Separation in a Thermoelectrogravitational Electrophoresis Column Without Reservoirs:

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Part I. Theoretical Development of the Transport Equation and Its Application to the Analysis of Steady State Batch Operation

The thermoelectrogravitational electrophoresis column without reservoirs has been conceived following the principle of the Clusius-Dickel thermal diffusion column. The transport equation approach in thermal diffusion developed by Jones and Furry to explain the behavior of a conventional thermogravitational thermal diffusion column has been applied to describe the electrophoretic separation in the thermoelectrogravitational electrophoresis column. Equations have been established for a system in which one single or one hypothetically single component is mobile and the other species are at their isoelectric points.

Theoretical calculations for the velocity profiles, temperature distribution, and the steady state batch separation factors have been made with field strength, temperature difference, membrane spacing, and electric mobility as variables, and expected trends of the results are discussed using the steady state solution of the transport equation for batch operation.

SCOPE

The objective of these studies was the experimental definition of a mathematical theory for a continuous thermoelectrogravitational liquid diffusion column without reservoirs in order to provide guidelines for the design of separation systems using these diffusional fluxes. The work is an extension of analysis for identical geometry for the thermal diffusion column without reservoirs.

CONCLUSIONS AND SIGNIFICANCE

Experimental results for the separation of bovine albumin from buffer solution showed that the theory gave qualitative predictions of the influence of design variables on separation and capacity consistent with previous results for liquid thermal diffusion columns of the same type. The preliminary theory suggests that moderate laboratory data will suffice for the design of larger scale continuous separations using both thermal and electro diffusion with convection.

The purpose of this work was to develop suitable mathematical theory and to explore the possibility of constructing thermoelectrogravitational electrophoresis columns without reservoirs and to obtain sufficient experimental data to establish the theory. In the present paper, a basic mathematical theory for theoretical analysis of such columns is developed. Two subsequent papers will be devoted to the presentation of further theoretical development and experimental work and a discussion of the results obtained. A summary of previously reported experimental apparatus is presented in Prabhudesai (1965), and there are several relevant papers (Bier Milan, 1957; Dobry and Finn, 1958; Gutfreund, 1943; Kirkwood, 1941; Mel, 1900; Pauli, 1924; Polson, 1953; Strain, 1952; Van de Wonde and Davis, 1960; Winston et al., 1963; Wunderley, 1952).

ELECTROPHORESIS COLUMN THEORY

Following the Clusius-Dickel (1939) column, the principle of a batch electrophoresis column without reservoirs is illustrated in Figure 1. Unlike a thermal diffusion column, the solution of components to be separated is placed between two semipermeable membranes (instead of impervious metal plates) backed by two coextensive plate electrodes, by means of which an electrical field can be

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applied across the solution. A temperature gradient can also be established by adjusting the temperatures of the two buffer solutions flowing past the two membranes. Since both electrical and temperature fields can be employed if beneficial, this separation column will be termed a thermoelectrogravitational electrophoresis column.

In what follows, essentially only the isoelectric procedure is considered because the model assumes only one mobile species in a fluid field. The separation is therefore restricted to systems which can be considered as binary with only one mobile component. A multicomponent system must be considered as a binary system by taking the solvent and all isoelectric species as one component and all the mobile species together as the other component. Mass averaged properties for electrical mobility and ordinary diffusivity can be used for the hypothetical mobile component.

SELECTION OF MATHEMATICAL PROCEDURE FOR ANALYSIS

The Furry, Jones, and Onsager (FJO) procedure (1939) is commonly used in thermal diffusion. This FJO procedure of analysis can accommodate the boundary conditions required by both the steady state batch case and the continuous flow case. Moreover, even though it is approximate, it yields a nonlinear differential equation for the transport of a component in a column, which can be further simplified to an ordinary first-order linear differential equation and solved for a variety of cases of column operation. This procedure has been employed in thermal diffusion (Boyer and Powers, 1961; Crownover and Powers, 1962; Fleming and Powers, 1963; Powers, 1961; Powers and Wilke, 1957; Vichare and Powers, 1961) to describe the behavior of a transient batch column and a continuous flow column with or without vertical or horizontal barriers. The FJO transport equation is also easily modified to describe concentrated dilute and intermediate concentration binary solution systems. Although the original FJO procedure did not include the effect of concentration difference on density (Forgotten Effect), it can be accounted for in the FJO procedure by methods that have been developed by deGroot et al.(1943) and later by Baldschweiler (1961), Von Halle (1959), and Horne and Bearman (1962). Because of the similarity between thermal diffusion and electrophoresis column operation, the FJO procedure can be adapted to the analysis of the combined effect of electrophoresis and thermal diffusion. For these reasons, the FJO procedure will be used here for the mathematical description of the electrophoresis column.

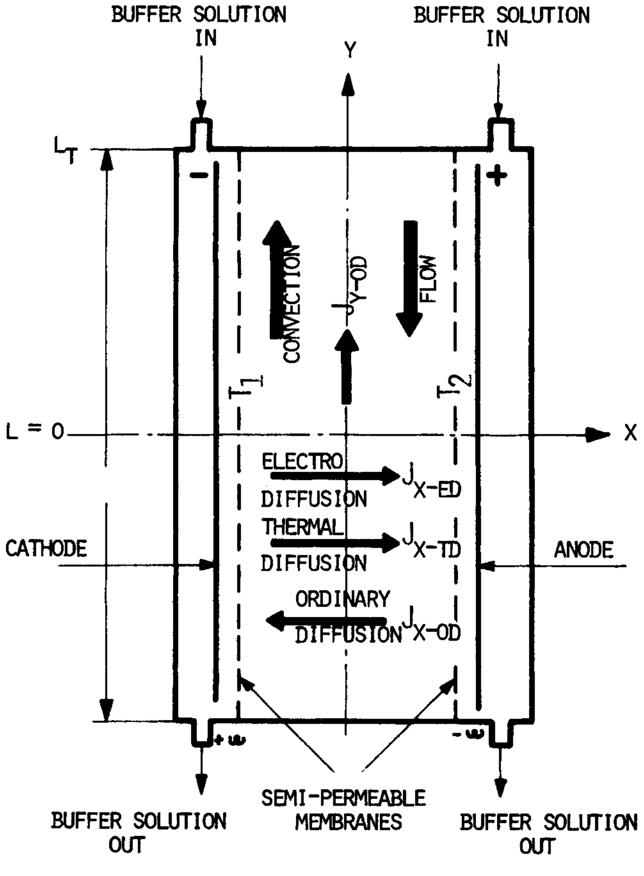

Fig. 1. Principle of operation and major fluxes in a batch thermoelectrogravitational column without reservoirs.

