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Thermosolutal transport phenomena in large Lewis number electrochemical systems

H. D. JIANG, S. OSTRACH† and Y. KAMOTANI

Department of Mechanical and Aerospace Engineering, Case Western Reserve University,
Cleveland, OH 44106, U.S.A.

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Abstract—A detailed scaling analysis of transport phenomena by laminar natural convection along a vertical flat plate is made for multiple-component electrochemical systems. The convective flow is generated by both horizontal temperature and concentration gradients under limiting current conditions. Both binary and well-supported ternary electrolytes are considered. Thicknesses of the thermal and solutal boundary layers, concentration variations of all species in each solutal layer, and the heat and mass transport rates are estimated for electrochemical systems with large Lewis numbers and buoyancy ratios. The solutal boundary layer structure is constructed for the well-supported electrochemical system. The results from the present scaling analysis are compared with available analytical results and experimental data.

INTRODUCTION

Natural convection generated by both solutal and thermal buoyancy forces is referred to as thermosolutal convection. These forces may either augment or oppose each other. In recent years, attention has been focused on thermosolutal convection due to horizontal temperature and concentration gradients, because this somewhat simulates the horizontal Bridgman crystal growth process. By employing an electrochemical system, copper-sulfate acid solution ($\text{H}_2\text{SO}_4 + \text{CuSO}_4 + \text{H}_2\text{O}$), a series of experimental investigations have been conducted in shallow enclosures by Kamotani *et al.* [1], Wang and Chuang [2], Ostrach *et al.* [3], and Jiang *et al.* [4]. In the experiments, the thermal buoyancy force either oppose, or augment the solutal buoyancy force. The interaction of the boundary layers and the driving forces results in complex flow structures. Three flow regimes were identified, the multilayer, secondary cell, and mixed flow patterns [4]. The multilayer flow is steady while both secondary cell and mixed flow are unsteady [5], which also holds for the mass and heat transfer processes corresponding to each flow.

Somers [6], Mathers *et al.* [7] and Wilcox [8] performed analytical studies of thermosolutal convection along a vertical flat plate for a nonelectrolytic solution which contains only one species. To consider the thermal effect on mass transport, they proposed a combined Rayleigh number, $RA = Gr_S \pm Le^{1/2} Gr_T$ (“+” sign for the augmenting cases and “−” sign for the opposing cases), where Le is the Lewis number which is a ratio of the Schmidt number, Sc , to the Prandtl number, Pr . Gr_S and Gr_T represent the solutal and thermal Grashof numbers, respectively. They found

that the dimensionless mass transfer rate, namely the Sherwood number, Sh , is correlated with RA by an one-fourth power dependency. The ratio of thicknesses of the thermal to solutal boundary layers, namely the δ_T/δ_S , was found to be proportional to the square root of Le . These results are accurate only for situations when both Pr and Sc are greater than one, as well as when Le approaches unity, as indicated by Wilcox [8]. For thermosolutal systems with large Le a new scaling law needs to be derived.

In general, transport phenomena in an electrochemical system is different from that in a nonelectrolytic system. If the reacting species, say the cupric ions C_{++} , is consumed in the surface reaction faster than it is supplied by transport through the solution, it is eventually depleted at the electrode surface and the current reaches a limiting value, which is referred to as the limiting current. It is known that under the limiting current condition, mass transport process in the electrochemical system is controlled by solutal diffusion and convection. This, by no means indicates that the transport phenomena in the electrochemical systems become the same as that in the nonelectrolytic systems. First, the electrochemical system must satisfy the electroneutrality condition in the bulk solution, except in the so-called electric double layer. Secondly, the migration contribution to mass transport does not apply for the nonelectrolytic system. Therefore, the solutal boundary layer structure as well as the corresponding flow field and concentration distributions of the species for an electrochemical system with multiple species differ, in general, from that for a nonelectrolytic system.

The scaling analysis has been proven to be a successful approach to gain physical insight into natural convection heat transfer along the flat plate [9]. To understand thermosolutal convection in non-

† Author to whom correspondence should be addressed.

NOMENCLATURE

C', C	dimensionless, and dimensional concentration [mol m ⁻³]	Greek symbols	
ΔC	concentration variation [mol m ⁻³]	α_T	thermal diffusivity [m ² s ⁻¹]
D	diffusion coefficient [m ² s ⁻¹]	β_S	volumetric coefficient of solutal expansion, $(\partial\rho/\partial C)/\rho$ [m ³ mol ⁻¹]
F	Faraday's constant [C equiv. ⁻¹]	β_T	volumetric coefficient of thermal expansion, $-(\partial\rho/\partial T)/\rho$ [K ⁻¹]
f	coefficient, F/RT [mol (equiv. V) ⁻¹]	Γ	ratio of concentration variations, equation (32)
g	gravitational acceleration [m s ⁻²]	γ_{TS}	ratio of thermal to solutal boundary layers, δ_T/δ_S
GR	combined Grashof number	δ	boundary layer thickness [m]
Gr_S	solutal Grashof number, $g\beta_S\Delta CH^3\nu^{-2}$	Λ	difference of charge numbers, $(Z_{++} - Z_+)$ [equiv. mol ⁻¹]
Gr_T	thermal Grashof number, $g\beta_T\Delta TH^3\nu^{-2}$	ν	kinematic viscosity [m ² s ⁻¹]
H	length of flat plate or length scale in Y direction [m]	ρ	density [kg m ⁻³]
L	length scale in X direction [m]	ϕ', Φ	dimensionless, and dimensional [V] potential
Le	Lewis number, $Sc/Pr = \alpha/D$	$\Delta\Phi$	potential variation [V]
N	buoyancy ratio, $\beta_S\Delta C/\beta_T\Delta T$	ψ'	concentration ratio, C/C_R .
Nu	Nusselt number	Subscripts	
p'	dimensionless pressure	B	bulk property
Pr	Prandtl number, ν/α_T	D	diffusion
R	universal gas constant [J (mol K) ⁻¹]	i	interface between the inner and outer solutal layers for the well-supported electrolyte
RA	combined Raleigh number	I	inner solutal boundary layer
Ra_S	solutal Rayleigh number, $Gr_S Sc$	R	reference property or characteristic value
Ra_T	thermal Rayleigh number, $Gr_T Pr$	S	solutal property
Re	Reynolds number, $V_R L_R^2/H_R \nu$	s	electrode surface
Sc	Schmidt number, ν/D	T	thermal property
Sh	Sherwood number	V	velocity or flow property
T', T	dimensionless, and dimensional [K] temperature	Φ	migration
ΔT	temperature variation [K]	0	outer solutal boundary layer
u', U	dimensionless, and dimensional [m s ⁻¹] velocities normal to the flat plate	+	hydrogen ions
v', V	dimensionless, and dimensional [m s ⁻¹] velocities parallel with the flat plate	=	sulphate ions
x', X	dimensionless, and dimensional [m] coordinates normal to the flat plate	++	cupric ions.
y', Y	dimensionless, and dimensional [m] coordinates parallel with the flat plate	Superscripts	
z	charge number of a species [equiv. mol ⁻¹].	b	binary electrolyte
		w	well-supported electrolyte.

