# LINEAR ANALYSIS OF THE FREE-CONVECTIVE STABILITY OF A BINARY ELECTROLYTE SOLUTION IN AN ELECTROCHEMICAL CELL WITH HORIZONTAL ELECTRODES

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*The influence of the electrode reaction kinetics on the critical Rayleigh number for a binary electrolyte solution situated between flat horizontal electrodes has been investigated. The equations of motion of an incompressible viscous fluid in the Boussinesq approximation and the material balance equations with the electrical neutrality condition have been used as a mathematical model. Analytical and numerical solutions of the linear stability problem have been obtained. The influence of the kinetic parameters of the electrode reaction (exchange current density, transport number of cations) and the transport properties of the solution on the critical value of the Rayleigh number has been investigated.*

**Keywords:** *free convection, convective instability, binary electrolyte, electrochemical cell.*

**Introduction.** In an electrochemical cell with flat electrodes, free convection can arise due to the appearance of a solution density gradient as a result of the proceeding of electrochemical reactions under diffusion or mixed diffusion-kinetic conditions provided that the concentration (density) of the solution decreases near the lower electrode and increases near the upper electrode. Free convection can arise only on the condition that the Rayleigh number exceeds the critical value of $Ra_{cr}$. At smaller Rayleigh numbers the system is in a state of mechanical equilibrium. In the general case, the conditions for the appearance of free convection in electrochemical systems differ from the conditions in thermal systems. At current densities lower than the limiting one, when the electrical neutrality condition is fulfilled with a high degree of accuracy, the volume electric charge can be neglected. This makes it possible to eliminate the migration terms between the ion migration equations and obtain for the concentration an equation analogous to the convective heat-transfer equation. For thermal convection in a horizontal plane fluid layer bounded by solid walls whose temperatures are held constant, the critical Rayleigh number is equal to 1707.62 [1, 2]. The same critical Rayleigh value was also obtained with the use of linear stability theory in an electrochemical system with a binary electrolyte [3]. In so doing, it was assumed that the concentration perturbations on the electrodes were equal to zero. However, as a result of experimental studies of the convective instability of an aqueous solution of $CuSO_4$ in an electrochemical cell with flat copper horizontal electrodes, much smaller values of $Ra_{cr}$ were obtained [4, 5].

In [4], it was established that under galvanostatic conditions $Ra_{cr}$ varies from 1351.7 ± 34.7 to 763.3 ± 85.7 with a variation of the copper sulfate concentration from 1.2 to 5 mmol and of the interelectrode spacing from 0.64 to 1.07 mm. For the mean value of the critical Rayleigh number, 1132 ± 210 was taken, although, as noted in [4], the $Ra_{cr}$ value increases as the current density approaches the limiting value. The discrepancy between the experimental and theoretical critical Rayleigh numbers, as the authors of [4] see it, is due to the insufficiently thorough preparation of the electrode surfaces and the proceeding of electrolysis only on a part of it. Under potentiostatic conditions, a somewhat higher value of $Ra_{cr}$ equal to 1540 was obtained [5], which, however, is also smaller than the theoretical value of the critical Rayleigh number for thermal convection. Analogous experimental results were also reported in [6]. Evidently, such significant discrepancies between experiments and theory cannot be explained by experimental errors alone.

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One factor capable of influencing the convective stability of the binary electrolyte solution is the volume electric charge formed in the solution when electric current passes through it. Analytical and numerical investigations of the influence of the volume charge on the convective stability of the binary electrolyte solution [7–13] showed that at current densities close to the limiting ones, depending on the electrochemical system parameters (diffusion coefficients of cations and anions, dielectric constant, viscosity and density of the electrolyte) the Coulomb forces can both increase and decrease the system's stability [11]. However, it seems to be impossible to explain the decrease in the stability of the binary electrolyte solution at small current densities by the influence of the volume charge.

Another factor influencing the stability of the binary electrolyte solution is associated with the influence of the kinetics of electrode reactions [14–19]. Taking account of the latter leads to a change in the type of boundary conditions for perturbations of ion concentrations. In [14–19], it was suggested to use homogeneous boundary conditions of the third kind which in the limiting cases reduce to boundary conditions of the first or second kind. In the former case corresponding to nonpolarizable electrodes, the critical Rayleigh number is equal to 1707.62, and in the latter case corresponding in the opinion of the authors of [15, 17], to the galvanostatic regime of electrolysis, $Ra_{cr} = 720$. The use of boundary conditions of the third kind permits obtaining $Ra_{cr}$ in the 720–1707.62 range, which agrees with the experimental data of [4–6].

However, the methods for taking into account the electrode reaction kinetics used in [14–19] have a number of disadvantages. First, it is assumed that electrode potential perturbations have equal values throughout the electrode surface while concentration perturbations are considered to be periodic. Second, the relation between current and electrode potential perturbations is established with account for the properties of the external circuit. Third, it is assumed that the convective stability depends on the electrolysis conditions (potentiostatic or galvanostatic ones). In actual fact, electrolysis conditions should not be related to the critical Rayleigh number, although they influence the free convection arising from convective instability.

The aim of the present work is to investigate the convective stability of the horizontal layer of the binary electrolyte solution with account for the kinetics of electrode reactions and the relationship between the concentration and electric potential fields and to determine the dependences of $Ra_{cr}$ on the electrochemical system parameters.

**Formulation of the Problem.** In the Boussinesq approximation and in the approximation of electrical neutrality of the solution, the equations of motion of an incompressible viscous fluid and ion transfer in the layer of binary electrolyte solution between two flat horizontal electrodes can be written in the following form [1, 2, 20]:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \, \mathbf{v} = -\frac{1}{\rho_{in}} \nabla p + \nu \Delta \mathbf{v} - \mathbf{e}_z \frac{g \, (\rho - \rho_{in})}{\rho_{in}} \,, \quad \mathrm{div} \, (\mathbf{v}) = 0 \,,$$

$$\frac{\partial c_1}{\partial t} = \mathrm{div} \left( D_1 \nabla c_1 + \frac{F z_1 D_1 c_1}{RT} \nabla \varphi \right) - \mathbf{v} \nabla c_1 \,, \tag{1}$$

$$\frac{\partial c_2}{\partial t} = \mathrm{div} \left( D_2 \nabla c_2 + \frac{F z_2 D_2 c_2}{RT} \nabla \varphi \right) - \mathbf{v} \nabla c_2 \,, \quad z_1 c_1 + z_2 c_2 = 0 \,.$$

The density of a solution containing two kinds of ions can be expressed in terms of the concentration of only one kind of ion, since for the concentration of ions of the other kind it is found definitively from the electrical neutrality condition. Let us assume that the solution density is defined by the expression

$$\rho - \rho_{in} = \frac{\partial \rho}{\partial c_1} (c_1 - c_{1,in}) \,. \tag{2}$$

We will assume that on the electrodes the following electrochemical reaction involving cations is proceeding:

$$M^{z_1} + z_1 e^- \leftrightarrow M \,. \tag{3}$$

The boundary conditions for the system of equations (1) have the form

$$\mathbf{v}\big|_{z=0,z=H} = 0 , \quad \left(\frac{\partial c_2}{\partial z} + \frac{Fz_2 c_2}{RT}\frac{\partial \varphi}{\partial z}\right)\Bigg|_{z=0,z=H} = 0 , \tag{4}$$

$$Fz_1 D_1\left(\frac{\partial c_1}{\partial z} + \frac{Fz_1 c_1}{RT}\frac{\partial \varphi}{\partial z}\right)\Bigg|_{z=0} = -i_{\text{ex}}\left[\exp\left(-\frac{(1-\alpha)\,z_1 F}{RT}\,(\varphi + E_0)\right) - \frac{c_1}{c_{1,\text{in}}}\exp\left(\frac{\alpha z_1 F}{RT}\,(\varphi + E_0)\right)\right]\Bigg|_{z=0} , \tag{5}$$

$$Fz_1 D_1\left(\frac{\partial c_1}{\partial z} + \frac{Fz_1 c_1}{RT}\frac{\partial \varphi}{\partial z}\right)\Bigg|_{z=H} = i_{\text{ex}}\left[\exp\left(\frac{(1-\alpha)\,z_1 F}{RT}\,(u - \varphi - E_0)\right) - \frac{c_1}{c_{1,\text{in}}}\exp\left(-\frac{\alpha z_1 F}{RT}\,(u - \varphi - E_0)\right)\right]\Bigg|_{z=H} .$$

The first equation in (4) expresses the adhesion condition for a viscous fluid, and the second one corresponds to the absence of anion transfer through the electrode–electrolyte interface. Relations (5) are Butler–Volmer equations for the electrochemical reaction (3).

