

CHEMICAL AND HYDRODYNAMIC STABILITY IN ELECTROCHEMICAL CELLS WITH A ROTATING DISK ELECTRODE

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Abstract. Polarization curves experimentally obtained in the electro-dissolution of iron in a 1 M H_2SO_4 solution using a rotating disk as the working electrode present a current instability region within the range of applied voltage in which the current is controlled by mass transport in the electrolyte. According to the literature (Barcia, 1992) the electro-dissolution process leads to the existence of an axial viscosity gradient in the interface metal-solution, which leads to a deviation from von Kármán's classical solution for rotating disk flow. On two previous papers, Pontes et al (*J. of the Braz. Soc. Mechanical Sciences*, Vol. XXIV, pp. 139, 2002, and *Phys. of Fluids*, Vol. 16, No. 3, pp. 707, 2004) showed that stability of the steady flow, affected by a time-independent viscosity gradient pointing in the axial directions, is strongly affected by the stratified viscosity profile. In this work, we go one step beyond, by considering the stability of the hydrodynamic field coupled, through the viscosity, to the chemical field originated by the transport of one species. A phenomenological law is assumed, relating the viscosity to the concentration of chemical species. The steady state of the problem is obtained and a linear stability analysis of the coupled fields is made. The resulting eigenvalue-eigenfunction problem is presented, as well as some neutral stability curves associated with stationary perturbations, for Schmidt numbers $Sc = 2000$, usually found in the electro-dissolution of iron in sulfuric acid.

keywords: Rotating Disk, Hydrodynamic Stability, Electrochemistry

1. Introduction

Electrochemical cells using a rotating disk electrode are a widely used experimental tool in electrochemistry, due the simplicity of the setup and the fact that the mass flux is independent of the radial position along the disk, at steady state conditions (Levich, 1962). Furthermore, the rate of transfer of ions close of the electrode is conveniently controlled by imposing an adequate angular velocity to the electrode. This rate of transfer defines the maximum steady state current attained in an experiment.

Two current instabilities are observed in the region where the current is controlled by mass transport (Ferreira et al., 1994). The first instability is intrinsic to the system, while the current instability close to the active-passive transition is affected by the output impedance of the control equipment. This instability can be suppressed by using a negative feedback resistance (Epelboin et al., 1979), that gives rise to a continuous transition.

Most explanations presented in the literature for the current instabilities are based on mechanisms proposing a FeSO_4 film precipitated at the electrode surface (Russel and Newman, 1986). In fact, changes in the ohmic voltage drop due to precipitation and dissolution of a FeSO_4 film provide an acceptable explanation for the instability observed in the active/passive transition region, coupled with the output impedance of the control

equipment. However, this model can not be generalized to explain oscillations observed at the beginning of the current plateau. Indeed, using electro-hydrodynamic (EHD) impedance measurements (Tribollet and Newman, 1983), Barcia *et al.* (Barcia *et al.*, 1992) studied the electro-dissolution of iron electrodes in 1 M H_2SO_4 at the current plateau, before and after the first instability region. They propose that the electro-dissolution process leads to the existence of a viscosity gradient in the diffusion boundary layer, which could affect the stability of the hydrodynamic field and explain the observed current instability.

To investigate the importance of the hydrodynamics in the electro-dissolution of iron, Ferreira *et al.* (Ferreira *et al.*, 1994) and Geraldo *et al.* (Geraldo *et al.*, 1998) studied the influence of the viscosity on the current oscillations observed at the beginning of the current plateau region of the above described experiment. These authors found that increasing the bulk electrolyte viscosity – and therefore decreasing the Reynolds number of the experiment – by adding glycerol to the solution, the current signals evolve from chaotic to periodic, and to a stationary regime, where the instability is suppressed. They also found that the current oscillations are enhanced by an increase in the angular velocity of the electrode.

The existence of a hydrodynamic instability in rotating disk flow has been the object of a number of investigations, both experimental and theoretical in the case of fluids with uniform viscosity. The main result shows that the steady flow becomes unstable beyond a certain non-dimensional distance from the axis of rotation.

The flow develops corotating vortices which spiral outward with their axes along logarithmic spirals of angle $90^\circ + \varepsilon$ ($\varepsilon \approx 13^\circ$) with respect to radius of the disk. Malik (Malik, 1986) determined the neutral stability curve for stationary vortex disturbances, which turn with the angular velocity of the disk. Neutral curves were presented in the $\alpha \times R$, $\beta \times R$ and $\varepsilon \times R$ planes for zero-frequency disturbances, where α and β are the components of the real perturbation wave-vector along the radial and azimuthal directions and ε is the angle between the perturbation and the radial direction, given by $\varepsilon = \tan^{-1} \beta/\alpha$. The critical Reynolds number was found to be in good agreement with experimental results, at a value of $R = 285.36$.

A comprehensive review of the literature on the subject, concerning research made until 1989 can be found in the paper by Reed and Saric (Reed and Saric, 1989).

