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

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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.

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 interelectrode 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
A	parameter, $\overline{Ra}_{\mathrm{c}}^{2/3}$
c_m	concentration of ions of mth type
C_1	dimensionless concentration of electroactive ions, $\frac{c_1}{2c_{1_{\mathrm{b}}}}$
C_4	dimensionless concentration of fictitious ions, $\frac{z_3c_4}{2\alpha c_{1_{\mathrm{b}}}(z_3-z_2)}\frac{\partial\rho}{\partial c_2}$
$\widehat{C}_m$	modified dimensionless small disturbance of concentration of ions of mth type, $\widetilde{C}_m/Ra$
D_m	diffusion coefficient of ions of mth type
D_4	diffusion coefficient of supporting electrolyte, $\frac{D_2D_3(z_3-z_2)}{z_3D_3-z_2D_2}$
D^*	mutual diffusion coefficient, $\frac{D_1}{D_2}\left[\frac{n_2}{n_1}D_1-\frac{D_3(z_3-z_2)+(D_3-D_2)z_1}{z_3D_3-z_2D_2}D_2-\frac{n_2-n_1}{n_1}D_4\right]$
$\overline{D}_4$	dimensionless diffusion coefficient of supporting electrolyte, $\frac{D_4}{D_1}$
$\overline{D}^*$	dimensionless mutual diffusion coefficient, $\frac{z_3D^*}{\alpha D_1(z_3-z_2)}\frac{\partial\rho}{\partial c_2}$
F	Faraday number
g	gravitational acceleration
Gr	Grashof number, $\frac{2gH^3c_{1_{\mathrm{b}}}\alpha}{\rho_{\mathrm{b}}\nu^2}$
H	distance between electrodes
k_X, k_Y	projections of wave vector onto the coordinate axis X and Y, respectively
k	wave number, $\sqrt{k_X^2+k_Y^2}$
$\bar{k}$	modified wave number, $k\sqrt{\tau/Sc_1}$
M_m	designation of ions of mth type
n	number of electrons exchanged in the electrode reaction, $(z_1n_1-z_2n_2)$
n_m	stoichiometric coefficient of ions of mth type
p	pressure
P	dimensionless pressure, $\frac{H^2}{\rho_{\mathrm{b}}\nu D_1}p$
R	gas constant
Ra_1	Rayleigh number of electroactive ion, $Sc_1\cdot Gr$
Ra	Rayleigh number of electrolyte with three types of ions, $\frac{\beta}{2}Ra_1$
$\overline{Ra}$	modified Rayleigh number of electrolyte with three types of ions, $Ra\cdot(\tau/Sc_1)^{3/2}$
Sc_1	Schmidt number, $\frac{\nu}{D_1}$
$S_1(\varsigma)$	amplitude of small perturbation of concentration of electroactive ions
$S_4(\varsigma)$	amplitude of small perturbation of concentration of fictitious ions
$W_Z(\varsigma)$	amplitude of small perturbation of vertical component of hydrodynamic velocity
t	time
τ	dimensionless time, $\frac{\nu}{H^2}t$
T	temperature
$\mathbf{v}$	hydrodynamic velocity
$\mathbf{V}$	dimensionless hydrodynamic velocity, $\frac{H}{D_1}\mathbf{v}$
x, y, z	axial, spanwise and normal coordinate
X, Y, Z	dimensionless axial, spanwise and normal coordinate, $\frac{x}{H}$, $\frac{y}{H}$, $\frac{z}{H}$
z_m	charge number of ions of mth type

Greek symbols

α	densification coefficient of electrolyte with three types of ions, $\frac{\partial\rho}{\partial c_1}+\frac{z_1-z_3n_2D_1/n_1D_2}{z_3-z_2}\frac{\partial\rho}{\partial c_2}$
β	dimensionless parameter, $\frac{1+\sqrt{\overline{D}_4}}{1+\sqrt{\overline{D}_4+\overline{D}^*}}$
Δ_2	two-dimensional Laplacian, $\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}$
ε	relative concentration of electroactive ions, $\frac{c_{1_{\mathrm{b}}}}{c_{3_{\mathrm{b}}}}$
ϕ	electric potential
$\boldsymbol{\gamma}$	unity vector directed vertically downwards
ν	kinematic viscosity of electrolyte
ρ	density of electrolyte
$\frac{\partial\rho}{\partial c_m}$	densification coefficient of ions of mth type
ς	self-similar variable, $(Sc_1/\tau)^{1/2}Z$

Subscripts

b	bulk state
c	critical conditions

Overbars

—	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]:

$$\begin{aligned}
&\frac{\partial\mathbf{v}}{\partial t}+(\mathbf{v}\cdot\nabla)\mathbf{v}=-\frac{1}{\rho_{\mathrm{b}}}\nabla p+\nu\Delta\mathbf{v}+\frac{\boldsymbol{\gamma}g}{\rho_{\mathrm{b}}}(\rho-\rho_{\mathrm{b}}),\\
&\mathrm{div}(\mathbf{v})=0,\\
&\frac{\partial c_1}{\partial t}=D_1\Delta c_1+\frac{Fz_1D_1}{RT}(\nabla c_1\nabla\varphi+c_1\Delta\varphi)-\mathbf{v}\nabla c_1,\\
&\frac{\partial c_2}{\partial t}=D_2\Delta c_2+\frac{Fz_2D_2}{RT}(\nabla c_2\nabla\varphi+c_2\Delta\varphi)-\mathbf{v}\nabla c_2,\\
&\frac{\partial c_3}{\partial t}=D_3\Delta c_3+\frac{Fz_3D_3}{RT}(\nabla c_3\nabla\varphi+c_3\Delta\varphi)-\mathbf{v}\nabla c_3,\\
&z_1c_1+z_2c_2+z_3c_3=0.
\end{aligned}\tag{1}$$

