THEORY OF PAPER ELECTROPHORESIS. II.*

SOLUTION OF CONTINUITY EQUATION BY ANALOGUE COMPUTER

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A method was elaborated to solve the continuity equation for paper electrophoresis by an analogue computer, based on a transformation of the basic partial differential equation to a system of ordinary differential equations. The solution was performed for linear distribution functions with due regard to diffusion, slow attainment of equilibrium and flow of electrolyte.

In the previous work[1] we derived the following equation of continuity for paper electrophoresis:

$$\frac{1}{H}\frac{\delta^2 c}{\delta t^2} + \left(\frac{1}{H}\frac{dv(x)}{dx} + \frac{1}{p_0}\frac{df(c)}{dc}\right)\frac{\delta c}{\delta t} - D\frac{\delta^2 c}{\delta x^2} + \left(V + v(x) + v(c) + c\frac{dv(c)}{dc}\right)\frac{\delta c}{\delta x} -$$

$$- \frac{D}{H}\frac{\delta^3 c}{\delta x^2\,\delta t} + \frac{1}{H}\left(V + v(x) + v(c) + c\frac{dv(c)}{dc}\right)\frac{\delta^2 c}{\delta x\,\delta t} +$$

$$+ \frac{1}{H}\left(2\frac{dv(c)}{dc} + c\frac{d^2 v(c)}{dc^2}\right)\frac{\delta c}{\delta t}\frac{\delta c}{\delta x} + c\frac{dv(x)}{dx} = 0 ,\qquad (1)$$

where c denotes concentration of the substance to be separated, $f(c)$ separation function, t time, p_0 porosity, D diffusion coefficient, H coefficient of transfer of the separated substance from the electrolyte to the solid phase, x distance, V constant velocity component, $v(x)$ velocity component that depends on concentration of the substance to be separated.

We shall now deal with the solution of Eq. (1) with the aid of an analogue computer for cases where the distribution function (*i.e.* the dependence of concentration of the migrating substance in the stationary phase on its concentration in the base electrolyte) is linear. Further we shall assume a constant potential gradient along the paper strip during the whole experiment.

CALCULATION

Apparatus

We used a small electronic analogue computer, "Meda II" type differential analyzer (Aritma, Prague), supplemented with twenty operational amplifiers, nine function generators of the type "Digef 12", five calculators "Senas II", two $x - y$ recorders "Bak II" with a monitoring oscilloscope and a digital voltohⁱameter "VOM" (all accessories from the same firm).

Principle of the Method

Partial differential equations cannot be solved directly on the Meda II type differential analyzer.* An approximate solution can be obtained in a similar way as with numerical methods: the partial differentiation with respect to one variable is replaced by differences formed by dividing the definition range of this variable into a sufficiently large number of equal steps, and the partial differentiation with respect to the other variable is replaced by an ordinary one. Thus, the partial differential equation is transformed to a system of ordinary ones.

In the case of column electrophoresis where the dependence of concentration on time in a given place is important (at the end of the column), it would be advantageous to replace the real (experimental) time by the computer time and to perform the calculation for discrete distances. However, in paper electrophoresis we are interested in the concentration distribution along the paper strip ($c - x$ dependence) at different times. Therefore we replace the x coordinate by the computer time and use discrete real time values $t_0 = 0$, $t_1 = h, \ldots t_n = nh$. The approximate solution in the n-th point depends only on the x coordinate and is denoted as $c_n \equiv c(t_n, x)$.

The first time derivative is expressed approximately[2] as $(\partial c(x, t)/\partial t)_{t = t_n} \approx \Delta c_n/h$ and the second as $(\partial^2 c(x, t)/\partial t^2)_{t = t_n} \approx \Delta c_n^2/h^2$.

Discussion of Difference Formulas

The accuracy of the solution depends on the difference formulas used and on the distance of neighbouring points h, and can be improved by decreasing h and using more accurate approximation formulas. In both cases more accessories for the computer are needed. Decreasing h results in a larger number of steps, *i.e.* in more differential equations in the transformed system; therefore more basic operational units are necessary. With the same step width h, more accurate difference formulas are based on more points resulting in the need of a larger number of summing amplifiers in the computer program. (A table of difference formulas for the first and second derivatives can be found in ref.[2])

The influence of various difference formulas for the first derivative on the con-

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*   The computer programs for all mentioned calculations are available by the authors.

centration profile of the zone was studied on the solution of the simplest variant of Eq. (1):

$$(K/p_0)(\partial c/\partial t) + (EU/\gamma)(\partial c/\partial x) = 0 , \qquad (2a)$$

transformed suitably as follows:

$$pc_n = -K_0 \Delta c_n , \qquad (2b)$$

where $p = d/dx$ and $K_0 = K\gamma/Ehp_0U$. (Assumptions involved in this equation are mentioned in further text.) This equation was chosen because its solution is known: the initial concentration profile of the zone moves without change along the x axis and the symmetry is preserved.