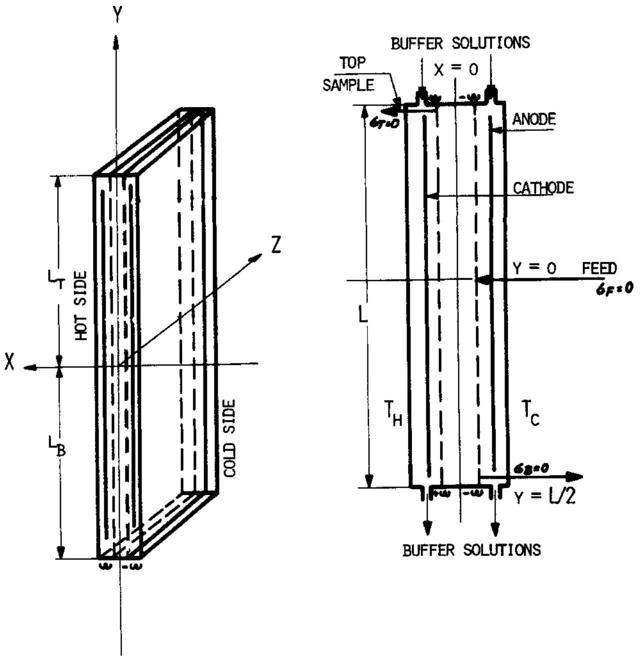

Fig. 2. Coordinate system for batch thermoelectrogravitational column.

PHENOMENOLOGICAL FORMULATION

For the formulation of phenomenological theory of the column, consider a solution at a certain pH in which there are several components (for example, proteins) P_1, P_2, P_3, —P_n having electric mobilities U_{1s}, U_{2s}, U_{3s},—U_{ns}. The solution is placed in a batch thermoelectrogravitational column without reservoirs which has a direct current electric field and a temperature field applied across the membranes. The coordinate system to be employed for analysis is illustrated in Figure 2. The two membranes are separated by a distance equal to 2ω and the column is imagined to be separated into two sections, top and bottom, vertically, at the line $y = 0$.

Since we are considering only the isoelectric procedure in this development, the fluxes for a single component can be easily written. If there is more than one mobile component, the fluxes could be written for a hypothetical component with C_H—the mass fraction concentration of the hypothetical component given by

$$C_H = \sum_{n=1}^{m} C_n \qquad (1)$$

and the electric mobility of the hypothetical single component given by

$$U_H = \sum_{n=1}^{m} C_n U_{ns} \Big/ \sum_{n=1}^{m} C_n \tag{2}$$

We will denote the concentration of mobile species (as a single component) by C_1 and its mobility by U_{1s}. In the same manner, a mass averaged ordinary diffusivity (D_{1s}) and thermal diffusion coefficient (α_{1s}) can also be written. The fluxes for the mobile component can now be written as:

In the x direction:

Flux due to electric field

$$J_{x-ED} = \rho\left[-U_{1s}\frac{dV}{dx}\right]C_1C_s \tag{3}$$

Flux due to thermal field

$$J_{x-TD} = \rho\left[-\frac{\alpha_{1s}D_{1s}}{T}\frac{dT}{dx}\right]C_1C_s \tag{4}$$

Flux due to ordinary diffusion

$$J_{x-OD} = -\rho D_{1s}\frac{\partial C_1}{\partial x} \tag{5}$$

In the y direction:

Flux due to ordinary diffusion in vertical direction

$$J_{y-OD} = -\rho D_{1s}\frac{\partial C_1}{\partial y} \tag{6}$$

In the above equations, ρ = average density (g/cc), C_s = mass fraction concentration of solvent, V = voltage at a point along x direction, and T = temperature which is a function of x. In order to obtain a simplified mathematical description of the electrophoresis column, the following assumptions will now be made:

1. There are no gradients in the z direction, which implies the assumption that the width is infinite in z direction; therefore, edge effects are negligible.
2. Temperature and voltage gradients occur only in the x direction.
3. The column length is very large so that end effects can be neglected.
4. In order to evaluate the properties of the solution in the column such as average viscosity and mean average density, an integrated average temperature $\overline{T}$ may be used.
5. The electric mobility, the thermal diffusion constant, and the ordinary diffusivity are all constant at all positions in the column.
6. Laminar flow conditions exist between the membranes.

