

BASIC PRINCIPLES OF RADIAL CHROMATOGRAPHY

V. V. RACHINSKII

Timiryazev Academy of Agriculture, Moscow A-8 (U.S.S.R.)

SUMMARY

The equations of dynamic sorption are considered in the case of radial cylindrical symmetry. The basic quantitative regularities of radial chromatography are deduced from these equations.

In the case of radial-cylindrical dynamic sorption there is an additional factor of front deformation, namely the dependence of flow rates on radius.

The effect of this factor is considered in the cases of different shapes of sorption isotherms for frontal and elution chromatography.

It is shown that reproducible migration coefficients of the chromatographic zones R_F in radial chromatography, as in linear chromatography, can be obtained only in the case of linear sorption isotherms of the substances.

Radial chromatography is one of the most effective rapid methods of separation and analysis of complicated mixtures of substances¹.

The theory of this modification of chromatography, however, has not been sufficiently developed.

If we consider the essential principles and specific peculiarities of radial chromatography in the light of general theory of dynamic sorption and chromatography², from the physical point of view, radial chromatography is based on a process of dynamic sorption in the cylindrical field of the mobile phase migration rates (radial-cylindrical dynamic sorption).

We shall commence with the theoretical consideration of the given problem by presenting the general equations.

Let us assume that dynamic sorption of any substance takes place in a complex field of migration rates in three dimensions. In this case the full equation of mass equilibrium in the process of isothermal dynamic sorption will read as follows²:

$$\frac{\partial n}{\partial t} + \frac{\partial N}{\partial t} + \operatorname{div} (n\vec{u}) = D^* \Delta \vec{u} \quad (1)$$

where n and N are the volume concentrations of the substance to be sorbed in the liquid (or gaseous) phase and in the sorbent respectively, expressed as the mass of the substance per unit volume occupied by the sorption medium, t = time, \vec{u} = the vector of the rate of migration of the substance through the sorbing medium, D^* = effective coefficient allowing for the supplementary longitudinal (diffusional and quasi-dif-

fusional) effects of transport (isotropic character of this coefficient is assumed), $\text{div} =$ the divergence operator, and $\Delta =$ the Laplace operator.

In accordance with the rules known for the transformation of the Cartesian coordinates into cylindrical ones in vector calculation, the equilibrium equation of dynamic sorption in cylindrical coordinates is expressed as:

$$\begin{aligned} \frac{\partial n}{\partial t} + \frac{\partial N}{\partial t} + \frac{1}{\rho} \cdot \frac{\partial(\rho n u_\rho)}{\partial \rho} + \frac{1}{\rho} \cdot \frac{\partial(n u_\varphi)}{\partial \varphi} + \frac{\partial(n u_z)}{\partial z} = \\ = D^* \left[\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial n}{\partial \rho} \right) + \frac{1}{\rho^2} \cdot \frac{\partial^2 n}{\partial \varphi^2} + \frac{\partial^2 n}{\partial z^2} \right] \end{aligned} \quad (2)$$

If in the cylindrical field of flow

$$(u_\rho \neq 0, u_\varphi = 0, u_z = 0, \frac{\partial n}{\partial \varphi} = 0, \frac{\partial n}{\partial z} = 0)$$

eqn. (2) becomes simplified as follows:

$$\frac{\partial n}{\partial t} + \frac{\partial N}{\partial t} + \frac{1}{\rho} \frac{\partial}{\partial \rho} (\rho n u_\rho) = D^* \frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial n}{\partial \rho} \right) \quad (3)$$

If the longitudinal effects are neglected ($D^* = 0$), the equation is still further simplified to:

$$\frac{\partial n}{\partial t} + \frac{\partial N}{\partial t} + \frac{1}{\rho} \frac{\partial}{\partial \rho} (\rho n u_\rho) = 0 \quad (4)$$

An equation is now derived for a change of radial flow rate in a cylindrical field. We assume a cylindrical sorbent block (sorber) and introduction of the solution of the substance undergoing sorption at a constant rate of

$$dV/dt = \dot{V} \quad (V = \text{volume of the solution})$$

from the axis z , the height of the sorber being z_0 and its radius ρ being of infinite length.