electrolytic solutions, Ostrach [10] performed a global scaling analysis which covered wide parametric ranges. A detailed scaling analysis of thermosolutal convection in large Le electrochemical systems with multiple species has not been reported in the literature. In the present study the analysis is performed so as to understand transport phenomena in the systems.

A major purpose of the present analysis is to determine how the electroneutrality and migration affect the solutal boundary layer structure and corresponding concentration profiles of all species in solutal boundary layers for the systems. The second motivation of the work is to derive a new scaling law

to describe thermosolutal transport processes, which is appropriate to the large Le systems. To achieve these goals, a new approach of force balances somewhat different from the traditional one needs to be developed.

GENERAL BASIC EQUATIONS

The consideration is given to transport phenomena of the thermosolutal convection in the previously mentioned copper-sulfate acid solution. The electrolyte is an incompressible and dilute electrochemical system with three components, the cupric, sulfate and

hydrogen ions. Natural convection is generated by both horizontal temperature and concentration gradients along a vertical flat electrode. For the sake of simplicity, only the convection near the hot cathode is analyzed, and the thermal buoyancy force is imposed so as to augment the solutal one. Figure 1 represents the sketch of a steady, two-dimensional thermosolutal convection with $Pr > 1$ and $Le \gg 1$ in a binary electrochemical system, namely the cupric sulfate solution, in which no sulfate acid is added.

It is well known that the electrolytic solution is electrically neutral, except within an electric double layer very close to the electrode which is of the order of 10μ in thickness. This condition is expressed by

$$Z_{++}C_{++} + Z_{=}C_{=} + Z_{+}C_{+} = 0, \quad (1)$$

$++$, $=$, and $+$ represent the cupric, sulphate and hydrogen ions, respectively. In the present analysis, the effect of the double layer on transport processes is neglected.

Transport processes in the present system are diffusion, migration and convection. Therefore, the equations of hydrodynamics need to be considered. In the present analysis the physical properties of electrolytes are considered to be constant and the Boussinesq approximation is applied for the thermal and solutal buoyancy terms. The dimensionless forms of these equations are as follows. The continuity equation is

$$\frac{U_R}{L_R} \frac{\partial u'}{\partial x'} + \frac{V_R}{H_R} \frac{\partial v'}{\partial y'} = 0. \quad (2)$$

To satisfy the mass flux balance in equation (2), we have $U_R H_R \sim V_R L_R$. By using this relation the momentum equations become

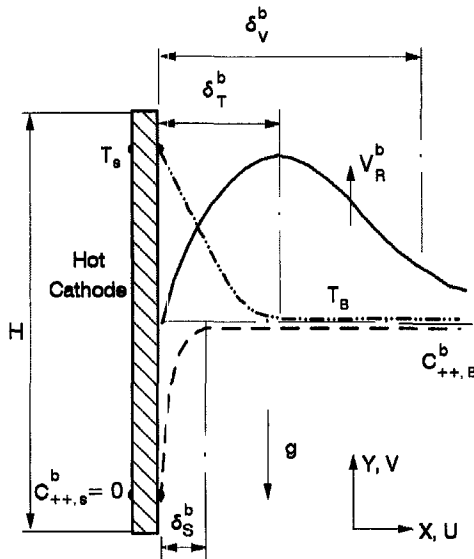


Fig. 1. Sketch of the thermosolutal convection along a flat plate for a binary electrolyte subjected to augmenting thermal and solutal buoyancy forces.

$$u' \frac{\partial u'}{\partial x'} + v' \frac{\partial u'}{\partial y'} = -\frac{\partial p'}{\partial x'} + \frac{1}{Re} \left(\frac{\partial^2 u'}{\partial x'^2} + \frac{L_R^2}{H_R^2} \frac{\partial^2 u'}{\partial y'^2} \right) \quad (3)$$

$$u' \frac{\partial v'}{\partial x'} + v' \frac{\partial v'}{\partial y'} = -\frac{L_R^2}{H_R^2} \frac{\partial p'}{\partial y'} + \frac{1}{Re} \left(\frac{\partial^2 v'}{\partial x'^2} + \frac{L_R^2}{H_R^2} \frac{\partial^2 v'}{\partial y'^2} \right) + \left(\frac{L_R}{H_R} \right)^4 \left(\frac{Gr_T}{Re^2} T' - \sum_z \frac{Gr_{s,z}}{Re^2} C'_z \right) \quad (4)$$

where $\alpha = ++, =$ and $+$. Note that the determination of $\beta_{s,\alpha}$ for all species is interrelated by the electroneutrality condition.

The energy equation describes the heat transfer process, and is written as

$$u' \frac{\partial T'}{\partial x'} + v' \frac{\partial T'}{\partial y'} = \frac{1}{Pr Re} \left(\frac{\partial^2 T'}{\partial x'^2} + \frac{L_R^2}{H_R^2} \frac{\partial^2 T'}{\partial y'^2} \right). \quad (5)$$

The mass transfer process in the electrochemical system is described by not only convection and diffusion, but also migration. Therefore, for the species α , mass transport equation is defined as

$$u' \frac{\partial C'_\alpha}{\partial x'} + v' \frac{\partial C'_\alpha}{\partial y'} = \frac{1}{Sc_\alpha Re} \left[\left(\frac{\partial^2 C'_\alpha}{\partial x'^2} + \frac{L_R^2}{H_R^2} \frac{\partial^2 C'_\alpha}{\partial y'^2} \right) + \frac{f Z_\alpha C_{\alpha,R} \Delta \Phi_R}{\Delta C_{\alpha,R}} \left(\frac{\partial^2 \phi'}{\partial x'^2} + \frac{L_R^2}{H_R^2} \frac{\partial^2 \phi'}{\partial y'^2} \right) \psi'_\alpha + f Z_\alpha \Delta \Phi_R \left(\frac{\partial C'_\alpha}{\partial x'} \frac{\partial \phi'}{\partial x'} + \frac{L_R^2}{H_R^2} \frac{\partial C'_\alpha}{\partial y'} \frac{\partial \phi'}{\partial y'} \right) \right] \quad (6)$$

where $f = F/RT$ and $Sc_\alpha = \nu/D_\alpha$. On the right hand side of the equation, the first two terms represent the diffusion while the last four terms the migration.

