Centrifugal convection in a two-layer system of reacting miscible fluids

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Abstract. The authors study the effect of uniform rotation on the system of two reacting miscible liquids placed in a cylindrical Hele-Shaw cell. The cell performs a rotation with a constant velocity around the axis of symmetry resulting in a radially directed inertial field. The initial configuration of the system is statically stable and consists of two concentric layers of aqueous solutions of acid and base, which are spatially separated. When liquids are brought into contact, a neutralization reaction begins, which is accompanied by the release of salt. In this work, we obtain a system of governing equations and present the results of numerical simulation. We found that reaction-diffusion processes lead to the formation of a non-monotonic density profile with a potential well. If the rotation rate gradually increases, then a cellular convection pattern can develop in the potential well. We found that with further growth of the control parameter, the periodicity of the pattern is violated due to the influence of another convective instability, which independently develops in the domain close to the axis of rotation. The action of the inertial field results in the ejection of some convective vortices from the potential well.

1. Introduction

Since the world of chemical reactions is rich, the researchers dealing with the chemo-hydrodynamics are focused on studying the effect of the model reaction with relatively simple, but nonlinear kinetics. The neutralization reaction is ideal for this role [1]. The most popular initial configuration of a convective system, which can be relatively easily realized in an experiment, includes two spatially separated reactant solutions. If the liquids are miscible (for example, both solutions are aqueous), then immediately after bringing them into contact, a narrow transition zone with a reaction front is formed between them. The faster the reaction rate, the thinner this zone. The results of experiments by different authors [2–4] have shown that the reaction proceeds frontally in a gravity field and is accompanied by the onset of the convective motion caused by the difference in the diffusion rates of the reacting components. The emerging convective state is a disordered finger-like structure spreading on both sides of the transition zone. In this case, the mass transfer still occurs under the control of diffusion, which leads to a slow reaction rate. In the paper [5], the authors attempted to classify all possible types of buoyancy-driven instabilities arising in two-layer miscible systems based on the study of the asymptotic of long evolution times of the system. The classification is based on the assumption that the processes that occur above and below the reaction front are reliably separated by an interlayer of liberated salt. Therefore, one should
consider their features apart. The main conclusion of this classification is that a neutralization reaction does not give rise to new types of instabilities, but rather changes the features of previously well-known instability mechanisms: the instability of double diffusion (DD), diffusion layer convection (DLC), and Rayleigh-Taylor instability (RT). However, the classification given in [5], as it was soon shown in [6], is not complete since there is a reaction regime under the control of energetic convection in the form of a shock wave with a front oriented perpendicular to the force of gravity. This chemoconvection mode occurs when the density of the upper layer is approximately equal to the density of the lower layers. It is important to note that this effect has been confirmed experimentally for a homologous series of reactants [6]. Besides, the diffusion coefficients of reactants dissolved in water were shown to depend on the concentration of species, and this can lead to a periodic system of chemoconvective cells, which resembles the Rayleigh-Benard convection in its regularity.

In this work, we study the reaction-diffusion-convection processes developing under not a constant, but of a space-variable inertial field, which is created due to the centrifugation of the two-layer reacting system around its axis of symmetry. In addition to spatial inhomogeneity, the centrifugal field can be tuned by changing the rotation frequency, which also gives the system new degrees of freedom.

2. Mathematical formulation

Let us consider a two-layer system of miscible reacting liquids placed in a cylindrical Hele-Shaw (HS) cell rotating at a constant angular velocity $\Omega = \Omega_0 \gamma$. Here, $\Omega_0$ is the absolute value of the angular velocity, $\gamma$ is a unit vector directed along the rotation axis (Fig. 1a).

![Figure 1. Schematic representation of the Hele-Shaw cell in cylindrical coordinates (a), the initial configuration of solutions – top view (b)](image)

Let us denote the radius of the HS cell as $R$ and its gap width as $h$. The necessary condition for the Hele-Shaw approximation requires $R \gg h$. The sufficient condition requires that the convective structures that can potentially arise as a result of pattern formation be much larger than the HS cell gap. The description of the system in the framework of the coordinate system rotating together with the body leads to the appearance of Coriolis and centrifugal forces. In what follows, we neglect the influence of static gravity. Thus, the inertial field acts on a fluid element along with the layer, which makes it possible to assume that possible fluid flow would be quasi-two-dimensional.

