

Analysis of Facilitated Transport through Fixed Site Carrier Membranes*

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Abstract:

A simple mathematical model for facilitated mass transport with a fixed site carrier membrane was derived by assuming an instantaneous, microscopic concentration (activity) fluctuation. The concentration fluctuation, developed due to the reversible chemical reaction between carrier and solute, could cause the higher chemical potential gradient and the facilitated transport. For mathematical formulation, an analogy was employed between the mass transfer for the facilitated transport with fixed site carrier membrane and the electron transfer in a parallel resistor-capacitor (RC) circuit. For the single RC model, it was assumed that a single capacitor represented the total carrier and a solute could not inter-diffuse between matrix and carrier, allowing only two diffusional pathways. This assumption was relaxed by adopting a serial combination of the parallel RC circuit. Here, a solute diffuses in two elements (matrix or carrier) can exchange its pathway, exhibiting four diffusional pathways. The current models were examined against experimental data and the agreement was exceptional.

** This is dedicated to Professor Sun-Tak Hwang in University of Cincinnati to commemorate his sixtieth birthday.*

INTRODUCTION

Facilitated transport has been an attractive goal in gas and liquid separations, because mass transport is enhanced by a carrier in addition to a normal Fickian diffusion. A carrier in a facilitated transport membrane reacts specifically and reversibly with a solute from its mixture. The carrier binds with the solute on a higher potential side and releases it to a lower one, resulting in a facilitated transport. Most of the facilitated transport phenomena investigated has been in liquid membranes, which are problematic because they can be unstable.

The facilitated transport with fixed site carrier membrane can be unique in providing stability as well as both high permeability and permselectivity. In the case of normal Fickian diffusion membrane, there has been frequently observed a trade-off between permeability and permselectivity [1]. Therefore, polymeric membranes with fixed site carriers have been the subject of much recent investigation. Typical applications are air separation with metallo-porphyrins [2-4] or metal-Schiff's bases [5-8], acid gas (i.e. CO₂ and SO₂) separation with amine carriers [9] and ion transport [10-11].

A few mathematical models have been developed to analyze the facilitation phenomena in a fixed site carrier membrane. The dual sorption model has been commonly employed, because it is conceptually analogous to the mass transport in a facilitated transport membrane with fixed site carriers [2-4] and it has a mathematical simplicity. The dual sorption model was originally developed to interpret the sorption behavior of gases or vapors in glassy polymers [12]. However, it does not provide for the dependency of the permeability of the matrix, the exchange rate of solute between carrier and matrix and the membrane thickness.

A more rigorous analysis of the facilitated transport in a fixed site carrier membrane was presented by introducing a concept of "the effective diffusion coefficient" between fixed site carriers by Noble [13-14]. In his analysis, the concentration of unreacted, fixed carrier was assumed to be constant, implying a large excess of carrier. A mathematical model was developed for this case of excess carrier, and it was identical to that of facilitated transport in liquid membranes developed by Smith and Quinn [15]. It reduced to the dual sorption transport model at low solute partial pressure [13]. Experimentally, facilitation behavior has been observed at low concentrations of carrier [4]. In this case the concentration of uncomplexed carrier will diminish

as the solute pressure increases, violating the excess carrier assumption. This causes the model predictions to deviate gradually from the experimental data as the solute pressure increases.

Cussler et al.[16] analyzed fixed site facilitated transport with a concept of "limited mobility of chained carriers". They assumed that no uncomplexed solute can exist in the membrane, and the reaction between a carrier and solute occurs only at the surface of the membrane, and is fast. The mobility of chained carrier, commonly pending on side chain, can allow the complex to encounter a second, uncomplexed carrier, resulting in a facilitated transport. However, diffusion is only allowed over a limited distance due to the limited mobility of the chained carriers, which, in turn, leads to a percolation threshold. The existence of a percolation threshold is unlikely for many systems because facilitated transport has been experimentally observed with the low concentration of carriers, as low as 0.6 wt % [5].

Here, two papers accepted for publication in the Journal of Membrane Science were summarized [17,18]. A simple mathematical model was proposed by assuming pressure or concentration fluctuations in the membrane. An analogy between electron transport in a single parallel resistor-capacitor (RC) circuit and mass transport in a facilitated transport membrane with fixed carriers was applied to develop the model. The single RC model was expanded to the series of the single parallel RC circuit to accommodate four diffusional pathways. The two models were then examined against the experimental data on oxygen transport through poly(dimethyl siloxane), (PDMS), poly(butyl methacrylate) (PBMA) and poly(methyl methacrylate) (PMMA) with metallo-porphyrin carrier by Ohyanagi et al [2].