Under the limiting current condition, the concentration of cupric ions at the electrode surface, C_{++s} , reduces to zero,

$$C_{++s} = 0. \quad (7)$$

To satisfy the electroneutrality condition given in equation (1) for the ternary electrolyte, the concentration of inert species, sulphate ions ($C_{=s}$) and hydrogen ions (C_{+s}), at the surface must have finite values

$$C_{=s} = \text{finite}, \quad C_{+s} = -Z = C_{=s}/Z_+ \quad (8)$$

these values are unknown *a priori* and will be estimated later. The potential at the electrode surface can be chosen arbitrarily to be zero

$$\phi = \phi_s = 0.$$

SCALING ANALYSIS

In the present study, only natural convection with large Gr_T and Gr_s is analyzed, since it is relevant to the past experimental work of interest to us and to most practical applications. For large Gr_T , a viscous boundary layer δ_V exists. For the copper-sulfate acid

solution, $Sc_x \gg 1$ and $Pr > 1$, which are true for most aqueous electrolytes. Then thinner thermal and solutal boundary layers, δ_T and δ_S , coexist with δ_V . The boundary layer structure and the corresponding flow field have great influence on both heat and mass transport processes.

By employing the approach used by Ostrach [9, 10], the thickness of the thermal boundary layer can be estimated. Inside the layer, thermal convection balances with conduction while thermal buoyancy with viscous, which lead to

$$\delta_T \sim HRa_T^{-1/4} \quad (9)$$

and

$$V_T \sim \frac{\nu}{H} \frac{Ra_T^{1/2}}{Pr}. \quad (10)$$

δ_T and V_T are the thickness of the layer and the thermal reference velocity in the layer, respectively. Replacing Pr and Gr_T by Sc and Gr_S , the solutal layer thickness δ_S and reference velocity V_S are found. The ratio of thicknesses of the solutal to the thermal boundary layers can be defined as [1]

$$\frac{\delta_T}{\delta_S} \sim (LeN)^{1/4}, \quad (11)$$

and the ratio of reference velocities is

$$\frac{V_T}{V_S} \sim \left(\frac{Le}{N}\right)^{1/2}, \quad (12)$$

where $Le = Sc/Pr = \alpha_T/D$, and $N = Gr_S/Gr_T = \beta_S \Delta C / \beta_T \Delta T$.

Equations (11) and (12) provide a guideline for the boundary layer structure. Thermal and solutal boundary layers may coexist in three different ways: (a) $LeN \gg 1$, $\delta_T > \delta_S$; (b) $LeN \sim 1$, $\delta_T \sim \delta_S$; and (c) $LeN \ll 1$, $\delta_T < \delta_S$. For each type of layer structure, three kinds of flow patterns are possible: (1) $Le \gg N$, $V_T > V_S$; (2) $Le \sim N$, $V_T \sim V_S$; and (3) $Le \ll N$, $V_T < V_S$. Due to space limitations, the present analysis focuses on the case with

$$LeN \gg 1 \quad \text{and} \quad Le \gg N > 1 \quad (13)$$

because it is relevant to the experimental works [1–4] and to most aqueous electrolytes used in industrial applications. The remaining cases will be presented elsewhere. For a binary electrolyte, these conditions indicate that $\delta_V > \delta_T > \delta_S$ and $V_T > V_S > 0$, and therefore the boundary layer structure and the flow field can be constructed as shown in Fig. 1.

Without loss of generality, the cupric ions Cu^{++} , the sulphate ions SO_4^- , and the hydrogen ions H^+ of the copper-sulfate acid solution are assumed to be completely dissolved in water. Molecular diffusivities of these ions differ and diffusivity ratios of the ions at infinite dilution can be defined by solutal Lewis numbers as [11]

$$Le_{+,++} = \frac{D_+}{D_{++}} = 12.93, \quad Le_{-,++} = \frac{D_-}{D_{++}} = 1.48. \quad (14)$$

To obtain meaningful scales of the solutal boundary layers and the concentration profiles of the ions in the layers for the electrochemical system, we must consider not only the multiple diffusivities of the solution but also the electroneutrality and migration. Next, a detailed scaling analysis is carried out for two limiting cases, a binary electrolyte and a well-supported electrolyte.

Binary electrolyte

When the sulfuric acid H_2SO_4 is absent, the ternary electrolyte $H_2SO_4 + CuSO_4 + H_2O$ becomes a binary system $CuSO_4 + H_2O$. The binary electrolyte consists of two species, namely anions Cu^{++} and cations SO_4^- . These species tend to separate when the diffusivities of the constituents differ. During the separation a charge density is generated to prevent further separation. As a result, a potential gradient is created and migration can no longer be neglected. The migration speeds up the ions with the smaller diffusivity and slows down the ions with the larger diffusivity, until the two diffusion processes are adjusted to an equal rate. In order to estimate the potential variation, an apparent diffusivity can then be introduced to describe the real diffusion processes. The apparent diffusivities for both SO_4^- and C^+ ions are defined by a linear combination of the migration and the diffusion terms on right hand side of equation (6)

$$D_{++}^b \sim D_{++} \left[1 + Z_{++} (f \Delta \Phi_R^b) \frac{\Delta C_{+,R}^b + C_{+,R}^b}{\Delta C_{+,R}^b} \right] \quad (15)$$

$$D_{-}^b \sim D_{-} \left[1 + Z_{-} (f \Delta \Phi_R^b) \frac{\Delta C_{-,R}^b + C_{-,R}^b}{\Delta C_{-,R}^b} \right] \quad (16)$$

where the superscript ^b represents the binary system and

$$\Delta \Phi_{\alpha,R}^b = \Phi_{\alpha,B}^b - \Phi_{\alpha,S}^b, \quad C_{\alpha,R}^b = \frac{1}{2}(C_{\alpha,B}^b + C_{\alpha,S}^b)$$

$$\Delta C_{\alpha,R}^b = C_{\alpha,B}^b - C_{\alpha,S}^b, \quad \alpha = ++ \text{ and } =.$$

