

TRANSFERENCE OF AMPHIPHILIC MOLECULES FROM A FLAT INTERFACE TO A FINITE SYSTEM BY CONVECTIVE DIFFUSION

P. Contreras *, C. Podina ** and Mihaela Olteanu **

An expression of transference of amphiphilic molecules in a finite system has been derived. This effort completes the equation presents in the literature of colloids that were written for free diffusion, semi-finite systems. The processes occur from a flat interface to a bulk by convective diffusion. The partial differential equation of Fick's second law was converted by Laplace transforms in an ordinary equation and thus an equation of concentration as a function of time t and position x was obtained. This equation permits to obtain from values of concentration in the time, the global and the micellar diffusion coefficients.

Introduction

The phenomenon of molecular transference by convective diffusion, in interface-solution systems has been subject of diverse studies. Most of them are related with the absorption of amphiphilic species at liquid-liquid or air-liquid interfaces [1÷3]. The process, that is consequence of the chemical potential gradient, has been described in concordance with the Fick's second law equation [4]. Using free diffusion technique as experimental procedure the diffusion coefficient has been calculated for a semi-finite system [5].

Results and Discussion

In this work an equation for a finite system was obtained from the Fick's second law equation changing the boundaries conditions. The expressions give us the possibility to obtain concentration variations in a system of known length. The model is illustrated in the Fig. 1, a monostate of molecules organized and oriented that occupy the available interfacial area of constant concentration C_{in} in contact with a bulk of concentration C_A . The bottom of vessel, where the concentration is zero, is separated a distance $x=l$ from the interface. We mimic the phenomena of transference interface-bulk that occurs in a simple test tube containing two immiscible phases (usually oil and water), with amphiphilic molecules concentrated initially in one of the phases.

Experimental values of C_A , obtained from a radioactive tracer technique was used to test the equation applicability [6].

* PDVSA – INTEVEP, Apartado, 76343 – Caracas 1070A, Venezuela

** University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry, Bd. Regina Elisabeta No. 4-12, Bucharest, Romania

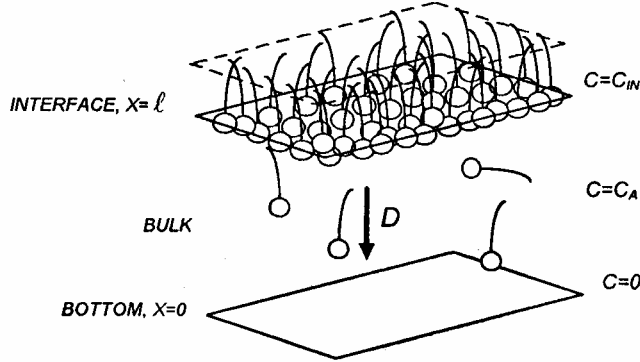


Fig. 1: Model of the finite system proposed, a flat interface containing a monolayer of concentration C_m at $x=l$, in contact with a bulk solution of concentration C_A of length l . The transference occurs by convective diffusion D , to the bulk.

Equation of convective diffusion from the interface

Mass balance and equations of variation for a finite system were the started points in this work. Our mathematics treatment has had it base in the conservation of mass expressed in terms of the equation of continuity [7].

Considering the balance for a component A , at any volume element fitted in the space, in aqueous we have:

$$\frac{\partial C_A}{\partial t} + (\nabla \cdot N_A) = 0 \quad (1)$$

where, C_A is the total molar concentration of A , ∇ Nabla operator and N_A the density of molar flow of A . according with the first Fick's law N_A in stationary coordinates can be expressed as:

$$N_A = x_A(N_A + N_B) - CD\nabla x_A \quad (2)$$

where x_A is the molar fraction of A (C_A/C), N_B the density of molar flow of B (the solvent), C the total molar concentration, D the translation diffusion coefficient of A in B . The first term of the eq. 2, represents the vector that results of the fluid global movement. The second one represents the diffusion in parallel with the global flow,

$$\frac{\partial C_A}{\partial t} + (\nabla \cdot C_A v) = \left(\nabla \cdot CD\nabla \frac{C_A}{C} \right) \quad (3)$$

and

$$\frac{\partial C_A}{\partial t} + (v\nabla C_A) = D\nabla^2 C_A \quad (4)$$

Finally the equation expressed in rectangular coordinates is:

$$\frac{\partial C_A}{\partial t} + \left(v_x \frac{\partial C_A}{\partial x} + v_y \frac{\partial C_A}{\partial y} + v_z \frac{\partial C_A}{\partial z} \right) = D \left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right) \quad (5)$$

Convection currents are particularly significant only in the vicinity of the interface due to the Marangoni instabilities [8], and then eq. 5 is transformed by simplification of the velocity terms. In general, it would be a process occurring in three dimensions, but the experimental devices allow a concentration gradient to exist in one direction only. It can be reduced to a one-dimensional problem and will be treated as such here. Changes of the concentration are considered only in x directions.

