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Nonlinearity and Stationary Phase Nonequilibrium

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Abstract

A combination of the nonequilibrium method of Giddings and a statistical moment operator method is used to formulate the stationary phase contributions to the *r*th statistical moment in nonlinear chromatography. It is shown that these do not differ essentially from those of the mobile phase.

INTRODUCTION

In a recent series of papers (*1–3*) a theoretical analysis of the effect of isotherm nonlinearity on the statistical moments of chromatographic peaks was made. In these studies only mobile phase nonequilibrium contributions were considered. The present paper is an extension of the theory to include contributions arising from nonequilibrium in the stationary phase, and it will be shown that these do not differ essentially from that of the mobile phase. The method employed is a combination of the nonequilibrium theory of Giddings (*4*) and the operator method used in the moments studies mentioned above. Since the application of the nonequilibrium theory to the case of single site adsorption chromatography is discussed in detail in Giddings' book (*4*), only an outline

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of the extension to nonlinear distribution isotherms will be given. For convenience, symbolism will as far as possible be chosen to conform to that of Giddings.

THEORY

Concentration, Nonlinearity, and Nonequilibrium Parameters

The concentration of the solute in the mobile and stationary phases, C_m and C_s, are defined by

$$C_m = m_m/V_m \tag{1}$$

$$C_s = m_s/V \tag{2}$$

where m_m and m_s denote the masses of solute in the mobile and stationary phases, and V_m and V are the mobile phase and column volumes, respectively. The equilibrium departure terms ϵ_m and ϵ_s for the mobile and stationary phases are introduced by means of the equations

$$C_m = C_m^*(1 + \epsilon_m) \tag{3}$$

and

$$C_s = C_s^*(1 + \epsilon_s) \tag{4}$$

where C_m^* and C_s^* denote the equilibrium values of C_m and C_s.

At equilibrium, C_s^* is related to C_m^* through the nonlinear distribution isotherm (e.g., Ref. *1*)

$$\begin{aligned} C_s^* &= K_1C_m^* + K_2(C_m^*)^2 \\ &= \epsilon k_1C_m^* + \epsilon k_2(C_m^*)^2 \end{aligned} \tag{5}$$

where

$$\epsilon = V_m/V \tag{6}$$

is the void fraction and

$$K_1 = \epsilon k_1 \tag{7}$$

$$K_2 = \epsilon k_2 \tag{8}$$

are isotherm parameters.

The total mass of solute in the column is given by

$$\begin{aligned} m &= m_s + m_m \\ &= C_sV + C_mV_m \end{aligned} \tag{9}$$

and also by

$$m = C_s^*V + C_m^*V_m \tag{10}$$

From Eqs. (3), (4), (9), and (10) the following relationship between ϵ_s and ϵ_m is obtained

$$\epsilon_s = -\frac{C_m^*}{C_s^*}\epsilon\epsilon_m \qquad (11)$$

Relation of Mass Transfer Kinetics to Nonequilibrium and Nonlinearity

If it is assumed that only the adsorption rate constant is concentration dependent, then the mobile phase mass transfer term s_m is given by

$$\begin{aligned} s_m &= \left(\frac{dC_m}{dt}\right)_{\text{mass transfer}} \\ &= \frac{1}{\epsilon}k_dC_s - (k_{a_1} + k_{a_2}C_m)C_m \qquad (12) \end{aligned}$$

Equation (12) conforms to the nonlinear distribution isotherm (Eq. 5) since at equilibrium $s_m = 0$ and

$$\begin{aligned} C_s^* &= \epsilon\left(\frac{k_{a_1}}{k_d}\right)C_m^* + \epsilon\left(\frac{k_{a_2}}{k_d}\right)(C_m^*)^2 \\ &= \epsilon k_1C_m^* + \epsilon k_2(C_m^*)^2 \qquad (13) \end{aligned}$$

where k_1 and k_2 are now given by

$$k_1 = k_{a_1}/k_d \qquad (14)$$

and

$$k_2 = k_{a_2}/k_d \qquad (15)$$

Substitution of Eqs. (3) and (4) into Eq. (12) gives

$$s_m = \frac{1}{\epsilon}k_d\{C_s^*\epsilon_s - [\epsilon k_1C_m^* + 2\epsilon k_2(C_m^*)^2]\epsilon_m\} \qquad (16)$$

where Eq. (13) has been used and the term in ϵ_m^2 has been neglected. By using Eq. (11), ϵ_s may be eliminated from Eq. (16) to give

$$s_m = -k_d\epsilon_mC_m^*(1 + k_1)(1 + \lambda C_m^*) \qquad (17)$$

where

$$\lambda = 2k_2/(1 + k_1) \qquad (18)$$

is the nonlinearity parameter (see, e.g., Refs. *1–3*).

