

行政院國家科學委員會專題研究計畫 成果報告

自簡單系統的可測擴散參數估計複雜系統的擴散參數

計畫類別：個別型計畫

計畫編號：NSC91-2113-M-009-018-

執行期間：91年08月01日至92年12月31日

執行單位：國立交通大學應用化學系

計畫主持人：陳振興

計畫參與人員：高大宇、張文益，吳承昌

報告類型：精簡報告

處理方式：本計畫可公開查詢

中 華 民 國 93 年 2 月 4 日

行政院國家科學委員會補助專題研究計畫

成果報告
期中進度報告

自簡單系統的可測擴散參數估計複雜系統的擴散參數

計畫類別： 個別型計畫 整合型計畫

計畫編號：NSC 91 - 2113 - M - 009 - 018

執行期間：91年08月01日至92年12月31日

計畫主持人：陳振興 國立交通大學應用化學系

計畫參與人員：高大宇、張文益，吳承昌

成果報告類型(依經費核定清單規定繳交)： 精簡報告 完整報告

本成果報告包括以下應繳交之附件：

赴國外出差或研習心得報告一份

赴大陸地區出差或研習心得報告一份

出席國際學術會議心得報告及發表之論文各一份

國際合作研究計畫國外研究報告書一份

處理方式：除產學合作研究計畫、提升產業技術及人才培育研究計畫、
列管計畫及下列情形者外，得立即公開查詢

涉及專利或其他智慧財產權， 一年 二年後可公開查詢

執行單位：國立交通大學應用化學系

中 華 民 國 93 年 02 月 04 日

中文摘要

關鍵詞: 傳輸矩陣、泰勒級數展開、平均首度通過時間、延滯時間

我們先行求出 Laplace domain 下的傳輸矩陣的形式是 Laplace variable s 的泰勒級數展開式，展開係數可用成份薄板的可測擴散參數表示，如延滯時間、滲透係數正向及反向前導時間，及其高階矩擴散參數。有了這個工具之後，複合體擴散諸參數就可以用成份薄板的擴散參數表示。於是我們不必要直接測量複合體的擴散係數而由成份薄片的擴散參數組合即可。以平均首度通過時間為例，闡明此新法之應用。

Abstract

Key word: transmission matrix, Taylor's expansion, mean first passage time, time lag

The membrane transport in terms of transmission matrix, $T(s)$, in the Laplace domain has been extended to a more useful formulation. This is achieved with the help of a combination of the uses of the matrix transport equations appropriate for initial conditions of void concentration or saturated equilibrium within the membrane and the theorem $\det[T(s)] = 1$. This new formulation gives $T(s)$ in power series of the Laplace variable, s , with the expansion coefficients as the algebraic functions of the experimentally measurable parameters: permeability, time lag, forward and backward time leads and their higher moments. The utility of this new formulation of the transmission matrix is illustrated in the estimation of the time moments for the first passage and residence times, which are not measurable directly from the experiments.

Background, Purpose and Significance of the Investigation

Permeation transport across membranes is of great importance in science and technology, and has played a crucial role in such diversified fields as chemical sensors,^{1,2} controlled release,^{3,4} separation processes,⁵ protection against pollution,⁶ electrodialysis,⁷ to name just a few. In practical applications, three modes of membrane transport are employed:⁸ (a) absorptive permeation, zero and the activities at the upstream and downstream faces are at a constant level a_0 (b) forward and/or backward desorptive permeation, (c) desorption, For heterogeneous membranes, where the diffusivity $D(x)$ and partition coefficient $K(x)$ depending on position, the permeation can be mathematically described by the Smoluchowski equation⁹⁻¹¹

$$\frac{\partial}{\partial t} \rho(x, t) = \frac{\partial}{\partial x} D(x) K(x) \frac{\partial}{\partial x} \frac{\rho(x, t)}{K(x)}. \quad \text{The complete knowledge about the membrane permeation}$$

entails the full time-dependent solution to the diffusion equation subject to appropriate boundary and initial conditions. Unfortunately such a solution is seldom obtained except for some simple, trivial cases. Thus one is usually satisfied with a few diffusion parameters characteristic of the permeation such as permeation (P), time lag (t_L) for absorptive and time lead (t_+) for desorptive permeation and their higher moments.^{12,13} All these permeation parameters can be obtained directly from the suitably designed experiments. Theoretically, they can also be formulated via the Taylor expansion of the transmission matrix, $T(s)$, in power series of s with the expansion coefficients expressed in terms of the repeated integrals of $[K(x)D(x)]^{-1}$ and $K(x)$ ¹⁴ or by the method of repeated integration of the diffusion equation.^{9,15}

However, these formulations are useful only in the cases where the functions $K(x)$ and $D(x)$ are known beforehand.