Faller (Faller, 1991) determined the neutral stability curves for setup configurations consisting of rotating or stationary disks and flows approaching the disk with (rotating flow) or without (stationary flow) bulk angular velocity. Critical Reynolds number for the case of rotating disk and stationary fluid was found as 69.4.

Lingwood (Lingwood, 1995) presented the neutral curve for vortices turning with several angular velocities and theoretical results concerning the asymptotic response of the flow to an impulsive excitation exerted in the flow at a certain radius at $t = 0$. Additionally, Lingwood's work addresses the case where the wavenumber component along the radial direction, α , is complex, leading to an exponential growth along that direction. The curve for this case defines the region of absolute instability, with a critical Reynolds number of $R = 510.625$.

It is well known that boundary layers can be destabilized by increasing the viscosity close to the wall and stabilized by decreasing, through heating or cooling the wall (Schlichting and Gersten, 1999). Schäfer *et al.* (Schäfer *et al.*, 1995) deduced an asymptotic expression for the critical Reynolds number for moderate temperature differences in boundary layers developed over flat plates, taking into account the temperature dependency of the viscosity. Turkyilmazoglu Cole and Gajjar (Turkyilmazoglu *et al.*, 1998) studied the influence of heat transfer on the convective and absolute instability of compressible boundary layers in rotating disk flow.

On two previous papers, Pontes *et al.* (Pontes *et al.*, 2002, Pontes *et al.*, 2004) showed that stability of the steady flow, affected by a time-independent viscosity gradient pointing in the axial directions, is strongly affected by the stratified viscosity profile. In this work, we go one step beyond, by considering the stability of the hydrodynamic field, coupled through the viscosity, to the chemical field originated by the transport of one species. A phenomenological law is assumed, relating the viscosity to the concentration of chemical species. The steady state of the problem is obtained and a linear stability analysis of the coupled fields is made. The resulting eigenvalue-eigenfunction problem is presented, as well as some neutral stability curves, for Schmidt numbers $Sc = 2000$, usually found in the electro-dissolution of iron electrodes in sulfuric acid.

Four linear stability analysis are presented in this work. All four cases address the stability of base state with respect to perturbations turning with the angular velocity of the rotating electrode. The first case, denoted as case No. 1, refers to fluids with constant viscosity (see Malik, 1986 and Pontes *et al.*, 2004) and is presented for purposes of comparison with the new results. The three other cases refer to fluids with variable viscosity and Schmidt number $Sc = 2000$, corresponding to the the Schmidt number found in the actual electrochemical problem. Case No. 2 refers to problems with sensitivity factor $\gamma = \frac{1}{\nu(\infty)} \frac{d\nu}{dC} = 0.05$. Cases Nos. 3 and 4 refer to problems with $\gamma = 1$ and 5, respectively, the last one corresponding to the value found in the actual electrochemical problem. All variable viscosity cases were studied assuming the same phenomenological law relating concentration of the relevant chemical species and fluid viscosity, as discussed below.

2. The Base State

The steady hydrodynamic field coupled to the transport of a chemical species is an extension of the well known von Kármán (von Kármán and Angew, 1921) exact solution of the continuity and Navier-Stokes equations for laminar rotating disk-flow, written in a rotating coordinate frame turning with the disk angular velocity Ω .

The continuity, momentum, and concentration equations on a rotating frame are given by:

$$\mathbf{div} \mathbf{v} = 0 \quad (1)$$

$$\frac{D\mathbf{v}}{Dt} = -2\boldsymbol{\Omega} \times \mathbf{v} - \frac{1}{\rho} \mathbf{grad} p + \frac{1}{\rho} \mathbf{div} \boldsymbol{\tau} \quad (2)$$

$$\frac{Dc}{Dt} = \mathbf{div} (D \mathbf{grad} c) \quad (3)$$

where $\boldsymbol{\tau}$ is the Newtonian viscous stress tensor.

Assuming that the stationary chemical species concentration depends only on the axial direction, the stationary coupled fields are governed by:

$$\frac{\partial v_r}{\partial r} + \frac{v_r}{r} + \frac{\partial v_z}{\partial z} = 0 \quad (4)$$

$$v_r \frac{\partial v_r}{\partial r} - \frac{v_\theta^2}{r} + v_z \frac{\partial v_r}{\partial z} = 2\Omega v_\theta + \nu \left(\frac{2}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_r}{\partial r} \right) - \frac{2v_r}{r^2} \right) + \frac{\partial}{\partial z} \left(\nu \frac{\partial v_r}{\partial z} \right) \quad (5)$$

$$v_r \frac{\partial v_\theta}{\partial r} + \frac{v_r v_\theta}{r} + v_z \frac{\partial v_\theta}{\partial z} = -2\Omega v_r + \frac{\nu}{r^2} \frac{\partial}{\partial r} \left(r^3 \mu \frac{\partial}{\partial r} \left(\frac{v_\theta}{r} \right) \right) + \frac{\partial}{\partial z} \left(\nu \frac{\partial v_\theta}{\partial z} \right) \quad (6)$$

