CHEMICAL ENGINEERING TRANSACTIONS

VOL. 70, 2018

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Timothy G. Walmsley, Petar S. Varbanov, Rongxin Su, Jiří J. Klemeš
Copyright © 2018, AIDIC Servizi S.r.l.
ISBN 978-88-95608-67-9; **ISSN** 2283-9216

DOI: 10.3303/CET1870097

Thermocapillary Instability in the Nonstationary Process of Gas Absorption. Effect of Lewis and Prandtl Numbers on The Critical Time

Evgeny F. Skurygin*, Taras A. Poroyko

Yaroslavl State Technical University, Yaroslavl, Russia
skouryguine@rambler.ru

Theoretical analysis of the development of surface convection in the transient process of gas absorption by an initially motionless layer of liquid was carried out. The main resistance to mass transfer is concentrated in the liquid phase. Convective instability is caused by the temperature dependence of the surface tension. Linear analysis showed a strong dependence of the critical time on the viscosity of the liquid. On the basis of the simplified nonlinear model that does not use semi-empirical assumptions, approximate estimates of the critical time from physical characteristics are obtained. The problem was solved in a two-dimensional formulation. The concentration of the absorbed substance is represented as the sum of the three terms of the Fourier series on the coordinate directed along the gas - liquid interface. Equations for the temperature and the fluid velocity are linearized. Nonlinearity was taken into account only in the equations for concentration. The calculations are compared with known experimental data.

1. Introduction

Thermocapillary instability, also known as the Marangoni effect, is of interest in its ability to exert a strong influence on the mass transfer rate at the liquid-gas interface (Scriven et al., 1959). The latter has practical application for chemical-technological processes associated with the contact of liquid and gaseous phases (Nepomnyashchiy, 2002). The Marangoni effect is of practical importance in medicine and ecology, for example, in the processes of purifying gases from impurities; absorption of carbon dioxide by water, collection of organic liquids from the surface (Molder et al., 2002). Modern problems of air and water purification were discussed in work of Phang et al. (2017). The effectiveness of new solvents for absorbing CO_2 from the atmosphere was experimentally studied in (Ahmad et al, 2017).

The process of gas absorption in liquid proceeds in the diffusion regime only up to a certain critical time, after which it is replaced by more intense convective mode (Plevan, 1966). The problem is to determine the physical characteristics of the system under which the convective instability arises and to calculate the critical time for the transition of the process to the convective regime. Theoretical estimates of the mass transfer rate under conditions of thermocapillary convection (Dil'man et al., 1998) are applicable in a limited range of parameters.

The purpose of this paper is to estimate the critical time depending on physical characteristics on the basis of theoretical analysis and numerical simulation of the process.

2. Statement of the problem - basic equations

The transient process of gas absorption by an initially motionless layer of a liquid of infinite thickness is considered. The main resistance to mass transfer is concentrated in the liquid phase. Convective instability is caused by the temperature dependence of the surface tension. The process is determined by the following equations

Please cite this article as: Skurygin E.F., Poroyko T.A., 2018, Thermocapillary instability in the nonstationary process of gas absorption. effect of lewis and prandtl numbers on the critical time , Chemical Engineering Transactions, 70, 577-582 DOI:10.3303/CET1870097

$$\begin{aligned}&\frac{\partial c}{\partial t}+\mathbf{v}\nabla c-D\Delta c=0, \qquad \frac{\partial T}{\partial t}+\mathbf{v}\nabla T-\chi\Delta T=0,\\&\frac{\partial}{\partial t}\omega+(\mathbf{v}\nabla)\omega\ \text{-}\nu\Delta\omega=0, \quad \omega=\text{-}\frac{\partial v_z}{\partial x}+\frac{\partial v_x}{\partial z}\\&\nabla\mathbf{v}=0.\end{aligned} \tag{1}$$

where *c* is the concentration of the absorbed substance in the liquid, *T* is the temperature, *v = (*v_x*,* v_z*)* is the liquid velocity vector, *D* is the diffusivity*,* χ - the thermal diffusivity, ν - the kinematic viscosity of the liquid, and *t* is the time. The problem solved in a two-dimensional formulation. The coordinate x is directed along the liquid-gas boundary, z is directed deep into the liquid along the normal to the free surface, the value z = 0 corresponds to the interphase boundary.

