A simplified nonlinear model of the Marangoni instability in gas absorption

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Abstract. The process of gas absorption into initially motionless liquid layer is investigated. The convective instability caused by the temperature dependence of the surface tension. The critical time of transition of the process to unstable convective regime, as well as the intensity of mass transfer in a surface convection are estimated numerically. The mathematical model includes the equations of convective diffusion, thermal conduction and fluid motion. The problem was solved numerically in the two-dimensional formulation. In the coordinate along the interface the concentration of the absorbed substance is represented by three terms of the trigonometric Fourier series. A difference approximation of equations with an exponentially changing grid in the direction normal to the interface is used. The simulations results agree with the well-known experimental data on the absorption of carbon dioxide in water.

Introduction

In the well-known experiments for the physical gas absorption by liquid layer the process goes in diffusion mode, only to a certain critical time, and then turn into more intense convective [1-3]. A linear stability analysis of the absorption process by frozen-time assumption was performed in [2, 4]. In order to estimate the intensity of mass transfer in the convective mode a semi-empirical formula was used in [3]. Critical time obtained by frozen-time assumption is a stationary point of the process, corresponding to the beginning of the joint growth of perturbations of concentration of absorbable material, temperature and velocity of the fluid. Transition of the process to convective mode occurs at a later time when the disturbances will reach the necessary intensity. For the process of carbon dioxide absorption in water the critical time [1, 3] exceeds a stationary point about 1000 times. In [5] it is shown that the reason for the long delay is the high viscosity of the fluid. Curently no available numerical estimates of the critical time and the intensity of mass transfer in a surface convection obtained without involving semiempirical hypotheses. The purpose of this paper is to construct a simplified non-linear model to assess these characteristics, as well as checking its adequacy by comparison with experimental data.

2.   The formulation of the problem. The main equations

We consider non-stationary process of gas absorption by initially fixed bed fluid of infinite thickness. The liquid interacts with the gas phase, wherein component *A* is contained. The component

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A is absorbed by liquid, its concentration in the gas phase is maintained constant, in the liquid phase, its concentration in the beginning of the process is c_∞. The main resistance to heat and mass transfer during the absorption is concentrated in the liquid phase. The liquid temperature at the beginning of the process is constant and equal T_∞. Convective instability caused by the temperature dependence of surface tension.

The absorption process in the presence of surface convection is described by a system of the equations of convective diffusion, thermal conductivity [9] and the motion of a viscous fluid [10]

$$\frac{\partial c}{\partial t} + \mathbf{v}\nabla c - D\Delta c = 0, \tag{1}$$

$$\frac{\partial T}{\partial t} + \mathbf{v}\nabla T - \chi\Delta T = 0, \tag{2}$$

$$\frac{\partial}{\partial t}\omega + (\mathbf{v}\nabla)\omega - \nu\Delta\omega = 0, \quad \omega = -\frac{\partial v_z}{\partial x} + \frac{\partial v_x}{\partial z}, \tag{3}$$

$$\nabla\mathbf{v} = 0, \tag{4}$$

where c is the concentration of component A in the liquid, T -temperature, $\mathbf{v} = (v_x, v_z)$ - vector of fluid velocity, D and χ are molecular diffusivity and thermal diffusivity, ν - kinematic viscosity of the fluid, t - time,

The problem is considered in a two-dimensional setting. The x coordinate is directed along the interface, the coordinate z – directed normal to the surface, the value z =0 corresponds to the gas-liquid interface. The boundary conditions for the system of equations (1) - (4) are as follows.

$$c = c_B, \quad D\frac{\partial c}{\partial z} = \Delta H\lambda\frac{\partial T}{\partial z}, \quad v_z = 0, \quad \rho\nu\frac{\partial v_x}{\partial z} = \varepsilon\frac{\partial T}{\partial x} \quad \text{for } z = 0. \tag{5}$$

$$\frac{\partial c}{\partial z} -> 0, \quad T = -> T_\infty, \quad v_x -> 0, \quad v_z -> 0 \quad \text{for } z = \infty. \tag{6}$$

where ΔH - specific heat of solution, $\lambda = \rho c_p\chi$ - thermal conductivity of the fluid, ρ - its density, c_p - specific heat capacity, ε - negative temperature coefficient of surface tension, c_B - equilibrium concentration of component A in the liquid corresponding to its partial pressure in the gas phase [11]: Initial conditions can be represented in the following form:

$$c(x,z,t) = c_\infty + f_c(x,z), \quad T(x,z,t) = T_\infty + f_T(x,z),$$
$$v_x(x,z,t) = f_{vx}(x,z), \quad v_z(x,z,t) = f_{vz}(x,z) \quad \textit{for } t = 0 \tag{7}$$

Zero values of the functions f_c, f_T, f_{vx}, f_{vz} correspond to the absorption process in a motionless liquid. The flux density of an absorbable material at the interface j is equal to:

$$j(x,t) = -D\frac{\partial c(x,z,t)}{\partial z}\big|_{z=0}, \tag{8}$$

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In the case of motionless liquid we have:

$$j^{(0)}(t) = (c_B - c_\infty)\left(\frac{D}{\pi t}\right)^{1/2};$$ (9)

where the superscript (0) corresponds to a stationary liquid.

