Dynamics of a soluble surfactant and evolution of daughterly concentration tongue in a Hele–Shaw cell

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Abstract. The origin and evolution of a concentration tongue, which is generated in the volume of a fluid due to the non-uniform desorption of a soluble surfactant, is investigated theoretically by the method of direct numerical simulation. Initially, a film of the soluble surfactant is located on the surface of the fluid that fills up the thin vertical rectangular slot (Hele–Shaw cell), heated non-uniformly from above. The intensity of desorption into the volume is determined by the compression of the film, caused by the Marangoni force, acting along the upper boundary in opposite direction to the tangential component of temperature gradient. The dynamics of concentration tongue depends on the intensity of a creeping convective flow, which is produced in the volume jointly by the Archimedean and thermocapillary forces. The spatial motion of the fluid and the process of an admixture exchange between the surface and the volume in the Hele–Shaw cell are carried out in the plane of wide vertical boundaries of the cavity. This permits to simulate numerically and clearly visualize behaviour of the contaminants in multifarious fluid systems.

1. Introduction
The investigation and control in a practice of the origin and dynamics of contaminants in various liquid systems, related to the technological applications and natural phenomena, play an important role in human life. It is especially difficult to govern by the complex distributions of a molecular admixture in a liquid solution, if the contaminant is located as on the surface as in the volume of the matter. Actually, there are many technological problems of extraction and further removal of some molecular components from the matter in a physics, chemistry, biology, geology and engineering technologies. Sometimes the spreading of contaminant takes extremely bizarre form, which can have even the fractal nature. The complex structures are obtained as a result of self-organization in chemistry [1], environmental science [2,3], applied hydrodynamics [4,5] and so on. The most non-trivial problems take place in the case of mutual action of the surface effects and the volume phenomena [6-9] because the physical laws of the molecular substance behaviour in the volume and on the surface are differ for all liquids.

In this paper we consider the evolution of a soluble surface-active substance on the free boundary of a liquid matter and its following penetration into the volume due to the process of desorption. The hydrodynamic system is heated non-uniformly therefore the complex diffusive and convective mass transfer of an admixture takes place in the cavity. On the other hand, our cavity has a simple geometry, namely a thin vertical rectangular slot is used in the course of numerical simulation. This geometry permits to build theoretical model and at the same time to visualize experimentally the dynamics of the...
contaminant in a liquid. It is found that the creeping liquid jet, saturated by the admixture, can have the neutral buoyancy in the medium with an inhomogeneous temperature and this flow can keep a form like a concentration tongue for a long time.

2. Statement of the problem
The hydrodynamic system under consideration is composed of a vertical rectangular slot that is filled up with a liquid, which has the free upper boundary (figure 1). At the initial moment of time the uniform film of a heavy soluble surfactant is located at this boundary. The cavity is heated from above non-uniformly. Namely, the heat flux permeates the surface in such a way that it has a linear profile along the x-axis. When the height and width of the cavity are much more than the thickness one ($H, L \gg 2d$), it is called as a Hele – Shaw cell. This geometry is suitable for experimental methods of investigation and numerical calculations [10,11] because the stable regular and chaotic convective regimes with parallel trajectories to the wide sides are observed in such cavity in a broad range of governing parameters.

The heavy component, floating on the upper free boundary of the liquid, is surface-active and soluble substance. It can turn from the surface phase into the volume one and back as a result of processes desorption and adsorption.

Figure 1. Geometry of the problem. Coordinate system.

The heat- and mass transfer in a volume can be described by the following system of equations in Boussinesq approximation [12]:

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

(1)

$$\frac{\partial T}{\partial t} + (\mathbf{v} \cdot \nabla) T = \chi \Delta T,$$

(2)

$$\frac{\partial C}{\partial t} + (\mathbf{v} \cdot \nabla) C = D \Delta C,$$

(3)