For a solution containing three types of ions, which is obtained of two source substances (for example $CuSO_4$ and H_2SO_4), the electrolyte density can be expressed in terms of concentrations of two types of ions, because the concentration of ions of the third type is uniquely determined by the electroneutrality condition. For the sake of definiteness, assume that the electrolyte density is expressed as follows:

$$\rho - \rho_b = \frac{\partial\rho}{\partial c_1}(c_1 - c_{1_b}) + \frac{\partial\rho}{\partial c_2}(c_2 - c_{2_b}). \tag{2}$$

Assume that the following reaction proceeds on the electrodes:

$$n_1 M_1^{z_1} + ne \leftrightarrow n_2 M_2^{z_2} + a n_1 M_1, \tag{3}$$

Eq. (3) describes both redox reactions ($a = 0$, $n_2 \neq 0$) and the reactions of cathodic deposition (anodic dissolution) of metal ($a = 1$, $n_1 = 1$, $n_2 = 0$). In some cases, the reduction (for example, of $[Fe(CN_6]^{3+})$ proceeds at the cathode and the oxidation of $[Fe(CN_6]^{2+})$ proceeds at the anode; in other cases, metal (copper, for example) cations discharge on the cathode and form on the anode.

For the limiting-current mode, the boundary conditions for set of Eq. (1) are as follows:

$$\begin{aligned}
&\mathbf{v}|_{z=0,z=H} = 0\\
&c_1|_{z=0} = 0, c_1|_{z=H} = 2c_{1_b}\\
&\left[n_2 D_1\left(\frac{\partial c_1}{\partial z} + \frac{Fz_1 c_1}{RT}\frac{\partial\varphi}{\partial z}\right) = -n_1 D_2\left(\frac{\partial c_2}{\partial z} + \frac{Fz_2 c_2}{RT}\frac{\partial\varphi}{\partial z}\right)\right]\Bigg|_{z=0,z=H}\\
&\left(\frac{\partial c_3}{\partial z} + \frac{Fz_3 c_3}{RT}\frac{\partial\varphi}{\partial z}\right)\Bigg|_{z=0,z=H} = 0.
\end{aligned} \tag{4}$$

Assume that the concentration of indifferent electrolyte considerably exceeds the concentration of electroactive electrolyte, i.e. the following condition is fulfilled

$$\varepsilon = \frac{c_{1_b}}{c_{3_b}} \ll 1. \tag{5}$$

We will estimate the relative diffusion and migration terms in the equations of ionic transfer and the corresponding boundary conditions at $\varepsilon \ll 1$. We denote the difference in the concentration of the first electrolyte component between the cathode and the anode by $\delta c_1 \sim \varepsilon c_{3_b}$. From the electroneutrality condition, the estimates for the concentration differences for the second and the third types of ions are as follows:

$$\begin{aligned}
&\delta c_2 \sim \delta c_1 \sim \varepsilon c_{3_b},\\
&\delta c_3 \sim \delta c_1 \sim \varepsilon c_{3_b}.
\end{aligned} \tag{6}$$

Thus, for all electrolyte components, the relative diffusion terms are identical and proportional to ε. To estimate the derivatives of electric potential, we use the equation of electric charge conservation:

$$\sum_{m=1}^{3} z_m D_m \Delta c_m + \nabla\varphi \sum_{m=1}^{3}\frac{Fz_m^2 D_m}{RT}\nabla c_m + \Delta\varphi\sum_{m=1}^{3}\frac{Fz_m^2 D_m c_m}{RT} = 0, \tag{7}$$

which is a consequence of equations of ion transfer (1) and the electroneutrality condition. Taking into account that $\sum_{m=1}^{3} z_m D_m \Delta c_m \sim \varepsilon c_{3_b}$, $\sum_{m=1}^{3}\frac{Fz_m^2 D_m}{RT}\nabla c_m \sim \varepsilon c_{3_b}$, $\sum_{m=1}^{3}\frac{Fz_m^2 D_m c_m}{RT} \sim c_{3_b}$ and $\Delta\phi \sim \nabla\phi$, we obtain the following estimates: $\Delta\phi \sim \varepsilon$, $\nabla\phi \sim \varepsilon$.

To the linear in small parameter ε approximation, system of Eq. (1) takes the form:

$$\begin{aligned}
&\frac{\partial\mathbf{v}}{\partial t} + (\mathbf{v}\cdot\nabla)\mathbf{v} = -\frac{1}{\rho_b}\nabla p + \nu\Delta\mathbf{v} + \frac{\gamma g}{\rho_b}\left[\frac{\partial\rho}{\partial c_1}(c_1 - c_{1_b}) + \frac{\partial\rho}{\partial c_2}(c_2 - c_{2_b})\right],\\
&\mathrm{div}(\mathbf{v}) = 0,\\
&\frac{\partial c_1}{\partial t} = D_1\Delta c_1 - \mathbf{v}\nabla c_1,\\
&\frac{\partial c_2}{\partial t} = D_2\Delta c_2 + \frac{Fz_2 D_2 c_{2_b}}{RT}\Delta\varphi - \mathbf{v}\nabla c_2,\\
&\frac{\partial c_3}{\partial t} = D_3\Delta c_3 + \frac{Fz_3 D_3 c_{3_b}}{RT}\Delta\varphi - \mathbf{v}\nabla c_3,\\
&z_1 c_1 + z_2 c_2 + z_3 c_3 = 0.
\end{aligned} \tag{8}$$

Based on these estimates, the equations for ion fluxes at the electrodes (the third and the fourth equations in (4)) can be presented as follows:

$$\begin{aligned}
&\left[n_2 D_1\frac{\partial c_1}{\partial z} = -n_1 D_2\left(\frac{\partial c_2}{\partial z} + \frac{Fz_2 c_{2_b}}{RT}\frac{\partial\varphi}{\partial z}\right)\right]\Bigg|_{z=0,z=H}\\
&\left(\frac{\partial c_3}{\partial z} + \frac{Fz_3 c_{3_b}}{RT}\frac{\partial\varphi}{\partial z}\right)\Bigg|_{z=0,z=H} = 0.
\end{aligned} \tag{9}$$