The flow rate at a distance ρ from the axis will then be:

$$u_\rho = \dot{V}/2\pi\rho z_0\kappa = K/\rho \quad (5)$$

where $K = \dot{V}/2\pi z_0\kappa = \text{const.}$, and $\kappa =$ porosity, *i.e.* the decrease in radial flow is inversely proportional to the distance from the axis.

If the flow takes place in the opposite direction, *i.e.* towards the axis, then

$$u_\rho = -K/\rho \quad (6)$$

If the last term of the left hand side of eqn. (4) is developed and the expression for (5) or (6) is used,

$$\frac{\partial n}{\partial t} + \frac{\partial N}{\partial t} + u_\rho \frac{\partial n}{\partial \rho} = 0 \quad (7)$$

is obtained, where $u_\rho = \pm K/\rho$ (the rate is positive for filtration from the axis and negative for filtration towards the axis).

Let us now consider frontal equilibrium dynamic sorption for filtration from the axis.

The equation of the sorption isotherm in its general form is:

$$N = f(n) \quad (8)$$

In this case eqns. (7) and (8) will describe radial-cylindrical equilibrium sorption dynamics of one component. Assuming that the initial condition of the problem of frontal dynamic sorption is given by an initial continuous distribution (which may be differentiated)

$n = \varphi(\varrho)$, and then the problem of Cauchy can be formulated.

Let us first find the general integral of the system of eqns. (7) and (8).

By eliminating the variable N from these equations we obtain

$$\frac{\delta n}{\delta t} + v_{n,\varrho} \frac{\delta n}{\delta \varrho} = 0 \quad (9)$$

where

$$v_{n,\varrho} = \frac{u_{\varrho}}{1 + f'(n)} = \frac{K}{\varrho[1 + f'(n)]} \quad (10)$$

$f'(n)$ is a derivation of the isotherm (8) according to concentration.

The characteristic equation for (9) will be as follows:

$$\frac{dt}{1} = \frac{d\varrho}{v_{n,\varrho}} \quad (11)$$

which implies that $v_{n,\varrho} = d\varrho/dt$, the migration rate of a given concentration point of the dynamic sorption front.

Formula (10) can be considered to be the expression of Wicke's law concerning radial-cylindrical sorption dynamics. But, in contrast to the expression of Wicke's law concerning linear dynamic sorption, the migration rate of a given concentration point in radial-cylindrical dynamic sorption is not a constant value and depends on the coordinate ϱ ; it decreases with an increasing ϱ . From (11) taking into account (10) we obtain:

$$\varrho d\varrho - \frac{K}{1 + f'(n)} dt = 0 \quad (12)$$

The integral of this equation will be:

$$\xi = \varrho^2 - \lambda_n t, \quad (13)$$

where

$$\lambda_n = 2K/[1 + f'(n)]$$

Then the general solution of eqn. (11) will be as follows:

$$n = \Phi(\xi) = \Phi(\varrho^2 - \lambda_n t) \quad (14)$$

where $\Phi(\xi)$ stands for any arbitrary function of the integral (13). As can be easily verified, it satisfies eqn. (11).

Let us proceed to the solution of Cauchy's problem.

If $t = 0$, the characteristic integral (13) is $\xi = \varrho^2$ and, since the initial condition is $n = \varphi(\varrho)$ or $n = \varphi(\sqrt{\xi})$, and the solution of the problem of Cauchy can be expressed as follows:

$$n = \varphi (\sqrt{\varrho^2 - \lambda n t}), \quad (15)$$

from which it follows that

$$\varrho^2 - \lambda n t = [\bar{\varphi}(n)]^2, \quad (16)$$

or

$$\varrho = \sqrt{\varrho_0^2 + \lambda n t}, \quad (17)$$

where $\varrho_0 = \bar{\varphi}(n)$ stands for the initial coordinate of a given concentration point of the front of the initial distribution.

If $\varrho_0 \rightarrow 0$, then

$$\varrho = \sqrt{\lambda n t}. \quad (18)$$

In this way, eqn. (17) appears to be the solution of Cauchy's problem sought for.

It permits the calculation of the coordinate ϱ for a given concentration n at any time.

