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A NEW "SMALL-t" EXPANSION AND COMPARISON WITH "LARGE-t" EXPANSION

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INTRODUCTION

Solution to Fick's diffusion equation using expansions which favor the evaluation of data with large values of time have been used here for several years to analyze permeation measurements. This type of expansion converges fast in the larger time range. The first term is good enough for diffusivity calculations in the range of large values of time. But many terms must be included for evaluations in the short initial time interval.

Another solution by Laplace transformation of the diffusion equation is studied here. This solution gives an expansion in the short interval which converges fast. This new expansion is complementary to the "large-t" expansion and is discussed in this report. The advantage is that more data from pumpout and breakthrough permeation experiments can now be used in the statistical evaluation of diffusivity.

SUMMARY AND CONCLUSION

1. The "Large-t" expansion is a solution of the diffusion equation solved by an assumption of time-space variable separation. The "Small-t expansion is another solution of the diffusion equation solved by Laplace transformation.

2. The "Large-t" expansion converges fast in the large time range and a new "Small-t" expansion converges fast in the small time range. These two expansions are complementary to each other.

3. Permeation measurements can be treated by either expansion by including many terms and by a non-linear least square program. But the first term with simple linear regression gives accurate results by using one or the other expansion depending upon the time range of the data being treated.

DISCUSSION

1. Permeation Measurement Methods

Most permeation measurements are made by either "Breakthrough" or "Pump-Out" methods.[1]

(a) Brief "Breakthrough" method description

Both sides of a sample are under vacuum initially. Applying a fixed pressure of a gas on one side, the flow rate is measured on the other side of the sample until steady state is obtained. The relative flow rate is defined by

$$y = \frac{J_s - J(t)}{J_s} \qquad 1$$

where $J(t)$ and J_s are the flow rates at time t and final steady state, respectively.

(b) Brief "Pump-Out" method description

One side of a sample is under a fixed pressure of gas and the other side is under vacuum. The flow of the gas through the sample is under steady state initially. Pumping out quickly on the high pressure side, the flow rate is then measured on the initially evacuated side until the flow reaches a minimum signal limit. The relative flow rate is defined by

$$y = \frac{J(t)}{J_s} \qquad 2$$

where $J(t)$ and J_s are the flow rates at time t and the initial steady state, respectively.

2. "Small-t" and "Large-t" Expansions

The diffusion equation has been solved in two different approaches[2-4]; (1) by an assumption of space-time variable separation, and (2) by Laplace transformation. The convergency of the infinite series expansion depends on the range of time. The "Large-t" expansion, a solution by space-time variable separation, converges fast in the large time range. The "Small-t" expansion, a solution by Laplace transformation, converges fast in the range of small time.

The relative flow rate by "Large-t" expansion[1,5] is

$$y = -2 \sum_{n=1}^{\infty} (-1)^n \exp \left[- \frac{n^2 \Pi^2 Dt}{\ell^2} \right] \qquad 3$$

where D is the diffusivity of the gas through the sample and ℓ is the thickness of the sample. As t increases the higher terms in the summation contribute little. Approximately then

$$y \simeq 2 \exp \left[-\Pi^2 Dt/\ell^2 \right] \qquad 4$$

The slope on the semilog plot gives diffusivity by the relation:

$$\frac{\partial \ell n y}{\partial t} = - \left(\frac{\Pi}{\ell} \right)^2 D \qquad 5$$

The relative flow rate by "Small-t" expansion is

$$y = 1 - \frac{2\ell}{\sqrt{\Pi D t}} \sum_{n=o}^{\infty} \exp \left[- \frac{(2n+1)^2 \ell^2}{4Dt} \right] \qquad 6$$

The details of the derivation are in the Appendix. As t decreases the higher terms in the summation contribute little. By rearrangement

$$\ell n [(1-y) \sqrt{t}] = \ell n \left[\frac{2\ell}{\sqrt{\Pi D}} \right] - \frac{\ell^2}{4DT} + \ell n \left\{ 1 + \sum_{n=1}^{\infty} \exp \left[- \frac{(2n+1)^2 \ell^2 - \ell^2}{4Dt} \right] \right\} \qquad 7$$

In the small time range the last term on the right hand side is negligible. From the slope

$$\frac{d \ \ell n \ [(1-y)\sqrt{t}]}{d(1/t)} = - \frac{\ell^2}{4D} \qquad 8$$

diffusivity can be calculated.

