

**THEORY OF PAPER ELECTROPHORESIS. III.\***  
**SOLUTION OF CONTINUITY EQUATION**  
**FOR NONLINEAR DISTRIBUTION FUNCTIONS**

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In the preceding communication<sup>1</sup> the equation of continuity was solved for the case of a linear distribution function and constant potential gradient, and the influence of various factors on the concentration of the substance migrating in the electric field was considered. The present work deals with the case where the distribution function is not linear. An analogous case is obtained when the migrating compound is a weak electrolyte. The potential gradient will be considered constant as in the preceding work.

The calculations were performed analogously as in the preceding work<sup>1</sup> by the difference method on the same analogue computer.\*\*

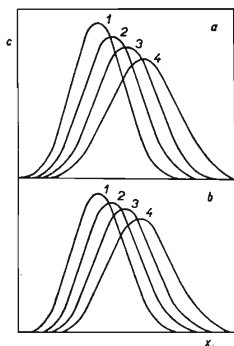


FIG. 1

Solution of Eq. (1a) for  $f'(c)$  Depending Linearly on  $c$

A  $f(c)$  is convex; B  $f(c)$  is concave with respect to the  $c$  axis. Curve numbers give  $n$  values.

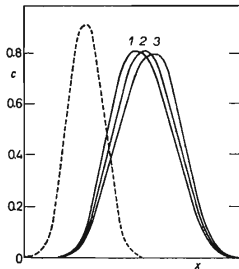


FIG. 2

Solution of Eq. (1a) for  $n = 4$

1  $f'(c)$  proportional to  $c$ ,  $f(c)$  concave to  $c$  axis; 2  $f'(c) = 0$ ; 3  $f'(c)$  proportional to  $c$ ,  $f(c)$  convex to  $c$  axis. Dashed curve corresponds to initial distribution,  $n = t = 0$ .

\* Part II: This Journal 36, 2123 (1971).

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

## RESULTS AND DISCUSSION

## Electrophoresis without Flow of Base Electrolyte

When the separation isotherm is not linear, the continuity equation involving diffusion and nonequilibrium (Eq. (2a) in reference<sup>1</sup>) takes the form

$$(f'(c)/p_0)(\delta c/\delta t) + (EU/\gamma)(\delta c/\delta x) = 0 \quad (1a)$$

(for meaning of symbols see reference<sup>1</sup>). On denoting  $\gamma/Ehp_0U = K_1$  and using the same difference formulas as previously (Eq. (3) in reference<sup>1</sup>) we can replace Eq. (1a) by the following system of ordinary differential equations:

$$\begin{aligned} pc_n &= K_1 f'(c) c_{n-1} - 0.66 K_1 f'(c) c_n - 0.34 K_1 f'(c) c_{n+1}, \\ pc_n &= K_1 f'(c) c_{n-1} - K_1 f'(c) c_n, \end{aligned} \quad (1b)$$

where the former expression holds for  $n = 1$  to 3, the latter for  $n = 4$ . The solution is shown graphically in Fig. 1. The deformation of the concentration profiles of the zone is more distinct in Fig. 2, where besides the initial concentration profile of the zone also the concentration profiles for  $n = 4$  and for three different distribution functions are shown. It is seen that the medium concentration profile of the zone (curve 2) corresponding to a linear distribution function remains symmetrical, whereas with nonlinear distribution functions the zone becomes unsymmetrical and either the front (curve 3) or the rear (curve 1) part of the zone sharpens.

For comparison, we attempted to determine the distribution function from the diffusion (rear) part of curve 3 in Fig. 2. We used the Glueckauf method<sup>2</sup>, but in a modified form. This method assumes that the width of the zone at the beginning of the experiment is negligible against the distance  $x$  in which the elution curve is measured. Since this assumption is not fulfilled in our

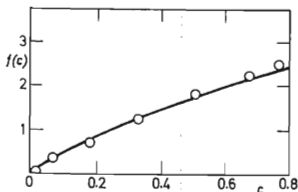


FIG. 3

Distribution Function  $f(c)$  Used in Calculating Curve 3 in Fig. 2 (Solid Curve) and Recalculated from Eq. (3) (Circles)