CONCENTRATION PROFILE IN A FIXED SITE CARRIER MEMBRANE

In a facilitated transport membrane, a carrier reversibly reacts with a specific component of solute mixture. Because of the reaction, the local solute concentration in the membrane will be instantaneously perturbed from its average. For Fick's law with a constant diffusion coefficient, the steady state concentration or pressure profile is linear. In the facilitated transport membranes, a reversible chemical reaction between solute and carrier continuously occurs. If one looks at the membrane microscopically to molecular level, the local solute concentration dissolved in a matrix will be diminished instantaneously when the solute reacts with the carrier to make solute-carrier complex. When the backward reaction takes place, the solute-carrier complex will release the solute into the matrix. The local solute concentration would be, then, increased instantaneously

from its average concentration. But the time-averaged concentration maintains constant at a given position and linear across the membrane. This implies that the solute concentration profile will be instantaneously deviated from the linearity. In other words, the original linear concentration profile could be perturbed by the reversible chemical reaction, resulting in the fluctuated concentration profile. Figure 1 shows the proposed actual concentration profile. Although the extent of the concentration fluctuation is expected to be very small, it is exaggerated in Figure 1.

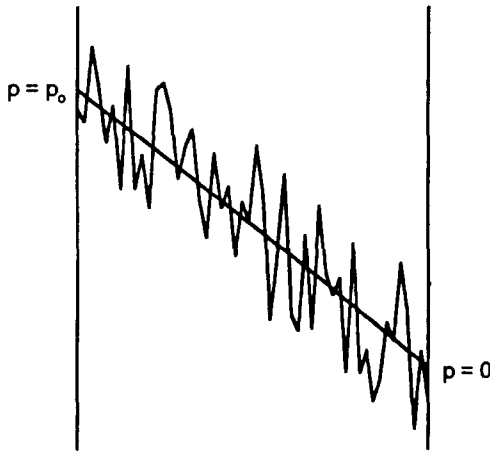


Figure 1. A fluctuated pressure profile in a facilitated transport membrane with fixed site carrier at steady state.

Consider an inhomogeneous system whose composition everywhere differs only slightly from the average composition, and with small composition gradients, ∇c . Its free energy, G , is [19]

$$G = \int [g(c) + \kappa(\nabla c)^2] dV \quad (1)$$

Here $g(c)$ is the free-energy density of homogeneous system of composition c , and κ is positive. $\kappa(\nabla c)^2$ is the additional free energy density if the system is in a composition gradient [17]. Equation (1) demonstrates that the free energy will be higher in the inhomogeneous system compared to the homogeneous system. The inhomogeneous system corresponds to the facilitated membrane with fluctuated concentration while the homogeneous system to the membrane with the linear, unperturbed concentration profile. According to equation (1), the chemical potential of solute, a gradient of the free energy and a driving force for diffusion, in the facilitated transport membrane will be increased due to the fluctuated concentration profile. The increased chemical

potential, in turn, leads to a higher solute flux resulting in the facilitated transport. Consequently, the pressure fluctuation could cause facilitation.

ANALOGY BETWEEN RC CIRCUIT AND FACILITATED TRANSPORT.

In a facilitated transport membrane with fixed site carrier, two transport modes would be parallelly operating: normal diffusion mode through matrix and carrier-mediated mode. This overall mass transport phenomenon is analogous to that of electron transfer in a single parallel resistor-capacitor (RC) circuit when an alternating voltage is applied. This is because the capacitor momentarily holds electrons from a high potential side and transfers them to a lower one in the field of an alternating voltage. The function of the capacitor in an alternating voltage is analogous to that of the fixed site carrier in the facilitated membrane. Thus, two modes for electron transfer in the single RC circuit are concurrently working. Figure 2-A depicts the analogy between the mass transport in a fixed site carrier membrane and the electron transfer in the single RC circuit and the analogy is summarized in Table 1.

