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MASS, CHARGE, MOMENTUM AND ENERGY CONSERVATION IN ELECTROPHORETIC FRACTIONATION SYSTEMS*

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1. INTRODUCTION

As an analytical and small-scale preparative technique (*i.e.*, at the milligram to microgram level), electrophoresis has acquired a prominent status among modern physico-chemical separation methods on account of its versatility, ease of implementation and, most importantly, its extremely high resolving power. Since the adaptation by Tiselius¹ in 1937 of the moving-boundary method for the fractionation and analysis of complex protein mixtures, progress has accelerated rapidly. Numerous applications to chemical, biological, biochemical and medical systems have led to a significant number of important discoveries and to the synthesis of other electrophoretic apparatus with improved resolving capacity and operating characteristics^{2,3}.

As a large-scale preparative technique, on the other hand, electrophoresis has not achieved the same degree of success. Because of the high non-linear interactions among the governing mass, charge, momentum and energy transport processes, straightforward scale-up procedures are not effective or may be completely inapplicable. The main difficulty stems from the Joule heating mechanism, which is inherently present in any system through which an electric current is conducted. As the physical dimensions of the apparatus are increased, it becomes increasingly

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difficult to remove this internally dissipated energy, which generally varies proportionally to the square of the local electric field strength or, equivalently, to the square of the current. An attempt to reduce the Joule heat effect, then, would necessarily have to emanate from either an increase in the cooling capacity of the system (which has the disadvantages of spatially varying temperature distributions and enhanced instrumentation complexity) or from a reduction in the current or field strength. Buffer systems of the appropriate ionic strength may be selected in order to accomplish the latter. However, it is evident that this is in direct contrast to the requirements of rapid and high-resolution separations. The optimization criteria are consequently apparent: maximize the Joule heat dispersion and transfer with the system's surroundings, minimize the thermal convection currents and maximize the electric field strength in order to achieve rapid fractionations with the best possible resolution.

It must be further pointed out, however, that even with the attainment of a successful solution to this optimization problem, other significant practical difficulties remain. An example is the recovery of fractionated components of mixtures in polyacrylamide gel electrophoresis.

In this review, previously reported investigations are summarized, and the fundamental mass, momentum and energy transport relationships applicable to multi-component flowing mixtures are presented. These relationships are subsequently limited to macromolecular mixtures with non-interacting components and, on dimensionally analysing the resulting equations, two dimensionless parameters are found, one of which is associated with the mass transport mechanism (E_r) and the other with the thermal energy dissipation mechanism (Je).

2. ANALYSIS OF PREVIOUS INVESTIGATIONS

The combined effect of the various transport processes present in electrophoretic fractionation systems are considered from two standpoints: one at the single particle or microscopic level, where the primary objective is to determine the interactions among the uniformly applied electrostatic field, the composition of the electrolytic solution, the structure of the electrical double layer and the induced electrophoretic mobility, and the other at the macroscopic level where quantitative expressions are sought for the concentration distributions of the macromolecular mixture components and the associated velocity, temperature and electrical potential distribution.

The behavior of single isolated particles has been studied extensively. Smoluchowski^{4,5} at the turn of the century, derived an expression for the electrophoretic mobility of a non-conducting particle with a small double layer thickness when compared with the particle's radius of curvature throughout its surface. A decade later, Hückel^{4,6} obtained a similar expression applicable to small spherical particles for which the ratio of radius of curvature to double layer thickness is small, and the frictional resistance on the particle by the medium is given by Stokes' law. Subsequently, Henry^{7,8}, Booth^{7,9} and Overbeek and co-workers^{7,10} generalized the above theories by incorporating into the analysis the four principal forces believed to be acting on a particle in a stationary state of electrophoretic motion. These included the force exerted by the electrostatic field on the charge of the particle, the Stokes'

frictional resistance, a retardation force due to the influence of the electrostatic field on the ions in the diffuse double layer and a relaxation force which attempts to restore the original symmetrical configuration of the electrical double layer. The specific form of the electrophoretic mobility relationships obtained by these investigators are given in a later section. Other extensions to non-spherical particles and to systems with intra-particle interactions are also available¹¹⁻¹³ and can be consulted for further details on the diversity and complexity of the phenomena.