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

(4)

where $\mathbf{v}$, $p$, $T$, $C$ are the fields of velocity, pressure, temperature and volume concentration, respectively; $\nu$, $\chi$, $D$ are the coefficients of kinematic viscosity, thermal diffusivity and diffusion, $\rho$ is the density of the fluid, $\beta_T$ and $\beta_C$ are the coefficients of thermal and concentration expansion, $g$ is the magnitude of gravity acceleration, $\gamma$ is the unit vector, directed vertically upward.
In addition to equations (1) – (4), the transfer of soluble surfactant along the free surface satisfies the equation of surface component [13]:

\[ \frac{\partial \Gamma}{\partial t} + \nabla \cdot (\mathbf{v} \Gamma) = D_s \Delta \Gamma + k_\text{s} C \left( 1 - \frac{\Gamma}{\Gamma_s} \right) - k_\text{d} \Gamma , \]  

(5)

where \( \Gamma(x, z, t) \) is the two-dimensional field of surfactant concentration, \( D_s \) is the coefficient of surface diffusion, \( k_\text{s}, k_\text{d} \) are the coefficients of adsorption and desorption. Index \( s \) under the symbols \( \nabla \) and \( \Delta \) (nabla and Laplace operators, respectively) means the differentiation on coordinates \( x \) and \( z \) in the plane of interface. Adsorption term in the equation (5) includes the mechanism of saturation of the surface concentration. Thus, the constant \( \Gamma_s \) corresponds to the concentration of saturation.

The lateral boundaries of the cavity are impermeable, so that:

\[ x = 0, L : \quad \frac{\partial \Gamma}{\partial x} = C \frac{\partial C}{\partial x} = 0 , \quad y = 0 : \quad \frac{\partial C}{\partial y} = 0 . \]

Temperature and velocity on the rigid boundaries are determined by the following conditions:

\[ x = 0, L, \quad y = 0 : \quad T = 0, \quad \mathbf{v} = 0 . \]

The conditions for temperature and concentration on the free boundary follow from the equation for the heat flux and mass conservation law:

\[ y = H : \quad \kappa \frac{\partial T}{\partial y} = A \left( 1 - \frac{x}{L} \right) , \quad -D \frac{\partial C}{\partial y} = k_\text{s} C \left( 1 - \frac{\Gamma}{\Gamma_s} \right) - k_\text{d} \Gamma , \]

\[ A \text{ and } \kappa \text{ are the characteristic heat flux and thermal conductivity.} \]

In the course of theoretical and experimental study [14], devoted to the dynamics of an insoluble surfactant in analogous statement, the characteristic concentration difference was extremely small that allowed to use the Gibbs isotherm in numerical simulation. In our case, the characteristic difference may be significant, so that more general isotherm must be taken. To solve our problem we use the Lengmuir isotherm:

\[ \sigma = \sigma_0 + RT \Gamma_s \ln \left( 1 - \frac{\Gamma}{\Gamma_s} \right) . \]

Here \( R \) is the ideal gas constant, \( \sigma \) is the surface tension in the presence of surfactant, \( \sigma_0 \) – surface tension of pure liquid. Thus, the balance of tangential stresses on the free boundary is:

\[ y = H : \quad \eta \frac{\partial \Gamma}{\partial y} = \sigma_0 \frac{\partial T}{\partial x} + RT \frac{\partial \Gamma}{\partial x} \ln \left( 1 - \frac{\Gamma}{\Gamma_s} \right) \frac{\partial T}{\partial x} - \frac{RT}{1 - \frac{\Gamma}{\Gamma_s}} \frac{\partial \Gamma}{\partial x} , \]

where \( \eta \) is the dynamic viscosity.

This problem is solved in the terms of non-dimensional variables. The units of length, time, velocity, temperature, pressure, volume and surface concentrations are taken as \( d, d^2/\nu, \chi/d, \Theta, \rho \nu g/d^2, C_0 \) and \( \Gamma_s \). Here \( C_0 \) is the initial volume concentration of surfactant. The non-dimensional system of equations has the following form:

\[ \frac{\partial \mathbf{v}}{\partial t} + \frac{1}{\text{Pr}} (\mathbf{v} \nabla) \mathbf{v} = -\nabla p + \Delta \mathbf{v} + (\text{Ra}_t T - \text{Ra}_c C) \mathbf{y} , \]

\[ \text{Pr} \frac{\partial T}{\partial t} + (\mathbf{v} \nabla) T = \Delta T , \quad \frac{\partial C}{\partial t} + \frac{1}{\text{Sc}} (\mathbf{v} \nabla) C = \frac{1}{\text{Sc}} \Delta C , \]

