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ZBIGNIEW JAN GRZYWNA

DYFUZYJNY TRANSPORT MASY W MEMBRANACH HETEROGENICZNYCH REGULARNYCH

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SPIS TREŚCI

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Autor składa serdeczne podziękowania Prof. John H. Petropoulosowi i Jego Współpracownikom z Nuclear Research Centre "Demokritos" w Atenach za owocną współpracę podczas rocznego (1981/82) pobytu autora w NRC.

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Prof. Józefowi Podkówce i Kolegom z Zespołu Podstaw Chemii Fizycznej i Fizykochemii Polimerów Instytutu Fizykochemii i Technologii Polimerów należą się szczególne podziękowania za wprowadzenie mnie, kilkanaście lat temu, w trudną problematykę dyfuzji w membranach polimerowych.

WYKAZ SKRÓTÓW

a - aktywność termodynamiczna
c - stężenie penetrante
D - współczynnik dyfuzji
erfc - dopełnienie funkcji błędu Gaussa
f - współczynnik aktywności
H(y) - obraz struktury dyfuzyjnej (P(x)S(x)/PS)
J - dyfuzyjny strumień masy
l - grubość membrany
L - opóźnienie czasowe
m - współczynnik ruchliwości
MHR - membrana heterogeniczna regularna
M - masa penetrante na jednostkę powierzchni membrany (sorpcja)
P - współczynnik przenikalności
p - ciśnienie (prężność pary)
Q - masa penetrante na jednostkę powierzchni membrany (przenikanie)
RRC - równanie różniczkowe cząstkowe
RRZ - równania różniczkowe zwyczajne
RS - różnice skończone
R - uniwersalna stała gazowa
S - współczynnik rozpuszczalności
T - temperatura
t - czas
μ - potencjał chemiczny

OPIS INDEKSÓW

o - standardowy (lub stały)
p - ciśnieniowy
R - reservoir (na zewnątrz membrany)
T - termodynamiczny

1. WPROWADZENIE

1.1. Cel pracy

Praca ma charakter teoretyczny i dotyczy dyfuzyjnego transportu gazów i par przez membrany stałe, których własności dyfuzyjne są funkcją położenia wewnątrz membrany i zmieniają się w sposób ciągły regularnie - membrany heterogeniczne regularne (MHR).

Trzy zasadnicze cele przyświecają niniejszej pracy:

- efektywne rozwiązanie zagadnienia nieustalonego transportu masy w MHR. Uzyskane rozwiązania umożliwiają wyprowadzenie formuł analitycznych ośmiu metod eksperymentalnego badania tego transportu. Te z kolei pozwalają na stworzenie systemu analizy, komplementarnego z systemem opóźnień czasowych. Faktem o istotnym znaczeniu jest stwierdzenie, które z owych ośmiu formuł zachowują własność liniowości dla wybranych struktur dyfuzyjnych membrany,
- rozwiązanie tzw. zagadnienia pierwotnego dyfuzji, czyli przewidywania własności dyfuzyjnych układu na podstawie znanej struktury dyfuzyjnej membrany,
- stworzenie możliwości wykrywania struktury dyfuzyjnej membrany na podstawie pomiarów własności dyfuzyjnych układu w stanie nieustalonym, czyli rozwiązanie jednego z tzw. zagadnień odwrotnych.

1.2. Rozważania wstępne

Zagadnienia rozpatrywane w tej pracy dotyczą generalnie dyfuzyjnego transportu masy (dyfuzji) małych cząstek gazów lub par (penetrant) w/lub przez ciało stałe, zwykle polimer (ośrodek dyfuzji, membrana).

W celu scharakteryzowania powyższego systemu dyfuzyjnego przyjęto trzy współczynniki [1-4] : rozpuszczalności (podziału) lub sorpcji (S), dyfuzji (D_T) oraz przenikalności (przepuszczalności) (P).

Pierwszy z nich charakteryzuje podział penetranta między ośrodek dyfuzji a fazę zewnętrzną w równowadze, co można zapisać, wychodząc z równości potencjałów chemicznych penetranta, w obu fazach

$$\mu_R = \mu^{x)} \tag{1.1}$$

x) Znaczenie użytych symboli - patrz Wykaz Skrótów.

i co implikuje relacje [4]

$$S = (a/a_R)_{równ} = \exp\left[-\frac{\Delta\mu^o}{RT}\right], \qquad (1.2)$$

gdzie $\Delta\mu^o$ oznacza różnicę potencjałów chemicznych standardowych penetranta w obu fazach.

W przypadku gdy wybrano identyczne stany standardowe w ośrodku dyfuzji i fazie zewnętrznej (tj., gdy $\Delta\mu^o = 0$), współczynnik podziału równa się jedności. Wykorzystując relację $a = f.c$, równanie (1.2) zapisuje się często w postaci

$$\tilde{S} = (c/a_R)_{równ.}, \qquad (1.3)$$

gdzie: $\tilde{S} = 1/f$.

Dla gazowych penetrantów pod umiarkowanymi ciśnieniami można przyjąć $a_R = p/p_o$ i wtedy równanie (1.3) przyjmuje postać

$$S_p = (c/p)_{równ.}, \qquad (1.4)$$

gdzie: $S_p = \tilde{S}/p_o$.

Termodynamiczny współczynnik dyfuzji D_T można wprowadzić opierając się na zasadzie termodynamiki nierównowagowej. Upraszczając znacznie pełny wywód Baranowskiego [4] można napisać:

$$J = -D_T\left(1 + \frac{\partial \ln f}{\partial \ln c}\right)\frac{\partial c}{\partial x} = -D_T\frac{\partial \ln a}{\partial \ln c}\frac{\partial c}{\partial x} = -D_T\tilde{S}\frac{\partial a}{\partial x}, \qquad (1.5)$$

gdzie $D_T = D_1^{id}$ z pracy [4], tj. współczynnikowi dyfuzji w układach idealnych, dla których czynnik termodynamiczny redukuje się. Równanie (1.5) można ostatecznie przedstawić w formie

$$J = -P\frac{\partial a}{\partial x}, \qquad (1.6)$$

gdzie $P = D_T.\tilde{S}$, jest współczynnikiem przenikalności.

Zdefiniowana powyżej grupa współczynników charakteryzuje różne (w tym tylko dwie niezależne) własności układów dyfuzyjnych, a więc:

a) Współczynnik rozpuszczalności (S) jest parametrem równowagowym (analogicznym do stałej równowagi reakcji chemicznej) i miarą wielkości sorpcji ośrodka dyfuzji.
b) Współczynnik (termodynamiczny) dyfuzji (D_T) jest parametrem kinetycznym (analogicznym do stałej szybkości reakcji chemicznej) i miarą szybkości poruszania się cząstek penetranta w ośrodku dyfuzji.

c) Współczynnik przenikalności (P) jest iloczynem dwóch powyższych, lecz często jest bardzo użyteczny, gdyż jest miarą szybkości z jaką cząstki penetranta przechodzą przez membranę (folię). W wielu przypadkach zastosowania membran, właśnie P jest poszukiwanym współczynnikiem a nie S i D_T indywidualnie.

Trzeba podkreślić, że nieco inaczej definiuje się ten współczynnik w biofizyce błon [5]. Jak już wspomniano, termodynamika nierównowagowa oferuje pełny, fenomenologiczny opis procesu dyfuzji. Na potrzeby jednak tej pracy (proces izotermiczny, dwuskładnikowy, jednowymiarowy) wystarczy przypomnieć, że najprostszą formą równań fenomenologicznych, opisujących dyfuzję, jest tzw. I prawo Ficka

$$J = -D\frac{\partial c}{\partial x}, \qquad (1.7)$$

gdzie D jest rzeczywistym współczynnikiem dyfuzji [4].
Porównanie (1.7) oraz (1.5) daje relację

$$D = D_T\frac{d \ln a}{d \ln c} \equiv D_T\left(1 + \frac{\partial \ln f}{\partial \ln c}\right). \qquad (1.8)$$

Zastosowanie lokalnego równania bilansu do równań (1.6) i (1.7) daje odpowiednio:

$$\frac{\partial(S\,.\,a)}{\partial t} = \frac{\partial}{\partial x}\left[P\frac{\partial a}{\partial x}\right] \qquad (1.9)$$

oraz

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D\frac{\partial c}{\partial x}\right]. \qquad (1.10)$$

Rozróżnia się generalnie trzy kategorie układów dyfuzyjnych:

a) układ fickowski idealny: D i S = const, co implikuje równości: P = = constans oraz $D \equiv D_T$. W tym przypadku równania (1.9) i (1.10) są identyczne,
b) układ fickowski: D i S są tu funkcjami stężenia (lub aktywności). W tych przypadkach równanie (1.10) jest wygodniejsze w użyciu niż równanie (1.9),
c) układ anomalny lub niefickowski: D_T i S są również funkcjami innych zmiennych (oprócz stężenia), np. współrzędnych (heterogeniczne ośrodki dyfuzji) lub czasu (polimer relaksujący), lub wszystkich trzech jednocześnie. W tym przypadku należy stosować równanie (1.9), użycie równania (1.10) może prowadzić do nieprawidłowych rezultatów [6].

Przedmiotem rozważań niniejszej pracy są niektóre układy zawarte w punkcie c), takie mianowicie, których własności zależą w sposób ciągły od położenia. W tym przypadku równanie (1.9) przyjmuje postać

$$S(x)\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[P(x)\frac{\partial c}{\partial x}\right] \tag{1.11}$$

i opisuje dyfuzyjny transport masy w takich układach, jak:

- folie z kopolimerów szczepionych,
- laminaty ciągłe,
- folie semikrystaliczne z pewną funkcją rozdziału krystalitów wzdłuż osi x,
- membrany porowate z rozdziałem porów wzdłuż osi x,
- membrany polimerowe plastyfikowane, z których ubyła część plastyfikatora, powodując nierównomierny rozdział ilości pozostałej wzdłuż osi x,
- membrany powierzchniowe utlenione,
- membrany biologiczne itp. układy o ciągłym (regularnym) rozkładzie własności dyfuzyjnych, pod warunkiem, że użyte stężenia (ciśnienia) gazów i par nie są zbyt duże.

1.3. O możliwościach rozwiązywania zagadnień granicznych w MHR

Równanie (1.11) jest równaniem różniczkowym cząstkowym (RRC), liniowym, parabolicznym II rzędu o współczynnikach funkcyjnych (zmiennych). Rozwiązywanie równań tego typu (z reguły bardzo uciążliwe) jest ogólnie możliwe za pomocą trzech grup metod [7]:

1) analitycznych,
2) analitycznych przybliżonych,
3) numerycznych.

Powyższego podziału nie należy traktować zbyt dosłownie. We współczesnych metodach obliczeniowych nakładają się bowiem często cechy charakterystyczne metod, które należą do różnych grup [8]. Należy również podkreślić, że efektywność większości metod, używanych obecnie do obliczeń jest zbliżona (niezależnie od grupy, do której należą), tj. pozwalają one uzyskać rozwiązania z dowolną dokładnością [7, 9].

Przykładem zastosowania jednej z metod pierwszej grupy, tj. rozdzielenia zmiennych, może być praca Barrera [10]. W odniesieniu do nieco prostszego równania, tj.

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D(x)\frac{\partial c}{\partial x}\right] \tag{1.12}$$

oraz liniowej funkcji $D(x) = D_0(1 + ax)$ uzyskał on rozwiązanie

$$c = c_1 + (c_2 - c_1)\frac{\ln(1 + ax)}{\ln(1 + al)} - \sum_n \pi Y_0(W_0)\left(\frac{c_0 - c_2}{Y_0(W_2)}\right) + \frac{c_1 - c_0}{Y_0(W_0)} \cdot V_0(W)\exp(-D_0\alpha_n^2 t), \tag{1.13}$$

gdzie α_n (wartości własne) otrzymuje się jako n-ty dodatni pierwiastek równania

$$J_0(2\sqrt{\alpha})\, Y_0\left[2\sqrt{\alpha(1 + al)}\right] - J_0\left[2\sqrt{\alpha(1 + al)}\right] \cdot Y_0(2\sqrt{\alpha}) = 0 \tag{1.14}$$

J_0 i Y_0 są funkcjami Bessela zerowego rzędu, odpowiednio pierwszego i drugiego rodzaju, $W = 2\sqrt{\alpha_n(1 + ax)}$ i $W_0 = 2\sqrt{\alpha_n}$, V_0 natomiast dane jest relacją

$$V_0(W) = Y_0(W_0)J_0(W) - J_0(W_0)Y_0(W). \tag{1.15}$$

Równanie (1.14) może być rozwiązane tylko metodami przybliżonymi (najlepiej numerycznie), co powoduje, że uzyskane rozwiązanie ma podobny, tj. przybliżony charakter.

Na marginesie tych rozważań warto jednak zanotować, że uzyskiwanie rozwiązań dokładnych jest rzadkością, nawet w klasie równań o stałych współczynnikach. Typową formą rozwiązań zagadnień granicznych jest postać szeregu nieskończonego [2, 11], którego sumy nie znamy.

Rozwiązanie efektywne (służące do konkretnych obliczeń) jest z konieczności przybliżone (z dowolną jednak dokładnością) przez skończoną sumę kolejnych n wyrazów szeregu.

W grupie metod analitycznych przybliżonych największą rolę odgrywają metody perturbacyjne [12, 13] (pewne znaczenie praktyczne mają też metody wariacyjne [7, 12]).

Nieco dokładniej zostanie omówiona metoda regularnej perturbacji, z uwagi na konieczność wprowadzenia korekt matematycznych do wcześniejszych prób jej zastosowania przez innych autorów [12]. Idea metody regularnej perturbacji w odniesieniu do równania (1.11) jest następujące. Postuluje się, że funkcje: $S(x)$ oraz $P(x)$ można przedstawić w postaci:

$$S(x) = S_0\left[1 + \epsilon H(x)\right], \qquad P(x) = P_0\left[1 + \epsilon F(x)\right], \tag{1.16}$$

gdzie:

S_o, P_o - stałe, $H(x)$, $F(x)$ - znane funkcje, zaś $\epsilon \ll 1$ jest parametrem perturbacyjnym.

Niech warunki graniczne opisują proces sorpcji symetrycznej [12], tzn.:

$$a(x,o) = 0, \qquad a(o,t) = a(l,t) = a_o. \tag{1.17}$$

Ponieważ $H(x)$ i $F(x)$ nie zależą od czasu, możemy rozwiązanie równania (1.11) napisać w formie równania o zmiennych rozdzielonych [12]

$$a(x,t) = a_o + \sum_{n=0}^{\infty} B_n^o \cdot f_n(x) \cdot e^{-\lambda_n t} \tag{1.18}$$

Istotą powyższego zagadnienia jest znalezienie B_n, f_n i λ_n.
Zakładając, że $f_n(x)$ oraz λ_n można rozwinąć w szeregi potęgowe względem ϵ

$$f_n(x) = f_n^o(x) + \epsilon f_n^1(x) + \epsilon^2 f_n^2(x) + \ldots$$
$$\lambda_n = \lambda_n^o + \epsilon \lambda_n^1 + \epsilon^2 \lambda_n^2 + \ldots \tag{1.19}$$

podstawiamy równania (1.16) - (1.19) do równania (1.11), otrzymując układ równań różniczkowych zwyczajnych postaci:

$$O(\epsilon) \begin{cases} \dfrac{\lambda_n^o}{D_o} f_n^o(x) + \dfrac{d^2}{dx^2} f_n^o(x) = 0 \\ f_n^o(o) = f_n^o(1) = 0 \end{cases} \tag{1.20}$$

$$O(\epsilon^2) \begin{cases} \dfrac{d^2}{dx^2} f_n^1(x) + \dfrac{\lambda_n^o}{D_o} f_n^1(x) + \left(\dfrac{\lambda_n^o}{D_o} H(x) + \dfrac{\lambda_n^1}{D_o}\right) f_n^o(x) + \\ + \dfrac{d}{dx}\left[H(x) + F(x)\right] \dfrac{d}{dx} f_n^o(x) + \left[H(x) + F(x)\right] \dfrac{d^2}{dx^2} f_n^o(x) = 0 \\ f_n^1(o) = f_n^1(1) = 0 \end{cases} \tag{1.21}$$

dla $n = 0,1,2,\ldots$

Równanie (1.20) oraz (1.21) wraz z warunkami (1.17) pozwalają wyliczyć kolejne wartości B_n, f_n i λ_n w równaniu (1.18) i tak: z równania (1.20) oraz warunków (1.17) otrzymujemy [2, 11]

$$a(x,t) = a_o - \frac{4a_o}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin \frac{(2n+1)\pi}{l} x \exp\left[-\frac{D_o \pi^2 (2n+1)^2}{l^2} t\right], \tag{1.22}$$

tzn.:

$$B_n^o = -\frac{4a_o}{\pi(2n+1)},$$
$$f_n^o = \sin \frac{(2n+1)\pi}{l} x, \tag{1.23}$$
$$\lambda_n^o = \frac{D_o \pi^2 (2n+1)^2}{l^2}.$$

Rozwinięcie funkcji $f_n^1(x)$ w szereg wg funkcji własnych $f_n^o(x)$ (które tworzą układ zupełny) oraz równanie (1.21), umożliwiają obliczenie wartości λ_n^1, tzn.

$$\lambda_n^1 = 2\lambda_n^o \left\{ \left\langle F(x) \sin^2 \frac{(2n+1)\pi}{l} x \right\rangle_l + \left\langle \left[H(x) + F(x)\right] \cos^2 \frac{(2n+1)\pi}{l} x \right\rangle_l - \left\langle \left[H(x) + F(x)\right] \sin^2 \frac{(2n+1)\pi}{l} x \right\rangle_l \right\}, \tag{1.24}$$

gdzie:

$$\langle \ldots\ldots \rangle_l = \frac{1}{l} \int_o^l (\ldots\ldots)\, dx$$

Równanie (1.21) zapisane w postaci

$$\frac{d^2 f_n^1(x)}{dx^2} + \frac{\lambda_n^o}{D_o} f_n^1(x) = T(x), \tag{1.25}$$

gdzie

$$T(x) = -\left(\left(\frac{\lambda_n^o}{D_o} H(x) + \frac{\lambda_n^1}{D_o}\right) f_n^o(x) + \frac{d}{dx}\left[H(x) + F(x)\right] \frac{d}{dx} f_n^o(x) + \right.$$
$$\left. + \left[H(x) + f(x)\right] \frac{d^2}{dx^2} f_n^o(x)\right),$$

daje metodą "wariacji stałych" rozwiązanie

$$f_n^1(x) = \left[\frac{1}{\pi(2n+1)} \int_0^1 T(x)\cos\frac{(2n+1)\pi}{1}x\,dx \right] \sin\frac{(2n+1)\pi}{1}x$$

$$- \left[\frac{1}{\pi(2n+1)} \int_0^1 T(x)\sin\frac{(2n+1)\pi}{1}x\,dx \right] \cos\frac{(2n+1)\pi}{1}x. \qquad (1.26)$$

Tak więc rozwiązania perturbacyjne równania (1.11) z dokładnością do $O(\varepsilon^2)$ ma postać (1.18), z uwzględnieniem (1.23) oraz (1.24) i (1.26). Procedura określania wielkości λ_n^1 oraz $f_n^1(x)$ stwarza możliwość rekurencji, pozwalającej uzyskiwać kolejne λ_n^i oraz $f_n^i(x)$, czyli rozwiązania dokładniejsze niż $O(\varepsilon^2)$.

Inną szeroką klasą metod o podobnej do zreferowanej powyżej idei - są metody znane pod nazwą WKB(Wentzel, Kramers i Brillouin). Jedna z metod WKB jest podstawą niniejszego opracowania i jako taka jest omówiona szczegółowo w pracy [I].

Metody numeryczne oferują cały szereg możliwości rozwiązania równania (1.11) [14, 15].

Metoda elementu skończonego [16] wydaje się być najsilniejszą z metod numerycznego rozwiązywania równań różniczkowych cząstkowych (RRC) [17]. W przypadku jednak liniowych RRC, prostych geometrii ośrodka dyfuzji i stałych warunków granicznych, metoda różnic skończonych (RS) [18] jest ciągle metodą szeroko stosowaną [2, 19, 20]. Istota metody RS (zwanej też metodą siatek [21]), w przypadku jednowymiarowego równania dyfuzji, polega, na zbudowaniu dwuwymiarowej siatki (x,t), w węzłach której należy obliczyć wartości aktywności (stężeń), aproksymując ich pochodne cząstkowe przez odpowiednie różnice skończone. Procedura ta zamienia problem rozwiązania RRC na problem rozwiązania układu liniowych równań algebraicznych. Metoda ta, mimo że prosta w swej naturze, jak większość metod przybliżonych, nastręcza czasami znaczne kłopoty w zastosowaniu. Głównym problemem bywa stwierdzenie, czy otrzymane w węzłach siatki wartości numeryczne a_{ij} (ih, jk) są wystarczająco dobrym przybliżeniem wartości dokładnych. Z praktycznego punktu widzenia, bardzo ważną cechą metody jest szybkość zbieżności otrzymanych rezultatów do rozwiązania dokładnego przy zagęszczaniu siatki. Zbyt wolna zbieżność bowiem, może przekreślić użyteczność tej metody ze względu na: znaczny czas obliczeń komputerowych, wymaganą pamięć a wreszcie błędy zaokrągleń.

Szczegóły rozwiązań zastosowanych w tej pracy przedstawiono w poz. [IV] i [V].

2. SPIS OPUBLIKOWANYCH PRAC AUTORA WCHODZĄCYCH W ZAKRES NINIEJSZEJ ROZPRAWY

[I] An application of WKB approximation to transient diffusion in inhomogeneous membranes. Part 1 General solutions by Zbigniew J. Grzywna and Harry L. Frisch Polish Journal of Chemistry 1-3, 1984.

[II] An application of WKB approximation to transient diffusion in inhomogeneous membranes. Part 2 Sorption by Zbigniew J. Grzywna and Harry L. Frisch Polish Journal of Chemistry 1-3, 1984.

[III] An application of WKB approximation to transient diffusion in inhomogeneous membranes. Part 3 Permeation by Zbigniew J. Grzywna and Harry L. Frisch Polisch Jornal of Chemistry 1-3, 1984.

[IV] Transient Diffusion Kinetics in Media Exibiting Axial Variation of Diffusion Properties. Part 1 Sorption Kinetics by Zbigniew J. Grzywna and John H. Petropoulos J.C.S. Faraday Trans 2 (Journal of Chemical Physics) 79, 571-584, 1983.

[V] Transient Diffusion Kinetics in Media Exibiting Axial Variations of Diffusion Properties. Part 2 Permeation Kinetics by Zbigniew J. Grzywna and John H. Petropoulos J.C.S. Faraday Trans. 2 (Journal of Chemical Physics) 79, 585-597, 1983.

Uwaga: Odwołania do powyższych prac mają miejsce w tekście poprzez liczby rzymskie w nawiasach kwadratowych w odróżnieniu od pozostałej literatury oznaczonej liczbami arabskimi w takich samych nawiasach.

3. OMÓWIENIE STANU BADAŃ DYFUZJI GAZÓW I PAR W MHR NA PODSTAWIE OPUBLIKOWANEGO WCZEŚNIEJ MATERIAŁU

3.1. Metoda WKB jako matematyczna podstawa uzyskanych wyników [I]

Konkretne sytuacje fizyczne narzucają zwykle zarówno formę jak i sposób rozwiązania opisujących je równań różniczkowych. Niewłaściwe dobranie formy rozwiązania prowadzi najczęściej do nieefektywnych numerycznie i skomplikowanych obliczeń. W przypadku zagadnień granicznych, opartych na równaniu (1.11), istota powyższego problemu sprowadza się do właściwego dobrania formy rozwiązania odpowiednio w obszarze krótkich i długich czasów. Rozwiązania te, z reguły w postaci szeregów nieskończonych, uznaje się za właściwie dobrane, jeżeli wykazują dostatecznie szybką zbieżność w odpowiednich dla siebie obszarach zastosowań.