The summations up to the third term of the "Small-t" and "Large-t" expansion approximations are compared with the exact value of the relative flow rates in Table 1. In the range where y is larger than 0.1 only one term of the "Small-t" expansion is required. One term of the "Large-t" expansion is sufficient in the range where y is smaller than 0.4. These two expansions are complementary to each other in the evaluation of actual test data. The comparisons are shown in Figure 1.

APPENDIX

Derivation of "Small-t" Expansion

The diffusion equation for one dimensional flow is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[D\frac{\partial C}{\partial x}\right] \qquad \text{A-1}$$

If D is constant, we have

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad \text{A-2}$$

By Laplace transformation

$$\int_0^\infty e^{-pt}\frac{\partial^2 C}{\partial x^2}\,dt = \frac{\partial^2}{\partial x^2}\int_0^\infty e^{-pt}C\,dt = \frac{\partial^2 \overline{C}}{\partial x^2} \qquad \text{A-3}$$

where

$$\overline{C} = \int_0^\infty e^{-pt}C\,dt \qquad \text{A-4}$$

We also have

$$\int_0^\infty e^{-pt}\left(\frac{\partial C}{\partial t}\right)dt = \left[Ce^{-pt}\right]_0^\infty + p\int_0^\infty Ce^{-pt}dt \qquad \text{A-5}$$

$$= -C(t=o) + p\overline{C}$$

The diffusion equation, A-2, is

$$\frac{\partial^2 C}{\partial x^2} - \frac{p}{D}\,\overline{C} + \frac{C(t=o)}{D} = 0 \qquad \text{A-6}$$

(i) For the "Breakthrough" process we have C(t=0)=0 and

$$\frac{\partial^2 C}{\partial x^2} - q^2\,\overline{C} = 0 \qquad \text{A-7}$$

where

$$q^2 = \frac{p}{D} \qquad \text{A-8}$$

The solution of the equation A-7 is

$$\overline{C} = C_A e^{-qx} + C_B e^{qx} \qquad \text{A-9}$$

By boundary conditions for t>o

$$\text{At } x = 0,\ C = C_o,\ \overline{C} = C_o/p \qquad \text{A-10}$$

$$\text{At } x = \ell,\ C = 0,\ \overline{C} = 0$$

the constants in equation A-9, C_A and C_B are solved by A-9, and A-10.

$$C_A + C_B = C_o/p$$

$$C_A e^{-q\ell} + C_B e^{q\ell} = 0 \qquad \text{A-11}$$

which give

$$C_A = \frac{Co}{p} \frac{1}{1-e^{-2q\ell}}$$

$$C_B = \frac{Co}{p} \frac{e^{-2q\ell}}{1-e^{-2q\ell}} \qquad \text{A-12}$$

The solution A-9 is

$$\overline{C} = \frac{Co}{p} \frac{1}{1-e^{-2q\ell}} \left[e^{-qx} - e^{qx - 2q\ell}\right] \qquad \text{A-13}$$

By expansion

$$(1-e^{-2q\ell})^{-1} \sum_{n=o}^{\infty} e^{-2qn\ell} \qquad \text{A-14}$$

We have

$$\overline{C} = C_o \sum_{n=o}^{\infty} \left[\frac{e^{-q(2n\ell+x)}}{P} - \frac{e^{-q\{2(n+1)\ell-x\}}}{p}\right] \qquad \text{A-15}$$