In previous works, we have reported the dependence of the diffusion coefficients of the substances on their concentrations. For sake of definiteness, let us consider a specific pair of reactants for which we previously developed the diffusion model tested in [6]. Let A denote the concentration of an aqueous solution of nitric acid HNO$_3$, and B stands for the concentration of sodium hydroxide NaOH. The initial
system configuration is shown in Fig. 1b. The contact of two solutions leads to the onset of a neutralization reaction producing water and sodium nitrate NaNO$_3$. In a simplified form, the kinetics of this reaction can be defined as

$$A + B \rightarrow S$$

(1)

where the water production and heat release were neglected. One can notice that the wide sidewalls of the HS cell are usually made from glass, which transmits significant heat because of the thermal conductivity coefficients of water and glass are nearly the same. In comparison with the concentration effects, the thermal effects can be controlled to a greater extent during the experiment. Thermally insulated walls enhance the role of heat, while perfectly conductive walls make the heat effect negligible.

We rewrite the problem in a dimensionless form using the following measurement units: length — $h$, time — $h^2/D_{A0}$, velocity — $D_{A0}/h$, pressure — $\rho D_{A0}/h^2$, and concentration — $A_{lim}$, where $D_{A0}$ stands for the tabular value of the diffusion coefficient of the fastest of the three substances (nitric acid), $A_{lim}$ is the maximum value of the acid concentration, up to which the approximation for the concentration-dependent diffusion (CDD) effect works well, $\rho$ and $\nu$ are density and kinematic viscosity of the fluid, respectively. Then we obtain the following nonlinear system of dimensionless convection–reaction–diffusion equations written in a two-field formulation in terms of the stream function $\Psi$ and the vorticity $\Phi$:

$$\Delta \Psi + \Phi = 0,$$

$$\frac{1}{Sc} \left( \frac{\partial \Phi}{\partial t} + \frac{6}{5r} \frac{\partial (r \Phi)}{\partial r} \right) = \Delta \Phi - 12 \Phi - \frac{\partial (R \ C)}{\partial \varphi},$$

$$\frac{\partial C}{\partial t} + \frac{1}{r} \frac{\partial (r C \varphi)}{\partial r} = \nabla \cdot (D \nabla C) + ID_{A0}AB,$$

(2)

where $C = (A, B, S)$ stands for the vector of concentrations, $R = (R_A, R_B, R_S)$, $D = (D_A, D_B, D_S)$, and $I = (-1, -1, 1)$.

Several dimensionless similarity criteria have appeared in the system of equations (2). The Schmidt number $Sc = \nu/D_{A0}$ characterizes the ratio of the characteristic diffusion times of the solute (acid) and the diffusion of the momentum of the solvent element (water). For the set of substances under consideration, this parameter is $Sc = 317$. The Damköhler number $Da = h^2/\alpha A_{lim}/D_{A0}$ is the ratio of the characteristic diffusion time of the fastest reactant to the characteristic reaction time. The neutralization reaction is considered to be fast so that reactants do not have time to penetrate deep into the solution of its paired species. Therefore, the reaction between two initially separated solutions proceeds in a narrow zone called the reaction front. In the paper [7], the authors estimated the value of the kinetic constant of the neutralization reaction. The obtained range was from 102 to 105. In this work, we take the value $Da = 10^3$ that falls within the range defined in [7].

The set of Rayleigh concentration numbers appeared in (2) determine the buoyancy effects in solutions of the corresponding substances under the centrifugal force field:

$$R_A = \frac{\beta_A R \Omega^2 A_{lim} h^2}{\nu D_{A0}}, \quad R_B = \frac{\beta_B R \Omega^2 A_{lim} h^2}{\nu D_{B0}}, \quad R_S = \frac{\beta_S R \Omega^2 A_{lim} h^2}{\nu D_{S0}}.$$  

(3)

The CDD effect is key to this work. We assume for simplicity that each diffusion coefficient depends only on the concentration of its substance and the data set falls in the experimentally defined range on a straight line $f(x) = a + bx$, where $x$ is the concentration, $a$ and $b$ are some constants. These linear laws in a dimensionless form, then, are

$$D_A(A) = 0.881 + 0.158A, \quad D_B(B) = 0.594 - 0.087B, \quad D_S(S) = 0.478 - 0.284S.$$  

(4)

Finally, we formulate the boundary and initial conditions. The boundary conditions are
\[ r = R : \Psi = 0, \quad \frac{\partial \Psi}{\partial r} = 0, \quad \frac{\partial A}{\partial r} = 0, \quad \frac{\partial B}{\partial r} = 0, \quad \frac{\partial S}{\partial r} = 0. \] (5)