Ilustrację powyższego niech będzie rozwiązanie problemu symetrycznej sorpcji fickowskiej idealnej, dane odpowiednio w obszarze krótkich i długich czasów, relacjami [2]:

$$c = c_0 \left\{ \sum_{n=0}^{\infty} (-1)^n \operatorname{erfc} \frac{(2n+1)l-x}{2\sqrt{Dt}} + \sum_{n=0}^{\infty} (-1)^n \operatorname{erfc} \frac{(2n+1)l+x}{2\sqrt{Dt}} \right\} \tag{3.1}$$

$$c = c_0 \left\{ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cos \frac{(2n+1)\pi x}{l} \exp\left[- \frac{D(2n+1)^2 \pi^2 t}{l^2} \right] \right\}. \tag{3.2}$$

Próby zastosowania powyższych równań "na odwrót", tzn. równ. 3.1 w obszarze długich czasów, a równ. 3.2 w obszarze krótkich czasów, powodują konieczność sumowania znacznej liczby (od kilkudziesięciu wzwyż) wyrazów odpowiednich szeregów, podczas gdy stosowane właściwie dają rozwiązania bardzo szybkozbieżne (jeden, najwyżej dwa wyrazy).

Zupełnie podobnie przedstawia się problem z zastosowaniem metody WKB do równania (1.11). Właściwie dobrane wersje, z wielu możliwych do zastosowania, pozwaliła na względnie zwarte przedstawienie rozwiązań w obu obszarach.

W pracy zastosowano oryginalną (tj. rozszerzoną na obszar długich czasów) wersję opisanej przez Kamkego metody WKB [I]. Wyżej wymieniona metoda spełnia dwa praktycznie ważne warunki:

- daje prostą możliwość rekurencji,
- pozwala uzyskać rozwiązania bez konieczności postulowania jawnych postaci funkcji występujących w równaniu (1.11).

Jedynym, nietrudnym do spełnienia założeniem, w przypadku zastosowania metody WKB, jest warunek, by występujące w równaniu (1.11) funkcje (współczynniki równania) były "wolno zmienne" [I]. Sens tego założenia zostanie wyjaśniony w rozdziale 5.

3.2. Problem pierwotny dyfuzji w MHR [II, III]

Według Frischa [22] problem pierwotny dyfuzji powstaje wtedy, gdy znamy postacie funkcji S(x) i P(x) (a więc i $D_T(x)$) i pytamy o rozwiązania równania (1.11), spełniające odpowiednie warunki graniczne.
Można to zilustrować schematycznie w formie:

$$\begin{matrix} [\text{znane}] & & [\text{poszukiwane}] \\ S(x),\ P(x) & \Longrightarrow & \left\{ \begin{matrix} c \\ J \\ M \\ Q \\ L \\ \cdot \\ \cdot \\ \cdot \end{matrix} \right\} \end{matrix} \tag{3.3}$$

Konkludując zauważmy, że sformułowanie Frischa jest dość precyzyjne, wystarczy bowiem znać c(x,t), by wyliczyć wszystkie pozostałe wielkości schematu (3.3).

3.3. Problem odwrotny dyfuzji w MHR [IV, V]

Najkrótsze przedstawienie istoty problemu odwrotnego dyfuzji w membranach polegałoby na zmianie zwrotu strzałki ze schematu (3.3), tzn.:

$$\begin{matrix} [\text{znane}] & & [\text{poszukiwane}] \\ \left\{ \begin{matrix} c \\ J \\ M \\ Q \\ L \\ \cdot \\ \cdot \\ \cdot \end{matrix} \right\} & \Longrightarrow & S(x),\ P(x) \end{matrix} \tag{3.4}$$

Schemat (3.4) mówi zatem o sytuacji, kiedy wiemy, że równania (1.11) opisuje dany układ dyfuzyjny oraz zmierzyliśmy doświadczalnie takie wielkości, jak; rozkład stężenia lub opóźnienie czasowe czy masę czynnika penetrującego, pochłoniętego przez membranę w danym czasie i pytamy się, jakie informacje o współczynnikach równania (1.11) można przez to uzyskać?

Pytanie to jest bardzo ważne i aktualne w badaniach dyfuzyjnych, jako że mówi o strukturze ośrodka dyfuzji w układach, w których już nieznaczne zmiany tej struktury wpływają w istotny sposób na większość własności sorpcyjno-dyfuzyjnych.

4. METODY I SYSTEMY BADANIA DYFUZYJNEGO TRANSPORTU MASY W MEMBRANACH

Odpowiedź na pytanie - co to jest metoda badania dyfuzji - ma podstawowe znaczenie w tej pracy. Bez zagłębienia się w zawiłości, analizowane raczej przez metodologię nauk, można by tę odpowiedź sformułować następująco: jest to każdy opis analityczny, wynikający z rozwiązania danego zagadnienia brzegowego, wiążący mierzone wielkości układu dyfuzyjnego [23, 24]. Uściślając nieco powyższe zdanie, należy dodać, że nie uwzględnia się opisów identycznych, mimo że wynikają z różnych zagadnień granicznych (np. obszar krótkich czasów sorpcji niesymetrycznej i przenikania). Jest sprawą oczywistą, że w przypadku procesu fickowskiego idealnego (D = = const) wartości współczynników dyfuzji, otrzymane którąkolwiek z wielu powyższych metod, są identyczne. W przypadku jednak każdego innego procesu, otrzymane wartości są różne i to właśnie wykorzystano do zbudowania efektywnego systemu analizy układów dyfuzyjnych [IV, V].

Sprawą o podstawowym znaczeniu przy tworzeniu takiego systemu jest wybór punktu odniesienia, z którym porównujemy otrzymane różnymi metodami wartości pewnych wielkości fizycznych. W systemach, opóźnień czasowych [2, 25] oraz referowanym w tej pracy wybrano, jako punkt odniesienia stan stacjonarny przenikania masy przez membranę. Stan stacjonarny oferuje bowiem wszystko, czego oczekuje się od punktu odniesienia: jest łatwy do zrealizowania, powtarzalny i stały (patrz 4.2). Definiuje się go zwykle relacją [2]

$$J_s = \frac{D_e \cdot c_o}{l} = \frac{D_e \cdot S_p \cdot p_o}{l}, \qquad (4.1)$$

gdzie J_s jest stacjonarnym strumieniem dyfuzyjnym.

4.1. System opóźnień czasowych

Przedstawimy tu tylko główną ideę systemu, odsyłając zainteresowanego czytelnika po szczegóły do prac źródłowych [23, 25]. Ograniczymy się do eksperymentu przenikania reprezentowanego przez krzywą $Q^s(l,t)$ z rys. 1 [III].

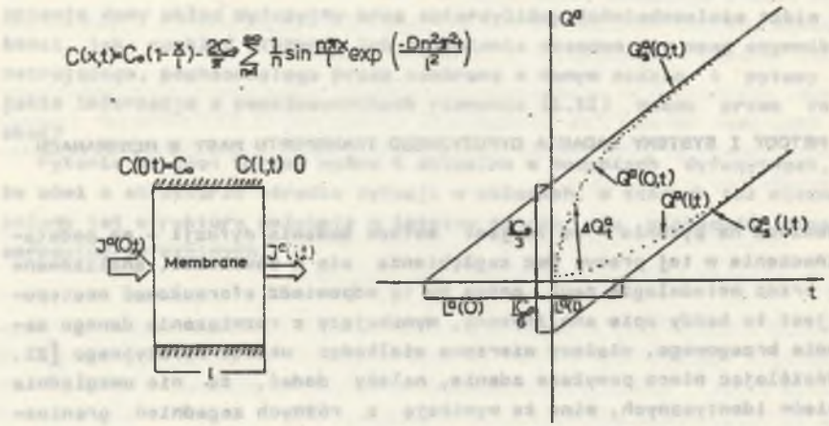

Fig. 1

W przypadku procesu fickowskiego idealnego, opóźnienie czasowe $L^a(l)$ dane jest relacją [26]:

$$L^a(l) = \frac{l^2}{6D} \tag{4.2}$$

Jeżeli teraz obliczymy D_a z równania (4.1) (co wyznacza się z eksperymentu sorpcji równowagowej) i wstawimy do równania (4.2)

$$L_a^a = \frac{l^2}{6D_a} \tag{4.3}$$

to tak wyznaczone opóźnienie czasowe $L_a^a(l)$ jest różne od danego relacją (4.2) o pewną wartość, którą nazwiemy $L_E^a(l)$, tzn.

$$L^a(l) = L_a^a(l) + L_E^a(l). \tag{4.4}$$

Wielkość $L_E^a(l)$ może być nazwana "niefickowską nadwyżką" opóźnienia czasowego.

W podobny sposób otrzymuje się "niefickowskie nadwyżki" pozostałych opóźnień czasowych i ich kombinacji algebraicznych [25]. Różne własności "niefickowskich nadwyżek" opóźnień czasowych związane z różnymi typami procesów niefickowskich pozwalają na identyfikację tych procesów i pewną ich charakterystykę [25].

Tabela 1

Lp.	Formuła analityczna metody	Uwagi
1	$\frac{Q_t^a}{Q_\infty} = 2\sqrt{\frac{D_1}{\pi l^2}}\, t^{1/2}$	Krótkie czasy. Sorpcja niesymetryczna
2	$\frac{M_t^a}{M_\infty} = 4\sqrt{\frac{D_{1M}}{\pi l^2}}\, t^{1/2}$	Krótkie czasy. Sorpcja symetryczna
3	$\left[\ln 1 - \frac{Q_t^a}{Q_\infty}\right] = \ln\frac{8}{\pi^2} - \frac{D_2\pi^2}{4l^2}\, t$	Długie czasy. Sorpcja niesymetryczna
4	$\ln\left[1 - \frac{M_t^a}{M_\infty}\right] = \ln\frac{8}{\pi^2} - \frac{D_{2M}\pi^2}{l^2}\, t$	Długie czasy. Sorpcja symetryczna
5	$\ln\left[t^{1/2} \cdot J^a(l,t)\right] = \ln\left[2C_0\left(\frac{D_4}{\pi}\right)^{1/2}\right] - \frac{l^2}{4D_3 t}$	Przenikanie. Krótkie czasy
6	$\ln\left[Q^a(l,t) - Q_a^a(l,t)\right] = \ln\frac{2lC_0}{\pi^2} - \frac{D_5\pi^2}{l^2}\, t$	Przenikanie. Długie czasy
7	$\frac{\Delta Q_t^a}{\Delta Q_a^a} = 4\sqrt{\frac{D_6}{\pi l^2}}\, t^{1/2}$	Sorpcja w przepływie. Krótkie czasy
8	$\ln\left[Q_a^a(0,t) - Q^a(0,t)\right] = \ln\frac{2lC_0}{\pi^2} - \frac{D_7\pi^2}{l^2}\, t$	Przenikanie. Długie czasy
9	$\ln\left[1 - \frac{\Delta Q_t^a}{\Delta Q_a^a}\right] = \ln\frac{8}{\pi^2} - \frac{D_8\pi^2}{l^2}\, t$	Sorpcja w przepływie. Długie czasy

gdzie:

Q_t^a, M_t^a - masa penetranta w folii na jednostkę powierzchni po czasie t w procesie sorpcji,

$M_\infty = Q_\infty = C_0 \cdot l$,

$J^a(l,t)$ - dyfuzyjny strumień masy w punkcie $x = l$,

$Q^a(l,t)$ - masa penetranta na jednostkę powierzchni wypływająca z membrany po czasie t,

$Q^a(0,t)$ - masa penetranta na jednostkę powierzchni, wnikająca do membrany po czasie t,

$\Delta Q_t^a = Q^a(0,t) - Q^a(l,t)$.

Indeksy: a - stacjonarny, ∞ - równowagowy.

4.2. System metod niestacjonarnych [II, III, IV, V]

W skład systemu wchodzi osiem metod badania dyfuzji D1 - D8 [II, III], co przedstawia tabela 1. Istota analizy danego układu dyfuzyjnego, w ramach omawianego systemu, polega na porównaniu wartości D_i obliczonych ze współczynników kierunkowych oraz przesunięć I_i, otrzymanych ww. metodami z wartościami "idealnymi" tych parametrów. Wartości "idealne" uzyskuje się odpowiednio z relacji (17-20) [II] oraz (1-5) [III] przez wstawienie w miejsce D_i wartości D_e, tj. wartości współczynnika dyfuzji obliczonego ze wzoru (4.1) na podstawie eksperymentu. Wielkość D_e posiada status zupełnie wyjątkowy w zbiorze D_i, co podkreślone jest przymiotnikiem "eksperymentalny", mimo że pozostałe wartości D_i też przecież oznacza się eksperymentalnie. Wartość D_e jest stała i średnia, w różnym jednak sensie, zależnie od typu procesu dyfuzji, tzn.:

(1) w procesie dyfuzji, w którym $D = D(c)$

$$D_e = \frac{1}{C_o}\int_0^{C_o} D(c)dc \qquad (4.5)$$

(2) w procesie dyfuzji, w którym $D = D(x)$

$$D_e = l\left[\frac{2}{S}\int_0^1 dx/P(x)\right]^{-1} \qquad (4.6)$$

(3) w procesie dyfuzji, w którym $D = D(t)$

$$D_e = \lim_{t\to\infty} D(t) = D(\infty) \qquad (4.7)$$

5. UWAGI KOŃCOWE

Obiektem rozważań w pracy były membrany heterogeniczne regularne, tj. membrany homogeniczne w mikro- a heterogeniczne w makroskali, o regularnym ciągłym rozkładzie heterogeniczności (sytuacja dokładnie odwrotna tj. heterogeniczność w mikro- a homogeniczność w makroskali mają miejsce w przypadku typowych membran heterogenicznych [10]). Wydaje się, że pierwszy problem postawiony w tej pracy, tj. stworzenie podstaw teoretycznych systemu metod niestacjonarnych badania dyfuzji w ww. membranach, został w pełni rozwiązany. Konieczność stworzenia takiego systemu, współdziałającego z systemem opóźnień czasowych, była już sygnalizowana od pewnego czasu [25, 27]. Na uwagę zasługuje fakt dokonania istotnych korekt we właściwym matematycznym traktowaniu rozwiązywanych zagadnień i to zarówno w przypadku metody WKB [I], jak i regularnej perturbacji równania (1.21) - - (1.26).

Porównanie przydatności metod WKB oraz regularnej perturbacji wypada, w tym przypadku, zdecydowanie na korzyść tej pierwszej. Ograniczenie stosowania metody WKB warunkiem "wolnej zmienności" występujących w równaniu (1.11) funkcji jest podyktowane koniecznością spełnienia relacji typu [I]

$$\left|\frac{P''(x)}{2\,P(x)} - \frac{P'(x)^2}{4\,P(x)^2}\right| \ll \frac{\beta}{D(x)}. \qquad (4.8)$$

Nie powoduje to zbyt dużych problemów nawet w przypadkach, gdy stosunek wartości maksymalnej do minimalnej funkcji $P(x)$ w przedziale zmienności wynosi kilkanaście i więcej. (Należy zauważyć, że warunek "wolnej zmienności" funkcji jest zgodny z fizykalnym modelem MHR).

Natomiast w przypadku metody regularnej perturbacji warunek $\epsilon \ll 1$ poważnie ogranicza praktyczną użyteczność rozwiązań. Zgodnie z celem pracy stwierdzono liniowość w opisach analitycznych obszaru długich czasów i brak takiej liniowości dla rozwiązań używanych w obszarze krótkich czasów. Fakt braku liniowości w opisach analitycznych eliminuje je co prawda z grupy metod D1 - D8 [II, III], niemniej jednak można ten fakt wykorzystać w inny sposób w ramach omawianego systemu, a mianowicie do identyfikacji charakteru procesu (patrz końcowe fragmenty tego rozdziału).

Problem korzyści płynących z rozwiązania zagadnienia pierwotnego jest oczywisty (choćby z punktu widzenia kosztów badań teoretycznych w porównaniu z kosztami eksperymentów) pod warunkiem, że dysponuje się analitycznym przedstawieniem struktury dyfuzyjnej membrany. Określenie takiej

struktury jest możliwe, czego przykładem są udane próby wykonane z membranami porowatymi [25, 28]. Trzeci i ostatni problem podjęty w tej pracy, to próba rozwiązania problemu odwrotnego transportu masy w membranach heterogenicznych regularnych [IV, V]. Polega ona na możliwie najdokładniejszym określaniu postaci funkcji H(y). H(y) jest funkcją złożoną, której analiza pozwala na wnioskowania o zachowaniu się funkcji S(x) i $D_T(x)$ a przez to i o strukturze dyfuzyjnej membrany [25]. Przedstawiona praca, oprócz analizy teoretycznej dyfuzyjnego transportu masy w membranach heterogenicznych regularnych, formułuje także system niestacjonarnych metod badania układów dyfuzyjnych i wskazuje na jego wielorakę przydatność.

Dyfuzyjny transport masy w membranach można fenomenologicznie podzielić na procesy zależne od stężenia, położenia i czasu, co schematycznie da się przedstawić w postaci:

D(c,x,t)

D(c,x) D(x,t) D(c,t)

Do D(c) D(x) D(t)

Możliwość identyfikacji danego procesu, a następnie jego systematyczne badanie, to problemy o fundamentalnym znaczeniu praktycznym. System D1-D8 zapewnia obie te możliwości [29].

LITERATURA

[1] Crank J., Park G.S.: Diffusion in Polymers. Academic Press, 1963, ss. 1, 5, 6, 170.

[2] Crank J.: The Mathematics of Diffusion. Clarendon Press, Oxford 1975 sc. ed., ss. 2, 18, 45-46, 47-48, 203-209.

[3] Nikolajev N.I.: Difuzja w Membranach. Moskwa, Chimia, 1980, ss. 44-45, 129.

[4] Baranowski B.: Nierównowagowa Termodynamika w Chemii Fizycznej. PWN, Warszawa 1974, ss. 101-102, 105, 121.

[5] Przestalski St.: Błony Komórkowe. Encyklopedia Fizyki Współczesnej. Praca zbiorowa, PWN, Warszawa 1983, s. 721.

[6] Erdey-Gruz T.: Transport Phenomena in Agueos Solutions. Akademia Kiado, Budapest 1974, ss. 145-146.

[7] Williams W.E.: Partial Differential Equations. Clarendon Press, Oxford 1980, ss. 318-342.

[8] Hartnett J.P., Irvinc Jr. I.F.: Advances in Heat Transfer. Academic Press, 1972, ss. 3-19.

[9] Potter D.: Metody obliczeniowe Fizyki. PWN, Warszawa 1977, ss. 57-59, 77-79.

[10] Barrer R.M.: poz. 1, rozdział 6, ss. 197-200.

[11] Jost W.: Diffusion in Solids. Liquids and Gases Academic Press, 1960 ss. 36-37, 42-44.

[12] Frisch H.L., Bdzil J.B.: J. Chem. Phys., 62, 12, 4804 (1975).

[13] Tsang T.: IEC, 52, 8, 707 (1960).

[14] Marczuk G.I.: Analiza Numeryczna Zagadnień Fizyki Matematycznej. PWN Warszawa 1983, ss. 56-125, 415-419.

[15] Demidowicz B.P., Maron I.A., Szuwałowa E.J.: Metody Numeryczne. Cz. II. PWN, Warszawa 1965, ss. 250-264, 303-306.

[16] Strang G., Fix G.: An Analysis of the Finite Element Method. Prentice-Hall, New York 1973, ss. 5-11, 171-178.

[17] Jain R., Schultz J.S.: J. Membrane Sci. 11, 79 (1982).

[18] Smith G.D.: Numerical Solutions of Partial Differential Equations. Finite Difference Method. Clarendon Press, Oxford 1978, sec. ed. ss. 11-55.

[19] Petropoulos J.H.: J. Polymer Sci. Phys. Ed. 12, 35 (1974).

[20] Grzywna Z.J., Petropoulos J.H.: IUPAC Conference, Athens 1982.

[21] Michlin S.G., Smolicki C.L.: Metody Przybliżone Rozwiązywania Równań Różniczkowych i Całkowych. PWN, Warszawa 1970, ss. 63-183.

[22] Frisch H.L.: J. Membrane Sci., 3, 149 (1978).

[23] Grzywna Z.J., Podkówka J.: Bull. Acad. Polon. Sci, 10, 811 (1976).

[24] Grzywna Z.J.: Praca Doktorska. Politechnika Śląska, 1978 (nie publikowana).

[25] Teimillis K., Petropoulos J.H.: J. Phys. Chem. 81, 2185 (1977).

[26] Frisch H.L.: J. Phys. Chem. 61, 93 (1957).

[27] Amarantos S.G., Tsimillis K., Sawakis C., Petropoulos J.H.: J. Membrane Sci. 13, 259 (1983).

[28] Petropoulos J.H., Roussis P.P.: J. Chem. Phys. 48, 4619 (1968).

[29] Grzywna Z.J.: VI Ogólnopolskie Seminarium. Membrany Syntetyczne i Polimery Reaktywne. Toruń 1983, Materiały Seminarium, C2.

DYFUZYJNY TRANSPORT MASY W MEMBRANACH HETEROGENICZNYCH REGULARNYCH

S t r e s z c z e n i e

Praca dotyczy dyfuzyjnego transportu masy w membranach heterogenicznych regularnych, tj. w ośrodkach dyfuzji, których własności zmieniają się w sposób ciągły (regularnie).

W pierwszej części pracy wprowadzono niezbędne pojęcia i równania, dające sposobność właściwego spojrzenia na rozpatrywany proces. Przedstawiono również najczęściej stosowane metody matematyczne, ze szczególnym uwzględnieniem metody regularnej perturbacji, z uwagi na wprowadzenie korekt w stosunku do jej wcześniejszych zastosowań.

Część druga natomiast jest próbą zwartego przedstawienia zasadniczych osiągnięć autora w opracowaniu pełnego opisu matematycznego badanych zjawisk, jak również w stworzeniu podstaw teoretycznych ich eksperymentalnego badania.

Kolejno zatem przedstawiono:

- walory zastosowanej metody WKB, gdzie na szczególne podkreślenie zasługuje fakt istotnych korekt i uogólnień wniesionych do wcześniejszych prób jej zastosowania przez różnych autorów,
- istotę problemu pierwotnego i odwrotnego dyfuzji w membranach. Pierwszy jest okazją do zastanowienia się nad wzajemną relacją kosztów i możliwością badań teoretycznych i doświadczalnych. Drugi, daje możliwość określenia struktury dyfuzyjnej ośrodka dyfuzji,
- system metod niestacjonarnych eksperymentalnego badania dyfuzji na tle systemu opóźnień czasowych, z możliwościami wykorzystania go do badania wszelkich procesów dyfuzyjnego transportu masy w membranach.

ДИФФУЗНЫЙ ТРАНСПОРТ МАССЫ В ГЕТЕРОГЕНИЧЕСКИХ РЕГУЛЯРНЫХ МЕМБРАНАХ

Р е з ю м е

Работа касается диффузного транспорта массы в гетерогенных регулярных мембранах, т.е. в среде диффузии, особенности которой изменяются непрерывно (регулярно).

В 1 части работы приведены необходимые понятия и управления употребляемые в дальнейшем. Даны также часто используемые математические методы, с особенным учётом метода регулярной пертурбации, в виду внесённых поправок по её практическому применению.

Во 2 части сделана попытка конденсированного представления достижений автора в разработке полного математического описания исследуемых явлений, а также в разработке теоретических основ их экспериментального исследования.

И так представлены:

- примечательности применённого метода ВКБ, где особенно внимание обращает факт существенных коррект и обобщений внесённых автором в ранее имеющиеся испытания с применением этого метода разными авторами,
- суть первичной и обратной проблем диффузии в мембранах. Первая проблема - это подходящий случай, для того, чтобы обдумать взаимную зависимость между стоимостью и возможностью теоретических и экспериментальных исследований. Вторая проблема даёт возможность диффузной структуры диффузной среды,
- система нестационарных методов экспериментального исследования диффузии на фоне систем временного запаздывания, с возможностью использования её для исследования всевозможных диффузных процессов транспорта масом в мембранах.