In the limiting cases $i_{\text{ex}} \gg i$ and $i_{\text{ex}} \ll i$, the Butler–Volmer equations (5) reduce to the Nernst equations

$$(\varphi + E_0)\big|_{z=0} = -\frac{RT}{z_1 F}\ln\frac{c_1}{c_{1,\text{in}}}\Bigg|_{z=0} , \quad (u - \varphi - E_0)\big|_{z=H} = \frac{RT}{z_1 F}\ln\frac{c_1}{c_{1,\text{in}}}\Bigg|_{z=H} \tag{6}$$

or the Tafel equations

$$Fz_1 D_1\left(\frac{\partial c_1}{\partial z} + \frac{Fz_1 c_1}{RT}\frac{\partial \varphi}{\partial z}\right)\Bigg|_{z=0} = i_{\text{ex}}\frac{c_1}{c_{1,\text{in}}}\exp\left(\frac{\alpha z_1 F}{RT}\,(\varphi + E_0)\right)\Bigg|_{z=0} , \tag{7}$$

$$Fz_1 D_1\left(\frac{\partial c_1}{\partial z} + \frac{Fz_1 c_1}{RT}\frac{\partial \varphi}{\partial z}\right)\Bigg|_{z=H} = i_{\text{ex}}\exp\left(\frac{(1-\alpha)\,z_1 F}{RT}\,(u - \varphi - E_0)\right)\Bigg|_{z=H} .$$

The Nernst equations (6) correspond to the limiting case $i_{\text{ex}} \gg i$. Noteworthily, the expressions between square brackets on the right-hand sides of the Butler–Volmer equations differ slightly from zero, and, therefore, the rates of the forward and backward reactions can be assumed to be equal and the reaction itself — reversible. The Tafel equations (7) correspond to the other limiting case $i_{\text{ex}} \ll i$. Here the value of the expression between square brackets on the right-hand sides of Eqs. (5) is large, which is only possible at a significant potential shift from the equilibrium value. The rate of the back reaction is much lower therewith than the rate of the forward electrochemical reaction, and, therefore, the contribution of the backward reaction can be neglected and the reaction itself can be thought to be irreversible.

Although Eqs. (6) and (7) follow from the Butler–Volmer relations immediately, they will be considered separately in what follows for the following reasons: 1) they are often used in the literature in investigating the mass transfer in electrochemical systems; 2) explicit expressions for the electrode potential are obtained from them, while in using the Butler–Volmer equations the electrode potential is determined as a result of the numerical solution of the nonlinear equation; 3) the derivative of the electroactive ion concentration does not enter into the Nernst equation (6), i.e., the latter establishes no relation between the concentration and the electrode potential on the one hand and the current density on the other.

The electrolyte anions do not participate in the electrochemical reaction; therefore, the anion flows on the electrodes are equal to zero and the current density on the electrodes can be given as follows:

$$i\big|_{z=0} = -Fz_1 D_1\left(\frac{\partial c_1}{\partial z} + \frac{Fz_1 c_1}{RT}\frac{\partial \varphi}{\partial z}\right)\Bigg|_{z=0} = -Fz_1 D_1\frac{z_2 - z_1}{z_2}\frac{\partial c_1}{\partial z}\Bigg|_{z=0} ,$$

$$i\big|_{z=H} = -Fz_1 D_1\left(\frac{\partial c_1}{\partial z} + \frac{Fz_1 c_1}{RT}\frac{\partial \varphi}{\partial z}\right)\Bigg|_{z=H} = -Fz_1 D_1\frac{z_2 - z_1}{z_2}\frac{\partial c_1}{\partial z}\Bigg|_{z=H} . \tag{8}$$

The unperturbed steady state of the stagnant electrolyte can be characterized by either the current density $\bar{i}$, or the applied voltage $\bar{u}$, or the anode potential $\bar{u} - \bar{\varphi} - E_0$, or the cathode potential $-(\bar{\varphi} + E_0)$. Of these four quantities, only one can be specified. It is most convenient to use for the parameter characterizing the unperturbed steady state of the stagnant electrolytic solution the current density referred to its limiting density in the stagnant solution. The latter corresponds to the limiting rate of the electrode reaction when the concentration of cations on the cathode decreases to zero, and the concentration of cations on the anode increases to $2c_{1,\text{in}}$. The dimensionless current density in the stagnant electrolyte $(\bar{I} = -\bar{i}/i_{\text{lim}})$ can vary from 0 to 1, the difference between the electroactive cation concentrations on the anode and the cathode being equal to $2c_{1,\text{in}}\bar{I}$.

Assuming the diffusion coefficients to be constant and using the electrical neutrality condition, to eliminate the migration terms between the cation and anion transfer equations, let us write the system of equations (1) in the following dimensionless form:

$$\frac{\partial \mathbf{V}}{\partial \tau} + \frac{1}{\text{Sc}}(\mathbf{V}\cdot\nabla)\mathbf{V} = -\nabla P + \Delta\mathbf{V} - \mathbf{e}_z \, \text{Ra}\left(C_1 - \frac{1}{2I}\right), \quad \text{div}\,(\mathbf{V}) = 0 \,, \tag{9}$$

$$\text{Sc}\,\frac{\partial C_1}{\partial \tau} = \Delta C_1 - \mathbf{V}\nabla C_1\,, \quad \frac{D_1 - D_2}{z_1 D_1 - z_2 D_2}\Delta C_1 + (C_1\Delta\Phi + \nabla C_1\nabla\Phi) = 0 \,.$$

Eliminating the concentration of anions and the migration term for cations between relations (5), (7), we obtain the following relations for the boundary conditions in dimensionless form:

$$\mathbf{V}\big|_{Z=0,Z=1} = 0\,, \quad \left(\frac{\partial C_1}{\partial Z} + z_2 C_1\frac{\partial\Phi}{\partial Z}\right)\bigg|_{Z=0,Z=1} = 0\,, \tag{10}$$

$$\frac{\partial C_1}{\partial Z}\bigg|_{Z=0} = -\frac{\bar{I}_{\text{ex}}}{\bar{I}}\left[\exp\left(-(1-\alpha)z_1\Phi\right) - 2\bar{I}C_1\exp(\alpha z_1\Phi)\right]\big|_{Z=0}\,, \tag{11}$$

$$\frac{\partial C_1}{\partial Z}\bigg|_{Z=1} = \frac{\bar{I}_{\text{ex}}}{\bar{I}}\left[\exp\left((1-\alpha)z_1(\bar{U}-\Phi)\right) - 2\bar{I}C_1\exp\left(-\alpha z_1(\bar{U}-\Phi)\right)\right]\big|_{Z=1}\,,$$

$$\Phi\big|_{Z=0} = -\frac{1}{z_1}\ln 2\bar{I}C_1\big|_{Z=0}\,, \quad (\bar{U}-\Phi)\big|_{Z=1} = \frac{1}{z_1}\ln 2\bar{I}C_1\big|_{Z=1}\,, \tag{12}$$

$$\frac{\partial C_1}{\partial Z}\bigg|_{Z=0} = 2\bar{I}_{\text{ex}}C_1\exp(\alpha z_1\Phi)\big|_{Z=0}\,, \quad \frac{\partial C_1}{\partial Z}\bigg|_{Z=1} = \frac{\bar{I}_{\text{ex}}}{\bar{I}}\exp\left((1-\alpha)z_1(U-\Phi)\right)\bigg|_{Z=1}\,. \tag{13}$$

The system of equations (9) with boundary condition (10)–(13) has a stationary solution for the stagnant solution. To investigate the stability of the steady state, it is necessary to determine the behavior of the small perturbations. If they decay with time, then the system is in the steady state, which corresponds to the absence of convection. Otherwise, the system is unstable and, therefore, convective motion of the electrolyte will arise.

**Stationary Solution for a Stagnant Electrolyte.** The stationary solution of problem (9)–(13) has the form

$$\bar{C}_1(Z) = \bar{C}_{1,c} + Z\,, \quad \bar{\Phi}(Z) = \bar{\Phi}(0) - \frac{1}{z_2}\ln\frac{1 + (2Z-1)\bar{I}}{1 - \bar{I}}\,. \tag{14}$$

From the boundary conditions (11)–(13) for determining $\bar{\Phi}(0)$ and $\bar{U}$ we obtain the following relations:

$$\overline{I} = -\overline{I}_{ex} \left[ \exp\left(-(1-\alpha) z_1 \overline{\Phi}(0)\right) - (1-\overline{I}) \exp\left(\alpha z_1 \overline{\Phi}(0)\right) \right],$$

$$\overline{I} = \overline{I}_{ex} \left[ \exp\left((1-\alpha) z_1 (\overline{U} - \overline{\Phi}(1))\right) - (1+\overline{I}) \exp\left(-\alpha z_1 (\overline{U} - \overline{\Phi}(1))\right) \right], \tag{15}$$

$$\overline{\Phi}(0) = -\frac{1}{z_1} \ln(1-\overline{I}), \quad \overline{U} = \Phi(1) + \frac{1}{z_1} \ln(1+\overline{I}), \tag{16}$$

$$\overline{I} = \overline{I}_{ex} (1-\overline{I}) \exp(\alpha z_1 \Phi(0)), \quad \overline{I} = \overline{I}_{ex} \exp((1-\alpha) z_1 (\overline{U} - \overline{\Phi}(1))). \tag{17}$$

In view of (10), $\overline{\Phi}(1)$ is defined as

$$\overline{\Phi}(1) = \overline{\Phi}(0) - \frac{1}{z_2} \ln \frac{1+\overline{I}}{1-\overline{I}}. \tag{18}$$

Relations (14)–(18) permit determining by the values of the dimensionless current density $\overline{I}$ the stationary distributions of the concentration and potential in the interelectrode gap in the stagnant solution.