At the macroscopic level, many investigations have been conducted to elucidate the importance of the various factors that affect electrophoretic separations, including buffer composition, ionic strength, pH, temperature, electric field intensity, fractionation time and zone stability. Analytical studies addressed to quantitative descriptions of such factors, however, have been scarce and mostly confined to isothermal systems with constant physical parameters and mobilities. Cann and Goad¹⁴ considered mass transport in non-reacting and reversibly reacting systems under isothermal conditions and constant electrostatic field strength. Typically, they stipulated that the components of the macromolecular mixture interact either through acid-base dissociative reactions of the type



or through associative reactions of the form



with each species possessing a characteristic net charge, electrophoretic mobility and diffusion coefficient. Integrating these chemical reactions with diffusion and electromigration processes, they derived mass conservation conditions as

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left(D_i \frac{\partial C_i}{\partial x} \right) - \frac{\partial(\mu_i E C_i)}{\partial x} + r_i \quad (1)$$

which they solved analytically or numerically to arrive at the electrophoretic patterns. Following a similar procedure for isotachopheresis, Coxon and Binder¹⁵ also considered systems modeled by the above differential relationship. The chemical reaction terms were absent from their analysis, however, and the applied electric force followed Poisson's equation:

$$\nabla \cdot E = \frac{z}{\epsilon} \sum_i C_i$$

More recently, Ries *et al.*¹⁶ extended the work of Philpot¹⁷ and described quantitatively the combined effects of diffusion, convection and electromigration under isothermal conditions and constant transport properties, including electrophoretic mobilities. The bulk velocity profile in the planar, forced-flow electrophoretic system was taken as parabolic with diffusion in all three coordinate directions, *i.e.*, the transient distribution of the mixture constituents was stated as

$$\frac{\partial C_i}{\partial t} + v_x \frac{\partial C_i}{\partial x} - \mu \frac{\partial C_i}{\partial z} = D_i \left(\frac{\partial^2 C_i}{\partial x^2} + \frac{\partial^2 C_i}{\partial y^2} + \frac{\partial^2 C_i}{\partial z^2} \right) \quad (2)$$

with the appropriate boundary and initial conditions. This model was recognized by the authors as the slit-flow analog of the classical Taylor dispersion problem¹⁸. Their analytical solution reflected quantitatively a significantly large Taylor dispersion dependence, and qualitatively a decrease in fractionation efficiency with increasing electromigration velocities and Peclet numbers. Other investigations addressed to isothermal systems described by convective-diffusion differential relationships of the above type include those by Weiss and Rodbard¹⁹ (pore gradient electrophoresis), Lee and Lightfoot²⁰ and Krishnamurthy and Subramanian²¹ (field-flow fractionation), and Ries and Lightfoot²² and Lee *et al.*²³ (ultrafiltration and electrophoresis).

Quantitative studies of temperature distributions within electrophoretic cells have been confined to one-dimensional conductive systems with no convective energy transport and constant density, specific heat and thermal conductivity:

$$\frac{\partial T_E}{\partial t} = k_E \nabla_{e1}^2 T_E + Q_E(T_E)/\rho_E C_{pE} \text{ (electrolytic solution)}$$

$$\frac{\partial T_w}{\partial t} = k_w \nabla_{e1}^2 T_w \text{ (cell wall)}$$

Martin and Everaerts²⁴, with negligible cell wall effects, analysed the parabolic distributions which arise under additional constraints of constant electrical conductivity and uniform wall temperature. Coxon and Binder²⁵, Hinckley²⁶ and Brown and Hinckley²⁷ treated cells of both circular and rectangular cross-section under transient and stationary conditions. The energy source was held constant and the electrical conductivity was taken to vary linearly with cell temperature, *i.e.*,

$$Q_E(T_E) = E^2 \sigma_E^0 (1 + \alpha T_E)$$

3. FUNDAMENTAL TRANSPORT RELATIONSHIPS

The application of the fundamental principles of mass, momentum and energy conservation to a flowing mixture, either via the arbitrary control volume approach or the more classical theory^{28,29}, gives rise to the following continuity, motion and energy equations, respectively:

Overall continuity:

$$\frac{D\rho}{Dt} + \rho(\nabla \cdot v) = 0 \quad (3)$$

Component continuity:

$$\frac{D\rho_i}{Dt} = -\nabla \cdot j_i - \rho_i(\nabla \cdot v) + r_i \text{ (} i = \text{fluid mixture components)} \quad (4)$$

Motion:

$$\rho \frac{Dv}{Dt} = -\nabla p - \nabla \cdot \tau + \rho g + \sum_i \rho_i \hat{F}_i \quad (5)$$

