行政院國家科學委員會專題研究計畫成果報告

(1)反應／擴散之延遲時間及平均首度通過時間之研究 (2)以 NMR 和 IR 研究乙醯苯胺在溶液中自結合

(1) The Study of Time Lag and Mean First Passage Time for Membrane Diffusion Accompanying Reaction (2) NMR and IR of Self-Association of Acetanilides in Various Solution

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一、中文摘要

本研究企圖將非均勻擴散隨伴著反應，從數學的觀點，可以視為純粹非均勻擴散。上述的條件是要將擴散質在介質的配分係數作適當的修正為等效配分係數。從而，為純粹擴散而設計的傳輸矩陣便可以借過來給擴散/反應系統使用。而處理延滯時間及平均首度通過時間也可以依照以往的方法處理。

關鍵詞：擴散/反應，等效分配係數，傳輸矩陣，延滯時間，平均首度通過時間。

Abstract:

This project is to attempts to treat the system of inhomogeneous diffusion accompanying a first order reaction as a pure inhomogeneous diffusion. This is possible, from the mathematical point of view, if the partition coefficient of the latter is modified to an effective one. Thus, the transmission matrix designed for the diffusion without reaction can be transcribed to the diffusion/reaction system. The time lag and mean first passage time problems can be treated in the same way as the pure diffusion system.

Keywords: diffusion/reaction, effective partition coefficient, transmission matrix, time lag, mean first passage time
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二、緣由與目的

Diffusion is a ubiquitous phenomenon in physical and biological world.[1] It

occurs in electrochemistry,[2] colloidal science,[3] semiconductor device fabrication and operation,[4] solid state physics,[5] and drug delivery,[6] to name only a few. Sometimes a chemical reaction accompanying diffusion, such as accurring in chemical sensor,[7] in membrane reactor[8] and drug delivery across skin with metabolism.[6] In such cases diffusion and reaction cannot be treated separately, i.e., they must be mingled together.

It is always desirable to have a complete scenario of the process of diffusion/reaction. This is possible only for some very simple cases whose diffusion/reaction equation has a complete analytic solution. In other more complicated cases, some diffusion parameters such as permeability, P, time lag, t_L, and mean first passage time, t_{mfp}, are resorted to.[9-13] As a matter of fact, P and t_L are crucial parameters to estimate the total release at the downstream side as a function of time, Q(t), via a linear asymptote, $Q(t) = P(t - t_L)$, when the experiment are set up that the initial concentration within the membrane is void, and the boundary conditions at the upstream and downstream sides are constant and zero concentrations, respectively.[11] The mean first passage time is used to be characterized the time elapsed for a diffusant particle lingering in the diffusion domain when it is initially at a particular position.[12] Formulae to calculate P, t_L and t_{mfp} are well known for the pure diffusion system. However, when it comes to diffusion with reaction, their expressions are found only in some simple cases. The general theory related to this subject still has some room to develop.

三、結果與討論
（一）結果

Inhomogeneous diffusion accompanying reaction can be repressed in mathematical form

$$\frac{\partial}{\partial t}\rho(x,t) = \frac{\partial}{\partial x}D(x)K(x)\frac{\partial}{\partial x}\frac{\rho(x,t)}{K(x)} - k(x)\rho(x,t) \tag{1}$$

where D(x), K(x) and k(x) are diffusivity, partition coefficient and rate constant, respectively, and $\rho(x,t)$ is the diffusant concentration.

with $\rho(x,t) = [g(x)]^{-1}\tilde{\rho}(x,t)$, and after some lengthy algebraic operation , eq. (1) can be partitioned into two parts, one corresponding to the steady state equation for g(x),

$$\frac{\partial}{\partial x}D(x)K(x)\frac{\partial}{\partial x}\frac{g(x)}{K(x)} - k(x)g(x) = 0 \tag{2}$$

the other is for $\tilde{\rho}(x,t)$ obeying the new equation

$$\frac{\partial}{\partial t}\tilde{\rho}(x,t) = \frac{\partial}{\partial x}D(x)K(x)g^2(x)\frac{\partial}{\partial x}\frac{\tilde{\rho}(x,t)}{g^2(x)K(x)} \tag{3}$$

If, further, we name $\tilde{K}(x) = g^2(x)K(x)$ as the effective partition coefficient, then eq. (3) can be cast into a standard from of pure inhomogeneous diffusion equation with diffusivity, D(x), and partition coefficient, $\tilde{K}(x)$, to be

$$\frac{\partial}{\partial t}\tilde{\rho}(x,t) = \frac{\partial}{\partial x}D(x)\tilde{K}(x)\frac{\partial}{\partial x}\frac{\tilde{\rho}(x,t)}{\tilde{K}(x)} \tag{4}$$

Thus, we have established the equivalence between diffusion and diffusion/reaction upon modifying K(x) to $\tilde{K}(x) = g^2(x)K(x)$

（二）討論

    With this establishment of the equivalence

1. The time lag can be expressed for diffusion/reaction after replacing K(x) by $\tilde{K}(x)$ to be

$$t_L = \frac{\int_0^h \tilde{K}(x)\int_0^x \frac{dy}{D(y)\tilde{K}(y)}\int_x^h \frac{dy}{D(y)\tilde{K}(y)}dx}{\int_0^h \frac{1}{D(x)\tilde{K}(x)}dx} \tag{5}$$

2. The mean first passage time for a particle initially at x_0 for both sides x = 0 and x = h being absorbing now reads

$$t_{mfp} = \int_{x_0}^h \frac{1}{D(x)\tilde{K}(x)}\int_0^x \tilde{K}(y)dydx - \frac{\int_{x_0}^h \frac{1}{D(x)\tilde{K}(x)}dx \int_0^h \frac{1}{D(x)\tilde{K}(x)}\int_0^x \tilde{K}(y)dydx}{\int_0^h \frac{1}{D(x)\tilde{K}(x)}dx} \tag{6}$$

3. For upstream side (x = 0) being reflecting downstream side (x = h) being absorbing, the mean first passage time becomes

$$t_{mfp} = \int_{x_0}^h \frac{1}{D(x)\tilde{K}(x)}\int_0^x \tilde{K}(y)dydx \tag{7}$$

4. If x = 0 is absorbing, while x = h is reflecting, the corresponding entity now becomes

$$t_{mfp} = \int_0^{x_0} \frac{1}{D(x)\tilde{K}(x)}\int_x^h \tilde{K}(y)dydx \tag{8}$$

Eqs. (6)-(8) are obtained by replacing K(x) by $\tilde{K}(x)$ from the corresponding known equations of the pure diffusion

The result of another subproject, NMR and IR of self-association of Acetanilide in various solvents, has been published in **Zeitschrift fur Physikalische Chemie**, <u>215</u>, 447-459 (2001) under the title *NMR Study of Self-Association of Acetanilide in Chloroform, Acetonitrile and Dimethyl Sulphoxide.*

（三）計劃結果自評

We have established, mathematically, the equivalence between diffusion and diffusion with reaction after a modification of the partition coefficient from K(x) to $\tilde{K}(x) = g^2(x)K(x)$, where $g(x)$ is the steady-state solution of the diffusion/reaction equation. This establishment enables us to treat the problem of diffusion/reaction along the line used for pure diffusion problem.

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