$$v_r \frac{\partial v_z}{\partial r} + v_z \frac{\partial v_z}{\partial z} = -\frac{1}{\rho} \frac{\partial p}{\partial z} + \nu \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_r}{\partial r} \right) + 2 \frac{\partial^2 v_z}{\partial z^2} \right) + 2 \frac{\partial \nu}{\partial z} \frac{\partial v_z}{\partial z} \quad (7)$$

$$v_z \frac{\partial c}{\partial z} = \frac{\partial D}{\partial z} \frac{\partial c}{\partial z} + D \frac{\partial^2 c}{\partial z^2} \quad (8)$$

where c is the chemical species concentration and D is its diffusion coefficient in the electrochemical cell electrolyte.

The steady solution takes the form:

$$\bar{v}_r = r \Omega F(z) \quad (9)$$

$$\bar{v}_\theta = r \Omega G(z) \quad (10)$$

$$\bar{v}_z = (\nu(\infty) \Omega)^{1/2} H(z) \quad (11)$$

$$\bar{p} = \rho \nu(\infty) \Omega P(z) \quad (12)$$

$$\bar{c} = C_\infty + (C_0 - C_\infty) C(z) \quad (13)$$

where $\nu(\infty)$ is the bulk viscosity, far from the electrode surface. Equations (9–13) are introduced in the dimensional continuity and Navier-Stokes equations. Defining the bulk Schmidt number $Sc = \nu(\infty)/D(\infty)$, and the sensitivity factor $\gamma = \frac{1}{\nu(\infty)} \frac{d\nu}{dC}$ leads to the following system of equations for F , G , H and P :

$$2F + H' = 0 \quad (14)$$

$$F^2 - (G + 1)^2 + HF' = \nu^* F'' + \gamma F' C' \quad (15)$$

$$2F(G + 1) + HG' = \nu^* G'' + \gamma G' C' \quad (16)$$

$$P' + HH' = 2\gamma C' H' + \nu^* H'' \quad (17)$$

$$Sc HC' = \frac{1}{\nu^*} C'' + \frac{1}{\nu^{*2}} \gamma (C')^2 \quad (18)$$

Here, we refer to the nondimensional viscosity $\nu^* = \nu(z)/\nu(\infty)$, and to the nondimensional diffusivity $D^* = D(z)/D(\infty)$. We assume that the Stokes-Einstein equation is strictly valid, which implies that $D^* \nu^* = 1$ and that $d\nu^*/dC$ is constant. The bulk Schmidt number, Sc , and the sensitivity factor γ , define the slope of the viscosity profile close to the electrode surface.

Boundary conditions for F , G , H , and C are $F = H = P = G = 0$, $C = 1$ when $z = 0$, $F = H' = C = 0$, $G = -1$ when $z \rightarrow \infty$.

Figure 1 shows the non-dimensional viscosity and velocity profiles obtained by numerical integration of Eqs. (14–18) and used in the four cases of the stability analysis presented in this work. Curves No. 1 refer to fluids with constant viscosity; Curves No. 2, 3 and 4 refer to fluids with viscosity profiles obtained with $\gamma = 0.05, 1$ and 5 , respectively and $Sc = 2000$. In all cases, the fluid viscosity decays to the bulk value at $z = 0.3$ approximately. These viscosity profiles follow a trend similar to the one of the concentration profile of Fe^{++} , which is produced at the interface by the electrodisolution (Calabrese Barton and West, 2001).

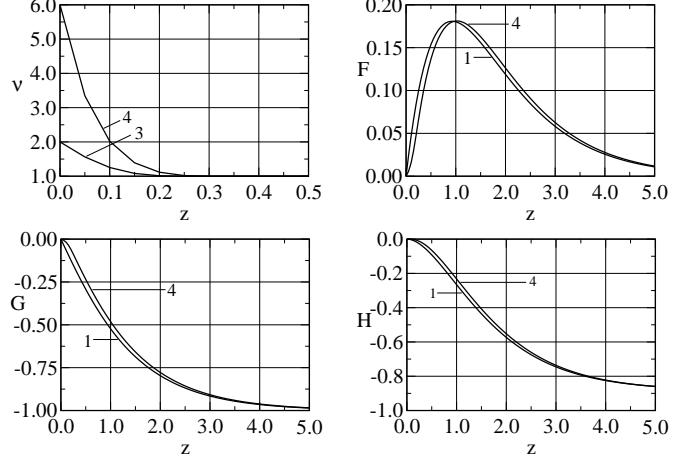


Figure 1: Dimensionless viscosity, ν , and velocity profiles F , G and H . Curves No. 1 refer to constant viscosity fluids. Curves No. 3 and 4, to variable viscosity fluids. Curves No. 3: $\gamma = 1$; Curves No. 4: $\gamma = 5$. In all cases, $Sc = 2000$.

