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MOMENT ANALYSIS IN NON-LINEAR FRONTAL-ELUTION AND ELUTION CHROMATOGRAPHY*

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SUMMARY

Analytical formulae are presented for the statistical moments of an output chromatographic curve for non-linear distribution isotherms at a very narrow feed band ("elution chromatography"). Non-linear "frontal-elution chromatography", *i.e.*, the case of a very wide feed band, is also considered. The analytical expressions characterize the position and the width of sorption and desorption boundaries of the output curve. The column length at which a constant configuration of the sorption (or desorption) boundary is attained is dependent on the curvature of the isotherm and on the plate height. The results have been confirmed experimentally.

INTRODUCTION

Broadening of chromatographic zones accompanying the movement of solute through a porous medium reduces the efficiency of resolution in chromatographic columns. The effect results from the finite rate of mass transport between the phases (kinetics) and from various irregularities in the flow caused by the disordered porous structure which are described by the longitudinal diffusion coefficient, D (ref. 1).

The broadening of zones leads to their overlapping to an extent which depends on the width of the zones and on the distance between them. The width of chromatographic bands is dependent, among other things, on the linearity of the distribution isotherm.

The parameters which characterize the movement and broadening of chromatographic zones have been quantitated theoretically for linear distribution isotherms[2–12] by the use of statistical moments. In the case of non-linear distribution isotherms, the statistical moments of elution curves have often been interpreted by use of computer simulations[13–17]. This paper presents an attempt to obtain analytical formulae for the statistical moments of an chromatographic output curve in non-

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linear elution at very narrow and at very wide feed bunds. The treatment which is described is applicable equally to all forms of gas and liquid chromatography.

THEORETICAL

The quantitative description of the effects of non-linearity in chromatographic profiles is difficult due to the necessity of solving the non-linear differential equations that describe mass transport by the mobile phase in a chromatographic column:

$$\frac{\partial a'}{\partial t} + \frac{\partial c'}{\partial t} + u\frac{\partial c'}{\partial x} = D\frac{\partial^2 c'}{\partial x^2} \tag{1}$$

$$\frac{\partial a'}{\partial t} = \Psi(a', c') \tag{2}$$

where c' is the concentration of the solute in the mobile phase, a' is the mass of the solute in the stationary phase per unit volume of the mobile phase, u is the linear velocity of the mobile phase, D is the longitudinal diffusion coefficient and x is the distance along the column. An approximate solution of eqns. 1 and 2 has been proposed[16-18] based on the use of statistical moments together with expansion into series in the non-linearity parameter of the isotherm. The small-parameter method is suitable for arbitrary concave and convex isotherms with small deviations from linearity. The expression describing such isotherms in terms of dimensionless concentration, $c = c'/c_0$, can be presented as

$$f(c) = \gamma(c + \varepsilon c^2) \tag{3}$$

where c_0 is the maximum value of the concentration c', γ is Henry's coefficient and ε (which equals $[f(1) - \gamma]/\gamma$) is the non-linearity parameter of the isotherm. Concave ($\varepsilon > 0$), linear ($\varepsilon = 0$) and convex ($\varepsilon < 0$) isotherms are presented in Fig. 1.

The solution of eqns. 1 and 2 at $|\varepsilon| \ll 1$ can be approximately presented as

$$c(x,t) = c_{(0)}(x,t) + \varepsilon c_{(1)}(x,t) \tag{4}$$

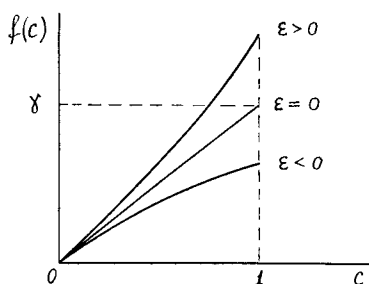where $c_{(0)}$ is the solution of eqns. 1 and 2 for the linear isotherm γc and c_1 is the first

Fig. 1. Concave ($\varepsilon > 0$), linear ($\varepsilon = 0$) and convex ($\varepsilon < 0$) distribution isotherms; c = dimensionless concentration.
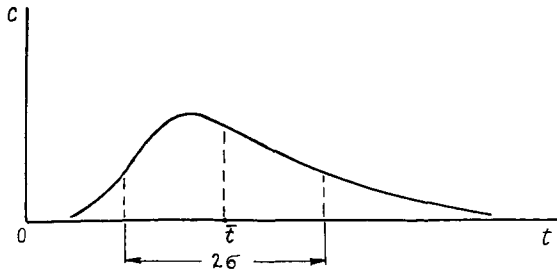
Fig. 2. Output concentration curve in elution chromatography; $\sigma = \sqrt{\overline{(t - \bar{t})^2}}$.