Consequently the eq. 5 is,

$$\frac{\partial C_A}{\partial t} = D \left(\frac{\partial^2 C_A}{\partial x^2} \right) \quad (6)$$

In our case boundary conditions for $0 < x < l, t > 0$ are:

$$C_A(x, 0) = C_{A_0}$$

$$C_A(0, t) = 0$$

$$C_A(l, t) = C_{in}$$

where C_{A_0} , is the initial concentration of A in the aqueous phase, $C_A(0, t)$ is the concentration on the bottom of the tube that always is taken as zero and C_{in} the interfacial concentration.

This partial differential equation of convective diffusion is converted in an ordinary equation by the Laplace transforms \mathcal{L} and resolved as follow [9,10]

$$sC_A - C_A(x, 0) = \frac{D d^2 c_A}{dx^2} \quad \text{or} \quad \frac{d^2 c_A}{dx^2} = \frac{sc_A}{D} - \frac{C_{A_0}}{D} \quad (7)$$

where s is the Laplace parameter, $c_A = c_{A(o,s)} = \mathcal{L} \{C_A(x, t)\}$ [4]. From border conditions and by Laplace transform, if $c_{A(o,s)} = 0$ and $c_A(l, s) = C_{in}/s$, we have the general solution with α and β as the constant of the equation:

$$c_A = \alpha \cosh \sqrt{s/D} x + \beta \sinh \sqrt{s/D} x + \frac{C_{A_0}}{s} \quad (8)$$

where β is zero due to the condition established above and then α :

$$\alpha = \frac{C_{in} - C_{A_0}}{s \cosh \sqrt{s/D} l} \quad (9)$$

Thus, the eq. 8 is,

$$c_A = \frac{C_{A_0}}{s} + (C_{in} - C_{A_0}) \frac{\cosh \sqrt{s/D} x}{s \cosh \sqrt{s/D} l} \quad (10)$$

The inverse of the first term is C_{A_0} , the inverse of the second one, without the term $(C_{in} - C_{A_0})$ is:

$$\frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{e^{st} \cosh \sqrt{s/Dx}}{s \cosh \sqrt{s/Dl}} ds \quad (11)$$

that is equal at the sum of all the integer rest, in the simple poles present:

$$s = 0, \quad \sqrt{s/Dl} = (n - (1/2))\pi i \quad n = 0, \pm 1 \pm 2, \dots$$

$$s = 0, \quad s = -\frac{(2n-1)^2 \pi^2 D}{4l^2} \quad n = 0, 1, 2, 3, \dots$$

where: the rest in $s=0$ is $\lim_{s \rightarrow 0} (s) \left(\frac{e^{st} \cosh \sqrt{s/Dx}}{s \cosh \sqrt{s/Dl}} \right) = 1$

the rest in $s = -\frac{(2n-1)^2 \pi^2 D}{4l^2} = s_n$ is

$$\begin{aligned} & \lim_{s \rightarrow s_n} (s - s_n) \left(\frac{e^{st} \cosh \sqrt{s/Dx}}{s \cosh \sqrt{s/Dl}} \right) = \\ & = \left\{ \lim_{s \rightarrow s_n} \frac{s - s_n}{\cosh \sqrt{s/Dl}} \right\} \left\{ \lim_{s \rightarrow s_n} \frac{e^{st} \cosh \sqrt{s/Dx}}{s} \right\} = \\ & = \left\{ \lim_{s \rightarrow s_n} \frac{1}{(\sinh \sqrt{s/Dl})(l/2\sqrt{Ds})} \right\} \left\{ \lim_{s \rightarrow s_n} \frac{e^{st} \cosh \sqrt{s/Dx}}{s} \right\} = \\ & = \frac{4(-1)^n}{(2n-1)\pi} e^{-(2n-1)^2 \pi^2 Dt/4l^2} \cos \frac{(2n-1)\pi x}{2l} \end{aligned}$$

and we obtain the solution using L'Hospital,

$$C_A(x,t) = C_{in} + \frac{4(C_{in} - C_{A_0})}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{2n-1} e^{-(2n-1)^2 \pi^2 Dt/4l^2} \cos \frac{(2n-1)\pi x}{2l} \quad (12)$$

This equation permits us to calculate the concentration of A as a function of x and t , for a system of finite length l and a diffusion coefficient D .

Curves of concentration as a function of the distance x can be obtained for a value of D , in each period of time (Fig. 2).

