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Displacement Development on Ion Exchangers. A Comparison of Steady-State Profile Equations in the Chromatographic and the Distillation Models

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Abstract

After showing in a rigorous manner that when the chromatographic model is adopted to describe displacement development phenomena, HETP is twice as big as HETP in the countercurrent resin-solution model analogous to the distillation model, different equations are given for the steady-state profile according to the origin of the plates: origin where the molar fraction is 0.5, origin at the point of initial molar fraction, and origin at the middle of the band. The distance from the middle of the band to the initial molar fraction zone is given as well as molar fractions at the ends of the band.

INTRODUCTION

Displacement development on an ion exchange resin column is a choice technique for the separation of close species for preparation purposes (*1*). Let us bear in mind that it consists in displacing an A + B mixture band to be separated between the initial ion I of the resin and the developing ion D, selected so that the band conserves a constant length. This occurs if the order of affinities for the resin is I ≪ A < B ≪ D.

When the length of the column where the displacement takes place approaches an infinite value, the A and B species repartition in the band approaches a particular repartition at a steady-state for which different relations have been proposed.

In this way an assimilation of the chromatographic column into a distillation column working at total reflux (the resin being displaced countercurrent to the solution) and the use of the plate theory developed in distillation enabled Tremillon to propose the following expression (*2*): If x is the molar fraction of the most fixed specie in resin (B) in the P plate, and if the chosen origin of plates is the one where $x = 0.5$ by numbering the plates according to an increase of the B content, we have

$$\frac{x}{1 - x} = K^p \tag{1}$$

which corresponds to a bilogarithmic repartition of the species A and B in the band symmetrical with respect to the plate where $x = 0.5$.

Relation (1) is, in fact, the equation of a band of infinite length displaced on a column which is itself of infinite length (Fig. 1).

If we now consider a band of a definite length of P theoretical plates brought to steady-state, the species distribution will be a portion of the previous bilogarithmic curve and will be symmetric with respect to the origin only if the molar fraction of the initial mixture equals 0.5 (as much of A as of B).

Moreover, by using the plates theory, applied this time to the working of the column in a fixed bed (immovable resin, solution flowing on the resin) and not at countercurrent, Conrard et al. (*3*) proposed the following expression of the molar fraction x of the most fixed specie by the resin in the plate of order n, when the chosen origin of the plates is the one where $x = x_0$, molar fraction of the initial mixture, and when the equilibrium constant K is close to unity ($K = 1 + \varepsilon$, $\varepsilon \ll 1$):

$$x = \frac{1}{1 + \dfrac{1 - x_0}{x_0} \exp(-2n\varepsilon)} \tag{2}$$

an expression which can also be formulated as

$$\frac{x}{1 - x} = \frac{x_0}{1 - x_0} \exp(2n\varepsilon) \tag{3}$$

We therefore decided to compare expressions (1) and (2) and to discuss their importance for the practical determination of species distribution in a band at the steady-state.

CHROMATOGRAPHIC PLATE AND DISTILLATION PLATE

In classical chromatography in a fixed bed, the resin phase is immovable and the solution flows in contact with the resin. To apply the plate theory,