order solution of eqns. 1 and 2. On substituting eqn. 4 into eqns. 1 and 2 we obtain, to the first approximation, linearized partial differential equations with linear boundary conditions. From these equations the ordinary differential equations for the statistical moments of the output curve (at $x =$ constant), or for the moments of the distribution of concentration along the column (at $t =$ constant), can be easily derived.

Previously[18–21], we have derived the analytical relations for the statistical moments in two variants of the problem: equilibrium non-linear chromatography at $D \neq 0$, and non-equilibrium non-linear chromatography at $D = 0$.

Here we shall consider two modes of chromatographic operation for which the names "elution" and "frontal-elution" have been suggested[22]. In "elution chromatography" the feed band width, L_0 is sufficiently small, i.e., $L_0 < \frac{1}{2} \sqrt{LH}$ where L is the column length and H is the height equivalent to a theoretical plate (HETP). In this case the output curve may be considered as a distribution curve or as a probability-density curve. Any distribution curve can be described by statistical moments which represent in particular such important parameters of an elution curve as its centre of gravity, width (dispersion) (Fig. 2) and distortion or skewness[2–19].
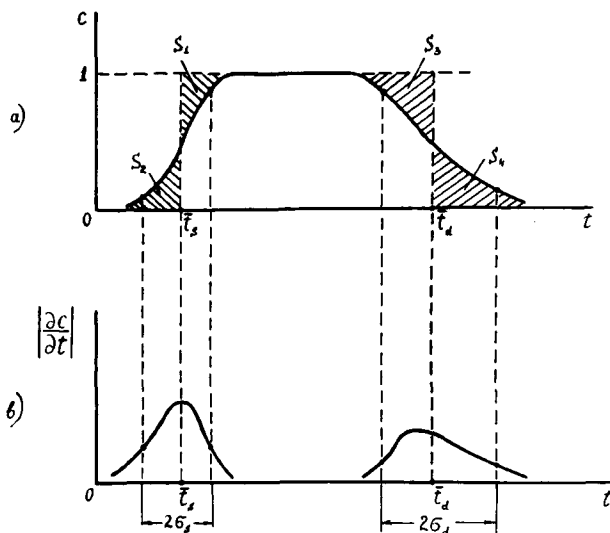

Fig. 3. (a), Output concentration band in frontal-elution chromatography; (b), the corresponding functions $\partial c / \partial t$ for the sorption and desorption boundaries of the band (for details see text).

In "frontal-elution chromatography" the feed band is very wide, $L_0 > 6\sqrt{LH}$, and a plateau of constant height, c_0, appears on the output concentration curve (Fig. 3a). The chromatographic band in this case has two frontal boundaries (sorption and desorption) that are sufficiently separated to exclude considerable interaction. Each boundary may be considered as an integral probability curve. The functions $\partial c/\partial t$ for the sorption boundary and $-\partial c/\partial t$ for the desorption boundary represent probability-density curves (Fig. 3b). Analytical expressions have been obtained for the statistical moments which characterize these curves. As can be seen from Fig. 3, the first moments, $\bar{t}_s$ and $\bar{t}_d$, and the second central moments, $\sigma_s{}^2$ and $\sigma_d{}^2$, determine the centre of gravity and the width of the sorption and desorption boundaries respectively. The vertical lines through the centres of gravity, $\bar{t}_s$ and $\bar{t}_d$, define boundaries so that $S_1 = S_2$ and $S_3 = S_4$ (Fig. 3a). To our knowledge, moment analysis has not been used in frontal-elution non-linear chromatography. In this paper part of the theoretical results obtained in refs. 18–20 are reported, but we shall restrict ourselves to the relations which describe the moments of the output chromatographic curve in equilibrium chromatography.