Let us now analyse the effect of Wicke's law (see eqn. (10)) on the course of deformation of the dynamic sorption front with respect to the shape of the sorption isotherm.

FRONTAL DYNAMIC SORPTION

Let us consider the course of deformation of the front in the case of the three kinds of sorption isotherm, *viz.* convex, concave and linear.

On application of Wicke's law (10) to radial-cylindrical dynamic sorption, the migration rate of the concentration points of the front depends not only on the concentration n but also on the coordinate ϱ , *i.e.* there are two factors which influence the migration rate of the front—namely the sorption isotherm (8) and the flow rate (5).

In the *convex isotherm*, the sorption isotherm is a factor which narrows the diffuse front (the points of lower concentration moving more slowly than those of higher concentration). The flow-rate factor (which is inversely proportional to ϱ) will appear to slow down the migration rate of all points along the front. But in a diffuse front, the concentration points more remote from the axis will show, at any given moment, a lower speed than those situated closer to the axis. Consequently, the flow-rate factor will also appear to narrow the dynamic sorption front. Hence, with a convex isotherm, gradual narrowing of the diffuse front must occur. Since the factors which cause diffusion act continuously under actual conditions, stabilization of the dynamic sorption front must occur at some asymptotic stage of dynamic sorption. Since in radial-cylindrical sorption dynamics with a convex isotherm, two factors narrowing the front are in action, the stabilization of the front will take its course more effectively and the width of the stationary front will be less (if the other conditions are identical), than in the sorption dynamics in columns.

Linearity in a sorption isotherm is a factor which conserves the diffuseness of the front. For this reason only one factor narrowing the front will exist in the case of a linear sorption isotherm—namely the flow rate. Thus, in this case too, formation of a stable front should be expected in the asymptotic stage of the process.

A *concave* sorption isotherm is a factor causing progressive diffuseness of the front. The flow rate, which is a factor narrowing the front, cannot prevent this. Thus, *e.g.*, in keeping with (18), the diffuseness of the front will be proportional to \sqrt{t} . This

diffusion of the front, however, is less pronounced than in column chromatography where the diffusion in the case of a concave isotherm is proportional to t^2 . In this way radial-cylindrical dynamic sorption is thus, a more effective technical procedure than the dynamic sorption in columns.

Let us now consider a special idealised, but very important, case of frontal sorption dynamics, in which only one single concentration point n_0 (concentration of the entering solution) exists at the entrance to the cylindrical sorber, *i.e.* at the axis, while the corresponding concentration in the sorbent $N_0 = f(n_0)$ (instantaneous equilibrium) and no disturbing factors (kinetic or quasidiffusional) are present.

In this case the dynamic sorption is described by a special solution of eqn. (9): $n = \text{const}$. This solution is interpreted as conservation of the constancy of the concentration n_0 and N_0 in the process of dynamic sorption. This must result in the formation and migration of a stabilized discontinuous dynamic sorption front.

For the calculation of the flow rate of such a stabilized discontinuous front the following equilibrium equation of the substance undergoing sorption is used:

$$n_0 v_\varrho dt \cdot 2\pi \varrho z_0 \kappa = (n_0 + N_0) v_\varrho dt \cdot 2\pi \varrho z_0 \kappa, \quad (19)$$

in which v_ϱ stands for the sought-for migration rate of the stationary front.

From eqn. (19) we obtain

$$v_\varrho = \frac{d\varrho}{dt} = v_\varrho \cdot \frac{n_0}{n_0 + N_0} = \frac{K}{\varrho} \cdot \frac{h}{1 + h}, \quad (20)$$

where $h = n_0/N_0$, *i.e.* the partition ratio.

Eqn. (20) may be considered as an expression of Wilson's law for the radial-cylindrical dynamic sorption.

As shown by eqn. (20) the flow rate of the stabilized front is not a constant; it depends on the coordinate ϱ .

On integrating eqn. (20) we obtain:

$$\varrho = \sqrt{\frac{2Kh}{1+h}} t. \quad (21)$$

From eqn. (5) the formula for the movement of the front of the solvent may be obtained as follows:

$$\frac{d\varrho_F}{dt} = \frac{K}{\varrho_F} \quad (22)$$

from which

$$\varrho_F = \sqrt{2Kt} \quad (23)$$

is obtained by integration.