As a result of the presence of migration terms in set (8) and boundary conditions (9), the ion transfer equations are non-linear and coupled and, hence, difficult to solve. From boundary conditions (9) and the electroneutrality condition, to the linear in small parameter ε approximation, it follows:

$$\frac{\partial}{\partial z}\left(\frac{n_2 D_1}{n_1 D_2}c_1 + c_2 + c_3\right)\Bigg|_{z=0,z=H} = 0. \tag{10}$$

Introducing a new variable

$$c_4 = \frac{n_2 D_1}{n_1 D_2}c_1 + c_2 + c_3 \tag{11}$$

and expressing concentrations c_2 and c_3 in terms of c_1 and c_4

$$\begin{aligned}
&c_2 = \frac{z_3}{z_3 - z_2}c_4 + \frac{z_1 - z_3 n_2 D_1/n_1 D_2}{z_3 - z_2}c_1,\\
&c_3 = -\frac{z_2}{z_3 - z_2}c_4 - \frac{z_1 - z_2 n_2 D_1/n_1 D_2}{z_3 - z_2}c_1
\end{aligned} \tag{12}$$

set of Eq. (8) and boundary conditions (4), (9) can be presented in the following dimensionless form:

$$\begin{aligned}&\frac{\partial \mathbf{V}}{\partial \tau}+\frac{1}{Sc_1}(\mathbf{V}\cdot\nabla)\mathbf{V}=-\nabla P+\Delta\mathbf{V}+\gamma Ra_1(C_1-0.5+C_4-C_{4_\mathrm{b}})\\&\mathrm{div}(\mathbf{V})=0\\&Sc_1\frac{\partial C_1}{\partial \tau}=\Delta C_1-\mathbf{V}\nabla C_1\\&Sc_1\frac{\partial C_4}{\partial \tau}=\overline{D}_4\Delta C_4-\mathbf{V}\nabla C_4+\overline{D}^{*}\Delta C_1\end{aligned}\tag{13}$$

$$\begin{aligned}&\mathbf{V}|_{Z=0,Z=1}=0\\&C_1|_{Z=0}=0, C_1|_{Z=1}=1\\&\left.\frac{\partial C_4}{\partial Z}\right|_{Z=0,Z=1}=0.\end{aligned}\tag{14}$$

To investigate the stability of undisturbed state, that is, a solution of system (13) for stagnant electrolyte, the perturbations of dependent variables are introduced

$$C_1=\overline{C}_1+\widetilde{C}_1,\quad C_4=\overline{C}_4+\widetilde{C}_4,\quad \mathbf{V}=\widetilde{\mathbf{V}},\quad P=\overline{P}+\widetilde{P}.\tag{15}$$

To the linear approximation, the equations for disturbed electrolyte motion are

$$\begin{aligned}&\frac{\partial \widetilde{\mathbf{V}}}{\partial \tau}=-\nabla\widetilde{P}+\Delta\widetilde{\mathbf{V}}+\gamma Ra_1(\widetilde{C}_1+\widetilde{C}_4)\\&\mathrm{div}(\widetilde{\mathbf{V}})=0\\&Sc_1\frac{\partial \widetilde{C}_1}{\partial \tau}=\Delta\widetilde{C}_1-\widetilde{V}_Z\frac{\partial \overline{C}_1}{\partial Z}\\&Sc_1\frac{\partial \widetilde{C}_4}{\partial \tau}=\overline{D}_4\Delta\widetilde{C}_4-\widetilde{V}_Z\frac{\partial \overline{C}_4}{\partial Z}+\overline{D}^{*}\Delta\widetilde{C}_1.\end{aligned}\tag{16}$$

After double application of curl operator to the first equation of set (16), this set can be reduced to three equations in functions $\widetilde{C}_1,\ \widetilde{C}_4,\ \widetilde{V}_Z$

$$\begin{aligned}&\frac{\partial \Delta\widetilde{V}_Z}{\partial \tau}=\Delta^2\widetilde{V}_Z-Ra_1(\Delta_2\widetilde{C}_1+\Delta_2\widetilde{C}_4)\\&Sc_1\frac{\partial \widetilde{C}_1}{\partial \tau}=\Delta\widetilde{C}_1-\widetilde{V}_Z\frac{\partial \overline{C}_1}{\partial Z}\\&Sc_1\frac{\partial \widetilde{C}_4}{\partial \tau}=\overline{D}_4\Delta\widetilde{C}_4-\widetilde{V}_Z\frac{\partial \overline{C}_4}{\partial Z}+\overline{D}^{*}\Delta\widetilde{C}_1.\end{aligned}\tag{17}$$

The conditions and the critical time of onset of convection can be determined by solving the perturbation Eq. (17). Solution of set of Eq. (17) depends on the solution of undisturbed problem, which should be found preliminary.

3. Solution of stability problem

In the absence of convection, the distribution of concentration depends solely on the vertical coordinate Z. This allows to write the equations of undisturbed state in the following form:

$$Sc_1\frac{\partial \overline{C}_1}{\partial \tau}=\frac{\partial^2\overline{C}_1}{\partial Z^2},\quad Sc_1\frac{\partial \overline{C}_4}{\partial \tau}=\overline{D}_4\frac{\partial^2\overline{C}_4}{\partial Z^2}+\overline{D}^{*}\frac{\partial^2\overline{C}_1}{\partial Z^2}.\tag{18}$$