\[ \frac{\partial \Gamma}{\partial t} + \frac{1}{\text{Sc}_s} \nabla^2 (\mathbf{v} \Gamma) = \frac{1}{\text{Sc}_s} \Delta \Gamma + k_s C (1 - \Gamma) - k_d \Gamma , \]

where

\[ \text{Ra}_t = \frac{g \beta}{\nu} \frac{\rho_d d^3}{\chi} , \quad \text{Ra}_c = \frac{g \rho_c C_0 d^3}{\nu} , \quad \text{Pr} = \frac{\nu}{\chi} , \quad \text{Sc} = \frac{\nu}{D} , \quad \text{Sc}_s = \frac{\nu}{D_s} , \quad k_s = \frac{k_s C_d d^2}{\Gamma_s \nu} , \quad k_d = \frac{k_d d^2}{\nu} , \]
i.e. Ra_T, Ra_c are the thermal and concentration Rayleigh numbers, correspondingly; Pr, Sc are the Prandtl and Schmidt numbers, Sc_s is the surface analogue of Schmidt number, k, k_c are the coefficients of adsorption and desorption in non-dimensional form.

Corresponding boundary conditions in non-dimensional form take place:

\[ x = 0, \quad \frac{\partial \Gamma}{\partial x} = \frac{\partial C}{\partial x} = 0, \quad y = 0, \quad \frac{\partial C}{\partial y} = 0, \quad (6) \]
\[ x = 0, \quad \frac{\partial T}{\partial y} = 0, \quad y = 0: \quad T = 0, \quad \psi = 0, \quad (7) \]
\[ y = h: \quad \frac{\partial T}{\partial y} = a(1-x), \quad \frac{\partial C}{\partial y} = \text{Sc}(k_c C(1-\Gamma) - k \Gamma), \quad (8) \]

where l, h are the non-dimensional length and height of the cell; k = \Gamma_c/dC_s, a = dA/d\Theta.

The boundary problem under discussion is solved in the terms of stream function \( \psi \) and vorticity \( \varphi \):

\[ \nu_x = -\frac{\partial \psi}{\partial x}, \quad \nu_y = \frac{\partial \psi}{\partial y}, \quad \varphi = \frac{\partial \psi}{\partial y} - \frac{\partial \psi}{\partial x}. \]

The fields of stream function and temperature were expanded with the basis functions in accordance with the idea of Hele – Shaw approximation:

\[ \psi = \psi(x, y, t) \cos(\pi z/2), \quad T = \theta(x, y, t) \cos(\pi z/2). \]

After the exclusion of pressure we apply the procedure of averaging to the system of equations and write it in the final form:

\[ \frac{\partial \varphi}{\partial t} + \frac{8}{3\pi \text{Pr}} \left( \frac{\partial \psi}{\partial y} \frac{\partial \varphi}{\partial x} - \frac{\partial \psi}{\partial x} \frac{\partial \varphi}{\partial y} \right) = \frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} - \frac{\pi^2}{4} \varphi - \text{Ra}_\tau \frac{\partial \theta}{\partial x} + \text{Ra}_c \frac{\partial C}{\partial x}, \quad (9) \]
\[ \text{Pr} \frac{\partial \theta}{\partial t} + \frac{8}{3\pi} \left( \frac{\partial \psi}{\partial y} \frac{\partial \theta}{\partial x} - \frac{\partial \psi}{\partial x} \frac{\partial \theta}{\partial y} \right) = \frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} - \frac{\pi^2}{4} \theta, \quad \varphi = \Delta \psi, \quad (10) \]
\[ \frac{\partial C}{\partial t} + \frac{8}{3\pi \text{Pr}} \left( \frac{\partial \psi}{\partial y} \frac{\partial C}{\partial x} - \frac{\partial \psi}{\partial x} \frac{\partial C}{\partial y} \right) = \frac{1}{\text{Sc}} \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right), \quad (11) \]
\[ \frac{\partial \Gamma}{\partial t} + \frac{2}{\pi \text{Pr}} \frac{\partial}{\partial x} \left( \frac{\partial \psi}{\partial y} \Gamma \right) = \frac{1}{\text{Sc}_s} \frac{\partial^2 \Gamma}{\partial x^2} + k_c C(1-\Gamma) - k \Gamma. \quad (12) \]