Energy:

$$\rho \frac{DU}{Dt} = -\nabla \cdot q - (pI + \tau)/\nabla v + \sum_i j_i \cdot \hat{F}_i$$

For purposes of thermal systems analysis, the last expression can be more conveniently rewritten as

$$\begin{aligned} \rho C_v \frac{DT}{Dt} = & -\nabla \cdot q - (pI + \tau)/\nabla v + \delta \nabla \cdot v + \\ & + \sum_i [(\nabla \cdot j_i) + r_i] [\bar{U}_i/M_i + \delta \bar{V}_i/M_i] + \sum_i j_i \cdot \hat{F}_i \end{aligned} \quad (6)$$

with

$$\delta = p - T(\partial p/\partial T)$$

Following Hirschfelder *et al.*²⁸, the mass flux of the individual species can be broken down into a contribution due to the concentration (ordinary diffusion), temperature (thermal diffusivity, the Soret effect) and pressure (pressure diffusion) gradients present locally within the fluid mixture, and a contribution due to the externally applied forces (forced diffusion):

$$j_i = j_i^{(c)} + j_i^{(T)} + j_i^{(p)} + j_i^{(F)} \quad (7)$$

Similarly, the thermal energy flux can be broken down into contributions emanating from ordinary thermal conduction and energy transport due to concentration gradients (the Dufour effect), molecular diffusion and radiation:

$$q = q^{(T)} + q^{(c)} + q^{(d)} + q^{(r)} \quad (8)$$

The last term in eqn. 5 represents the momentum imparted on the fluid mixture due to the influence of the externally applied forces, and the last term in eqn. 6 corresponds to the work done (energy dissipated) by the migrating molecules in overcoming the external forces.

4. ELECTROPHORETIC TRANSPORT RELATIONSHIPS FOR NON-INTERACTING MACROMOLECULAR MIXTURES

General expressions for the mass and energy flux components included in eqns. 7 and 8 have been obtained by Hirschfelder *et al.*²⁸ through the thermodynamics of irreversible processes and the Onsager reciprocal relations approach. Of such fluxes, specifically as related to electrophoretic systems, mass fluxes resulting from temperature and pressure diffusion mechanisms, and also energy fluxes resulting from concentration, molecular diffusion and radiation mechanisms, are neglected. Consequently, as a function of the corresponding transport coefficients, the following expressions hold:

Ordinary diffusion:

$$j_i^{(c)} = \frac{C^2}{\rho RT} \sum_j M_i M_j D_{ij} \left[x_j \sum_{\substack{k \\ k \neq j}} \left(\frac{\partial \bar{G}_j}{\partial x_k} \right) \right]_{\substack{T, P, x_s \\ s \neq j, k}} \nabla x_k$$

Forced diffusion:

$$j_i^{(F)} = - \frac{C^2}{\rho RT} \cdot \sum_j M_i M_j D_{ij} \left[x_j M_j (\hat{F}_j - \sum_k \frac{\rho_k}{\rho} \cdot \hat{F}_k) \right]$$

Heat conduction:

$$q^{(T)} = -k \nabla T$$

In this form these expressions are rather unmanageable, as the partial molal Gibbs free energies are temperature, pressure and composition dependent, and the transport coefficients, D_{ij} , are multi-component diffusion parameters whose values are difficult to obtain either theoretically or experimentally. Note that in addition, generally $D_{ij} \neq D_{ji}$ for other than binary systems.

To arrive at a quantitatively suitable set of transport equations, it will be assumed that the interactions along the macromolecular mixture constituents are negligible and that, consequently, the mixture behaves ideally. For each constituent, then, the combined binary form of the concentration and forced diffusion flux is

$$J_i = -D_i \nabla C_i + \left(\frac{D_i C_i}{RT} \right) F_i \quad (9)$$

Also, if viscous dissipation mechanisms and pressure variations are insignificant, eqn. 6 may be transformed into

$$\rho C_v \frac{DT}{Dt} = \nabla \cdot (k \nabla T) + \sum_i \bar{U}_i r_i + \sum_i J_i \cdot F_i \quad (10)$$