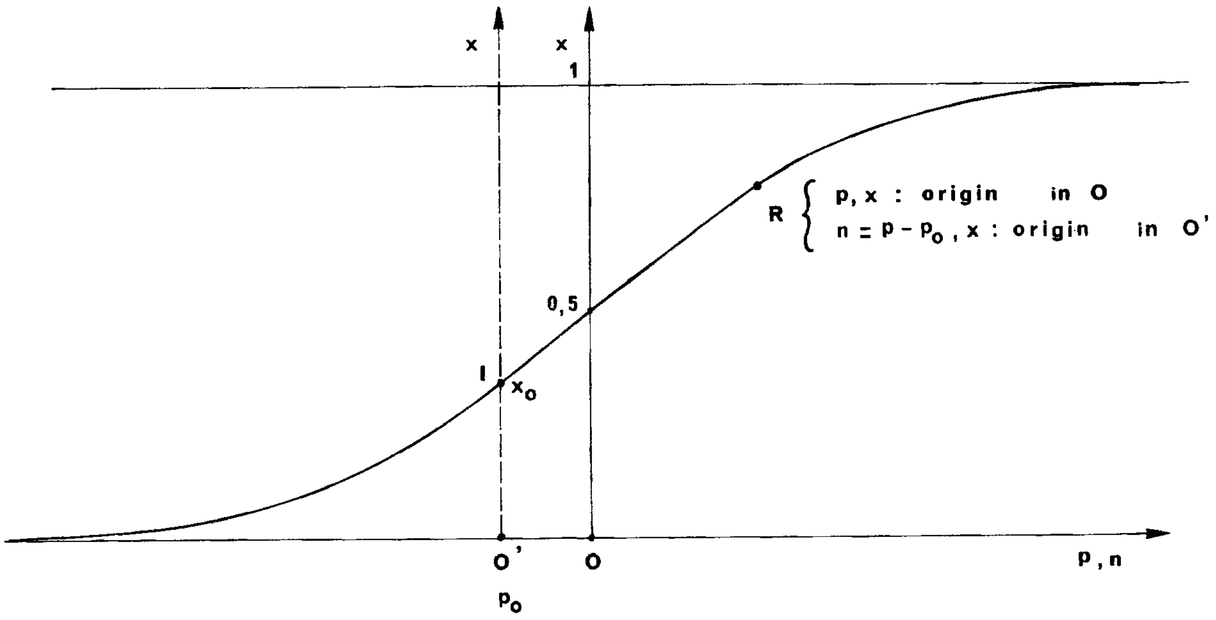

FIG. 1. Steady-state repartition in displacement development. Infinite length band. Various coordinates systems.

it is supposed that after equilibrium is reached in each of a series of "reactors" containing both resin and solution, the solution phase of each reactor is transferred to the following one. Each "reactor" constitutes a "chromatographic plate."

In distillation, the working of a plate column with an upward moving phase (i.e., the vapor) and a downward moving phase (i.e., the liquid) is considered. It is thus a countercurrent situation. The height of a "distillation" plate is the distance between two sections of the column working at total reflux (no withdrawal), so that an equilibrium relation between the vapor from the upper section and the liquid from the lower section can be formulated.

It is therefore essential, in order to link Relation (1), established according to the "distillation" model, and Relation (2), deduced from the "chromatographic" model, to first compare the plate height defined by these two models.

Glueckauf (*4*) showed intuitively that the height of the chromatographic plate was twice the height of the distillation plate. A rigorous demonstration is offered as follows.

Let us consider a distillation column having been working for an infinite length of time with a total reflux at both ends, and therefore brought to the steady state in the case of an A + B mixture, with A more volatile than B:

$$K_{AB} = \frac{y_A \cdot x_B}{y_B \cdot x_A}$$

where y represents the molar fractions in the vapor phase and x the molar fractions in the liquid phase ($y_A > y_B$, $K_{AB} > 1$).

Supposing that the column contains P_D distillation plates or P_C chromatographic plates, we will calculate the front composition in function of the back composition of the column according to the two models considered. By identifying both expressions we thus obtain the relation between P_D and P_C.

"Distillation" Model

Figure 2 illustrates the countercurrent working of a fractionating column, where V_n is the vapor flow rate from plate n, L_n is the liquid flow rate from plate n, x_n is the molar fraction in A of liquid from plate n, and y_n is the molar fraction in A of steam from plate n.

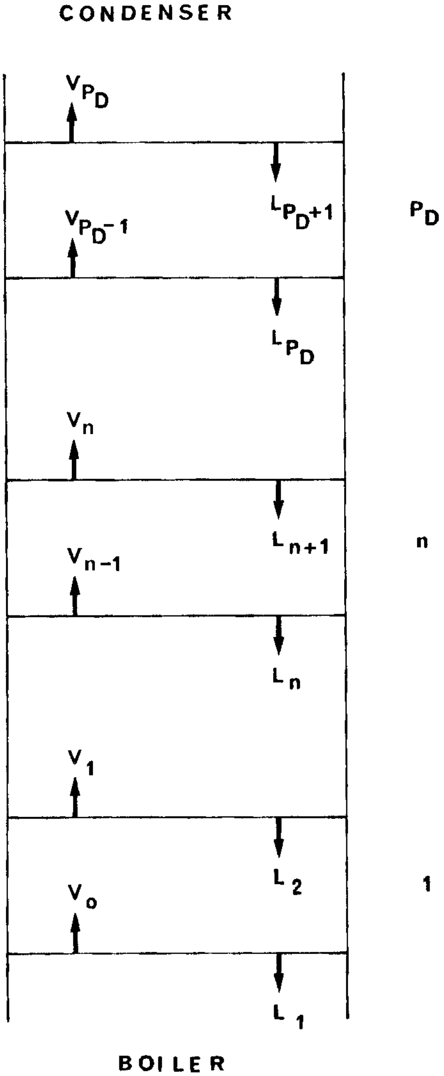

FIG. 2. Schema of the countercurrent working of a fractionating column.