Let us start with the expressions for the moments of the $c(L, t)$ output curve in the elution mode[19]

$$\bar{\tau} \equiv \frac{u\bar{t}}{1 + \gamma} = L + H + \frac{\varepsilon\chi}{\sqrt{2\pi}} \cdot L_0 \sqrt{2N} \tag{5}$$

$$\mu_2 \equiv \frac{u^2\overline{(t - \bar{t})^2}}{(1 + \gamma)^2} = LH + 2H^2 + \frac{\varepsilon\chi}{2\sqrt{2\pi}} \cdot L_0 H \sqrt{2N} \tag{6}$$

$$\mu_3 \equiv \frac{u^3\overline{(t - \bar{t})^3}}{(1 + \gamma)^3} = 3LH^2 + 8H^3 - \frac{\varepsilon\chi}{4\sqrt{2\pi}} \cdot L_0 H^2 \left[(2N)^{3/2} - \frac{21}{8} \sqrt{2N}\right] \tag{7}$$

$$\bar{t} = \int_0^\infty tc(L,t) \, dt \Big/ \int_0^\infty c(L,t) \, dt; \; \chi = \frac{\gamma}{1 + \gamma} \tag{8}$$

$$\overline{(t - \bar{t})^n} = \int_0^\infty (t - \bar{t})^n c(L,t) \, dt \Big/ \int_0^\infty c(L,t) \, dt \quad n = 2, 3, \text{etc.} \tag{9}$$

N is the number of theoretical plates in the column. Using the above method the following equations were obtained for the first and the second moments characterizing the sorption and desorption boundaries of the output curve in frontal-elution equilibrium chromatography[20]:

$$\bar{\tau}_s \equiv \frac{u\bar{t}_s}{1 + \gamma} = (1 + \varepsilon\chi)\left(L - L_0 + \frac{H}{2}\right) \tag{10}$$

$$\mu_{2s} \equiv \frac{u^2\sigma_s{}^2}{(1 + \gamma)^2} = (1 + 2\varepsilon\chi) H (L - L_0) + \varepsilon\chi \cdot \frac{4}{3} \sqrt{\frac{H}{\pi}} (L - L_0)^{3/2} +$$
$$+ \varepsilon\chi \cdot \frac{9H^{3/2}}{4\sqrt{\pi}} \sqrt{(L - L_0)} + K_1 \tag{11}$$

$$\bar{\tau}_d = \frac{u \cdot \bar{t}_d}{1 + \gamma} = (1 + \varepsilon\chi)\left(L + \frac{H}{2}\right) \tag{12}$$

$$\mu_{2d} \equiv \frac{u^2 \cdot \sigma_d^2}{(1 + \gamma)^2} = (1 + 2\varepsilon\chi) \cdot HL - \varepsilon\chi \cdot \frac{4}{3}\sqrt{\frac{H}{\pi}} \cdot L^{3/2} -$$

$$- \varepsilon\chi \cdot \frac{9H^{3/2}}{4\sqrt{\pi}}\sqrt{L} + K_2 \tag{13}$$

Here $\sigma_s^2 = \overline{(t - \bar{t}_s)^2}$, $\sigma_d^2 = \overline{(t - \bar{t}_d)^2}$ and K_1 and K_2 are constants. Substitution of $L_0 = 0$ into eqns. 10 and 11 yields equations which are in agreement with similar relations for the theory of non-equilibrium frontal-sorption dynamics[21]. Expressions 10 and 11 at $L_0 = 0$ can be used for estimation of the retention time and of the width of the output profile in the case of equilibrium frontal-sorption dynamics.

It follows from eqns. 10 and 12 that the centres of gravity $\bar{t}_s$ and $\bar{t}_d$ (Fig. 3a) pass along the column at a rate $v_0 = u/(1 + \gamma + \gamma\varepsilon)$. According to Weyde and Wicke[23], the rate of the point of the front at height c is $v_c = u/[1 + df(c)/dt]$. Thus the centres of gravity $\bar{t}_s$ and $\bar{t}_d$ move with the same velocity as the point of the front at height $c = \frac{1}{2}(c' = c_0/2)$. This velocity is larger for convex (smaller for concave) isotherms than for linear isotherms.