The following approximation formulas for the stationary point time t_{st} and the corresponding wavenumber k_{st} are obtained in [4]

$$t_{st} = \pi(1 + 3\pi^{1/3}Le^{-1/3} + 12Le^{-2/3})t_*,$$ (10)

$$k_{st} = (2^{-1}\pi^{-2/3}Le^{1/6} - 0.7Le^{-1/6} + 0.9Le^{-1/2})z_*^{-1}.$$ (11)

Where $Le = \chi / D$ is Lewis number.

$$z_* = \frac{\lambda\rho\nu}{\varepsilon\Delta Hc_*}\left(\frac{\chi}{D}\right)^{1/2}; \quad t_* = \frac{1}{D}\left(\frac{\lambda\rho\nu}{\varepsilon\Delta Hc_*}\right)^2;$$ (12)

are characteristic length and time scales. As already mentioned, the time t_{st} corresponds to the beginning of the joint growth of perturbations in the absorption process.

3. A simplified nonlinear model.

Let us represent the instantaneous values of concentration, temperature and velocity as follows:

$$c(z,x,t) = c_0(z,t) + c_1(z,t)\cos(kx) + c_2(z,t)\cos(2kx)$$ (13)

$$T(z,x,t) = T_0(z,t) + T_1(z,t)\cos(kx) + T_2(z,t)\cos(2kx)$$ (14)

$$v_z(z,x,t) = v_1(z,t)\cos(kx) + v_2(z,t)\cos(2kx)$$ (15)

$$v_x(z,x,t) = v_{x1}(z,t)\cos(kx) + v_{x2}(z,t)\cos(2kx),$$
$$v_{x1} = \frac{-1}{k}\frac{\partial v_1}{\partial z}; \quad v_{x2} = \frac{-1}{2k}\frac{\partial v_2}{\partial z};$$ (16)

The wave number k is chosen to be 0.5 k_{st}. This choice of the wavenumber provides the most rapid growth in the second Fourier component of concentration.

The equations for all components of the velocity and temperature linearized. The nonlinearity considered only the equation of concentration. The equations of the model are as follows:

$$\frac{\partial c_0}{\partial t} - D\frac{\partial^2}{\partial z^2}c_0 = -\frac{1}{2}\frac{\partial}{\partial z}(v_1 c_1 + v_2 c_2).$$ (17)

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$$\frac{\partial c_1}{\partial t} - D(\frac{\partial^2}{\partial z^2} - k^2)c_1 = -\frac{1}{2}\frac{\partial}{\partial z}(2v_1 c_0 + v_2 c_1 + v_1 c_2) + c_0\frac{\partial v_1}{\partial z} - \frac{1}{2}c_2\frac{\partial v_1}{\partial z} + \frac{1}{4}C_1\frac{\partial v_2}{\partial z} \tag{18}$$

$$\frac{\partial c_2}{\partial t} - D(\frac{\partial^2}{\partial z^2} - 4k^2)c_2 = -\frac{1}{2}\frac{\partial}{\partial z}(2v_2 c_0 + v_1 c_1) + c_0\frac{\partial v_2}{\partial z} + c_1\frac{\partial v_1}{\partial z} \tag{19}$$

$$\frac{\partial T_0}{\partial t} - \chi\frac{\partial^2}{\partial z^2}T_0 = 0 \tag{20}$$

$$\frac{\partial T_n}{\partial t} - \chi\left(\frac{\partial^2}{\partial z^2}T_n + n^2 k^2 T_n\right) = -v_n\frac{\partial T_0}{\partial Z}; \quad n = 1,2 \tag{21}$$

$$\left(\frac{\partial}{\partial t} - v(\frac{\partial^2}{\partial z^2} - n^2 k^2)\right)(\frac{\partial^2}{\partial z^2} - n^2 k^2)v_n = 0, \quad n=1,2. \tag{22}$$

The initial conditions for zero Fourier components of the concentration and temperature are specified in the following form:

$$c_0(z,t) = c_\infty, \quad T_0(z,t) = T_\infty \quad for \ t = 0 \tag{23}$$

Concentration perturbation of different intensities and different spatial scales were set for non-zero components in the initial conditions,

$$c_n(z,t) = \begin{cases} \alpha_n(c_B - c_\infty) & for \ z < Z_n z_* \\ 0 & for \ z > Z_n z_* \end{cases} \quad for \ t = 0, \quad n = 1,2 \tag{24}$$

where α_n - intensities of disturbances, Z_n - their spatial scales in the direction normal to the surface. The initial perturbations of velocity and temperature are equal to zero

$$v_n(z,t) = 0, \quad T_n(z,t) = 0 \quad for \ t = 0, \quad n = 1,2 \tag{25}$$

4.   The simulations results

The simulations were performed for the case of *Le = 79, Pr = 7*, which corresponds to the absorption of carbon dioxide by water. Simulations were carried out using Matlab software. Exponentially varying mesh built on the z coordinate, Feldberg difference approximation is used [12, 13].