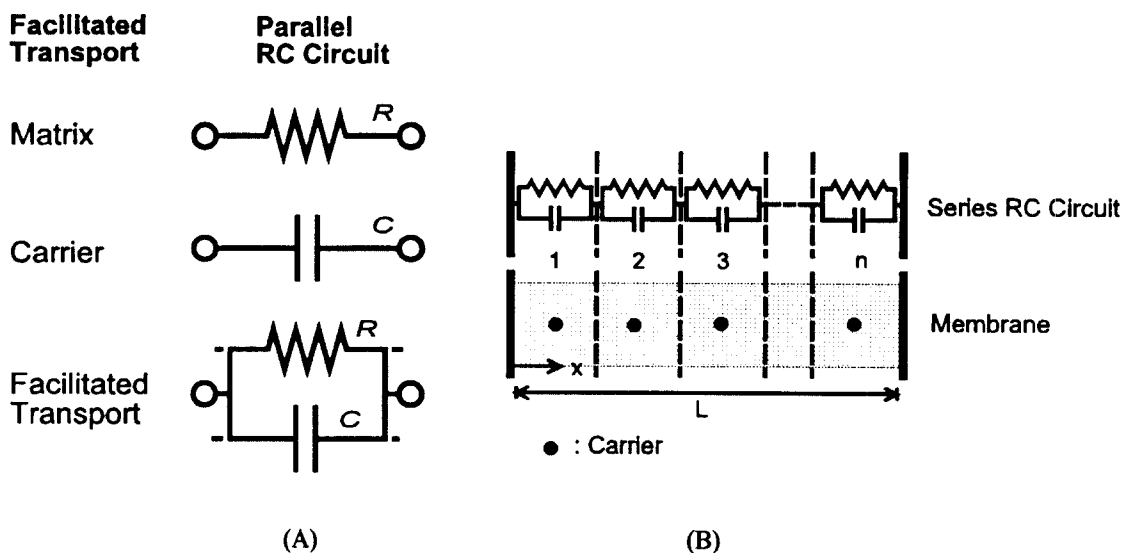


Figure 2. Schematic analogy between mass transfer in fixed site carrier membrane and electron transfer: (A) for the single RC circuit, and (B) for the series RC circuit.

Table 1. Analogy between Electron Transfer in RC circuit and Mass Transfer in Facilitated Membrane with Fixed Site Carriers

	Electron Transfer	Mass Transfer
Governing Law	Ohm's Law ($j=\sigma V/L$)	Fick's Law ($J=\bar{P} p_o/L$)
Driving Force	Voltage Gradient (V/L)	Pressure Gradient (p_o/L)
Proportionality	Conductivity (σ)	Permeability (\bar{P})
Capacitor	Charge ($q=CV$)	Solute-Carrier Complex ($C_{AB}=C_B^o K p_a/(1+K p_a)$)

In the single RC circuit model, it is further assumed that a single capacitor represents the total carrier in the membrane and a solute cannot inter-diffuse between matrix and carrier. This allows only two independent diffusional pathways: normal diffusion and carrier-mediated transport. However, in reality, a solute can in two elements (matrix or carrier) can exchange its pathway, exhibiting four diffusional pathways. Thus, the assumption can be relaxed by adopting a series of the single RC circuit as illustrated in Figure 2-B.

ELECTRON TRANSPORT IN PARALLEL RC CIRCUIT

If an alternating voltage V (as in equation(2)) is applied to the RC circuit,

$$V = V_r + V_d \sin(\omega t) \quad (2)$$

then the ratio of the conductivity of the single RC circuit to a purely resistive circuit is:

$$\frac{\sigma_{rc}}{\sigma} = 1 + \alpha_v \sqrt{1 + \left(\frac{2\pi fCL}{\sigma A_s}\right)^2} \quad (3)$$

The corresponding ratio for the series RC circuit is

$$\frac{\sigma_{rc}}{\sigma} = 1 + \alpha_v \sqrt{n^2 + \left(\frac{2\pi fCL}{\sigma A_s}\right)^2} \quad (4)$$

where n is the number of the single RC circuit in the series RC circuit as shown in Figure 2-B.

MASS TRANSPORT IN FIXED SITE CARRIER MEMBRANE

When a *constant* solute pressure is applied to a fixed site carrier membrane and the solute pressure on the downstream side is maintained at zero, the local solute pressure of the membrane will be fluctuated as described previously owing to the continuous reversible reaction between carrier and solute. The fluctuating local pressure could be random and can not be, thus, expressed easily by a simple mathematical form. For mathematical simplicity, it is assumed to be a simple sine function as with the alternating voltage in an RC circuit.

$$p = p_a + p_d \sin(\omega t) \quad (5)$$

p_a and p_d are the time-averaged pressure and the pressure fluctuation, respectively, at a given position in a membrane. The time-averaged pressures at the membrane surfaces are $p=p_0$ and $p=0$ for upstream and downstream sides, respectively .