The equation of the tangential stresses balance is

\[ \varphi = \text{Ma} \left( \ln(1-\Gamma) \frac{\partial \theta}{\partial x} - \frac{\partial \Gamma}{\partial t} \frac{1}{1-\Gamma} \right) - \text{Ma}_\tau \frac{\partial \theta}{\partial x}, \quad (13) \]

where Ma and Ma\_\tau are Marangoni numbers:

\[ \text{Ma} = \frac{\text{R} \Gamma_c \theta d}{\chi \eta}, \quad \text{Ma}_\tau = \frac{\sigma_c \Theta d}{\chi \eta}, \quad \sigma_c = -\frac{\partial \Gamma}{\partial T}, \quad \sigma_{\text{et}} = -\frac{\partial \sigma_c}{\partial T}, \]

\( \sigma_{\text{et}} \) – temperature non-uniformity of surface tension of the pure liquid.

3. Numerical procedure

The system of differential equations (9) – (12) together with the boundary conditions (6) – (8), (13) was solved numerically with the help of the finite difference method [15]. The algorithm was developed in accordance with the explicit scheme of solution the partial differential equations and was based on the two-field technique. The code was written using programming language Fortran-90. One-sided and central differences were used to approximate the derivatives with respect to the time and the coordinates, respectively. The time step was taken from the analysis of stability of the numerical procedure. The successive upper relaxation method was applied in the course of the solution the Poisson equation for the stream function. The evolution of concentration, temperature and velocity fields kept track during the calculations. The formulation of our problem admits the appearance of a concentration boundary layer, which resolvability demands to make the decomposition of the numerical grid. For aspect ratio \( L/H = 12/5 \) the working grid with the number of nodes 251 \times 169 was used in calculations with fixed size of the mesh along the coordinates \( x \) and \( y \). The water was chosen
as working liquid with heavy surface active component. Initial conditions were non-disturbed fields of stream function ($\psi = 0$), vorticity ($\varrho = 0$), temperature ($\vartheta = 0$), volume and surface concentrations ($C_0 = 1, \Gamma = 0.2$). Governing parameters had the following values: $Ra_T = 600$, $Ra_C = 1000$, $a = 0.011$, $k = 0.002$, $k_+ = 0.0017$, $k_+ = 0.013$, $Sc = 1500$, $Sc_S = 150$, $Pr = 7$.

![Figure 2](image2.png)

Figure 2. Convergence of the method: 1 – discrepancy for the total kinetic energy, 2 – discrepancy for the maximum of stream function.

Numerical procedure was carried out with the parallelization technology OpenMP, which increased the effectiveness by 20%. On the other hand the geometry of the problem is simple and it is not necessary to generate non-uniform numerical grid. The results of the analysis of numerical convergence are presented in the figure 2 for different values of the total nodes number $N = N_1 \cdot N_2$.

4. Results of calculation

In the process of surfactant transition along the interface under the influence of thermocapillary force, the surface-active component is accumulated nearby the “cold” narrow side of the cavity. It leads to the intensive penetration of the surfactant from the interface into volume. Thus, the desorption flux originates in the colder corner of the cell. Then admixture begins to move with the volume flow via the cavity to the “hot” lateral boundary of the cavity (figure 3, a-c). After that the contaminant transfers upward to the interface, depleted with surfactant. At the final stage, as a result of adsorption and transformation into the surface phase the heavy component again moves along the interface with the thermocapillary current.