The boiler supplies the column from the bottom with a V_0 vapor flow rate; the condenser sweeps back the whole of the vapor coming from plate P_D with a V_{P_D} rate flow and sends back the liquid in the column with an L_{P_D+1} rate flow. Since the column works at a total reflux,

$$V_{P_D} = L_{P_D+1}$$

$$V_0 = L_1$$

In the same way, whatever the plate n may be, we have

$$V_n = L_{n+1}$$

Furthermore, when the steady-state is reached, the distribution in the column of A (and B) no longer varies. The quantity of A which goes from the bottom to the top of any section of the column is equal to the quantity which goes from the top to the bottom. With

$$V_n y_n = L_{n+1} x_{n+1}$$

and in particular at the extremity of the column

$$V_{P_D} y_{P_D} = L_{P_D+1} x_{P_D+1}$$

$$V_0 y_0 = L_1 x_1$$

then, whatever n may be:

$$y_n = x_{n+1} \tag{4}$$

Furthermore, since in a plate there is equilibrium between the liquid and the vapor, we have

$$\frac{y_n}{1 - y_n} \frac{1 - x_n}{x_n} = K$$

that is,

$$y_n = \frac{K x_n}{1 + (K - 1) x_n} \tag{5}$$

and, according to Eq. (4),

$$x_{n+1} = \frac{K x_n}{1 + (K - 1) x_n}$$

therefore, the relation between the molar fraction x_{P_D+1} of the liquid swept back by the condenser to the top part of the column and the molar fraction x_1 of the liquid flowing from the Plate 1 boiler is

$$x^{P}_{D+1} = \frac{K_{P_D} x_1}{1 + (K^{P_D} - 1)x_1} \tag{6}$$

"Chromatographic" Model

The fractionating column holding P_C chromatographic plates must work continuously and no longer be countercurrent. Transfer of the vapor phase of each plate to the next one is followed by a first equilibrium between the liquid and vapor phases of each plate (which for Plate 1 corresponds to the total vaporization of the liquid and for plate P_{C+1} to the total condensation of the steam coming from plate P_C), then transfer of liquid of each plate to the preceding one and a new equilibrium leading to a final state after the equivalent of the "plate displacement" in a chromatographic column.

Here V_n and L_n are the vapor and liquid quantities of plate n, and x_n and y_n are the A molar fractions, respectively, in the liquid and the vapor of plate n.

The chromatographic working process of the fractionating column is schematized on Fig. 3. V_n, L_n, x_n, and y_n have been written with upper indexes to designate the initial state of equilibrium before transfer (d), the intermediate state of equilibrium (i), and the final state of equilibrium (a).

Quantitative vaporization and condensation in Plates 1 and P_{C+1}, corresponding to reflux, enable us to write:

$$L_1{}^d = V_1{}^i$$

$$V_{P_C}{}^d = L^i_{P_C+1}$$

In the same way, the absence of any accumulation of mass in the column implies that the vapor quantity going from one plate to the next one, during vapor transfer, is equal to the liquid quantity going from the same plate to the preceding one during the liquid transfer, which enables us to write

$$V_{n-s}{}^d = L_{n-1}{}^i$$

Furthermore, with the mass conservation in plate n during the equilibrium following the vapor transfer, we can write