A DIFFUSIVE MASS TRANSPORT IN REGULAR HETEROGENOUS MEMBRANES

S u m m a r y

The present paper concerns the diffusive mass transport in regular heterogenous membranes i.e. in media exibiting a continuous gradation in diffusion properties along the diffusion axis. In the introductory part of the paper all main ideas and equations are introduced as well as most of the mathematical methods with special attention to regular perturbation (where some corrections with respect to the previvus treatments are made) are presented.

The second part, is a fairly compact presentation of both: a full mathematical description of aforementioned systems, and such of the theoretical background necessary for the practical use of transient - state analysis.

There are presented in turn:

- advantages of the WKB method used, where the special attention is called to the fact of a serious corrections and generalizations made comparing with the earlier published work,
- the merit of "direct" and "inverse" problems in diffusion through membranes. First of them, is an occasion to think over the interrelations between costs and possibilities of theoretical and experimental investigations. Second, offers possibilities of determination the diffusional structure of the membrane,
- the transient state analysis system of experimental approach to diffusion in regular heterogenous membrane on the background of time lags system, with possibilities of using it to all kinds of processes.

AN APPLICATION OF WKB APPROXIMATION TO TRANSIENT DIFFUSION IN INHOMOGENEOUS MEMBRANES

Part I. GENERAL SOLUTIONS

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Stosując metodę WKB znaleźliśmy ogólne rozwiązania równania dyfuzji "kierunkowej" (do trzeciego przybliżenia włącznie) odpowiednio w obszarze krótkich i długich czasów. Przeprowadziliśmy analizę porównawczą z poprzednio uzyskanymi rezultatami, zapewniając równocześnie krótki przegląd metod WKB w przypadku nieobecności punktów osobliwych danego równania różniczkowego. Poprawiliśmy błędy poprzednich opracowań.

We have found the general solutions of the "directional" diffusion equation (up to the third approximation) valid for early and late times, respectively, by the WKB method. These solutions are discussed and compared with those previously given. A short review of the WKB methods is also provided in case of the absence of transition points of the O.D.E. as well as the errors inherent in previous treatments are corrected.

A mathematical description of transient unidimensional diffusion in inhomogeneous membranes [1, 2] is a problem of considerable interest for many reasons. It is enough to say that "practically" there are no homogeneous membranes and the transient state provides most of the necessary information for quantitative description of the diffusional system.

The partial differential equation (P.D.E) which governs this "directional" [3] mass transport process has a form [1, 3]

$$s(x)\,\frac{\partial u}{\partial t} = \frac{\partial}{\partial x}\left[P(x)\,\frac{\partial u}{\partial x}\right] \tag{1}$$

where t is the time; $P(x) = D_T(x)S(x)$ is the ("thermodynamic") permeability coefficient and $a(x,t)$ is the activity of the penetrant in the solid. The later is defined as equal to the penetrant activity in the external phase at equilibrium and is related to the concentration of penetrant in the solid by $c = S \cdot a$ (c.f. Ref. 1).

To solve the initial boundary value problems based on eq. (1) in general i.e. without the explicitly given functional forms on $P(x)$ and $S(x)$ we have applied the WKB method (independently derived by Wentzel, Kramers and Brillouin, hence the name) putting the previous eq. (1) into the Sturm-Liouville (SL) form [4]. It is necessary to notice that three different methods under the same name WKB (method) Approximation are reported in literature.

The first method, referred to by Pearson [5] as Liouville-Green (or WKB) Approximation, consists in the transformation of the SL equation as follows:

$$\frac{d^2y}{dx^2} - f(x)y = 0 \tag{2}$$

into the linear O.D.E. of the second order with constant coefficients in three steps:

(i) On transforming to ξ (any thrice-differentiable function) as independent variable and setting

$$w = \left(\frac{d\xi}{dx}\right)^{1/2} y \tag{3}$$

we find that eq. (2) becomes

$$\frac{d^2w}{d\xi^2} = \left[\dot{x}^2 f(x) - \frac{1}{2}\{x,\xi\}\right]w \tag{4}$$

Here, the dot signifies differentiation with respect to ξ and $\{x,\xi\}$ is the Schwarzian derivative.
The foregoing change of the variable is called the Liouville transformation.

(ii) If we now prescribe

$$\xi = \int f^{1/2}(x)dx \tag{5}$$

then $\dot{x}^2 f(x) = 1$

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[x] Some authors use the name JWKB [6] or WKBJ [7] or AA method [11].

(iii) Neglect of the Schwarzian derivative enables eq. (4) to be solved exactly and this leads to the following general solution of eq. (2).

$$y = A\, f^{-1/4}(x)\exp\left[\int f^{1/2}(x)dx\right] + B\, f^{-1/4}(x)\exp\left[-\int f^{1/2}(x)dx\right] \tag{6}$$

where A and B are arbitrary constants.

The second WKB method is presented by Mathews and Walker [8]. They recalled the O.D.E. of the form

$$\frac{d^2y}{dx^2} + f(x)y = 0 \tag{7}$$

and stated that the WKB method provides an approximate solution to it, provided $f(x)$ satisfies certain restrictions, which may be summarized in the phrase "$f(x)$ is slowly varying".

The solution of eq. (7) is guessed to have a form

$$y = \exp\left[i\,\Phi(x)\right] \tag{8}$$

where $i = \sqrt{-1}$.

Substituting eq. (8) into eq. (6) we get

$$-\left[\Phi'(x)\right]^2 + i\Phi''(x) + f(x) = 0 \tag{9}$$

where the differentiation with respect to x is indicated by dashes.

If we assume $|\Phi''(x)| \ll |f(x)|$, then a first approximation is

$$\Phi'(x) = \pm f^{1/2}(x);\ \Phi(x) = \pm\int f^{1/2}(x)dx \tag{10}$$

A second approximation can be found by iteration from eq. (10)

$$\Phi''(x) \cong \pm\frac{1}{2} f(x)^{-1/2}\, f(x) \tag{11}$$

Substituting this estimate into eq. (9), we finally get

$$\Phi(x) \cong \pm\int f^{1/2}(x)dx + \frac{1}{4}\ln f(x) \tag{12}$$

The two choices of sign give two (approximate) solutions which may be combined to give the general solution

$$y(x) \cong f^{-1/4}(x)\left\{A\exp\left[i\int f^{1/2}(x)dx\right] + B\exp\left[-i\int f^{1/2}(x)dx\right]\right\} \tag{13}$$

It is evident that this approach gives eq. (6) when use it to eq. (2).

Before proceeding to the third version of the WKB method, let us notice that we can put eq. (1) into a form of the SL equation with a parameter

$$\frac{d^2y}{dx^2} = \left\{\rho^2 f(x) + g(x)\right\} y \tag{14}$$

Eq. (14) is an object of the third version of the WKB Approximation given by Kemke [9].

The Kemke's approach consists in the transformation of eq. (14) into the associated Riccati equation by substitution

$$y = \exp\left[\rho \int U(x)\,dx\right] \tag{15}$$

After differentiating twice eq. (15) and substituting it into eq. (14), we get

$$\rho U'(x) + \rho^2\, U(x)^2 - \rho^2\, f(x) - g(x) = 0 \tag{16}$$

i.e. Riccati equation associated with eq. (14).

The solution of eq. (16) is postulated to have a form of asymptotic expansion (note that the use of asymptotic behaviour is made with respect to parameter ρ).

$$U(x) = \sum_{n=0}^{\infty} U_n(x)\rho^{-n} \tag{17}$$

Substituting eq. (17) and its derivative into eq. (16), we can get an explicit form of the subsequent forms of eq. (17), i.e.

$$U_o = \pm\sqrt{f(x)}$$

$$U_1 = -\frac{f'(x)}{4\,f(x)}$$

$$U_2 = \pm\frac{1}{2}\, f(x)^{-1/2}\left[g(x) + \frac{f''(x)}{4\,f(x)} - \frac{5}{16}\frac{f'(x)^2}{f(x)^2}\right] \tag{18}$$

$$U_3 = \frac{1}{4}\frac{g(x)f'(x)}{f(x)^2} - \frac{1}{4}\frac{g'(x)}{f(x)} + \frac{9}{32}\frac{f'(x)f''(x)}{f(x)^3} - \frac{15}{64}\frac{f'(x)^3}{f(x)^4} - \frac{1}{16}\frac{f'''(x)}{f(x)^2}$$

$$\vdots$$

$$U_{n+1} = -\frac{1}{2U_o}\left(U_n' + \sum_{p=1}^{n} U_p U_{n+1-p}\right); \quad n \geq 2$$

Substituting eq. (17) via (18) into eq. (15) we get two linearly independent solutions (for plus and minus, respectively) which constitute the general solution of eq. (14). The sense of the WKB method referred to by Pearson remains the same in case of eq. (14), although the LG Approximation (eq. 6) stands here only for the first term in the asymptotic expansion. We have used the WKB asymptotics referred to by Kemke throught this paper for its simplicity and easily detectable connection with perturbation theory.

An early-time approximation

Comparing eq. (1) and (14), it is evident that a series of transformation is necessary to put eq. (1) into a form required by the WKB procedure.

First of all, the P.D.E ought to be transformed into the O.D.E of the same order. Following Ref. 10, we have applied the Laplace transformation to eq. (1), getting

$$S(x)\beta\bar{a}(x) = \frac{d}{dx}\left[P(x)\,\frac{d\bar{a}}{dx}\right] \tag{19}$$

where β is a parameter whose real part is positive and large enough to make the Laplace transformation convergent and a bar over the letter indicates the entity which is transformed. Let us notice that eq. (19) is the SL equation in which $S(x)$ stands for "weighting function" (always positive or zero) and $\bar{a}(x)$ are the eigenfunctions joined with the corresponding eigenvalues β .

Comparing eq. (19) with eq. (14), we can see that the next step to follow is some transformation by which the first derivative in eq. (19) will disappear effectively. There are a few possibilities, however, the most convenient here is

$$\bar{a} = w\, P(x)^{-1/2} \tag{20}$$

After differentiating twice eq. (20) and substituting it into eq. (19), we get finally [10]

$$w''(x) - w(x)\left[\frac{\beta}{D(x)} + G(x)\right] = 0 \tag{21}$$

that is the form of O.D.E. desired by the third version of the WKB method where

$$G(x) = \frac{P''(x)}{2P(x)} - \frac{P'(x)^2}{4P(x)^2} \tag{22}$$

The general solution of eq. (21) can be obtained from eq. (15) via (17) and (18) by setting

$$\rho^2 \equiv \beta$$

$$f(x) \equiv D(x)^{-1} \tag{23}$$

$$g(x) \equiv G(x)$$

$$y(x) \equiv w(x)$$

Namely,

$$w(x,\beta) = D(x)^{1/4}\left\{A \exp\left[\sqrt{\beta}\Phi_0(x) - \frac{1}{\sqrt{\beta}}\Phi_2(x) - \frac{1}{\beta}\Phi_3(x) + O(\beta^{-3/2})\right] + B \exp\left[-\sqrt{\beta}\Phi_0(x) + \frac{1}{\sqrt{\beta}}\Phi_2(x) - \frac{1}{\beta}\Phi_3(x) + O(\beta^{-3/2})\right]\right\} \tag{24}$$

where A and B are arbitrary constans, term $\Phi_1(x) = \frac{1}{4}\int_0^x \left[\ln D(y)\right]' dy$ has been replaced before paranthesis as a common factor equal to $D(x)^{1/4}$ for both linearly independent solutions, and

$$\Phi_0(x) = \int_0^x dy/D(y)^{1/2}$$

$$\Phi_2(x) = -\frac{1}{32}\int_0^x D(y)^{1/2}\left[16\, G(y) + \frac{3\, D'(y)^2}{D(y)^2} - \frac{4\, D''(y)}{D(y)}\right]dy \tag{25}$$

$$\Phi_3(x) = -\frac{1}{64}\int_0^x \left\{\frac{3\, D'(y)^3}{D(y)^2} - \frac{6\, D'(y)D''(y)}{D(y)} + 4\, D'''(y) - 16\left[G(y)D(y)\right]\right\} dy$$

A L a t e - t i m e a p p r o x i m a t i o n

In this case, the "technique" of deriving the form of eq. (14) required by the WKB method, differs from that of the "early-time" one.

Instead of using the Laplace transform we postulate (following Ref. 10) a solution of eq. (1) to be represented by

$$a(x,t\to\infty) = a_0 - b(x)\exp\left[-\gamma t\right] \tag{26}$$

where $a_0 = a(x,\infty)$ and γ is parameter.

Substituting the derivatives of eq. (26) into eq. (1), we get

$$\frac{d}{dx}\left[P(x)\,\frac{db(x)}{dx}\right] + \gamma S(x)b(x) = 0 \tag{27}$$

that is the desired SL equation.

The next step in this procedure is identical with the previous one i.e. substitution of

$$b(x) = P(x)^{-1/2}w(x) \tag{28}$$

enables us to get rid of the first order derivative from eq. (27) and get finally

$$w''(x) + w(x)\left[\gamma/D(x) + G(x)\right] = 0 \tag{29}$$

where $G(x)$ is given by eq. (22).

Joining the second and third versions of the WKB method cited above, we can conclude that the solution of eq. (29) has the form:

$$w(x) = \exp\left[i\sqrt{\gamma}\int_0^x U(y)dy\right] \tag{30}$$

where $U(x)$ is given by eq. (17) with γ instead of β and the subsequent approximations i.e. terms of $U(x)$ are:

$$U_0(x) = \pm f^{1/2}(x)$$

$$U_1(x) = \frac{1}{4}\frac{f'(x)}{f(x)}$$

$$U_2(x) = \pm\frac{1}{2} f^{-1/2}(x)\left[\frac{5}{16}\frac{f'(x)^2}{f(x)^2} - \frac{f''(x)}{4\, f(x)} - G(x)\right] \tag{31}$$

$$U_3(x) = -i\,\frac{1}{4}\,G(x)f'(x) - \left[\frac{1}{4}\frac{G'(x)}{f(x)} + \frac{9}{32}\frac{f'(x)f''(x)}{f(x)^3} - \frac{15}{64}\frac{f'(x)^3}{f(x)^4} - \frac{f'''(x)}{16\, f(x)^2}\right]$$

$$\vdots$$

$$U_{n+1} = -\frac{1}{2U_0}\left[U_n' + \sum_{p=1}^{n} U_p U_{n+1-p}\right]; \quad n \geq 2$$

Considering that $f(x) = D(x)^{-1}$, we can write the general solution of eq. (29) via eq. (30) and (31) in the form as given below:

$$w(x,\gamma) \cong D(x)^{1/4}\left\{A \exp\left[i\sqrt{\gamma}\,\Phi_0(x) + \frac{1}{\sqrt{\gamma}}\,\Phi_2(x) - \frac{1}{\gamma}\,\Phi_3(x) + O(\gamma^{-3/2})\right] + \right.$$

$$\left. + B \exp\left[-i\sqrt{\gamma}\,\Phi_0(x) - \frac{1}{\sqrt{\gamma}}\,\Phi_2(x) + \frac{1}{\gamma}\,\Phi_3(x) + O(\gamma^{-3/2})\right]\right\} \qquad (32)$$

or using Euler's formulae

$$w(x,\gamma) \cong D^{1/4}(x)\left\{A_0 \sin\left[\sqrt{\gamma}\,\Phi_0(x) + \frac{1}{\sqrt{\gamma}}\,\Phi_2(x) + O(\gamma^{-3/2})\right] + \right.$$

$$\left. + B_0 \cos\left[\sqrt{\gamma}\,\Phi_0(x) + \frac{1}{\sqrt{\gamma}}\,\Phi_2(x) + O(\gamma^{-3/2})\right]\right\} \qquad (33)$$

where $\Phi_0(x)$, $\Phi_2(x)$ and $\Phi_3(x)$ are given by eq. (25).

Notice that it was necessary to join both $\Phi_3(x)$ with A and B, respectively.

Taking into consideration eq. (28) and (33), we can rewrite eq. (26) as shown below:

$$a(x,t\to\infty) = a_0 - D(x)^{-1/4}\,S(x)^{-1/2}\left\{A_0 \sin\left[\sqrt{\gamma}\,\Phi_0(x) + \frac{1}{\sqrt{\gamma}}\,\Phi_2(x) + \right.\right.$$

$$\left.\left. + O(\gamma^{-3/2}) + B_0 \cos\left[\sqrt{\gamma}\,\Phi_0(x) + \frac{1}{\sqrt{\gamma}}\,\Phi_2(x) + O(\gamma^{-3/2})\right]\right\} \exp\left[-\gamma t\right] \qquad (34)$$

Results and discussion.

One of the tasks of this work was to present, as simply as possible, the WKB Approximation and various possibilities that exist among the methods covered by this name.

Although all the versions give the same final results, the way to get them - very important in calculus - differs from each other. The most convenient procedure seems to be that presented by Kamke for its simplicity and univocal character. It is interesting to notice that in the Kamke's approach (and similar in this respect of Mathews and Walker) the zero approximation solution exists i.e.eq. (15) with U_0 term which does not exist in L-G method. The zero approximation "U_0" arising from eq. (17), when $\beta\to\infty$ provides an exact solution of unperturbed equation that is

$$w''(x) - w(x)\,\frac{\beta}{D(x)} = 0 \qquad (35)$$

Eq. (22) ought to be called consequently a "perturbed" term under condition

$$|G(x)| \ll \frac{\beta}{D(x)} \qquad (36)$$

In case of the equation with oscilatory type solution i.e. eq. (32) condition $\gamma\to\infty$ does not hold [13] and as a result of it two terms inside the brackets of eq. (29) are comparable.

It causes the "perturbation principle" to differ from that of the early-time solution [13]. Namely, to see if the eq. (32), taken only up to the $\Phi_0(x)$ (first approximation), is an exact solution of any D.E. let us differentiate it twice with respect to x, getting

$$w''(x) + w(x)\left[\frac{\gamma}{D(x)} + g(x)\right] = 0 \qquad (37)$$

where

$$g(x) = \frac{3}{16}\,\frac{D'(x)^2}{D(x)^2} - \frac{D''(x)}{4\,D(x)}$$

Comparing eqs. (29) and (37) it can be seen that eq. (32) of the first approximation is an exact solution to eq. (37) and approximate to eq. (29) under condition

$$|g(x)| \gg |\Delta g(x)| \qquad (38)$$

where

$$\Delta g(x) = g(x) - G(x)$$

It will be convenient in further discussions to comment the obtained results in terms of the behaviour of the early and late times separately and to compare then with those given in Ref. 13.

(a) E a r l y - t i m e s o l u t i o n

It is instructive to see why we actually call eq. (24) "the short-time solution". The reasons for that are provided by the sense of the Laplace transform operator used with respect to eq. (1)

$$S(x)\int_0^\infty e^{-\beta t}\,\frac{\partial a}{\partial t}\,dt = \frac{\partial}{\partial x}\int_0^\infty e^{-\beta t}\,P(x)\,\frac{\partial a}{\partial x}\,dt \qquad (39)$$

It is clear from eq. (39) that $t\to 0 \Leftrightarrow \beta\to\infty$

Condition $\beta \to \infty$ leads to $\lim_{\beta\to\infty} A/B \to 0$ and eq. (24) can be read finally

$$w(x,\beta) \cong B\, D(x)^{1/4} \exp\left[-\sqrt{\beta}\,\Phi_0(x) - \frac{1}{\sqrt{\beta}}\,\Phi_2(x) + \frac{1}{\beta}\,\Phi_3(x) + O(\beta^{-3/2})\right] \tag{40}$$

Taking into consideration eq. (20), we can write

$$\bar{a}(x,\beta) \cong B\, D(x)^{-1/4}\, S(x)^{-1/2} \exp\left[-\sqrt{\beta}\,\Phi_0(x) - \frac{1}{\sqrt{\beta}}\,\Phi_2(x) + \frac{1}{\beta}\,\Phi_3(x) + O(\beta^{-3/2})\right] \tag{41}$$

The last point, which has left here to deal with, is the inverse Laplace transformation of eq. (41). There is no, however a simple way to perform it i.e. use of the tables of the ready formulae. We can see later (Part II and III of this series) that there is such a possibility in the further stage of calculus of the initial-boundary value problems.

Comparing eq. (40) with that previously given one must notice the difference in the sign of the power of $D(x)$ namely, incorrectly used minus [14] as well as in the functions being analogue of $\Phi_2(x)$, presented in a logarithmic form [10], there is a number of typographical errors.

It is interesting to compare eq. (40) with the corresponding one in Ref. 13 namely eq. (22). They are formally identical, if we put $D(x) = H(y)$ and $S(x) = 1$, but their physical sense differs very much from each other. Eq. (40) describes the real activity (or concentration for $c = S$. a) distribution when the inverse Laplace transform of it is taken i.e.

$$a(x,t) \cong \frac{B}{2\pi i}\, D(x)^{-1/4}\, S(x)^{-1/2} \int_{c-i\infty}^{c+i\infty} \exp\left[\sqrt{\beta t} - \sqrt{\beta}\,\Phi_0(x) + \frac{1}{\sqrt{\beta}}\,\Phi_2(x) + \frac{1}{\beta}\,\Phi_3(x) + \ldots\right] d\beta \tag{42}$$

where c is chosen so that all the singular points of eq. (40) lie to the left of the line $\mathrm{Re}\{\beta\} = c$ in the complex β plane, while identical procedure with respect to eq. (22) in Ref. 13 gives a virtual concentration distribution.

(b) L a t e - t i m e s o l u t i o n

In this case, the reasons for using the name "late-time solutions" are provided by eq. (26). There is no, however any information about how to treat γ. In the previous approach [10], the WKB asymptotics were applied formally in the same way to early-time case (with appropriate note).

Recently [13], it has been shown that γ approaches limited comparable with $G(x)$, value and that it leads to the different formal treatment.

Comparing these results with those previously given, it is worthwhile to notice that eq. (34) provides a real activity distribution along the x-axis for sufficiently late periods of time, while that of Ref. 13, namely eq. (38), gives a virtual one. Similarly to the early-time case, the sign of power of $D(x)$ in eq. (33) was improperly used as minus in the corresponding equation of Ref. 10. It implicates a series of changes in further calculus.

Finally, we can conclude that most of the necessary relations for analysis of diffusional systems with heterogeneous membranes can be calculated when general solutions of eq. (1) are provided. It will be shown in Parts II and III of this series.

Acknowledgment

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REFERENCES

[1] Petropoulos J.H., Reussis P.P.: J. Chem. Phys. 50, 3951 (1969).
[2] Frisch H.L., Fargeas G., Chui S.T.: J. Phys. Chem. 83, 2787 (1979).
[3] Petropoulos J.H.: J. Polymer Sci. Phys. Ed. 12, 35 (1974).
[4] Birkhoff G., Rota G.C.: Ordinary Differential Equations Wiley, 3rd Ed. 1980.
[5] Pearson K.: Handbook of Applied Mathematics, Van Nostran 1975.
[6] Frömen N., Frömen P.O.: JWKB Approximation, North Holland Publ. Comp. 1965.
[7] Morse P.M., Feshbach H.: Methods for Theoretical Physics, Part II Mc Graw Hill Book Comp. 1953.
[8] Mathews J., Walker R.L.: Mathematical Methods of Physics Benjamin Inc. 1973.
[9] Kamke E.: Differentialgleichungen, Lösungsmethoden und Lösungen 3rd Ed., Chelsea Publ. Comp. New York 1959.
[10] Frisch H.L.: J. Phys. Chem. 82, 1559 (1978).
[11] Jeffreys B.S.: In Quantum Theory, I. Elements, ed. by D.R. Bates Academic Press, New York 1961.
[12] Wylie C.R.: Advanced Engineering Mathematics, Mc Graw-Hill, 1975.
[13] Grzywna Z.J., Petropoulos J.H.: Faraday Trans. II, 79, 571 (1983).
[14] Frisch H.L., Edzil J.B.: J. Chem. Phys., 62, 4804 (1975).