**Equations for Perturbations.** To analyze the stability of the stationary solution (14) of the system of equations (9), consider the behavior of the small perturbations of the cation concentration, the electric potential, the hydrodynamic velocity, and the pressure $\widetilde{C}_1$, $\widetilde{\Phi}$, $\widetilde{\mathbf{V}}$, and $\widetilde{P}$:

$$C_1 = \overline{C}_1 + \widetilde{C}_1, \quad \Phi = \overline{\Phi} + \widetilde{\Phi}, \quad \mathbf{V} = \widetilde{\mathbf{V}}, \quad P = \overline{P} + \widetilde{P}. \tag{19}$$

Taking into account only the terms linear with respect to perturbations and eliminating the pressure from the equations of motion (9), we get

$$\frac{\partial \Delta \widetilde{V}_Z}{\partial \tau} = \Delta^2 \widetilde{V}_Z - \mathrm{Ra} \left( \frac{\partial^2 \widetilde{C}_1}{\partial X^2} + \frac{\partial^2 \widetilde{C}_1}{\partial Y^2} \right), \quad \mathrm{Sc} \frac{\partial \widetilde{C}_1}{\partial \tau} = \Delta \widetilde{C}_1 - \widetilde{V}_Z,$$

$$\frac{D_1 - D_2}{z_1 D_1 - z_2 D_2} \Delta \widetilde{C}_1 + \widetilde{C}_1 \frac{\partial^2 \overline{\Phi}}{\partial Z^2} + \overline{C}_1 \Delta \widetilde{\Phi} + \frac{\partial \widetilde{C}_1}{\partial Z} \frac{\partial \overline{\Phi}}{\partial Z} + \frac{\partial \overline{C}_1}{\partial Z} \frac{\partial \widetilde{\Phi}}{\partial Z} = 0. \tag{20}$$

We shall seek a solution of the system of equations (20) in the form of "normal" perturbations

$$\widetilde{V}_Z(X, Y, Z, \tau) = \hat{V}_Z(Z) \exp(\lambda \tau + j(k_X X + k_Y Y)),$$

$$\widetilde{C}_1(X, Y, Z, \tau) = \hat{C}_1(Z) \exp(\lambda \tau + j(k_X X + k_Y Y)), \tag{21}$$

$$\widetilde{\Phi}(X, Y, Z, \tau) = \hat{\Phi}(Z) \exp(\lambda \tau + j(k_X X + k_Y Y)).$$

The introduction of the variable

$$\hat{Q} = \frac{z_1}{z_1 - z_2} (\hat{C}_1 + z_2 \overline{C}_1 \hat{\Phi}) \tag{22}$$

permits reducing, in view of (21), the last equation in system (20) to an inhomogeneous modified Bessel equation. As a result of passing to the variable $\hat{Q}$, from relations (20) we obtain the following system of equations for the amplitudes of "normal" perturbations:

TABLE 1. Expressions for the Parameters Taking into Account the Electrode Reaction Kinetics

| Parameters | Type of boundary conditions | | |
| --- | --- | --- | --- |
| | Butler–Volmer equation (11) | Nernst equation (12) | Tafel equation (13) |
| $M_0$ | $\frac{1}{\overline{C}_{1,c}}\left(1-\alpha\frac{z_1}{z_2}\right)+\frac{2\overline{I}_{ex}}{1-\overline{I}}\left(1-\frac{z_1}{z_2}\right)\exp\left(-(1-\alpha)z_1\overline{\Phi}(0)\right)$ | $1$ | $\frac{1}{\overline{C}_{1,c}}\left(1-\alpha\frac{z_1}{z_2}\right)$ |
| $L_0$ | $1$ | $0$ | $1$ |
| $N_0$ | $-\frac{\alpha}{\overline{C}_{1,c}}\left(1-\frac{z_1}{z_2}\right)-\frac{2\overline{I}_{ex}}{1-\overline{I}}\left(1-\frac{z_1}{z_2}\right)\exp\left(-(1-\alpha)z_1\overline{\Phi}(0)\right)$ | $-1$ | $-\frac{\alpha}{\overline{C}_{1,c}}\left(1-\frac{z_1}{z_2}\right)$ |
| $M_1$ | $-\frac{1-\alpha}{\overline{C}_{1,a}}\frac{z_1}{z_2}+2\overline{I}_{ex}\left(1-\frac{z_1}{z_2}\right)\exp\left(-\alpha z_1(\overline{U}-\overline{\Phi}(1))\right)$ | $1$ | $-\frac{1-\alpha}{\overline{C}_{1,a}}\frac{z_1}{z_2}$ |
| $L_1$ | $1$ | $0$ | $1$ |
| $N_1$ | $-\frac{1-\alpha}{\overline{C}_{1,a}}\left(1-\frac{z_1}{z_2}\right)-2\overline{I}_{ex}\left(1-\frac{z_1}{z_2}\right)\exp\left(-\alpha z_1(\overline{U}-\overline{\Phi}(1))\right)$ | $-1$ | $-\frac{1-\alpha}{\overline{C}_{1,a}}\left(1-\frac{z_1}{z_2}\right)$ |

$$\lambda(D^2-k^2)\hat{V}_Z=(D^2-k^2)^2\hat{V}_Z+k^2\operatorname{Ra}\hat{C}_1,\quad \lambda\operatorname{Sc}\hat{C}_1=(D^2-k^2)\hat{C}_1-\hat{V}_Z,$$

$$[\overline{C}_1^2 D^2-\overline{C}_1 D+(1-k^2\overline{C}_1^2)]\hat{Q}=A\overline{C}_1^2(D^2-k^2)\hat{C}_1.\tag{23}$$

In view of relations (11)–(19) (21), and (22), the boundary conditions for the system of equations (23) will be written as

$$\hat{V}_Z(0)=D\hat{V}_Z(0)=\hat{V}_Z(1)=D\hat{V}_Z(1)=0,$$

$$\hat{Q}(0)-\overline{C}_{1,c}D\hat{Q}(0)=0,\quad \hat{Q}(1)-\overline{C}_{1,a}D\hat{Q}(1)=0,\tag{24}$$

$$M_0\hat{C}_1(0)-L_0 D\hat{C}_1(0)+N_0\hat{Q}(0)=0,\quad M_1\hat{C}_1(1)+L_1 D\hat{C}_1(1)+N_1\hat{Q}(1)=0.$$

The expressions for the coefficients $M_0$, $L_0$, $N_0$, $M_1$, $L_1$, and $N_1$ for different types of boundary conditions are given in Table 1.

The general solution of the last equation of (23) has the form

$$\hat{Q}(Z)=A(\overline{C}_{1,c}+Z)[s_1(Z)I_0(k\overline{C}_{1,c}+kZ)+s_2(Z)K_0(k\overline{C}_{1,c}+kZ)],\tag{25}$$

where

$$s_1(Z)=\int_0^Z K_0(k\overline{C}_{1,c}+k\gamma)(D^2-k^2)\hat{C}_1 d\gamma+d_1;\quad s_2(Z)=-\int_0^Z I_0(k\overline{C}_{1,c}+k\gamma)(D^2-k^2)\hat{C}_1 d\gamma+d_2.$$

Determining $d_1$ and $d_2$ from the boundary conditions (24), we obtain the values of interest to us for the function $\hat{Q}$ at the layer boundaries:

$$\hat{Q}(0) = - \frac{A \int_0^1 [K_1(k\overline{C}_{1,a}) I_0(k\overline{C}_{1,c} + kZ) + I_1(k\overline{C}_{1,a}) K_0(k\overline{C}_{1,c} + kZ)] (D^2 - k^2) \hat{C}_1 dZ}{k [I_1(k\overline{C}_{1,a}) K_1(k\overline{C}_{1,c}) - K_1(k\overline{C}_{1,a}) I_1(k\overline{C}_{1,c})]},$$

$$\hat{Q}(1) = - \frac{A \int_0^1 [K_1(k\overline{C}_{1,c}) I_0(k\overline{C}_{1,c} + kZ) + I_1(k\overline{C}_{1,c}) K_0(k\overline{C}_{1,c} + kZ)] (D^2 - k^2) \hat{C}_1 dZ}{k [I_1(k\overline{C}_{1,a}) K_1(k\overline{C}_{1,c}) - K_1(k\overline{C}_{1,a}) I_1(k\overline{C}_{1,c})]}.$$

(26)