With these assumptions and previously defined fluxes, a material balance around a differential element of the solution space over an infinitesimal time increment yields, in the limit, the following partial differential equation having one term with a nonconstant coefficient:

$$\rho\frac{\partial C_1}{\partial t} = D_{1s}\left(\frac{\partial^2 C_1}{\partial x^2} + \frac{\partial^2 C_1}{\partial y^2}\right) + \left[\frac{\alpha_{1s}D_{1s}}{\overline{T}}\frac{dT}{dx} + U_{1s}\frac{dV}{dx}\right]\frac{\partial C_1C_s}{\partial x} - v(x)\frac{\partial C_1}{\partial y} \tag{7}$$

where m is amount of solution per unit length of column and $v(x)$ is the laminar velocity profile, a function of x only. At the membrane walls, the net transfer of the mobile component due to ordinary, electric, and thermal diffusion must be zero since the membrane is semipermeable and does not allow molecules of either the mobile or the isoelectric component to pass through its pores. Therefore any solution to Equation (7) must be subject to the boundary condition that:

$$-D_{1s}\frac{\partial C_1}{\partial x} + \left[U_{1s}\frac{dV}{dx} + \frac{\alpha_{1s}D_{1s}}{\overline{T}}\frac{dT}{dx}\right]C_1C_s = 0 \quad \text{at} \quad x = +\omega,\ -\omega \tag{8}$$

(Hereafter, the subscripts on D and U will be dropped for convenience as only one component is considered.)

In addition to the condition expressed in Equation (8), a solution to Equation (7) must also satisfy the material balance equation around each section of the column:

$$\tau = B\rho\int_{-\omega}^{\omega} C_1\, v(x)\, dx - B\rho\int_{-\omega}^{\omega} D\frac{\partial C_1}{\partial y}\, dx \tag{9}$$

where B is column width (cm), in the z direction (assumed constant), ρ = average density g/cm^3 at $\overline{T}$, and τ = net transport of component 1 down the column, g/sec. Equations (7), (8), and (9), together with a relation for $v(x)$ to be derived later, provide a basis for an adequate mathematical description of a thermoelectrodiffusion column subject to the assumptions made. But the nonlinear form of the basic partial differential equation [Equation (7)], the nonconstant coefficient involved in $v(x)$, and the associated boundary conditions make it difficult to obtain a rigorous mathematical solution. A simplified transport equation will therefore be obtained by application of the FJO procedure.

The form of Equation (7) will be simplified by making further assumptions as follows:

7. Vertical diffusion will be neglected as compared to transport by vertical convection, that is, $D\,\frac{\partial^2 C_1}{\partial y^2} << v(x)\,\frac{\partial C_1}{\partial y}$.
8. Only the steady state solution will be considered so that $\frac{\partial C_1}{\partial t} = 0$.
9. Flow between parallel membranes is laminar so that convective backmixing is negligible.
10. The voltage gradient $\frac{dV}{dx}$ can be replaced by E, the electric field strength by definition,
11. E is assumed constant.
12. Also, it will be assumed that $\frac{dT}{dx}$ can be replaced by an average value $\frac{\overline{dT}}{dx}$ to take into account the dependence of T on x.

When these assumptions are applied to Equation (7), one obtains

$$D\frac{\partial^2 C_1}{\partial x^2} + \left(UE + \frac{\alpha_{1s}D}{\overline{T}}\cdot\frac{\overline{dT}}{dx}\right)\frac{\partial C_1C_s}{\partial x} - v(x)\frac{\partial C_1}{\partial y} = 0 \tag{10}$$

The boundary conditions of Equation (8) are also modified to give

$$D \frac{\partial C_1}{\partial x} + \left(UE + \frac{\alpha_{1s} D}{\bar{T}} \cdot \frac{\overline{dT}}{dx} \right) C_1 C_s = 0 \quad \text{at} \quad x = +\omega, -\omega \tag{11}$$

Application of the FJO procedure with the use of Equation (9), (10), and (11) yields for the transport of the component down the column the equation

$$\tau = \overline{C_1 C_s} \left[B\rho \left(\frac{UE}{D} + \frac{\alpha_{1s}}{\bar{T}} \frac{\overline{dT}}{dx} \right) \right] \int_{-\omega}^{\omega} \int_{-\omega}^{x} v(x)\, dx\, dx - \frac{d\overline{C_1}}{dy} \frac{B\rho}{D} \left[\int_{-\omega}^{\omega} \left(\int_{-\omega}^{x} v(x)\, dx \right)^2 dx \right] - B\rho D \left(\int_{-\omega}^{\omega} dx \right) \frac{d\overline{C_1}}{dy} \tag{12}$$

A superbar (on C) indicates the mean value (of C) taken at $x = 0$. In addition to the assumptions listed before, the derivation of Equation (12) involves the following assumptions:

13. The product C_1C_s is essentially independent of x.
14. $\dfrac{\partial C_1}{\partial y}$ is independent of x, so that all x dependence is retained within the integrals.
15. The mean concentration at $x = 0$ will be satisfactory for defining the y dependence of composition.

Given a velocity distribution, all expressions within the brackets in Equation (12) can be integrated to yield constant coefficients. Let these coefficients be defined as

$$H = B\rho \left(\frac{UE}{D} + \frac{\alpha_{1s}}{\bar{T}} \frac{\overline{dT}}{dx} \right) \int_{-\omega}^{\omega} \int_{-\omega}^{x} v(x)\, dx\, dx \tag{13}$$

$$K_c = \frac{B\rho}{D} \int_{-\omega}^{\omega} \left[\int_{-\omega}^{x} v(x)\, dx \right]^2 dx \tag{14}$$

$$K_d = B\rho D \int_{-\omega}^{\omega} dx \tag{15}$$

Further K_c and K_d can be combined together as

$$K = K_c + K_d \tag{16}$$

The above expressions are similar in form to those obtained for thermal diffusion columns (Furry et al., 1939; Jones and Furry, 1946; Powers and Wilke, 1957). Their final form will depend upon the nature of the velocity profile $v(x)$ which is discussed subsequently.

With the above definitions of column transport coefficients, the equation for the transport of the component down the column is given by

$$\tau = H\, \overline{C_1 C_s} - K \frac{d\overline{C_1}}{dy} \tag{17}$$

This is the transport equation for a batch thermoelectrogravitational column. Although it is simple in form, it is still a nonlinear differential equation because of the presence of the product term $\overline{C_1C_s}$. This equation has been derived with the assumption of a steady state batch operation of the electrophoresis column. With certain modifications, it can also be used to describe the continuous flow steady state and transient batch operations of the column. These applications will be considered in subsequent papers, but the evaluation of the velocity profile and temperature distribution required for evaluation of column transport coefficients H and K must be considered first.