3. Perturbations of the Base State

We turn now to the question of the stability of the steady configurations of the hydrodynamic field described in Sec. (2), with respect to infinitesimally small disturbances.

Variables are made non-dimensional as follows: radial and axial coordinates are divided by the reference length $(\nu(\infty)/\Omega)^{1/2}$, velocity components are divided by the reference velocity $r_e\Omega$, pressure is divided by the reference pressure $\rho(r_e\Omega)^2$, viscosity is divided by the bulk value, $\nu(\infty)$ and time and the eigenvalue of the linearized problem are divided by the time required by a particle, turning with the azimuthal velocity $r_e\Omega^2$, to move a distance equal to the reference length, $(\nu(\infty)/\Omega)^{1/2}$. Here, r_e is the dimensional coordinate along the radial direction where the stability analysis is made. We define also the Reynolds number by the relation:

$$R = r_e \left(\frac{\Omega}{\nu(\infty)} \right)^{1/2} \quad (19)$$

The nondimensional concentration is defined by

$$c^* = \frac{C_T - C_\infty}{C_S - C_\infty}$$

where C_S and C_∞ are the saturation and bulk concentrations of the relevant chemical species.

Therefore, dropping the asterisks, the equations in nondimensional form are given by:

$$\mathbf{div} \mathbf{v} = 0 \quad (20)$$

$$\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \mathbf{grad} \mathbf{v} = -\frac{2}{R} \mathbf{e}_z \times \mathbf{v} - \mathbf{grad} p + \frac{1}{R} \mathbf{div} \tau \quad (21)$$

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \mathbf{grad} c = \frac{1}{RSc} \mathbf{div} (D \mathbf{grad} c) \quad (22)$$

The hydrodynamic field is written in the form of the von Kármán solution plus a perturbation. The steady and perturbation variables are identified with a bar and a tilde, respectively. Therefore:

$$\begin{aligned} v_r &= \bar{v}_r + \tilde{v}_r & v_\theta &= \bar{v}_\theta + \tilde{v}_\theta & v_z &= \bar{v}_z + \tilde{v}_z \\ p &= \bar{p} + \tilde{p} & C_T &= \bar{c} + \tilde{c} \end{aligned}$$

The perturbed variables are introduced in the evolution equations. Subtracting the steady state solution, and neglecting the nonlinear terms containing products of the perturbations, the small amplitude perturbations evolution equations are given by

$$\frac{1}{r} \frac{\partial}{\partial r} (r \tilde{v}_r) + \frac{1}{r} \frac{\partial \tilde{v}_\theta}{\partial \theta} + \frac{\partial \tilde{v}_z}{\partial z} = 0 \quad (23)$$

$$\begin{aligned} \frac{\partial \tilde{v}_r}{\partial t} + \bar{v}_r \frac{\partial \tilde{v}_r}{\partial r} + \tilde{v}_r \frac{\partial \bar{v}_r}{\partial r} + \frac{\bar{v}_\theta}{r} \frac{\partial \tilde{v}_r}{\partial \theta} - 2 \frac{\bar{v}_\theta \tilde{v}_\theta}{r} + \bar{v}_z \frac{\partial \tilde{v}_r}{\partial z} + \tilde{v}_z \frac{\partial \bar{v}_r}{\partial z} = 2\Omega v_\theta - \frac{1}{\rho} \frac{\partial \tilde{p}}{\partial r} + \\ \frac{1}{\rho} \left(\frac{1}{r} \frac{\partial}{\partial r} (r \tilde{\tau}_{rr}) + \frac{1}{r} \frac{\partial \tilde{\tau}_{r\theta}}{\partial \theta} - \frac{\tilde{\tau}_{\theta\theta}}{r} + \frac{\partial \tilde{\tau}_{rz}}{\partial z} \right) \end{aligned} \quad (24)$$

$$\frac{\partial \tilde{v}_\theta}{\partial t} + \bar{v}_r \frac{\partial \tilde{v}_\theta}{\partial r} + \tilde{v}_r \frac{\partial \tilde{v}_\theta}{\partial r} + \frac{\bar{v}_\theta}{r} \frac{\partial \tilde{v}_\theta}{\partial \theta} + \frac{\tilde{v}_\theta \tilde{v}_\theta + \tilde{v}_r \bar{v}_\theta}{r} + \bar{v}_z \frac{\partial \tilde{v}_\theta}{\partial z} + \tilde{v}_z \frac{\partial \tilde{v}_\theta}{\partial z} = -2\Omega v_r - \frac{1}{\rho r} \frac{\partial \tilde{p}}{\partial \theta} + \frac{1}{\rho} \left(\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \tilde{\tau}_{r\theta}) + \frac{1}{r} \frac{\partial \tilde{\tau}_{\theta\theta}}{\partial \theta} + \frac{\partial \tilde{\tau}_{\theta z}}{\partial z} \right) \quad (25)$$