The initial conditions are formulated as it follows:

\[ \begin{align*}
  t = 0: & \quad r \leq R/\sqrt{2} : \quad \Psi = 0, \quad A = \gamma_A, \quad B = 0, \\
  t = 0: & \quad r > R/\sqrt{2} : \quad \Psi = 0, \quad A = 0, \quad B = \gamma_B,
\end{align*} \] (6)

where

\[ \gamma_A = A_0 / A_{\text{lim}}, \quad \gamma_B = B_0 / A_{\text{lim}}. \] (7)

3. Results of numerical simulation

As we have shown earlier in the work [6], the control parameter of the problem is the ratio of the initial concentrations of solutions \( \gamma = \gamma_A / \gamma_B \) defined by (7). The initial configuration of the system remains statically stable down to the lowest value \( \gamma = R_A/R_B \approx 0.83 \), which determines the state of equal densities of central and peripheral layers (i.e. isopycnic line). We demonstrated that there exists a bifurcation point \( \gamma^* \) for \( \gamma > R_A/R_B \) that separates the onset of two fundamentally different regimes of reaction-diffusion-convection processes. In the range \( R_A/R_B < \gamma < \gamma^* \), the traveling shock-like wave mode is realized which proceeds under the control of convection. In the case \( \gamma > \gamma^* \), the transfer processes are controlled by diffusion. In this case, convection also can take place, but its intensity is determined by diffusion processes. In this paper, we restrict ourselves to considering the effect of centrifugal action in the case \( \gamma > \gamma^* \). For definiteness, let us fix the initial concentrations at the values \( \gamma_A = 0.667 \) and \( \gamma_B = 0.667 \) (\( \gamma = 1 \)) and trace how the type of instability changes with increasing rotation frequency. The Rayleigh number \( R_A \) unambiguously determines the intensity of rotation in the system, but we should keep in mind that the centrifugal force increases with distance from the axis of rotation, therefore, the inertial effect will be different at different points of the HS cell. Thus, the Rayleigh numbers defined by (3) characterize the centrifugal force at the edge of the cuvette. In what follows, we present preliminary results of the numerical simulation of the nonlinear problem (2), (4)--(6) obtained for different values of \( R_A \). The problem has been solved by the finite-difference method; the details of the computational scheme are given in [8]. It is convenient to present the numerical results not for individual concentration fields, but for the total density, which is an addition to the density of the solvent:

\[ \hat{\rho}(t,r,\varphi) = A(t,r,\varphi) + \frac{R_A}{R_s} B(t,r,\varphi) + \frac{R_A}{R_s} S(t,r,\varphi). \] (8)

In contrast to the static gravity field, in this problem, we can change the intensity of the inertial field. When the rotation frequency is low, the HS cell is in microgravity. In this case, the inertial force can not give rise to the chemoconvective motion of the fluid. Fig. 2 shows the time evolution frames obtained for \( R_A = 1.6 \times 10^3 \), which corresponds to an overload of 0.02g at the edge of the HS disk. One can see from the figure that there exists a reaction-diffusion base state, which gives rise to two statically stable potential wells in the density field. Potential wells are concentric, one of them is closer to the axis of rotation and wider, and the other is located further and narrower. The wells occur when an emerging component (salt) starts to accumulate near the reaction front creating a potential barrier near the reaction zone. The numerical simulation of the time evolution of the base state shows that the shape and depth of the wells practically do not change with time, and the width slowly increases under the influence of diffusion processes (Fig. 2a-c).
Figure 2. Time evolution of the dimensionless density field at times: 0.2 (a), 0.6 (b), 1.0 (c) demonstrating the motionless state at $R_A = 1.6 \cdot 10^3$ (approximately 0.02g measured at the edge of the disk).