In consequence of the surfactant desorption into the volume the concentration tongue originates in the liquid, which preserves its form notwithstanding to the conductive and convective diffusion. This mechanism is connected with a gradual cooling of the mixture during the downflow. The height of separation point depends on volume concentration of surfactant and intensity of the creeping flow. It should be noted, that convective pattern and corresponding field of concentration can be various in dependence on chosen surface-active component. In our case for the taken heavy surface-active substance, it is possible to find the conditions, for which concentration tongue has the neutral buoyancy (figure 3) and appears in a middle of the Hele – Shaw cell. In the case of chosen parameters the density of contaminant at this height is approximately equal to the density of surrounding liquid. This leads to predominantly horizontal transfer of surfactant in the direction to opposite side of the cavity. The velocity of admixture transfer in the volume is much smaller, than on the surface, nonetheless, at definite moment of time the heavy component reaches the “hot” lateral side. Then the contaminant is accumulated under the interface and becomes the adsorptive source of admixture from the volume onto the surface. According to the results of calculations, the system arrives to the steady state after the time $t = 30$ in non-dimensional units, that corresponds to approximately 120 s (figure 3d). Thus, the fields of stream function (figure 4a), vorticity, temperature (figure 4b) and
concentration are practically stationary. Only extremely weak diffusion bit by bit washes out this pattern.

![Figure 3](image3.png)

**Figure 3.** Fields of volume concentration for \( \text{Ma} = 1000, \text{Ma}_T = 3000; a-d \) \( t = 2, 10, 15, 30 \).

![Figure 4](image4.png)

**Figure 4.** Fields of stream function \((a)\) and temperature \((b)\) for \( \text{Ma} = 1000, \text{Ma}_T = 3000 \) at the time moment \( t = 30 \).

According to the surfactant profile in figure 5a and its comparison with the field of volume concentration the most part of the interface is depleted. Under the contamination region there are quite intensive concentration fluxes along the free surface, which can lead to formation of the concentration boundary layer. Its thickness can be estimated by the formula:

\[
\delta \sim \frac{1}{\sqrt{\text{Re} \cdot \text{Sc}}} = \frac{D}{\sqrt{\text{Re} \cdot \text{Sc} \cdot U}}
\]

where \( \text{Re} \) is the Reynolds number, \( U \) is the characteristic velocity, which was equal in calculations to \( U \sim 6 \cdot 10^{-4} \) m/s. Non-dimensional value of the layer thickness estimated as \( \delta \approx 0.3 \), what means, that 12 numerical nodes must correspond to concentration boundary layer.

This problem represents the generalization of the research [14] for insoluble surfactant, so that there can be analogous of stagnant point, dividing interface on two regions: free and covered by surfactant. As previous research demonstrated, in the vicinity of this point there must be a kink of temperature, velocity and surfactant profiles. After the passage along the free region, the velocity of a liquid under the surfactant film turns to be zero. However, the multiformity of surfactant properties leads to big amount of possible regimes. The small variation of parameters of the working fluid can
completely change preferable pattern of this system. The results of calculations show that there is no completely free region on the interface because of continuous adsorption of surfactant from the volume.

5. Conclusion
The behavior of a heavy soluble surfactant film on the surface of a non-uniformly heated liquid has been considered numerically. It is found that there are conditions, for which the concentration tongue

Figure 5. Profiles of surfactant concentration \((a)\) and velocity \((b)\): \(1 - \text{Ma} = 100, \text{Ma}_T = 300, 2 - \text{Ma} = 1000, \text{Ma}_T = 1000.\)

Figure 6. Profiles of temperature: \(1 - \text{Ma} = 100, \text{Ma}_T = 300, 2 - \text{Ma} = 1000, \text{Ma}_T = 1000.\)

In contrast to the problem with insoluble surfactant, the surface active component does not form a quasi-rigid film on the surface. In other words, there is quite intensive transfer of soluble surfactant along whole interface (figure 5\(b\)). As a consequence the profile of temperature does not have any kinks and almost linear (figure 6).
of neutral buoyancy originates in the volume of the cavity. As a result, the levitation of the concentration tongue is observed for a long time. The key role in this phenomenon belongs to the mutual action of thermocapillary force and desorption, which lead to the accumulation of heavy surfactant in the cold area of the interface and cause its consequent penetration into the volume. After the motion along the cold vertical wall downward, the surfactant cools and jointly equates the density with surrounding liquid. Near the middle of the vertical side of the cavity it changes the stream of the current, separates from the lateral boundary and begins to move in horizontal direction with the following accumulation nearby the opposite side. Some time later the surfactant partially again adsorbs on the surface and the steady state is settled.

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