The boundary conditions given in the following form:

$$\begin{aligned}&c=c_B, \quad \Delta HD\frac{\partial c}{\partial z}=\lambda\frac{\partial T}{\partial z}, \quad \mathrm{v}_z=0, \quad \rho\nu\frac{\partial \mathrm{v}_x}{\partial z}=\varepsilon\frac{\partial T}{\partial x} \quad for\ z=0.\\&\frac{\partial c}{\partial z}\to 0, \quad T\to T_\infty, \quad \mathrm{v}_x\to 0, \quad \mathrm{v}_z\to 0 \quad for\ \ z\ =\infty.\end{aligned} \tag{2}$$

where c_B is the equilibrium concentration at the liquid-gas interface, ΔH is the specific heat of dissolution, $\lambda=\rho c_p\chi$ - the thermal conductivity of the liquid, ρ - its density, c_p - the specific heat capacity, and the ε - temperature coefficient of surface tension.

The initial conditions are as follows:

$$\begin{aligned}&c(x,z,t)=c_\infty+f_c(x,z), \quad T(x,z,t)=T_\infty+f_T(x,z),\\&\mathrm{v}_x(x,z,t)=f_{vx}(x,z), \quad \mathrm{v}_z(x,z,t)=f_{vz}(x,z) \ \ for\ t=0\end{aligned} \tag{3}$$

The functions f_c, f_T, f_{vx}, f_{vz} represent the initial values of the perturbations of concentration, temperature, and fluid velocity.

3. Linear analysis

Let us represent the values of concentration, temperature and velocity as the sum of the unperturbed values, corresponding to diffusion into a stationary liquid, and a sinusoidally varying small perturbations

$$\begin{aligned}&c(\mathbf{r},t)=c^{(0)}(z,t)+c^{(1)}(z,t)\cos kx; \quad T(\mathbf{r},t)=T^{(0)}(z,t)+T^{(1)}(z,t)\cos kx;\\&v_z(\mathbf{r},t)=\mathrm{v}^{(1)}(z,t)\cos kx.\end{aligned} \tag{4}$$

The index (1) corresponds to a small perturbation; r is the radius vector, k is the wave number. Linearized equations for small perturbations and the corresponding boundary conditions have the following form

$$\begin{aligned}&\left(\frac{\partial}{\partial t}-D\Delta\right)c^{(1)}=-\mathrm{v}^{(1)}\frac{\partial c^{(0)}}{\partial z}, \quad \left(\frac{\partial}{\partial t}-\chi\Delta\right)T^{(1)}=-\mathrm{v}^{(1)}\frac{\partial T^{(0)}}{\partial z}, \quad \left(\frac{\partial}{\partial t}-\nu\Delta\right)\Delta\mathrm{v}^{(1)}=0,\\&\Delta=\frac{\partial^2}{\partial z^2}-k^2\end{aligned} \tag{5}$$

$$\begin{aligned}&c^{(1)}=0, \quad \rho c_p\chi\frac{\partial T^{(1)}}{\partial z}=\Delta HD\frac{\partial c^{(1)}}{\partial z}, \quad \mathrm{v}^{(1)}=0, \quad \rho\nu\frac{\partial^2\mathrm{v}^{(1)}}{\partial z^2}=k^2\varepsilon T^{(1)} \quad for \qquad z=0\\&\frac{\partial c^{(1)}}{\partial z}0 \quad \mathrm{v}^{(1)}\to 0 \quad \frac{\partial \mathrm{v}^{(1)}}{\partial z}\to 0 \quad \frac{\partial T^{(1)}}{\partial z}\to 0\ for\ z\to\infty,\end{aligned} \tag{6}$$