To satisfy the electroneutrality condition, an apparent diffusivity D^b must be equal to both D_{++}^b and D_{-}^b . The reference potential change $\Delta \Phi_R^b$ is determined by using equations (15) and (16) with the electroneutrality condition to yield

$$f \Delta \Phi_R^b \sim \frac{(D_{++} - D_{-})}{(Z_{-} D_{-} - Z_{++} D_{++})} \frac{\Delta C_R^b}{(C_R^b + \Delta C_R^b)}. \quad (17)$$

Substitution of equation (17) into either equation (15) or equation (16) results in

$$D^b \sim \frac{D_{++}D_=(Z_{++}-Z_-)}{Z_{++}D_{++}-Z_-D_=} \quad (18)$$

This result was derived by Levich [12] in a somewhat different manner. The present approach will be used in the later discussion. An apparent Schmidt number Sc^b is defined as

$$Sc^b = \frac{\nu}{D^b} = \frac{\nu(Z_{++}D_{++}-Z_-D_-)}{D_{++}D_=(Z_{++}-Z_-)} \quad (19)$$

and the thickness of the solutal layer for the binary system can be estimated by using equation (9) as

$$\frac{\delta_S^b}{H} \sim (Ra_S^b)^{-1/4}, \quad Ra_S^b = Sc^b Gr_S^b, \quad (20)$$

$$Gr_S^b = \frac{g\beta_S^b C_{+,B}^b H^3}{\nu^2}$$

Physically, equation (20) indicates that only one solutal boundary layer can be defined even though two species with different diffusivities exist in the solution. The mass transfer process behaves like a single species. In contrast, in a nonelectrolytic solution two solutal boundary layers must exist for two species with different diffusivities. The results demonstrate that the electroneutrality and the migration have significant effect on the solutal boundary layer structure of the electrochemical system. In general, we conclude that for any electrochemical system with multiple components, if diffusivities of all species differ, the electroneutrality condition requires these two species whose diffusivities are the largest among that of all species, to share a single solutal boundary layer.

Well-supported electrolyte

A ternary system $H_2SO_4 + CuSO_4 + H_2O$ in which the concentration of H_2SO_4 is much greater than that of $CuSO_4$ in the bulk solution, is referred to as the well-supported electrolyte, which has been widely used in mass transfer study and various applications. Although the diffusivities of H^+ , Cu^{++} and SO_4^- differ as given in equation (14), H^+ and SO_4^- cannot diffuse independently due to electroneutrality as we concluded previously. Therefore, the entire solutal boundary layer must be constructed in two parts, an inner layer $\delta_{S,1}^w$ where concentrations of all ions vary and an outer layer $\delta_{S,0}^w$ where the concentration of cupric ions remains constant. In $\delta_{S,0}^w$, H^+ and SO_4^- behave like the binary electrolyte and share the common solutal layer. The superscript w represents the well-supported system. The relative magnitudes of all four boundary layers for the present thermosolutal system are

$$\delta_v > \delta_T > \delta_{S,0}^w > \delta_{S,1}^w \quad (21)$$

In $\delta_{S,0}^w$, the bulk concentration of the reactant Cu^{++} , is much smaller than those of SO_4^- and H^+ and, therefore, one concludes that

$$\frac{\Delta C_{+,0}^w}{C_{+,0}^w} \ll 1 \quad \text{and} \quad \frac{\Delta C_{-,0}^w}{C_{-,0}^w} \ll 1 \quad (22)$$

where $\Delta C_{\alpha,0}^w = C_{\alpha,B}^w - C_{\alpha,i}^w$ with $\alpha = +$ and $-$. Similar to what we did for the binary system, the apparent diffusivities $D_{+,0}^w$ for H^+ and the $D_{-,0}^w$ for SO_4^- are defined as

$$D_{+,0}^w = D_+ \left[1 + Z_+ (f\Delta\Phi_0^w) \frac{C_{+,0}^w}{\Delta C_{+,0}^w} \right] \quad (23)$$

$$D_{-,0}^w = D_- \left[1 + Z_- (f\Delta\Phi_0^w) \frac{C_{-,0}^w}{\Delta C_{-,0}^w} \right] \quad (24)$$

By equating equation (23) with equation (24) due to electroneutrality, one obtains an estimate of the potential variation $\Delta\Phi_0^w$

$$f\Delta\Phi_0^w \sim \frac{\Delta C_{-,2}^w}{C_{-,2}^w} \frac{(D_+ - D_-)}{(Z_- D_- - Z_+ D_+)} \quad (25)$$

By introducing equation (25) into either equations (23) or (24), the apparent diffusivity $D_0^w = D_{0,++}^w = D_{0,-}^w$ is determined

$$D_0^w \sim \frac{D_+ D_- (Z_+ - Z_-)}{(Z_+ D_+ - Z_- D_-)} \approx 3.61 D_{++} \quad (26)$$

where data given in equation (14) have been used in the calculation.

In $\delta_{S,1}^w$, the variation of the concentration of Cu^{++} has to be taken into account, and the apparent diffusivities for all the ions are defined by linear combinations of the migration and diffusion terms on right hand side of equation (6),

$$D_{+,1}^w = D_+ \left[1 + Z_+ (f\Delta\Phi_1^w) \frac{C_{+,1}^w}{\Delta C_{+,1}^w} \right] \quad (27)$$

$$D_{-,1}^w = D_- \left[1 + Z_- (f\Delta\Phi_1^w) \frac{C_{-,1}^w}{\Delta C_{-,1}^w} \right] \quad (28)$$

$$D_{++,1}^w = D_{++} \left[1 + Z_{++} (f\Delta\Phi_1^w) \frac{C_{++,1}^w}{\Delta C_{++,1}^w} \right] \quad (29)$$

where $\Delta C_{\alpha,1}^w = C_{\alpha,i}^w - C_{\alpha,s}^w$ with $\alpha = +, =$ and $++$. Subscript $_1$ denotes the interface between the inner and outer solutal layers. Equating these apparent diffusivities leads to

$$f\Delta\Phi_1^w = \frac{(D_{++} - D_+)}{D_+} \frac{\Delta C_{+,1}^w}{Z_+ C_{+,1}^w} \quad (30)$$

$$f\Delta\Phi_1^w = \frac{(D_{++} - D_-)}{D_-} \frac{\Delta C_{-,1}^w}{Z_- C_{-,1}^w} \quad (31)$$