$$V_{n-1}{}^d + L_n{}^d = V_n{}^i + L_n{}^i \tag{7}$$

Therefore

$$V_n{}^i = L_n{}^d$$

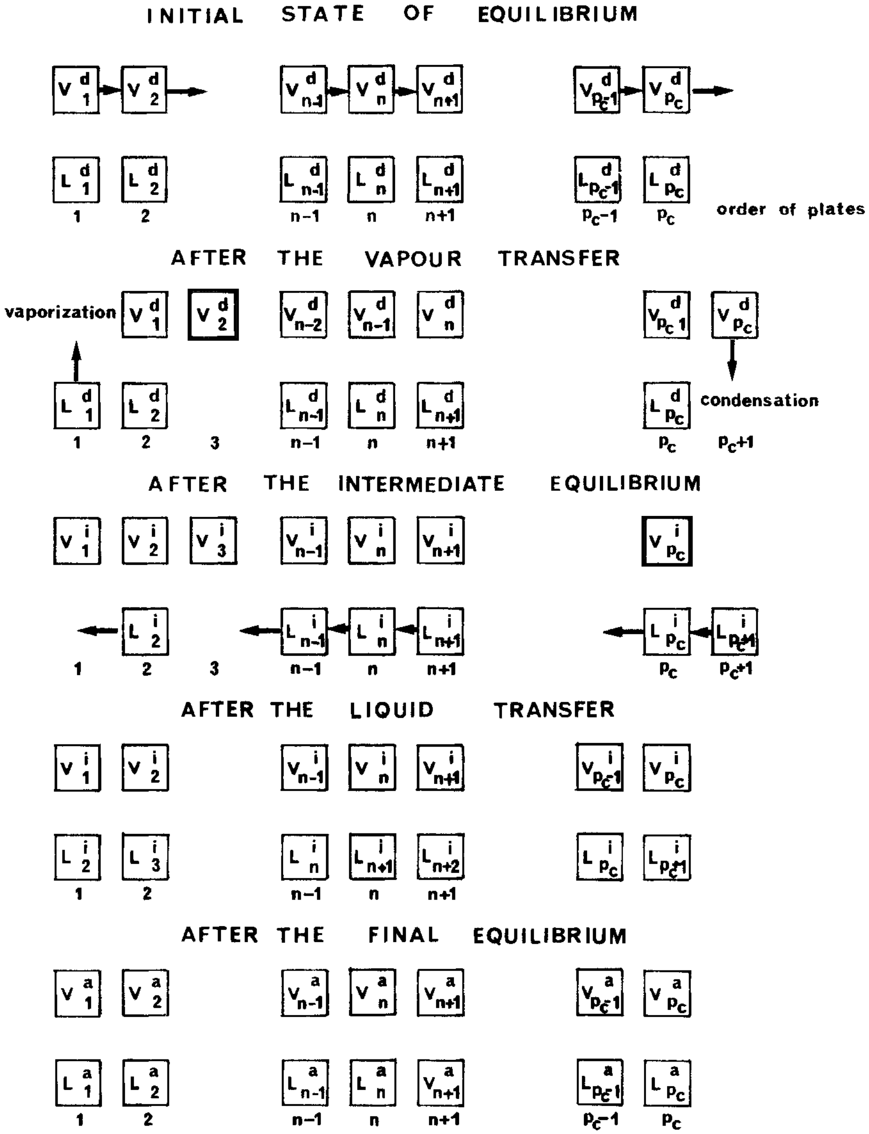

FIG. 3. Schema of the chromatographic working of a fractionating column.

When steady-state is reached, the repartition of A in the column no longer varies. Let us write that the quantity of A in plate n, after intermediate equilibrium following vapor transfer, is conserved. We have

$$V_{n-1}{}^{d}y_{n-1}{}^{d} + L_{n}{}^{d}x_{n}{}^{d} = V_{n}{}^{i}y_{n}{}^{i} + L_{n}{}^{i}x_{n}{}^{i} \tag{8}$$

By comparing Equalities (7) and (8), we deduce that steady-state requires

$$y_{n-1}{}^{d} = x_{n}{}^{i}$$

$$y_{n}{}^{i} = x_{n}{}^{d}$$

Now, Relation (5) expressing the liquid–steam equilibrium is verified:

$$y_{n}{}^{i} = x_{n}{}^{d} = \frac{Kx_{n}{}^{i}}{1 + (K-1)x_{n}{}^{i}} = \frac{Ky_{n-1}{}^{d}}{1 + (K-1)y_{n-1}{}^{d}}$$

and

$$y_{n-1}{}^{d} = \frac{Kx_{n-1}{}^{d}}{1 + (K-1)x_{n-1}{}^{d}}$$

Therefore

$$x_{n}{}^{d} = \frac{K^{2}x_{n-1}{}^{d}}{1 + (K^{2}-1)x_{n-1}{}^{d}}$$

which enables us to express $x_{P_C}{}^{d}$ in relation to $x_1{}^{d}$:

$$x_{P_C}{}^{d} = \frac{K^{2(P_C-1)}x_1{}^{d}}{1 + (K^{2(P_C-1)} - 1)x_1{}^{d}}$$

We deduce that the composition of the condensed vapor in front, $y_{P_C}{}^{d}$, in relation to the composition of the vaporizing liquid at the back, $x_1{}^{d}$, is

$$y_{P_C}{}^{d} = \frac{Kx_{P_C}{}^{d}}{1 + (K-1)x_{P_C}{}^{d}}$$

$$y_{P_C}{}^{d} = \frac{K^{2(P_C-1)}x_1{}^{d}}{1 + (K^{2(P_C-1)} - 1)x_1{}^{d}} \tag{9}$$

Identification of Both Relations

If models are applied to the same column, the Expressions (5) and (9) are identical. This yields

$$P_D = 2P_{C-1}$$

If P_C is large, 1 is negligible compared to $2P_C$, and we have

$$P_D \sim 2P_C$$

The number of countercurrent distillation plates is therefore clearly twice the number of chromatographic plates.