EVALUATION OF VELOCITY PROFILE

Assuming the flow in the column is Newtonian and using the Navier-Stokes equation for a Newtonian fluid, one has

$$\frac{\eta}{g_c} \frac{d^2 v(x)}{dx^2} - \frac{dP}{dy} - \frac{\rho g}{g_c} = 0 \tag{18}$$

With P the fluid pressure, η the viscosity, g the gravitational acceleration and g_c the units conversion from force to momentum rate. Differentiation of Equation (18) with respect to x yields (assuming dP/dy independent of x)

$$\frac{d^3 v(x)}{dx^3} = \frac{g}{\eta} \frac{d\rho}{dx} \tag{19}$$

For the case of a single mobile component, $d\rho/dx$ is given by

$$\frac{d\rho}{dx} = \frac{\partial \rho}{\partial T} \frac{dT}{dx} + \frac{\partial \rho}{\partial C_1} \cdot \frac{\partial C_1}{\partial x} \tag{20}$$

Thus, for the evaluation of $d\rho/dx$, it is necessary to determine the two terms on the right hand side of Equation (20).

EVALUATION OF TEMPERATURE DISTRIBUTION

In deriving material balance Equation (7), $\overline{dT}/dx$ and $\bar{T}$ were both employed. To obtain values of these and the value of dT/dx required in Equation (20) for evaluation of the velocity profile $v(x)$, an expression for temperature distribution is required. In an electrophoresis column, an amount of heat Q cal/s/cm³ (given by $Q = k_e E^2$ where E is the electric field strength, volt/cm, and k_e is the electrical conductivity of the solution) is evolved, and this will influence the temperature distribution and the value of $\bar{T}$. With the assumption of steady state heat transfer and constant voltage gradient to stabilize the electrical and thermal fields and constant thermal conductivity for solution, an energy balance on an incremental volume of solution yields a differential equation relating T and x as

$$\frac{d^2 T}{dx^2} + \frac{Q}{k} = 0 \tag{21}$$

where k is the thermal conductivity of solution. Solving Equation (21) subject to the boundary conditions:

$$\begin{aligned} T &= T_2 \quad \text{at} \quad x = +\omega \\ T &= T_1 \quad \text{at} \quad x = -\omega \end{aligned} \tag{21a}$$

gives

$$T - T_{av} = \frac{Q}{2k} (\omega^2 - x^2) + \frac{x \Delta T}{2\omega} \tag{22}$$

where

$$\Delta T = T_2 - T_1, \text{ and } T_{av} = \frac{T_1 + T_2}{2} \tag{23}$$

whence

$$\frac{dT}{dx} = -\frac{Q}{k} x + \frac{\Delta T}{2\omega} \tag{24}$$

$$\bar{T} = \frac{1}{2\omega} \int_{-\omega}^{+\omega} T\, dx = \frac{T_1 + T_2}{2} + \frac{Q\omega^2}{3k} \tag{25}$$

and

$$\frac{\overline{dT}}{dx} = \frac{1}{2\omega} \int_{-\omega}^{+\omega} \frac{dT}{dx}\, dx = \frac{\Delta T}{2\omega} \tag{26}$$

EVALUATION OF CONCENTRATION GRADIENT

The second term in Equation (20) is the measure of change in density caused by the concentration difference and in thermal diffusion it is called the Forgotten Effect. When interpreting thermal diffusion data, this effect is usually assumed negligible. This may be a poor approximation even in thermal diffusion as pointed out by deGroot (1943), Von Halle (1959), and Horne and Bearman (1962). The electric field force is much stronger than the thermal diffusion field force and since its effect is reflected in the concentration difference that results, the concentration gradient term will not be negligible in the electrophoresis column case. Explicit determination of $\overline{\partial C_1}/\partial x$ is not possible independently of the velocity and therefore, following the above authors, it will be assumed that some average value of $\overline{\partial C_1}/\partial x$ can be used. With this assumption and taking $\beta_T = -\partial\rho/\partial T$ and $\beta_C = \partial\rho/\partial\overline{C}_1$ as constants, substitution of dT/dx from Equation (24) into Equation (19) gives the following relation:

$$\frac{d^3v(x)}{dx^3} = \frac{g}{\eta}\left(\frac{Q\beta_T}{k}x - \frac{\beta_T\Delta T}{2\omega} - \beta_C\frac{\overline{\partial C_1}}{\partial x}\right) \tag{27}$$

By virtue of the relation $\int_{-\omega}^{\omega} v(x)\,dx = 0$ for the batch case and the boundary conditions

$$v(x) = 0 \quad \text{at} \quad x = -\omega,\ \omega$$

the solution of Equation (27) is given by

$$v(x) = \frac{g}{\eta}\left(\frac{\beta_TQ}{24k}x^4 - \frac{1}{6}\left(\frac{\beta_T\Delta T}{2\omega} - \beta_C\frac{\overline{dC_1}}{dx}\right)\right.$$
$$\left.(x^3 - \omega^2x) - \frac{\beta_TQ\omega^2}{20k}x^2 + \frac{\beta_TQ}{120k}\omega^4\right) \tag{28}$$

EVALUATION OF $\overline{\partial C_1}/\partial x$

If one follows the procedure suggested first by deGroot (1943) and later by Von Halle (1959), the following expression for $\overline{\partial C_1}/\partial x$ results:

$$\frac{\overline{\partial C_1}}{\partial x} = 0.3\frac{UE}{D}\overline{C}_1 \tag{29}$$

