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A Modified Random Walk Method for Plate Height Calculations

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NOTE

A Modified Random Walk Method for Plate Height Calculations

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Summary

A modified random walk method, based on the Aris integrals, has been formulated for the evaluation of plate height contributions. The method is simple to apply, yet yields values in exact correspondence with that obtained from Giddings' nonequilibrium theory.

INTRODUCTION

The two main methods currently available for the calculation of plate heights in chromatography are the generalized nonequilibrium (GNE) theory and the simple random walk (SRW) approach. Their relative merits are adequately discussed by Giddings (*1*). The GNE theory was developed specifically to handle the important mass-transfer terms in the plate height equation, i.e., the terms of the form $C'a^2u/D_R$,

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where C' = constant dependent on the geometry, the flow profile, and the mass distribution coefficient k, a = characteristic length, u = average longitudinal flow velocity, and D_R = column radial dispersion coefficient. The crucial shortcoming of the SRW theory is its inability to yield exact C' values. The modified random walk (MRW) approach described below represents an attempt to remedy this deficiency and is based on the recognition of the possibility of interpreting the integrals derived by Aris (*2*) in terms of a random walk mechanism.

THEORY

It has been shown previously (*3*) that the effective longitudinal diffusion coefficient D_e which is related to the local plate height H by

$$\mathrm{H} = 2D_e(1 + k)/u \tag{1}$$

is the product of three factors

$$D_e = \Lambda \cdot v^2 \cdot \Delta t \tag{2}$$

where v is the effective axial velocity of the random walk relative to the mean zone velocity during the time Δt, i.e., the average time required to complete a single random walk step. Λ is a multiplicative constant which includes the conditional transition probability. In the present treatment Λ will fill the role of an adjustable empirical constant and will be required to absorb the proportionality constant in the formulations of v and Δt. This semiempirical approach has been adopted since there is, in theories of a probabilistic nature, always the danger of fortuitous numerical agreement based on fallacious reasoning. In short, the method employed will consist of casting the Aris integrals, for the specific case of the coated capillary, in the form defined by Eq. (2). This automatically fixes the value of Λ in the subsequent generalizations of these integrals.

The resistance to mass-transfer contributions to the effective diffusion coefficient arising from nonequilibrium in the mobile and stationary phases have been formulated by Aris (*2*) as

$$D_{em} = \int_0^{r_1} (1 + k)\frac{r_1^2\, dr}{2rD_R}\left\{\int_0^r \frac{1}{(1 + k)}\cdot\frac{2\pi r'\, dr'}{\pi r_1^2}\left[u(r') - \frac{u}{1 + k}\right]\right\}^2 \tag{3}$$

and

$$D_{es} = \int_{r_1}^{r_2} \frac{(1+k)}{r} \cdot \frac{(r_2^2 - r_1^2)}{2rD_R} \left\{ \int_r^{r_2} \frac{k}{1+k} \cdot \frac{2\pi r'\, dr'}{\pi(r_2^2 - r_1^2)} \left[u(r') - \frac{u}{1+k} \right] \right\}^2 \tag{4}$$

where the integrals have been rearranged to facilitate a random walk interpretation.

It is obvious that these equations represent summations over all radial elements of thickness Δr in which resistance to radial mass transfer is experienced. This implies that the cross section is supposed to consist of a superposition of cylindrical shells of thickness Δr, each of which may be considered as an independent source of band broadening. The plate height contribution of an arbitrary element may thus be computed by allowing $D_R \rightarrow \infty$ in all regions except the one under consideration. This assumption corresponds to the additivity theorem in Giddings' work. Despite its intuitive plausibility, a rigorous proof is still lacking. An important corollary of this "theorem" is the possibility of treating the mobile and stationary phases as separate entities. Consider first a contribution from a single Δr element in the mobile phase. The factor

$$\Delta t_m = (1+k)\frac{r_1^2\, \Delta r}{4rD_R} \tag{5}$$

is seen to be of the order of the time required by a number of molecules, equal to that contained in the cross section, to have diffused through the barrier presented by the element of thickness Δr. This follows since the time for a δ distribution to spread out into a Gaussian, with standard deviation $\sigma = \Delta r$, is given by

$$\Delta t = (\Delta r)^2/2D_R \tag{6}$$

This would apply to molecules initially located within Δr; the time required for all the molecules within the cross-sectional slice to have been scattered by diffusion within Δr to either the inner or the outer side of Δr will be larger by a factor of the order $\pi r_1^2(1+k)/(2\pi r\, \Delta r)$. Similarly the Δt time for a stationary phase element is found to be of the order

$$\Delta t_s = \frac{(1+k)}{k} \cdot \frac{(r_2^2 - r_1^2)\Delta r}{4rD_R} \tag{7}$$