$$\frac{\partial \tilde{v}_z}{\partial t} + \bar{v}_r \frac{\partial \tilde{v}_z}{\partial r} + \frac{\bar{v}_\theta}{r} \frac{\partial \tilde{v}_z}{\partial \theta} + \tilde{v}_z \frac{\partial \tilde{v}_z}{\partial z} + \tilde{v}_z \frac{\partial \tilde{v}_z}{\partial z} = -\frac{1}{\rho} \frac{\partial \tilde{p}}{\partial z} + \frac{1}{\rho} \left(\frac{1}{r} \frac{\partial}{\partial r} (r \tilde{\tau}_{rz}) + \frac{1}{r} \frac{\partial \tilde{\tau}_{\theta z}}{\partial \theta} + \frac{\partial \tilde{\tau}_{zz}}{\partial z} \right) \quad (26)$$

$$\frac{\partial \tilde{c}}{\partial t} + \bar{v}_r \frac{\partial \tilde{c}}{\partial r} + \frac{\bar{v}_\theta}{r} \frac{\partial \tilde{c}}{\partial \theta} + \tilde{v}_z \frac{\partial \tilde{c}}{\partial z} + \tilde{v}_z \frac{d\tilde{c}}{dz} = \bar{D} \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \tilde{c}}{\partial r} \right) + \frac{1}{r} \frac{\partial}{\partial \theta} \left(\frac{1}{r} \frac{\partial \tilde{c}}{\partial \theta} \right) + \frac{\partial^2 \tilde{c}}{\partial z^2} \right) + \frac{d\bar{D}}{dz} \frac{\partial \tilde{c}}{\partial z} + \tilde{D} \frac{\partial^2 \tilde{c}}{\partial z^2} + \frac{\partial \tilde{D}}{\partial z} \frac{d\tilde{c}}{dz} \quad (27)$$

Expanding the stress tensor components and simplifying using the continuity equation, results in

$$\frac{1}{r} \frac{\partial}{\partial r} (r \tilde{v}_r) + \frac{1}{r} \frac{\partial \tilde{v}_\theta}{\partial \theta} + \frac{\partial \tilde{v}_z}{\partial z} = 0 \quad (28)$$

$$\begin{aligned} \frac{\partial \tilde{v}_r}{\partial t} + \bar{v}_r \frac{\partial \tilde{v}_r}{\partial r} + \tilde{v}_r \frac{\partial \tilde{v}_r}{\partial r} + \frac{\bar{v}_\theta}{r} \frac{\partial \tilde{v}_r}{\partial \theta} - 2 \frac{\bar{v}_\theta \tilde{v}_\theta}{r} + \bar{v}_z \frac{\partial \tilde{v}_r}{\partial z} + \tilde{v}_z \frac{\partial \tilde{v}_r}{\partial z} &= 2 \frac{\tilde{v}_\theta}{R} - \frac{\partial \tilde{p}}{\partial r} + \\ \frac{1}{R} \left[\tilde{\nu} \left(\frac{\partial^2 \tilde{v}_r}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2 \tilde{v}_r}{\partial \theta^2} + \frac{\partial^2 \tilde{v}_r}{\partial z^2} + \frac{1}{r} \frac{\partial \tilde{v}_r}{\partial r} - \frac{2}{r^2} \frac{\partial \tilde{v}_\theta}{\partial \theta} - \frac{\tilde{v}_r}{r^2} \right) + \frac{d\tilde{\nu}}{dz} \left(\frac{\partial \tilde{v}_z}{\partial r} + \frac{\partial \tilde{v}_r}{\partial z} \right) + \right. \\ \left. \tilde{\nu} \left(\frac{\partial^2 \tilde{v}_r}{\partial z^2} + \frac{1}{r} \frac{\partial \tilde{v}_r}{\partial r} - \frac{\tilde{v}_r}{r^2} \right) + 2 \frac{\partial \tilde{v}_r}{\partial r} \frac{\partial \tilde{\nu}}{\partial r} + \frac{\partial \tilde{\nu}}{\partial z} \frac{\partial \tilde{v}_r}{\partial z} \right] & \quad (29) \end{aligned}$$