The three circuit parameters, α_v , C and f in equations (3) and (4) will be transformed into corresponding mass transport parameters as summarized in Table 2.

Table 2. Analogy and Physical Meanings of Parameters for Electron and Mass Transfer

Electron Transfer	Mass Transfer	Definition	Physical Meanings
α_v	α_p	p_d/p_0	extent of pressure fluctuation
C	H_a	$A_s L \frac{C_B^0 \ln(1 + Kp_0)}{p_0}$	total amount of complex AB per unit pressure in a given volume
f	k_2		backward reaction constant

From the analogy between V and p, σ and \bar{P} , α_v and α_p , C and H_s , and f and k_2 described above, equation (3) for the single RC circuit can readily be rewritten for the facilitated transport in fixed site carrier membrane as

$$\frac{\bar{P}_f}{\bar{P}} = 1 + \left(\frac{p_d}{p_0}\right) \sqrt{1 + \left[\frac{2\pi k_2 L^2 C_B^0 \ln(1 + Kp_0)}{\bar{P} p_0}\right]^2} \quad (6)$$

This simplifies to

$$\frac{\bar{P}_f}{\bar{P}} = 1 + \left(\frac{p_d}{p_0}\right) \frac{2\pi k_2 L^2 C_B^0 \ln(1 + Kp_0)}{\bar{P} p_0} \quad (7)$$

because equation (8) is generally true for normal experimental conditions

$$\left[\frac{2\pi k_2 L^2 C_B^0 \ln(1 + Kp_0)}{\bar{P} p_0}\right]^2 \gg 1 \quad (8)$$

For the series RC model, equation (4) can be transformed to

$$\frac{\bar{P}_f}{\bar{P}} = 1 + \left(\frac{p_d}{p_0}\right) \sqrt{n^2 + \left[\frac{2\pi k_2 L^2 C_B^0 \ln(1 + Kp_0)}{\bar{P} p_0}\right]^2} \quad (9)$$

This equation reduces to that for the single RC circuit model when $n=1$.

If each layer contains only one carrier in the direction of diffusion (x-direction), n can be interpreted as the number of carrier molecules that a solute can meet in its unidirectional diffusion pathway. It is further assumed that the minimum area necessary for diffusion of a solute would be equivalent to the cross-sectional area of the solute. Thus, the area will be πr_s^2 where r_s is the kinetic radius of the solute. Then,

$$n = N_A C_B^0 (\pi r_s^2 L) \quad (10)$$

Equation (10) can be reduced to one when only one carrier is present, as is for the single RC circuit model, in the unidirectional diffusion pathway.

Equations (6) and (9) show that the facilitation factor $F (= \bar{P} / \bar{P})$ increases with increasing p_d/p_o , k_2 , L , C_B^0 , and K . However, it decreases with \bar{P} and p_o . Note, in particular, that F is linearly proportional to p_d , k_2 , C_B^0 and L^2 , and inversely to \bar{P} according to equation (7).

For convenience, equation (6) can be converted to a nondimensional form as follows when $\bar{P} = DS$ and $C_A^* = Sp_o$.

$$F = 1 + \alpha_p \sqrt{1 + [2\pi\psi\gamma \ln(1 + \Delta)]^2} \quad (11)$$

Table 3. Definitions and Their Physical Meanings of Dimensionless Parameters in Facilitated Transport.

$F = \bar{P} / \bar{P}$	facilitation factor
$\alpha_p = p_d/p_o$	the extent of pressure fluctuation
$\psi = k_2 L^2 / D$	the time scale ratio of diffusion to chemical reaction.
$\gamma = C_B^0 / C_A^*$	the ratio of the total carrier concentration to the solute solubility by Henry's law ($C_A^* = Sp_o$)
$\Delta = Kp_o$	the combined driving force for facilitated transport

Equation (11) again reduces to

$$F = 1 + 2\pi\alpha_p \psi \gamma \ln(1 + \Delta) \quad (12)$$

when equation (8) holds.

For the series RC circuit, equation (9) can also be converted to

$$F = 1 + \alpha_p \sqrt{n^2 + [2\pi\psi\gamma \ln(1 + \Delta)]^2} \quad (13)$$

The definitions and their physical meanings of the dimensionless parameters in equations (11) and (13) are summarized in Table 3.