Eliminating the relations for the function $\hat{Q}$ from the system of equations (23) and the boundary conditions (24), we have finally

$$\lambda (D^2 - k^2) \hat{V}_Z = (D^2 - k^2)^2 \hat{V}_Z + k^2 \operatorname{Ra} \hat{C}_1, \quad \lambda \operatorname{Sc} \hat{C}_1 = (D^2 - k^2) \hat{C}_1 - \hat{V}_Z;$$

(27)

$$\hat{V}_Z(0) = D\hat{V}_Z(0) = \hat{V}_Z(1) = D\hat{V}_Z(1) = 0, \quad M_0 \hat{C}_1(0) - L_0 D\hat{C}_1(0) + N_0 \hat{Q}(0) = 0,$$

$$M_1 \hat{C}_1(1) + L_1 D\hat{C}_1(1) + N_1 \hat{Q}(1) = 0.$$

(28)

The system of equations (27) coincides with the corresponding system of equations for the problem of stability of an inhomogeneously heated fluid. The only difference is in the boundary conditions (28) for the perturbation amplitude of the cation concentration on the electrodes: along with the concentration and its derivative, the boundary conditions, as is seen from (26), include also the $\hat{C}_1$-containing integrals and its second derivative $D^2\hat{C}_1$. Integrating by parts, we can eliminate the second-order derivatives from the boundary conditions

$$\int_0^1 I_0(k\overline{C}_{1,c} + kZ) D^2\hat{C}_1 dZ = I_0(k\overline{C}_{1,a}) D\hat{C}_1(1) - I_0(k\overline{C}_{1,c}) D\hat{C}_1(0) - k\int_0^1 I_1(k\overline{C}_{1,c} + kZ) D\hat{C}_1 dZ,$$

$$\int_0^1 K_0(k\overline{C}_{1,c} + kZ) D^2\hat{C}_1 dZ = K_0(k\overline{C}_{1,a}) D\hat{C}_1(1) - K_0(k\overline{C}_{1,c}) D\hat{C}_1(0) + k\int_0^1 K_1(k\overline{C}_{1,c} + kZ) D\hat{C}_1 dZ.$$

(29)

The homogeneous system of equations (27) with homogeneous boundary conditions (28) has a nontrivial solution only at certain values of $\lambda$ which in the general case can be complex.

**Determination of the Type of Neutral Perturbations.** Because of the integral boundary conditions for the concentration perturbation amplitude, it is impossible to determine analytically the type of neutral perturbations. Therefore, we made an approximate estimate of the possible values of the imaginary part of the eigenvalues for the stability boundary, i.e., at $\lambda_r = 0$. Two methods were used to perform the estimation:

(1) by solving the system of equations (27) by the Galerkin method with the use of the simplest approximations for the velocity and concentration perturbation amplitudes for the fundamental mode;

(2) by solving the problem numerically by the collocation method with the use of Chebyshev polynomials as basis functions [21, 22].

In the Galerkin method, the following approximations were used:

$$\hat{V}_Z = Z^2 (1 - Z)^2, \quad \hat{C}_1 = -a_0 - a_1 Z + a_2 Z^2.$$

(30)

The coefficients $a_0$, $a_1$, and $a_2$ have positive values, with $a_1 > a_2$, which corresponds to a larger perturbation amplitude of the concentration on the anode as compared to such on the cathode. By means of the Galerkin method it has been obtained that for neutral perturbations of the fundamental mode the imaginary part of the eigenvalue of $\lambda$ has a zero value, i.e., convection arises from monotonic perturbations.

In solving numerically the system of differential equations (27) with the boundary conditions (28), the initial value problem was reduced to the generalized problem on the eigenvalues for the system of linear algebraic equations whose solution at given values of Ra and $k$ permits finding the spectrum of eigenvalues of $\lambda$. At a given wave number $k$ the Rayleigh number Ra($k$) corresponding to neutral perturbations was determined by the Newton method.

As a result of numerical calculations at various values of the system parameters, it has been established that in all cases at positive values of the Rayleigh number, to the stability boundary there correspond monotonic perturbations, i.e., for the problem under consideration the "stability change" principle is fulfilled and convection arises from monotonic perturbations.

**Approximate Analytical Solution for Monotonic Neutral Perturbations.** In this case, at $\lambda = 0$ the system of equations (27) takes on the form

$$(D^2 - k^2)^2 \, \hat{V}_Z + k^2 \, \text{Ra} \, \hat{C}_1 = 0 , \quad (D^2 - k^2) \, \hat{C}_1 - \hat{V}_Z = 0 . \tag{31}$$

In view of (31), for $\hat{Q}(0)$ and $\hat{Q}(1)$ determined by (26) we have

$$\hat{Q}(0) = - \frac{A \int_0^1 [K_1 (k\overline{C}_{1,a}) I_0 (k\overline{C}_{1,c} + kZ) + I_1 (k\overline{C}_{1,a}) K_0 (k\overline{C}_{1,c} + kZ)] \, \hat{V}_Z dZ}{k \, [I_1 (k\overline{C}_{1,a}) K_1 (k\overline{C}_{1,c}) - K_1 (k\overline{C}_{1,a}) I_1 (k\overline{C}_{1,c})]} ,$$

$$\hat{Q}(1) = - \frac{A \int_0^1 [K_1 (k\overline{C}_{1,c}) I_0 (k\overline{C}_{1,c} + kZ) + I_1 (k\overline{C}_{1,c}) K_0 (k\overline{C}_{1,c} + kZ)] \, \hat{V}_Z dZ}{k \, [I_1 (k\overline{C}_{1,a}) K_1 (k\overline{C}_{1,c}) - K_1 (k\overline{C}_{1,a}) I_1 (k\overline{C}_{1,c})]} . \tag{32}$$

The general solution of the second equation in system (31) has the form

$$\hat{C}_1 (Z) = p_1 \exp (kZ) + p_2 \exp (- kZ) + \frac{1}{2k} \left( \exp (kZ) \int_0^Z \hat{V}_Z \exp (- k\gamma) \, d\gamma - \exp (- kZ) \int_0^Z \hat{V}_Z \exp (k\gamma) \, d\gamma \right). \tag{33}$$

The values of the integration constants are determined from the boundary conditions (28):

$$p_1 = \left\{ N_0 (M_1 - kL_1) \exp (- k) \, \hat{Q}(0) - (M_0 + kL_0) \left[ N_1 \hat{Q}(1) + \frac{M_1 + kL_1}{2k \exp (- k)} \int_0^1 \hat{V}_Z \exp (- kZ) \, dZ \right. \right.$$

$$\left. \left. - \frac{M_1 - kL_1}{2k \exp (k)} \int_0^1 \hat{V}_Z \exp (kZ) \, dZ \right] \right\} \Big/ \left[ (M_0 + kL_0) (M_1 + kL_1) \exp (k) - (M_0 - kL_0) (M_1 - kL_0) \exp (- k) \right],$$

$$p_2 = \left\{ - N_0 (M_1 + kL_1) \exp (k) \, \hat{Q}(0) + (M_0 - kL_0) \left[ N_1 \hat{Q}(1) + \frac{M_1 + kL_1}{2k \exp (- k)} \int_0^1 \hat{V}_Z \exp (- kZ) \, dZ \right. \right.$$

$$\left. \left. - \frac{M_1 - kL_1}{2k \exp (k)} \int_0^1 \hat{V}_Z \exp (kZ) \, dZ \right] \right\} \Big/ \left[ (M_0 + kL_0) (M_1 + kL_1) \exp (k) - (M_0 - kL_0) (M_1 - kL_0) \exp (- k) \right]. \tag{34}$$

Giving the approximation of the perturbation amplitude of the vertical velocity component in the form

$$\hat{V}_Z = Z^2 (1 - Z)^2 , \tag{35}$$

TABLE 2. Values of Coefficients $b_{n,m}$ in the Expression for $\hat{Q}(0)$

| $n$ | $m$ | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| 1 | −0.00568 | 0.16902 | 0.04516 | 0.01201 |
| 2 | 0.73451 | −2.53469 | −0.17879 | −1.53647 |
| 3 | −0.00690 | 0.53816 | 0.07178 | 0.56973 |
| 4 | −0.00007 | −0.04560 | −0.00452 | −0.06805 |

TABLE 3. Values of Coefficients $d_{n,m}$ in the Expression for $\hat{Q}(1)$

| $n$ | $m$ | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| 1 | 0.00125 | 0.04926 | −0.08808 |
| 2 | 0.71601 | 1.83638 | −0.86395 |
| 3 | −0.00417 | −0.21243 | 0.16255 |

multiplying the first equation in (31) by $\hat{V}_Z$, and integrating with respect to $Z$ from 0 to 1, we find the Rayleigh number from the following relations:

$$
\mathrm{Ra} = -\frac{\displaystyle\int_0^1 \hat{V}_Z (D^2 - k^2)\, \hat{V}_Z dZ}{k^2 \displaystyle\int_0^1 \hat{V}_Z \hat{C}_1 dZ} .
\tag{36}
$$

Making calculations by relation (36) at various values of the wave number, we obtain a neutral curve whose minimum corresponds to the critical values of the wave number and the Rayleigh number.