In other words, the height equivalent to a theoretical plate (HETP) when a chromatographic model is adopted to describe phenomena is twice as large as HETP h_D when a countercurrent resin-solution model similar to the distillation one is adopted:

$$\frac{h_C}{h_D} = 2 - \frac{1}{P_C} \sim 2$$

DISTRIBUTION AT STEADY-STATE

Relation (1), established by considering the countercurrent model, becomes, if the chromatographic plate is adopted,

$$\frac{x}{1 - x} = K^{2p} \tag{10}$$

But Relations (1) and (2) are not applied to the same axis system because the origin corresponds to $x = 0.5$ for Eq. (1) and to $x = x_0$ for Eq. (2). A point R with coordinates (p, x) in the first system (Fig. 1) has the coordinates $(n = p - p_0, x)$ in the second one, with

$$\frac{x_0}{1 - x_0} = K^{2p_0}$$

(p_0 is considered negative in the figure).

In the axis system with $x = x_0$ as the origin, $p = n + p_0$ and Eq. (10) becomes

$$\frac{x}{1 - x} = K^{2p_0}K^{2n}$$

Therefore

$$\frac{x}{1 - x} = \frac{x_0}{1 - x_0} K^{2n} \tag{11}$$

If K is close to 1, we have

$$K^{2n} = (1 + \varepsilon)^{2n} \sim \exp 2n\varepsilon$$

the error is about 5% for $n = 500$ with $\varepsilon = 0.01$, and for $n = 5$ with $\varepsilon = 0.1$. With bands of the usual length (a few hundred plates), the approximation implies that $K < 1.02$.

$$\frac{x}{1 - x} \sim \frac{x_0}{1 - x_0} \exp(2n\varepsilon) \tag{12}$$

In other words, when expressed in the same axis system ($x = x_0$) and with the same model, Relations (1) and (2) are strictly equivalent.

Remarks

1. If $x_0 \ll 1$ (the mixture to be separated contains a very weak proportion of the elements most fixed by the resin) and if $P\varepsilon \ll 1$ (short band), then x is also small compared to 1 and Eq. (12) becomes

$$x \sim x_0 \exp(2n\varepsilon) \sim x_0(1 + 2n\varepsilon)$$

As shown in Eq. (3), the distribution is linear and symmetric with respect to x_0. Let us insist on the fact that equating $\exp 2n\varepsilon$ with $1 + 2n\varepsilon$ practically implies $P\varepsilon < 0.2$.

2. Expression (10) enables easy calculation, as a function of K of the number of plates on which a band lies at steady-state within limits of 2%, for example, from $x = 0.01$ to $x = 0.99$. If $x = 0.01$

$$x/(1 - x) \sim 10^{-2} = K^{2p}; \qquad p = -1/\log K$$

If $x = 0.99$

$$x/(1 - x) \sim 10^{2} = K^{2p}; \qquad p = 1/\log K$$

The bandwidth within 2% limits in the number of plates is therefore:

TABLE 1

K	ΔP
10	2
5	3
2	7
1.5	12
1.1	50
1.01	500
1.001	5000

$$\Delta p = 2/\log K$$

when $K = 1 + \varepsilon$, $\log K = 0.43 \ln K \sim 0.43\varepsilon$

$$\Delta p \sim 5/\varepsilon$$

which yields the values in Table 1.

The order of magnitude agrees with the experimental results given by Tremillon (*2*).

POSITION OF THE BAND MIDDLE

The band is symmetrical only if $x_0 = 0.5$ (and in the particular case where $x_0 \ll 1$, $P\varepsilon \ll 1$).

When $x_0 \neq 0.5$ it is essential, in order to construct a steady-state band shape, to know the abscissa M of the middle of the band with respect to the point where the composition of the initial mixture x_0 is taken as the plate origin (Fig. 4).