$$\begin{aligned} \frac{\partial \tilde{v}_\theta}{\partial t} + \bar{v}_r \frac{\partial \tilde{v}_\theta}{\partial r} + \tilde{v}_r \frac{\partial \tilde{v}_\theta}{\partial r} + \frac{\bar{v}_\theta}{r} \frac{\partial \tilde{v}_\theta}{\partial \theta} + \frac{\bar{v}_r \tilde{v}_\theta + \tilde{v}_r \bar{v}_\theta}{r} + \bar{v}_z \frac{\partial \tilde{v}_\theta}{\partial z} + \tilde{v}_z \frac{\partial \tilde{v}_\theta}{\partial z} &= -2 \frac{\tilde{v}_r}{R} - \frac{1}{r} \frac{\partial \tilde{p}}{\partial \theta} + \\ \frac{1}{R} \left[\tilde{\nu} \left(\frac{\partial^2 \tilde{v}_\theta}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2 \tilde{v}_\theta}{\partial \theta^2} + \frac{\partial^2 \tilde{v}_\theta}{\partial z^2} + \frac{1}{r} \frac{\partial^2 \tilde{v}_\theta}{\partial r} + \frac{2}{r^2} \frac{\partial \tilde{v}_r}{\partial \theta} - \frac{\tilde{v}_\theta}{r^2} \right) + \frac{d\tilde{\nu}}{dz} \left(\frac{1}{r} \frac{\partial \tilde{v}_z}{\partial \theta} + \frac{\partial \tilde{v}_\theta}{\partial z} \right) + \right. \\ \left. \tilde{\nu} \left(\frac{\partial^2 \tilde{v}_\theta}{\partial z^2} + \frac{1}{r} \frac{\partial \tilde{v}_\theta}{\partial r} - \frac{\tilde{v}_\theta}{r^2} \right) + \frac{2\tilde{v}_r}{r^2} \frac{\partial \tilde{\nu}}{\partial \theta} + \frac{\partial \tilde{\nu}}{\partial z} \frac{\partial \tilde{v}_\theta}{\partial z} \right] & \quad (30) \end{aligned}$$

$$\begin{aligned} \frac{\partial \tilde{v}_z}{\partial t} + \bar{v}_r \frac{\partial \tilde{v}_z}{\partial r} + \tilde{v}_r \frac{\partial \tilde{v}_z}{\partial r} + \frac{\bar{v}_\theta}{r} \frac{\partial \tilde{v}_z}{\partial \theta} + \bar{v}_z \frac{\partial \tilde{v}_z}{\partial z} + \tilde{v}_z \frac{\partial \tilde{v}_z}{\partial z} &= -\frac{\partial \tilde{p}}{\partial z} + \\ \frac{1}{R} \left[\tilde{\nu} \left(\frac{\partial^2 \tilde{v}_z}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2 \tilde{v}_z}{\partial \theta^2} + \frac{\partial^2 \tilde{v}_z}{\partial z^2} + \frac{1}{r} \frac{\partial \tilde{v}_z}{\partial r} \right) + 2 \frac{d\tilde{\nu}}{dz} \frac{\partial \tilde{v}_z}{\partial z} \right. \\ \left. 2\tilde{\nu} \frac{\partial^2 \tilde{v}_z}{\partial z^2} + \frac{\partial \tilde{\nu}}{\partial r} \left(\frac{\partial \tilde{v}_z}{\partial r} + \frac{\partial \tilde{v}_r}{\partial z} \right) + \frac{1}{r} \frac{\partial \tilde{\nu}}{\partial \theta} \left(\frac{\partial \tilde{v}_\theta}{\partial z} + \frac{1}{r} \frac{\partial \tilde{v}_z}{\partial \theta} \right) + 2 \frac{\partial \tilde{\nu}}{\partial z} \frac{\partial \tilde{v}_z}{\partial z} \right] & \quad (31) \end{aligned}$$

$$\begin{aligned} \frac{\partial \tilde{c}}{\partial t} + \bar{v}_r \frac{\partial \tilde{c}}{\partial r} + \frac{\bar{v}_\theta}{r} \frac{\partial \tilde{c}}{\partial \theta} + \tilde{v}_z \frac{\partial \tilde{c}}{\partial z} + \tilde{v}_z \frac{d\tilde{c}}{dz} &= \frac{1}{R Sc} \left[\bar{D} \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \tilde{c}}{\partial r} \right) + \frac{1}{r} \frac{\partial}{\partial \theta} \left(\frac{1}{r} \frac{\partial \tilde{c}}{\partial \theta} \right) + \frac{\partial^2 \tilde{c}}{\partial z^2} \right) + \right. \\ \left. \frac{d\bar{D}}{dz} \frac{\partial \tilde{c}}{\partial z} + \tilde{D} \frac{d^2 \tilde{c}}{dz^2} + \frac{\partial \tilde{D}}{\partial z} \frac{d\tilde{c}}{dz} \right] & \quad (32) \end{aligned}$$

The perturbed field is assumed as

$$\begin{pmatrix} v_r \\ v_\theta \\ v_z \\ p \\ C_T \end{pmatrix} = \begin{pmatrix} r\Omega F \\ r\Omega G \\ (\nu(\infty)\Omega)^{1/2} H \\ \rho\nu(\infty)\Omega P \\ C_\infty + (C_s - C_\infty) C \end{pmatrix} + A \begin{pmatrix} r_e \Omega f \\ r_e \Omega g \\ r_e \Omega h \\ \rho\nu(\infty)\Omega \pi \\ C_\infty + (C_s - C_\infty) c \end{pmatrix} \exp[i(\alpha r + \beta R\theta - \omega t)] + cc \quad (33)$$