With the help of the approximation for $\hat{V}_Z$, we obtained from (35) the approximate analytical expressions

$$
\hat{Q}(0) = -\frac{(1 - \bar{I})\, A}{\left(30 + \displaystyle\sum_{n=1}^4 k^n \sum_{m=1}^4 b_{n,m} \bar{I}^{m-1}\right) k^2}, \quad
\hat{Q}(1) = -\frac{(1 + \bar{I})\, A}{\left(30 + \displaystyle\sum_{n=1}^3 k^n \sum_{m=1}^3 d_{n,m} \bar{I}^{m-1}\right) k^2},
\tag{37}
$$

providing an error not exceeding 0.2%. The values of the coefficients $b_{n,m}$ and $d_{n,m}$ are given in Tables 2 and 3. From relations (37) it follows that at small values of the wave number, i.e., for long-wave perturbations, the following relations hold:

$$
\lim_{k \to 0} \hat{Q}(0) = -\frac{A(1 - \bar{I})}{30 k^2}, \quad
\lim_{k \to 0} \hat{Q}(1) = -\frac{A(1 + \bar{I})}{30 k^2} .
\tag{38}
$$

**Results and Discussion.** The stability of the binary electrolyte solution depends on six dimensionless parameters, namely, $A$, $\bar{I}$, $\bar{I}_{ex}$, $z_1$, $z_2$, and $\alpha$, which considerably complicates the analysis of the influence of the transport properties of the solution and the kinetic parameters of the electrode reaction on the critical values of the Rayleigh number and the wave number. The situation is simplified considerably if instead of the Butler–Volmer equations the Nernst equations or the Tafel equations corresponding to the limiting cases of reversible ($\bar{I}_{ex} \gg \bar{I}$) and irreversible ($\bar{I}_{ex} \ll \bar{I}$) electrode reactions are used. Let us consider these limiting cases in more detail.

*Reversible electrode reaction* ($\bar{I}_{ex} \gg \bar{I}$). In the case of the reversible electrode reaction, the stability of the binary electrolyte solution depends only on two dimensionless parameters: $A$ and $\bar{I}$. The coefficient $A$ characterizes the
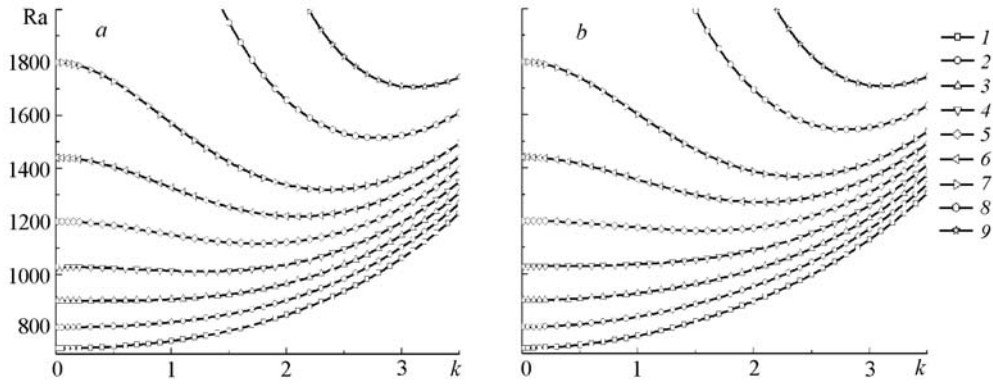
Fig. 1. Neutral curves for the reversible electrode reaction at $\bar{I} = 0.01$ (a) and $\bar{I} = 0.99$ (b) for various values of the parameter $A$: 1) 0.999; 2) 0.9; 3) 0.8; 4) 0.7; 5) 0.6; 6) 0.5; 7) 0.4; 8) 0.2; 9) 0.001.
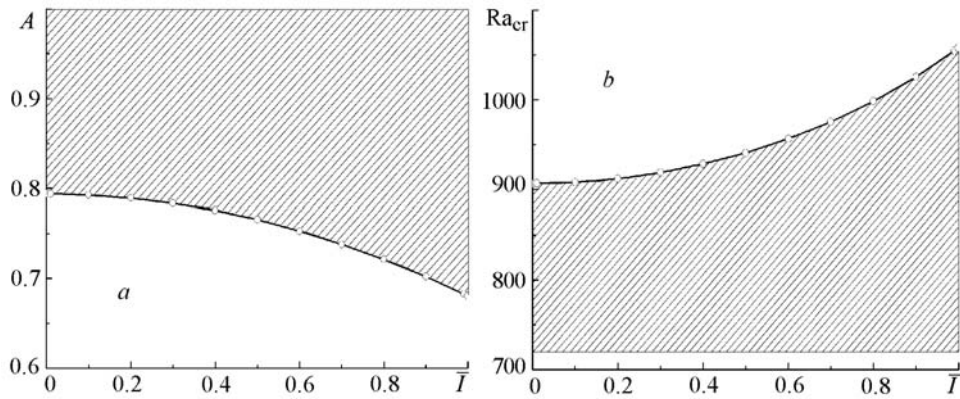


Fig. 2. Regions of values of the parameter $A$ (a) and the critical Rayleigh number (b) for the reversible electrode reaction corresponding to the long-wave instability.
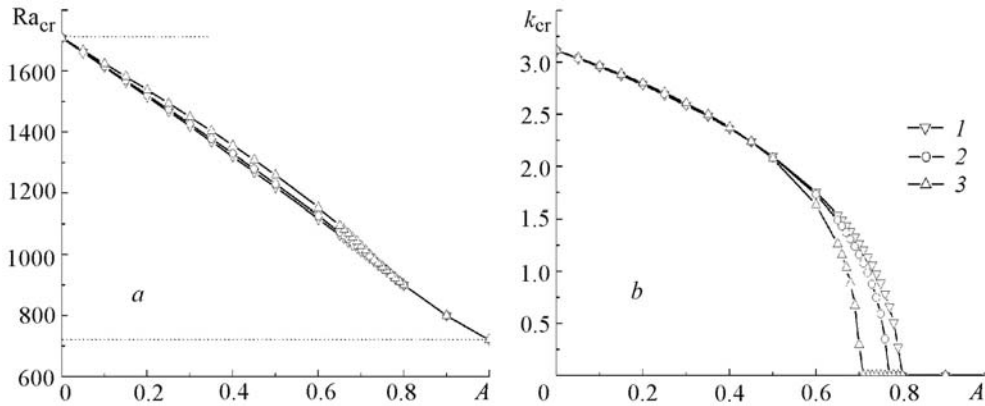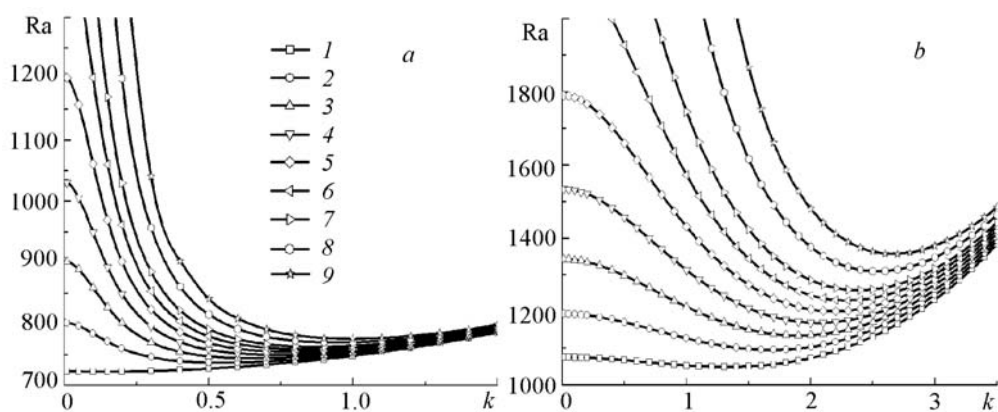


Fig. 3. Dependences of the critical value of the Rayleigh number (a) and the critical value of the wave number (b) for the reversible electrode reaction on the parameter $A$: 1) $\bar{I} = 0.001$; 2) 0.5; 3) 0.99.

transport properties of the solution and its value varies from 0 to 1. The zero value of $A$ is attained if the diffusion coefficient of anions is much higher than the diffusion coefficient of cations, i.e., at $D_2 \gg D_1$. We arrive at the largest value of $A$ in the opposite case. The dimensionless current density $\bar{I}$ also varies from 0 to 1.