In order to use expression (29), explicitly in the calculations of velocity profile, some average value of $\overline{C}_1$ is required. Here, it will be conveniently assumed that $\overline{C}_1 = C_0$. The expression for $\overline{\partial C_1}/\partial x$ then becomes

$$\frac{\overline{\partial C_1}}{\partial x} = 0.3\frac{UE}{D}C_0 \tag{30}$$

when the integral average of $\overline{\partial C_1}/\partial x$ given by Equation (30) is used in Equation (28), the final relation for $v(x)$ results

$$v(x) = \frac{g}{\eta}\left(\frac{\beta_TQ}{24k}x^4 - \frac{1}{6}\left(\frac{\beta_T\Delta T}{2\omega} - \beta_C\frac{0.3UEC_0}{D}\right)\right.$$
$$\left.(x^3 - \omega^2x) - \frac{\beta_TQ\omega^2}{20k}x^2 + \frac{\beta_TQ}{120k}\omega^4\right) \tag{31}$$

The evaluation of column transport constants H and K by integration of Equations (13), (14), and (15) using this relation for $v(x)$ [Equation (31)] is straightforward although tedious. The resulting expressions are complicated and are conveniently presented in terms of contributions of ΔT alone (subscript T), E alone (subscript E), the product of ΔT and E (subscript TE) and of ordinary diffusion (subscript d). Thus

$$H = H_T + H_{TE} + H_E \tag{32}$$

where

$$H_T = B\rho\frac{g\beta_T\Delta T}{\eta}\frac{\alpha_{1s}\Delta T}{\overline{T}}\frac{(2\omega)^3}{6!} \tag{32a}$$

$$H_{TE} = B\rho\frac{g\beta_T\Delta T}{\eta}\frac{UE}{D}\frac{(2\omega)^4}{6!} \tag{32b}$$

and

$$H_E = B\rho\frac{0.3UEg\beta_CC_0}{\eta D}\frac{UE}{D}\frac{(2\omega)^5}{6!} \tag{32c}$$

Similarly, the column transport coefficient K can be written in the following form:

$$K = K_T + K_{TE} + K_E + K_d \tag{33}$$

where

$$K_T = \frac{B\rho}{D}\left(\frac{g\beta_T\Delta T}{\eta}\right)^2\frac{(2\omega)^7}{9!}$$
$$-\frac{63}{8}\frac{B\rho}{D}\frac{g^2}{\eta^2}\frac{\beta_T{}^2\Delta TQ}{k}\frac{(2\omega)^9}{9!}$$
$$-\frac{1511}{640}\frac{B\rho}{D}\left(\frac{g\beta_TQ}{\eta k}\right)^2\cdot\frac{(2\omega)^{11}}{9!} \tag{33a}$$

$$K_{TE} = 2.0\frac{B\rho}{D}\cdot\frac{g\beta_T\Delta T}{\eta}\cdot\frac{0.3g\beta_CC_0UE}{\eta D}\cdot\frac{(2\omega)^8}{9!} \tag{33b}$$

$$K_E = -\frac{63}{8}\cdot\frac{B\rho}{D}\cdot\frac{g^2}{\eta^2}\cdot\frac{\beta_TQ}{k}\cdot\frac{0.3UE\beta_CC_0}{D}\cdot\frac{(2\omega)^{10}}{9!}$$
$$+\frac{B\rho}{D}\left(\frac{g}{\eta}\cdot\frac{0.3UEC_0\beta_C}{D}\right)^2\cdot\frac{(2\omega)^9}{9!} \tag{33c}$$

$$K_d = B\rho D\cdot(2\omega) \quad \text{(due to vertical diffusion)} \tag{33d}$$

Some experiments carried out without any applied electrical field and only with application of a temperature difference showed no separation for bovine albumin indicating $\alpha = 0$. The term H_T in Equation (32a) can therefore be set equal to zero in case of electrophoresis for this system and

$$H = H_{TE} + H_E \tag{32d}$$

APPLICATION OF THE TRANSPORT EQUATION TO STEADY STATE BATCH OPERATION

Equation (17) gives the net transport of the mobile component down the column for batch operation and is quite general in its ability to describe the operation of a thermoelectrogravitational column. Its application to steady state batch operation of the electrophoresis column without reservoirs is straightforward and requires the solution of the equation for $\tau = 0$ to get the concentration in the column as a function of position.

Since only dilute solutions are encountered in electrophoresis, $C_S \approx 1$ and Equation (17) applied to the bottom of the column reduces to

$$H_BC - K_B\frac{dC}{dy} = 0 \tag{34}$$

in which the superbar and subscript on C are dropped for convenience and subscript B denotes the bottom section of the column. The boundary conditions for the bottom section are given by

$$C = C_M \ @ \ y = 0 \qquad C = C_B \ @ \ y = L_B \tag{35}$$

With these boundary conditions, the solution of Equation (34) for the bottom section is

$$\frac{C_M}{C_B} = e^{-\frac{H_B L_B}{K_B}} \tag{36}$$

A similar solution for the top section of the column yields

$$\frac{C_M}{C_T} = e^{\frac{H_T L_T}{K_T}} \tag{37}$$

and the steady state separation factor q_s defined as the ratio of C_B to C_T is given by

$$q_s = C_B/C_T = e^{\frac{H_T L_T}{K_T}} \Big/ e^{-\frac{H_B L_B}{K_B}} \tag{38}$$

Further, if it is assumed that the two sections of the column are equal in length, that is, $L_B = L_T = L/2$ and if $H_B = H_T = H$ and $K_B = K_T = K$, then the steady state batch separation factor is given by

$$q_s = C_B/C_T = e^{2A} \tag{39}$$

where

$$A = HL/2K \tag{40}$$

Application of the transport equation to continuous flow and transient operations of the electrophoresis column is deferred to subsequent papers.

DISCUSSION

This theoretical development predicts the velocity profiles and the temperature distribution within a thermoelectrogravitational electrophoresis column and the steady state batch separation that is achieved as a function of the properties of the solution being treated, the column dimensions, and operating conditions.