where C and c are functions of z . Re-writing the variables in Eq. (33) in nondimensional form, the perturbed non-dimensional velocity components, pressure, and concentration are written as:

$$\begin{pmatrix} v_r \\ v_\theta \\ v_z \\ p \\ C_T^* \end{pmatrix} = \begin{pmatrix} rF/R \\ rG/R \\ H/R \\ p/R^2 \\ C \end{pmatrix} + A \begin{pmatrix} f \\ g \\ h \\ \pi \\ c \end{pmatrix} \exp[i(\alpha r + \beta R\theta - \omega t)] + cc \quad (34)$$

where ω is a complex number, with $\Re(\omega)$ and $\Im(\omega)$ being, respectively, the frequency and the rate of growth of the perturbation. Parameters α and β are the components of the perturbation wave-vector along the radial and azimuthal directions. For a given time, the phase of the perturbation is constant along branches of a logarithmic spiral, with the branches curved in the clockwise direction if β/α is positive and counter-clockwise, if negative. The structure turns counter-clockwise if ω/β is positive and clockwise, if negative.

Perturbation and steady state variables are introduced in the evolution equations, resulting in

$$i \left(\alpha - \frac{i}{r} \right) f + i \frac{R}{r} \beta g + h' = 0 \quad (35)$$

$$i \left(\frac{r}{R} \alpha F + \beta G - \omega \right) f + \frac{r}{R} F' h + i \alpha \pi - \frac{r}{R} F' \gamma c' - \frac{r}{R} F'' \gamma c = \frac{1}{R} \left(\nu f'' - \nu \left(\alpha^2 + \frac{R^2}{r^2} \beta^2 \right) f - F f + 2(G+1)g - H f' + i \alpha \nu' h + \nu' f' + 2i \alpha F \gamma c \right) + \frac{1}{R^2} \left(i \frac{R}{r} \nu \alpha f - 2i \frac{R^2}{r^2} \nu \beta g \right) - \frac{\nu}{R r^2} f \quad (36)$$

$$i \left(\frac{r}{R} \alpha F + \beta G - \omega \right) g + \frac{r}{R} G' h + i \frac{R}{r} \beta \pi - \frac{r}{R} (G'' \gamma c + G' \gamma c') = \frac{1}{R} \left(\nu g'' - \nu \left(\alpha^2 + \frac{R^2}{r^2} \beta^2 \right) g - F g - 2(G+1)f - H g' + i \frac{R}{r} \beta \nu' h + \nu' g' + \frac{2R}{r} i \beta F \gamma c \right) + \frac{1}{R^2} \left(i \frac{R}{r} \nu \alpha g - 2i \frac{R^2}{r^2} \nu \beta f \right) - \frac{\nu}{R r^2} g \quad (37)$$

$$i \left(\frac{r}{R} \alpha F + \beta G - \omega \right) h + \pi' - i \beta G' \gamma c - \frac{r}{R} i \alpha F' \gamma c = \frac{1}{R} \left(\nu h'' - \nu \left(\alpha^2 + \frac{R^2}{r^2} \beta^2 \right) h - H h' - H' h + 2\nu' h' + 2H'' \gamma c + 2H' \gamma c' \right) + \frac{i}{R r} \nu \alpha h \quad (38)$$

$$i \left(\frac{r}{R} \alpha F + \beta G - \omega \right) c + C' h = \frac{1}{R S c \bar{\nu}} \left(- \left(\alpha \bar{\alpha} + \frac{R^2}{r^2} \beta^2 \right) c + \frac{1}{\bar{\nu}} \left(\left(2 \frac{\bar{\nu}'}{\bar{\nu}} \gamma - \gamma' \right) C' - \gamma C'' \right) c - \left(\frac{\bar{\nu}'}{\bar{\nu}} + \frac{1}{\bar{\nu}} C' \gamma + S c \bar{\nu} H \right) c' + c'' \right) \quad (39)$$

Introducing the parallel flow hypothesis, eliminating the pressure, and dropping terms of order R^{-2} , leads to:

$$\begin{aligned} & (i\nu (D^2 - \lambda^2) (D^2 - \bar{\lambda}^2) + i\nu' D (2D^2 - \lambda^2 - \bar{\lambda}^2) + i\nu'' (D^2 + \bar{\lambda}^2) + \\ & R(\alpha F + \beta G - \omega) (D^2 - \bar{\lambda}^2) - R(\bar{\alpha} F'' + \beta G'') - iHD (D^2 - \bar{\lambda}^2) - \\ & iH' (D^2 - \bar{\lambda}^2) - iFD^2) h + (2(G+1)D + 2G') \eta + (R(\bar{\alpha} F' + \beta G') \gamma D^2 + \\ & (2R(\bar{\alpha} F'' + \beta G'') + 6i\bar{\lambda}^2 F) \gamma D + (R\bar{\lambda}^2 (\alpha F' + \beta G') + R(\bar{\alpha} F''' + \beta G''')) + \\ & 6i\bar{\lambda}^2 F') \gamma + (R(\bar{\alpha} F'' + \beta G'') + 6i\bar{\lambda}^2 F) \gamma') c = 0 \end{aligned} \quad (40)$$