Of various difference formulas for Δc_n, the following one proved to be most advantageous:

$$\Delta c_n = -c_{n-1} + 0.66c_n + 0.34c_{n+1} , \qquad (3)$$

leading to a stable solution; the concentration profile of the zone remains symmetrical (Fig. 1). The concentration decrease in the maximum will be discussed below.

Initial Conditions

Equation (1) is a general equation of paper electrophoresis. The experimental conditions (zonal and frontal electrophoreses) are characterized by different initial conditions. In zonal electrophoresis, where a narrow zone of the sample of width Δx is put on the start, we have:

$$t = 0 : \quad c = c_0 \quad \text{for} \quad 0 \leqq x \leqq \Delta x ; \quad c = 0 \quad \text{for} \quad x > \Delta x ,$$

$$t > 0 , \quad x \geqq 0 : \quad c \leqq c_0 .$$

This initial condition is of course only a rough approximation assuming a sharply limited zone within which the concentration c_0 is everywhere constant. It is used in the theory of chromatography and brings a considerable simplification when Δx is much smaller than the distance in which the concentration profile of the zone is measured.

In reality, the concentration distribution in the zone is governed by diffusion, the $c - x$ curve at a given time being very similar to the Gaussian distribution curve. If the latter is used as initial condition for the concentration profile of the zone it brings two advantages. First, the real state before starting the electrophoresis is better described, and second, when for $t = 0$, $0 < x < \Delta x$ is $0 < c \leqq c_0$, and for $t = 0$, $x = 0$ or $x \geqq \Delta x$ is $c = 0$, then also for $t > 0$, $x = 0$ must be $c = 0$. Then the

exact (zero value) boundary condition is introduced in all integrators during the computations. In the present work the starting zone is defined by the Gaussian distribution curve.

In the frontal method of paper electrophoresis where the solution of concentration c_0 is fed continuously to the boarder of the paper, we have:

$$t = 0: \quad c = c_0 \quad \text{for} \quad x = 0; \quad 0 < c < c_0 \quad \text{for} \quad 0 < x < \Delta x;$$

$$c = 0 \quad \text{for} \quad x \geqq \Delta x.$$

After the beginning of electrophoresis, three sections can be distinguished on the $c - x$ curve characterized as follows: $t > 0$, $c = c_0$ for $0 \leqq x \leqq x_a$; $0 < c < c_0$ for $x_a < x < x_b$; $c = 0$ for $x \geqq x_b$. An additional condition is $\Delta x \leqq x_b - x_a$. The solution of Eq. (1) with the mentioned initial conditions for the frontal method will be the subject of another work.
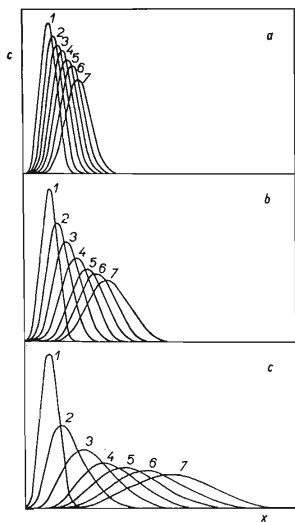

Fig. 1

Solution of Equation $(2a)$ for Various h Values

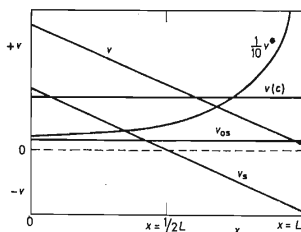a $h = 1$ min; b $h = 2$ min; c $h = 4$ min. The curve numbers give the n values.

Fig. 2

Dependence of Components of Rate of Flow of Electrolyte v on Distance x

L Denotes total length of paper strip, the meaning of other symbols is given in the text.

INFLUENCE OF VARIOUS FACTORS ON ZONE CONCENTRATION PROFILE

Influence of Longitudinal Diffusion and Slow Equilibration

Equation (2a), in which in addition to the mentioned assumptions of a linear adsorption isotherm ($f(c)/c = K$) and constant potential gradient ($v(c) = EU/\gamma$; $\partial E/\partial x =$ const.) also a mobile equilibrium ($\lim H^{-1} = 0$), negligible longitudinal diffusion, sucking and osmotic flows are assumed ($D = 0$, $V = v(x) = 0$), can be solved either by the differential or by the finite difference method. According to the differential method of solution[3] the starting concentration profile of the zone moves without any change along the x axis. Although Eq. (2a) does not involve the influence of diffusion and slow equilibration, the difference method simulates both these effects by the assumption of finite differences. The result is the well-known dispersion of the zone: the maximum concentration diminishes and the zone broadens. The result of the solution of Eq. (2a) by the difference method is shown in Fig. 1. The same result is obtained by solving the equation involving explicitly the influence of diffusion

$$(K/p_0)\,(\partial c/\partial t) + (EU/\gamma)\,(\partial c/\partial x) - D_{ef}(\partial^2 c/\partial x^2) = 0\,, \qquad (4)$$

by the differential method. The effective diffusion coefficient D_{ef} involves besides diffusion also the influence of slow equilibration. The D_{ef} value can be determined
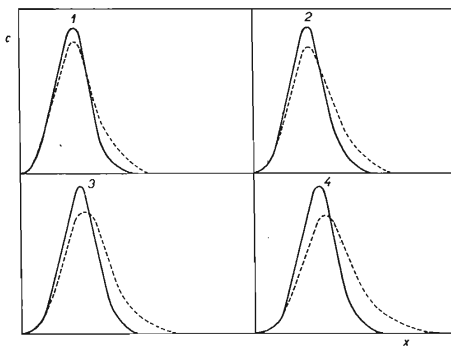