The inverse Laplace transformation on A-15 gives

$$C = C_o \sum_{n=o}^{\infty} \left[\text{erfc}\ \frac{2n\ell+x}{2\sqrt{Dt}} - \text{erfc}\ \frac{2(n+1)\ell-x}{2\sqrt{Dt}}\right] \qquad \text{A-16}$$

where

$$\text{erfe}(Z) = \frac{2}{\sqrt{\Pi}} \int_{Z}^{\infty} e^{-Z'^2} dZ'$$

$$= 1 - \frac{2}{\sqrt{\Pi}} \int_{0}^{Z} e^{-Z'^2} dZ' \qquad \text{A-17}$$

$$= 1 - \text{erf}(Z)$$

and

$$\frac{\partial}{\partial Z} (\text{erf } Z) = \frac{2}{\sqrt{\Pi}} \; e^{-Z^2} \qquad \text{A-18}$$

The flow rate J(t) is defined by

$$J(t) = -D \left(\frac{\partial C}{\partial x}\right)_{x=\ell} \qquad \text{A-19}$$

By equations A-16, A-17, A-18 and A-19, J(t) is

$$J(t) = 2C_o \sqrt{\frac{D}{\Pi t}} \sum_{n=o}^{\infty} \exp \left[- \frac{(2n+1)^2 \ell^2}{4Dt}\right] \qquad \text{A-20}$$

At the steady state

$$\frac{\partial C}{\partial t} = 0 = D \frac{\partial^2 C}{\partial x^2} \qquad \text{A-21}$$

and the boundary conditions we have

$$C = C_o(1 - \frac{X}{\ell}) \qquad \text{A-22}$$

and

$$J_s = \frac{DC_o}{\ell} \qquad \text{A-23}$$

The equations A-20 and A-23 give the relative flow rate

$$y = \frac{J_s - J(t)}{J_s} = 1 - \frac{2\ell}{\sqrt{\Pi Dt}} \sum_{n=o}^{\infty} \exp \left[- \frac{(2n+1)^2 \ell^2}{4Dt}\right] \qquad \text{A-24}$$

This is the final form of the "Breakthrough" case.

(ii) For the "pump-out" case at t = 0 (steady state)

$$\frac{\partial C_s}{\partial t} = 0 = D\left(\frac{\partial^2 C_s}{\partial x^2}\right)_{t=o} \qquad \text{A-25}$$

and $C_s = C_o\ (1 - \frac{x}{\ell})$ (A-22)

where $C_s = C(t=o)$

The equations, A-6 and A-22, lead to

$$\frac{\partial^2 \overline{C}}{\partial x^2} - \frac{p}{D} + \frac{C_s}{D} = 0 \qquad \text{A-26}$$

With definition of a new variable $\overline{C}'$

$$\overline{C}' = \frac{C_s}{p} - \overline{C} \qquad \text{A-27}$$

the equation A-26 is given by

$$\frac{\partial^2}{\partial x^2}\left[\frac{C_s}{p} - \overline{C}'\right] - \frac{p}{D}\left[\frac{C_s}{p} - \overline{C}'\right] + \frac{C_s}{D} = 0 \qquad \text{A-28}$$

But by A-25

$$\frac{\partial^2}{\partial x^2}\left[\frac{C_s}{p}\right] = 0 \qquad \text{A-29}$$

A-28 is now

$$-\frac{\partial^2}{\partial x^2}\overline{C}' + \frac{p}{D}\overline{C}' = 0 \qquad \text{A-30}$$

or

$$\frac{\partial^2 \overline{C}'}{\partial x^2} - q^2\overline{C}' = 0 \qquad \text{A-31}$$

where $q^2 = \frac{p}{D}$. This has same form as the equation A-7.

The boundary conditions for t > o

At x=o, C=o, C=o, $\overline{C}' = \frac{Co}{p}$ A-32

At $x=\ell$, C=o, $\overline{C}$=o, $\overline{C}'$=o

These are the same as conditions in A-10 except $\overline{C}'$ instead of $\overline{C}$. By A-15 the solution of A-31 is

$$\overline{C}' = Co \sum_{n=o}^{\infty} \left[\operatorname{erfc} \frac{2n\ell+x}{2\sqrt{Dt}} - \operatorname{erfc} \frac{2(n+1)\ell-x}{2\sqrt{Dt}} \right] \qquad \text{A-33}$$