If the critical time of onset of natural convection is significantly shorter than the characteristic time of transient process in the stagnant electrolyte, the solution of the set (18) corresponding to the limiting rate of cathodic reaction (3) near the cathode surface can be written as follows:

$$\overline{C}_1(Z,\tau)=\frac{1}{2}-\frac{1}{\sqrt{\pi}}\int_{\frac{Z}{2}\sqrt{\frac{Sc_1}{\tau}}}^{\infty}\mathrm{e}^{-u^2}\,\mathrm{d}u\tag{19}$$

$$\overline{C}_4(Z,\tau)=C_{4_\mathrm{b}}+\frac{\overline{D}^{*}[\overline{C}_1(Z,\tau)-0.5]}{1-\overline{D}_4}+\frac{\overline{D}^{*}}{\sqrt{\pi}(1-\overline{D}_4)}\int_{\frac{Z}{2}\sqrt{\frac{Sc_1}{\tau}}}^{\infty}\mathrm{e}^{-\frac{u^2}{\overline{D}_4}}\mathrm{d}u.\tag{20}$$

The set of equations of disturbed motion (17) involves the derivatives $\partial\overline{C}_1/\partial Z$ and $\partial\overline{C}_4/\partial Z$, which can be readily determined from Eqs. (19) and (20):

$$\frac{\partial \overline{C}_1}{\partial Z}=\frac{1}{2}\sqrt{\frac{Sc_1}{\pi\tau}}\mathrm{e}^{-\frac{Sc_1Z^2}{4\tau}},\quad \frac{\partial \overline{C}_4}{\partial Z}=\frac{\overline{D}^{*}}{2(1-\overline{D}_4)}\sqrt{\frac{Sc_1}{\pi\tau}}\left(\mathrm{e}^{-\frac{Sc_1Z^2}{4\tau}}-\mathrm{e}^{-\frac{Sc_1Z^2}{4\overline{D}_4\tau}}\right).\tag{21}$$

Taking into account the solution of undisturbed problem, set of equations for perturbations (17) will take the following form

$$\begin{aligned}&\frac{\partial \varDelta\widetilde{V}_Z}{\partial \tau}=\varDelta^2\widetilde{V}_Z-\beta(\varDelta_2\widehat{C}_1+\varDelta_2\widehat{C}_4)\\&Sc_1\frac{\partial \widehat{C}_1}{\partial \tau}=\Delta\widehat{C}_1-Ra\sqrt{\frac{Sc_1}{\pi\tau}}\mathrm{e}^{-\frac{Sc_1Z^2}{4\tau}}\widetilde{V}_Z\\&Sc_1\frac{\partial \widehat{C}_4}{\partial \tau}=\overline{D}_4\Delta\widehat{C}_4+\overline{D}^{*}\Delta\widehat{C}_1-\frac{Ra\overline{D}^{*}}{1-\overline{D}_4}\\&\qquad\times\sqrt{\frac{Sc_1}{\pi\tau}}\left(\mathrm{e}^{-\frac{Sc_1Z^2}{4\tau}}-\mathrm{e}^{-\frac{Sc_1Z^2}{4\overline{D}_4\tau}}\right)\widetilde{V}_Z.\end{aligned}\tag{22}$$

For convenience of comparison with known solutions of stability problem for stagnant liquid under the non-steady-state heat-transfer conditions, where a step change in temperature only of one horizontal plate is considered, the Rayleigh number Ra is defined by the difference between the electrolyte densities of bulk solution and solution adjacent to cathode.

Assuming that the perturbations of concentrations and vertical component of hydrodynamic velocity can be presented as follows [8]:

$$\begin{aligned}&\widehat{C}_1=S_1(\varsigma)\mathrm{e}^{\mathrm{i}(k_XX+k_YY)},\\&\widehat{C}_4=S_4(\varsigma)\mathrm{e}^{\mathrm{i}(k_XX+k_YY)},\\&\widetilde{V}_Z=\tau/Sc_1\cdot W_Z(\varsigma)\mathrm{e}^{\mathrm{i}(k_XX+k_YY)}.\end{aligned}\tag{23}$$

Taking into account (23) set (22) can be reduced to three ordinary differential equations in functions $W_Z(\varsigma)$, $S_1(\varsigma)$, and $S_4(\varsigma)$:

$$
\begin{aligned}
&(\Delta^2-\bar{k}^2)^2 W_Z = -\bar{k}^2\beta(S_1+S_4) - \frac{1}{Sc_1}\left(\frac{\varsigma}{2}\Delta^3 - \frac{\varsigma}{2}\bar{k}^2\Delta + \bar{k}^2\right)W_Z\\
&(\Delta^2-\bar{k}^2)S_1 = -\frac{\varsigma}{2}\Delta S_1 + \overline{Ra}\frac{W_Z}{\sqrt{\pi}}\mathrm{e}^{-\frac{\varsigma^2}{4}}\\
&\overline{D}_4(\Delta^2-\bar{k}^2)S_4 + \overline{D}^*(\Delta^2-\bar{k}^2)S_1\\
&\quad = -\frac{\varsigma}{2}\Delta S_4 + \overline{Ra}\frac{W_Z}{\sqrt{\pi}}\frac{\overline{D}^*}{(1-\overline{D}_4)}\left(\mathrm{e}^{-\frac{\varsigma^2}{4}} - \mathrm{e}^{-\frac{\varsigma^2}{4\overline{D}_4}}\right)
\end{aligned}
\tag{24}
$$

where $\Delta = \partial/\partial\varsigma$.

The boundary conditions for set of Eq. (24) can be presented as follows:

$$
\begin{aligned}
&W_Z(0)=0,\quad \Delta W_Z(0)=0,\quad S_1(0)=0,\quad \Delta S_4(0)=0\\
&W_Z(\varsigma_{\max})=0,\quad \Delta W_Z(\varsigma_{\max})=0,\quad S_1(\varsigma_{\max})=0,\quad \Delta S_4(\varsigma_{\max})=0.
\end{aligned}
\tag{25}
$$

To solve set (24), the shooting method is used. Calculations were performed on the uniform grid; the computational region dimension $\varsigma_{\max}$ was taken such that the effect of finite dimension on the calculated data was eliminated. In the numerical solution, the boundary eigenvalue problem for set of Eq. (24) was reduced to the Cauchy problem for a set of ordinary differential equations of the first order.