Mass Transfer Rate and Flow

A second expression for s_m may now be obtained by application of the near-equilibrium hypothesis $(\partial C_m/\partial t \approx \partial C_m{}^*/\partial t,\ \partial C_m/\partial z \approx \partial C_m{}^*/\partial z)$. The treatment is identical to that of Giddings with the exception that the relationship between the derivatives of the overall concentration C defined by (see Eqs. 10 and 13)

$$\begin{aligned} C &= m/V \\ &= \epsilon(1 + k_1)C_m{}^* + \epsilon k_2(C_m{}^*)^2 \end{aligned} \tag{19}$$

and $C_m{}^*$ now becomes

$$\frac{\partial C}{\partial t} = \epsilon(1 + k_1)(1 + \lambda C_m{}^*)\frac{\partial C_m{}^*}{\partial t} \tag{20}$$

and

$$\frac{\partial C}{\partial z} = \epsilon(1 + k_1)(1 + \lambda C_m{}^*)\frac{\partial C_m{}^*}{\partial z} \tag{21}$$

so that substitution into the mass conservation equation

$$\frac{\partial C_m}{\partial t} = s_m - u\frac{\partial C_m}{\partial z} \tag{22}$$

yields

$$s_m = \frac{1}{\epsilon(1 + k_1)(1 + \lambda C_m{}^*)}\left\{\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial z}\right\} \tag{23}$$

when the near-equilibrium hypothesis is applied.

The term $\partial C/\partial t$ in Eq. (23) may now be written in terms of $\partial C_m{}^*/\partial z$ by noting that

$$\frac{\partial C}{\partial t} = \epsilon\left(\frac{dC_m}{dt}\right)_{\text{flow}} = -\epsilon u\frac{\partial C_m}{\partial z} \approx -\epsilon u\frac{\partial C_m{}^*}{\partial z} \tag{24}$$

where the first equality follows since the net gain in C is due solely to mobile phase flow. s_m thus follows as

$$s_m = (1 - R')u\frac{\partial C_m{}^*}{\partial z} \tag{25}$$

where

$$R' = \frac{1}{(1 + k_1)(1 + \lambda C_m{}^*)} \tag{26}$$

From the two expressions for s_m (Eqs. 17 and 25), ϵ_m is obtained as

$$\epsilon_m = -\frac{R'(1 - R')u}{k_d}\frac{1}{C_m{}^*}\frac{\partial C_m{}^*}{\partial z} \tag{27}$$

The additional solute flux due to nonequilibrium

$$\Delta J = \epsilon_m C_m{}^* u$$

is thus given by

$$\Delta J = \frac{(R')(1 - R')u^2}{k_d}\frac{\partial C_m{}^*}{\partial z}$$

or, from Eq. (21), by

$$\Delta J = \frac{(R')^2(1 - R')u^2}{\epsilon k_d}\frac{\partial C}{\partial z} \tag{28}$$

Comparison of Eq. (28) with Fick's first law of diffusion

$$\Delta J = -D_{es}\frac{\partial C}{\partial z} \tag{29}$$

shows the effective diffusion coefficient, D_{es}, to be given by

$$D_{es} = \frac{(R')^2(1 - R')u^2}{\epsilon k_d} \tag{30}$$

The overall change of concentration with time is thus given by

$$\frac{\partial C}{\partial t} = -u_{es}\frac{\partial C}{\partial z} + \frac{\partial}{\partial z}D_{es}\frac{\partial C}{\partial z} \tag{31}$$

where the diffusional contribution follows from Eq. (29) and the equivalence of the two formulations of the diffusion equation (*5, 6*) while the flow contribution is obtained from Eqs. (21) and (24) with

$$u_{es} = R'u \tag{32}$$

DISCUSSION

Equation (31) is now in the required form for the moments analysis. u_{es} and D_{es} may also be written in terms of the total concentration by using the relation (see Eq. 19)

$$C_m{}^* = \frac{1}{\lambda}[-1 + (1 + \lambda' C)^{1/2}] \tag{33}$$

where

$$\lambda' = 2\lambda/\epsilon(1 + k_1) \tag{34}$$

Differentiation of the diffusional term may then be carried out. If $\lambda' C$ is assumed to be smaller than unity, the coefficients in the resulting differential equation may be expanded in a binomial series giving

$$\begin{aligned} \frac{\partial C}{\partial t} = & -U \sum_{n=0}^{\infty} \frac{(-\frac{1}{2})!}{n!(-\frac{1}{2} - n)!} (\lambda' C)^n \frac{\partial C}{\partial z} \\ & + D \sum_{n=0}^{\infty} \left\{ (1 + k_1) \frac{(-1)!}{n!(-1 - n)!} - \frac{(-\frac{3}{2})!}{n!(-\frac{3}{2} - n)!} \right\} (\lambda' C)^n \frac{\partial^2 C}{\partial z^2} \\ & + D\lambda' \sum_{n=0}^{\infty} \left\{ -(1 + k_1) \frac{(-2)!}{n!(-2 - n)!} + \frac{3}{2} \frac{(-\frac{5}{2})!}{n!(-\frac{5}{2} - n)!} \right\} (\lambda' C)^n \left[\frac{\partial C}{\partial z} \right]^2 \end{aligned} \tag{35}$$