The expression for M was given by Conrard et al. (*3*) for the case of equilibrium constants close to 1:

$$M = \frac{1}{2\varepsilon} \ln \left[\frac{1 - x_0}{x_0} \frac{\exp(2\varepsilon P x_0) - 1}{\exp \varepsilon P - \exp \varepsilon P(2x_0 - 1)} \right] \tag{13}$$

where P is the total number of band plates.

When the equilibrium constant is not close to 1, we replace ε by $\ln K$ in Eq. (13). Expressions (11) and (12) derive from each other by replacing K^{2n} by $e^{2n\varepsilon}$. Now, $K = e^{\ln K}$ and $K^{2n} = e^{2n \ln K}$.

We therefore have in the case of high equilibrium constants:

$$M = \frac{1}{2 \ln K} \ln \left[\frac{1 - x_0}{x_0} \frac{K^{2px_0} - 1}{K^p - K^{p(2x_0 - 1)}} \right] \tag{14}$$

It can be verified that this expression is obtained if we write that, owing to the mass conservation law, the mixture obtained by adding each species in the various plates has the initial composition x_0 (*3*).

Therefore, in order to construct a steady-state band shape, we have only to place on the curve of Eq. (10) the plate for which $x = x_0$, then to place, from this plate, the median plate M whose abscissa is calculated by Eq. (14) and then, finally, to place $P/2$ plates on both sides of M.

Remark

By multiplying the numerator and denominator in Eq. (13) by $\exp -\varepsilon P x_0$, we have the more symmetric expression

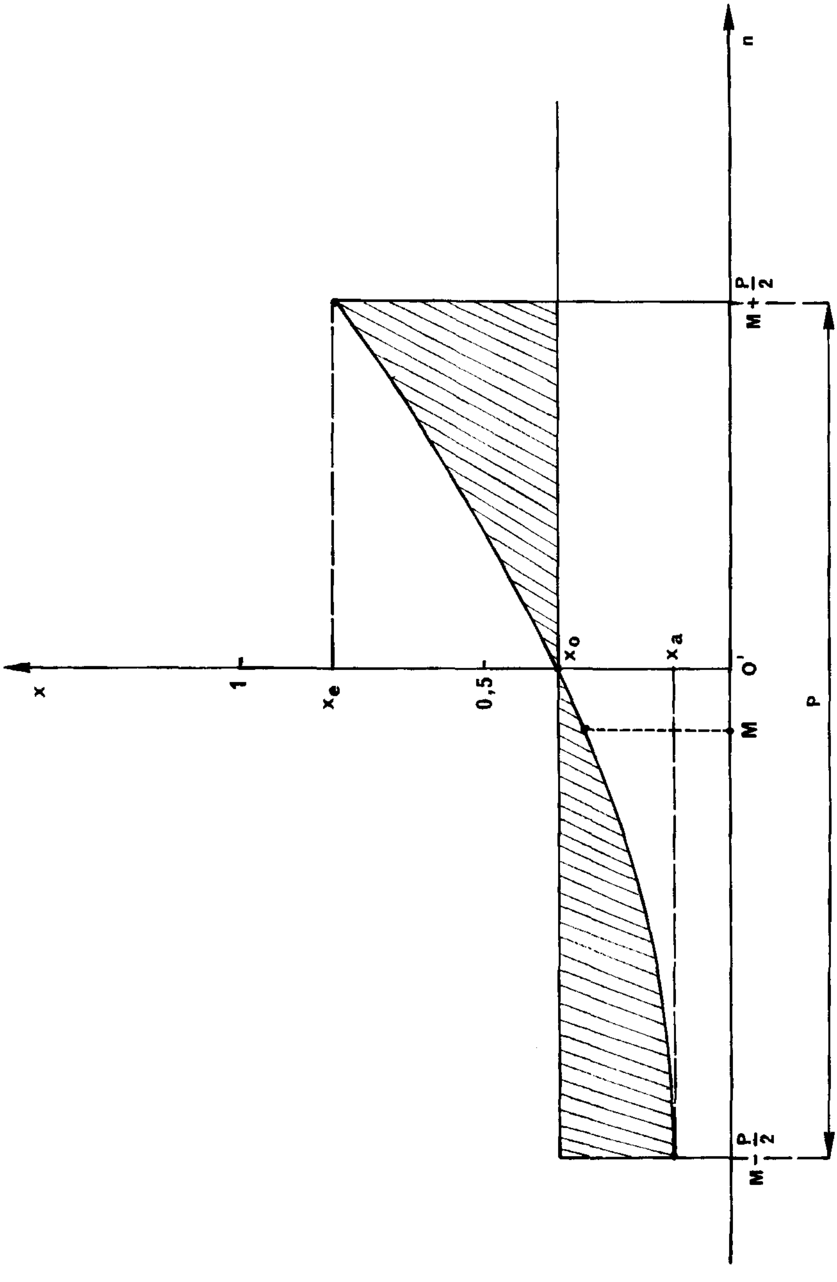

FIG. 4. Steady-state repartition. Nonsymmetric band of a given length (P plates and $x_0 \neq 0.5$).