Set of linear Eq. (24) is homogeneous; therefore, one boundary condition can be prescribed arbitrarily. This enables one to determine the unknown parameter $\overline{Ra}$. It was assumed that

$$\Delta^2 W_Z(0) = 2. \tag{26}$$

At a given $\bar{k}$, preliminary magnitudes of $\Delta^3 W_Z$ (0), $\Delta S_1(0)$, $S_4(0)$, and $\overline{Ra}$ were prescribed. Integrating set of Eq. (24) using the Runge–Kytta method of the fourth-order accuracy, $W_Z(\varsigma_{\max})$, $\Delta W_Z(\varsigma_{\max})$, $S_1(\varsigma_{\max})$, $\Delta S_4(\varsigma_{\max})$ were determined. In general case, they do not satisfy boundary conditions (25). The preliminary magnitudes of variables at $\varsigma = 0$ were refined using the Newton method from the discrepancy magnitude for boundary conditions prescribed at $\varsigma = \varsigma_{\max}$. Then $\bar{k}$ was changed in order to determine the critical Rayleigh number $\overline{Ra}_c = \min_{\bar{k}}\overline{Ra}(\bar{k})$, which corresponds to the onset of convective instability. The critical time of onset of non-steady-state convective instability can be determined by equation

$$
\begin{aligned}
&\tau_c = ASc_1 Ra^{-2/3}\\
&t_c = \frac{AH^2}{\nu}Sc_1 Ra^{-2/3}.
\end{aligned}
\tag{27}
$$

4. Results and discussion

For an electrolyte with three types of ions, under condition (5), when the migration transfer of electroactive component can be ignored, set of equations for the amplitudes of perturbations (24) contains four dimensionless parameters: $\overline{Ra}$, Sc_1, $\overline{D}_4$, $\overline{D}^*$, i.e. the critical Rayleigh number, which is determined by the change in the electrolyte density between the bulk and the cathode,

$$\Delta\rho = c_{1_b}\frac{1+\sqrt{\overline{D}_4}+\overline{D}^*}{1+\sqrt{\overline{D}_4}}\left(\frac{\partial\rho}{\partial c_1} + \frac{z_1 - z_3 n_2 D_1/n_1 D_2}{z_3 - z_2}\frac{\partial\rho}{\partial c_2}\right), \tag{28}$$

is a function of three parameters Sc_1, $\overline{D}_4$, $\overline{D}^*$. At high Schmidt numbers, the dependence of $\overline{Ra}$ on Sc_1 can be ignored. Thus, the critical $\overline{Ra}$ corresponding to the onset of instability depends on two dimensionless parameters $\overline{D}^*$ and $\overline{D}_4$.

As follows from set of Eq. (24), at $\overline{D}^* = 0$, the last equation of the system admits only zero solution, that is the supporting electrolyte has no effect on the critical Rayleigh number. In this case, set of Eq. (24) reduces to a set in the perturbations of vertical component of hydrodynamic velocity and concentration of electroactive component

$$
\begin{aligned}
&(\Delta^2-\bar{k}^2)^2 W_Z = -\bar{k}^2 S_1 - \frac{1}{Sc_1}\left(\frac{\varsigma}{2}\Delta^3 - \frac{\varsigma}{2}\bar{k}^2\Delta + \bar{k}^2\right)W_Z\\
&(\Delta^2-\bar{k}^2)S_1 = -\frac{\varsigma}{2}\Delta S_1 + \overline{Ra}\frac{W_Z}{2\sqrt{\pi}}\mathrm{e}^{-\frac{\varsigma^2}{4}}.
\end{aligned}
\tag{29}
$$

Eq. (29) are similar to the corresponding equations for a binary electrolyte with the Schmidt number Sc_1 and the densification coefficient α. Set of Eq. (29) coincides with equations for heat convection [8]. Numerical solving of set of Eq. (29) yielded the results coinciding with the data of [8].

First, the effect of the system parameters $\overline{D}^*$ and $\overline{D}_4$ on the undisturbed distributions of concentration and density in the diffusion layer growing with time was studied. As is seen from the results (Fig. 1), under certain conditions (provided that $\overline{D}^* > 0$), the distribution of density becomes non-monotonic due to the migration of supporting electrolyte; this will have an effect on the stability of electrolyte with three types of ions. Figs. 2 and 3 give the calculated critical Rayleigh numbers and the critical wave numbers at various magnitudes of system parameters. At a constant

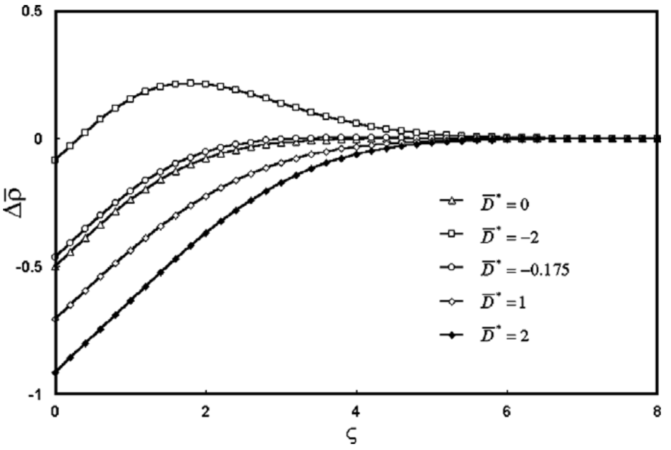

Fig. 1. The effect of D^* on the distribution of $\Delta\rho$ in the stagnant electrolyte.