The inverse Laplace transformation of $\overline{C} = (C_s/p) - \overline{C}'$ gives

$$C = C_s - Co \sum_{n=o}^{\infty} \left[\operatorname{erfc} \frac{2n\ell+x}{2\sqrt{Dt}} - \operatorname{erfc} \frac{2(n+1)\ell-x}{2\sqrt{Dt}} \right] \qquad \text{A-34}$$

The flow rate is then

$$J(t) = J_s - 2\ Co \sqrt{\frac{D}{\Pi t}} \sum_{n=o}^{\infty} \exp \left[- \frac{(2n+1)^2 \ell^2}{4Dt} \right] \qquad \text{A-35}$$

or the relative flow rate

$$y = \frac{J(t)}{J_s} = 1 - \frac{2\ell}{\sqrt{\Pi Dt}} \sum_{n=o}^{\infty} \exp \left[- \frac{(2n+1)^2 \ell^2}{4Dt} \right] \qquad \text{A-36}$$

This is the final form of the "pump-out" case and has exactly the same as equation A-24 for the "Breakthrough" case.

In both cases the relative flow rate is given by

$$y = 1 - \frac{2\ell}{\sqrt{\Pi Dt}} \sum_{n=o}^{\infty} \exp \left[- \frac{(2n+1)^2 \ell^2}{4Dt} \right]$$

For the "Pump-Out" case $y = J(t)/Js$ and

for the "Breakthrough" Case $y = J - J(t) /Js$.

REFERENCES

1. W. G. Perkins and D. R. Begeal, J. Chem. Phys. 54, 1683 (1971).

2. J. Crank, "The Mathematics of Diffusion," Oxford (1956).

3. H. S. Canslow and J. C. Jaeger, "Conduction of Heat in Solids." Oxford (1947).

4. R. M. Barrer, "Diffusion in and Through Solids," Cambridge (1951).

5. Computer program, DIFFUZ, in permeation calculation program package.

TABLE 1

Comparison of "Small-t" and "Large-t" Expansion with the Exact Values

$Z = \frac{Dt}{\ell^2}$	*"Small Time"* 1	2	3	*"Large Time"* 1	2	3	*Exact*
0.02	0.99997			1.64174	0.73366	1.07211	.99997
0.04	0.98911			1.34765	0.93534	0.99262	.98911
0.06	0.92858			1.10624	0.91904	0.92873	.92858
0.08	0.82472			0.90808	0.82308	0.82472	.82472
0.10	0.70710			0.74542	0.70682	0.70710	.70710
0.12	0.59441			0.61189	0.59437	0.59441	.59441
0.14	0.49433			0.50228	0.49432	0.49433	.49433
0.16	0.40870			0.41231	0.40869	0.40870	.40870
0.18	0.33682	0.33681		0.33845	0.33681		.33681
0.20	0.27711	0.27708		0.27782	0.27708		.27708
0.22	0.22780	0.22772		0.22806	0.22772		.22772
0.24	0.18725	0.18705		0.18720	0.18705		.18705
0.26	0.15399	0.15360		0.15367	0.15360		.15360
0.28	0.12680	0.12611		0.12614	0.12611		.12611
0.30	0.10467	0.10353		0.10355			.10355
0.32	0.08677	0.08499		0.08500			.08500
0.34	0.07236	0.06977		0.06977			.06977
0.36	0.06090	0.05727		0.05727			.05727
0.38	0.05192	0.04701		0.04701			.04701
0.40	0.04503	0.03859		0.03859			.03859
0.42	0.03989	0.03168		0.03168			.03168
0.44	0.03624	0.02601		0.02601			.03601
0.46	0.03385	0.02135		0.02135			.02135
0.48	0.03253	0.01753	0.01752	0.01752			.01752
0.50	0.03212	0.01439	0.01438	0.01438			.01438
0.60	0.03966	0.00540	0.00536	0.00536			.00536
0.70	0.05637	0.00218	0.00200	0.00200			.00200
0.80	0.07702	0.00126	0.00074	0.00074			.00074
0.90	0.09906	0.00143	0.00028	0.00028			.00028
1.00	0.12122	0.00229	0.00011	0.00010			.00010