This change is due to the diffusion from the bulk and the gradual saturation of the surface. Therefore the physical meaning of $c(o,t)$ requires it to be a monotonically increasing and limited function. The character of the diffusion flow with time (eq. [13] in (2) and eq. [15] in (3)) has to be similar. It decreases monotonically from a maximum value at the beginning, to zero at equilibrium.

If however we apply Cauchy's integral criterion to the integrals in eq. [13] of (2) and eq. [15] of (3), it can be shown that they are divergent in this interval. In this premise the following requirements should be satisfied:

If $\dfrac{\Phi(\tau)}{(t-\tau)^{\frac{3}{2}}} = f(\tau)$

is positiv and exists a number $\alpha > 1$ so that for τ near by t we have the relation

$$f(\tau)(t-\tau)^{\alpha} > d > o \qquad [8]$$

the integral $\int\limits_{0}^{t} f(\tau)d\tau$ is divergent. It is easy to see that these conditions are satisfied for instance when $\alpha = 5/4$.

The discontinuity of the diffusion flow expression makes doubtful the possibility of its integration, which follows in (2) and (3). In fact, with the help of eq. [8] and the mean values problem for integrals

$$\int\limits_{a}^{b} f(t)dt = f(\xi)(b-a),\ a \leqslant \xi \leqslant b \qquad [9]$$

one can show that the double integrals in eq. [14] of (2) and eq. [15] of (4) are also divergent.

$$M_2 = \frac{1}{2}\left(\frac{D}{\pi}\right)^{\frac{1}{2}} \int\limits_{0}^{t}\int\limits_{0}^{\tau} \frac{\Phi(z)}{(\tau-z)^{\frac{3}{2}}}\,dz\,d\tau$$

$$= \frac{1}{2}\left(\frac{D}{\pi}\right)^{\frac{1}{2}} \int\limits_{0}^{t} F(\tau)\,d\tau \geqslant m\,\frac{t}{2}\left(\frac{D}{\pi}\right)^{\frac{1}{2}}.$$
$$[10]$$

Here $m = \min F(\tau)$ for $\tau\varepsilon(o,t)$. As $F(\tau)$ is infinity for all $\tau\varepsilon(o,t)$ the integral in [10] does not exist.

The application of Cauchy's criterion to eq. [6] shows that it also does not correspond to the physical meaning of the subsurface concentration. Therefore the substitution of this expression in eq. [5] should lead to a new uncorrect resultformula [7]. But if we apply the same procedure to Hansen's expression, it becomes clear that it does not contain similar mathematical peculiarities.

This discrepancy and the already mentioned importance of the cited equation requires one to check there solutions once again. Such analysis of the derivation in (2) shows that the correct final result is reached after two imaccuracies following one after the other. The first is connected with the transition of eq. [12] to eq. [13] in (3):

$$\left(\frac{\partial C_2}{\partial x}\right)_{x=0} = -\frac{1}{(\pi Dt)^{\frac{1}{2}}}$$
$$\sum\limits_{r=0}^{\infty} \frac{(-1)^r t^r}{(2r-1)r!}\,\phi^{(r)}(t)$$
$$= -\frac{1}{2(\pi D)^{\frac{1}{2}}}$$
$$\sum\limits_{r=0}^{\infty} \frac{(-1)^r t^{r-\frac{1}{2}}}{r!(r-\frac{1}{2})}\,\phi^{(r)}(t). \qquad [11]$$

Formally one can write

$$\frac{t^{r-\frac{1}{2}}}{r-\frac{1}{2}} = \int\limits_{0}^{t} \frac{d\tau}{(t-\tau)^{\frac{3}{2}-r}} \qquad [12]$$

but this is true only for $r > o$, as for $r = o$ the right side integral is divergent. Using relation [12] formally the authors have obtained:

$$\left(\frac{\partial C_2}{\partial x}\right)_{x=0} = -\frac{1}{2(\pi D)^{\frac{1}{2}}}$$
$$\int\limits_{0}^{t} \frac{\sum\limits_{r=0}^{\infty} \frac{(-1)^r}{r!}\,\phi^{(r)}(t)(t-\tau)^r}{(t-\tau)^{\frac{3}{2}}}\,d\tau$$
$$[13]$$

Having in mind that the expression in the numerator is a Taylor series of $\phi(t)$ the last expression gives eq. [13] of (2).

The next integration of this divergent integral is carried out with the help of "Cauchy's theorem for *n*-times repeated integrals applied to non integer *n*" (eq. [19]–[21] of (2)). This generalization of the theorem is the second ungrounded step of the solution. An indirect demonstration will show the error. *Ward* and *Tordai* obtained the equality (eq. [21]–[22] of (2)):

$$\frac{d}{dt} \int_0^t \frac{\phi(\tau)}{(t-\tau)^{\frac{1}{2}}} \, d\tau = -\frac{1}{2} \int_0^t \frac{\phi(\tau)}{(t-\tau)^{\frac{3}{2}}} \, d\tau \ . \quad [14]$$

Here the right side gives infinity for every $\tau = t$, as it was shown earlier. The left side is convergent for all $o < t < t_{eq}$, which follows directly if the differentiation is carried out after a reorganization of the integral by integration by parts:

$$\frac{d}{dt} \int_0^t \frac{\phi(\tau)}{(t-\tau)^{\frac{1}{2}}} \, d\tau = \frac{\phi(+o)}{t^{\frac{1}{2}}} \Big]_0^t + \int_0^t \frac{\phi'(\tau)}{(t-\tau)^{\frac{1}{2}}} \, d\tau \ . \quad [15]$$

Another error was made by *Baret* in (3), who had applied the Laplace transformation to obtain $c(x,t)$ distribution.