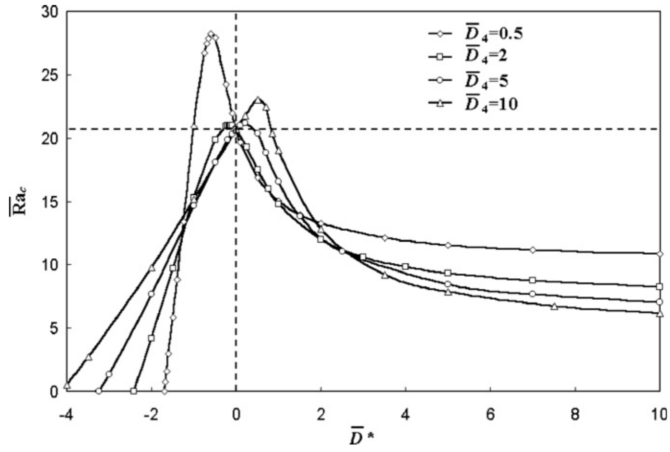

Fig. 2. Plots of critical Rayleigh number vs. the diffusion coefficient $\overline{D}^*$ at various $\overline{D}_4$.

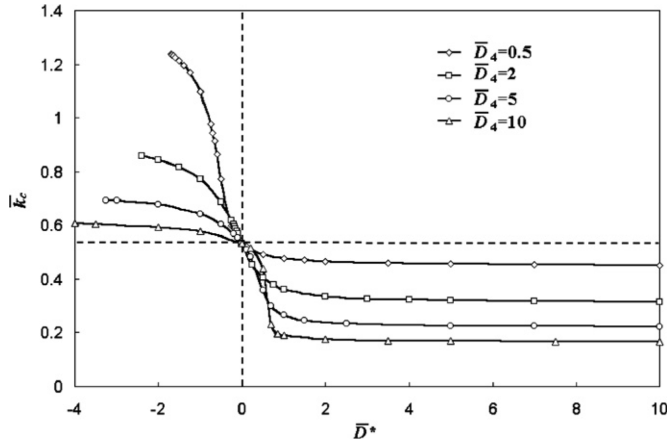

Fig. 3. Plots of critical wave number vs. the diffusion coefficient $\overline{D}^*$ at various $\overline{D}_4$.

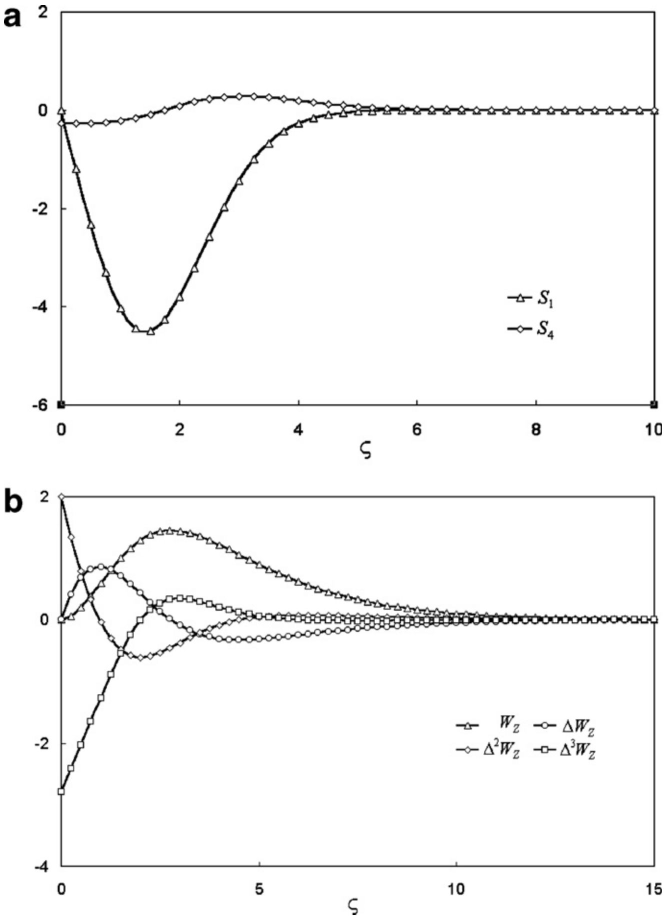

Fig. 4. The distribution of amplitudes of perturbations of (a) concentration and (b) vertical component of velocity and its derivatives at $\overline{D}_4 = 2$ and $\overline{D}^* = -0.175$.

$\overline{D}_4$, the dependence of critical Rayleigh number on $\overline{D}^*$ is described by the non-monotonic function with a local maximum. The maximum critical Rayleigh number is higher than the corresponding value for a binary electrolyte. However, an increase in stability is observed only in a small range of $\overline{D}^*$. To the right of the maximum (with an increase in $\overline{D}^*$) $\overline{Ra}_c$ decreases rather slowly, whereas to the left of the maximum (with a decrease in $\overline{D}^*$) the system stability steeply decreases up to $\overline{Ra}_c = 0$. In the vicinity of the extremum of $\overline{Ra}_c(\overline{D}^*)$ curve, the critical wave number decreases sharply.

At $\overline{D}_4 = 2$, the maximum $\overline{Ra}_c = 21.02$ is reached at $\overline{D}^* = -0.175$. An increased stability of electrolyte with three types of ions at these magnitudes of parameters is caused by the fact that at small $\overline{D}^*$ the amplitude of concentration perturbations S_4 is small; near the electrode, perturbations S_1 and S_4 are of the same sign slightly increasing stability, whereas, at a certain distance from the electrode, sign of perturbation S_4 is changed enhancing stability (Fig. 4). The sizes of zones, where perturbation amplitude S_4 has opposite signs, are approximately equal; therefore, a zone, which is farther from the electrode surface, has a stronger effect on stability; as a result, the system stability somewhat increases. With an increase in $\overline{D}^*$, the distribution of perturbation amplitude S_4 changes (Fig. 5): a zone, in which the perturbations of electroactive component concentration are partially compensated, shifts to the electrode surface and its size decreases, whereas a zone, in which perturbations S_1 and S_4 are of the same sign, is at a certain distance from the electrode, and the perturbation amplitude S_4 in this zone is rather large. This reduces the system stability. To the left of the maximum, with a decrease in $\overline{D}^*$, a zone, where perturbations S_1 and S_4 are of the same sign is retained; this zone increases with decreasing $\overline{D}^*$, while a zone, where S_1 and S_4 are of opposite sign, gradually decreases (Fig. 6). As a result, the system stability decreases rapidly. At negative $\overline{D}^*$, the distribution of variation in the density is non-monotonic; this also reduces stability.