A ratio of concentration variations of the sulphate to hydrogen ions in the inner solutal layer is determined by equating equations (30) and (31)

$$\frac{\Delta C_{-,1}^w}{\Delta C_{+,1}^w} = \frac{D_-}{D_+} \frac{(D_+ - D_{++})}{(D_{++} - D_-)} = \frac{1}{\Gamma} \approx -2.84 \quad (32)$$

where equation (14) has been used for the calculation. Substitution of either equations (30) or (31) into equation (29) yields

$$D_{++}^w = D_+ \left[1 + \frac{Z_{++}}{Z_+} \frac{(D_{++} - D_+)}{D_+} \frac{\Delta C_{+,i}^w}{C_{+,i}^w} \right]. \quad (33)$$

Since

$$\frac{\Delta C_{+,i}^w}{C_{+,i}^w} \ll 1 \quad \text{and} \quad \frac{Z_{++}}{Z_+} \frac{(D_{++} - D_+)}{D_+} \sim O(1) \quad (34)$$

one gets the apparent diffusivity in the inner solutal layer $\delta_{s,i}^w$

$$D_1^w = D_{+,i}^w = D_{=,i}^w = D_{+,i}^w = D_{++}. \quad (35)$$

Since the minor constituent, Cu^{++} is the only species taking part in the electrode reaction for the well-supported system, the concentration variation of inert species, SO_4^- and H^+ , must be of the same order of magnitude as that of the reactant, Cu^{++} . The electro-neutrality condition is satisfied microscopically at every location in the electrolyte, except in the electric double layer. By applying this condition at both sides of the solutal layer, one finds that concentration variations of Cu^{++} , SO_4^- and H^+ across the entire layer, are described by

$$\frac{\Delta C_{+,t}^w}{\Delta C_{=,t}^w} = \frac{C_{+,B}^w - C_{+,s}^w}{C_{=,B}^w - C_{=,s}^w} = \frac{Z_-}{\Lambda}, \quad (36)$$

$$\frac{\Delta C_{+,t}^w}{\Delta C_{=,t}^w} = \frac{C_{+,B}^w - C_{+,s}^w}{C_{=,B}^w - C_{=,s}^w} = -\frac{Z_-}{\Lambda}, \quad (37)$$

where $\Lambda = Z_{++} - Z_+$ and the subscript t denotes the total concentration variation. A summation of the local concentration variations in the inner and outer solutal layers should be equal to the total variation for each species

$$\Delta C_{=,t}^w = \Delta C_{=,i}^w + \Delta C_{=,0}^w \quad (38)$$

$$\Delta C_{+,t}^w = \Delta C_{+,i}^w + \Delta C_{+,0}^w. \quad (39)$$

The electroneutrality condition in $\delta_{s,0}^w$ requires that

$$Z_- C_{=,0}^w \approx -Z_+ C_{+,0}^w$$

$$\text{and} \quad Z_- \Delta C_{=,0}^w \approx -Z_+ \Delta C_{+,0}^w. \quad (40)$$

Solutions for $\Delta C_{=,i}^w$, $\Delta C_{=,0}^w$, $\Delta C_{+,i}^w$ and $\Delta C_{+,0}^w$ can be obtained from equations (37)–(40)

$$\Delta C_{=,0}^w = \frac{Z_+(Z_- - \Lambda\Gamma)}{Z_-(Z_- + Z_+\Gamma)} \Delta C_{+,i}^w \approx -0.35 C_{+,i}^w \quad (41)$$

$$\Delta C_{=,i}^w = \frac{-Z_{++}}{(Z_- + Z_+\Gamma)} \Delta C_{+,i}^w \approx 0.85 C_{+,i}^w \quad (42)$$

$$\Delta C_{+,0}^w = -\frac{(Z_- - \Lambda\Gamma)}{(Z_- + Z_+\Gamma)} \Delta C_{+,i}^w \approx -0.70 C_{+,i}^w \quad (43)$$

$$\Delta C_{+,i}^w = \frac{-Z_{++}\Gamma}{(Z_- + Z_+\Gamma)} \Delta C_{+,i}^w \approx -0.30 C_{+,i}^w. \quad (44)$$

Note that $\Delta C_{+,i}^w = C_{+,i}^w$ under the limiting current condition, and for the present system, $Z_- = -2$, $Z_{++} = 2$, $Z_+ = 1$. The value of Γ given in equation (32) has been used for the calculations. The thickness ratio of the outer to inner solutal layers is

$$\frac{\delta_{s,0}^w}{\delta_{s,i}^w} \sim \left(\frac{D_0^w}{D_{++}^w} \right)^{1/2} \sim 1.9. \quad (45)$$

The basis for equation (45) will be given later. By satisfying the boundary conditions given in equations (7) and (8), and connecting the concentration slopes described by equations (41)–(45) in both the inner and the outer solutal layers, one can construct the concentration profiles of all species in the entire solutal boundary layer. The dimensionless concentration difference profiles $\Delta C_{z,R}^w / C_{+,B}^w$ are plotted against the dimensionless solutal layer thickness, $\delta_{s,R}^w / \delta_{s,i}^w$ in Fig. 2. Letters s, i, and B in the figure represent the cathode surface, the interface which separates the inner and outer solutal layers, and the bulk electrolyte, respectively.