AN APPLICATION OF WKB APPROXIMATION TO TRANSIENT DIFFUSION IN INHOMOGENEOUS MEMBRANES

Part II. SORPTION

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W artykule przedstawiono dwie metody sorpcyjne, tzn. niesymetryczną i symetryczną, opisane na podstawie metody WKB jako część efektywnego systemu badania membran heterogenicznych. Równocześnie rozszerzono i poprawiono wiele rezultatów otrzymanych uprzednio.

In the present paper we provide two methods derived through the WKB Asymptotics i.e. unsymmetrical and symmetrical sorptions as a part of promising tool for the study of inhomogeneous membranes. At the same time we have extended and corrected the errors inherent in many of the results previously given.

In the preceding paper [1], we have dealt with the general solutions of the diffusion equation applied to the case of inhomogeneous membranes, appropriate for the early and late times, respectively, and obtained by the WKB method. The aim of this paper is to apply these results to the mathematical description of two experiments: unsymmetrical [2](one sided) and symmetrical (two sided) sorption.

In both methods the total amount of the mass accumulated in the medium as a function of time is only of interest. This amount can be calculated in two ways (for a unit cross-section)

(i) by integrating the concentration distribution C(x,t) in the appropriate region over x axis

$$M_t = \int_0^1 C(x,t)dx \equiv \int_0^1 S(x)s(x,t)dx \qquad (1)$$

(ii) by integrating the diffusion flow density through the particular interface over time

$$Q_t = -\int_0^t \left(D\,\frac{\partial C}{\partial x}\right)_{x=0} d\tau = -\int_0^t \left(P\,\frac{\partial a}{\partial x}\right)_{x=0} d\tau \qquad (2)$$

Both calculations give identical results for the unsymmetrical sorption, while for the symmetrical one we get the relation [3] as follows

$$M_t = Q_t + Q_t^* \qquad (3)$$

where

Q_t^* is the mass accumulated during a reverse flow.

It seems to be useful to discuss two types of sorption separately in terms of the early and late times, respectively.

Unsymmetrical sorption

It is a process in which the diffusion medium is initially equilibrated with penetrant at the activity a_1, and then exposed to the penetrant activity a_o at one of the surfaces $x = 0$ or $x = 1$ (for details see Fig. 1).

(a) Early-time relations

The terminology and symbolism used in Ref. 1 are followed here as far as possible.

According to eq. (19) of Ref. 1, the flux in the Laplace transform space has a form

$$J^a(x,\beta) = -P(x)\,\frac{d\bar{a}}{dx} \qquad (4)$$

where the bar over the letter indicates the transformed quantities.

Taking into consideration eq. (40) of Ref. 1 and the boundary condition $a(0,t) = a_o$ i.e. $\bar{a}(0,\beta) = a_o/\beta$ we get

$$J^a(x,\beta) \cong \frac{a_o\,P(o)}{\sqrt{\beta}}\,\Phi_o'(o) + \frac{a_o}{4\beta}\,D'(o)S(o) + \frac{a_o}{2\beta}\,D(o)S'(o) + \frac{a_o\,P(o)}{\beta^{3/2}}\,\Phi_2'(o) =$$

$$= \frac{a_o\,P(o)}{\beta^2}\,\Phi_3'(o) + O\left[\beta^{-5/2}\right] \qquad (5)$$

where differentiation with respect to x is indicated by dashes.

Inverting of the Laplace transform yields

$$J^a(x,t) \cong \frac{a_o}{\sqrt{\pi t}}\,S(o)D^{1/2}(o) + a_o\left[\frac{S'(o)D(o)}{2} + \frac{S(o)D'(o)}{4}\right] +$$

$$+ 2\sqrt{\frac{t}{\pi}}\,a_o\,P(o)\Phi_2'(o) - a_o\,t\,P(o)\Phi_3'(o) + O\left[t^{3/2}\right] \qquad (6)$$

Following eq. (2) we get

$$Q_t^a = \frac{2a_o}{\sqrt{\pi}}\,S(o)D^{1/2}(o)t^{1/2} + a_o\left[\frac{S'(o)D(o)}{2} + \frac{S(o)D'(o)}{4}\right]t +$$

$$+ \frac{4}{3}\,\frac{a_o\,P(o)\Phi_2'(o)}{\sqrt{\pi}}\,t^{3/2} - \frac{a_o\,P(o)\Phi_3'(o)}{2}\,t^2 + O\left[t^{3/2}\right] \qquad (7)$$

i.e. the total mass of the penetrant accumulated in the membrane as a function of time.

(b) Late-time relations

The first boundary condition $a(0,t) = a_o$ leads to the conclusion that B_o in eqs. (32) and (33) of Ref. 1 is equal to zero, while the second one enables us to calculate the smallest eigenvalue of, γ i.e. $\left.\frac{\partial a}{\partial x}\right|_{x=1} = 0$ leads to the equation as given below

$$\Theta'(\gamma,1)\,\mathrm{ctg}\,\Theta(\gamma,1) = \frac{D'(1)}{4\,D(1)} + \frac{S'(1)}{2\,S(1)} \qquad (8)$$

where

$$\Theta(\gamma,x) = \gamma^{1/2}\Phi_o(x) + \gamma^{-1/2}\Phi_2(x) + \ldots$$

Eq. (8) upon expansion to the first term in Θ becomes

$$\gamma = \frac{\pi^2}{4\Phi_o^2(1)} - \frac{D^{1/2}(1)\left[\frac{D'(1)}{2\,D(1)} + \frac{S'(1)}{S(1)}\right]}{\Phi_o(1)} \qquad (9)$$

The initial condition $a(x,o) = o$ applied to eq. (34) of Ref.1 let us, after integrating over $d\Theta$ from 0 to π and simple algebraic operations find

$$A_o = \frac{2a_o}{\pi}\int_0^1 D(x)^{1/4}S(x)^{1/2}\,\sin\Theta(\gamma,x)\,\Theta'(x,\gamma)\,dx \qquad (10)$$

In this case the total mass of the penetrant accumulated in the membrane as a function of time is found multiplying eq. (34) of Ref. 1 by $S(x)$ and integrating with respect to x from 0 to 1.

$$Q_\infty - Q_t^a = A_o \exp(-\gamma t) \int_0^1 D(x)^{-1/4}\, S(x)^{-1/2} \sin\Theta(\gamma,x)\,dx \qquad (11)$$

where $Q_\infty = a_o \cdot \bar{S} \cdot l$ and $\bar{S} = \frac{1}{l}\int_0^1 S(x)\,dx$ is the experimental solubility coefficient [2].

Symmetrical Sorption

In this experiment, the diffusion medium is initially equilibrated with penetrant at the activity a_1 and then exposed to the penetrant activity a_o at both sides $x = 0$ and $x = l$, while all the remaining surfaces of the membrane are blocked. In the typical experiment, the initial activity a_1 is equal to zero i.e. diffusion medium is initially evacuated.

(a) Early-time relations

It is clear from comparison of the two sorption processes defined above that in the homogeneous membranes $M_t = 2Q_t$ $M_\infty = Q_\infty$ where letters M and Q refer to symmetrical and unsymmetrical sorptions, respectively. In the inhomogeneous membranes, however, the relation (3) holds where Q_t^* is a mass of penetrant which enters the membrane at $x = l$ (or $x^* = 0$ where $x^* = l - x$), i.e.

$$M_t^a = \frac{2a_o}{\sqrt{\pi}}\left[S(o)D^{1/2}(o) + S(l)D^{1/2}(l)\right]t^{1/2} +$$

$$+ a_o\left[\frac{S'(o)D(o) + S'(l)D(l)}{2} + \frac{S(o)D'(o) + S(l)D'(l)}{4}\right]t +$$

$$+ \frac{4}{3}\frac{a_o}{\sqrt{\pi}}\left[P(o)\Phi_2'(o) + P(l)\Phi_2'(l)\right]t^{3/2} + \frac{a_o}{2}\left[P(o)\Phi_3'(o) + P(l)\Phi_3'(l)\right]t^2 + O(t^{3/2}) \qquad (12)$$

(b) Late-time relations

All the formulae which follow are derived from eq. (34) of Ref. 1 at the initial and boundary conditions assumed.

At the first boundary condition $a(0,t) = a_o$ it can be concluded that B in eq. (34) of Ref. 1 is equal to zero, while the second one $a(l,t) = a_o$ applied to eq. (34) of Ref. 1 yields

$$\Theta(\gamma,l) = \pi \qquad (13)$$

which, upon expansion to the first two terms in Θ, becomes [2]

$$\gamma = \frac{\pi^2}{\Phi_o^2(l)} - \frac{2\Phi_2(l)}{\Phi_o(l)} + \frac{\Phi_2(l)^2}{4\pi^2} \qquad (14)$$

The integration constant A_o has the same formal structure as in the unsymmetrical sorption i.e. eq. (9) including γ from eq. (14).

This formal similarity to the unsymmetrical sorption allows to derive the expression for the total mass of the penetrant accumulated in the membrane of the form of eq. (11)

$$M_\infty - M_t^a = A_o \exp(-\gamma t) \int_0^1 D(x)^{-1/4}\, S(x)^{-1/2} \sin\Theta(\gamma,x)\,dx \qquad (15)$$

where

$$M_\infty = Q_\infty \quad \text{and} \quad M_t^a = Q_t^a + Q_t^{a*}$$

Results and Discussion

We have proposed a mathematical description of two sorption processes, basing on the general solutions obtained by the WKB method in Part I of this series. The unsymmetrical sorption, recently proposed by Teimillis and Petropoulos [3], is a very promising way of analysis of the inhomogeneous membranes.

It presents at least two interesting aspects:

(i) there is no reverse flow when one experiment is performed;

(ii) the early and late periods of time of the process are longer comparing with symmetrical sorption.

The first point of these two offers possibility similar to permeation experiments, that is, enables the penetrant to pass through every region of different diffusion properties in a forward flow. The concept of this experiment strictly corresponds to the definition of the experimentally measured solubility coefficient in case of the "directional" system [3].

$$\bar{S} = \frac{1}{l}\int_0^1 S(x)\,dx \qquad (16)$$

The second item "promises" more experimental points in the two regions of time utilized in building up the diagnostic system of analysis of the anomalous diffusion [2].

We will keep here the convenience of discussion the early and late time behaviour separately.

(a) E a r l y - t i m e b e h a v i o u r

From the early-time behaviour it can be generally concluded that for inhomogeneous membranes the linearity between the mass of the penetrant accumulated in the membrane and the square root of time (assured by the Fickian process) is not preserved, as can be seen from eqs. (7) and (12).

From the other hand it is evident that eqs. (7) and (12) give the ideal Fickian formulae when D and S are constant [4], i.e.

$$Q_t^a = \frac{2a_o}{\sqrt{\pi}} S \cdot D^{1/2} \cdot t^{1/2} = 2\, Co\sqrt{\frac{Dt}{\pi}} \tag{17}$$

$$M_t^a = \frac{4a_o \cdot S \cdot D^{1/2} \cdot t^{1/2}}{\pi} = 4\, Co\sqrt{\frac{Dt}{\pi}} \tag{18}$$

Comparing eq. (12) with that previously given [5] (there is no unsymmetrical sorption available in the form suitable for comparison with eq. (7) one can notice the difference in the functional coefficient related to time at power one as a consequence of the difference between appropriate general solutions [1].

Note that it is possible to compare the present results with those given in Ref. 2, assuming formally $D(x) \equiv H(y)$, $S(x) \equiv 1$, $l \equiv 1$.

It has been pointed out [2] that the equations of the type (7) and (12) can be used to explain the shapes of the non-Fickian sorption kinetic curves. However, it is not possible to determine the diffusion coefficients in a simple way using these equations.

(b) L a t e - t i m e b e h a v i o u r

In contrary to the early-time behaviour, the linearity of $\ln(1 - Q_t^a/Q_\infty)$ vs t plot is preserved. It is interesting to see how the eqs. (11) and (15) look like for the ideal Fickian process i.e. when D and S are constant. Therefore,

$$\ln\left[1 - \frac{Q_t^a}{Q_\infty}\right] = \ln\frac{8}{\pi^2} - \frac{D_{2Q}^2 t}{4l^2} \tag{19}$$

and

$$\ln\left[1 - \frac{M_t^a}{M_\infty}\right] = \ln\frac{8}{\pi^2} - \frac{D_{2M}^2 t}{l^2} \tag{20}$$

When eqs. (19) and (20) are compared the following equalities can be noticed

$$Q_\infty \equiv M_\infty$$

$$D_2 \equiv D_{2M} \tag{21}$$

l = thickness of the whole membrane

Taking the above into account it can be concluded that the time scale of the two experiments differs markedly from each other what could be expected from the merit of the two methods (see Fig. 1).

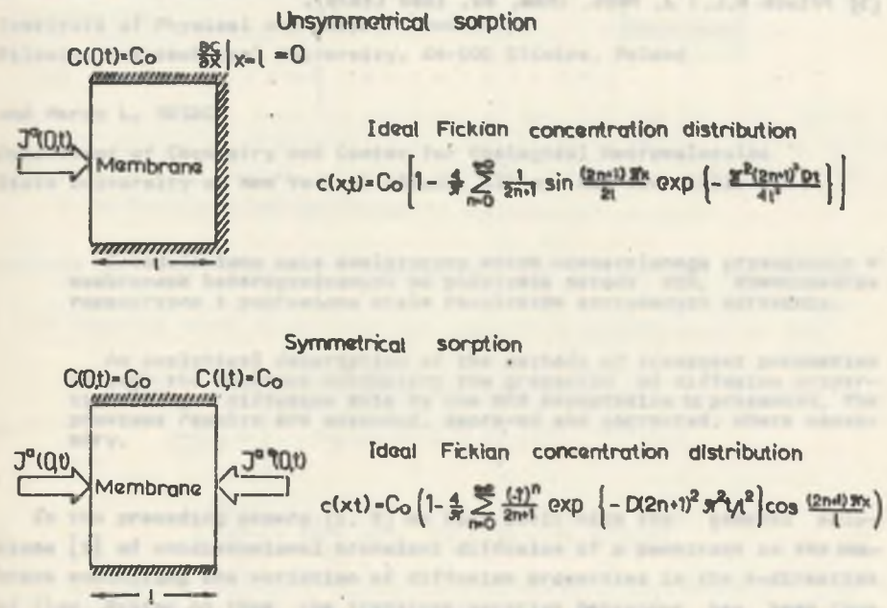

Fig. 1

Fig. 1. Illustration of Sorption Experiments

Returning back to the X-dependence system it is necessary to notice that $D_2 = D_{2M}$ is no longer valid what can be utilized, among others, in building up the system of detecting the functional form of $D = D(x)$ similarly to the approach recently presented [2].

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REFERENCES

[1] Grzywna Z.J., Frisch H.L.: Polish J. of Chem., the preceding paper.
[2] Grzywna Z.J., Petropoulos J.H.: J.C.S. Faraday 2, 79, 571 (1983).
[3] Tsimillis K., Petropoulos J.H.: J. Phys. Chem. 81, 23 (1977).
[4] Crank J.: The Mathematics of Diffusion, 2nd Edition, Clarendon Press, Oxford, 1975.
[5] Frisch H.L.: J. Phys. Chem. 82, 1559 (1978).

AN APPLICATION OF WKB APPROXIMATION TO TRANSIENT DIFFUSION IN INHOMOGENEOUS MEMBRANES

Part III. PERMEATION

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Przedstawiono opis analityczny metod nieustalonego przenikania w membranach heterogenicznych na podstawie metody WKB. Równocześnie rozszerzono i poprawiono wiele rezultatów otrzymanych uprzednio.

An analytical description of the methods of transient permeation through the membrane exhibiting the gradation of diffusion properties along a diffusion axis by the WKB Asymptotics is presented. The previous results are extended, improved and corrected, where necessary.

In the preceding papers [1, 2] we have dealt with the general solutions [1] of unidimensional transient diffusion of a penetrant in the membrane exhibiting the variation of diffusion properties in the x-direction of flow. Basing on them, the transient sorption behaviour has been then described mathematically. In the present paper we proceed to a similar study of transient permeation methods. The approach of Parts 1 and 2 is continued here and applied to the permeation experiment in which the surfaces of the membrane at $x = 0$ and $x = 1$ are kept at the constant activities a_0 and a_1 ($a_0 > a_1$), respectively, while all the remaining surfaces are blocked. In the typical experiment, the membrane is initially evacuated so $a(x,0) = 0$. This standard experimental situation will be illustrated with respect to adsorptive permeation case as shown in Fig.1. The interested reader may find full explanation elsewhere [3, 4, 5].

From Fig. 1 it can be seen that the upstream-downstream permeation curves can be divided into a few regions represented by different analytical

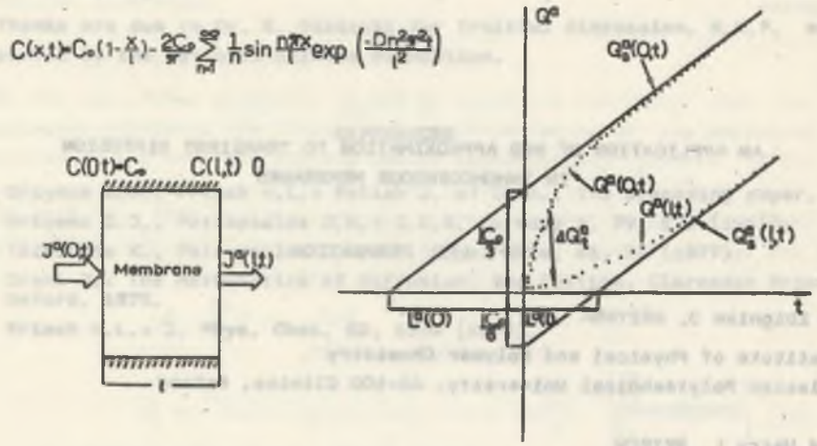

Fig 1

— 19 —

Fig. 1. Illustration of permeation experiments

description (methods) as has been suggested previously [6] and published recently [5, 7].

For an ideal Fickian diffusion, the formulas of these methods are as follows:

$$\ln\left[t^{1/2}\,.\,J(l,t)\right] = \ln\left(2\,C_0\left(\frac{D_4}{\pi}\right)^{1/2}\right) - \frac{l^2}{4\,D_3 t} \tag{1}$$

$$\ln\left[Q^a(l,t) - Q^a_s(l,t)\right] = \ln\frac{2lC_0}{\pi^2} - \frac{D_5\pi^2}{l^2}\,t \tag{2}$$

$$\frac{\Delta Q^a_t}{\Delta Q^a_s} = 4\sqrt{\frac{D_6 t}{\pi l^2}} \tag{3}$$

$$\ln\left[Q^a_s(0,t) - Q^a(0,t)\right] = \frac{2lC_0}{\pi^2} - \frac{D_7\pi^2}{l^2} \tag{4}$$

$$\ln\left[1 - \frac{\Delta Q^a_t}{\Delta Q^a_s}\right] = \ln\frac{8}{\pi^2} - \frac{D_8\pi^2}{l^2}\,t \tag{5}$$

where

$$\Delta Q_t = Q^a(0,t) - Q^a(l,t)$$

$$\Delta Q_s = \lim_{t\to\infty} \Delta Q_t$$

The problem considered in this paper is whether the analogues of the above formulas derived using the WKB Asymptotics for the case of inhomogeneous membranes still hold i.e. if they give straight lines within the appropriately chosen co-ordinate system.

We are going to answer this question in turn for early and late times permeation.

(a) E a r l y - t i m e p e r m e a t i o n

Let us present here the analogues of eqs. (1) and (3). To derive the first of than we differentiate eq. (24) given in Ref. 1. Taking into account eq. (20) of Ref. 1 and the boundary conditions for permeation in the Laplace transform space, i.e.

$$\bar{a}(0) = a_0/\beta, \quad \bar{a}(l) = 0 \tag{6}$$

we get

$$\bar{J}_{x=l} = \frac{2\,D(l)^{3/4}\,S(l)^{1/2}\,D(o)^{1/4}\,S(o)^{1/2}}{\beta}\,\vartheta'\exp(-\vartheta') \tag{7}$$

where

$$\vartheta'(x,l) = \beta^{1/2}\,\Phi_0(x) - \beta^{-1/2}\,\Phi_2(x) + O\left[\beta^{-3/2}\right]. \tag{8}$$

Expanding $\exp\left[-\beta^{-1/2}\,\Phi_2(x)\right]$ into series with accuracy $O\left[\beta^{-3/2}\right]$ we can write eq. (7) in the form

$$\bar{J}_{x=l} = 2\left[D(l)D(o)\right]^{1/4}\left[S(l)S(o)\right]^{1/2}\left\{\frac{1}{\sqrt{\beta}} + \frac{\Phi_2(l)}{\beta}\right\}\exp\left[-\beta^{-1/2}\,.\,\Phi_0(l)\right] \tag{9}$$

Inverting of the Laplace transform yields

$$J_{x=l} = 2\left[D(l)D(o)\right]^{1/4}\left[S(l)S(o)\right]^{1/2}\left\{\frac{1}{\sqrt{\pi t}}\exp\left(-\frac{\Phi_0(l)^2}{4\,t}\right) + \Phi_2(l)\left[1-\mathrm{erf}\left(\frac{\Phi_0(l)}{2\sqrt{t}}\right)\right]\right\} \tag{10}$$

For $t \to 0 \Leftrightarrow \frac{\Phi_o(1)}{\sqrt{t}} \to \infty$ and the erf function can be expanded to asymptotic series [9]

$$1 - \mathrm{erf}\left(\frac{\Phi_o(1)}{2\sqrt{t}}\right) \approx \exp\left(-\frac{\Phi_o(1)^2}{4t}\right)\frac{2\sqrt{t}}{\sqrt{\pi}\,\Phi_o(1)} \tag{11}$$

Considering the above, eq. (10) can be put into a final form of eq. (1) i.e.

$$\ln\left[J(1,t)\,.\,t^{1/2}\right] =$$

$$= \ln\left[\frac{2\left[D(1)D(o)\right]^{1/4} a_o\left[S(1)S(o)\right]^{1/2}}{\sqrt{\pi}}\,.\left[1 + \frac{2\Phi_2(1)}{\Phi_o(1)}\,t\right]\right] - \frac{\Phi_o(1)^2}{4t} \tag{12}$$

A derivation of the formula analogous to eq. (3) is very simple. It is enough to notice [5] that at sufficiently early times for the medium to be essentially semi-infinite

$$Q^a(0,t) \approx \Delta Q^a_t = Q^a_t \tag{13}$$

where the latter quantity refers to the unsymmetrical sorption experiment [2]; and

$$\Delta Q^a_s = \int_0^1 S(x)a_s(x)dx \tag{14}$$

where $a_s(x)$ is the stationary activity distribution given by [8]

$$a_s(x)/a_o = 1 - \left[\int_0^x dy/P(y) \Big/ \int_0^1 dy/P(y)\right] \tag{15}$$

(b) L a t e - t i m e p e r m e a t i o n

In this section the analogues of eqs. (2), (4) and (5) will be derived. The basis for that is eq. (34) of Ref. 1 in which a_o is replaced [8] by $a_s(x)$ and $B_o = 0$.

Taking it into consideration we can write eq. (10) given in Ref. 2 in the form

$$A_o = \frac{2}{\pi}\int_0^1 a_s(x)D(x)^{1/4}\,S(x)^{1/2}\,\sin\Theta(\vartheta,x)\Theta'(\vartheta,x)dx \tag{16}$$

To get the desired result, the activity distribution mentioned above must be first differentiated and multiplied by $P(x)$ to get the flux at $x = 1$.

$$J^a(1,t) = J^a_s(1,t) - A_o\,D(1)^{3/4}\,S(1)^{1/2}\Theta'(\vartheta,1)\exp(-\vartheta^{t}) \tag{17}$$

After integration of eq. (17) with respect to time from $\{\infty, t\}$ and taking logarithm, we get finally

$$\ln\left[Q^a(1,t) - Q^a_s(1,t)\right] = \ln\left[A_o\vartheta^{-1}D(1)^{3/4}\,S(1)^{1/2}\Theta'(\vartheta,1)\right] - \vartheta^{t} \tag{18}$$

where ϑ is given by eq. (14) of Ref. 2.