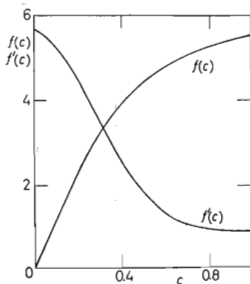


FIG. 4

$f(c)$  and  $f'(c)$  Functions Used in Calculating Curves in Fig. 5

case, we must use the integrated form of the de Vault equation with the integration constant

$$x = V/(f(c) + p_0) + S_x(c), \quad (2)$$

where  $S_x(c)$  is a function expressing the form of the zone at the beginning of the experiment ( $V = 0$ ). We introduce  $x_r = x - S_x(c)$ ;  $x_r$  denotes the distance by which a point corresponding to a certain concentration is shifted on the  $c - x$  curve during the experiment. The Glueckauf equation takes the form

$$f(c) = (cV + \mu)/x_r, \quad (3)$$

where  $\mu$  denotes in chromatography the amount of substance which remains in the column after the elution agent of volume  $V$  has flown through. In paper electrophoresis,  $\mu$  has the meaning of the total amount of substance from the start to a given point  $x$  or  $x_r$ , i.e.  $\int_0^x f(c) dx$ . The integration was replaced by summation, the  $c - x$  curve was divided into  $n$  sections and the  $\mu$  values in every section ( $\mu_1$  to  $\mu_n$ ) were calculated in turn. For the beginning of the curve we set  $\mu_1 = 0$ . The result of this calculation is shown in Fig. 3.

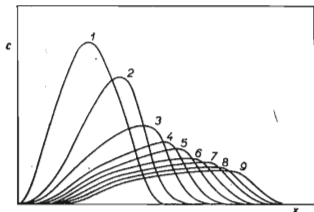


FIG. 5  
Solution of Eq. (1a) for  $f(c)$  According to Fig. 4  
Curve numbers give  $n$  values.

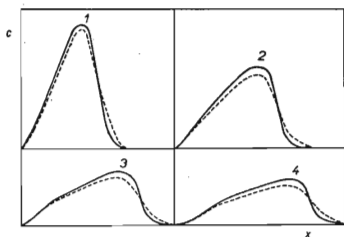


FIG. 6  
Solution of Eq. (4a) for  $f(c)$  According to Fig. 4 (Solid Curves)  
Curve numbers give  $n$  values. Dashed curves show the concentration profile without the influence of flow, other conditions being preserved.

The above calculations concern the solution of Eq. (1a) for the special case where the first derivative of the distribution function depends linearly on concentration. To obtain different forms of the distribution function,  $f(c)$ , we used diode function generators and recorded the  $c-x$  curves. One example of the  $f(c)$  function is shown in Fig. 4 and the corresponding results of calculation in Fig. 5. It is seen that the frontal part of the zone sharpens in accord with experience (since  $f(c)$  is convex with respect to the concentration axis) and the maximum concentration diminishes. Its most pronounced decrease is observed at the beginning of electrophoresis when the concentration is in the range corresponding to the greatest curvature of the distribution function.

#### Influence of Base Electrolyte Flow

If the distribution function is nonlinear and a flow of electrolyte in the paper takes place, it is necessary to solve the equation

$$(f'(c)/p_0)(\delta c/\delta t) + (v_{0s} + \frac{1}{2}aL - ax + EU/\gamma)(\delta c/\delta x) - ac = 0, \quad (4a)$$

which can be derived on introducing the nonlinear distribution function into Eq. (5a) of reference<sup>1</sup>. Analogously as in the preceding case we arrive at the equations

$$\begin{aligned} pc_n &= Q^*(K_1 f'(c) c_{n-1} - 0.66K_1 f'(c) c_n - 0.34K_1 f'(c) c_{n+1} + K_2 c_n), \\ pc_n &= Q^*(K_1 f'(c) c_{n-1} - K_1 f'(c) c_n + K_2 c_n), \end{aligned} \quad (4b)$$

where  $K_1 = 1/hp_0$ ; the former equation holds for  $n = 1$  to 3, the latter for  $n = 4$ . The solution of this system of equations is shown graphically in Fig. 6. As in the case of a linear  $f(c)$  function (cf. Fig. 3 in reference<sup>1</sup>), also in the present case the flow of electrolyte causes a sharpening of the frontal part of the zone, which of course is somewhat sharpened also by the influence of the special form of the  $f(c)$  function used.