The effect of migration on the stability of electrolyte containing three types of ions involves the variation in the density of stagnant solution near the electrodes due to the migration of supporting electrolyte and the perturbations of concentrations of supporting electrolyte ions. In

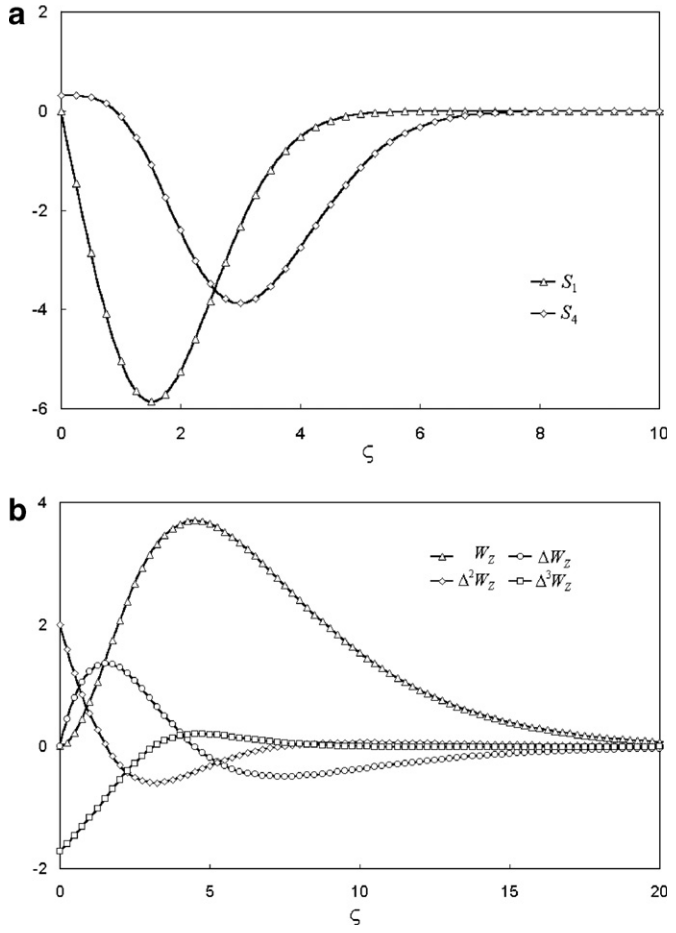

Fig. 5. The distribution of amplitudes of perturbations of (a) concentration and (b) vertical component of velocity and its derivatives at $\overline{D}_4 = 2$ and $\overline{D}^* = 1$.

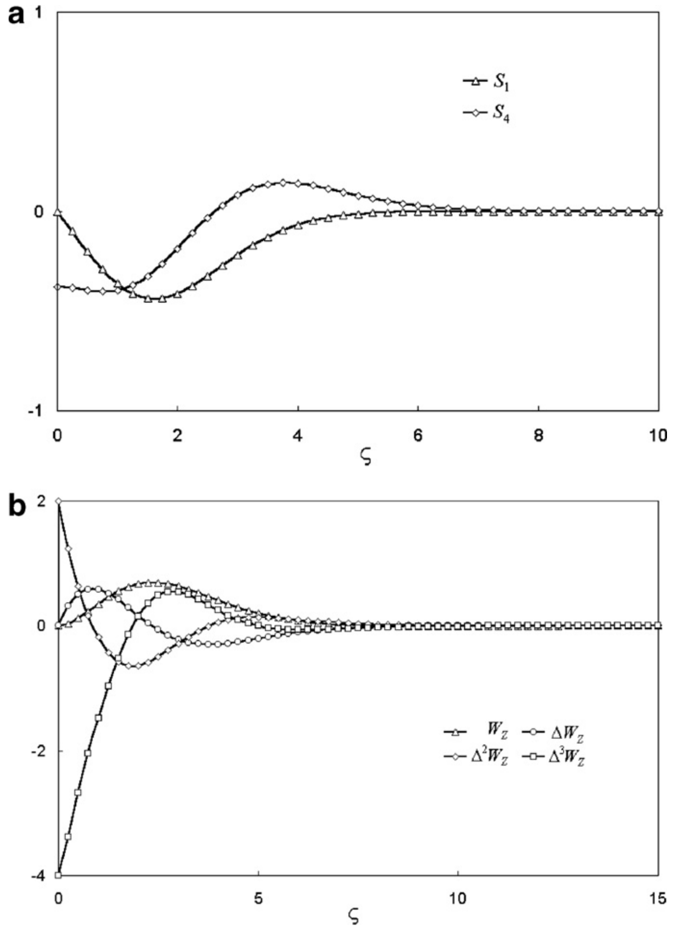

Fig. 6. The distribution of amplitudes of perturbations of (a) concentration and (b) vertical component of velocity and its derivatives at $\overline{D}_4 = 2$ and $\overline{D}^* = -2$.

the absence of migration, the solution density drop between the bulk and the cathode is

$$\Delta\rho = c_{1_b}\left(\frac{\partial\rho}{\partial c_1} - \frac{n_2 D_1}{n_1 D_2}\frac{\partial\rho}{\partial c_2}\right). \tag{30}$$