A similar procedure at the boundary $x = 0$ gives the formula for analogues of eq. (4) i.e.

$$\mathrm{Ln}\left[Q^a_s(0,t) - Q^a(0,t)\right] = \ln\left[A_o\vartheta^{-1}\,D(o)^{3/4}\,S(o)^{1/2}\Theta'(\vartheta,0)\right] - \vartheta^{t} \tag{19}$$

where ϑ is taken at the point $x = 0$.

The last formula we intend to describe is the analogue to eq. (5). Bearing in mind that it relates to the amount of the mass accumulated in the membrane in a function of time, we can make use of eq. (1) Ref. 2 for its derivation.

Let us recall the activity distribution during flow i.e.

$$a(x,t) \approx a_s(x) - A_o\,D(x)^{-1/4}\,S(x)^{-1/2}\,\sin\Theta(\vartheta,x)\exp(-\vartheta^{t}) \tag{20}$$

Eq. (20) upon multiplication by $S(x)$ and integration with respect to x from 0 to 1 yields (in a logaritmic form)

$$\ln\left[1 - \frac{\Delta Q^a_t}{\Delta Q_\infty}\right] = \ln\left\{\left[\int_0^1 a_s(x)dx\right]^{-1} A_o\int_0^1 D(x)^{-1/4}\,S(x)^{-1/2}\,\sin\Theta(\vartheta,x)dx\right\} - \vartheta^{t} \tag{21}$$

where $a_s(x)$ and A_o are given by eqs. (15) and (16), respectively.

Conclusions and Discussion

Similar to the preceding papers [1, 2] of this series the early and late time relations are discussed here separately.

Early-time

As can be seen from Fig. 1 there is the early-time section of the upstream curve which has not been discussed. It does not provide any new

information, since it is exactly the same as the early-time unsymmetrical sorption method (cf. ref. 2 and 5). Holstein-like relation i.e. eq. (12) does not provide a very accurate method of determining D_3 and D_4, mostly due to the slight but significant time dependence of the intercept. If we assume the first approximation to be valid, then we can get the form (part joined with time vanished) appropriate for comparing with the previous treatment [9]. Therefore, when eq. (1, 8) of Ref. 9 is compared with eq. (12), a number of necessary corrections can be made in the first term of the R.H.S. of eq. (1, 8), while in the second term of this equation only a paranthesis was wrongly placed, probably due to a typographical error. In case of the D_6 method it is evident from eqs. (12) and (13) as well as eq. (7) of Ref. 2 that no simple possibility of determining D is provided here, although this method is of some use in solving the "inverse problem" [5].

Late-time

The linearity of the late-time formulae is also preserved similar to the sorption relations. As can be seen from the appropriate equations, the following equality holds [5]

$$D_5 = D_7 = D_8 = D_{2M} = \frac{l^2}{\Phi_0(1)} - \frac{2\, l^2\, \Phi_2(1)}{\pi^2\, \Phi_0(1)} + \frac{l^2\, \Phi_2(1)^2}{4\pi^4} \qquad (22)$$

where D_{2M} is a diffusion coefficient obtained from the symmetrical sorption experiment [2]. Hence, it is sufficient to deal only with intercepts.

To compare our results with those previously given [8] let us write down the activity distribution in an explicit form

$$a(x,t) = a_s(x) - A_0\, D(x)^{-1/4}\, S(x)^{-1/2} \sin\Theta \exp(-\eta^{t}) \qquad (23)$$

with a constant of integration given here only up to the first approximation i.e.

$$A_0 = \frac{2}{\Phi_0(1)} \int_0^1 a_s(x) D(x)^{-1/4}\, S(x)^{1/2} \sin\Theta(\eta, x)\, dx \qquad (24)$$

Comparing eqs. (22) and (23) with the relevant formulae 4.17 and 4.18 given in Ref. 8 two small corrections should be introduced which are required with respect to the powers of D(x). Note that $S(x) \equiv k(x)$ and $X(1) \equiv \Phi_0(1)$.

It is interesting to know that these results can be compared with those previously given [5] due to a formal substitution

$$D(x) \equiv H(y)$$
$$S(x) \equiv 1 \qquad (25)$$
$$l \equiv 1$$

There is no, however, a simple opposite possibility.

Acknowledgment

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REFERENCES

[1] Grzywna Z.J., Frisch H.L.: Polish J. Chem. the procading paper Part 1.
[2] Grzywna Z.J., Frisch H.L.: ibid. Part 2.
[3] Crank J.: The Mathematics of Diffusion, Second Ed. Clarendon Press, Oxford 1975.
[4] Roussis P.P., Petropoulos J.H.: J.C.S. Faraday II, 72, 737 (1976).
[5] Grzywna Z.J., Petropoulos J.H.: J.C.S. Faraday II, 79, 585 (1983).
[6] Grzywna Z.J., Thesis Ph.D.: Silesian Polytechnical University, Gliwice, 1978.
[7] Asarantos S.G., Tsimillis K., Savvakis C., Petropoulos J.H.: J. Membrane Sci. 13, 259 (1983).
[8] Frisch H.L.: J. Phys. Chem. 82, 1559 (1978).
[9] Abramowitz M., Stegun I.: Handbook of Mathematical Functions, Dover Publ. Inc. 1965.

TRANSIENT DIFFUSION KINETICS IN MEDIA EXHIBITING AXIAL VARIATION OF DIFFUSION PROPERTIES

Part 1. SORPTION KINETICS

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Transient uni-dimensional sorption of a penetrant in a medium exhibiting a gradation in diffusion properties along the diffusion axis is considered. The effect of the mode and extent of the variation in diffusion properties on the kinetics of both "symmetrical" and "unsymmetrical" sorption processes is investigated systematically by numerical solution of a number of carefully chosen representative cases. A previous asymptotic analytical treatment is reconsidered, corrected where necessary, and further developed. Its practical usefulness is then assessed by comparison with the corresponding numerical results. The insight thus gained should permit a much more systematic and informative analysis of the transient sorption kinetic behaviour of experimental non-homogeneous solid-penetrant systems.

As part of a general study of "non-Fickian" or "anomalous" diffusion, it has been shown that a system consisting of a penetrant diffusing unidimensionally across a solid slab or membrane whose diffusion properties vary along the diffusion axis can be characterized (up to a certain point) by means of permeation time-lag analysis [1-6]. It has also been pointed out [6, 7] that analysis of the transient part of sorption or permeation curves should afford a means of characterizing such systems more fully. One method of doing this is to derive suitable moments from the aforesaid curves [8, 9]. Another, rather more promising, possibility is to attempt more detailed kinetic analysis of transient diffusion data along the lines indicated in ref. (6) and (7). This, in turn, requires development of the appropriate theoretical background. An important step in this direction is due to Frisch [10-12] who showed how asymptotic expressions appropriate to short and long times of transient sorption or permeation could be obtained by the WKB method. Nevertheless, the practical usefulness of

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these results is as yet limited; because of their approximate nature, the uncertainty of the degree of approximation involved and the complex and unwieldy expressions which result from the treatment of ref. (10) - (12).

In this and the following paper, we take advantage of the approach developed in ref. (1) and (6) to devise more general and compact asymptotic expansions. At the same time, we have extended, and corrected the errors inherent in, many of the results previously given. The present treatment also permits a fairly detailed exact study of transient diffusion behaviour by numerical solution of a limited number of representative cases of axial variation of diffusion properties. These numerical results further serve as a basis for assessing the extent of the validity and utility of the analytical asymptotic solutions.

THEORY

GENERAL CONSIDERATIONS

We consider a slab or membrane of thickness l and unit area in contact with an external phase of penetrant at constant activity. Diffusion occurs across the membrane (in the space $0 \leq X \leq l$) and is governed by "thermodynamic" diffusion and solubility (sorption) coefficients D_T and S, respectively, which are functions of X. We have [1, 10]

$$S \frac{\partial a}{\partial t} = \frac{\partial}{\partial X}\left(D_T S \frac{\partial a}{\partial X}\right) \equiv \frac{\partial}{\partial X}\left(P \frac{\partial a}{\partial X}\right) \tag{1}$$

where t is the time, $P(X) \equiv D_T(X)S(X)$ is the ("thermodynamic") permeability coefficient and $a(X,t)$ is the activity of penetrant in the solid. The latter is defined as equal to the penetrant activity in the external phase at equilibrium and is related to the concentration of penetrant in the solid, $C(X,t)$, by $C = Sa$ [cf. ref. (1)].

In a sorption experiment, the diffusion medium is initially equilibrated with penetrant at activity a_1 and then exposed to penetrant activity a_0 either (i) at one of the surfaces $X = 0$ or $X = l$ ("unsymmetrical sorption") or (ii) at both $X = 0$ and $X = l$ ("symmetrical sorption"), all remaining surfaces of the slab being blocked. The sorption experiment is terminated when equilibrium at activity a_0 is reached. Thus the following conditions are imposed on eqn (1):

$$a(X,t = 0) = a_1; \quad a(X,t \to \infty) = a_0 \tag{2}$$

and either (i) one of the alternative conditions

$$a(X = 0,t) = a_0; \quad \partial a(X = l,t)/\partial X = 0 \tag{3a}$$

$$a(X = l,t) = a_0; \quad \partial a(X = 0,t)/\partial X = 0 \tag{3b}$$

or (ii) the conditions

$$a(X = 0,t) = a(X = l,t) = a_0. \tag{4}$$

In each case the total amount of penetrant sorbed is measured as a function of t. In case (i) this will be denoted by Q_t for diffusion in the sense of increasing X [forward flow ; eqn (3a)] and by Q_t^* for diffusion in the sense of decreasing X [reverse flow ; eqn (3b)]. In case (ii) the symbol M_t will be used. The total amount sorbed up to the final equilibrium state ($t \to \infty$) is $Q_\infty = Q_\infty^* = M_\infty$. Absorption ($a_0 > a_1$) and desorption ($a_0 < a_1$) processes will be distinguished, where necessary, by superscripts a and d, respectively.

From measurements of equilibrium sorption and permeation steady-state flux, one may determine the effective solubility and diffusion coefficients given by [1, 6]

$$\tilde{S} = l^{-1} \int_0^l S(X)dX \tag{5}$$

$$\tilde{D} = l\left[S \int_0^l dX/P(X)\right]^{-1}. \tag{6}$$

Introduction into eqn (1) - (4) of the new variables

$$y = (l\tilde{S})^{-1} \int_0^X S(z)dz \tag{7}$$

$$\sigma \equiv \tilde{S}|a - a_1|, \quad \sigma_0 = \tilde{S}|a_0 - a_1| \tag{8}$$

$$\tau \equiv \tilde{D}t/l^2 \tag{9}$$

yields the standard diffusion equation form

$$\frac{\partial \sigma}{\partial \tau} = \frac{\partial}{\partial y}\left[H(y)\frac{\partial \sigma}{\partial y}\right] \tag{10}$$

with

$$H(y) \equiv D_T(X)S(X)^2/\tilde{D}\tilde{S}^2 \tag{11}$$

subject to the conditions

$$\sigma(y, \tau = 0) = 0 \tag{12}$$

and (i) for unsymmetrical sorption one of the alternative conditions (for Q_t and Q_t^*, respectively)

$$\sigma(y = 0, \tau) = \sigma_0; \quad \partial\sigma(y = 1, \tau)/\partial y = 0 \tag{13a}$$

$$\sigma(y = 1, \tau) = \sigma_0; \quad \partial\sigma(y = 0, \tau)/\partial y = 0 \tag{13b}$$

or (ii) for symmetrical sorption the conditions

$$\sigma(y = 0, \tau) = \sigma(y = 1, \tau) = \sigma_0. \tag{14}$$

The total amount of penetrant sorbed is given by

$$Q_t = \int_0^1 S(X)\left|a(X,t) - a_1\right| dX = \int_0^1 \sigma(y,t)dy; \quad Q_\infty = \sigma_0 \tag{15}$$

and similarly for Q_t^* and M_t.

For absorption and desorption experiments characterized by the same value of $|a_0 - a_1|$, condition (14) remains the same. Conditions (13a) and (13b) similarly remain the same, if there is simultaneous flow reversal. Hence

$$Q_t^a \equiv Q_t^{d*}; \quad Q_t^d \equiv Q_t^{a*}; \quad M_t^a \equiv M_t^d \tag{16}$$

thus halving the number of quantities to be calculated. One may further bear in mind that Q_t^{a*} for any $H(y)$ function is equivalent to Q_t^a for its mirror image about the plane $y = \frac{1}{2}$, namely for $H^*(y) \equiv H(1-y)$. Hence, in a study of unsymmetrical sorption kinetics which includes the appropriate mirror-image functions, it is sufficient to calculate Q_t^a [i.e. to utilize only conditions (13) above].

A S Y M P T O T I C A N A L Y T I C A L S O L U T I O N S

EARLY-TIME SORPTION KINETICS

We consider unsymmetrical sorption at sufficiently small times for the medium to be essentially semi-infinite. Thus, eqn (13) is replaced by the more restrictive conditions

$$\sigma(y = 0, \tau) = \sigma_0; \quad \sigma(y \to 1, \tau) \simeq 0. \tag{17}$$

After Laplace transformation and introduction of the variable

$$w(y) \equiv \bar{\sigma} H(y)^{1/2} \tag{18}$$

where $\bar{\sigma}(y,\beta)$ is the Laplace transform of $\sigma(y,\tau)$, eqn (10) reduces to [10, 12]

$$w''(y) - w'(y)\left[G(y) + \beta/H(y)\right] = 0 \tag{19}$$

where

$$G(y) = H''(y)/2H(y) - H'(y)^2/4H(y)^2 \tag{20}$$

and differentiation with respect to y is indicated by primes. Conditions (17) become

$$w(y = 0) = \sigma_0 H(0)^{1/2}/\beta; \quad w(y \to 1, \beta) \simeq 0. \tag{21}$$

The condition $\tau \to 0$ and hence $\beta \to \infty$ imposed here implies that $G(y)$ is small in comparison with the second term within the bracket in eqn (19). Hence [13]

$$w(y) = A \exp\left[\beta^{1/2}\Phi_0(y) + \Phi_1(y) - \beta^{-1/2}\Phi_2(y) - \beta^{-1}\Phi_3(y) + \ldots\right] +$$

$$+ B \exp\left[-\beta^{1/2}\Phi_0(y) + \Phi_1(y) + \beta^{-1/2}\Phi_2(y) - \beta^{-1}\Phi_3(y) + \ldots\right] \tag{22}$$

where

$$\Phi_0(y) = \int_0^y H(y)^{-1}dy$$

$$\Phi_1(y) = \frac{1}{4}\ln\frac{H(y)}{H(0)}$$

$$\Phi_2(y) = \frac{1}{8}\int_0^y H(z)^{1/2}\left[\frac{H'(z)^2}{4H(z)^2} - \frac{H''(z)}{H(z)}\right]dz = \frac{1}{8}\int_0^y H(z)^{1/2}g(z)dz \tag{23}$$

$$\Phi_3(y) = \frac{1}{16}\int_0^y H(z)\left[\frac{H'(z)^3}{4H(z)^3} - \frac{H'(z)H''(z)}{2H(z)^2} + \frac{H'''(z)}{H(z)}\right]dz.$$

Application of conditions (21) to eqn (22) leads to

$$A + B = \sigma_0 H(0)^{1/2}/\beta \tag{24}$$

and

$$A = 0. \tag{25}$$

Bearing in mind that

$$Q_t^* = \int_0^t q(x = 0, t')dt' = -\int_0^\tau H(0)\frac{\partial\sigma(y = 0, \tau')}{\partial y}d\tau, \tag{26}$$

where $q(x,t)$ is the diffusion flux density at x, the expression for the corresponding Laplace transform is [cf. eqn (18)]

$$\bar{q}(y = 0) = -H(0)\left(\frac{d\bar{\sigma}}{dy}\right)_{y=0} = \frac{\sigma_0}{2\beta}H'(0) - H(0)^{1/2}w'(0) \tag{27}$$

and, upon substitution in eqn (27) from eqn (22) - (25), Laplace transform inversion and integration, we obtain [cf. eqn (26)]

$$\frac{Q_t^*}{Q_\infty} \simeq \tau\left[\frac{H(0)}{\pi}\right]^{1/2} + \frac{H'(0)\tau}{4} + \left[\frac{H(0)\tau}{6}\right]^{3/2}\pi^{-1/2}\left[\frac{H'(0)}{H(0)} - \frac{H'(0)^2}{4H(0)^2}\right] +$$

$$+ \left[\frac{H(0)\tau}{32}\right]^2\left[\frac{H'(0)^3}{4H(0)^3} - \frac{H'(0)H''(0)}{2H(0)^2} + \frac{H'''(0)}{H(0)}\right] + O(\tau^{5/2}). \tag{28}$$

The corresponding expression for symmetrical sorption is simply

$$M_t^* \simeq Q_t^* + Q_t^{*\prime}. \tag{29}$$

LATE-TIME SORPTION KINETICS

When the sorption process is close to the final equilibrium, we have, according to Frisch [12]

$$\sigma(y,\tau) = \sigma_0 - \lambda(y)\exp(-\gamma\tau) \tag{30}$$

where $\gamma\tau$ is large, whereas λ satisfies

$$\gamma\lambda(y) = \frac{d}{dy}\left[H(y)\frac{d\lambda}{dy}\right] \tag{31}$$

and (i) in the case of unsymmetrical sorption

$$\lambda(y = 0) = 0; \quad \lambda'(y = 1) = 0 \tag{32}$$

or (ii) in the case of symmetrical sorption

$$\lambda(y = 0) = \lambda(y = 1) = 0. \tag{33}$$

Introduction of the variable

$$w(y) = \lambda(y)H(y)^{1/2} \tag{34}$$

reduces eqn (31) to

$$w''(y) + w(y)\left[\gamma/H(y) - G(y)\right] = 0 \tag{35}$$

where $G(y)$ is given by eqn (20). An asymptotic solution of eqn (35), subject to the condition $\lambda(y = 0) = 0$ [see eqn (32) and (33)], can be written (cf. the Appendix):

$$w(y) = A_0H(y)^{1/4}\sin\vartheta(\gamma,y) \tag{36}$$

where

$$\vartheta(\gamma,y) \equiv \gamma^{1/2}\Phi_0(y) + \gamma^{-1/2}\Phi_2(y) + \ldots \tag{37}$$

and $\Phi_0(y)$, $\Phi_2(y)$ are given by eqn (23). Substitution from eqn (34) and (36) in eqn (30) yields

$$\sigma(y,\tau) = \sigma_0 - A_0H(y)^{1/4}\sin\vartheta(\gamma,y)\exp(-\gamma\tau) \tag{38}$$

where A_0 may be evaluated with the aid of condition (12) as indicated in ref. (12)

$$A_0 \simeq \frac{2Q_\infty}{\pi}\int_0^1 H(y)^{1/4}\sin\left[\vartheta(\gamma,y)\right]\vartheta'(\gamma,y)dy. \tag{39}$$

On the other hand, with the remaining boundary condition [see eqn (32) and (33)], γ must satisfy one of the following conditions: (i) unsymmetrical sorption

$$\vartheta'(\gamma,1)\cot\left[\vartheta(\gamma,1)\right] = H'(1)/4H(1) \tag{40a}$$

which, upon expansion to the first term in ϑ [see eqn (37)] for sufficiently small $H'(1)/H(1)$, becomes

$$\gamma \simeq \frac{\pi^2}{4\Phi_0(1)^2} - \frac{H'(1)}{2H(1)^{1/2}\Phi_0(1)} \tag{40b}$$

or (ii) symmetrical sorption

$$\vartheta(\gamma,1) = \pi \tag{41a}$$

which, upon expansion to the first two terms in ϑ, becomes

$$\gamma \simeq \frac{\pi^2}{\Phi_0(1)^2} - \frac{2\Phi_2(1)}{\Phi_0(1)} + \frac{\Phi_2(1)^2}{4\pi^2}. \tag{41b}$$

Integration of eqn (38) with respect to y yields

$$Q_\infty - Q_t^a = A_0 \exp(-\gamma\tau) \int_0^1 H(y)^{-1/4} \sin\vartheta(\gamma,y)\,dy \tag{42}$$

with a similar equation for M_t^a.

NUMERICAL SOLUTIONS

The range $0 \leq y \leq 1$ was divided into N equal intervals and a time interval $\Delta\tau$ was chosen such that $\Delta\tau \leq \frac{1}{2} H_{max}^{-1}\Delta y^2$, where $\Delta y = N^{-1}$ and H_{max} was the maximum value of $H(y)$ in the range $0 \leq y \leq 1$.

Starting with the initial cindition (12), values of σ at each node i for $i = 1,2,3,\ldots,N-1$ were computed at successive times $\tau_n = n\Delta\tau (n = 1,2,\ldots)$ by repeated application of the numerical approximation of eqn (10), viz.

$$\sigma_i^+ = \sigma_i + \frac{\Delta\tau}{\Delta y^2}\left[H_j(\sigma_{i+1} - \sigma_i) - H_k(\sigma_i - \sigma_{i-1})\right] \tag{43}$$

where σ_i^+ and σ_i refer to times τ_{n+1} and τ_n, respectively, $H_j = \frac{1}{2}(H_i + H_{i+1})$ and $H_k = \frac{1}{2}(H_i + H_{i-1})$. The values of σ for nodes $i = 0,N$ follow from the appropriate boundary conditions, either eqn (13) or eqn (14). Application of the second condition (13) was effected simply by introducing an additional virtual node $N+1$, setting $\sigma_{N+1} = \sigma_{N-1}$ and applying eqn (43).

Alternatively, eqn (10) may be rewritten as

$$\frac{\partial\sigma}{\partial t} = H'(y)\frac{\partial\sigma}{\partial y} + H(y)\frac{\partial^2\sigma}{\partial y^2}$$

the corresponding numerical approximation being

$$\sigma_i^+ = \sigma_i + \frac{\Delta\tau}{\Delta y^2}\left[\frac{1}{2} H_i'\Delta y(\sigma_{i+1} - \sigma_{i-1}) + H_i(\sigma_{i+1} + \sigma_{i-1} - 2\sigma_i)\right]. \tag{44}$$

Eqn (43) and (44) gave comparable results and it proved difficult to decide in favour of either.

Finally, the quantities Q_t^a or M_t^a were obtained by Simpson integration [cf. eqn (15)].

COMPARISON WITH THE CORRESPONDING IDEAL SYSTEM

The behaviour of the diffusion systems studied here is best investigated [6, 7] by constructing suitable kinetic plots and comparing them with the corresponding linear kinetic plot expected from an ideal diffusion system characterized by constant diffusion and solubility coefficient $\tilde{D}$ and $\tilde{S}$ [cf. eqn (5) and (6)]. If the plot pertaining to the system under investigation is also linear, one may determine an effective or apparent diffusion coefficient (denoted by D_n, $n = 1,2,\ldots$) and/or other parameters, which may be compared with $\tilde{D}$ or other appropriate ideal values.

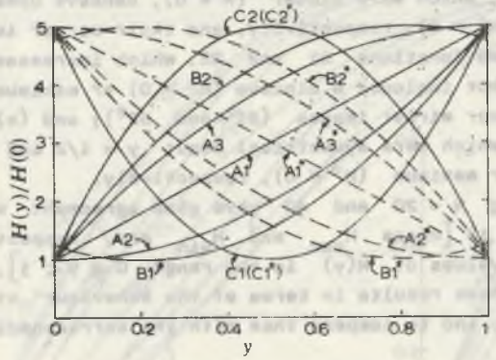

Fig. 1. Illustrations of $H(y)$ functions for $H_{max}/H_{min} = 5$

The following plots are useful here [6]

$$Q_t^a/Q_\infty = 2(D_1^a t/\pi l^2)^{1/2} = 2(D_1^a\tau/\tilde{D}\pi)^{1/2} \tag{45}$$

$$\ln(1 - Q_t^a/Q_\infty) = I_2^a - \pi^2 D_2^a t/4l^2 = I_2^a - \pi^2 D_2^a\tau/4\tilde{D} \tag{46}$$

for short- and long-time unsymmetrical sorption, respectively. The ideal value of I_2^*, the intercept at $\tau = 0$, is $I_2^0 = \ln(8/\pi^2)$. The corresponding expressions for symmetrical sorption are obtained by substituting 1/2 for 1 in eqn (45) and (46) and the relevant D^* and I^* values will be denoted by D^*_{1M}, D^*_{2M} and I^*_{2M}.