$$M = \frac{1}{2\varepsilon}\ln\left[\frac{1-x_0}{x_0}\frac{\operatorname{sh} P\varepsilon x_0}{\operatorname{sh} P\varepsilon(1-x_0)}\right] \tag{15}$$

and in the same way Eq. (14) becomes

$$M = \frac{1}{2\ln K}\ln\left[\frac{1-x_0}{x_0}\frac{\operatorname{sh} Px_0 \ln K}{\operatorname{sh} P(1-x_0)\ln K}\right]$$

BAND EXTREMITIES

Let us first give the expression of the number of plates N separating any two points of a band and whose molar fractions are x_1 and x_2. Expression (11) is

$$N = \frac{\ln\dfrac{x_1}{1-x_1}\dfrac{1-x_2}{x_2}}{2\ln K}$$

which is similar to the classical Fenske (*5*) distillation formula, within the limit of a factor of 2 in the denominator, owing to the fact that the number of chromatographic plates is half the number of countercurrent (distillation) plates.

In the case of constants close to 1, the expression becomes

$$\ln\frac{x_1}{1-x_1}\frac{1-x_2}{x_2} = 2N\varepsilon$$

If we now consider the enriched band extremity of molar fraction x_e and the poor one of molar fraction x_a, these two points have the characteristic of being symmetric with respect to the point middle of abscissa M.

Conrard (*6*) showed that when this is the case, we have

$$x_e/x_a = K^{2P(1-x_0)} \tag{16}$$

Since the Fenske formula can be applied to band extremities (with $N = P$), by combining it with Eq. (16) it is possible to deduce the explicit expressions giving x_e or x_a as functions of P, x_0, and K, and to calculate the molar fractions of the band extremities brought to steady-state only as functions of the quantities characteristic of the development displacement considered: band length, equilibrium constant, and composition of initial mixture.

For the enriched end:

$$x_e = \frac{K^{2P(1-x_0)} - K^{2P}}{1-K^{2P}}$$

For the poor end:

$$x_a = \frac{K^{2Px_0} - 1}{K^{2P} - 1}$$

Figure 5 represents the variation of x_e and x_a as functions of the molar fraction x_0 of initial mixture for various values of K and for 100 plates band.

In the case where $x_0 = 0.5$, the band is symmetric with respect to the point of the x_0 ordinate, and we have

