

Onset of natural convection of electrolyte on horizontal electrode under non-steady-state mass-transfer conditions

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Received 22 June 2006; received in revised form 10 October 2006

Available online 29 December 2006

Abstract

In this work, the problem of convective stability of electrochemical system (a horizontal electrode and a solution containing three types of ions) under the non-steady-state mass-transfer conditions is solved. A set of equations involving the Navier–Stokes equation for incompressible viscous liquid to the Boussinesq approximation, the ion-transfer equations that account for diffusion, migration, and convection, and the electroneutrality condition were used as the mathematical model. The problem is solved within the framework of linear theory of stability. The set of amplitude equations obtained for vertical component of hydrodynamic velocity and concentrations was solved numerically by the shooting method. As a result, the critical Rayleigh number, the wave number, and the critical time of onset of natural convection were determined. It is shown that the supporting electrolyte has a strong effect on the convective stability of the system.

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Keywords: Natural-convective instability; Electrochemical system; Onset time; Non-steady-state mass-transfer; Supporting electrolyte; Migration

1. Introduction

Natural convection of electrolyte, which arises in the electrochemical systems due to the variations in the electrolyte density, has a pronounced effect on the electrode reaction rate [1,2]. In the case of horizontal electrodes, natural convection of electrolyte arises only at the Rayleigh numbers Ra higher than a certain critical value Ra_c . The determination of Ra_c involves a study of stability of stagnant electrolyte under the steady-state mass-transfer conditions. In real systems, stability of stagnant electrolyte is disturbed before the steady-state distribution of concentrations is reached. Therefore, in recent years, non-steady-state convective instability has been studied. In this case, instability arises when the diffusion layers exist near each of electrodes and the distribution of concentrations of ions in the inter-electrode space has a complex, non-linear character. This

significantly complicates the theoretical analysis of the process. In this case, convective instability is characterized by a critical time t_c , i.e. a period of time from the beginning of experiment (for example, from the instant of imposing a voltage between the electrodes) to the onset of convection. The critical time can be determined by the analysis of stability of interrelated equations of liquid motion and ion-transfer equations. In [3–8] the problem of stability of stagnant fluid under the non-steady-state heat-transfer conditions was studied. The results of these studies can be used directly for the electrochemical systems with a binary electrolyte. In the multi-component electrochemical systems (with three or more types of ions), the distribution of electrolyte density over the diffusion layers depends both on electroactive and supporting electrolyte; this prevents the use of results, which were obtained for heat systems. The natural convection in the multi-component systems with horizontal electrodes was studied experimentally in several works [9–11]. Recently, the effect of stable thermal stratification on the onset of double-diffusive convection in the