The functionality between the externally applied electric forces and the net migration imparted on the individual components of the electrolytic solution must now be established. Pertaining to the ionic species, they may be viewed as point charges and, consequently,

$$F_i = z_i F (-\nabla \Phi)$$

Pertaining to the charged macromolecular components, on the other hand, the resultant force is directly dependent on the character of the particles' double layer and on the magnitude of the zeta potential. In its simplest form, assuming the presence of single, rigid and non-conducting particles with uniform dielectric constants and solution viscosity coefficients^{4,10}, the zeta potential can be expressed as

$$\zeta = \frac{Q}{\epsilon a} - \frac{Q}{\epsilon(a + 1/\lambda)}$$

For large ratios of radius of curvature to diffuse double layer thickness (λa),

$$\zeta = (3/2)Q/\epsilon a$$

and, on equating the electrical and viscous forces affecting the particle, Smoluchowski's equation is obtained for the particle electrophoretic mobility:

$$v = \zeta \epsilon / 4 \pi \mu$$

For small ratios of the radius of curvature to the diffuse double layer thickness,

$$\zeta = Q/\epsilon a$$

Similarly, if only forces of electrical and frictional origin are accounted for, Hückel's equation derives:

$$v = \zeta \epsilon / 6 \pi \mu$$

Incorporating surface conductivity distributions, solvent retardation effects and diffuse double layer asymmetries into the analysis, Henry⁸, Booth⁹ and Overbeek and co-workers^{7,10} derived generally flexible zeta potential relationships of the form

$$\zeta = \frac{Q}{\epsilon a} f(\lambda a)$$

and for the electrophoretic mobility

$$v = \frac{\zeta \epsilon}{6 \pi \mu} f(\lambda a)$$

where both analytical and graphical representations of $f(\lambda a)$ for Henry's equation (relaxation effects not included and λa small or large) and the more general case can be found in the references cited.

Generally then, the force exerted on the components of the electrolytic medium will be

$$F_i = \begin{cases} z_i F(-\nabla\Phi) & \text{ionic species} \\ [\zeta \epsilon a f(\lambda a)]_i \tilde{N}(-\nabla\Phi) & \text{charged particles or macromolecules} \end{cases}$$

$$= \gamma_i(-\nabla\Phi)$$

Consequently, the component continuity and energy equations result in

$$\frac{DC_i}{Dt} = \nabla \cdot (D_i \nabla C_i) + \nabla \cdot \left(\frac{D_i C_i \gamma_i}{RT} \right) \nabla \Phi - C_i (\nabla \cdot v) + r_i \quad (11)$$

$$e C_o \frac{DT}{Dt} = \nabla \cdot (k \nabla T) + \sum_i (D_i \gamma_i \nabla C_i) \nabla \Phi + \left(\sum_i D_i C_i \gamma_i^2 / RT \right) (\nabla \Phi \cdot \nabla \Phi) + \sum_i \bar{U}_i r_i \quad (12)$$

In addition to mass, momentum and energy conservation, electrophoretic systems must also uphold the electrical charge conservation principle. To arrive at an expression for such a principle, eqn. 11 is formally multiplied by the net particle charge, γ_i , and upon summing over all mixture components we obtain

$$\begin{aligned} \frac{\partial(\sum_i \gamma_i C_i)}{\partial t} &= \nabla \cdot (\sum_i D_i \gamma_i \nabla C_i) \\ &+ \nabla \cdot [(\sum_i D_i C_i \gamma_i^2 / RT) \nabla \Phi] - \nabla \cdot (\sum_i \gamma_i C_i v) = \nabla \cdot (\sum_i \gamma_i N_i) = \nabla \cdot i \end{aligned} \quad (13)$$

where all chemical reactions have been assumed to be electrically balanced. If the medium is said to be electrically neutral, *i.e.*,

$$\sum_i \gamma_i C_i = 0 \quad (14)$$

then, after some rearrangement, eqn. 13 yields an expression for the electrical potential:

$$\nabla^2 \Phi = - \frac{\nabla \cdot (\sum_i D_i \gamma_i \nabla C_i) + [\nabla(\sum_i D_i C_i \gamma_i^2 / RT)] \cdot \nabla \Phi}{\sum_i D_i C_i \gamma_i^2 / RT} \quad (15)$$

The following observations can be made:

(i) For the analysis of electrochemical systems composed of ionic species only, the component continuity expression (eqn. 11) reduces to the commonly encountered multi-component diffusion equation³⁰, for which the distribution of migrating species in dilute solutions is expressed as

$$\frac{\partial C_i}{\partial t} + v \cdot \nabla C_i = \nabla \cdot (D_i \nabla C_i) + \nabla \cdot (u_i C_i z_i F \nabla \Phi) + r_i$$

where the fluid mixture is assumed to be incompressible and use is made of the Nernst-Einstein relationship:

$$u_i = D_i / RT$$

(ii) The second and third terms in eqn. 12 constitute contributions due to Joule heating. Under more familiar circumstances of uniform compositions and no thermal energy exchange due to chemical reactions, this energy transport equation is simplified to give

$$e C_o \frac{DT}{Dt} = \nabla \cdot (k \nabla T) + \underbrace{\frac{i \cdot i}{\sum_i D_i C_i \gamma_i^2 / RT}}_{\text{Joule heating}}$$

(iii) The charge density movement and the flowing current density induce electric and magnetic fields which, according to Maxwell's equations, follow

$$\epsilon \frac{\partial \Phi_E}{\partial t} + i = \nabla \times B$$

$$\Phi_E = \nabla \cdot E = (1/\epsilon) \sum_i \gamma_i C_i$$

If the characteristic time constants for the system are such that the electrical processes respond significantly more quickly to temporal variations relative to the co-existing mass, momentum and thermal energy processes, then a pseudo-steady-state approximation with respect to Φ_E indicates

$$\frac{\partial(\sum_i \gamma_i C_i)}{\partial t} = \nabla \cdot i = \nabla \cdot (\nabla \times B) = 0$$

Consequently, this procedure in general is not equivalent to invoking the electro-neutrality condition as expressed by eqn. 14. In isotachopheresis with no convective currents present, this indeed holds true, as indicated by Moore³¹.

(iv) It is frequently stated³⁰ that the electroneutrality assumption does not imply Laplace's equation for the electrical potential. This is evident from eqn. 15, which for isothermal and uniform composition systems reduces to

$$\nabla^2 \Phi = 0$$

5. DIMENSIONAL ANALYSIS OF ELECTROPHORETIC TRANSPORT EQUATIONS

For purposes of reducing the total number of relevant dimensional system parameters to independent subsets of dimensionless groups, the electrophoretic transport eqns. 3, 5, 11, 12 and 15 will now be simplified (to reflect the predominant processes taking place in homogeneous and heterogeneous and in continuous and discontinuous electrophoretic systems) and cast in dimensionless form.

5.1. Convective electrophoretic systems

Forced-flow and continuous zone electrophoretic apparatus operate under incompressible flow conditions and with electrolytic fluid mixtures of constant viscosity. If electroosmotic effects are considered not to influence the development of the convective flow field, then, in dimensionless form, the governing transport relationships include the following:

Overall continuity:

$$\nabla \cdot v = 0$$

Motion:

$$\frac{\partial v}{\partial t} + (v \cdot \nabla)v = -\nabla p - \left(\frac{1}{Re}\right)\nabla \cdot \tau + \left(\frac{1}{Fr}\right)g$$

Component continuity:

$$\frac{\partial C_i}{\partial t} + v \cdot \nabla C_i = \left(\frac{1}{ReSc} \right) \nabla \cdot (\delta_i \nabla C_i) + \left(\frac{E_f}{ReSc} \right) \nabla \cdot [(\delta_i C_i \gamma_i / T) \nabla \Phi]$$

Energy:

$$\begin{aligned} \frac{\partial T}{\partial t} + v \cdot \nabla T &= \left(\frac{1}{RePr} \right) \nabla \cdot (k \nabla T) + \left(\frac{Je}{RePr} \right) [\Sigma_i \delta_i \gamma_i \nabla C_i] \nabla \Phi + \\ &+ \left(\frac{Je E_f}{RePr} \right) [\Sigma_i \delta_i C_i \gamma_i^2 / T] (\nabla \Phi \cdot \nabla \Phi) \end{aligned}$$

Charge:

$$\nabla^2 \Phi = - \frac{\frac{1}{E_f} \nabla \cdot (\Sigma_i \delta_i \gamma_i \nabla C_i) + (\nabla \Sigma_i \delta_i C_i \gamma_i^2 / T) \cdot \nabla \Phi}{\Sigma_i \delta_i C_i \gamma_i^2 / T}$$

The Reynolds, Schmidt, Froude and Prandtl numbers follow standard nomenclature (see *Definitions* in Section 7)^{29,30}, and the remaining dimensionless parameters are defined as

$$E_f = \gamma_e \Phi_0 / RT_0$$

and

$$Je = D_0 C_0 \gamma_0 \Phi_0 / k_0 T_0$$

E_f represents the ratio of mass transport due to the externally applied electric force to mass transport due to ordinary diffusion, and Je represents the ratio of thermal energy dissipated due to the externally applied electric force to thermal energy transport by conduction.