Traditionally, the data of non-stationary mass transfer at the gas-liquid interface are presented in the form according to the amount of the absorbed substance q versus the square root of time:

$$q(t) = \int_0^t j_0(t_1)dt_1, \qquad j_0(t) = -D\frac{\partial c_0}{\partial z}(t, z = 0), \tag{26}$$

where c_0, j_0 are zero Fourier components of concentration and flux density.
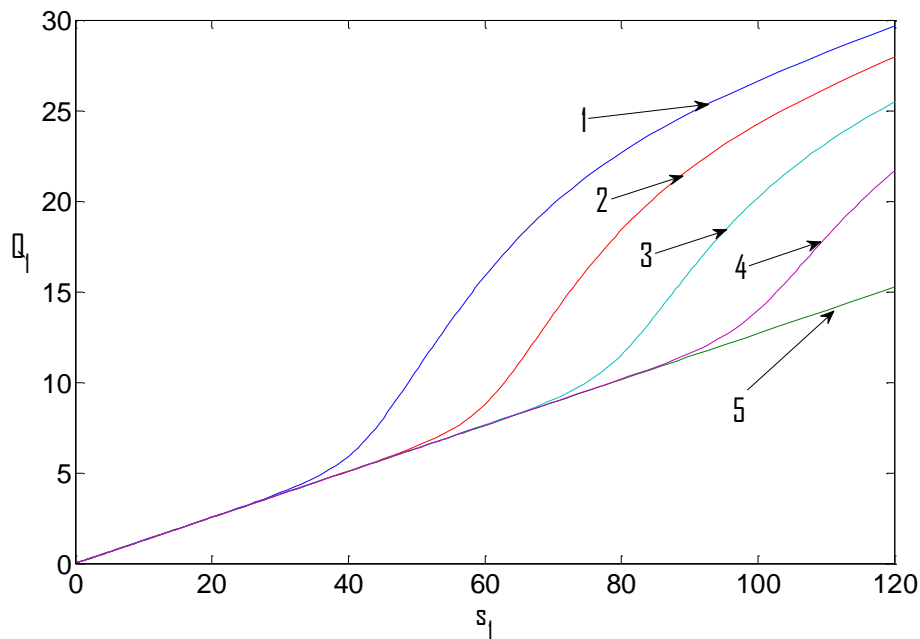
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Fig.1. The amount of adsorbed substance versus the square root of time. . $Z_1=Z_2=1$; 1 - $\alpha_1=\alpha_2=0.1$; 2 - $\alpha_1=\alpha_2=10^{-2}$; 3 - $\alpha_1=\alpha_2=10^{-3}$; 4 – $\alpha_1=\alpha_2=10^{-4}$; 5- mass transfer in the stationary liquid.

The results of simulations for different intensities of the initial perturbations are shown in Fig.1. The data are given in dimensionless variables:

$$Q_1 = \frac{q}{j_* t_*}; \quad s_1 = \sqrt{\frac{t}{t_*}} = \sqrt{\tau} \tag{27}$$

where

$$j_* = (c_B - c_\infty)(D/t_*)^{1/2} \tag{28}$$

is characteristic scale of flux density, the magnitude of t_* defined in (12). The moments of time when the amount of the absorbed substance under the conditions of surface convection begins to exceed the corresponding value in a stationary liquid are quite clearly visible in the chart. We define a critical time as the time at which the amount of absorbed substance under the conditions of surface convection exceeds the corresponding value for the motionless liquid on the threshold ε .

$$(Q_1 - Q_{1D})/Q_{1D} > \varepsilon \tag{27}$$

where Q_{1D} - amount of absorbed substance in a stationary liquid. The estimations of the critical time for various intensities of initial disturbances are represented in the Table 1.

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Table 1. Computational critical time.