The large value of the kinetic reaction constant guarantees almost instantaneous formation of a potential well after bringing the solutions into contact (Fig. 2a). In contrast, the onset and growth of chemoconvective instability require much more time. With an increase in the rotation frequency, one can observe the appearance of cellular convection in the potential well located further from the rotation axis, as well as a periodic system of plumes floating up to the center of the cell. Fig. 3 shows the sequential development of both instabilities at $R_A = 2.4 \cdot 10^4$ (about 0.3g). We can learn from the figure that a cellular structure appears at about $t = 0.6$ and acquires a mature form by the time $t = 0.8$. There are 52 convection cells on a circle of length $R/\sqrt{2}$. Therefore, the structure wavelength is about $l_{CDD} = 1.7$ (the wave number is $k_{CDD} = 3.7$). The characteristic wavelength of the plumes is $l_{DLC} = 6.4$ ($k_{DLC} = 0.9$). The DLC-convection plumes move to the center of the HS cell due to the low density of the reaction zone. The intensity of fluid flow in the vicinity of the rotation axis significantly decreases due to the weakening of the inertia field. Large-scale eddies being inherent in this instability define radial directions for intense injection of fresh acid to the periphery of the HS cell, which leads to the formation of a quasiperiodic structure of chemoconvective cells (Fig. 3b). Earlier we studied this effect for the case of a constant gravity field and an infinitely extended layer in detail. In the present problem, the instabilities grow near the reaction front, which has the shape of a circle and a finite length; therefore, synchronization occurs between the structures.

Figure 3. Time evolution of the dimensionless density field at times: 0.2 (a), 0.6 (b), 1.0 (c) demonstrating competition between the CDD and DLC instabilities at $R_A = 2.4 \cdot 10^4$ (approximately 0.3g measured at the edge of the disk).
Figure 4 illustrates the case of an inertial field that exceeds the static gravity field. The figure shows the frames of the time evolution of the density field at $R_A = 1.3 \cdot 10^5$ (it is approximately 1.3g). Here, we observe the irregular convective motion of liquid in potential wells almost from the very beginning of evolution. It is interesting to note that some convective cells leave the potential well under the action of the centrifugal force since fluctuations of the density field can exceed the height of the potential barrier farthest from the axis of rotation. These droplets of high density move in a radial direction and may even reach the edge of the disc (Fig. 4c). Notice that a high level of mixing in the central area is achieved already at $t = 1$.

(a)    (b)       (c)

Figure 4. Time evolution of the dimensionless density field at times: 0.2 (a), 0.6 (b), 1.0 (c) under a centrifugal action larger than static gravity: $R_A = 1.3 \cdot 10^5$ (approximately 1.3g measured at the edge of the disk)

The time evolution of the absolute value of the stream function maximum is shown in Figure 5 for each of the previously considered values of the Rayleigh number. A sharp increase in the stream function at the initial times corresponds to the development of instability within the potential well. This process continues until the sequence of cells is finally formed. It is obvious that convection becomes more intense with increasing rotation frequency. During rotation, the redistribution of density under the action of the centrifugal force leads to collision (competition) of vortices in the center of the HS cell, which explains the non-stationary nature of the dynamics of the stream function maximum shown in Figure 5.

Figure 5. Time evolution of the absolute value of the stream function maximum at different rotation intensities
4. Conclusion
In this work, we present a theoretical study of the effect of the uniform rotation on the development of chemoconvective instabilities arising in two-layer systems of miscible reacting liquids. We show that at low values of the rotation rate (if the inertia force measured at the edge of the HS cell is less than 0.1g), convection in the system does not develop at all. For higher values of the rotation speed, we observe two different types of chemoconvection, which excite in two potential wells separated by a potential barrier. An increase in the rotation speed of more than 1g leads to density fluctuations, which result in a chaos of fluid movement inside the potential wells. As a result, one can observe the phenomenon of the radial ejection of some chemoconvective cells outside the potential well.

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References
[1] De Wit A 2020 Annu. Rev. Fluid Mech. 52 531–555
[2] Zalts A, El Hasi C, Rubio D, Urena A and D’Onofrio A 2008 Phys. Rev. E 77 015304
[3] Asad A, Yang Y H, Chai C and Wu J T 2010 Chin. J. Chem. Phys. 23 513–520
[4] Almarcha C, R’Hon Y, De Decker Y, Trevelyan P M J, Eckert K and De Wit A, 2011 J. Phys. Chem. B 115 9739–9744
[5] Trevelyan P M J, Almarcha C and De Wit A, 2015 Phys. Rev. E 91 023001
[6] Bratsun D, Mizev A, Mosheva E and Kostarev K, 2017 Phys. Rev. E 96 053106
[7] Demin V A and Popov E A 2015 Bulletin of Perm University. Physics 5 44–50
[8] Utochkin V Y, Siraev R R and Bratsun D A, 2020 Comput. Contin. Mech. 13(2) 205–218