The solutal boundary layer structure and the corresponding concentration profiles shown in Fig. 2 for the well-supported electrochemical system is much different from that for the nonelectrolytic systems. First, for a ternary nonelectrolytic system in which all species have different diffusivities, there are three solutal layers instead of two for the present system. Secondly, it is noticed that the concentration profile of SO_4^- shows a maximum at the interface between

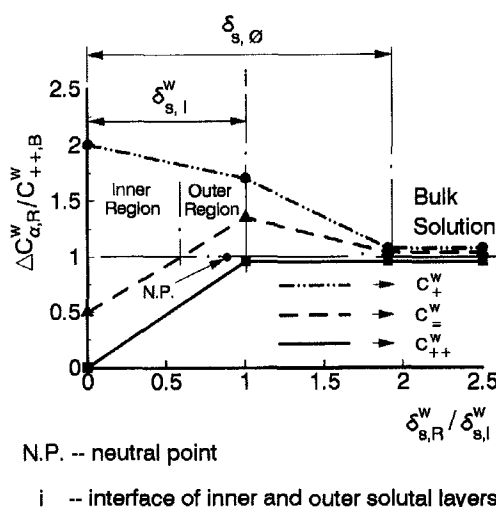


Fig. 2. Estimated concentration profiles of all species in solutal boundary layers for a well-supported electrolyte.

the inner and outer solutal layers due to electro-neutrality, which will not be possible for the non-electrolytic system. Finally, the solutal buoyancy force in the outer solutal layer is downward since concentrations of SO_4^- and H^+ are higher than while Cu^{++} is equal to the bulk values. However, the orientation of the solutal buoyancy force in the inner solutal layer is determined by the electrolyte density affected by the concentrations of all species. There are two regions in the inner solutal layer, an inner region near the electrode surface and an outer region near the interface, as shown in Fig. 2. In the entire inner region the concentrations of Cu^{++} and SO_4^- are lower than the bulk values, while that of H^+ is higher than the bulk value. Since the density variation generated by the ΔCu^{++} and ΔSO_4^- is greater than that by ΔH^+ in the region, the solutal buoyancy is upward. In the outer region, there is a neutral point marked by NP in Fig. 2 at which the density of the electrolyte becomes equal to that of the bulk solution. The density of the electrolyte is lower and higher than the bulk density of the electrolyte on the LHS and RHS of the point NP in the outer region, respectively. The orientation of the solutal buoyancy force in the entire inner solutal layer is determined, therefore, by the NP point rather than the interface of the inner and outer layers. In the portion of the solutal layer from NP to the electrode surface the solutal buoyancy is upward, while it is downward in the rest of the solutal layer.

In a numerical analysis of natural convection in an electrochemical system the same as the present one, Selman and Newman [13] demonstrated that the solution density gradient outward normal to the cathode surface is positive in the inner layer, while it is negative in the outer layer. The scaling results support the analysis and, furthermore, provides physical insight of the solutal boundary layer structure.

It would appear that the downward solutal buoyancy force in the outer portion of the solutal layer could cause bidirectional flow. No such flow exists in the present system since the magnitude of the downward solutal buoyancy force is less than upward one, as indicated by the scaling results. However, the downward buoyancy force modifies the density profiles and reduces the convection intensity as indicated in ref. [13]. The present system was used to study thermosolutal convection [1, 3, 4]. The parametric range of these experiments covered the cases in which $\delta_T > \delta_S$ and $V_T > V_S$. The upward thermal convection outside the solutal layer is strong enough to overwhelm the solutal downward effect. As a result, the thermosolutal convection along the electrode is unidirectional. The scales obtained above will be used to perform an analysis of heat and mass transfer correlation in the next section.

Transport correlations

Since the thermal and the solutal buoyancy forces act in regions with different length scales when $Le \gg 1$ ($\delta_T > \delta_S$), the thermal convection is stronger than the

solutal convection, even for the cases with $N > 1$. The thermal convection in the thermal layer enhances the solutal convection in the solutal layer. In order to obtain meaningful estimates of thicknesses of boundary layers and reference velocities in the layers, the effects of both the heat and mass transfer must be included in the force balances made in the momentum equations. To this end equations (3) and (4) are combined by eliminating pressure gradient terms, and equations (5) and (6) are introduced through derivatives of T and C

$$\begin{aligned} & \left(\frac{\partial^2 u'}{\partial x'^2} + \frac{L_R^2}{H_R^2} \frac{\partial^2 u'}{\partial y'^2} \right) v' - \left(\frac{\partial^2 v'}{\partial x'^2} + \frac{L_R^2}{H_R^2} \frac{\partial^2 v'}{\partial y'^2} \right) u' \\ &= \frac{1}{Re} \left(\frac{L_R}{H_R} \right)^4 \frac{\partial^3 u'}{\partial y'^3} - \frac{1}{Re} \frac{\partial^3 v'}{\partial x'^3} \\ &+ \frac{2}{Re} \frac{L_R^2}{H_R^2} \frac{\partial^3 u'}{\partial x'^2 \partial y'} + \frac{1}{Re^2} \left(\frac{L_R}{H_R} \right)^4 \\ &\times \left\{ \sum_x \frac{Gr_{S,\alpha}}{Sc_\alpha Re} \left(\frac{\partial^2 C'_\alpha}{\partial x'^2} + \frac{L_R^2}{H_R^2} \frac{\partial^2 C'_\alpha}{\partial y'^2} \right) \frac{1}{u'} \right. \\ &- \frac{Gr_T}{Pr Re} \left(\frac{\partial^2 T'}{\partial x'^2} + \frac{L_R^2}{H_R^2} \frac{\partial^2 T'}{\partial y'^2} \right) \frac{1}{u'} + Gr_T \left(\frac{v'}{u'} \frac{\partial T'}{\partial y'} \right) \\ &- \sum_x Gr_{S,\alpha} \left(\frac{v'}{u'} \frac{\partial C'_\alpha}{\partial y'} \right) + \sum_x \frac{Gr_{S,\alpha}}{Sc_\alpha Re} \\ &\times \left[\frac{fZ_\alpha C_{\alpha,R} \Delta\Phi_R}{\Delta C_\alpha} \left(\frac{\partial^2 \phi'}{\partial x'^2} + \frac{L_R^2}{H_R^2} \frac{\partial^2 \phi'}{\partial y'^2} \right) \psi'_\alpha \right. \\ &\left. + fZ_\alpha \Delta\Phi_R \left(\frac{\partial C'_\alpha}{\partial x'} \frac{\partial \phi'}{\partial x'} + \frac{L_R^2}{H_R^2} \frac{\partial C'_\alpha}{\partial y'} \frac{\partial \phi'}{\partial y'} \right) \right] \frac{1}{u'} \left. \right\}. \quad (46) \end{aligned}$$