Here he used the relation

$$L \left\{ \frac{x}{2(D\pi t^3)^{\frac{1}{2}}} \, e^{-\frac{x^2}{4Dt}} \right\} = e^{-x \left(\frac{p}{D}\right)^{\frac{1}{2}}} \quad [16]$$

which is only correct for $x > o$ (8). That is why his $c(x,t)$ expression coincides with that from (2), which is obtained by means of Green's function. However *Baret* needs to know $\left(\frac{\partial c}{\partial x}\right)_{x=0}$, and so letting $x \to o$ he gets the false equation [15] on page 899. To overcome the difficulties in integrating this divergent expression the author repeats the ungrounded application of "Cauchy's theorem".

We shall try to avoid the discrepancy mentioned above, and following the way chosen in (2) to obtain the solution in an uncontradictory manner. Starting from eq. [12] of (2) we make some easy transformations:

$$\left(\frac{\partial C_2}{\partial x}\right)_{x=0} = -\frac{1}{(\pi Dt)^{\frac{1}{2}}} \sum_{r=0}^{\infty} \frac{(-1)^r t^r \phi^{(r)}(t)}{r!(2r-1)}$$

$$= \frac{1}{(\pi D)^{\frac{1}{2}}} \sum_{r=0}^{\infty} \frac{(-1)^r}{r!} t^{r-\frac{1}{2}} \phi^{(r)}(t) \left(1 - \frac{2r}{2r-1}\right)$$

$$= \frac{1}{(\pi D)^{\frac{1}{2}}} \left[\frac{\phi(t)}{t^{\frac{1}{2}}} + \sum_{r=1}^{\infty} \frac{(-1)^r}{r!} \phi^{(r)}(t) t^{r-\frac{1}{2}} \right.$$
$$\left. - \sum_{r=1}^{\infty} \frac{(-1)^r}{(r-1)!} \phi^{(r)}(t) \frac{t^{r-\frac{1}{2}}}{2r-1} \right]$$

$$= \frac{1}{(\pi D)^{\frac{1}{2}}} \sum_{r=0}^{\infty} \frac{(-1)^r 2}{r!(2r+1)}$$
$$\left[\frac{2r+1}{2} \phi^{(r)}(t) t^{r-\frac{1}{2}} + \phi^{(r+1)}(t) t^{r+\frac{1}{2}} \right]$$

$$= \frac{1}{(\pi D)^{\frac{1}{2}}} \sum_{r=0}^{\infty} \frac{(-1)^r 2}{r!(2r+1)} \frac{d}{dt} \left(\phi^{(r)}(t) t^{r+\frac{1}{2}} \right)$$

$$= \frac{1}{(\pi D)^{\frac{1}{2}}} \frac{d}{dt} \sum_{r=0}^{\infty} \frac{(-1)^r}{r!} \phi^{(r)}(t) \int_0^t \frac{d\tau}{(t-\tau)^{\frac{1}{2}-r}}$$

$$= \frac{1}{(\pi D)^{\frac{1}{2}}} \frac{d}{dt} \int_0^t \frac{\phi(\tau)}{(t-\tau)^{\frac{1}{2}}} \, d\tau \ . \quad [17]$$

The integration of this expression has no difficulties:

$$M_2 = \int_0^t \left[-D \left(\frac{\partial C_2}{\partial x}\right)_{x=0} \right] d\tau$$

$$= -\left(\frac{D}{\pi}\right)^{\frac{1}{2}} \int_0^t \left[\frac{d}{d\tau} \int_0^t \frac{\phi(z)}{(\tau-z)^{\frac{1}{2}}} \, dz \right] d\tau$$

$$= -\left(\frac{D}{\pi}\right)^{\frac{1}{2}} \int_0^t \frac{\phi(\tau)}{(t-\tau)^{\frac{1}{2}}} \, d\tau \ . \quad [18]$$

Together with equation [8] of (2), this relation gives the total amount adsorbed at time *t*:

$$M = M_1 + M_2 = 2 C_0 \left(\frac{D}{\pi}\right)^{\frac{1}{2}} t^{\frac{1}{2}}$$

$$- \left(\frac{D}{\pi}\right)^{\frac{1}{2}} \int_0^t \frac{\phi(\tau)}{(t-\tau)^{\frac{1}{2}}} \, d\tau \, .$$

Another uncontradictory derivation of this formula has been made by *Hansen* (4). Carrying out the limiting transition $x \to o$ in the equation

$$C(x,p) = \frac{C_0}{p} - \frac{1}{D^{\frac{1}{2}}} [p \, \overline{M}(p)] \, e^{-x \left(\frac{p}{D}\right)^{\frac{1}{2}}} \cdot \frac{1}{p^{\frac{1}{2}}}$$

$$[19]$$

and solving the result with respect to $\overline{M}(p)$ he obtained eq. [3] after easy transformations. If however first transform eq. [19] and then let x tend to zero, we get the subsurface concentration formula [4]. The same expression can be obtained if we apply Abel's integral equation to eq. [3] as was done in (9). When we calculate the derivative correctly, having in mind that $M(+o) = o$, Hansen's result is found once again.