Another concern about diffusion transport is the moments of the first passage time^{10,11,16} and residence time.^{17,18} Ordinarily, neither are obtainable directly from the experiments. Mathematically the former can be obtained by solving the adjoint (or backward) diffusion equation^{10,11} and the latter by the Green's function of the diffusion equation.^{17,18} Again these tasks are feasible only when $K(x)$ and $D(x)$ are known ahead of time.

Method of Investigation and Results

Starting with the matrix transport equation and the appropriate initial and boundary conditions and a further use of the definitions of the experimentally accessible diffusion parameters for P (permeability), t_L (time lag), t_+ (forward time lead), t_- (backward time lead) and their higher moments, we are able to derive the Taylor's expansion of the transmission matrix in a power

series of Laplace variable, s , with the expansion coefficients as functions of the above mentioned parameters . Namely

$$\begin{bmatrix} \hat{a}_d(s) \\ \hat{J}_d(s) \end{bmatrix} = T(s) \begin{bmatrix} \hat{a}_u(s) \\ \hat{J}_u(s) \end{bmatrix} = \begin{bmatrix} T_{11}(s) & T_{12}(s) \\ T_{21}(s) & T_{22}(s) \end{bmatrix} \begin{bmatrix} \hat{a}_u(s) \\ \hat{J}_u(s) \end{bmatrix} \quad (1)$$

With

$$\begin{aligned} T_{12}(s) &= -\frac{1}{P} - \frac{t_L}{P} s - \frac{2t_L^2 - t_L^{(2)}}{2P} s^2 - \frac{6t_L^3 - 6t_L t_L^{(2)} + t_L^{(3)}}{6P} s^3 - \Lambda \\ &= -\beta_0 - \beta_1 s - \beta_2 s^2 - \beta_3 s^3 - \Lambda \end{aligned} \quad (2)$$

$$\begin{aligned} T_{22}(s) &= 1 + \bar{t}_+ s + \frac{2t_L \bar{t}_+ - \bar{t}_+^{(2)}}{2} s^2 + \frac{\bar{t}_+^{(3)} + 6\bar{t}_+ t_L^2 - 3t_L \bar{t}_+^{(2)} - 3t_L^{(2)} \bar{t}_+}{6} s^3 + \Lambda \\ &= \delta_0 + \delta_1 s + \delta_2 s^2 + \delta_3 s^3 + \Lambda \end{aligned} \quad (3)$$

$$\begin{aligned} T_{11}(s) &= 1 + \bar{t}_- s + \frac{2t_L \bar{t}_- - \bar{t}_-^{(2)}}{2} s^2 + \frac{\bar{t}_-^{(3)} + 6\bar{t}_- t_L^2 - 3t_L \bar{t}_-^{(2)} - 3t_L^{(2)} \bar{t}_-}{6} s^3 + \Lambda \\ &= \alpha_0 + \alpha_1 s + \alpha_2 s^2 + \alpha_3 s^3 + \Lambda \end{aligned} \quad (4)$$

$$\begin{aligned} T_{21}(s) &= -P[\bar{t}_+ + \bar{t}_-]s - \frac{P}{2}[2\bar{t}_+ \bar{t}_- - \bar{t}_+^{(2)} - \bar{t}_-^{(2)}]s^2 \\ &\quad - \frac{P}{6}[\bar{t}_+^{(3)} + \bar{t}_-^{(3)} - 3\bar{t}_+^{(2)} \bar{t}_- - 3\bar{t}_+ \bar{t}_-^{(2)} + 6t_L \bar{t}_+ \bar{t}_-]s^3 + \Lambda \end{aligned} \quad (5)$$

where $\bar{t}_+ = t_L - t_+$, $\bar{t}_+^{(2)} = t_L^{(2)} - t_+^{(2)}$, $\bar{t}_+^{(3)} = t_L^{(3)} - t_+^{(3)}$, $\bar{t}_- = t_L - t_-$, $\bar{t}_-^{(2)} = t_L^{(2)} - t_-^{(2)}$ and $\bar{t}_-^{(3)} = t_L^{(3)} - t_-^{(3)}$. The super index number in the parenthesis denotes the respective rank of moment, and the definition of i , i , i and i are self-explanatory.

Application

As an example, we consider the first passage time for a particle initially located at x_0 between a reflecting face x_u and an absorbing face x_d , $x_u < x_0 < x_d$.^{11,16} Solving this problem requires the matrix transport equation for an initial condition of δ -function type^{14,19}

$$\begin{bmatrix} \hat{a}_d(s) \\ \hat{J}_d(s) \end{bmatrix} = T(s) \begin{bmatrix} \hat{a}_u(s) \\ \hat{J}_u(s) \end{bmatrix} + T^*(s) \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (6)$$

where $T^*(s)$ is the transmission matrix for the subdomain from x_0 to x_d . After substitution of $\hat{J}_u(s) = 0$ and $\hat{a}_d(s) = 0$ into eqn. (6), the flux escaping the face x_d is calculated to be

$$\hat{J}_d(s) = \frac{T_{11}(s)T_{22}^*(s) - T_{21}(s)T_{12}^*(s)}{T_{11}(s)} \quad (7)$$