The values of $D_2^*/\bar{D} = 4\gamma/\pi^2$, $D^*_{2M}/\bar{D} = \gamma/\pi^2$, I_2^* and I^*_{2M} predicted by the analytical asymptotic treatment follow immediately upon comparison of eqn (42) and (46) and their symmetrical sorption analogues.

RESULTS AND DISCUSSION

The $H(y)$ functions employed in the numerical computations were chosen to be representative of most of the situations likely to be encountered in practice [1, 2] and were, for simplicity, second-degree polynomials subject to the condition [required by eqn (6), (7) and (11)]

$$\int_0^1 H(y)^{-1}dy = 1. \qquad (47)$$

These included (cf. fig. 1 and table 1) (a) three monotonic increasing functions A1, A2 and A3, which were linear ($H'' = 0$), concave upward ($H'' > 0$) and convex upward ($H'' < 0$), respectively, and their mirror images (A1*, A2* and A3*); (b) two functions B1 and B2, which increased over most of the range of y but included a minimum ($H'' > 0$) or maximum ($H'' < 0$), respectively, and their mirror images (B1* and B2*); and (c) two functions C1 and C2, which were symmetrical about $y = 1/2$ and exhibited a minimum ($H'' > 0$) or maximum ($H'' < 0$), respectively.

Computations using $N = 20$ and 40 gave good agreement with values of H_{max}/H_{min} up to 13 [where H_{max} and H_{min} are, respectively, the maximum and minimum values of $H(y)$ in the range $0 \leq y \leq 1$]. It is convenient to discuss these results in terms of the behaviour at short and long times separately and to compare them with the corresponding analytical predictions.

EARLY-TIME SORPTION KINETICS

Examples of the numerical results for unsymmetrical sorption are plotted according to eqn (45) in fig. 2. The slopes of these plots reflect the mean effective value of $H(y)$ over the range of y 'seen' by the penetrant at a given time. This value is $H(0)$ at $t = 0$ and then increases (decreases), if $H(y)$ is an increasing (decreasing) function, thus yielding concave (convex) upwards plots lying below (above) the ideal plot [6].

Table 1

Some characteristic parameters of the $H(y)$ functions used for $H_{max}/H_{min} = 5$. The characteristics of the $H^*(y)$ functions follow from $H^*(0) = H(1)$ and $H^{*\prime}(0) = -H'(1)$

H(y)	H(0)	H'(0)	H''	H(1)	H'(1)	$\Phi_0(1)$	$\Phi_2(1)$
A1	0.402	1.609	0	2.012	1.609	0.974	0.0877
A2	0.554	0	4.429	2.768	4.429	0.970	-0.435
A3	0.323	2.583	-2.582	1.614	0	0.974	0.441
B1	0.785	-1.571	7.854	3.142	6.283	0.971	-0.809
B2	0.299	2.989	-3.767	1.420	-0.747	0.975	0.608
C1	2.768	-8.857	17.714	2.768	8.857	0.970	-1.729
C2	0.323	5.165	-10.330	0.323	-5.165	0.974	1.752

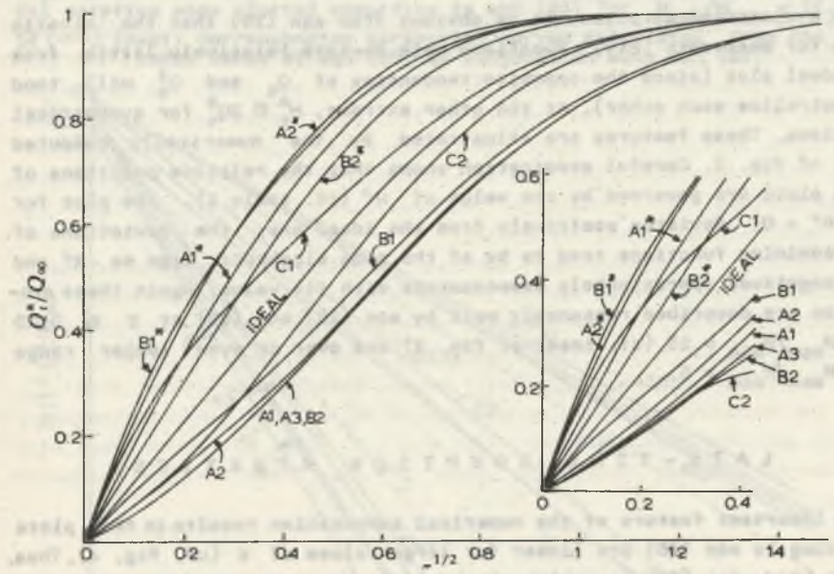

Fig. 2. Examples of numerically computed kinetic curves for the unsymmetrical sorption mode plotted according to eqn (45) for $H_{max}/H_{min} = 13$. Inset: Corresponding early-time curves calculated from the first three terms of eqn (28)

The rate at which $H(y)$ varies with y may be expected to determine the curvature of the relevant plot and its displacement relative to the ideal one. Thus, we see from fig. 2 that the most curved plots (which tend to approach the ideal one most closely at longer τ) are those for cases C1 and C2, where the variation of H with y is most rapid. An interesting situation arises in case B1, where the presence of a minimum near the surface $y = 0$ causes the relevant plot, which lies below the ideal one, to be initially convex upward.

The features noted above are represented reasonably well by eqn (28). Calculation shows that, even for a value of H_{max}/H_{min} as high as 13, the shapes and relative positions of the plots for the $H(y)$ functions considered here are correctly reproduced up to $\tau \approx 0{,}25$ (see inset of fig. 2). As shown by the lack of any appreciable initial linear part in many of these plots, the original theoretical expectation [10, 11] that the first term of eqn (18) would by itself provide a useful measure of approximation is not fulfilled. Inclusion of the second term, however, is sufficient to produce a pattern very similar to that obtained with four terms. These higher terms do not extend the range of validity of eqn (28) appreciably, but inclusion of the third term, at least, is required to reproduce the complicated shape of the sorption curve for function B1 noted above.

In symmetrical sorption, it is obvious from eqn (29) that the kinetic plots for monotonic $H(y)$ functions will deviate relatively little from the ideal plot (since the opposite tendencies of Q_t and Q_t^* will tend to neutralize each other). At the other extreme, $M_t^* \approx 2Q_t^*$ for symmetrical functions. These features are illustrated by the numerically computed plots of fig. 3. Careful examination shows that the relative positions of these plots are governed by the value of H'' (cf. table 1). The plot for A1 ($H'' = 0$) deviates positively from the ideal one; the deviations of the remaining functions tend to be of the same algebraic sign as H'' and of a magnitude approximately commensurate with its value. Again these properties are described reasonably well by eqn (28) and (29) at $\tau \lesssim 0.25$ for $H_{max}/H_{min} = 13$ (cf. inset of fig. 3) and over an even longer range for $H_{max}/H_{min} = 5$.

LATE-TIME SORPTION KINETICS

An important feature of the numerical computation results is that plots according to eqn (46) are linear for large values of τ (cf. fig. 4). Thus, on one hand, eqn (30) (on which the analytical treatment is based) is confirmed. On the other hand, the late-time sorption process can be described quantitatively by means of two parameters, namely $D_2^*(D_{2M}^*)$ and $I_2^2(I_{2M}^*)$.

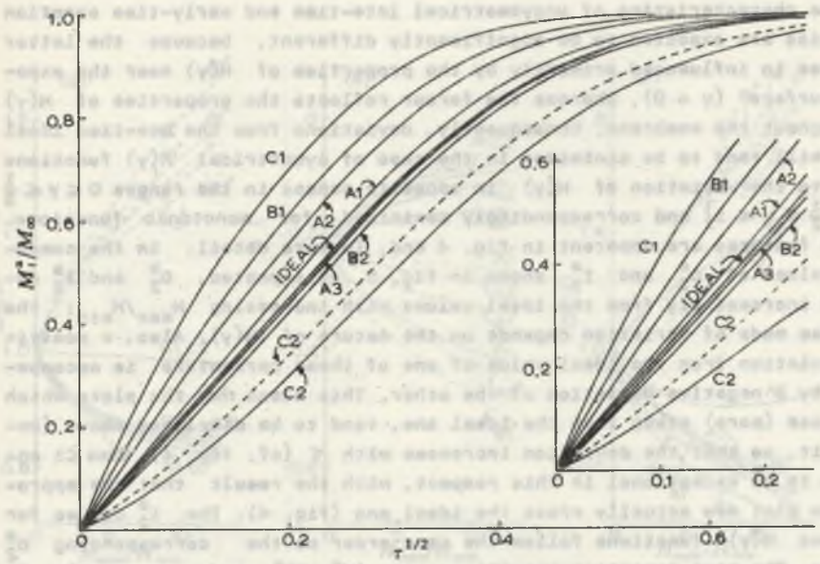

Fig. 3. Examples of numerically computed kinetic curves for the symmetrical sorption mode plotted according to eqn (45) for $H_{max}/H_{min} = 5$(...) or 13 (——) Inset: Corresponding early-time curves calculated from the first three terms of eqn (28) in conjunction with eqn (29)

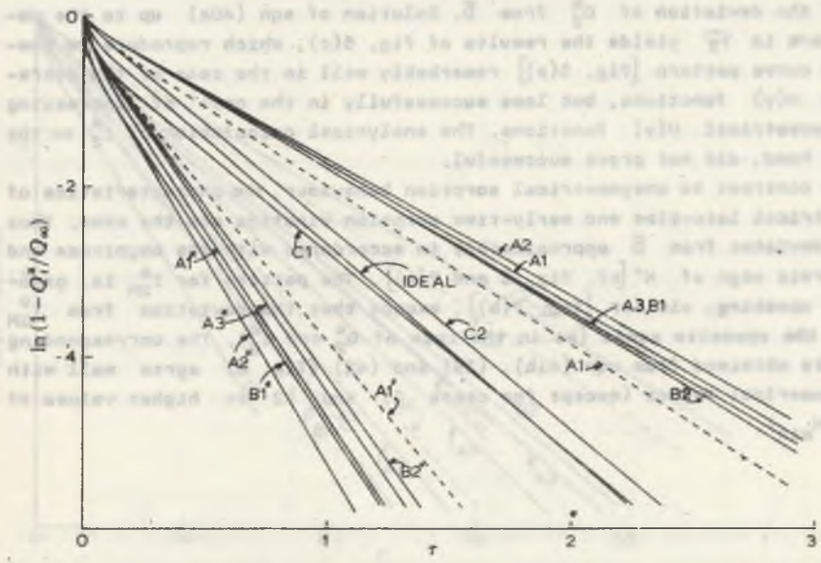

Fig. 4. Examples of numerically computed kinetic curves for the unsymmetrical sorption mode plotted according to eqn (46) for $H_{max}/H_{min} = 5$(...) or 13 (——)

The characteristics of unsymmetrical late-time and early-time sorption kinetics are expected to be significantly different, because the latter process in influenced primarily by the properties of $H(y)$ near the exposed surface ($y = 0$), whereas the forser reflects the properties of $H(y)$ throughout the membrene. Consequently, deviations from the late-time ideal plot will tend to be minimized in the case of symmetrical $H(y)$ functions [due to the variation of $H(y)$ in opposite senses in the ranges $0 \leq y \leq \frac{1}{2}$ and $\frac{1}{2} \leq y \leq 1$] and correspondingly maximized for monotonic functions. These features are apparent in fig. 4 and, in more detail, in the computed values of D_2^* and I_2^* shown in fig. 5. As expected, D_2^* and I_2^* deviate increasingly from the ideal values with increasing H_{max}/H_{min}; the precise mode of variation depends on the nature of $H(y)$. Also, a positive deviation from the ideal value of one of these parameters is accompanied by a negative deviation of the other. This means that the plots which are less (more) steep than the ideal one, tend to be displaced above (below) it, so that the deviation increases with τ (cf. fig. 4). Case C1 appears to be exceptional in this respect, with the result that the appropriate plot may actually cross the ideal one (fig. 4). The I_2^* curves for various $H(y)$ functions follow the same order as the corresponding D_2^* curves. The most important exceptions are A2*, B1* and especially C1 and C2 [cf. fig. 5(a) and (b)].

Bearing in mind that $\Phi_0(1) \neq 1$, (cf. table 1) the first analytical approximation to $\mathfrak{f}$, represented by eqn (40b), indicates correctly the sense of the deviation of D_2^* from $\tilde{D}$. Solution of eqn (40a) up to the cubic term in $\sqrt{\mathfrak{f}}$ yields the results of fig. 5(c), which reproduce the computed curve pattern [fig. 5(a)] remarkably well in the case of the decreasing $H(y)$ functions, but less successfully in the case of increasing and symmetrical $H(y)$ functions. The analytical calculation of I_2^*, on the other hand, did not prove successful.

By contrast to unsymmetrical sorption behaviour, the characteristics of symmetrical late-time and early-time sorption kinetics are the same. Thus D_{2M}^* deviates from $\tilde{D}$ approximately in accordance with the magnitude and algebraic sign of H'' [cf. fig. 6 and 7(a)]. The pattern for I_{2M}^* is, generally speaking, similar [fig. 7(b)], except that the deviation from I_{2M}^0 is in the opposite sense (as in the case of D_2^* and I_2^*). The corresponding results obtained from eqn (41b), (39) and (42) (fig. 8) agree well with the numerical values (except for cases C1 and C2 at higher values of H_{max}/H_{min}).

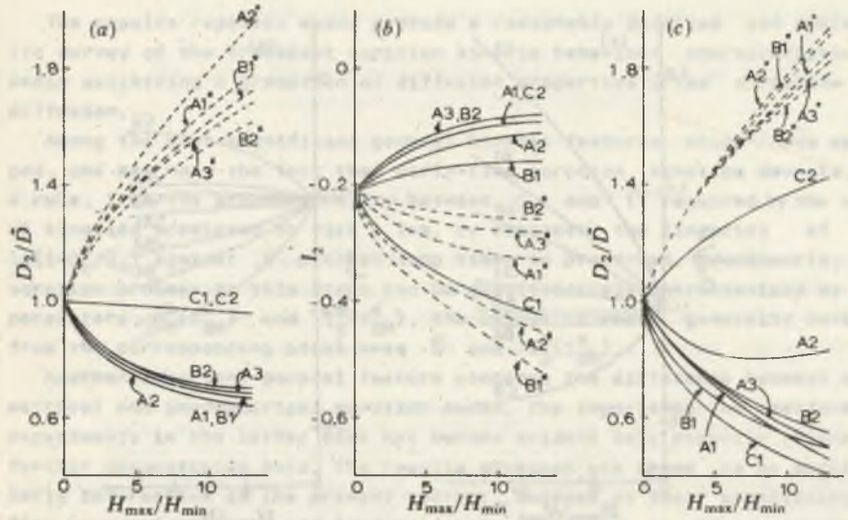

Fig. 5. Numerically computed values of (a) $D_2/\tilde{D}$ and (b) $I_2(I_2^0 = -0.210)$; (c) corresponding values of $D_2/\tilde{D}$ calculated from eqn (40a) (up to the cubic term in $\sqrt{\mathfrak{f}}$), (42) and (46)

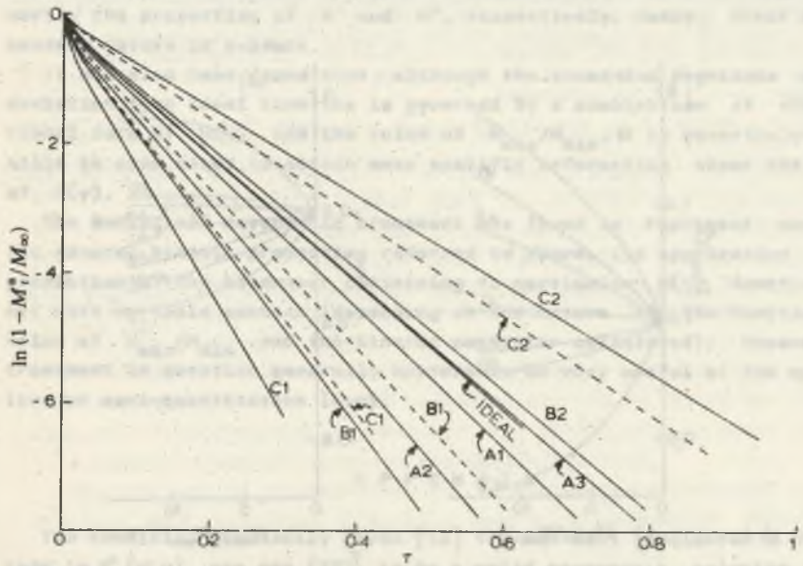

Fig. 6. Examples of numerically computed kinetic curves for the symmetrical sorption mode plotted according to eqn (46) for $H_{max}/H_{min} = 5$(...) or 13 (——)

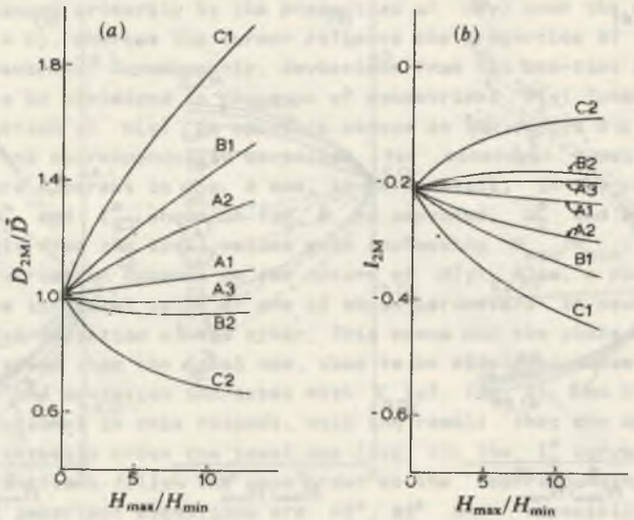

Fig. 7. Numerically computed values of (a) $D_{2M}/\bar{D}$ and (b) $I_{2M}(I^{o}_{2M} = -0.210)$

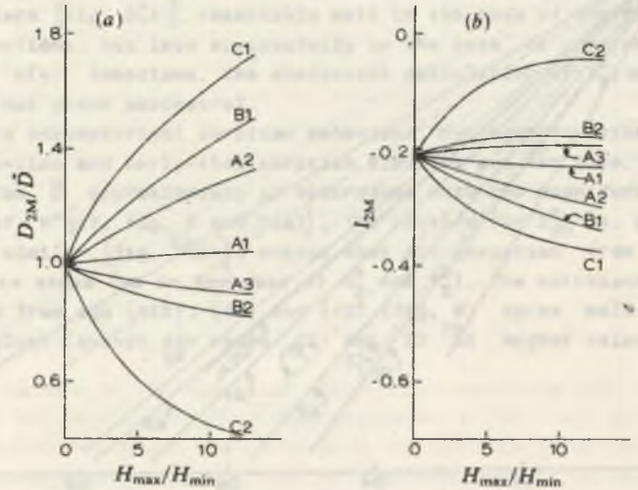

Fig. 8. Values of (a) $D_{2M}/\bar{D}$ and (b) I_{2M} calculated from equations for M_t identical to eqn (42) and (46) in conjunction with eqn (41b)

CONCLUSIONS

The results reported above provide a reasonably detailed and systematic survey of the transient sorption kinetic behaviour characteristic of media exhibiting a gradation of diffusion properties in the direction of diffusion.

Among the most significant general kinetic features which have emerged, one may note the fact that early-time sorption kinetics deviate, as a rule, from the proportionality between Q_t and $\sqrt{t}$ required by the ideal kinetics predicted by Fick's law. By contrast, the linearity of the $\ln(1-Q^{*}_{t}/Q_{\infty})$ against t plot at long times is preserved. Consequently, the sorption process at this stage can be quantitatively characterized by the parameters $D^{*}_{2}(D^{*}_{2M})$ and $I^{*}_{2}(I^{*}_{2M})$, the values of which generally deviate from the corresponding ideal ones $\bar{D}$ and $I^{o}_{2}(I^{o}_{2M})$.

Another important general feature concerns the difference between symmetrical and unsymmetrical sorption modes. The importance of performing experiments in the latter mode has become evident only recently [6] and is further demonstrated here. The results obtained are shown to be particularly informative in the present context, because of their sensitivity to flow reversal at short and long times. By contrast, in the symmetrical sorption mode, short- and long-time kinetic data convey the same kind of information. In terms of the asymptotic analytical treatment, it may be said that symmetrical and early-time unsymmetrical sorption reflect primarily the properties of H' and H'', respectively. Hence, their complementary nature is evident.

It has also been found that, although the sense and magnitude of the deviation from ideal kinetics is governed by a combination of the functional form of $H(y)$ and the value of H_{max}/H_{min}, it is nevertheless possible in some cases to obtain more specific information about the nature of $H(y)$.

The analytical asymptotic treatment was found to represent correctly the general kinetic properties referred to above. Its application to the prediction of the behaviour pertaining to particular $H(y)$ functions has met with variable success (depending on the nature of the function, the value of H_{max}/H_{min} and the kinetic parameter calculated). However, the treatment in question generally appears to be very useful at the qualitative or semi-quantitative level.

APPENDIX

The condition previously given [12] for eqn (36) [evaluated to the first term in $\vartheta'(\eta,y)$, see eqn (37)] to be a valid asymptotic solution of eqn (35) is that $G(y)$ should be negligible in comparison with $\eta H(y)^{-1}$. In

fact, eqn (36) becomes an exact solution of eqn (35) if $G(y)$ is replaced by another function $\bar{G}(y) \neq 0$. Accordingly, the proper condition for the validity of eqn (36) as an approximate solution of eqn (35) is

$$\left| \frac{\bar{G}(y) - G(y)}{\gamma H(y)^{-1} - G(y)} \right| \ll 1 \qquad (A1)$$

where $\bar{G}(y)$, to the first term in $\vartheta(\gamma,y)$, is given by

$$\bar{G}(y) = H''(y)/4H(y) - 3H'(y)^2/16H(y)^2. \qquad (A2)$$

Conditions (A1) and (A2) are found to be considerably less restrictive than the previous condition [12]. Condition (A1) is fulfilled more readily in the symmetrical than in the unsymmetrical sorption mode, because of the larger values of γ obtained in the forser case.

REFERENCES

[1] Petropoulos J.H. and Roussis P.P.: J. Chem. Phys. 1967, 47, 1491 and 1496.

[2] Petropoulos J.H. and Roussis P.P.: J. Chem. Phys., 1968, 48, 4619.

[3] Petropoulos J.H. and Roussis P.P.: J. Chem. Phys., 1969, 50, 3951.

[4] Petropoulos J.H. and Roussis P.P.: J. Chem. Phys., 1969, 51, 1332.

[5] Roussis P.P. and Petropoulos J.H.: J. Chem. Soc., Faraday Trans. 2, 1977, 73, 1025.

[6] Teimillis K. and Petropoulos J.H.: J. Phys. Chem., 1977, 81, 2185.

[7] Asarantos S.G., Teimillis K., Sevvakis C. and Petropoulos J.H.: J. Membr. Sci., to be published.

[8] Ash R., Barrer R.M. and Craven R.J.B.: J. Chem. Soc., Faraday Trans. 2, 1978, 74, 40.

[9] Frisch H.L., Forgacs G. and Chui S.T.: J. Phys. Chem., 1979, 83, 2787.

[10] Frisch H.L. and Bdzil J.: J. Chem. Phys., 1975, 62, 4804.

[11] Frisch H.L.: J. Membr. Sci., 1978, 82, 1559.

[12] Frisch H.L.: J. Phys. Chem., 1978, 83, 149.