Introducing the Rayleigh number $\widetilde{Ra}$, which is determined by the density drop (30), the net effect of migration on the stability can be presented using coefficient K_{mig}, which is the ratio between the critical Rayleigh numbers in the presence and in the absence of migration. For a binary electrolyte, the critical Rayleigh number is 20.67. Then, taking into account (30), we obtain:

$$K_{\text{mig}} = \frac{\widetilde{Ra}_c}{20.67} = \frac{\overline{Ra}_c}{20.67\alpha}\left(\frac{\partial\rho}{\partial c_1} - \frac{n_2 D_1}{n_1 D_2}\frac{\partial\rho}{\partial c_2}\right). \tag{31}$$

The method was used to determine the stability of four systems containing three types of ions: $KI + I_2$, $CuSO_4 + H_2SO_4$, $AgNO_3 + HNO_3$, and $K_3Fe(CN)_6 + K_4Fe(CN)_6$. Table 1 lists the parameters (taken from handbooks [15,16]) and the critical Rayleigh numbers for these systems. Only in the $AgNO_3 + HNO_3$ solutions the system stability is higher than that of a binary electrolyte; in all other cases under consideration, it is lower. For system $CuSO_4 + H_2SO_4$ two limiting cases were considered: com-

Table 1
Parameters of electrochemical systems with three types of ions and critical Rayleigh numbers

System	$10^9 \cdot D_1$ ($m^2\,s^{-1}$)	$10^9 \cdot D_2$ ($m^2\,s^{-1}$)	$10^9 \cdot D_3$ ($m^2\,s^{-1}$)	$\partial\rho/\partial c_1$ ($kg\,mol^{-1}$)	$\partial\rho/\partial c_2$ ($kg\,mol^{-1}$)	Sc_1	$\overline{D}_4$	$\overline{D}^*$	$\bar{k}_c$	$\overline{Ra}_c$	K_{mig}
$KI + I_2$	0.917	1.96	1.98	0.287	0.1210	1091	2.15	−0.687	0.717	18.20	0.73
$CuSO_4 + H_2SO_4$ (Cu^{2+}, H^+, SO_4^{2-})	0.750	9.00	1.00	0.156	0.0335	1333	3.27	−0.242	0.595	20.05	1.13
$CuSO_4 + H_2SO_4$ (Cu^{2+}, H^+, HSO_4^-)	0.750	9.00	1.90	0.156	0.0335	1333	4.18	−0.179	0.571	20.06	1.09
$AgNO_3 + HNO_3$	1.600	9.00	1.90	0.135	0.0340	625	1.96	−0.094	0.567	20.99	1.16
$K_3Fe(CN)_6 + K_4Fe(CN)_6$	0.740	0.890	1.96	0.226	0.167	1351	2.04	0.108	0.496	20.19	3.50

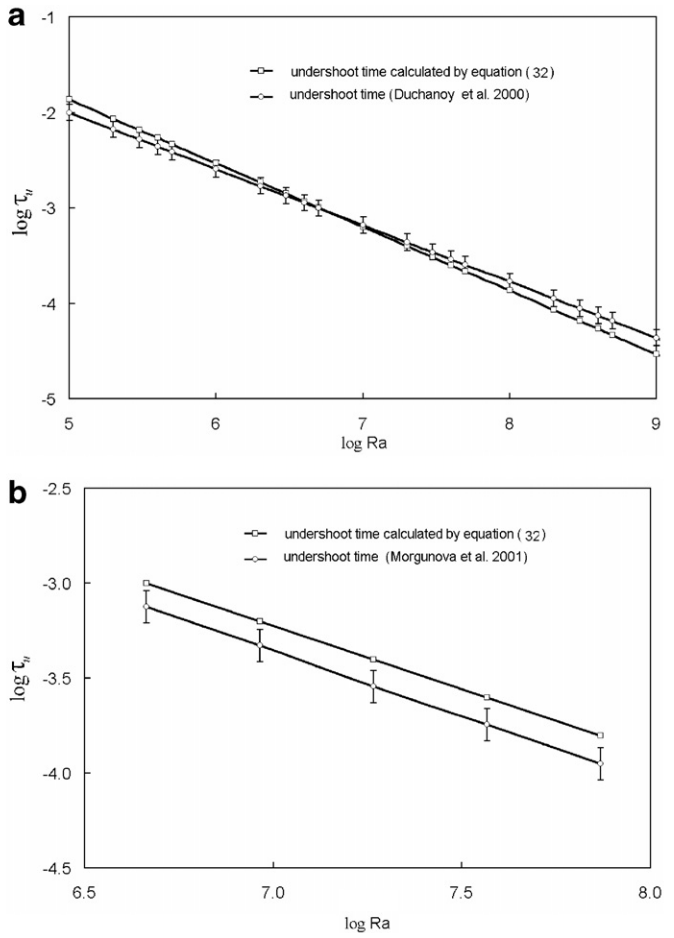

Fig. 7. Comparison of calculated and experimental undershoot times for the electrochemical systems with three types of ions: (a) $CuSO_4$–H_2SO_4 and (b) KI–I_2.

plete dissociation yielding SO_4^{2-} ions an incomplete dissociation yielding HSO_4^- ions (Table 1). The calculated undershoot times

$$\tau_u = 4\frac{\tau_c}{Sc_1}, \qquad (32)$$

corresponding to the minimum of the Sherwood number [8] agree well with the experimental data for $CuSO_4 + H_2SO_4$ and $KI + I_2$ systems (Fig. 7).

5. Conclusions

The problem of convective instability of electrochemical system containing three types of ions with an excess of supporting electrolyte and redox reaction or anodic dissolution (cathodic deposition) proceeding on the electrodes in the limiting-current mode under non-steady-state mass-transfer conditions is solved. It is found that the critical Rayleigh number and the critical time depend on the coefficients of electrolyte density and the diffusion coefficients of ions. Non-monotonic variation of electrolyte density in the diffusion layer near the electrode surface due to the migration of supporting electrolyte raise convective instability and decreases the critical time of onset of natural convection. The proposed method of determination of critical time takes into account the character of variation of density in multi-component electrochemical systems and enables to obtain t_c, which agree well with the experimental data.

Acknowledgements

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