Let us introduce the index $R_F = \varrho/\varrho_F$ which is well known in radial chromatography. From eqns. (22) and (23) we then obtain:

$$R_F = \sqrt{\frac{h}{1+h}} \quad (24)$$

By comparison we note that in linear chromatography, according to Wilson's law

$$R_F = \frac{h}{1+h} \quad (25)$$

If the process of dynamic sorption takes place on paper or thin layers (sheet chromatography), it may be convenient to express the formula (21) as follows:

$$P = \frac{2\pi Kh}{1+h} t \quad (26)$$

where $P = \pi q^2 =$ the area taken up by the zone of the substance to be sorbed on the sheet, *i.e.* the area of the zone increases proportionally with time.

ELUTION SORPTION DYNAMICS

Let us consider an ideal case: At the entrance to the cylindrical sorber an initial "rectangular" zone with a radius q_0 is formed and pure solvent is introduced at the entrance (from the axis). Let us assume that the initial zone contains the same solvent as that which is used for elution. Let us also suppose that dynamic sorption occurs under equilibrium conditions and that no other factors of frontal diffusion will operate. In this case both the fore and rear front of the zone must retain their discontinuous character during the process of elution. In keeping with Wilson's law (20), the fore front will migrate at a rate of v_1 and the rear front at a rate of v_2 and $v_1 < v_2$, because the coordinate of the rear front q_1 is smaller than the coordinate of the fore front q_2 . Thus the width of the zone is bound to decrease during the elution process.

The integration of eqn. (20) within the limits q_0 to q_1 —*i.e.* the migration of the fore front for a period t —gives:

$$q_1 = \sqrt{q_0^2 + \frac{2Kh}{1+h} t} \quad (27)$$

Similarly, the migration of the rear front of the zone for the same period will be

$$q_2 = \sqrt{\frac{2Kh}{1+h} t} \quad (28)$$

From eqns. (27) and (28) we obtain the dependence on time of the zone width during elution, as follows:

$$\delta q = q_1 - q_2 = q_0^2 / \left(\sqrt{\frac{2Kh}{1+h} t + q_0^2} + \sqrt{\frac{2Kh}{1+h} t} \right) \quad (29)$$

If

$$q_0 \ll \sqrt{2Kht/(1+h)}$$

then

$$\delta q = q_0^2/2 \sqrt{\frac{2Kh}{1+h} t} \quad (30)$$

i.e. if the time period is sufficiently large, the decrease in the width of the zone is inversely proportional to \sqrt{t} . If $t \rightarrow \infty$, we obtain $\delta q \rightarrow 0$. The decrease in the width of the zone represents the equilibrium effect and the area of the zone remains constant

during elution. In fact, the area of the ring with the radius q_1 , according to eqn. (27), will be as follows:

$$P_1 = P_0 + \frac{2\pi K h}{1 + h} t \quad (31)$$

where $P_0 = \pi q_0^2$, *i.e.* the area of the initial zone. The area of the ring with the radius q_2 will be, according to eqn. (28):

$$P_2 = \frac{2\pi K h}{1 + h} t \quad (32)$$

In accordance with eqns. (31) and (32), the area of the zone in the process of elution

$$P_1 - P_2 = P_0 = \pi q_0^2 = \text{const.} \quad (33)$$

In cases where factors which cause frontal diffusion operate during the process of the elution, the deformation of the fronts will depend, according to Wicke's law (10), on the shape of the sorption isotherm and the field of the flow rate. In the case of a convex sorption isotherm, the fore front of the zone will narrow under the influence of the convexity factor of the isotherm. This narrowing will become even more pronounced due to the influence of the flow rate of the mobile phase. In this way, in the presence of a convex sorption isotherm, the formation of a stabilized front can be expected at a certain stage of the elution type sorption dynamics. In the case of the rear front, the convexity factor of the sorption isotherm acts so as to broaden the front. This broadening, however, is partly compensated by the counteracting influence of the flow rate. For this reason the width of the rear front will not increase proportionally with time t , as it will in the case of linear sorption dynamics, but in proportion to \sqrt{t} , as follows from eqn. (18).