Eqns. 11 and 13 allow us to evaluate the column length, L_s (or L_d), at which a constant configuration of the sorption boundary for a convex isotherm (or desorption boundary for a concave isotherm) is attained:

$$L_s = L_0 + \frac{9\pi}{16} H\left(\frac{1 + 2\varepsilon\chi}{\varepsilon\chi}\right)^2, \ \varepsilon < 0 \tag{14}$$

$$L_d = \frac{9\pi}{16} H\left(\frac{1 + 2\varepsilon\chi}{\varepsilon\gamma}\right)^2, \quad \varepsilon > 0 \tag{15}$$

For example, when $\varepsilon\chi = -0.1$, $L_s = L_0 + 112H$ and when $\varepsilon\chi = 0.1$, $L_d = 255H$. The sorption boundary widens progressively for concave isotherms and the desorption boundary widens for convex isotherms. In these cases the widening of boundaries at large L is determined mainly by the second terms in eqns. 11 and 13. As can be seen from these equations, when L is large in non-linear chromatography the widening of the boundaries is represented by

$$u \cdot \sigma_s \approx H^{1/4} L^{3/4} \sqrt{\varepsilon}, \ \varepsilon > 0 \tag{16}$$

$$u \cdot \sigma_d \approx H^{1/4} L^{3/4} \sqrt{|\varepsilon|}, \ \varepsilon < 0 \tag{17}$$

It is well known[7] that in linear chromatographic systems the standard deviation, σ, of the boundary is determined by $u \cdot \sigma \approx \sqrt{HL}$. Thus, eqns. 14 and 15 can be used to calculate the length of the column at which a constant configuration of the sorption (or desorption) boundary is attained. The broadening of these boundaries at the outlet

TABLE I

VALUES OF THE MOMENTS $\bar{\tau}$, μ_2 AND μ_3 OF THE OUTPUT CURVE FOR COLUMNS OF VARIOUS LENGTHS FOR Ca^{2+}–Mg^{2+} EXCHANGE

$\gamma = 25.7$; $\varepsilon = -0.5$; $L_0 = 1.5$ cm; $H = 0.62$ cm.

L (cm)	$\bar{\tau}$ (cm)		μ_2 (cm^2)		μ_3 (cm^3)	
	Exptl.	Calculated according to eqn. 5*	Exptl.	Calculated according to eqn. 6*	Exptl.	Calculated according to eqn. 7*
27	23.1	24.9 (27.6)	13.0	16.7 (17.5)	34.4	53.8 (31.2)
34.5	29.9	32.1 (35.1)	20.0	21.2 (22.0)	60.7	72.4 (39.9)
40.4	35.4	37.7 (41.0)	24.0	24.8 (25.8)	79.6	88.0 (46.7)
46.4	41.0	43.5 (47.0)	28.1	29.8 (31.0)	81.2	96.0 (58.9)
51.8	45.7	48.8 (52.5)	31.6	32.3 (33.5)	115.5	116.4 (61.9)

* Values in parentheses: $\varepsilon = 0$.

of the column in non-linear frontal-elution chromatography can be estimated from eqns. 11 and 13.

EXPERIMENTAL

A set of output chromatographic curves for calcium and strontium with narrow and wide feed bands was obtained in order to check eqns. 5–13. The experiments were made with ion-exchange columns of different lengths, L (cross-section, 0.435 cm²), packed with KU-2-X6 (Mg) resin. Ion-exchange isotherms for Ca^{2+} and Mg^{2+}, and Sr^{2+} and Mg^{2+}, were recorded in static conditions at the same total concentration of the cations (0.5 g equiv./l). The distribution coefficient, γ, in eqns. 4–17 determines the slope of the tangent of the linear isotherm to the given non-linear isotherm at $c = 0$ (Fig. 1). The parameters γ and H were determined from column data, obtained for microconcentrations of calcium and strontium which provide conditions of linear chromatography, using eqns. 5 and 6 at $\varepsilon = 0$. The feed band was produced by passing appropriate quantities of calcium or strontium nitrate

TABLE II

VALUES OF THE MOMENTS $\bar{\tau}$, μ_2 AND μ_3 OF THE OUTPUT CURVE FOR COLUMNS OF VARIOUS LENGTHS FOR Sr^{2+}–Mg^{2+} EXCHANGE

$\gamma = 31.6$; $\varepsilon = -0.5$; $L_0 = 1.2$ cm.