FIG. 3

Solution of Equation (5a) (Full Curves)

The curve numbers give the n values. Dashed curves shown for comparison correspond to the concentration profile without the influence of electrolyte flow, other conditions being the same.

by analysis of the concentration profile of the zone obtained by solving Eq. $(2a)$ by the difference method for various values of the time interval h. The calculation is based on the Röck equation[4]: $D_{ef} = \Delta x^2/8t$, where Δx denotes width of the zone for $c = c_{max}e^{-1/2} \approx 0.607c_{max}$. To study the influence of diffusion and of slow equilibration, we used Eq. $(2b)$ in the form

$$pc_n = K_0 c_{n-1} - 0.66 K_0 c_n - 0.34 K_0 c_{n+1} ,$$

$$pc_n = K_0 c_{n-1} - K_0 c_n . \tag{2c}$$

The former equation was used for $n = 1$ to 5, the latter for $n = 6$. The coefficients in Eq. $(2a)$ were chosen as follows: $h = 1, 2$ and 4 min, $K = 2.8$, $\gamma = 1.2$, $p_0 = 2.8 \cdot 10^{-3}$ kg^{-3} m, $E = 10^3$ V/m, $U = 10^{-7}$ m^2 s^{-1} V^{-1}, hence in Eq. $(2c)$ $K_0 = 2 \cdot 10^5$; $1 \cdot 10^5$ and $0.5 \cdot 10^5$.

To calculate the effective diffusion coefficient, the Röck equation was rearranged to enable calculation from two concentration profiles of the zone at different times as follows: $D_{ef} = (\Delta x_2^2 - \Delta x_1^2)/8\Delta t$, where Δx_1 and Δx_2 are the widths of two zones corresponding to times t_2 and t_1; $\Delta t = t_2 - t_1$. The values needed for the calculation were determined from Fig. 1 and the D_{ef} value was calculated as $(3.3 \pm 0.7) \cdot 10^{-10}$ for $h = 1$ min, $(9.8 \pm 1.7) \cdot 10^{-10}$ for $h = 2$ min and $(22 \pm 5) \cdot 10^{-10}$ m/s for $h = 4$ min. At constant h, the D_{ef} value shows no significant dependence on n; the Röck equation is therefore well applicable. The expected increase of the D_{ef} value with h shows that the solution of Eq. $(2a)$ by the difference method simulates the influence of diffusion and slow equilibration.
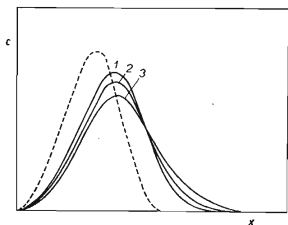

Fig. 4

Solution of Equation $(5a)$ for $n = 4$
Dashed curve corresponds to the boundary condition $(n = 0)$. The curves are numbered in the order of decreasing v_s/v values.

Influence of Electrolyte Flow

We shall deal with the solution of the equation

$$(K/p_0)(\partial c/\partial t) + (v_{0s} + \tfrac{1}{2}aL - ax + EU/\gamma)(\partial c/\partial x) - ac = 0 . \tag{5a}$$

We denote $K/p_0 h = K_1$, $a = K_2$, $v_{0s} + \frac{1}{2}aL - ax + EU/\gamma = v$, $1/v = v^*$. Eq. $(5a)$ can be transformed with the aid of difference formulas to a system of four ordinary differential equations:

$$pc_n = v^*(K_1 c_{n-1} - 0.66 K_1 c_n - 0.34 K_1 c_{n+1} + K_2 c_n),$$

$$pc_n = v^*(K_1 c_{n-1} - K_1 c_n + K_2 c_n), \tag{5b}$$

where the former expression applies for $n = 1$ to 3 and the latter for $n = 4$. The calculated rates of flow and their components are shown in Fig. 2. The results of solution of the system of equations $(5b)$ for different times and for various v values at a given time are presented graphically in Figs 3 and 4. The values of c and x are given in arbitrary units since no attempt was made to determine the parameter values. It is apparent from Figs 3 and 4 that the electrolyte flow exerts an influence on the concentration profile of the zone; it causes a sharpening of the zone head. This effect is due to diminishing the resulting velocity of motion of the ions with increasing distance from the start.

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