In this way, the effect of "tailing" in elution type sorption dynamics in the presence of a convex sorption isotherm also occurs in radial-cylindrical sorption dynamics. Tailing, however, is less pronounced than in the case of linear sorption dynamics.

In the case of a concave sorption isotherm the picture of elution dynamic sorption, while the factors of diffusion of the fronts operate, will be opposite to that which is encountered in the convex sorption isotherm. "Beards" will also form on the fore front as is the case in linear dynamic sorption. The width of the "beard" will increase in proportion to \sqrt{t} , but not however, to t , as would happen in linear sorption dynamics. The rear front in the case of a concave sorption isotherm must become stable.

Linearity of the sorption isotherm is a factor which conserves diffuseness. For this reason, in the case of a linear sorption isotherm when kinetic and quasi-diffusional factors operate, the only factor which counteracts diffuseness will be that of the flow-rate gradient. But even in this case, the degree of diffuseness of the fronts of the zones must be less than in the case of linear dynamic sorption. As a consequence of the shortening of the plateau range of the original zone, in a certain stage of the elution type sorption dynamics, a "band" of the substance to be sorbed will be present in the cylindrical sorber, the maximum of which will have to migrate at a rate of

$$v_{\max} = \frac{K}{q} \cdot \frac{h}{1 + h} \quad (34)$$

Distribution of the substance in the band requires special calculation. The migration of such a band can also be characterized by the coefficient

$$R_F = \rho_{\max}/\rho_F = \sqrt{h/(1+h)}.$$

It is of note that radial-cylindrical dynamic sorption (radial chromatography) resembles, in a certain sense, the so-called gradient dynamic sorption in chromatography. The gradient factor in radial-cylindrical sorption dynamics is a hyperbolic field ($u_\rho = K/\rho$) of the flow rate in the cylindrical sorber.

The gradient factor of the cylindrical velocity field acts as a factor which narrows the zone of the substance undergoing elution.

Neither in convex nor in concave isotherms, however, does the gradient cylindrical field of the flow rates of the mobile phase (as well as in the case of sorption dynamics in columns) fully preclude the influence of factors which cause diffuseness of the fronts. Since in the case of the convex and concave isotherm, the peak concentration after the disappearance of the plateau range will gradually change, the partition ratio h of the maximum of the elution band will also change. Only after the peak concentration has dropped to such low values as to cause the sorption isotherm to become linear, does the partition ratio h become stabilized. Under this condition, the migration rate of the maximum will be defined by the constant coefficient $R_F = \sqrt{h/(1+h)}$.

Reproducible migration coefficients of the chromatographic zones (R_F) in radial chromatography, as in linear chromatography, can only be obtained, if the sorption isotherms of the substances are linear.

REFERENCES

- 1 I. M. HAIS AND K. MACEK, *Paper Chromatography*, Publishing House of the Czechoslovak Academy of Sciences, Prague and Academic Press, London, 1963.
- 2 V. V. RACHINSKII, *The General Theory of Sorption Dynamics and Chromatography*, Consultants Bureau, New York, 1965.

DISCUSSION

HAIS: The relationship between the "linear" R_F value and the "radial" R_F value (R_R)

$$R_F = R_R^2$$

which has been derived by R. J. LE STRANGE and R. H. MÜLLER (*Anal. Chem.*, 26 (1954) 953), has been verified experimentally for paper chromatography by N. C. GANGULI (*Anal. Chim. Acta*, 12 (1955) 335). If somebody wants to do this for thin layers, he can begin with Dr. WOLLENWEBER's strips and disks exhibited upstairs. As far as I can judge from a first glance, they seem to bear out this relationship. In comparing linear and radial chromatography, Prof. RACHINSKII drew our attention primarily to the zone-sharpening effect of the gradient of mobile-phase flow-rate. This sharpening is convincingly represented in Dr. WOLLENWEBER's exhibits. There are further differences, especially those due to the geometry of the space into which evaporation occurs (if it does occur), which seem less amenable to theoretical treatment.