The method of "freezing" the time of the unperturbed solution is widely known in the linear analysis of nonstationary processes (Lick, 1965). According to the method, small perturbations vary in proportion to *exp(pt).* Solutions with Re *p*> *0* correspond to increasing, with Re p <0 - decaying, and with Re p = 0 - neutral or oscillatory perturbations. The method gives an underestimate of the critical time (Homsy et al, 1973), but the values obtained by this method have a fairly clear physical meaning. Neutral perturbations correspond to a stationary point of the perturbation amplitudes. Equations for perturbations at the stationary point are as follows:

$$(p - D\Delta)c_{st}^{(1)}(\mathrm{z}) = -\mathrm{v}^{(1)}{}_{st}(\mathrm{z})\frac{\partial c^{(0)}(\mathrm{t}_0,\mathrm{z})}{\partial z},\ \ (p - \chi\Delta)T_{st}^{(1)}(\mathrm{z}) = -\mathrm{v}^{(1)}{}_{st}(\mathrm{z})\frac{\partial T^{(0)}(\mathrm{t}_0,\mathrm{z})}{\partial z},\ \ (p - \nu\Delta)\Delta\mathrm{v}^{(1)}{}_{st}(z) = 0, \qquad (7)$$
$$\mathrm{Re}\,p = 0.$$

The time t_0 *(k)* at which the system of Eq(7) has nontrivial solutions corresponds to the termination of the damping and the beginning of the joint growth of the perturbations with the wave number *k*. We define the time t_{st} as the minimum value of t_0 *(k)* with respect to the wave numbers. The time t_{st} and the corresponding optimal wave number k_{st} can be represented in the following dimensionless form:

$$t_{st} = \tau_{st}(Le)t_*,\ k_{st} = K_{st}(Le)z_*^{-1},\ t_* = \frac{1}{D}\left(\frac{\lambda\mu}{\varepsilon\Delta H(c_* - c_\infty)}\right)^2,\ z_* = \frac{\lambda\mu}{\varepsilon\Delta H(c_* - c_\infty)}\sqrt{\frac{\chi}{D}} \qquad (8)$$

where $Le = \chi / D$ is the Lewis number, t_* and z_* are the characteristic scales of length and time.

For Le≥50, their numerical values with an error of not more than 5% are described by the following asymptotic approximation (Poroiko et al., 2013)

$$\tau_{st} = \pi(1 + 3\pi^{1/3}Le^{-1/3} + 12Le^{-2/3}),\quad K_{st} = (2^{-1}\pi^{-2/3}Le^{1/6} - 0.7Le^{-1/6} + 0.9Le^{-1/2}) \qquad (9)$$

In the case of absorption of carbon dioxide by water under normal conditions, the time of the stationary point is 0.15 s. The experimental time of transition of the process to the convective regime is 100 s. (Plevan, 1966). Let us consider the mechanism of such a long delay. The development of disturbances in the concentration of the absorbed substance, temperature and fluid velocity during absorption is determined by the competition between the forces of viscosity and surface tension. In the nonstationary process, the spatial scales of concentration, temperature and velocity increase, which leads to a decrease in the viscosity forces and, as is known, the process loses stability at a critical time. At times to a stationary point, $t<t_{st}$, the viscosity forces dominate, which lead to a decrease in the amplitude of velocity perturbations, and thus can delay the transition of the process to the convective regime. The approach of Poroyko et al. (2014) to analyze the transition of the process to the convective regime was used. The evolution of perturbations with wave numbers k_{st} passing through a stationary point is considered. Let us estimate the damping of such perturbations at times to a stationary point and their further development.

The problem for unperturbed values of concentration and temperature are solved together with Eq(5) and boundary conditions (6) for small perturbations. As an additional condition, we require passage of the perturbations through the stationary point:

$$c^{(1)}(z,t) = c_{st}^{(1)}(z),\quad T^{(1)}(z,t) = T_{st}^{(1)}(z),\quad \mathrm{v}^{(1)}(z,t) = \mathrm{v}^{(1)}{}_{st}(z)\quad for\ t = t_{st},\quad k = k_{st},\ p = 0 \qquad (10)$$