$$(2(G+1)D - iR(\alpha G' - \beta F')) h + (i\nu (D^2 - \lambda^2) + i\nu' D + R(\alpha F + \beta G - \omega) - iHD - iF) \eta + iR(\alpha G' - \beta F') \gamma c' + iR\alpha G'' \gamma c = 0 \quad (41)$$

$$R S c i (\alpha F + \beta G - \omega) c + R S c C' h - \frac{1}{\bar{\nu}} \left(-\bar{\lambda}^2 + \frac{1}{\bar{\nu}} \left(\left(2 \frac{\bar{\nu}'}{\bar{\nu}} \gamma - \gamma' \right) C' - \gamma C'' \right) c + \left(\frac{\bar{\nu}'}{\bar{\nu}} + \frac{1}{\bar{\nu}} C' \gamma + S c \bar{\nu} H \right) c' + c'' \right) = 0 \quad (42)$$

Eqs. (40 to 42) can be re-written as $\mathbf{AX} = \omega R \mathbf{BX}$:

$$\begin{pmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & & A_{33} \end{pmatrix} \begin{pmatrix} h \\ \eta \\ c \end{pmatrix} = \omega R \begin{pmatrix} B_{11} & & \\ & B_{22} & \\ & & B_{33} \end{pmatrix} \begin{pmatrix} h \\ \eta \\ c \end{pmatrix} \quad (43)$$

where the missing elements in the above matrices are null and the operators A_{ij} and B_{ij} are given by:

$$\begin{aligned} A_{11} &= a_{114} D^4 + a_{113} D^3 + a_{112} D^2 + a_{111} D + a_{110} & A_{12} &= a_{121} D + a_{120} & A_{13} &= a_{132} D^2 + a_{131} D + a_{130} \\ A_{21} &= a_{211} D + a_{210} & A_{22} &= a_{222} D^2 + a_{221} D + a_{220} & A_{23} &= a_{231} D + a_{230} \\ A_{31} &= a_{310} & & & A_{33} &= a_{332} D^2 + a_{331} D + a_{330} \\ B_{11} &= D^2 - \bar{\lambda}^2 & B_{22} &= 1 & B_{33} &= i S c \end{aligned}$$

Curves Nos. 2 - 4 show a large reduction on the critical Reynolds number for the cases of viscosity varying with the concentration field ($\gamma \neq 0$). Even though the steady state profiles (Fig. 1) are not appreciably affected by the viscosity variations, the stability of the flow is dramatically affected by the coupling of the chemical species through the viscosity field.

The above results are, qualitatively, in agreement with the experimental ones. Indeed, the system becomes more unstable as the angular velocity of the electrode increases, and more stable as the bulk viscosity increases, with addition of glycerol.

The results show that even a very small sensitivity factor (as low as 0.05) can produce a significant reduction in the critical Reynolds number for the values of Schmidt number found in actual electrochemical cells.

5. Conclusions

In this work we analyzed the behavior of the most unstable modes in rotating disk flow with a stratified viscosity depending on the concentration of a chemical species transported by the flow, and compared the results with existing results for the constant viscosity case.

The main conclusions of this work may be summarized as follows:

1. The proposed coupled hydrodynamic-chemistry model, with a stratified viscosity profile depending on the concentration of the chemical species, shows that, in all cases considered, the system becomes more unstable as the sensitivity factor increases.
2. The results show that even a very small sensitivity factor (as low as 0.05) can produce a significant reduction in the critical Reynolds number for the values of Schmidt number found in actual electrochemical cells.

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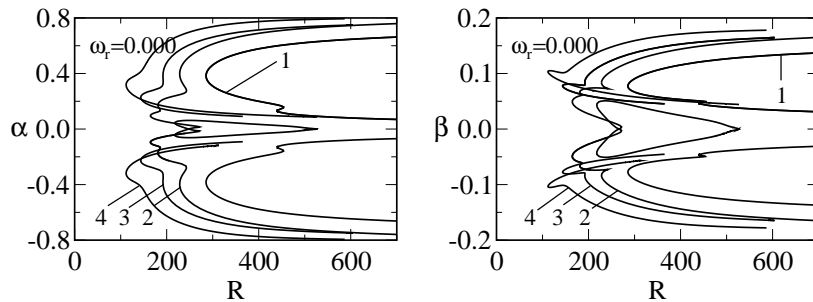


Figure 3: Neutral curves of stationary perturbations, for constant and variable viscosity fluids. Curves No. 1 refer to constant viscosity fluids. Curves No. 2, 3 and 4, to variable viscosity fluids. Curves No. 2: $\gamma = 0.05$; Curves No. 3: $\gamma = 1$; Curves No. 4: $\gamma = 5$. In all cases, $Sc = 2000$.

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