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Fig. 4. Neutral curves for the irreversible electrode reaction ($\alpha = 0.5$, $\left|z_1/z_2\right| = 1$) at $\overline{I} = 0.01$ (a) and $\overline{I} = 0.99$ (b) for various values of $A$: 1) 0.999; 2) 0.9; 3) 0.8; 4) 0.7; 5) 0.6; 6) 0.5; 7) 0.4; 8) 0.2; 9) 0.001.
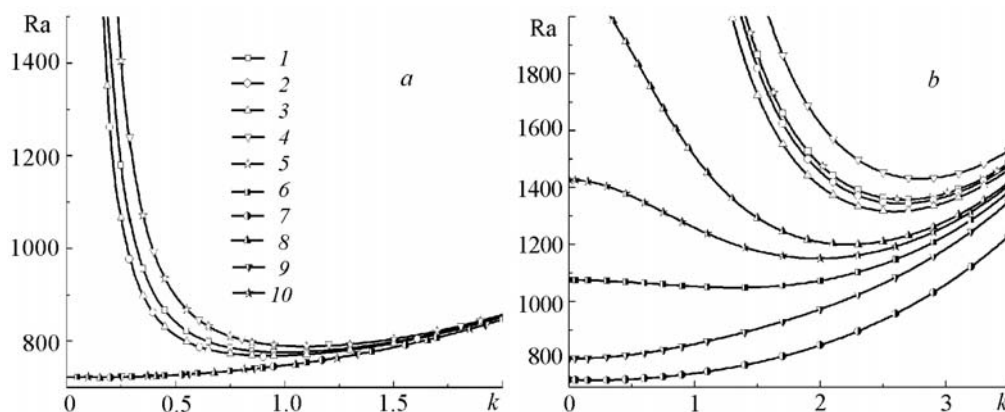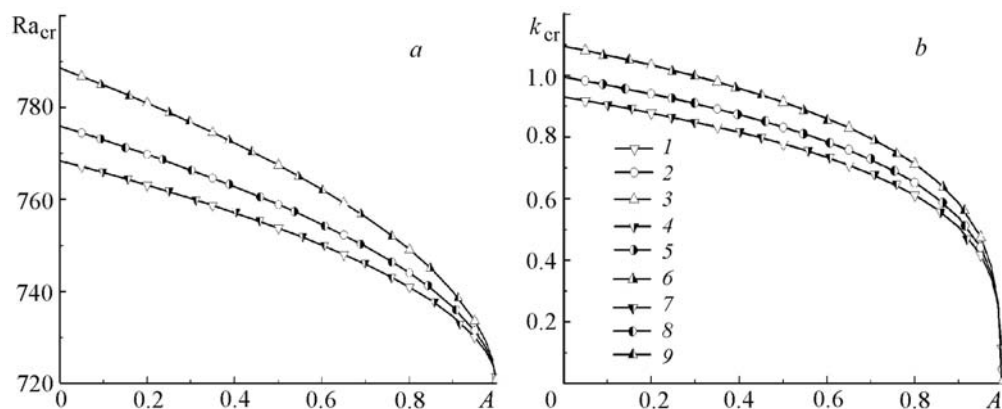


Fig. 5. Neutral curves for the irreversible electrode reaction at $\overline{I} = 0.01$ (a) and $\overline{I} = 0.99$ (b), $A = 0.01$ (1–5), $A = 0.999$ (6–10): 1, 6) $\alpha = 0.5$, $\left|z_1/z_2\right| = 1$; 2, 7) 0.25 and 0.5; 3, 8) 0.75 and 0.5; 4, 9) 0.25 and 2; 5, 10) 0.75 and 2.
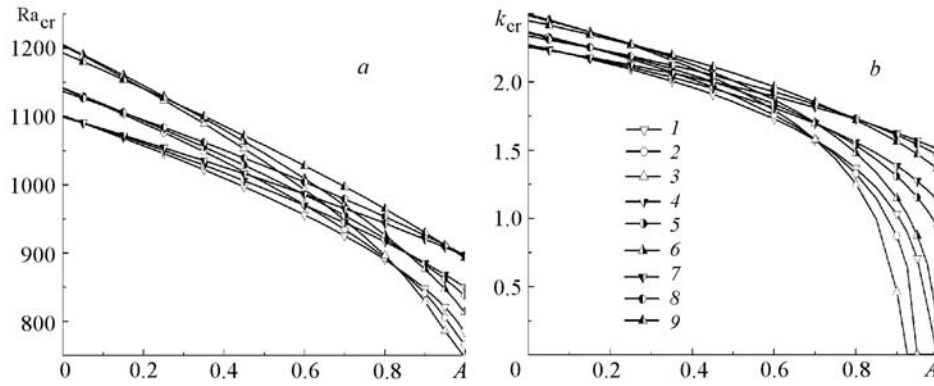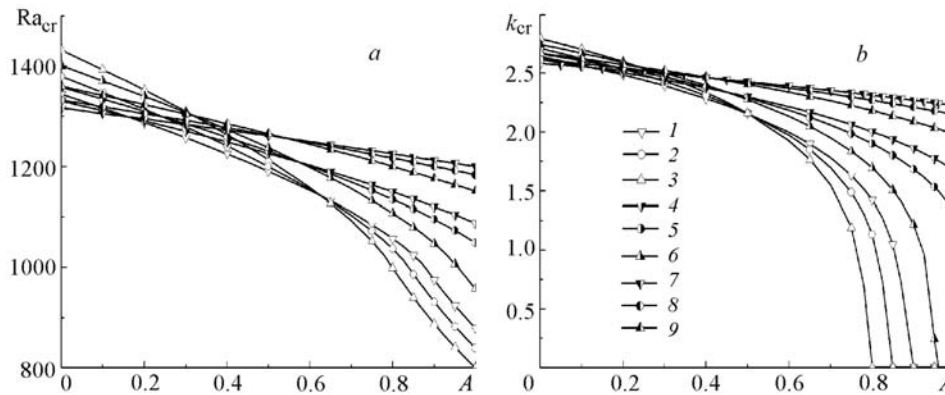


Fig. 6. Dependences of the critical value of the Rayleigh number (a) and the critical value of the wave number (b) for the irreversible electrode reaction on the parameter $A$ at $\overline{I} = 0.01$: $\alpha = 0.25$ (1–3), 0.5 (4–6), 0.75 (7–9); $\left|z_1/z_2\right| = 0.5$ (1, 4, 7), 1 (2, 5, 8), 2 (3, 6, 9).

For the reversible reactions, from the boundary conditions (28) and Table 1 it is seen that the perturbation amplitudes of the concentration and the function $\hat{Q}$ on these electrodes are equal, i.e.,

Fig. 7. Dependences of the critical value of the Rayleigh number (a) and the critical value of the wave number (b) for the irreversible electrode reaction on the parameter $A$ at $\bar{I} = 0.5$: $\alpha = 0.25$ (1–3), 0.5 (4–6), 0.75 (7–9); $\left| z_1/z_2 \right| = 0.5$ (1, 4, 7), 1 (2, 5, 8), 2 (3, 6, 9).



Fig. 8. Dependences of the critical value of the Rayleigh number (a) and the critical value of the wave number (b) for the irreversible electrode reaction on the parameter $A$ at $\bar{I} = 0.99$: $\alpha = 0.25$ (1–3), 0.5 (4–6), 0.75 (7–9); $\left| z_1/z_2 \right| = 0.5$ (1, 4, 7), 1 (2, 5, 8), 2 (3, 6, 9).

$$\hat{C}_1(0) = \hat{Q}(0), \quad \hat{C}_1(1) = \hat{Q}(1). \tag{39}$$

From relations (39) it follows that the concentration perturbation amplitudes on the electrodes linearly decrease with decreasing value of the parameter $A$ and at $A = 0$ they become equal to zero. A decrease in the concentration perturbation amplitudes on the electrodes increases the stability of the binary electrolyte solution and at $A = 0$ a critical value of the Rayleigh number equal to 1707.762 should be attained whatever the value of the dimensionless current density. An increase in $\bar{I}$ leads to an increase in $\hat{C}_1(0)$ and a decrease in $\hat{C}_1(1)$ (since the concentration perturbation amplitudes have negative values). However, the difference $\hat{C}_1(0) - \hat{C}_1(1)$ changes insignificantly and, therefore, the dimensionless current density should not have a marked effect on the stability of the binary electrolyte solution. Indeed, as is seen from Fig. 1, the neutral curves at $\bar{I} = 0.01$ and 0.99 differ insignificantly from each other. An interesting feature of the neutral curves is the finite value of the Rayleigh number at $k = 0$. As a result of the approximate analytical solution of (33)–(36), in view of relations (38) and (39), it has been obtained that for long-wave perturbations the Rayleigh number has a finite value:

$$\lim_{k \to 0} \mathrm{Ra} = \frac{720}{A}. \tag{40}$$

As is seen from Fig. 1, long-wave instability takes place not only at $A = 1$ and $\mathrm{Ra}_{cr} = 720$ but also at lower values of the parameter $A$. Figure 2 shows shaded ranges of values of the parameter $A$ (Fig. 2a) and critical values of the Rayleigh number (Fig. 2b) corresponding to the long-wave instability.
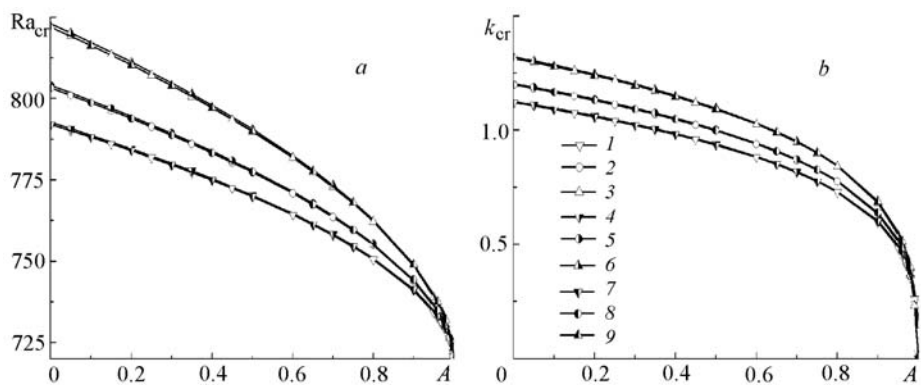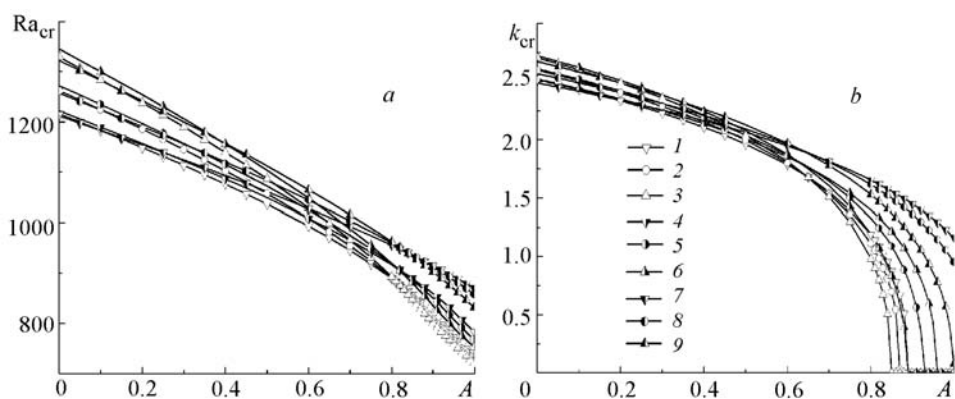
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Fig. 9. Dependences of the critical value of the Rayleigh number (a) and the critical value of the wave number (b) for the partly reversible electrode reaction on the parameter $A$ at $\bar{I} = 0.01$, $\bar{I}_0 = 0.01$: $\alpha = 0.25$ (1–3), 0.5 (4–6), 0.75 (7–9); $|z_1/z_2| = 0.5$ (1, 4, 7), 1 (2, 5, 8), 2 (3, 6, 9).
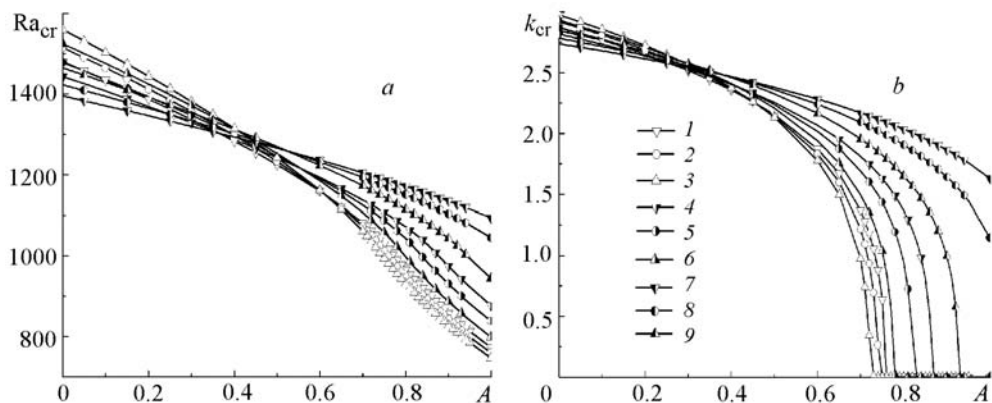


Fig. 10. Dependences of the critical value of the Rayleigh number (a) and the critical value of the wave number (b) for the partly reversible electrode reaction on the parameter $A$ at $\bar{I} = 0.5$, $\bar{I}_0 = 0.5$: $\alpha = 0.25$ (1–3), 0.5 (4–6), 0.75 (7–9); $|z_1/z_2| = 0.5$ (1, 4, 7), 1 (2, 5, 8), 2 (3, 6, 9).



Fig. 11. Dependences of the critical value of the Rayleigh number (a) and the critical value of the wave number (b) for the partly reversible electrode reaction on the parameter $A$ at $\bar{I} = 0.99$, $\bar{I}_0 = 0.99$: $\alpha = 0.25$ (1–3), 0.5 (4–6), 0.75 (7–9); $|z_1/z_2| = 0.5$ (1, 4, 7), 1 (2, 5, 8), 2 (3, 6, 9).

As the current density increases from 0 to 1, the parameter $A$ values at which long-wave instability takes place decrease slightly (approximately from 0.8 to 0.7) and correspond to a binary electrolyte in which the diffusion coefficient of cations is about twice that of anions.

The dependence of the critical value of the Rayleigh number on the parameter $A$ is close to linear (Fig. 3a) even upon going to the long-wave instability (Fig. 3b).

*Irreversible electrode reaction* $(\overline{I}_{ex} \ll \overline{I})$. In the case of the irreversible electrode reaction, the stability of the binary electrolyte solution depends not only on $A$ and $\overline{I}$ but also on $\alpha$ and $z_1/z_2$. In the case under consideration, the boundary conditions (28) will take the form

$$\left(1 - \alpha \frac{z_1}{z_2}\right)\hat{C}_1(0) - \frac{1 - \overline{I}}{2\overline{I}} D\hat{C}_1(0) - \alpha\left(1 - \frac{z_1}{z_2}\right)\hat{Q}(0) = 0 \,,$$

$$-\frac{z_1}{z_2}\hat{C}_1(1) + \frac{1 + \overline{I}}{2\overline{I}(1 - \alpha)} D\hat{C}_1(1) - \left(1 - \frac{z_1}{z_2}\right)\hat{Q}(1) = 0 \,.$$

(41)

Unlike the reversible reaction, in the case under consideration, even at $A = 0$, i.e., at $\hat{Q}(0) = \hat{Q}(1) = 0$, the concentration perturbation amplitudes on the electrodes are other than zero. This points to the fact that in the case of the irreversible electrode reaction, the critical value of the Rayleigh number equal to 1707.762 cannot be attained. At small current densities the coefficients of the derivatives in (41) are large and, therefore, $Ra_{cr}$ is close to the minimum value 720. At large current densities $\hat{C}_1(0) \to 0$, $\hat{C}_1(1) \to \frac{z_2}{z_1(1-\alpha)} D\hat{C}_1(1)$, i.e., the concentration perturbation amplitude on the anode is other than zero and, consequently, $Ra_{cr}$ should be less than the maximum value 1707.762.

With increasing parameter $A$, as for the reversible electrode reaction, the minima of the neutral curves are shifted into the region of smaller values of wave numbers (Figs. 4, 5) and smaller values of $Ra_{cr}$. At small current densities the critical value of the Rayleigh number does not depend on the exchange coefficient $\alpha$ (Fig. 6a), and the dependence of $Ra_{cr}$ on the charge ratio between ions is rather weak: as $|z_1/z_2|$ changes fourfold from 2 to 0.5, the greatest decrease in $Ra_{cr}$ constituting less than 3% is observed at $A = 0$, and at $A = 1$ the $Ra_{cr}$ value is practically independent of $|z_1/z_2|$ (Fig. 6a). The ranges of variation of the critical value of the Rayleigh number and the critical wave number are much narrower than for the reversible reaction: for the considered cases, as $A$ varies from 0 to 1, $Ra_{cr}$ changes from 790 to 720, and $k_{cr}$ changes from 1.1 to 0, the long-wave instability being attained only at $A = 1$ (Fig. 6b).

As the current density increases, the stability of the binary electrolyte solution begins to be influenced by the value of the transfer coefficient $\alpha$ (Figs. 7, 8). The character of the influence of $\alpha$ and $|z_1/z_2|$ depends on the value of the parameter $A$: at small values of $A$ a decrease in $\alpha$ and an increase in $|z_1/z_2|$ promote an increase in the stability, and at fairly large values, vice versa, they decrease it. This is explained by the fact that with increasing current density the perturbation amplitudes of electrode potentials increase and, therefore, the electric field produces a stronger effect on the concentration perturbation amplitudes on the electrodes. Moreover, at small values of the parameter $A$ the diffusion potential arising because of the difference between the values of the diffusion coefficients of ions impedes the transfer of cations and thus decreases the perturbation amplitude and increases the stability. Conversely, at large values of the parameter $A$ the diffusion potential promotes the transfer of cations, which leads to a decrease in the stability.