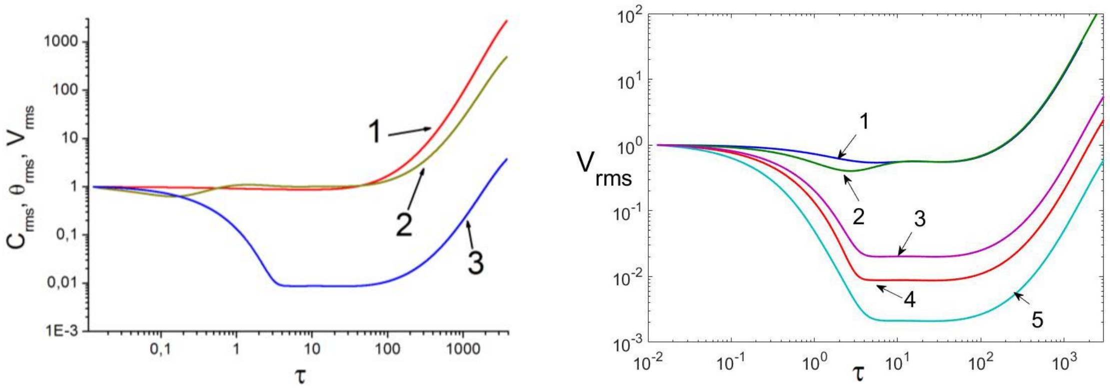
The solving of the equations for $t < t_{st}$ is an inverse problem for the evolution equations. The problem was solved by the method of selecting the initial conditions for $t = 0$. The latter are given in the form of linear combinations of Laguerre functions with coefficients determined from the requirement that conditions (10) be satisfied.

Figure 1(a) shows the numerical dependences of the root-mean-square values of the concentration C_{rms} temperature Θ_{rms}, and velocity V_{rms} perturbations versus time $t = \tau t_*$ for $Le = 79$, $\mathrm{Pr} = \nu / \chi = 7$. The data are presented in logarithmic coordinates.

In the time interval $\tau < \tau_{st}$, ($\tau_{st} = 8.57$), the intensity of the perturbation of concentration and temperature practically does not change, however, the intensity of the velocity perturbation sharply decays, its root- mean-square value decreases approximately 100-fold. The initial intensity of the velocity is restored at times approximately 2,000 t^*, which exceeds the time of the stationary point by about 250 times. The time of the stationary point corresponds to a pronounced minimum of velocity perturbations and cannot be the time of transition to the convective regime. The transition is possible only for many long times, when the perturbations reach the necessary intensity.

Let us note that such a strong attenuation of velocity perturbations and their long-term recovery is due to the high viscosity of the liquid; for the carbon dioxide-water system, the kinematic viscosity exceeds the thermal diffusivity by 7 times, and the diffusion coefficient by more than 500 times.

Figure 1(b) shows the time dependences of the root-mean-square velocity perturbations, raised for *Le = 79* and different values of the Prandtl number. With an increase in the Prandtl number, the intensity of velocity perturbations decreases, and the time of their restoration substantially increases. The latter allows us to conclude that the critical time for the transition of the process to the convective regime increases with increasing Prandl number.



(a) (b)

Figure 1: Intensity of disturbances as a function of time: (a) Pr=7, 1 – C_{rms}*, 2 -* θ_{rms}*, 3 -* V_{rms}*, (b) normal velocity perturbations, 1 – Pr=2, 2-Pr=4, 3-Pr=5, 4 - Pr=7, 5 - Pr=13*

4. Nonlinear analysis

Let us use the simplified nonlinear model (Skurygin et al, 2016) for an approximate estimate of the critical time. Let us represent the instantaneous values of concentration, temperature and velocity in the following form:

$$\begin{aligned}
&c(z,x,t) = c_0(z,t) + c_1(z,t)\cos(kx) + c_2(z,t)\cos(2kx)\\
&\mathrm{T}(z,x,t) = T_0(z,t) + T_1(z,t)\cos(kx) + T_2(z,t)\cos(2kx)\\
&\mathrm{v}_z(z,x,t) = \mathrm{v}_1(z,t)\cos(kx) + \mathrm{v}_2(z,t)\cos(2kx)\\
&\mathrm{v}_x(z,x,t) = \mathrm{v}_{x1}(z,t)\sin(kx) + \mathrm{v}_{x2}(z,t)\sin(2kx),\;\; \mathrm{v}_{x1} = \frac{-1}{k}\frac{\partial \mathrm{v}_1}{\partial z},\;\; v_{x2} = \frac{-1}{2k}\frac{\partial \mathrm{v}_2}{\partial z};
\end{aligned} \tag{11}$$

The wave number *k* was chosen equal to *0.5 k_{st}*. Such a choice of the wave number ensures the fastest growth of the second Fourier terms of the concentration and velocity. The equations for all terms of velocity and temperature are linearized. Nonlinearity is taken into account only in the concentration equations.