#### Influence of Partial Dissociation of Migrating Substance

We assume first that the contribution of conductivity of the migrating substance to the total conductivity of the electrolyte is negligible. On introducing this assumption and the relationship

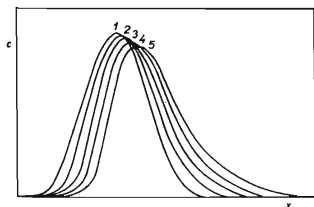


FIG. 7

Solution of Eq. (5a)

Curve numbers give  $n$  values.

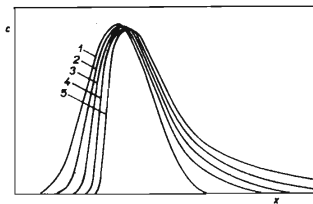


FIG. 8

Solution of Eq. (6a)

Curve numbers give  $n$  values.

for the dissociation constant (Eq. (16) in reference<sup>3</sup>) into the equation of continuity (Eq. (9) in reference<sup>3</sup>) we obtain

$$\frac{K}{p_0} \frac{\delta c}{\delta t} + \frac{EK_A U}{\gamma(K_A^2 + 4K_A c)^{1/2}} \frac{\delta c}{\delta x} = 0. \quad (5a)$$

This can be rearranged as in the preceding cases to the form suitable for the computer:

$$\begin{aligned} pc_n &= K_1 Q(c_{n-1} - 0.66c_n - 0.34c_{n+1}), \quad n = 1 - 3, \\ pc_4 &= K_1 Q(c_3 - c_4), \end{aligned} \quad (5b)$$

where  $K_1 = K\gamma/EhK_A p_0 U$  and  $Q = (K_A^2 + 4cK_A)^{1/2}$ . The modeling of these equations requires a relatively large number of operating units; it was therefore necessary to calculate the  $Q$  function in advance and to introduce it into the computer system with the aid of function generators. The final solution for  $K_A = 0.04$  is depicted in Fig. 7.

If the contribution of conductivity of the migrating compound is not negligible against that of the base electrolyte, then Eq. (14) rather than (16) in reference<sup>3</sup> is used to obtain

$$\frac{K}{p_0} \frac{\delta c}{\delta t} + \frac{K_a K_b K_A U}{\gamma[K_b - \frac{1}{2}K_A + \frac{1}{2}(K_A^2 + 4K_A c)^{1/2}]^2 (K_A^2 + 4K_A c)^{1/2}} \frac{\delta c}{\delta x} = 0. \quad (6a)$$

On setting  $[K_b - \frac{1}{2}K_A + \frac{1}{2}(K_A^2 + 4K_A c)^{1/2}]^2 (K_A^2 + 4K_A c)^{1/2} = Q^*$  and  $K\gamma/hK_a K_b K_A p_0 U = K_1^*$ , Eq. (6a) takes the form of (5b) where  $Q^*$  and  $K_1^*$  is substituted for  $Q$  and  $K_1$ . The result of solution is shown in Fig. 8.

It is obvious from Figs 7 and 8 that uncomplete dissociation of the migrating compound influences the concentration profile of the zone similarly as a distribution function that is concave with respect to the concentration axis: the rear part of the zone becomes sharper. This effect is more pronounced in the case where the contribution of conductivity of the compound under discussion is not negligible against that of the base electrolyte (Fig. 8), since the potential gradient in the zone decreases resulting in an additional sharpening of the rear part of the zone.

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#### REFERENCES

1. Vacík J., Fidler V.: This Journal 36, 2123 (1971).
2. Glueckauf E.: Nature 156, 748 (1945).
3. Vacík J.: This Journal 36, 1713 (1971).

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