The mean first passage time can be represented by

$$\mu_1 = \frac{\int_0^{\infty} t J_d(t) dt}{\int_0^{\infty} J_d(t) dt} = - \lim_{s \rightarrow 0} \frac{d}{ds} \hat{J}_d(s) \quad (8)$$

where the denominator represents the initial total amount which is equal to unity. Putting eqn. (7) into eqn. (8) followed by expanding the transition matrix elements in terms of eqns. (2), (3), (4) and (5), we obtain

$$\mu_1 = [\bar{t}_+ + \bar{t}_-] \frac{P}{P^*} - \bar{t}_+^* \quad (9)$$

Here the quantity associated with the superscript $*$ denotes the fact this quantity is to be specified to the subdomain, $x_0 < x < x_d$. The second moment of first passage time is also easily calculated by

$$\mu_2 = \frac{\int_0^{\infty} t^2 J_d(t) dt}{\int_0^{\infty} J_d(t) dt} = \lim_{s \rightarrow 0} \frac{d^2}{ds^2} \hat{J}_d(s)$$

$$= 2 t_L^* \bar{t}_+^* - \bar{t}_+^{(2)*} + \frac{P}{P^*} [\bar{t}_+^{(2)} + \bar{t}_-^{(2)} + 2 \bar{t}_-^2 - 2 t_L^* (\bar{t}_+ + \bar{t}_-)] \quad (10)$$

where $\bar{t}_+^* = t_L^* - t_+^*$ and $\bar{t}_+^{(2)*} = t_L^{(2)*} - t_+^{(2)*}$. Thus with each quantity on the right-hand sides of eqs 9 and 10 being experimentally accessible, μ_1 and μ_2 can be estimated.

Conclusion

With such a Taylor expansion of transmission matrix as a tool and in cooperation with appropriate matrix transport equations, the problems of time moments for first passage time, and residence time can be solved algebraically. As a result, various time moments can be expressed by the algebraic function of the above-mentioned measurable parameters. Thus, some experimentally inaccessible time moments can be estimated from permeation parameters measurable in appropriate permeation experiments. This methodology for the estimation of the time moments would provide a useful vehicle for the treatment of the membrane permeation and other problems in diffusive transports.

Acknowledgment

We are grateful to the National Science Council of Taiwan for the financial support of this work under Grant Nos. NSC 91 - 2113 - M - 009 - 018.

References

1. Madou, M. J.; Morrison, S. R. *Chemical Sensing with Solid State Devices*; Academic Press: Boston, **1989**.
2. Cattrall, R. W. *Chemical Sensor, Oxford Chemistry Primers*, No. 52; Oxford University Press: Oxford, **1997**.
3. Wood, D. A. In *Materials Used in Pharmaceutical Formulation*; Florence. A. T., Ed.; *Polymeric Material Used in Drug Delivery Systems*; Blackwell Scientific: Oxford, **1989**.

4. Smith, K. L.; Herbig, S. M. In *Membrane Handbook*; Ho, W. S.; Sirkar, K. K., Eds.; *Controlled Release*; Van Nostrand Reinhold: New York, **1992**.
5. Matsuura, T. *Synthetic Membranes and Membrane Separation Process*, CRC: Boca Raton, **1994**. Frisch, H. L.; Kloczkowski, A. *J. Colloid Interface Sci.* **1984**, 99, 404.
6. Mulder, M. *Basic Principles of Membrane Technology*; Kluwer: Dordrecht, 1991.
7. Frisch, H. L. *J. Phys. Chem.* **1978**, 82, 1559.
8. Chen, J. S.; Fox, J. L. *J. Chem. Phys.* **1988**, 89, 2278.
9. Zwanzig, R. *Proc. Natl. Acad. Sci. USA* **1988**, 85, 2029.
10. Szabo, A.; Schulten, K.; Schulten, Z. *J. Chem. Phys.* **1980**, 72, 4350.
11. Siegel, R. A. *J. Phys. Chem.* **1991**, 95, 2556.
12. Petropoulos, J. H. *Adv. Polym. Sci.* **1985**, 64, 93.
13. Chen, J. S.; Chang, W. Y. *J. Chem. Phys.* **2000**, 112, 4723.
14. Frisch, H. L.; Prager, S. T. *J. Chem. Phys.* **1971**, 54, 1451.
15. Weiss, G. H. *Adv. Chem. Phys.* **1967**, 13, 1.
16. Agmon, N. *J. Chem. Phys.* **1984**, 81, 3644.
17. Berzhkovskii, A. M.; Zaloj, V.; Agmon, N. *Phys. Rev.* **1998**, E57, 3937.
18. Chen, J. S.; Chang, W. Y. *J. Chem. Phys.* **1997**, 106, 8022.
19. Chen, J. S.; Chang, W. Y. *J. Chem. Phys.* **1997**, 107, 10709.