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Nomenclature

a	parameter	Sc_1	Schmidt number, $\frac{\nu}{D_1}$
A	parameter, $\overline{Ra}_c^{2/3}$	$S_1(\zeta)$	amplitude of small perturbation of concentration of electroactive ions
c_m	concentration of ions of m th type	$S_4(\zeta)$	amplitude of small perturbation of concentration of fictitious ions
C_1	dimensionless concentration of electroactive ions, $\frac{c_1}{2c_{1b}}$	$W_Z(\zeta)$	amplitude of small perturbation of vertical component of hydrodynamic velocity
C_4	dimensionless concentration of fictitious ions, $\frac{z_3 c_4}{2\alpha c_{1b}(z_3 - z_2)} \frac{\partial \rho}{\partial c_2}$	t	time
\widehat{C}_m	modified dimensionless small disturbance of concentration of ions of m th type, \widehat{C}_m/Ra	τ	dimensionless time, $\frac{\nu}{H^2} t$
D_m	diffusion coefficient of ions of m th type	T	temperature
D_4	diffusion coefficient of supporting electrolyte, $\frac{D_2 D_3 (z_3 - z_2)}{z_3 D_3 - z_2 D_2}$	\mathbf{v}	hydrodynamic velocity
D^*	mutual diffusion coefficient, $\frac{D_1}{D_2} \left[\frac{n_2}{n_1} D_1 - \frac{D_3(z_3 - z_2) + (D_3 - D_2)z_1}{z_3 D_3 - z_2 D_2} D_2 - \frac{n_2 - n_1}{n_1} D_4 \right]$	\mathbf{V}	dimensionless hydrodynamic velocity, $\frac{H}{D_1} \mathbf{v}$
\overline{D}_4	dimensionless diffusion coefficient of supporting electrolyte, $\frac{D_4}{D_1}$	x, y, z	axial, spanwise and normal coordinate
\overline{D}^*	dimensionless mutual diffusion coefficient, $\frac{z_3 D^*}{\alpha D_1 (z_3 - z_2)} \frac{\partial \rho}{\partial c_2}$	X, Y, Z	dimensionless axial, spanwise and normal coordinate, $\frac{x}{H}, \frac{y}{H}, \frac{z}{H}$
F	Faraday number	z_m	charge number of ions of m th type
g	gravitational acceleration	<i>Greek symbols</i>	
Gr	Grashof number, $\frac{2gH^3 c_{1b} \alpha}{\rho_b \nu^2}$	α	densification coefficient of electrolyte with three types of ions, $\frac{\partial \rho}{\partial c_1} + \frac{z_1 - z_3 n_2 D_1 / m_1 D_2}{z_3 - z_2} \frac{\partial \rho}{\partial c_2}$
H	distance between electrodes	β	dimensionless parameter, $\frac{1 + \sqrt{\overline{D}_4}}{1 + \sqrt{\overline{D}_4 + \overline{D}^*}}$
k_x, k_y	projections of wave vector onto the coordinate axis X and Y , respectively	Δ_2	two-dimensional Laplacian, $\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2}$
k	wave number, $\sqrt{k_x^2 + k_y^2}$	ε	relative concentration of electroactive ions, $\frac{c_{1b}}{c_{3b}}$
\bar{k}	modified wave number, $k \sqrt{\tau / Sc_1}$	ϕ	electric potential
M_m	designation of ions of m th type	$\boldsymbol{\gamma}$	unity vector directed vertically downwards
n	number of electrons exchanged in the electrode reaction, $(z_1 n_1 - z_2 n_2)$	ν	kinematic viscosity of electrolyte
n_m	stoichiometric coefficient of ions of m th type	ρ	density of electrolyte
p	pressure	$\frac{\partial \rho}{\partial c_m}$	densification coefficient of ions of m th type
P	dimensionless pressure, $\frac{H^2}{\rho_b \nu D_1} P$	ζ	self-similar variable, $(Sc_1 / \tau)^{1/2} Z$
R	gas constant	<i>Subscripts</i>	
Ra_1	Rayleigh number of electroactive ion, $Sc_1 \cdot Gr$	b	bulk state
Ra	Rayleigh number of electrolyte with three types of ions, $\frac{\beta}{2} Ra_1$	c	critical conditions
\overline{Ra}	modified Rayleigh number of electrolyte with three types of ions, $Ra \cdot (\tau / Sc_1)^{3/2}$	<i>Overbars</i>	
		—	undisturbed state
		~	small disturbance
		^	modified small disturbance

electrochemical systems has been studied theoretically by Kim et al. [12]; however, the migration of supporting electrolyte ions has been ignored.

2. Formulation of the problem

Within the framework of the Boussinesq approximation, the theory of dilute electrolytes, and under the assumption of electroneutrality, equations of flow of incompressible viscous liquid and the ion transfer in the electrolyte layer between two horizontal electrodes can be written as follows [1,2,13,14]:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = -\frac{1}{\rho_b} \nabla p + \nu \Delta \mathbf{v} + \frac{\gamma \mathbf{g}}{\rho_b} (\rho - \rho_b),$$

$$\text{div}(\mathbf{v}) = 0,$$

$$\frac{\partial c_1}{\partial t} = D_1 \Delta c_1 + \frac{Fz_1 D_1}{RT} (\nabla c_1 \nabla \phi + c_1 \Delta \phi) - \mathbf{v} \nabla c_1,$$

$$\frac{\partial c_2}{\partial t} = D_2 \Delta c_2 + \frac{Fz_2 D_2}{RT} (\nabla c_2 \nabla \phi + c_2 \Delta \phi) - \mathbf{v} \nabla c_2,$$

$$\frac{\partial c_3}{\partial t} = D_3 \Delta c_3 + \frac{Fz_3 D_3}{RT} (\nabla c_3 \nabla \phi + c_3 \Delta \phi) - \mathbf{v} \nabla c_3,$$

$$z_1 c_1 + z_2 c_2 + z_3 c_3 = 0.$$

(1)

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