*Partly irreversible electrode reaction* $(\overline{I}_{ex} \approx \overline{I})$. In the case of a partly irreversible reaction on the electrodes, the stability of the binary electrolyte solution depends on five parameters: $A$, $\overline{I}$, $\alpha$, $z_1/z_2$, and $\overline{I}_{ex}$. The last of these factors characterizing the electrode reaction rate has, in the given case, a finite value other than zero. Since, all other things being equal, the binary electrolyte solution in the case of the reversible reaction is more stable than in the case of the irreversible reaction, in the case under consideration only at $A < A^*$ should the critical values of the Rayleigh number satisfy the relations

$$Ra_{cr,irrev} \leq Ra_{cr,prev} \leq Ra_{cr,rev} \,, \quad 0 \leq A \leq A^* \,, \quad Ra_{cr,rev} \leq Ra_{cr,prev} \leq Ra_{cr,irrev} \,, \quad A^* \leq A \leq 1 \,,$$

(42)

where $A^*$ stands for the parameter $A$ values at the intersection point of the dependences $\text{Ra}_{\text{cr,rev}}(A)$ and $\text{Ra}_{\text{cr,irrev}}(A)$.

Figures 9–11 present the dependences of the critical values of the Rayleigh number and of the critical wave number on the parameter $A$ value at $\overline{I}_{\text{ex}} = \overline{I}$ and at various values of $\overline{I}$, $\alpha$, and $z_1/z_2$.

**Conclusions.** We have obtained a solution to the problem of convective stability of a binary electrolyte solution between two flat horizontal electrodes with account for the kinetics of electrode reactions and the electrode potential perturbations. The dimensionless parameters characterizing the convective stability of the solution have been determined. It has been shown that for the reversible electrode reaction the critical value of the Rayleigh number depends on the coefficient $A$ taking into account the transport properties of the solution (as the parameter $A$ varies from 0 to 1, the critical value of the Rayleigh number decreases from 1707.62 to 720) and the dimensionless current density. It has been established that for the irreversible electrode reaction $\text{Ra}_{\text{cr}}$ depends additionally on two dimensionless parameters, $\alpha$ and $|z_1/z_2|$. At small values of $A$ the stability decreases as compared to the reversible reaction, and at fairly large values of $A$ it increases. The dependences of $\text{Ra}_{\text{cr}}$ and $k_{\text{cr}}$ at various values of the system parameters have been obtained. A long-wave instability zone in which the critical values of the Rayleigh number exceed the minimum value equal to 720 has been revealed.

## NOTATION

$A = \dfrac{z_1}{z_1 - z_2}\left[1 - \dfrac{z_2(D_1 - D_2)}{z_1 D_1 - z_2 D_2}\right]$, dimensionless parameter characterizing the transport properties of the solution; $a_0$, $a_1$, $a_2$, coefficients of the function approximating the distribution of the concentration perturbation amplitude of cations; $b_{n,m}$, coefficients in the analytical expression for $\hat{Q}(0)$; $\overline{C}_{1,\text{a}} = \dfrac{1 + \overline{I}}{2\overline{I}}$, dimensionless concentration of cations on the anode; $\overline{C}_{1,\text{c}} = \dfrac{1 - \overline{I}}{2\overline{I}}$, dimensionless concentration of cations on the cathode; $C_m = \dfrac{c_m}{2c_{1,\text{in}}\overline{I}}$, dimensionless concentration of $m$th-type ions; $c_{1,\text{in}}$, initial concentration of cations, mole/m$^3$; $c_{\text{m}}$, concentration of $m$th-type ions, mole/m$^3$; $D = \dfrac{d}{dz}$, operator of differentiation with respect to $Z$; $D_{\text{eff}} = \dfrac{(z_1 - z_2)D_1 D_2}{z_1 D_1 - z_2 D_2}$, effective diffusion coefficient of the binary electrolyte, m$^2$/s; $D_m$ = diffusion coefficient of $m$th-type ions, m$^2$/s; $d_1$, $d_2$, integration constants; $d_{n,m}$, coefficients in the analytical expression for $\hat{Q}(1)$; $E_0$, equilibrium electrode potential, V; $\overline{\text{e}}$, electron; $\mathbf{e}_z$, unit vector directed vertically upwards; F, Faraday constant, K/mole; $g$, acceleration of gravity, m/s$^2$; $H$, interelectrode spacing, m; $I = \dfrac{i}{i_{\text{lim}}}$, dimensionless current density; $I_0$, $I_1$, modified zero- and first-order Bessel functions of the first kind, respectively; $I_{\text{ex}} = \dfrac{i_{\text{ex}}}{i_{\text{lim}}}$, dimensionless exchange current density; $i$, current density, A/m$^2$; $i_{\text{ex}}$, exchange current density, A/m$^2$; $i_{\text{lim}} = \dfrac{Fz_1(z_2 - z_1)D_1}{z_2}\dfrac{2c_{1,\text{in}}}{H}$, limiting current density for the stagnant binary electrolyte solution, A/m$^2$; $j = \sqrt{-1}$, imaginary part of a number; $K_0$, $K_1$, modified zero- and first-order Bessel functions of the second kind, respectively; $k = \sqrt{k_X^2 + k_Y^2}$, dimensionless wave number; $k_X$, $k_Y$, projections of the wave vector on the coordinate axes $X$ and $Y$, respectively; $L_0$, $L_1$, coefficients entering into the boundary conditions for concentration perturbation amplitudes (Table 1); M, metal participating in the electrochemical reaction; $M_0$, $M_1$, $N_0$, $N_1$, coefficients entering into the boundary conditions for concentration perturbation amplitudes (Table 1); $P = \dfrac{H^2}{\rho_{\text{in}}\nu D_{\text{eff}}}p$, dimensionless pressure; $p$, pressure, Pa; $p_1$, $p_2$, dimensionless integration constants; $\hat{Q} = \dfrac{z_1}{z_1 - z_2}(\hat{C}_1 + z_2 \overline{C}_1 \hat{\Phi})$, dimensionless variable; R, gas constant, J/(mole·K); Ra

$= \dfrac{2gH^3 c_{1,in} \bar{I}}{\rho_{in} \nu D_{eff}} \dfrac{\partial \rho}{\partial c_1}$, Rayleigh number of the binary electrolyte solution; $Sc = \dfrac{\nu}{D_{eff}}$, Schmidt number; $s_1$, $s_2$, dimensionless

integration constants; $T$, temperature, K; $t$, time, s; $U = \dfrac{Fu}{RT}$, dimensionless electrode voltage; $u$, electrode voltage, V;

$V = \dfrac{H}{D_{eff}} v$, dimensionless hydrodynamic velocity; $V_Z$, vertical component of the dimensionless hydrodynamic velocity;

$v$, hydrodynamic velocity, m/s; $X = \dfrac{x}{H}$, $Y = \dfrac{y}{H}$, $Z = \dfrac{z}{H}$, dimensionless Cartesian coordinates; $x$, $y$, $z$, Cartesian coordinates (the origin of coordinates is on the lower electrode (cathode), the $z$ axis is directed vertically upwards from the cathode to the anode), m; $z_m$, state of charge (valence) of $m$th-type ions; $\alpha$, transfer coefficient of cations; $\gamma$, auxiliary variable replacing the variable $Z$ in calculating certain integrals of functions depending on $Z$ with the upper limit of integration equal to $Z$; $\lambda = \lambda_r + j\lambda_i$, dimensionless decrement characterizing the time dependence of perturbation amplitudes; $\lambda_r$, $\lambda_i$, real and imaginary parts of the decrement, respectively; $\nu$, kinematic viscosity of the binary electrolyte

solution, m$^2$/s; $\rho$, density of the binary electrolyte solution, kg/m$^3$; $\dfrac{\partial \rho}{\partial c_m}$, mass coefficient of $m$th-type ions, kg/mole;

$\tau = \dfrac{\nu}{H^2} t$, dimensionless time; $\Phi = \dfrac{F(\varphi + E_0)}{RT}$, dimensionless electric potential, V. Subscripts: a, values of variables on the anode surface; c, values of variables on the cathode surface; cr, critical value; eff, effective diffusion coefficient; ex, exchange current density; i, imaginary part; in, values of variables corresponding to the initial concentration of the electrolytic solution (before current is switched on); irrev, irreversible; lim, limiting current density; prev, partly irreversible electrode reaction; r, real part; rev, reversible electrode reaction; $X$, $Y$, $Z$, projections on the corresponding coordinate axis; $^-$, unperturbed state; $\sim$, small perturbations; $^\wedge$, amplitude of small perturbations; $*$, parameter $A$ value at the intersection point of the dependences $Ra_{cr,rev}(A)$ and $Ra_{cr,irrev}(A)$.

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