For the binary electrolyte, both SO_4^- and H^+ share a single solutal layer as was previously mentioned. Reference parameters in the layer are

$$V_R = V_S^b, \quad H_R = \delta_S^b, \quad \Delta T_R = \Delta T_S^b, \quad D_R = D^b$$

as given in equation (18), and

$$\Delta C_{\alpha,R}^b = \Delta C_{+,R}^b = \Delta C_{-,R}^b = C_{+,B}^b$$

due to electroneutrality. Since $\delta_T > \delta_S^b$ the temperature difference ΔT_S^b needs to be rescaled by the total temperature variation across the thermal boundary layer

$$\Delta T_S^b \sim \frac{\delta_S^b}{\delta_T^b} \Delta T. \quad (47)$$

In the solutal boundary layer δ_S^b , the balance between the solutal convection and diffusion in equation (6) yields

$$V_S^b \sim \frac{v}{H} (Sc^b)^{-1} \left(\frac{H}{\delta_S^b} \right)^2. \quad (48)$$

The balance of the viscous term with both the solutal and thermal buoyancy terms in equation (46) yields

$$V_S^b \sim \frac{v}{H} (Sc^b)^{-1/2} \cdot (GR_S^b)^{1/2}$$

$$GR_S^b = Gr_S^b + \frac{\delta_S}{\delta_T^b} Le^b Gr_T^b \quad (49)$$

where the $Le^b = \alpha_T^b/D^b$. The Gr_S^b and Gr_T^b are defined by the $C_{+,B}^b$ and ΔT while the GR denotes the combined Grashof number. Combination of equations (48) and (49) leads to

$$\frac{\delta_S^b}{H} \sim (Sc^b GR_S^b)^{-1/4}. \quad (50)$$

In the thermal boundary layer δ_T^b , the V_S^b , δ_S^b , and ΔT_S^b are replaced by the V_T^b , δ_T^b , and ΔT . The balance between the thermal convection and diffusion in equation (5), and the balance of the viscous term with both the solutal and thermal buoyancy terms in equation (46) yield

$$\frac{\delta_T^b}{H} \sim (Pr^b GR_T^b)^{-1/4} \quad (51)$$

where

$$GR_T^b = (Le^b)^{-1} Gr_S^b + Gr_T^b \quad \text{and} \quad Pr^b = v/\alpha_T^b,$$

$$V_T^b \sim \frac{v}{H} (Pr^b)^{-1/2} (GR_T^b)^{1/2}. \quad (52)$$

A ratio of thicknesses of the thermal to solutal layers is defined by

$$\gamma_{TS}^b = \frac{\delta_T^b}{\delta_S^b} \sim (Le^b)^{2/5} \left[\left(\frac{\delta_T^b}{\delta_S^b} + \frac{Le^b}{N^b} \right) \left(1 + \frac{Le^b}{N^b} \right)^{-1} \right]^{1/5}$$

where

$$N^b = \frac{Gr_S^b}{Gr_T^b}. \quad (53)$$

Since $Le^b \gg N^b$ and $\delta_T^b > \delta_S^b$ equation (53) is reduced to

$$\gamma_{TS}^b = \frac{\delta_T^b}{\delta_S^b} \sim (Le^b)^{2/5}. \quad (54)$$

For thermosolutal systems with $Le^b \sim 1$, Somers [6] and Mathers *et al.* [7] found γ_{TS}^b is proportional to Le^b with a one-half power dependency. The analytical result obtained by Wilcox [8] indicates that this dependency no longer holds for systems with $Le^b > 1$. The present scaling result as given by equation (54) is plotted in Fig. 3 with the results by Somers [6] and Wilcox [8]. The new result provides an estimate more accurate than the scaling of the one-half power suggested by Somers [6]. A good agreement between the new scaling and Wilcox's result [8] is demonstrated for both $Le^b \sim 1$ and $Le^b > 1$ cases. Comparing with Wilcox's result, the present scaling is simple and is easy to apply to specific applications.

The dimensionless mass transfer coefficient, namely the Sherwood number, Sh^b , is inversely proportional to the dimensionless thickness of the solutal boundary layer

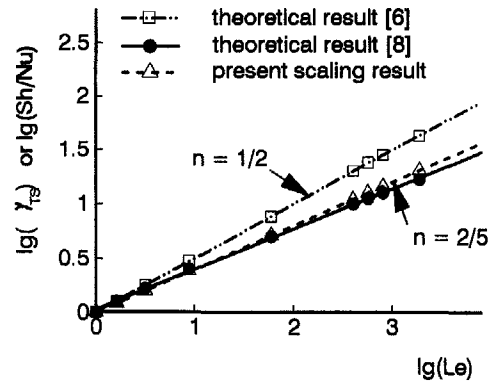


Fig. 3. Comparison of correlations of $\log(\gamma_{TS})$ or $\log(Sh/Nu)$ and $\log(Le)$ for both binary and well-supported electrolytes.

$$Sh^b \sim \frac{H}{\delta_S^b} \sim (Sc^b GR_S^b)^{1/4} \quad GR_S^b = Gr_S^b + (Le^b)^{3/5} Gr_T^b. \quad (55)$$

Equations (50) and (54) are used in the derivation of equation (55). This correlation is formally similar to that obtained by Somers [6], except that the coefficient $(Le^b)^{1/2}$ of Gr_T^b and the diffusivity D used in the Somers' result for a nonelectrolytic thermosolutal system has been replaced by $(Le^b)^{3/5}$ in equation (55) and D^b given in equation (18), respectively.

Similarly, the dimensionless heat transfer rate, namely the Nusselt number Nu^b , is inversely proportional to the dimensionless thickness of the thermal boundary layer

$$Nu^b \sim \frac{H}{\delta_T^b} \sim \frac{H}{\delta_S^b} \frac{\delta_S^b}{\delta_T^b} \sim Sh^b (Le^b)^{-2/5}, \quad (56)$$

where equations (54) and (55) have been used. The ratio of Sh^b to Nu^b is proportional to the two-fifth power of Le^b , which is also plotted vs Le^b in Fig. 3. When Le^b is large, the scaling of $(Le^b)^{2/5}$ given by equation (56), rather than that of the $(Le^b)^{1/2}$ reported by Somers [6], agrees well with the theoretical result obtained by Wilcox [8]. Both scalings merge as Le^b approaches unity.