The intensity of initial disturbances	Critical time t_{cr}	
	$\varepsilon=0.01$	$\varepsilon=0.1$
$\alpha_1 =\alpha_2 =0.1$, $Z_1=Z_2=1$	610 t_*	$10^3 t_*$
$\alpha_1 =\alpha_2 =0.01$, $Z_1=Z_2=1$	$2.2*10^3 t_*$	$3.2*10^3 t_*$
$\alpha_1 =\alpha_2 =0.001$, $Z_1=Z_2=1$	$4.1*10^3 t_*$	$6*10^3 t_*$
$\alpha_1 =\alpha_2 =0.0001$, $Z_1=Z_2=1$	$7.5*10^3 t_*$	$9.1*10^3 t_*$

Note that the time of stationary point is $t_{st}= 8.57 t_*$. As you can see, for the intensity of $\alpha_1=\alpha_2=0.1$ the critical time t_{cr} exceeds the stationary point t_{st} about 70 times for $\varepsilon = 0.01$ and about 120 times for $\varepsilon = 0.1$. Reducing the initial intensity 1,000 times the critical time estimation increases about 10 times, indicating its weak dependence of intensity on the initial perturbations. For the wide range of initial intensities the critical time is the same order of magnitude with the experimental value for the absorption of carbon dioxide, water, equal to 100 seconds, ie, about $6000 t_*$ [3].
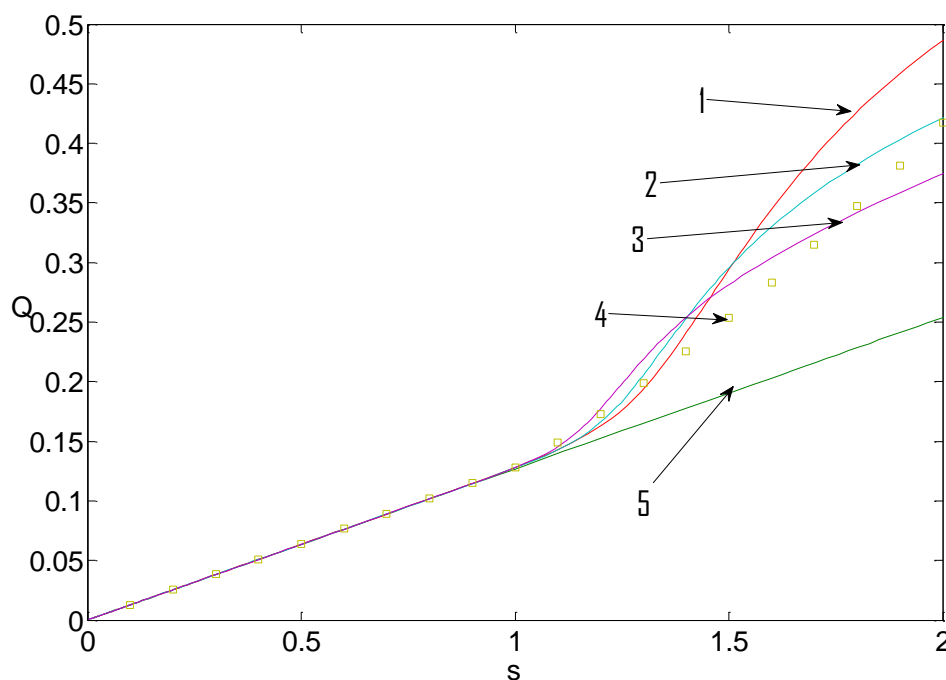

Fig.2. The amount of adsorbed substance depending on the square root of time. The data dimensionless on the critical time. $Z_1=Z_2=1$; 1 - $\alpha_1=\alpha_2=10^{-2}$; 2 - $\alpha_1=\alpha_2=10^{-3}$; 3 - $\alpha_1=\alpha_2=10^{-4}$; 4 - experimental data [3]; 5 - mass transfer in the stationary liquid.

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Let us represent data (26) dimensionless by the critical time calculated for $\varepsilon = 0.01$:

$$Q = \frac{q}{j_* \sqrt{t_* t_{cr}}}; \quad s = (t / t_{cr})^{1/2} \qquad (28)$$

Fig.2 shows the results of simulations for the initial disturbances with the intensity of 0.01 and below. The function Q (s) is weakly dependent on the initial conditions, the curves 1 and 3 correspond to the initial intensity of disturbances varies 100 times. Comparing with the well-known experimental data [3] shows that the function Q (s) qualitatively correctly describes the transition of the absorption process from diffusion to convective mode. On the chart you can see quite clearly that at a critical time (s = 1) the dependence of Q (s) is changing its functional. In the beginning of the convection mode, s <1.5, i.e. t <2t$_{cr}$, the numerical values of Q(s) are consistent with the experimental data [3].

5.   Conclusions

The simplified non-linear model agrees with the experimental data for the case of low intensities of initial perturbations of concentration. Accounting only three terms in Fourier series of concentration versus the coordinate along the interface one can correctly describe the intensity of mass transfer in the beginning of the convective regime.

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