To describe the trend of the results that would be expected, theoretical temperature distributions, velocity profiles, and steady state batch separation factors were calculated at various conditions approximating those used in experimental work for the transport of bovine albumin in boric acid-borax and phosphate buffers. Data for these calculations were obtained from literature and are listed in Prabhudesai (1965).

DISCUSSION OF THEORETICAL RESULTS

Temperature Distribution

Equation (22) shows that the temperature distribution in an electrophoresis column will not be linear. The magnitude of the group given by

$$\theta = Q/2k \ \Delta T = 0.24 \ k_e \ E^2/2k \ \Delta T$$

will determine the extent to which the linearity of temperature distribution will be affected. For small values of field strength E, that is, as $\theta \rightarrow 0$, the temperature distribution in an electrophoresis column should be about linear since the first term $\theta(\omega^2 - x^2)$ will be negligible. At much higher values of Q, corresponding to very small column volumes operating at rather high E (say 50 volts/cm), the effect would be more pronounced.

Velocity Distribution

The velocity profile given by Equation (31) is a function of field strength E, temperature difference ΔT, spacing 2ω, and the electric mobility U. The effect of heat evolution on the velocity profile is represented by the terms containing the heat evolution variable Q which is negligibly small for small values of E. The velocity distribution should, therefore, be substantially unaffected by the generation of heat in the column at low field strengths. In such a case, the velocity distribution will be essentially given by

$$v(x) = \frac{1}{6}\left[\frac{g\beta_T\Delta T}{2\eta} + \frac{0.3g\beta_C UEC_0}{\eta D}\right](x^3 - \omega^2 x) \tag{41}$$

Figure 3a and 3b illustrate some typical theoretically calculated velocity distributions in an electrophoresis column for bovine albumin. It is seen that the contribution to the total convective velocity due to temperature difference is relatively important only at very low field strengths. At higher field strengths, the velocity profile is mostly determined by the field strength E and the electric mobility of the component U.

COLUMN TRANSPORT COEFFICIENTS AND STEADY STATE BATCH SEPARATIONS

The column transport coefficients H and K determine the separation that can be obtained in an electrophoresis column. Column constant H is a measure of the diffusion of the species in the horizontal direction under the influence of an electric field while column constant K is related to the laminar convective flow in the column. Transport coefficient H [Equation (32)] is independent of the electrical conductivity of solution and, therefore, independent of heat generation in the cell. The column constant K may also be independent of the heat generation term at low values of field strength E, corresponding to negligible heat generation Q.

Equation (39) predicts theoretically the steady state

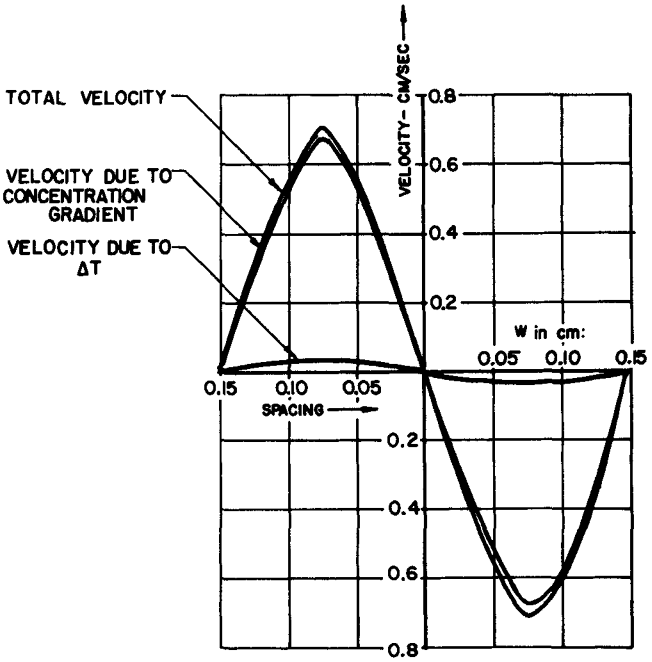

Fig. 3a. Theoretical velocity profile at $\Delta T = 8.5°C$, $E = 0.0423$ volt/cm, $2\omega = 0.30$ cm.

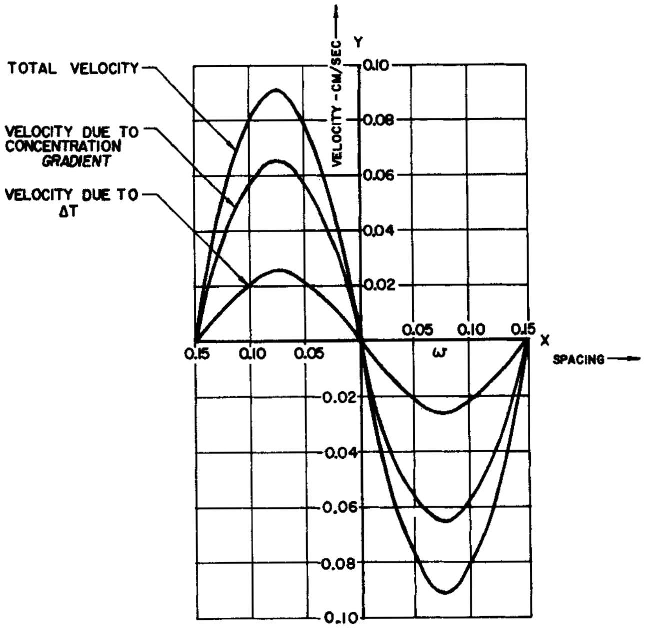

Fig. 3b. Theoretical velocity profile at $\Delta T = 8.5°C$, $E = 0.423$ volt/cm, $2\omega = 0.30$ cm.