A general expression for the rth moment can now be obtained by operating on both sides of Eq. (35) with the rth moment operator

$$\frac{1}{m_0} \int_{-\infty}^{+\infty} \chi^r \, dz \tag{36}$$

where m_0 (constant) is the zeroth moment and χ is given by z or $(z - \langle z \rangle)$ for ordinary or central moments, respectively. The rate of change of the rth moment, m_r, follows as

$$\begin{aligned} \frac{dm_r}{dt} = & \; r m_{r-1} \frac{d\chi}{dt} + \frac{rU}{m_0} \sum_{n=0}^{\infty} \frac{(-\frac{1}{2})!}{(n + 1)!(-\frac{1}{2} - n)!} (\lambda')^n \int_{-\infty}^{+\infty} \chi^{r-1} C^{n+1} \, dz \\ & + \frac{r(r - 1)D}{m_0} \sum_{n=0}^{\infty} \left\{ (1 + k_1) \frac{(-1)!}{(n + 1)!(-1 - n)!} \right. \\ & \left. - \frac{(-\frac{3}{2})!}{(n + 1)!(-\frac{3}{2} - n)!} \right\} (\lambda')^n \int_{-\infty}^{+\infty} \chi^{r-2} C^{n+1} \, dz \end{aligned} \tag{37}$$

The effective transport equation for elution under conditions where only mobile phase nonequilibrium is considered is given by

$$\frac{\partial C}{\partial t} = -u_{em}\frac{\partial C}{\partial z} + \frac{\partial}{\partial z} D_{em} \frac{\partial C}{\partial z} \tag{38}$$

which is simply the equation previously used (*1–3*) rewritten in terms of the total concentration. u_{em} and D_{em} are convenient abbreviations for

$$u_{em} = U/(1 + \lambda' C)^{1/2} \tag{39}$$

$$D_{em} = D_e/(1 + \lambda' C)^{1/2} \tag{40}$$

A procedure similar to that above yields

$$\frac{dm_r}{dt} = rm_{r-1}\frac{d\chi}{dt} + \frac{rU}{m_0}\sum_{n=0}^{\infty}\frac{(-\frac{1}{2})!}{(n+1)!(-\frac{1}{2}-n)!}(\lambda')^n \times \int_{-\infty}^{+\infty} \chi^{r-1}C^{n+1}\,dz + \frac{r(r-1)D_e}{m_0}\sum_{n=0}^{\infty}\frac{(-\frac{1}{2})!}{(n+1)!(-\frac{1}{2}-n)!}(\lambda')^n \times \int_{-\infty}^{+\infty} \chi^{r-2}C^{n+1}\,dz \tag{41}$$

Although the expressions are given to an arbitrary order in λ', inclusion of terms up to and including second order are usually adequate.

The integrals appearing in Eqs. (37) and (41) are seen to be identical, so that the results obtained earlier (*1–3*) for mobile phase nonequilibrium can be directly applied with minor modifications to the present situation. Indeed, the velocity terms in Eqs. (37) and (41) are seen to be identical while the diffusional terms differ merely by a characteristic coefficient. There are thus no novel phenomena associated with stationary phase nonequilibrium contributions in nonlinear chromatography, which confirms the intuitive views expressed in a previous paper (*2*).

SYMBOLS

C	overall solute concentration (Eq. 19)
C_m	solute concentration in mobile phase (Eq. 1)
$C_m{}^*$	equilibrium value of C_m

C_s	concentration of adsorbed solute (Eq. 2)
C_s^*	equilibrium value of C_s
D	effective diffusion coefficient due to stationary phase nonequilibrium ($\lambda = 0$)
D_e	effective diffusion coefficient due to mobile phase nonequilibrium ($\lambda = 0$)
D_{em}	D_e for $\lambda \neq 0$
D_{es}	D for $\lambda \neq 0$
ΔJ	additional solute flux due to nonequilibrium
K_i	($i = 1, 2$) parameters in nonlinear distribution isotherm (Eq. 5)
k_i	($i = 1, 2$) $= K_i/\epsilon$
k_{ai}	($i = 1, 2$) parameters in concentration dependent adsorption rate coefficient (Eq. 12)
k_d	desorption rate constant (Eq. 12)
m	$= m_s + m_m$: total mass of solute
m_m	mass of solute in mobile phase
m_r	rth moment
m_s	mass of solute in stationary phase
r	number indicating rth moment
R'	convenient parameter (Eq. 26)
s_m	mobile phase mass transfer term (Eq. 12)
t	time
U	$= u/(1 + k_1)$
u	mobile phase flow velocity
u_{em}	effective velocity coefficient with mobile phase nonequilibrium
u_{es}	effective velocity coefficient with stationary phase nonequilibrium
V	column volume
V_m	mobile phase volume
z	axial distance coordinate

Greek Letters

ϵ_m	mobile phase equilibrium departure term
ϵ_s	stationary phase equilibrium departure term
ϵ	void fraction (Eq. 6)
λ	nonlinearity parameter (Eq. 18)
λ'	convenient nonlinearity parameter (Eq. 34)
χ	$= z$ or $z - \langle z \rangle$ (Eq. 36)

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