Equation (12) is straight forward, i.e., F increases linearly with α_p , ψ and γ and logarithmically with $(1+\Delta)$. It is interesting to note that ψ , defined as k_2L^2/D , has been referred to as the inverse of the diffusion Deborah number [20,21], the Damkohler number [13-14] and the square of the Thiele modulus [16]. In the earlier treatments of Noble [13] and Cussler et al. [16], ψ is assumed to be large. In other words, mass transport is diffusion limited. According to the experimental data for PDMS, PBMA and PMMA membranes with metallo-porphyrin provided by Ohyanagi et al. [2], it is, however, close to unity as shown in Table 4, implying that the diffusion and the chemical reaction time scales are competitive.

RESULTS

Equation (7) demonstrates an inverse relationship between F and \bar{P} , and p_{O_2} , which was frequently observed experimentally [2-5,8]. A linear relationship between F and C_B^0 , which was also observed experimentally in different systems [9-11,16]. However, the experimental data for cobalt Schiff base carrier in poly[(octyl methacrylate)-*co*-4-(vinyl pyridine)] matrix provided by Tsuchida et al. [5] did not give a linear relationship. In the case of the high concentration of the cobalt Schiff base carrier, Woehle et al. [6,7] suggested that the carrier formed dimers and lost their reaction activity with oxygen. This could cause the deviation from linearity at the high concentrations of the cobalt Schiff base carrier. An interesting point to note is that F increases with L^2 . Figure 3 is a plot of permeability of oxygen through a poly(styrene-*co*-vinylpyridine) membrane with cobalt Schiff base carrier with the square of its thickness [22]. As can be seen, the linear relationship was observed, validating the validity of the current model.

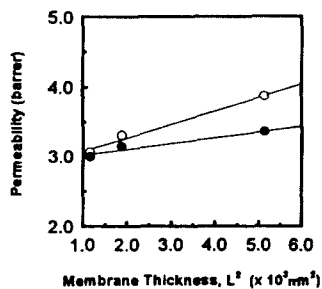


Figure 3. A plot of permeability \bar{P}_f vs L^2 .

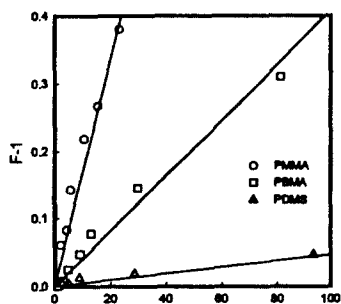


Figure 4. A plot of $F-1$ vs

$[1/p_0][2\pi k_2 L^2 C_B^0 / \bar{P}][\ln(1+Kp_0)/p_0]$
for the single model.

$[1/p_0][2\pi k_2 L^2 C_B^0 / \bar{P}][\ln(1+Kp_0)/p_0]$

Table 4. The Parameter Values for the Model Calculation².

	P	D	C_B^0	k_2	K	ψ	p_d (single)	n	p_d (series)
	(barrer)	(cm^2/sec)	(mol/cm^3)	($1/\text{sec}$)	($1/\text{cmHg}$)		(cmHg)	(ser)	(cmHg)
PDMS ^a	760	1.9×10^{-5}	2.02×10^{-5}	0.1	0.37	2.11	4.72×10^{-4}	229	5.22×10^{-4}
PBMA ^b	8.4	7.0×10^{-7}	2.29×10^{-5}	0.023	0.053	1.18	4.01×10^{-3}	78	4.59×10^{-3}
PMMA ^b	0.55	2.2×10^{-7}	2.58×10^{-5}	0.0028	0.052	0.46	1.68×10^{-2}	88	1.71×10^{-2}

a : membrane thickness $L=2.0 \times 10^{-2}$ (cm)

b : membrane thickness $L=6.0 \times 10^{-3}$ (cm)

The current model is next examined with the experimental data for the permeability of oxygen through PDMS, PBMA and PMMA containing metallo-porphyrin [2]. The parameters \bar{P} , k_2 , and K were independently measured by Ohyanagi et al. [2] and the n values are calculated from equation (10). Figure 4 demonstrates a linear relationship between $F-1$ and $[1/p_0][2\pi k_2 L^2 C_B^0 / \bar{P}][\ln(1+Kp_0)/p_0]$ for the single RC model. The linear relationship was also found between $F-1$ and $(1/p_0)[n^2 + \{(2\pi k_2 L^2 C_B^0 / \bar{P}) \ln(1+Kp_0) / p_0\}^2]^{1/2}$ for the series RC model. From the linear relationship, p_d is estimated for each membrane. All parameter values are summarized in Table 4. As expected, the p_d and α_p values are very small. The p_d value increases with the glass transition temperature of polymers.