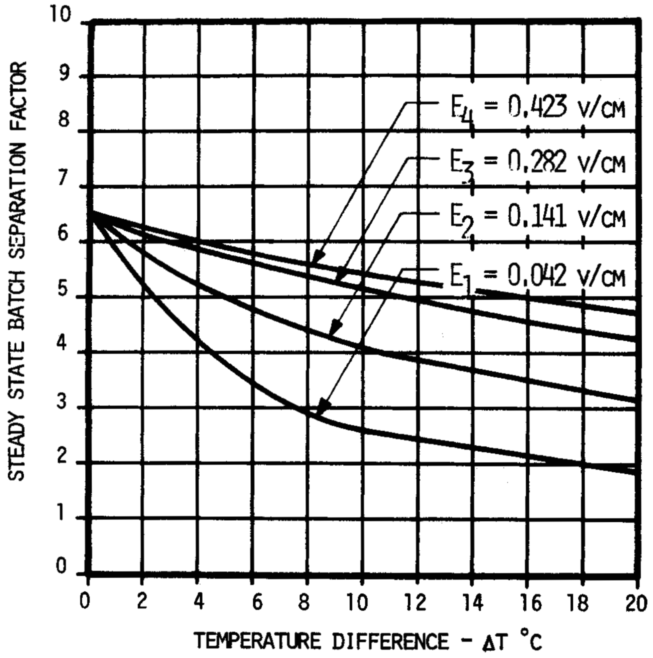

Fig. 4. Theoretical steady state batch separation factors as a function of temperature difference.

batch separation factors (q_s) and is especially useful to predict and test the effect of various parameters entering into H and K on the steady state batch separation that could be obtained. Taking logarithms of both sides of Equation (39), one obtains

$$\ln(q_s) = \frac{HL}{K} \tag{42}$$

Thus, for constant H and K, the steady state separation will be proportional to the length of the column.

Figures 4, 5, and 6 present theoretical results predicted on the basis of Equation (39) and the expressions for H and K, using the properties of buffered (pH = 8.6) bovine albumin at 4°C, using $2\omega = 0.1354$ cm. and $L = 145$ cm. It may be observed from the figures that the steady state separation appears to decrease with ΔT and approaches a limiting value (Figure 4), the steady state separation for ΔT not zero increases very rapidly at low values of E (Figure 5) and appears to reach a limiting value, and the effect of membrane spacing is tremendous, the separations being very high at low membrane spacing

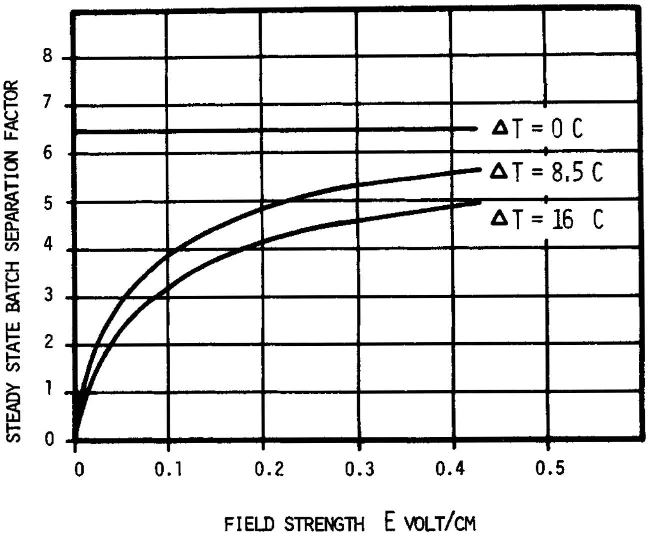

Fig. 5. Theoretical steady state batch separation factors as a function of field strength E at various ΔT.

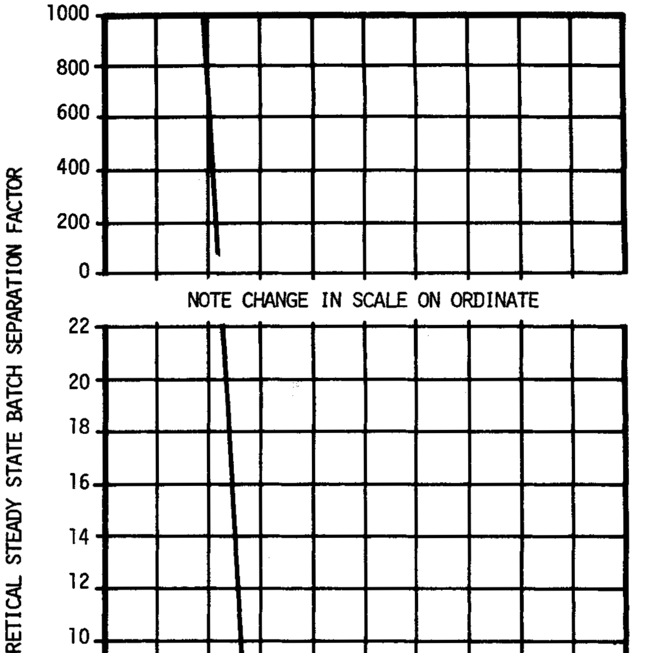

Fig. 6. Theoretical steady state separation factors as a function of membrane spacing for $\Delta T = 0$, and $E = 0.282$ volt/cm.

(Figure 6). The latter is evident from the functional forms of H and K. For constant physical properties and constant other dimensions of the column, the dependence of H and K on 2, the membrane spacing, is given by the following functional forms:

$$H = a(2\omega)^4 + b(2\omega)^5 \tag{45}$$

$$K = a' + b'\,(2\omega)^8 + c'\,(2\omega)^9 \tag{46}$$

Thus, with an increase in (2ω), K increases correspondingly more than H and H/K decreases very rapidly giving very low separations at high membrane spacings. These calculations must account for the decrease in viscosity and corresponding decrease in diffusivity (Stokes-Einstein equation) with an increase in average temperature which would occur as the temperature difference was increased, assuming that the cold wall was held constant at 4°C. The calculations show that for this system, terms including Q can be neglected, but that depending upon the relative sizes of the temperature and electric field several terms may contribute significantly to the total value of H and K.