L (cm)	H (cm)	$\bar{\tau}$ (cm)		μ_2 (cm^2)		μ_3 (cm^3)	
		Exptl.	Calculated according to eqn. 5*	Exptl.	Calculated according to eqn. 6*	Exptl.	Calculated according to eqn. 7*
25	0.52	25.5	23.4 (25.5)	12.6	13.0 (13.5)	22.6	34.3 (20.8)
31.2	0.52	28.8	29.1 (31.5)	14.0	16.0 (16.8)	31.7	44.6 (25.2)
36.3	0.52	34.0	34.1 (36.8)	18.6	19.0 (19.7)	55.0	52.1 (28.8)
43.3	0.39	37.8	40.3 (43.6)	16.8	16.5 (17.1)	35.8	47.3 (19.7)
53.4				20.9	19.5 (20.2)	57.5	57.4 (21.6)

* Values in parentheses: $\varepsilon = 0$.

(or of a mixture of one of them with magnesium nitrate) through the column at a total concentration of 0.5 g equiv./l. Elution was carried out with magnesium nitrate (0.5 g equiv./l) at a flow-rate of 2 ml/cm^2·min. The non-linearity parameter, ε, was calculated from experimental ion-exchange isotherms of Ca^{2+} and Mg^{2+} and of Sr^{2+} and Mg^{2+}.

RESULTS AND DISCUSSION

Statistical moments were calculated from the experimental output curves and compared with the corresponding values calculated according to eqns. 5–7 for the elution mode and according to eqns. 10–13 for the frontal-elution mode of operation. Results obtained for the elution mode are presented in Tables I and II. In order to estimate the effect of non-linearity, the moments were calculated for the linear isotherm and are presented in the fourth column of the tables. Eqn. 5 indicates that for a convex isotherm the first moment $\bar{t}$ (or $\bar{\tau}$) is smaller than for a linear isotherm tangent to it, i.e., in the case of a convex isotherm the main mass of substance leaves the column earlier than in a linear chromatographic system. Experimental and theoretical values of the first moments are in good agreement.

The second central moment, μ_2, characterizes the widening of the chromatographic band at the outlet of the column. Comparison of μ_2 and $\mu_2(\varepsilon = 0)$ in Tables I and II indicates that the correction to the linear term in eqn. 6 is small even for isotherms with large deviations from linearity ($\varepsilon = -0.5$). The values of the second moments calculated according to eqn. 6 are usually higher than the experimental values, while those determined from the relation obtained for non-equilibrium chromatography at $D = 0$ (which is not presented here) are lower[24].

The value of the third central moment, μ_3 in eqn. 7, is affected most by the non-linearity of the isotherm. This moment determines the asymmetry of the output elution curve. The data of Tables I and II show that eqn. 7 adequately represents the quantitative measure of the asymmetry of the chromatographic curve for non-linear isotherms. A satisfactory agreement is observed between the experimental data and the theoretical data. The positive values of μ_3, reflect the fact that for convex isotherms the front boundary of the chromatographic output curve is steeper than that of the rear boundary.

TABLE III

VALUES OF THE MOMENTS $\bar{\tau}$ AND μ_{2d} OF THE OUTPUT CURVE OBTAINED IN FRONTAL-ELUTION CHROMATOGRAPHY ON COLUMNS OF VARIOUS LENGTHS FOR Ca^{2+}–Mg^{2+} EXCHANGE

$\gamma = 24$; $\varepsilon = -0.3$; $H = 0.8$ cm; $L_0 = 27.6$ cm.

L (cm)	$\bar{\tau}_s$ (cm)		$\bar{\tau}_d$ (cm)		μ_{2d} (cm^2)	
	Exptl.	Calculated according to eqn. 10	Exptl.	Calculated according to eqn. 12	Exptl.	Calculated according to eqn. 13
36.3	6.0	6.3	26.7	25.8	59.9	58.5
41	9.6	9.7	30.5	29.0	70.1	68.7
45.3	12.2	12.6	33.1	32.0	74.8	78.7
50.4	15.7	16.2	36.6	35.6	83.2	91.0

The values of the first, $\bar{\tau}_s$ and $\bar{\tau}_d$, and the second, μ_{2d}, moments calculated from the experimental curves and from eqns. 10, 12 and 13 are presented in Table III; the calculated and experimental values are in good agreement.

CONCLUSION

Eqns. 5–17 were derived on the assumption that the non-linearity parameter, ε, is relatively small. The isotherm with a large deviation from linearity ($\varepsilon = -0.5$) gives theoretical and experimental results which are in agreement. This fact makes it possible to recommend eqns. 5–17 for quantitative evaluation of the width and of the retention time of a chromatographic curve in non-linear elution and frontal-elution chromatography.

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