[13] Kamke E.: Differentialgleichungen, Losungsmethoden und Losungen (Chelsea Publishing Co., New York, 3rd edn, 1959), vol. 1, p. 139.

TRANSIENT DIFFUSION KINETICS IN MEDIA EXHIBITING AXIAL VARIATION OF DIFFUSION PROPERTIES

Part 2. PERMEATION KINETICS

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Transient-state permeation of a penetrant across a slab or membrane exhibiting a gradation in diffusion properties along the diffusion axis is investigated by the methods used in the preceding analogous study of sorption kinetics. Early - and late - time transient permeation kinetics at both upstream and downstream surfaces of the membrane have been examined, in turn, in a systematic manner. It has been shown that proper analysis of data of this kind (hitherto largely unexploited in experimental practice) is potentially capable of furnishing important information about the mode and extent of the spatial variation of diffusion properties, which partly parallels and partly augments the information deducible from sorption kinetics or permeation time lags. The results of this and the preceding paper provide much of the theoretical background necessary for the practical use of transient-state analysis in a manner analogous to the method of time-lag analysis previously developed.

In the preceding paper [1] we called attention to the importance of studying theoretically the kinetics of uni-dimensional transient diffusion of a penetrant in a slab or membrane exhibiting variation of diffusion properties in the direction of flow X. We then proceeded to carry out such a study of transient sorption behaviour, in relation to the mode and extent of the variation of diffusion properties with X, by obtaining numerical solutions for a number of carefully selected representative examples. The solutions in question were also used as a basis for assessing the practical utility of the corresponding asymptotic analytical results obtained by combinning the WKB treatment introduced by Frisch [2-4] with that of Petropoulos and coworkers [5, 6]. In the present paper we proceed to a similar study of transient permeation kinetics.

The interest of experimenters has previously been confined to what we may here call early-time downstream absorptive permeation kinetics [7-9]

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but Amarantos et al [10] have recently called attention to the potential practical value of the kinetic analysis of other kinds of transient permeation data. All types of kinetic analysis proposed by Amarantos et al [10] are considered here and the appropriate asymptotic analytical expressions are obtained as in ref. (1) (previous results [4] being again corrected where necessary).

The terminology and symbolism of ref. (1) and (6) are followed here as far as possible.

THEORY

GENERAL CONSIDERATIONS

The treatment of ref. (1) is followed here and applied to a permeation experiment, in which the surfaces of the slab or membrane at $X = 0$ and $X = 1$ are maintained at constant penetrant activities a_0 and $a_1 (a_0 > a_1)$ respectively, all remaining surfaces being blocked, i.e.

$$a(X = 0,t) = a_0; \quad a(X = 1,t)\ a_1. \tag{1}$$

The amount of penetrant which enters the membrane at $X = 0$, $Q(0,t)$, or leaves it at $X = 1$, $Q(1,t)$, is measured. The membrane is initially pre-equilibrated either (i) at penetrant activity a_1 (absorptive permeation designated by superscript a), i.e.

$$a(X,t = 0) = a_1 \tag{2}$$

or (ii) at penetrant activity a_0 (desorptive permeation designated by superscript d), i.e.

$$a(X,t = 0) = a_0. \tag{3}$$

The experiment is terminated when $Q(0,t)$ and $Q(1,t)$ have attained their respective linear steady-state asymptotes, $Q_s(0,t)$ and $Q_s(1,t)$, to the required experimental precision. Flow reversal [cf. ref. (1) and (5)] may be represented by substituting eqn (1) by

$$a(X = 0,t) = a_1; \quad a(X = 1,t) = a_0. \tag{4}$$

Putting $X^* = 1 - X$, we may define $Q^*(0,t) \equiv Q(X^* = 0,t)$ and $Q^*(1,t) \equiv Q(X^* = 1,t)$.

For permeation experiments characterized by the same value of $(a_0 - a_1)$, the following relations hold [4, 6]:

$$Q^a(0,t) = Q^{d*}(1,t); \quad Q^d(1,t) = Q^{a*}(0,t) \tag{5a}$$

$$Q^a(1,t) = Q^{a*}(1,t) = Q^d(0,t) = Q^{d*}(0,t). \tag{5b}$$

The relations, together with the fact that Q^* for $S(X)$ and $D_T(X)$ is identical with Q for $S^*(X)$ and $D_T^*(X)$ (where the latter functions are the mirror images of the former about the midplane of the membrane) [1,5] mean that consideration of permeation characterized by conditions (1) and (2) is sufficient to cover the results pertaining to conditions (3) and (4) also. More precisely and making use of the transformation of the diffusion equation in terms of the variables y and τ, defined by eqn (7) and (9) of ref. (1), respectively, and of

$$\sigma \equiv \bar{S}(a - a_1); \quad \sigma_0 = \bar{S}(a_0 - a_1) \tag{6}$$

we need only consider the set of boundary conditions

$$\sigma(y = 0,\tau) = \sigma_0; \quad \sigma(y = 1,\tau) = 0; \quad \sigma(y,\tau = 0) = 0 \tag{7}$$

and calculate $Q^a(0,t)$ and $Q^a(1,t)$. Having calculated these quantities for a given function $H(y)$, characterization of its mirror-image function $H^*(y)$ requires only one additional calculation, namely $Q^a(0,t)$. Alternatively, calculation of $Q^a(0,t)$, $Q^a(1,t)$ and $Q^d(1,t)$ for $H(y)$ yields all the results necessary for the characterization of $H^*(y)$ also.

Instead of $Q^a(0,t)$ and $Q^d(0,t)$, one may consider the net amount of penetrant absorbed by, or desorbed from, the membrane

$$\Delta Q_t^a \equiv Q^a(0,t) - Q^a(1,t); \quad \Delta Q_\infty^a \equiv Q_s^a(0,t) - (Q_s^a(1,t) \tag{8a}$$

$$\Delta Q_t^d \equiv Q^d(1,t) - Q^d(0,t); \quad \Delta Q_\infty^d \equiv Q_s^d(1,t) - Q_s^d(0,t) \tag{8b}$$

for which the following relations hold

$$\Delta Q_t^a = \Delta Q_t^{d*}; \quad \Delta Q_t^d = \Delta Q_t^{a*}. \tag{9}$$

Eqn (9) are analogous to eqn (5) and to eqn (16) of ref. (1). Furthermore for permeation and symmetrical sorption experiments related by $a_0 - a_1 = |a_0 - a_1|$ [cf. eqn (6) and eqn (8) of ref. (1)] we have [4]

$$M_1 = \Delta Q_t^a + \Delta Q_t^d = \Delta Q_t^a + \Delta Q_t^{a*}. \tag{10}$$

A N A L Y T I C A L A S Y M P T O T I C S O L U T I O N S

EARLY-TIME PERMEATION KINETICS

At sufficiently small times for the medium to be essentially semi-infinite [eqn (17) of ref. (1)], $Q^a(0,t) \simeq \Delta Q^a_t \simeq Q^a_t$, where the latter quantity refers to an unsymmetrical sorption experiment with $|a_0 - a_1| = a_0 - a_1$.

To evaluate $Q^a(1,t)$, the treatment of ref. (1) for unsymmetrical sorption is followed up to eqn (24), after replacing the condition $\sigma(y-1,\beta) \simeq 0$ (cf. eqn (17) of ref. (1)] by the less restrictive $\sigma(y = 1, \beta) = 0$, whilst still keeping τ small and hence β large. This leads to substitution of the condition $w(y-1,\beta) \simeq 0$ [cf. eqn (21) of ref. (1)] by

$$w(y = 1, \beta) = 0 \tag{11}$$

which, in turn, causes eqn (25) of ref. (1) to be replaced by

$$A/B = -\exp - 2\left[\beta^{1/2}\Phi_0(1) + \beta^{-1/2}\Phi_2(1) + \ldots\right] \tag{12}$$

From eqn (18) and (22) - (24) of ref. (1) in combination with eqn(11) and (12) here, the Laplace transform of the flux density at $y = 1$ is given by

$$\bar{q}(y = 1) = -H(1)\bar{\sigma}'(y = 1,\beta) = -H(1)^{1/2}w'(y = 1,\beta)$$

$$\simeq 2\sigma_0\beta^{-1}H(0)^{1/4}H(1)^{3/4}\left[\beta^{1/2}H(1)^{-1/2} - H(1)^{1/2}\beta^{-1/2}g(1)/8 + \ldots\right]$$

$$\times \exp\left[-\beta^{1/2}\Phi_0(1) + \Phi_2(1)/\beta^{1/2} + \ldots\right](1 - A/B). \tag{13}$$

Bearing in mind that $A/B << 1$ [cf. eqn (12)], we obtain, after expanding the second exponential factor in eqn (13),

$$\bar{q}(y=1) = 2\sigma_0\left[H(0)H(1)\right]^{1/4}\left[\beta^{-1/2} + \beta^{-1}\Phi_2(1) + \ldots\right]$$

$$\times \exp\left[-\beta^{1/2}\Phi_0(1)\right].$$

Laplace transform inversion and expansion of the resulting error function term finally yields [bearing in mind that $\sigma_0 = Q_\infty$; cf. eqn (15) of ref. (1)]

$$q(y=1,\tau) = dQ^a(1,t)/d\tau = 2Q_\infty\left[H(0)h(1)\right]^{1/4}(\pi\tau)^{-1/2}$$

$$\times\left[1 + 2\Phi_2(1)\tau/\Phi_0(1) + \ldots\right]\exp\left[-\Phi_0(1)^2/4\tau\right]. \tag{14}$$

Eqn (14) may, of course, be integrated to obtain $Q^a(1,t)$, but it is more useful in the above form [see Appendix of ref. (10) for details].

LATE-TIME PERMEATION KINETICS

The treatment applicable here follows that for symmetrical sorption, [1, 4] i.e. eqn (30), (31) and (33) - (42) of ref. (1), except for the substitution of σ_0 in eqn (30), (38) and (39) of ref. (1) by $\sigma_s(y)$ which refers to the steady state of permeation. By putting $\partial\sigma/\partial\tau = 0$ in eqn (10) of ref. (1) and appropriate integration under conditions (7), we find

$$\sigma_s(y) = \sigma(y,\tau\to\infty) = \sigma_0\int_y^1 H(z)^{-1}\,dz\Big/\int_0^1 H(y)^{-1}dy \tag{15}$$

$$q_s = -H(y)\sigma_s'(y) = \sigma_0 \tag{16}$$

where the denominator of eqn (15) is unity by eqn (47) of ref. (1) and q_s is the steady-state flux density. Thus, eqn (38), (39) and (42) of ref. (1) are replaced, respectively, by

$$\sigma(y,\tau) \simeq \sigma_s(y) - A_1H(y)^{1/4}\sin\vartheta(\gamma,y)\exp(-\gamma\tau) \tag{17}$$

$$A_1 \simeq \frac{2Q_\infty}{\pi}\int_0^1 H(y)^{1/4}\vartheta'(\gamma,y)\sin\vartheta(\gamma,y)\left[\int_y^1 H(z)^{-1}\,dz\right]dy \tag{18}$$

$$\Delta Q^a_\infty - \Delta Q^a_t \simeq A_1\exp(-\gamma\tau)\int_0^1 H(y)^{-1/4}\sin\vartheta(\gamma,y)dy \tag{19}$$

where Q_∞ refers to a sorption experiment with $|a_0 - a_1| = a_0 - a_1$ and γ is given by eqn (41) of. ref. (1).

If eqn (17) is differentiated with respect to y and multiplied by H(y) the flux densities $q(y,\tau)$ at the upstream and downstream surfaces of the membrane are obtained by setting $y = 0$ or 1, respectively. Eqn (23), (37) and (41) of ref. (1) show that $\vartheta(\gamma,y) = 0, \pi$ for $y = 0, 1$, respectively, yielding finally

$$q_s - q(y,\tau) = \pm A_1H(y = 0,1)^{3/4}\vartheta'(\gamma;\, y = 0, 1)\exp(-\gamma\tau) \tag{20}$$

where the positive sign applies to $y = 0$ and the negative sign to $y = 1$ and A_1 is given by eqn (19). Integration of eqn (20) between τ and $\tau\to\infty$ then yields

$$Q_s^a(0,t) - Q^a(0,t) = A_1 \vartheta^{-1} H(0)^{3/4} \vartheta'(\vartheta,0)\exp(-\vartheta\tau) \tag{21}$$

$$Q^a(1,t) - Q_s^a(1,t) = A_1 \vartheta^{-1} H(1)^{3/4} \vartheta'(\vartheta,1)\exp(-\vartheta\tau). \tag{22}$$

An alternative approach involves integration of eqn (10) of ref. (1) with respect to the space coordinate once in the range y-1 and a second time [after dividing throughout by H(y)] in the range 0-1 [cf. ref. (11)] Then, after integration of the l.h.s. by parts and application of eqn 16) and of eqn (48) of ref. (1), we obtain finally

$$q_s - q(y = 1,\tau) = \int_0^1 \frac{\partial\sigma}{\partial\tau}\left[\int_0^y H(z)^{-1}\, dz\right]dy. \tag{23}$$

Integration of eqn (23) between τ and $\tau \to \infty$ then yields

$$Q^a(1,t) = \int_0^1 \left[\sigma_s(y) - \sigma(y,\tau)\right]\left[\int_0^y H(z)^{-1}\, dz\right]dy. \tag{24}$$

Substitution into eqn (24) from eqn (17) then gives finally

$$Q^a(1,t) - Q_s^a(1,t) = A_1 \exp(-\vartheta\tau) \int_0^1 H(y)^{-1/4} \sin\vartheta'(\vartheta,y)\left[\int_0^y H(z)^{-1}\, dz\right] dy. \tag{25}$$

The corresponding expressions for $Q_s^a(0,t) - Q^a(0,t)$ are obtained immediately by combining eqn (24) or (19) and (25) with eqn (8).

NUMERICAL SOLUTIONS

Transient-state solutions of eqn (10) of ref. (1) subject to conditions (7) were obtained by means of eqn (43) or (44) of ref. (1) (for i=1,2,... ...,N-1) using the method described therein. The computation was continued up to a time τ_∞ sufficiently long to ensure approach to the steady state to the desired extent.

The steady-state solution was obtained independently by setting the second term on the r.h.s. of eqn (43) or (44) of ref. (1) equal to zero and solving the resulting set of simultaneous equations for i=1,2,...,N-1 Ideally, this solution should satisfy eqn (16); but, in fact, the value of q_s at different nodes, q_{si}, tends to vary because of the errors inherent in the representation of eqn (10) of ref. (1) by either eqn (43) or (44) of ref. (1). Accordingly, q_s was equated to the integral mean value of q_{si}, i.e.

$$q_s = \int_0^1 - H(y)\, \sigma_s'(y)dy. \tag{26}$$

The integration in eqn (26) was performed by Simpson's rule like all other integrations.

Evaluation of ΔQ_t^a and ΔQ_∞^a is straightforward

$$\Delta Q_t^a = \int_0^1 \sigma(y,\tau)dy; \qquad \Delta Q_\infty^a = \int_0^1 \sigma_s(y)dy$$

but some care is required in the case of $q(y = 1, \tau \to 0)$ and $Q^a(y = 1, \tau \to \infty)$. The direct method based on $q(y=1,\tau) = -H(1)\,\sigma'(y=1,\tau)$ and subsequent integration to obtain $Q^a(y=1,\tau)$ involves a significant numerical differentiation error [12]. Eqn (23) offers another possibility, but $q(y=1,\tau)$ is now obtained as a small difference between two relatively large quantities when $\tau \to 0$. On the other hand, eqn (24) yields the quantity $Q^a(y=1,\tau) - Q_s^a(y=1,\tau)$ required at long times directly and was found satisfactory for this purpose. A third method, based on [12]

$$Q^a(y = 1,\tau) = Q^a(y = 1/2,\tau) - \int_{1/2}^1 \sigma(y,\tau)dy$$

and $q(y = 1,\tau) = dQ^a(y = 1,\tau)/d\tau$ was found to be reasonably satisfactory at both short and long τ. Here, $Q^a(y = 1/2,\tau)$ is obtained by integration of $q(y = 1/2,\tau)$; the latter requires evaluation of $\sigma'(y = 1/2,\tau)$, which is more accurate than that of $\sigma'(y = 1,\tau)$ [12]. This was the method usually chosen for short τ. Nevertheless, reasonable concordance with the above alternative methods was usually found.

COMPARISON WITH THE CORRESPONDING IDEAL SYSTEM

Proceeding in the manner explained in ref. (1), the quantities computed in the previous subsection were used to construct suitable kinetic plots which are linear for ideal systems. In the present case they may be non-linear, or they may be linear (or nearly so) but characterized by effective diffusion coefficients D_n (n = 1,2,...) and other parameters which differ from $\bar{D}$ or other pertinent ideal values.

Following ref. (10) we have

(a) at short times

$$\ln\left[\sqrt{\tau}\, dQ^{*}(1,t)/d\tau\right] = \ln 2Q_{\infty}(D_4^{*}/\tilde{D}\pi)^{1/2} - \tilde{D}/4D_3^{*}\tau \qquad (27)$$

$$Q^{*}(0,t)/Q_{\infty} = 2(D_1^{*}\tau/\tilde{D}\pi)^{1/2} \qquad (28)$$

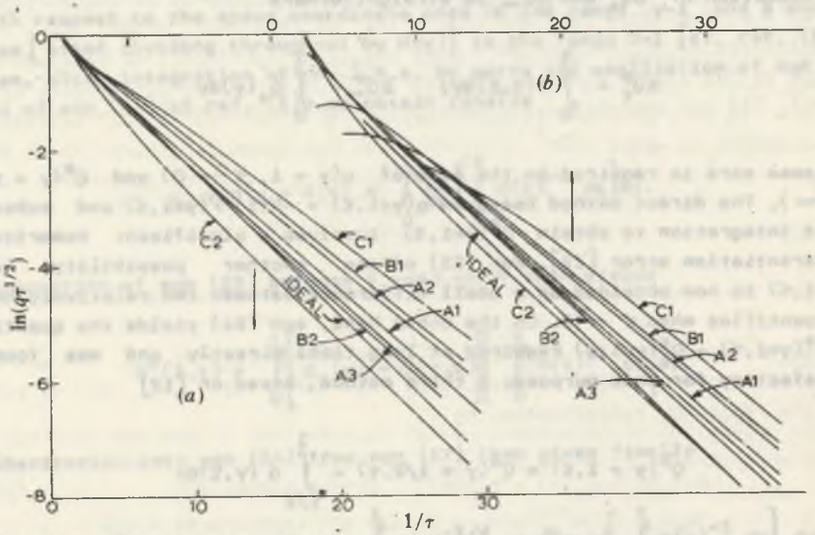

Fig. 1. Examples of early-time $Q^{*}(1,t)$ kinetic curves plotted according to eqn (27) with $H_{max}/H_{min} = 13$: (a) computed numerically; (b) calculated by means of eqn (14)

$$\Delta Q_t^{*}/\Delta Q_{\infty}^{*} = 4(D_6^{*}\tau/\tilde{D}\pi)^{1/2} \qquad (29)$$

(b) at long times

$$\ln\left\{\left[Q^{*}(1,t) - Q_s^{*}(1,t)\right]/Q_{\infty}\right\} = I_5^{*} - \pi^2 D_5^{*}\tau/\tilde{D} \qquad (30)$$

$$\ln\left\{\left[Q_s^{*}(0,t) - Q^{*}(0,t)\right]/Q_{\infty}\right\} = I_7^{*} - \pi^2 D_7^{*}\tau/\tilde{D} \qquad (31)$$

$$\ln(1 - \Delta Q_t^{*}/\Delta Q_{\infty}^{*}) = I_8^{*} - \pi^2 D_8^{*}\tau/\tilde{D} \qquad (32)$$

where the ideal values of the intercepts I are $I_5^{0} = I_7^{0} = \ln(2/\pi^2)$ and $I_8^{0} = \ln(8/\pi^2)$.

RESULTS AND DISCUSSION

Numerical computations were carried out for all the H(y) functions of ref. 1 (see table 1 and fig. 1 therein). The results for N = 20 and N = 40 generally showed good agreement. They were analysed and compared with the predictions of the analytical treatment as in ref. (1).

EARLY-TIME PERMEATION KINETICS

Examples of the numerical results for $Q^{*}(1,t)$ plotted according to eqn (27) are shown in fig. 1(a). The reliability of these plots at various τ was assessed on the basis of the agreement between the numerical results obtained (i) for N = 20 and N = 40, (ii) by the use of different methods (see) previous section), (iii) for H(y) and $H^{*}(y)$ functions making use of eqn (5) and (iv) for the ideal plot. In consequence, it appeared advisable not to rely on the results for $\tau \leq 0{,}05$ in most cases. The plots of fig. 1(a) for different H(y) functions follow the same order as those for symmetrical sorption [fig. 6 of ref. (1)] with C2 lowest and C1 highest. There is some difference, however, in that the deviations from the ideal plot are here positive in all cases except C2, although the latter plot shows a tendency to cross the ideal one at lower τ. Another noteworthy feature of the results is that, although the ideal plot can be considered to be linear up to $\tau \approx 0{,}3$, the other plots exhibit deviations from linearity in this time range which are usually small but noticeable. Consequently, precise values of D_3^{*} and D_4^{*} are not obtainable; those given in fig. 2 should be treated as indicative only. With this reservation, some features of fig. 2 are noteworthy. In particular, the lines of $D_3^{*}/\tilde{D}$

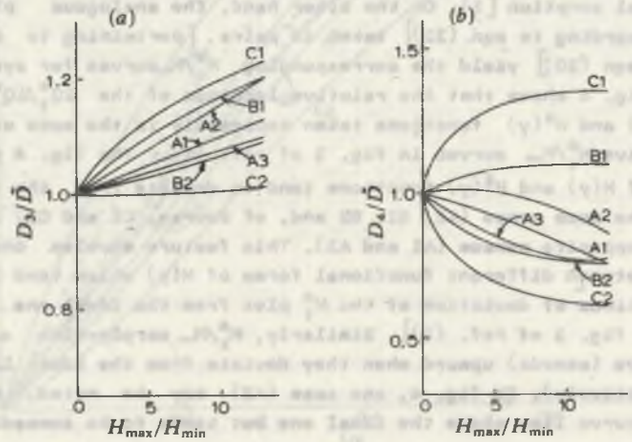

Fig. 2. Indicative values of (a) $D_3/\tilde{D}$ and (b) $D_4/\tilde{D}$ derived from numerically computed kinetic curves

and $D_4^a/\bar{D}$ for various H(y) follow the same order [by contrast with symmetrical sorption, see fig. 7 of ref. (1)] and they deviate from unity in opposite senses (cf. some pertinent experimental observations [6, 10]) or sometimes, in the same sense depending on the functional form of H(y).

Comparison of eqn (14) with eqn (27) shows that the analytical treatment accounts for the aforementioned non-linearity of the early-time plots of fig. 1(a) and predicts that it should be most pronounced in cases C1 and C2, where $\Phi_2(1)/\Phi_0(1)$ is the largest [see table 1 in ref. (1)]. This is confirmed by the numerical results. The results of detailed calculations with eqn (14) are given in fig. 1(b) for direct comparison with fig. 1(a). The shape of the numerically computed lines is reproduced correctly at small τ and so is their relative position, including the fact that the C2 plot lies below the ideal one and shows a tendency to cross it at low τ. The calculated values of D_3^a and D_4^a [cf. eqn (14) and (27)]

$$D_3^a/\bar{D} = \Phi_0(1)^{-2}$$

$$D_4^a/\bar{D} = [H(0)h(1)]^{1/2}[1 + 2\Phi_2(1)\tau/\Phi_0(1)]^2 \qquad (33)$$

are shown in fig. 3 for direct comparison with fig. 2. As can be seen from these figures and the above results, the analytical treatment meets with a large measure of success in the present context.