For the well-supported electrolyte, two solutal layers need to be considered as previously mentioned. In the outer layer $\delta_{S,0}^w$, the reference parameters are: $V_R = V_{S,0}^w$, $L_R = \delta_{S,0}^w$, $H_R = H$, $D_{z,0}^w = D_0^w$, $\Delta C_{+,R}^w = 0$, $\Delta C_{x,R}^w = \Delta C_{z,0}^w$, and $\alpha = +$ and $=$, in which D_0^w , $\Delta C_{=,0}^w$ and $\Delta C_{-,0}^w$ are given in equations (26), (41) and (43). The solutal buoyancy force in $\delta_{S,0}^w$ tends to retard the convective flow near the electrode surface, since it opposes the solutal buoyancy force in the inner layer $\delta_{S,1}^w$. Equation (26) shows that $Le_{0,++} = D_0^w/D_{++}$ is in order of unity and therefore equation (53) becomes

$$\gamma_{S,01}^w = \delta_{S,0}^w/\delta_{S,1}^w \sim Le_{0,++}^{1/2} = (D_0^w/D_{++})^{1/2}, \quad (57)$$

where $\gamma_{s,0}^w$ is the ratio of thicknesses of the outer to inner solutal layers.

In the inner layer $\delta_{s,1}^w$, the reference parameters are: $V_R = V_{s,1}^w$, $L_R = \delta_{s,1}^w$, $H_R = H$, $D_{\alpha,1}^w = D_{\alpha,++}$, $\Delta C_{\alpha,R}^w = C_{\alpha,1}^w$, and $\alpha = ++$, $+$ and $=$, in which $D_{\alpha,1}^w$, $\Delta C_{\alpha,1}^w$ and $\Delta C_{\alpha,1}^w$ are given in equations (35), (42) and (44). In a manner similar to that for a binary electrolyte, we obtain

$$V_{s,1}^w \sim \frac{v^w}{H} (Sc_{\alpha,++}^w)^{-1/2} (GR_{s,1}^w)^{1/2} \quad Sc_{\alpha,++}^w = v^w/D_{\alpha,++} \quad (58)$$

$$\frac{\delta_{s,1}^w}{H} \sim (Sc_{\alpha,++}^w GR_{s,1}^w)^{-1/4} \quad (59)$$

$$Sh^w \sim (Sc_{\alpha,++}^w GR_{s,1}^w)^{1/4} \quad (60)$$

where the combined Grashof number $GR_{s,1}^w$ is defined as

$$GR_{s,1}^w = Gr_S^w + (Le_{\alpha,++}^w)^{3/5} \cdot Gr_T \quad (61)$$

and

$$Gr_S^w = \frac{g\Delta\rho_s^w H^3}{\rho^w (v^w)^2} = \sum_{\alpha} Gr_{s,\alpha,1}^w - (Le_{0,++}^w)^{1/2} (Gr_{s,=,0}^w + Gr_{s,+,0}^w).$$

The Gr_S^w denotes the integrated solutal Grashof number and $\alpha = ++$, $+$ and $=$. Note that solutal Grashof numbers with subscript $_1$ and $_0$ are defined by the physical properties and concentration variations in the inner and outer solutal layers, respectively. The concentration variations are given in equations (41)–(44). Concentration variations of all species in the both inner and outer solutal layers contribute to the density variation.

In general, mass transport correlation for the present system is

$$Sh^w = C' (Sc_{\alpha,++}^w GR_{s,1}^w)^n \quad (62)$$

n is found to be 1/4 by using the scaling result as given by equation (60) and C' is an arbitrary constant which is determined by experimental results. The experimental data reported by Jiang *et al.* [4] are used to verify equation (62). The data are plotted in Fig. 4 to compare with the scaling result. The data fit well with the one-fourth power line up to $(Sc_{\alpha,++}^w GR_{s,1}^w)^{11}$ and then deviate from the line. The deviation appears to indicate the transition of flow into the turbulent regime. By extrapolating the one-fourth power line C' is found to be 0.71.

Similar to the binary system, the ratio of Sh^w to Nu^w for the well-supported system is

$$\frac{Sh^w}{Nu^w} \sim \gamma_{TS}^w = \frac{\delta_T^w}{\delta_{s,1}^w} \sim (Le_{\alpha,++}^w)^{2/5}. \quad (63)$$

Both Sh^w/Nu^w and γ_{TS}^w are also plotted vs $Le_{\alpha,++}^w$ in

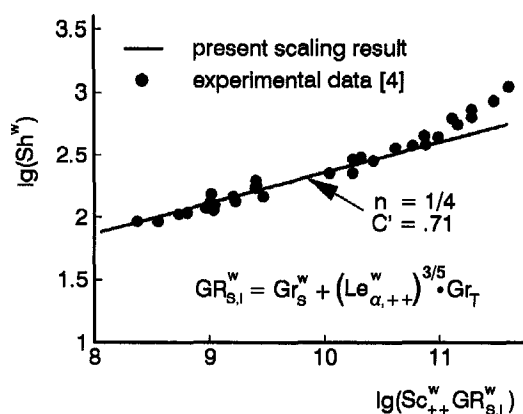


Fig. 4. Mass transport correlation for a well-supported electrolyte.

Fig. 3 and the conclusions drawn for the binary system apply for the well-supported system.

CONCLUSIONS

A scaling analysis has been successfully applied to study transport phenomena of thermosolutal convection in multiple-component electrochemical systems. Due to the interaction of diffusion and migration the solutal boundary layer structures of electrochemical systems are found to be very different from that of nonelectrolytic systems.

For a ternary electrolyte, such as cupric-sulphate-acid solution, the hydrogen and sulphate ions must share a single solutal boundary layer to satisfy the electroneutrality condition. Therefore, only two solutal layers, the inner and outer layers, can be defined and their thicknesses have been estimated. Concentration profiles of the sulphate, hydrogen and cupric ions are estimated in both inner and outer layers, respectively. It is noticed that the concentration of the sulphate ions reaches a maximum at the interface between the inner and outer layers. As a result, the solutal buoyancy force is upward in the inner portion of the entire solutal layer, and downward in the outer portion of the layer.

A new approach which considers the effects of heat and mass transfer simultaneously with the momentum transport is developed to study transport correlation for the thermosolutal convection. It is found that the ratio of thermal to solutal boundary layers as well as the ratio of the Sherwood to Nusselt numbers are proportional to the two-fifths power of the Lewis number. The scaling results are compared with both analytical results and experimental data and satisfactory agreements are demonstrated.

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