No separation could be observed for this system at zero field strength, so that it was concluded that thermal diffusion was negligible and the value of H_T was taken as zero.

SUMMARY

A new apparatus, the thermoelectrogravitational electrophoresis column without reservoirs, has been proposed to carry out electrophoretic separations using the advantage offered by laminar convection flow as in thermal diffusion columns.

The Furry, Jones, and Onsager procedure developed for the mathematical analysis of thermal diffusion columns has been applied to the proposed column. Equations have been established for temperature distribution and velocity distribution to account for the effect of both electrical and thermal fields. A transport equation to describe the transport down the column in terms of two column transport coefficients H and K has been derived and solved for the steady state batch operation of a column. The effect of temperature difference, electrical field strength, and spacing on the steady state batch separation is discussed in terms of the transport coefficients H and K.

In a subsequent paper, the transport equation derived here will be extended to the mathematical analysis of a continuous-flow electrophoresis column without reservoirs. An experimental thermoelectrogravitational column will be described in the results compared with the theory developed.

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NOTATION

A = $HL/2K$ defined by Equation (40)
A_T = A for top section of column
A_B = A for bottom section of column
a, a' = general constants
b, b' = general constants
B = column width
B = subscript to identity streams leaving from bottom of column
c, c' = general constants
C = mass fraction of mobile component
C_0 = mass fraction of mobile component in feed
C_s = mass fraction of solvent together with isoelectric component
C_1 = concentration of component 1 mobile
C_M = concentration (mass fraction) of mobile component at feed point of column
C_B = mass fraction of mobile component 1 at the bottom of column
C_T = mass fraction of component 1 at the top of the column
C_S = mass fraction of solvent
$\overline{C}$ = average concentration at $x = 0$
D = diffusion constant
D_{1s} = diffusion constant for the mobile component in solvent
E = field strength
g = local acceleration due gravity
g_c = dimensional constant
H = column transport coefficient defined by Equation (32); H_E–Equation (32c); H_{TE}–Equation (32b); H_T–Equation (32a); H_T–H for top section, H_B–H for bottom section, subscript H for hypothetical component
J = mass flux, g/cm^2
k = thermal conductivity of solution
k_e = electrical conductivity of solution
K = column transport coefficient defined by Equation (33); K_d–Equation (33d); K_E–Equation (33c); K_{TE}–Equation (33b); K_T–Equation (33a); K_T–K for top section; K_B–K for bottom section
L = total column length, L_T–L for top section, L_B–length for bottom section
P = pressure in the column
Q = heat generated in the column per unit volume
q_s = steady state batch separation factor
T = temperature T_1–that of colder membrane; T_2–that of hot membrane; $\overline{T}$–integrated average temperature
ΔT = temperature difference between hot and cold membranes
U = electrophoretic mobility
V = voltage
$v(x)$ = general velocity distribution function
x = axis normal to membrane
y = axis parallel to membrane
z = axis perpendicular to x, y plane

Greek Letters

α_{1s} = thermal diffusion constant for component 1
β_T = rate of change in density with temperature
β_C = rate of change in density with concentration
η = coefficient of viscosity
ρ = density
τ = amount of component 1 passing through a cross section of electrophoresis column normal to the membranes
2ω = spacing between hot and cold semipermeable membranes
θ = dimensionless group $0.24k_e\,E^2/2K\,\Delta T$ indicating the heat evolution

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Part II. Steady State Operation of Continuous Flow Column: Theory and Experiment

In Part I of this paper, a thermoelectrogravitational electrophoresis column without reservoirs was proposed for preparative electrophoretic separations. The Furry, Jones, and Onsager procedure in thermal diffusion was applied to develop a transport equation, and its solution for the steady state batch case was employed to demonstrate some typical effects of temperature difference, electric field strength, and membrane spacing on the predicted steady state batch separation in the column.

In this part, a theory is first developed from mathematical analysis of a continuous-flow thermoelectrogravitational column without reservoirs by modification of the transport equation to take into account the bulk flow through the column.

An experimental center-fed thermoelectrogravitational electrophoresis column and the related equipment used to obtain experimental data to test the theory are described. Further, experimental separation factors as a function of flow rates ranging from 0 to 10 g/min for the bovine albumin system at two *p*H values (8.6 and 6.0) were obtained using two membrane spacings (0.1354 and 0.3018 cm respectively) at four different electric field strengths (0.0423 to 0.423 volt/cm) and for three different temperature differences of 0°C, 8.5°C, and 16°C. Experimental data indicated that meaningful separations could be obtained using thermoelectrogravitational columns but that the temperature difference has an adverse effect on electrophoretic separation.

Analysis of the experimental flow data showed that theory and experiment are not in quantitative agreement. However, there was general, qualitative agreement between theory and experiment for the dependence of separation on field strength, temperature difference, membrane spacing and mobility of the component.

In Part I, a qualitative description of the proposed thermoelectrogravitational electrophoresis column was presented and a mathematical theory was developed for its analysis using the Furry, Jones, and Onsager procedure for thermal diffusion.

The purpose of Part II is to extend the application of the transport equation developed in Part I to the continuous-flow operation of a thermoelectrogravitational column, to describe in detail the construction of such a column to obtain laboratory experimental data, and to present the experimental results and compare them with the theory.

THEORY

Figure 1 illustrates an experimental continuous flow thermoelectrogravitational electrophoresis column. The transport equation derived by consideration of the steady state batch operation was (for the bottom section)

$$\tau_B = H_B C - K_B \frac{dC}{dy} \tag{1}$$

This equation must be modified to account for the flow through the column resulting from continuous withdrawal