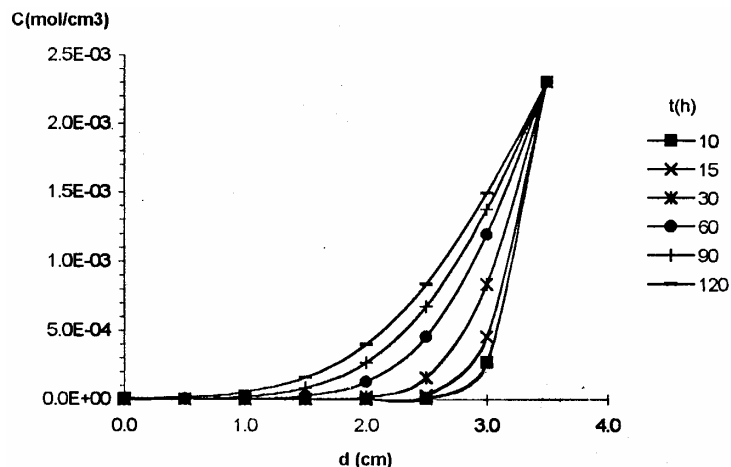


Fig. 2: Theoretical concentration of the acid in the aqueous phase as a function of position x in the tube, for different times. Hypothetical diffusion coefficient $D = 0.005004 \text{ cm}^2/\text{h}$ and interfacial concentration $C_i = 0.0023 \text{ mol}/\text{cm}^3$.

From this set of values is possible to obtain the mean concentration. After, a family of theoretical curves is drawn (Fig. 3), changing the diffusion coefficient values. If on these curves, the experimental value of concentration changes versus t for one finite system problem is plotted, the values of D as a function of t are estimated in the intersection points (Fig. 3).

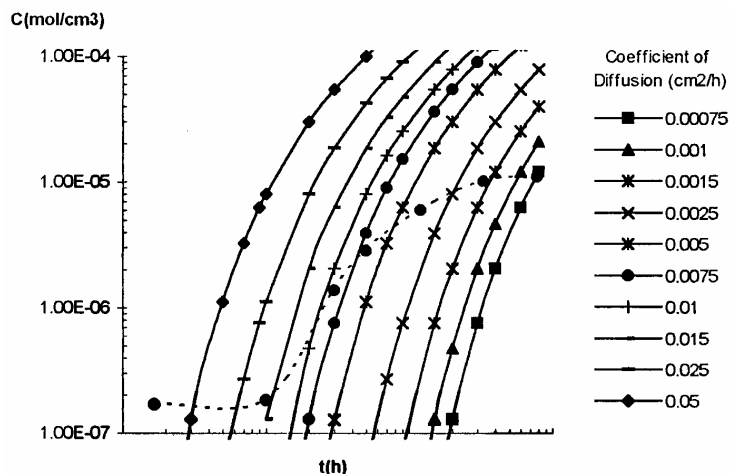


Fig. 3: Theoretical acid concentration vs. time for different coefficient of diffusion. Experimental concentration values have been represented by the symbol (●).

In the case of amphiphilic molecules, D represents the global diffusion coefficient, after the critical micellar concentration (CMC). There, we have the contribution of monomer and micelle aggregates. Thus, if we know the monomeric contribution it is possible to calculate the micellar contribution D_m from D .

Conclusions

A mathematical expression for the transference of amphiphilic molecules from a flat interface to a finite system has been derived. With this equation is possible to obtain theoretical curves that together with experimental values of concentration changes as a function of time, give us the diffusion coefficient D . Additionally, the micellar diffusion coefficient D_m , can be obtained for a system after the CMC.

REFERENCES

1. Bois, A. G. (1971) *Kolloid – Z. Z. Polymere* **249**, 1144 – 7.
2. Danov, K., Vlahovska, P., Horozov, T., Dushkin, C., Kralchevsky, P., Mehreteab, A., Broze, G. (1996) *J. Colloids Interface Sci.* **183**, 223 – 35.
3. Kralchevsky, P., Radkov, Y., Denkov, N. (1993) *J. Colloids Interface Sci.* **161**, 361 – 5.
4. Olteanu, M. (1993) *Coloizi*, Editura Universității din București, București, 35 – 41.
5. Mandru, I., Ceacareanu, D. (1976) *Chimia Coloizilor și Suprafețelor – Metode Experimentale*, Editura Tehnică, București, 104 – 109.
6. Contreras, P., Olteanu, M., Podină, C. (2001) *Journal of the Brazilian Chemical Society*, in press.
7. Bird, R., Stewart, W., Lightfoot, E. (1982) *Transport Phenomena*, John Wiley & Sons, New York, 18 – 2 & 18 – 10.
8. Sterling, C., Scriven, L. E. (1959) *A. I. Ch. E.* **5**, 514.
9. Zill D. (1986) *A First Course in Differential Equations with Applications*, PWS Publishers, USA, 156 – 161.
10. Spigel, M. (1987) *Schaum's Outline of Laplace Transforms*, McGraw Hill, USA, 221 – 36.