The discrepancy between eq. [4] and eq. [6] is due to a wrong back transformation of the equation

$$C(o,p) = - \left(\frac{p}{D}\right)^{\frac{1}{2}} \overline{M}(p) - \frac{C_0}{p}$$

$$[20]$$

(see p. 901 of (3)). Here again a formal application of the general relation

$$L^{-1} \{p^n\} = \frac{t^{-1-n}}{(1-n)!}$$

$$[21]$$

takes place. It is limited for $n < o$, where n is an integer, but *Baret* has used it for $n = 1/2$ and obtained

$$L^{-1} \{p^{\frac{1}{2}}\} = - \frac{t^{-\frac{3}{2}}}{2\pi^{\frac{1}{2}}} \, .$$

$$[22]$$

This result leads to the divergent integral in eq. [6]. Moreover, according to the theorem for the region of existence of the Laplace transformation, the function $F(p)$ is the transformation of a function $f(t)$, if $\lim_{p \to \infty} F(p) = o$. This demand is not fulfilled here, so that eq. [22] contradicts the cited theorem.

The substitution of the correct expression for $c(o,t)$ in [5] leads to a new equation for $\frac{dM}{dt}$, instead of that on p. 901 of (4):

$$\frac{dM}{dt} = A \cdot \left[C_0 - \frac{1}{(\pi D)^{\frac{1}{2}}} \int_0^t \frac{M'(\tau)}{(t-\tau)^{\frac{1}{2}}} \, d\tau \right]$$
$$[M_\infty - M(t)] - B M(t) \qquad [23]$$

or

$$\frac{dM}{dt} = A \cdot \left[C_0 - \frac{1}{(\pi D)^{\frac{1}{2}}} \frac{d}{dt} \int_0^t \frac{M(\tau)}{(t-\tau)^{\frac{1}{2}}} \, d\tau \right]$$
$$\cdot [M_\infty - M(t)] - B \cdot M(t) \, . \qquad [23a]$$

All other equations derived in the same manner (eq. [49]–[54] of (10)) may be used after their correction, changing only the term $\int_0^t \frac{M(\tau)}{(t-\tau)^{\frac{1}{2}}} \, d\tau$ by the term $\frac{d}{dt} \int_0^t \frac{M(\tau)}{(t-\tau)^{\frac{1}{2}}} \, d\tau$ or $\frac{d}{dt} \int_0^t \frac{M(\tau)}{(t-\tau)^{\frac{1}{2}}} \, d\tau$, when $M(o) = 0$.

Nomenclature

c	= concentration
c_0	= bulk surfactant concentration
x	= distance from the surface
t	= time
t_{eq}	= time for reaching the equilibrium
D	= diffusion coefficient
M	= number of adsorbed molecules per cm^2
M_∞	= number of adsorbed molecules when $c_0 \to \infty$
v_a	= adsorption rate
v_d	= desorption rate
A	= adsorption rate constant
B	= desorption rate constant
ϕ	= subsurface concentration
p	= the complex variable in Laplace transformation
L, L^{-1}	= right and back Laplace transformation operators.

Summary

In the present paper an analysis of *Ward* and *Tordai's*, *Baret's*, and *Hansen's* solutions which describe the diffusion stage of the adsorption kinetics is carried out. It is shown that (2) and (3) imply

expressions inconsistent with the physical picture of the process. A correction is proposed which removes the contradictions.

Further in (3) and again in (10) *Baret* has given equations for the rate of adsorption when the latter simultaneously depends on the diffusion transport and on the transition between dissolved and adsorbed states. These formulas are also corrected with respect to the expression for the subsurface concentration.

Zusammenfassung

Die vorliegende Arbeit führt eine Analyse der Arbeiten von *Ward* und *Tordai* (2), *Baret* (3) und *Hansen* (4) durch, die sich mit der Lösung der Diffusionsvorgänge in der Adsorptionskinetik befassen. Es wird gezeigt, daß in (2) und (3) Ausdrücke enthalten sind, die unvereinbar sind mit dem physikalischen Sachverhalt dieses Prozesses. Eine Korrektur, die diese Widersprüche beseitigt, wird vorgeschlagen.

Ferner hat *Baret* in (3) und in (10) Gleichungen angegeben, die die Geschwindigkeit der Adsorption beschreiben, wenn diese gleichzeitig vom Diffusionstransport und vom Übergang zwischen gelöster und adsorbierter Phase bestimmt wird. Diese Formeln werden ebenfalls korrigiert unter Berücksichtigung des Ausdrucks für die Subsurface-Konzentration.

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