Figure 5 depicts the model predictions for the single RC model and the series RC model and the experimental data on PDMS membrane containing metallo-porphyrin carrier. The results for the dual sorption model was also included as a reference. The parameter values used in the two models are the same except p_d for the current model and D_{AB} for the dual sorption. Please refer to the reference number 4 for the mathematical equation of the dual sorption model. The agreement between the experimental data and the current model is exceptional even in the high pressure region, where the dual sorption model markedly deviate. The series RC model is more accurate than the single RC model, but, as can be seen, their difference is minor. Both models also match the oxygen permeability data for PBMA and PMMA with less than 5 %.

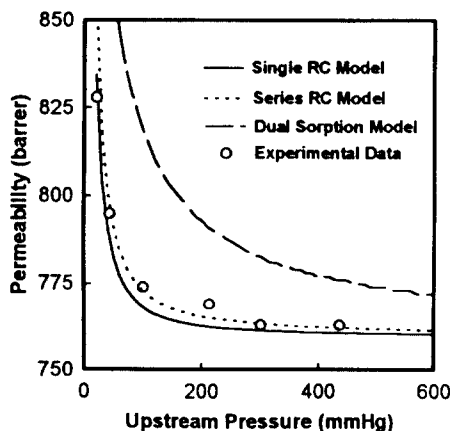


Figure 6. Comparison between the model predictions and experimental results on oxygen transport in PDMS membrane containing metallo-porphyrin carrier:

CONCLUSIONS

The local solute concentration in the facilitated transport membrane with fixed site carrier was assumed to be instantaneously fluctuated because of the continuous reversible reaction between solute and carrier. The fluctuated concentration resulted in a higher free energy, higher chemical potential and higher flux for facilitation. From the analogy between electron transport in an RC circuit and facilitated transport in a fixed site carrier membrane, a new simple mathematical model was developed. It was found that the facilitation phenomena could possibly be explained by a pressure or concentration fluctuation in the membrane. The model was examined against experimental data and showed an excellent agreement. Finally, the extent of pressure fluctuation α_p is found to be very small but can significantly affect the facilitation behavior.

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NOMENCLATURE

- A_s : surface area
 C : capacitance
 C_A^- : concentration of solute in matrix ($C_A^- = Sp_0$) [mol/cm³]
 C_{AB} : concentration of complex AB [mol/cm³]
 C_B^0 : initial carrier concentration loaded [mol/cm³]
 D : diffusion coefficient of solute through matrix [cm²/sec]
 dV : differential volume in equation (1)
 f : frequency in alternating voltage [1/sec]
 F : facilitation factor ($= \bar{P} / \bar{P}$)
 G : total free energy of system
 $g(c)$: free energy density of homogeneous system of composition c
 H_s : average total amount of complex AB per unit pressure in a given volume of membrane [mol/cmHg]
 j : total electron flux
 J : mass flux [mol/cm² sec]
 k_1 and k_2 : forward and reverse reaction constants of between solute and carrier [1/cmHg sec] and [1/sec]
 K : reaction equilibrium constant of between solute and carrier [1/cmHg]
 L : membrane thickness [cm]
 n : number of layers
 p : pressure (equation (5)) [cmHg]
 p_0 : time-averaged pressure at membrane surface [cmHg]

- p_a : time-averaged pressure (equation (5)) [cmHg]
 p_d : pressure fluctuation (equation (5)) [cmHg]
 \bar{P} : permeability of matrix [mol cm/cm²sec cmHg]
 \bar{P}_f : permeability of facilitated transport membrane [mol cm/cm²sec cmHg]
 q : charge
 S : Henry's law solubility coefficient of solute in matrix ($S=C_A^{\sim}/p_0$)
[mole/cm³cmHg]
 t : time [sec]
 V : voltage
 V_a : average voltage applied
 V_d : voltage fluctuation

Greek letter

- $\alpha_p = p_d/p_0$: the extent of pressure fluctuation
 $\alpha_v = V_d/V_a$: the extent of voltage fluctuation
 $\gamma = C_B^0/C_A^{\sim}$: the ratio of the carrier concentration, C_B^0 , loaded to the solute concentration in matrix (Henry's law; $C_A^{\sim} = Sp_0$).
 $\Delta = Kp_0$: the combined driving force for facilitated transport.
 κ : positive parameter in equation (1)
 σ : conductivity in a resistor circuit
 σ_{rc} : conductivity in a resistor-capacitor circuit
 $\psi = k_2L^2/D$: the time scale ratio of diffusion to chemical reaction.
 $\omega = 2\pi f$: angular velocity