As already pointed out in the previous section and implied by eqn (45) of ref. (1) and by eqn (30), early-time plots of $Q^a(0,t)/Q_\infty$ or $\Delta Q^a(0,t)/Q_\infty$ according to eqn (30) will simply reproduce the corresponding curves for unsymmetrical sorption [1]. On the other hand, the analogous plots of $\Delta Q_t^a/\Delta Q_\infty^a$ [according to eqn. (31)] taken in pairs [pertaining to H(y) and H*(y); see eqn (10)] yield the corresponding M_t^a/M_∞ curves for symmetrical sorption. Fig. 4 shows that the relative location of the $\Delta Q_t^a/\Delta Q_\infty^a$ curves of the H(y) and H*(y) functions taken separately is the same as that of the respective M_t^a/M_∞ curves in fig. 3 of ref. (1). The fig. 4 plots for each pair of H(y) and H*(y) functions tend to deviate from the ideal one either in the same sense (A2, B1, B2 and, of course, C1 and C2) or, more rarely, in opposite senses (A1 and A3). This feature enables one to discriminate between different functional forms of H(y) which tend to produce similar kinds of deviation of the M_t^a plot from the ideal one [e.g. A1 and A2, cf. fig. 3 of ref. (1)]. Similarly, M_t^a/M_∞ early-time curves tend to be concave (convex) upward when they deviate from the ideal line negatively (positively). In fig. 4, one case (A2) may be noted, where the early-time curve lies above the ideal one but tends to be concave upward.

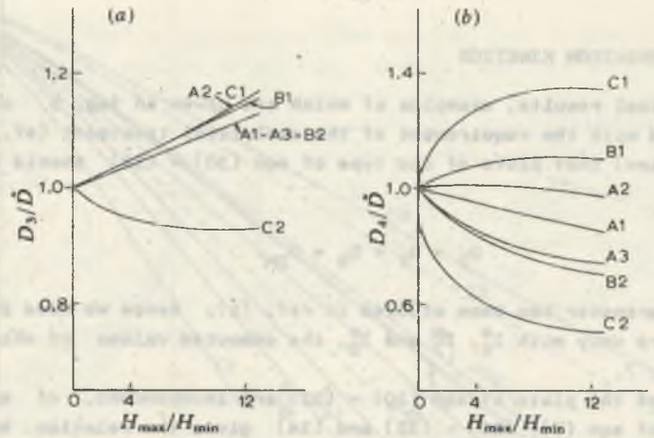

Fig. 3. Values of (a) $D_3/\bar{D}$ and (b) $D_4/\bar{D}$ calculated by eqn (33)

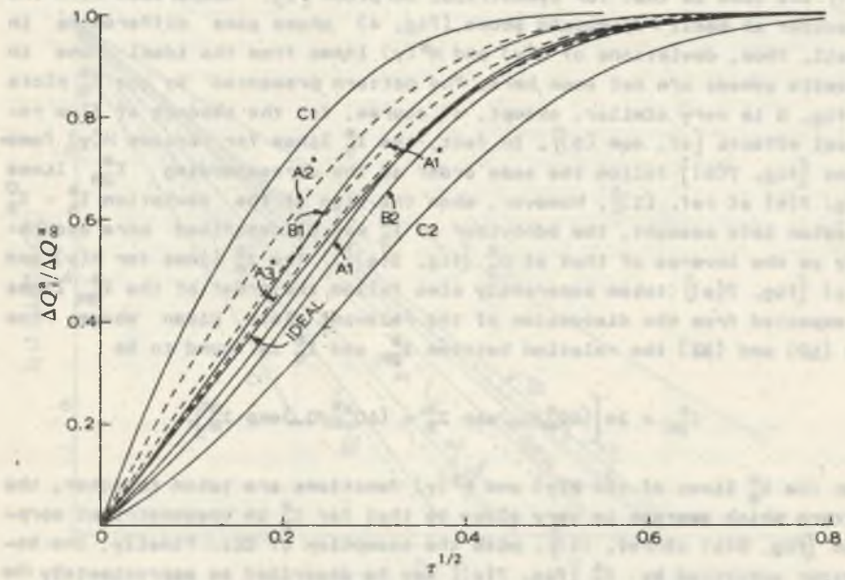

Fig. 4. Numerically computed $\Delta Q_t^a/\Delta Q_\infty^a$ curves for H(y) (——) and H*(y) (---) functions plotted according to eqn (29) for H_{max}/H_{min} = 13

LATE-TIME PERMEATION KINETICS

The numerical results, examples of which are given in fig. 5 and 6, are in accord with the requirement of the analytical treatment (cf. theoretical section) that plots of the type of eqn (30) - (32) should be linear and

$$D_5 = D_7 = D_8 = D_{2M}. \qquad (34)$$

The latter parameter has been studied in ref. (1); hence we need concern ourselves here only with I_5^*, I_7^* and I_8^*, the computed values of which are shown in fig. 7.

Only two of the plots of eqn (30) - (32) are independent, of course. Combination of eqn (8), (30) - (32) and (34) gives the relation between I_5^*, I_7^* and I_8^* as

$$I_8^* = \ln\left[(Q_\infty/\Delta Q_\infty^*)(\exp I_5^* + \exp I_7^*)\right].$$

In fig 5, the lines for the corresponding H(y) and H*(y) functions lie close together, so that the general pattern in either case is [cf. eqn (10)] the same as that for symmetrical sorption [1]. Comparison with the behaviour at small t discussed above (fig. 4) shows some differences in detail. Thus, deviations of H(y) and H*(y) lines from the ideal one in opposite senses are not seen here. The pattern presented by the I_5^* plots of fig. 6 is very similar, except, of course, for the absence of flow reversal effects [cf. eqn (5)]. In fact, the I_5^* lines for various H(y) functions [fig. 7(b)] follow the same order as the corresponding I_{2M}^* lines [fig. 7(b) of ref. (1)]. However, when the sign of the deviation $I_5^* - I_5^0$ is taken into account, the behaviour of I_5^* may be described more accurately as the inverse of that of D_3^* [fig. 3(a)]. The I_8^* lines for H(y) and H*(y) [fig. 7(a)] taken separately also follow the order of the I_{2M}^* lines as expected from the discussion of the relevant plots given above. From eqn (10) and (32) the relation between I_{2M}^* and I_8^* is found to be

$$I_{2M}^* = \ln\left[(\Delta Q_\infty^*/Q_\infty)\exp I_8^* + (\Delta Q_\infty^{*\prime}/Q_\infty)\exp I_8^{*\prime}\right].$$

When the I_8^* lines of the H(y) and H*(y) functions are taken together, the pattern which emerges is very close to that for I_2^* in unsymmetrical sorption [fig. 5(b) of ref. (1)], with the exception of C1. Finally, the behaviour exhibited by I_7^* [fig. 7(c)] may be described as approximately the inverse of that of D_2^* [fig. 5(a) of ref. (1)].

Calculation of I_8^* by eqn (19) in conjunction with eqn (32) [cf. fig. 8 (a)] reproduces the pattern of the numerical results [fig. 7(a)] satisfactorily. Similar success was achieved in the calculation of I_5^* by means of

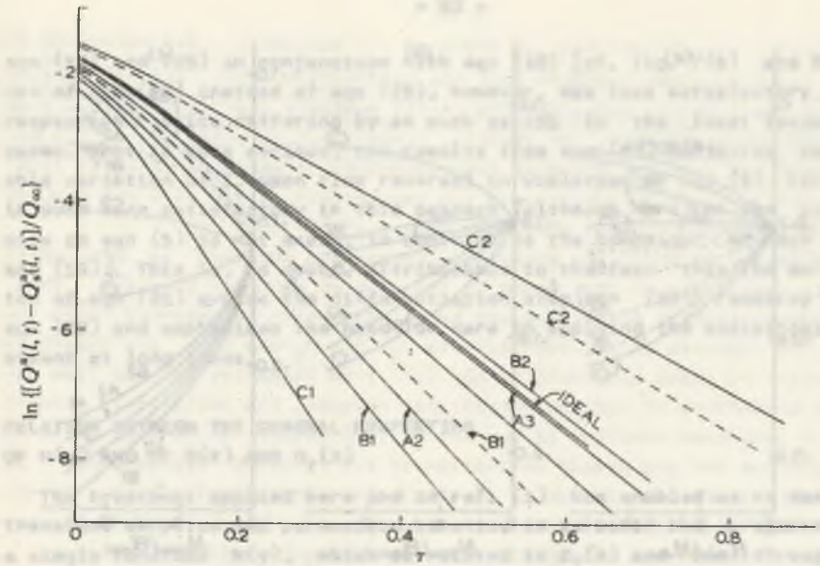

Fig. 5. Nummerically computed $\Delta Q_t^*/\Delta Q_\infty^*$ curves for H(y) (——) and H*(y) (---) functions plotted according to eqn (32) for H_{max}/H_{min} = 13

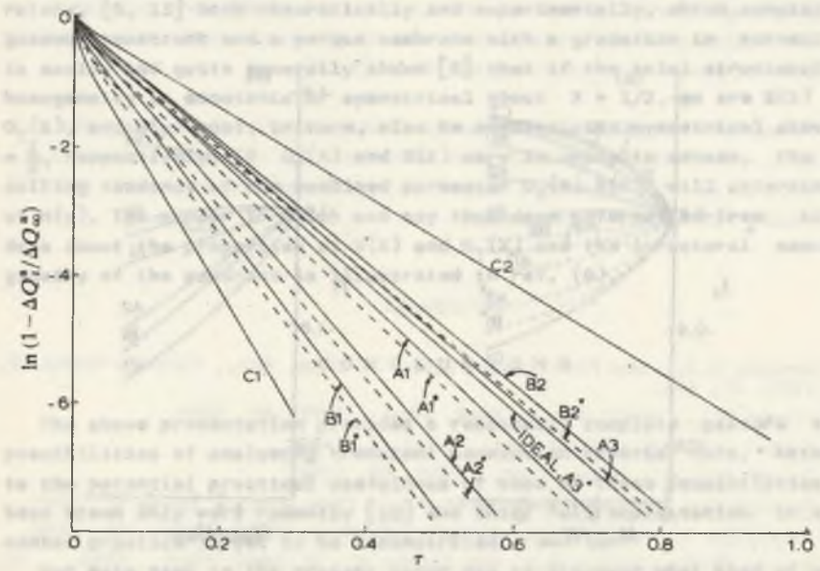

Fig. 6. Numerically computed $Q^*(l,t)$ curves plotted according to eqn (30) for H_{max}/H_{min} = 5(---) or 13 (——)

LATE-TIME PERMEATION KINETICS

The numerical results, examples of which are given in fig. 5 and 6, are in accord with the requirement of the analytical treatment (cf. theoretical section) that plots of the type of eqn (30) - (32) should be linear and

$$D_5 = D_7 = D_8 = D_{2M}. \qquad (34)$$

The latter parameter has been studied in ref. (1); hence we need concern ourselves here only with I_5^a, I_7^a and I_8^a, the computed values of which are shown in fig. 7.

Only two of the plots of eqn (30) - (32) are independent, of course. Combination of eqn (8), (30) - (32) and (34) gives the relation between I_5^a, I_7^a and I_8^a as

$$I_8^a = \ln\left[(Q_\infty/\Delta Q_\infty^a)(\exp I_5^a + \exp I_7^a)\right].$$

In fig 5, the lines for the corresponding H(y) and H*(y) functions lie close together, so that the general pattern in either case is [cf. eqn (10)] the same as that for symmetrical sorption [1]. Comparison with the behaviour at small τ discussed above (fig. 4) shows some differences in detail. Thus, deviations of H(y) and H*(y) lines from the ideal one in opposite senses are not seen here. The pattern presented by the I_5^a plots of fig. 6 is very similar, except, of course, for the absence of flow reversal effects [cf. eqn (5)]. In fact, the I_5^a lines for various H(y) functions [fig. 7(b)] follow the same order as the corresponding I_{2M}^a lines [fig. 7(b) of ref. (1)]. However, when the sign of the deviation $I_5^a - I_5^0$ is taken into account, the behaviour of I_5^a may be described more accurately as the inverse of that of D_3^a [fig. 3(a)]. The I_8^a lines for H(y) and H*(y) [fig. 7(a)] taken separately also follow the order of the I_{2M}^a lines as expected from the discussion of the relevant plots given above. From eqn (10) and (32) the relation between I_{2M}^a and I_8^a is found to be

$$I_{2M}^a = \ln\left[(\Delta Q_\infty^a/Q_\infty)\exp I_8^a + (\Delta Q_\infty^{a*}/Q_\infty)\exp I_8^{a*}\right].$$

When the I_8^a lines of the H(y) and H*(y) functions are taken together, the pattern which emerges is very close to that for I_2^a in unsymmetrical sorption [fig. 5(b) of ref. (1)], with the exception of C1. Finally, the behaviour exhibited by I_7^a [fig. 7(c)] may be described as approximately the inverse of that of D_2^a [fig. 5(a) of ref. (1)].

Calculation of I_8^a by eqn (19) in conjunction with eqn (32) [cf. fig. 8 (a)] reproduces the pattern of the numerical results [fig. 7(a)] satisfactorily. Similar success was achieved in the calculation of I_5^a by means of

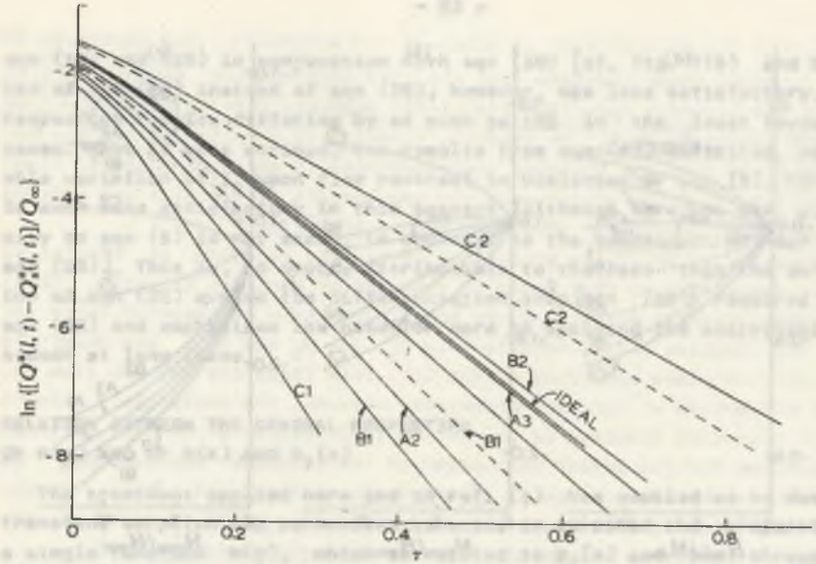

Fig. 5. Numerically computed $\Delta Q_t^a/\Delta Q_\infty^a$ curves for H(y) (——) and H*(y) (---) functions plotted according to eqn (32) for H_{max}/H_{min} = 13

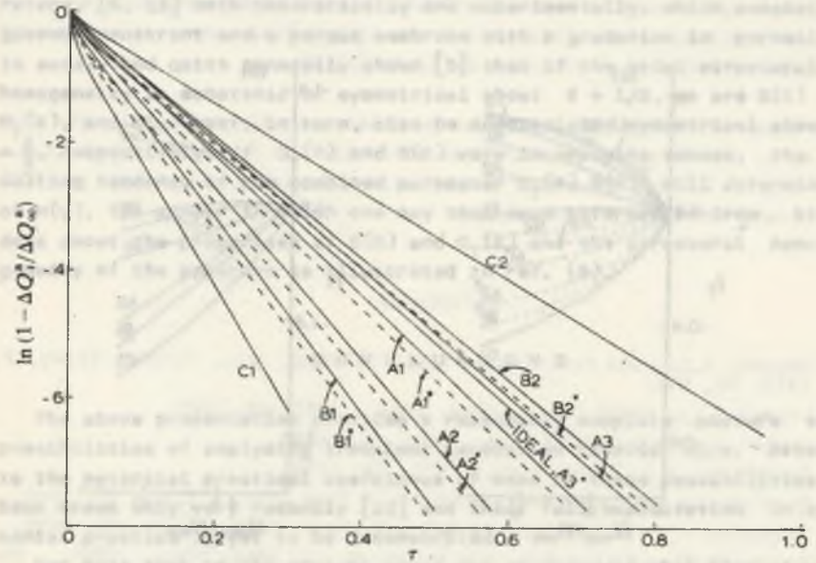

Fig. 6. Numerically computed $Q^a(1,t)$ curves plotted according to eqn (30) for H_{max}/H_{min} = 5(---) or 13 (——)

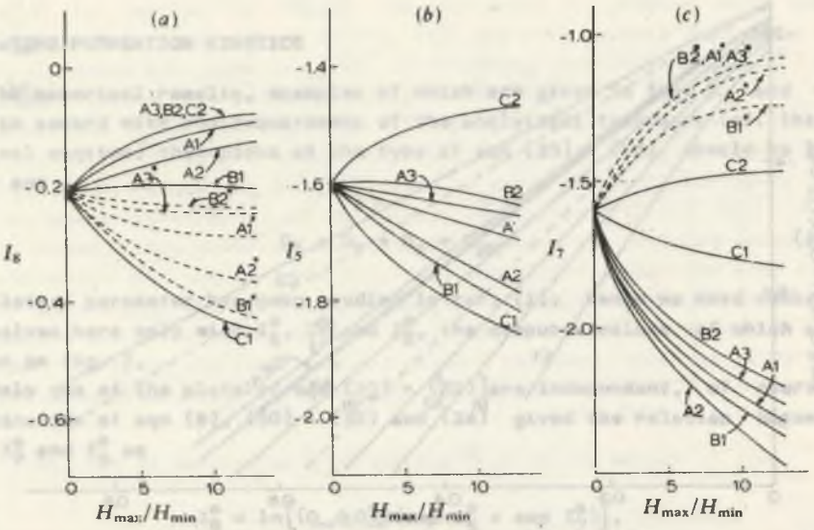

Fig. 7. Numerically computed values of (a) I_8^*, (b) I_5^* and (c) I_7^* (I_8^0 = = -0,210, $I_5^0 = I_7^0$ = -0,596)

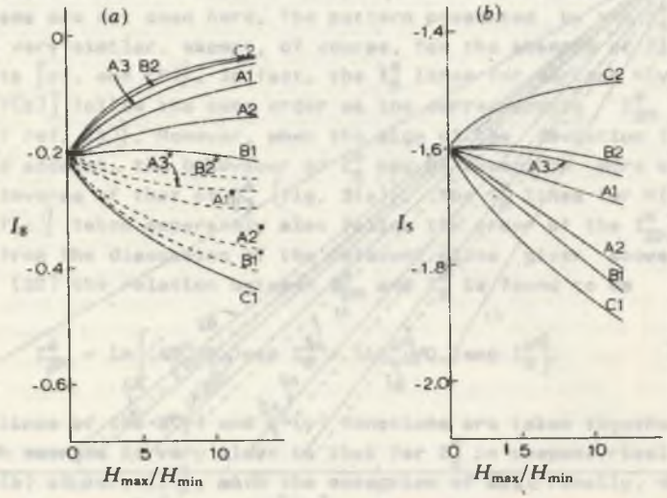

Fig. 8. Values of (a) I_8^* and (b) I_5^* calculated by means of eqn (19) and (32) by eqn (25) and (30), respectively

eqn (18) and (25) in conjunction with eqn (30) [cf. fig. 7(b) and 8(b)]. Use of eqn (22) instead of eqn (25), however, was less satisfactory, the respective results differing by as much as 15% in the least favourable cases. What is more serious, the results from eqn (22) exhibited noticeable variation of I_5^* upon flow reversal in violation of eqn (5). Eqn (25) is much more satisfactory in this respect [although here too the conformity to eqn (5) is not exact, in contrast to the behaviour of eqn (14) and (19)]. This is, no doubt, attributable to the fact that the derivation of eqn (25) avoids the differentiation step [eqn (20)] required for eqn (22) and emphasizes the need for care in applying the analytical treatment at long times.

RELATION BETWEEN THE GENERAL PROPERTIES OF H(y) AND OF S(X) AND $D_T(X)$

The treatment applied here and in ref. (1) has enabled us to describe transient sorption and permeation kinetics in terms of the properties of a single function H(y), which is related to $D_T(X)$ and S(X) through eqn (7) and (11) of ref. (1). The problem of passing from H(y) to S(X) and $D_T(X)$ is facilitated by the fact that the latter functions have a common physical origin, namely an axial gradation in membrane structure. A good specific example of this is afforded by the systems studied in our laboratory, [6, 13] both theoretically and experimentally, which consist of a gaseous penetrant and a porous membrane with a gradation in porosity. It is easily and quite generally shown [5] that if the axial structural non-homogeneity is monotonic or symmetrical about X = 1/2, so are S(X) and $D_T(X)$, and H(y) must, in turn, also be monotonic or symmetrical about y = = $\frac{1}{2}$, respectively. If $D_T(X)$ and S(X) vary in opposite senses, the resulting tendency of the combined parameter $D_T(X)\,S(X)^2$ will determine that of H(y). The manner in which one may thus draw information from kinetic data about the properties of S(X) and $D_T(X)$ and the structural non-homogeneity of the membrane is illustrated in ref. (6).

CONCLUSIONS

The above presentation provides a reasonably complete picture of the possibilities of analysing transient permeation kinetic data. Attention to the potential practical usefulness of some of these possibilities has been drawn only very recently [10] and their full exploitation in experimental practice is yet to be demonstrated.

Our main task in the present paper was to discover what kind of useful information can be expected from kinetic analyses of this nature for the purpose of characterizing penetrant-membrane systems exhibiting spatial variation of diffusion properties along the axis of permeation. The re-

sults reported above indicate that the information which can be derived in such cases partly parallels and partly augments that obtainable from sorption kinetics. Thus, for example, symmetrical sorption curves are here decomposed into two branches (corresponding to opposite senses of flow) the position of which relative to the appropriate ideal plot can provide more detailed information about the nature of H(y).

The extent to which the analytical asymptotic approach is successful here is comparable to that found in the case of sorption kinetics. Thus, the general kinetic properties are again adequately represented. These include the identity of the coefficients D_5, D_7, D_8 and D_{2M}, the departure of early-time plots according to eqn (27) from linearity and the flow reversal properties of various parameters. However, the analytical treatment of late-time kinetics is subject to limitations which must be taken into account for the proper derivation of the relevant expressions, as was shown in the calculation of I_5^a above. For purposes of a more detailed kinetic analysis the asymptotic treatment is again found to be very useful, as a rule, at the qualitative and semi-quantitative level.

The potential practical usefulness of transient-state kinetic analysis for the qualitative or semi-quantitative characterization of diffusion systems with spatially varying diffusion properties has already been illustrated in a preliminary way [6, 10]. The results of the present and preceding papers provide much of the theoretical background necessary for the full exploitation of this method as a diagnostic tool in a manner analogous to permeation time-lag analysis [5, 6].

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REFERENCES

[1] Grzywna Z.J., and Petropoulos J.H.: J. Chem. Soc., Faraday Trans. 2, 1983, 79, 571.
[2] Frisch H.L., Bdzil J.: J. Chem. Phys., 1975, 62, 4804.
[3] Frisch H.L.: J. Member. Sci., 1978, 3, 149.
[4] Frisch H.L.: J. Phys. Chem., 1978, 82, 1559.
[5] Petropoulos J.H. and Roussis P.P. J. Chem. Phys., 1967, 47, 1946.
[6] Tsimillis K. and Petropoulos J.H.: J. Phys. Chem., 1977, 81, 2185.
[7] Rogers W.Wm., Buritz R.S. and Alpert D.: J. Appl. Phys., 1954, 25, 868.
[8] Meares P.: J. Appl. Polym. Sci. 1965, 9, 917.
[9] Ash R., Barrer R.M. and Edge A.V.: J. Chem. Soc. Faraday Trans. 1, 1976, 72, 2777.

[10] Amarantos S.G., Tsimillis K., Savvakis C. and Petropoulos J.H.: J. membr. Sci, to be published.
[11] Frisch H.L.: J. Phys. Chem., 1957, 61, 93.
[12] Petropoulos J.H. and Roussis P.P.: J. chem. Phys., 1969, 50, 3951.
[13] Petropoulos J.H. and Roussis P.P.: J. Chem. Phys. 1968, 48, 4619.

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