5.2. Heterogeneous electrophoretic systems

For electrophoretic systems with supporting media and a stagnant electrolytic solution (*i.e.*, $v = 0$), such as polyacrylamide gel electrophoresis with continuous or discontinuous buffer regions, the corresponding set of dimensionless transport relationships has the following form:

Component continuity:

$$\frac{\partial C_i}{\partial t} = \nabla \cdot (\delta_i \nabla C_i) + E_f \nabla \cdot [(\delta_i C_i \gamma_i / T) \nabla \Phi]$$

Energy:

$$\frac{\partial T}{\partial t} = Le \nabla \cdot (k \nabla T) + LeJe [\Sigma_i \delta_i \gamma_i \nabla C_i] \nabla \Phi + LeJe E_f [\Sigma_i \delta_i C_i \gamma_i^2 / T] (\nabla \Phi \cdot \nabla \Phi)$$

5.3. Electrophoretic systems with natural convection

Homogeneous electrophoretic systems with no externally applied pressure gradients develop natural convection currents which, when included in the analysis of the electrophoretic transport relationships, give rise to the following:

Overall continuity:

$$\nabla \cdot v = 0$$

Motion:

$$\frac{\partial v}{\partial t} + (v \cdot \nabla)v = -\nabla \cdot \tau - GrgT$$

Component continuity:

$$\frac{\partial C_i}{\partial t} + v \cdot \nabla C_i = \left(\frac{1}{Sc}\right) \nabla \cdot (\delta_i \nabla C_i) + \left(\frac{E_f}{Sc}\right) \nabla [\delta_i C_i \gamma_i / T] \nabla \Phi$$

Energy:

$$\begin{aligned} \frac{\partial T}{\partial t} + v \cdot \nabla T = & \left(\frac{1}{Pr}\right) \nabla \cdot (k \nabla T) + \left(\frac{Je}{Pr}\right) \sum_i \delta_i \gamma_i \nabla C_i \cdot \nabla \Phi + \\ & + \left(\frac{JeE_f}{Pr}\right) \left[\sum_i \delta_i C_i \gamma_i^2 / T\right] (\nabla \Phi \cdot \nabla \Phi) \end{aligned}$$

It may be observed that, because of the electroneutrality condition, the charge conservation eqn. 11 is explicitly invariant to changes in fluid velocity distributions. Nevertheless, implicitly, it remains affected by such velocity distributions through the concentration gradients of the mixture components.

6. CONCLUSION

As large-scale preparative apparatus, electrophoretic systems have been severely limited by Joule heating and the difficulties encountered in its exchange with the system's surroundings. Rapid and highly demarcated fractionations are sought with minimal energy utilization. This, however, is necessarily accompanied by large localized voltage gradients and electrical current densities that enhance electrical energy dissipation, natural convection currents and broadening of concentration distributions. Operating parameters for optimal separations must then be obtained through an integrated analysis of the prevailing transport processes within the electrophoretic cell. To this end, mass, momentum, energy and charge conservation relationships (eqns. 3, 5, 11, 12 and 15) have been derived for electrophoretic fractionation systems. Fundamental simplifying assumptions include negligible mass transport due to thermal and pressure gradient effects, negligible thermal energy transport due to concentration gradients, molecular diffusion and thermal radiation, infinitely dilute macromolecular mixtures with no interactions among their constituents (*i.e.*, pseudo-binary solutions), ionic species considered as point charges and macromolecular species taken as non-conducting charged particles each surrounded

by a characteristic electrical double layer, and electrically neutral electrolytic mixtures.

In view of the high coupling and complexity of the derived conservation relationships, their complete solutions are seldom realized. Consequently, dimensional analysis was utilized to arrive at dimensionless parameters that can now be used to simplify such differential relationships, and to establish empirical correlations for analysis and design purposes. The resulting dimensionless parameters are E_f (the ratio of mass transport due to the applied electrical force to mass transport due to ordinary diffusion) and Je (the ratio of thermal energy dissipated due to the applied electrical force to thermal energy transport by conduction).