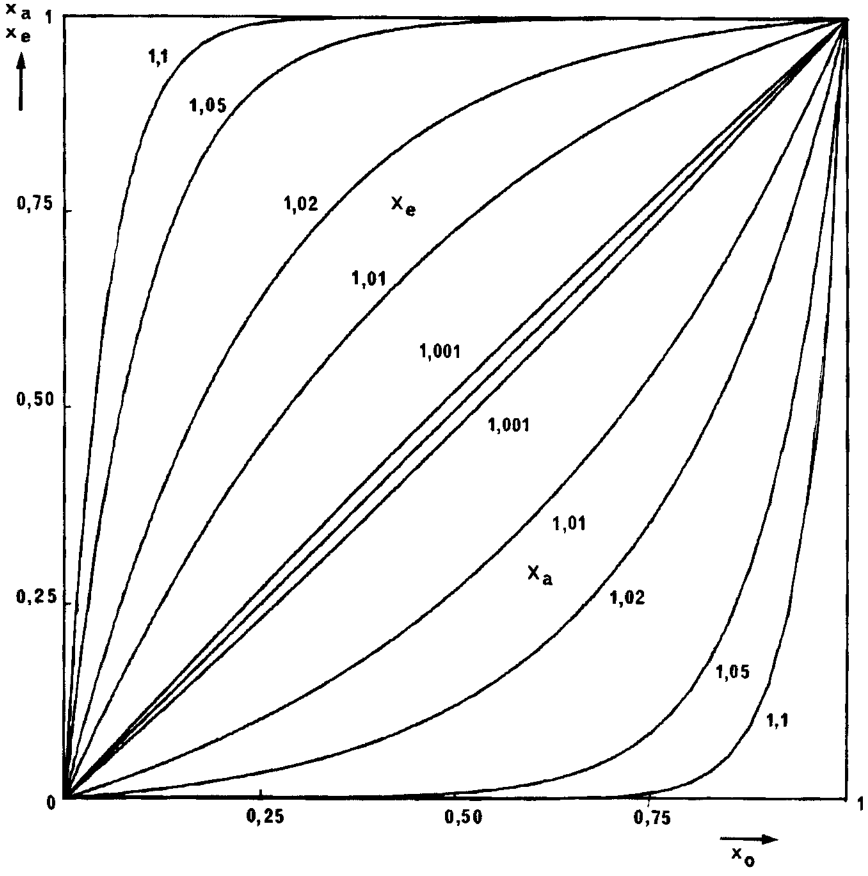

FIG. 5. Variation of molar fractions of an enriched extremity x_e (curves situated above first diagonal) and a poor one x_a (curves stituated below first diagonal) as a function of x_0 for various values of K. Steady-state, 100 plates band.

TABLE 2[a]

Nature of the band	Origin	Repartition at the steady-state	Abscissa M of the band middle with respect to the origin
Band of infinite length	$x = 0.5$	$\frac{x}{1-x} = K^{2P}$	$M = 0$
Band of finite length; any value of K	$x = x_0$	$\frac{x}{1-x} = \frac{x_0}{1-x_0} K^{2n}$ or $x = \frac{1}{1 + \frac{1-x_0}{x_0} K^{-2n}}$ or $n = \frac{1}{2 \ln K}\left(\ln \frac{x}{1-x} - \ln \frac{x_0}{1-x_0}\right)$	$M = \frac{1}{2 \ln K} \ln\left[\frac{1-x_0}{x_0} \frac{\operatorname{sh} P x_0 \ln K}{\operatorname{sh} P(1-x_0) \ln K}\right]$
Band of finite length; K close to 1; $K = 1 + \varepsilon$, ε small	$x = x_0$	$\frac{x}{1-x} = \frac{x_0}{1-x_0} \exp(2n\varepsilon)$ or $x = \frac{1}{1 + \frac{1-x_0}{x_0} e^{-2n\varepsilon}}$ or $n = \frac{1}{2\varepsilon}\left(\ln \frac{x}{1-x} - \ln \frac{x_0}{1-x_0}\right)$	$M = \frac{1}{2\varepsilon} \ln\left[\frac{1-x_0}{x_0} \frac{\operatorname{sh} P\varepsilon x_0}{\operatorname{sh} P\varepsilon(1-x_0)}\right]$
Short band; K close to 1; $x_0 \ll 1$; $P\varepsilon \ll 1$	$x = x_0$	$x = x_0(1 + 2n\varepsilon)$	$M = 0$
Band of finite length; any value of K	Band middle	$x = \frac{\frac{x_0}{1-x_0} K^{2(z+M)}}{1 + \frac{x_0}{1-x_0} K^{2(z+M)}}$	—
Band of finite length; K close to 1	Band middle	$x = \frac{\frac{x_0}{1-x_0} \exp 2\varepsilon(z+M)}{1 + \frac{x_0}{1-x_0} \exp 2\varepsilon(z+M)}$	—

[a] Plate order: Origin at $x = 0.5$: p. Origin at $x = x_0$: n. Origin at the band middle: z.

$$x_e = \frac{K^P}{1 + K^P}$$

$$x_a = \frac{1}{1 + K^P}$$

with $x_e/x_a = K^P$. If the band is very long, $x_e \to 1$ and $x_a \to 0$.

CONCLUSIONS

If we take into account the fact that the height of a "chromatographic" plate is twice the height of a distillation plate, relations which give the steady-state distribution in a band developed by displacement in ion exchanger chromatography, and which we obtain by either model, are strictly equivalent.

The shape obtained is a fraction of a bilogarithmic curve, generally nonsymmetrical (except if $x_0 = 0.5$), whose middle point position has been specified with respect to the origin taken at the point where the composition of original mixture x_0 is found.

Various expressions have been given which depend on whether we had an equilibrium constant of any value or one close to 1.

Table 2 summarizes the various equations to be used in different cases which we may encounter by *always* adopting the *chromatographic* plate.

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