The factor

$$v_m = \int_0^r \frac{1}{(1+\mathrm{k})} \cdot \frac{\pi r^2}{\pi r_1^2} \cdot \frac{2\pi r'\, dr'}{\pi r^2} \left[u(r') - \frac{u}{1+k} \right] \tag{8}$$

in Eq. (3) will now be interpreted as expressing the effective axial velocity v_m of the random walk during the time Δt_m. The v is seen to be an average velocity relative to the mean solute velocity, $u/(1 + k)$, weighted at each r by the probability of finding a representative molecule in the mobile phase on that particular side of Δr. The total random walk is symmetrical so that it should be immaterial whether the effective velocity is taken in the inner or the outer regions (relative to Δr). That this is indeed the case is seen by explicit formulation of v for the outer region. Following the arguments outlined above, this yields

$$v_m = \int_0^{r_1} \mathrm{d}v_m + \int_{r_1}^{r_2} dv_s - \int_0^r dv_m \tag{9}$$

where dv_m follows from Eq. (8). The dv_s is similarly defined by the expression for the effective random walk velocity relative to a stationary phase element [see Eq. (4)]:

$$v_s = \int_r^{r_2} dv_s$$

$$= \int_r^{r_2} \frac{k}{(1+\mathrm{k})} \cdot \frac{\pi(r_2^2 - r^2)}{\pi(r_2^2 - r_1^2)} \cdot \frac{2\pi r' dr'}{\pi(r_2^2 - r^2)} \left[u(r') - \frac{u}{1+k} \right] \tag{10}$$

The sum of the first two integrals in Eq. (9) is zero, however, since all velocities are taken relative to the mean solute velocity $u/(1 + k)$. Since the velocities are squared in the final expression for D_e, the difference in sign is irrelevant, and it is thus immaterial whether the effective velocity of the inner or the outer region is taken. For mobile phase elements, the inner velocity is more convenient whereas the outer is more appropriate for elements located in the stationary phase. Comparison of the above results with the exact expressions, Eqs. (3) and (4), fixes the value of Λ at $\Lambda = 2$.

DISCUSSION

The results for the coated capillary outlined above may now readily be generalized to other chromatographic situations. In order to check

TABLE 1

Model	$k\Delta t/1 + k$	$(1 + k)\, v_s/k$	H
Uniform film of depth d	$\frac{d}{\Delta y}\cdot\frac{(\Delta y)^2}{2D_s}$	$\int_0^x - \frac{udx}{(1 + k)d}$	$\frac{2}{3}\cdot\frac{k}{(1 + k)^2}\cdot\frac{ud^2}{D_s}$
Cylinder of radius a	$\frac{\pi a^2}{2\pi r\, \Delta r}\cdot\frac{(\Delta r)^2}{2D_s}$	$\int_0^r - \frac{u}{(1 + k)}\cdot\frac{2\pi r'\, \mathrm{d}r'}{\pi a^2}$	$\frac{1}{4}\cdot\frac{k}{(1 + k)^2}\cdot\frac{ua^2}{D_s}$
Sphere of radius a	$\frac{\frac{4}{3}\pi a^3}{4\pi r^2\, \Delta r}\cdot\frac{(\Delta r)^2}{2D_s}$	$\int_0^r - \frac{u}{(1 + k)}\cdot\frac{4\pi(r')^2\, dr'}{\frac{4}{3}\pi a^3}$	$\frac{2}{15}\cdot\frac{k}{(1 + k)^2}\cdot\frac{ua^2}{D_s}$

for the concistency of the MRW method, a variety of stationary phase models was considered and compared with that of the GNE theory. The results are summarized in Table 1. In all cases exact correspondence was obtained. (A value of $\Lambda = 2$ was used in all the calculations.)

CONCLUSION

The MRW method presents an alternative method for the calculation of the mass-transfer terms in the plate height equation. Its advantages are simplicity and a direct link with the underlying physical processes. At present it is formally less satisfying than the GNE theory; the *ab initio* calculation of the Λ factor will have to await a more sophisticated treatment. Its main application is envisaged as an aid in the development of more reliable approximate methods for plate height calculations.

SYMBOLS

a	characteristic length (e.g., radius of cylinder)
C'	parameter in mass-transfer term
D_e	effective longitudinal diffusion coefficient
D_{em}	mobile phase contribution to D_e
D_{es}	stationary phase contribution to D_e
D_R	column radial dispersion coefficient

D_s	stationary phase diffusion coefficient
H	plate height
k	mass distribution coefficient
r	radial coordinate
r_1	radius of mobile phase region of coated capillary
r_2	inside radius of empty chromatographic column
t	time
u	average longitudinal carrier flow velocity
$u(r)$	radial velocity profile
v	effective axial velocity of random walk
v_m	v for mobile phase
v_s	v for stationary phase
y	coordinate measuring depth of stationary phase in uniform film model
A	multiplicative constant [Eq. (2)]

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