7. SYMBOLS

a	particle radius
B	magnetic field
C	local concentration, total concentration
C_p, C_v	specific heat
D	binary diffusion coefficient
D_{ij}	multi-component diffusion coefficients
$\frac{D}{Dt}$	substantial time derivative
E	voltage gradient
E_f	ratio of mass transport due to externally applied electrical force to mass transport due to ordinary diffusion
F	external force
\hat{F}_i	applied external force per unit mass of component i
Fr	Froude number
f	zeta potential relationship describing particle-electrical double layer forces
g	gravitational force
\bar{G}	partial molal Gibbs free energy
Gr	Grashof number
HA	uncharged solution constituent
H^+	hydrogen ion
I	unit tensor
i	current density
j	mass flux with respect to fluid mass average velocity
J	mass flux with respect to fluid molal average velocity
Je	ratio of thermal energy dissipated due to externally applied electrical force to thermal energy transport by conduction
k	thermal conductivity
Le	Lewis number
M	molecular weight
N	mass flux with respect to stationary coordinate system
\bar{N}	Avogadro's number
P	protein molecule; macromolecular ion
$P(HA)_i$	protein-uncharged solution constituent complex
PH_i	macromolecular ion

Pr	Prandtl number
P	static pressure
Q	thermal energy source; particle charge
q	energy flux
R	gas law constant
r	reaction rate
Re	Reynolds number
Sc	Schmidt number
T	temperature
t	time
U	internal energy
\bar{U}	partial molal internal energy
u	Nernst–Einstein mobility
\bar{V}	partial molal volume
v	velocity
v_x	bulk velocity in x -direction
x	molar fraction; spatial coordinate
y	spatial coordinate
z	ionic charge; spatial coordinate

Greek symbols

α	temperature coefficient
γ	charge per gram-mole; charge per gram-ion
$\nabla_{e_1}^2$	one-dimensional Laplacian operator in e_1 direction
δ	dimensionless binary diffusivity coefficients
ϵ	dielectric constant
ζ	zeta potential
λa	ratio of radius of curvature to diffuse double layer thickness
λ^{-1}	thickness of diffuse double layer
μ	mobility; fluid viscosity
ν	electrophoretic mobility
ρ	density
σ_E^0	electrical conductivity at a nominal temperature T_0
τ	stress tensor
$\bar{\Phi}$	electrical potential
Φ_E	electric flux

Subscripts

E	electrolytic solution
i	solution constituent
0	characteristic quantities
w	cell wall

Superscripts

- (c) concentration
 (d) thermal diffusion
 (r) radiation
 (T) temperature, thermal
 (F) external force
 (p) pressure

Definitions

$$\text{Reynolds number} = \frac{\text{convective forces}}{\text{viscous forces}}$$

$$\text{Froude number} = \frac{\text{convective forces}}{\text{gravitational forces}}$$

$$\text{Grashof number} = \frac{(\text{buoyancy forces}) (\text{convective forces})}{(\text{viscous forces})^2}$$

$$(\text{Reynolds number}) (\text{Prandtl number}) = \frac{\text{convective energy transport}}{\text{conductive energy transport}}$$

$$(\text{Reynolds number}) (\text{Schmidt number}) = \frac{\text{convective mass transport}}{\text{ordinary diffusion mass transport}}$$

$$\text{Lewis number} = \frac{\text{conductive energy transport}}{\text{ordinary diffusion mass transport}}$$

8. SUMMARY

Electrophoretic fractionation systems have been used extensively in chemistry, biology, biochemistry and medicine. However, such applications have been confined to analytical-scale systems, with limited extension to preparative or large-scale engineering systems. The major difficulties encountered in the analysis and design of such systems are pointed out, and mass, momentum, energy and charge conservation relationships are derived that incorporate the effects of the composition of the electrolytic solution on the microscopic structure of the electrical double layer and the associated macroscopic concentration, velocity, temperature and electrical potential distributions. Two dimensionless parameters are found in the analysis of electrophoretic fractionation systems: the ratio of mass transport due to the applied electrical force to mass transport due to ordinary diffusion, and the ratio of thermal energy dissipated due to the applied electrical force to thermal energy transport by conduction. These, together with other normally occurring dimensionless transport parameters such as the Reynolds, Schmidt, Froude, Prandtl, Nusselt and Lewis numbers, are essential in establishing theoretical and empirical correlations for analysis and design purposes.

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