For zero Fourier terms of concentration and temperature, the initial conditions were given as for unperturbed values:

$$c_0(z,t) = c_\infty, \quad T_0(z,t) = T_\infty \quad for \;\; t = 0 \tag{12}$$

For nonzero Fourier terms of the concentration, the initial conditions were given as perturbations of various intensities and different spatial scales:

$$c_n(z,t) = \begin{cases} \alpha_n c_* & for\ z < Z_n \mathrm{z}_* \\ 0 & for\ z > Z_n \mathrm{z}_* \end{cases} \quad for\ t = 0, \quad n = 1,2 \tag{13}$$

Where α_n - the intensity of the perturbations, Z_n - their spatial scales in the direction normal to the surface. The perturbations of velocity and temperature at the initial instant were set to zero.

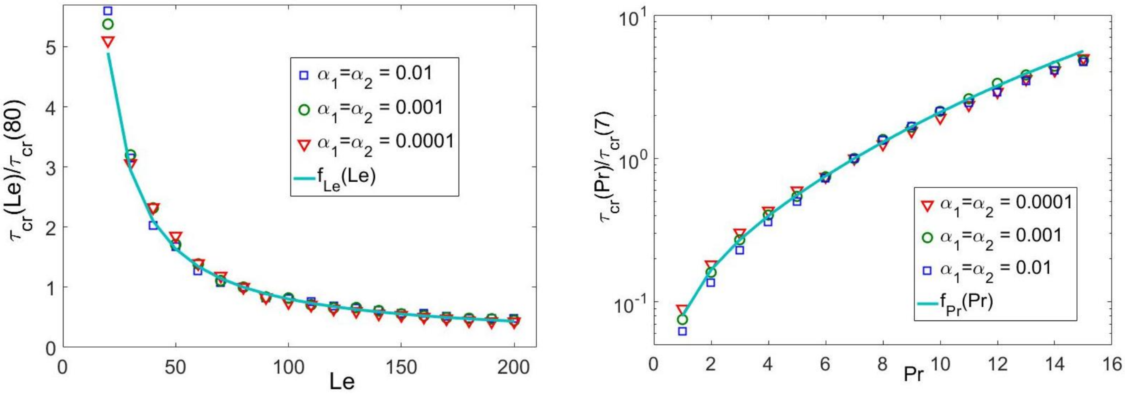
The critical time is defined as the time at which perturbations developing during the absorption process can be observed experimentally (Trouette et al, 2012). Let us define the critical time t_{cr} as the time at which the amount of absorbed substance under surface convection exceeds the corresponding value for a stationary liquid by 1 %.

$$t_{cr} = t_* \tau_{cr}(\mathrm{Pr}, Le, P) \tag{14}$$

where $P = (\alpha_1, Z_1, \alpha_2, Z_2)$ is a set of parameters characterizing the initial intensity of the perturbations.

Figure 2(a) presents the results of calculations of the critical time as a function of the Lewis number for *Pr = 7* and various initial intensities of the concentration perturbations. The data are normalized for a critical time at *Le=80*. Figure 2(b) shows the results of calculations of τ_{cr} as a function of the Prandtl number for *Le = 80* and the same initial perturbation intensities. The data are normalized to values at *Pr* = 7. The calculated values are aligned along the curves determined by the following formulas:

$$f_{Le}(Le) = 0.1 + 0.8\left(\frac{80}{Le}\right) + 0.1\left(\frac{80}{Le}\right)^2, \quad f_{\Pr}(\Pr) = 0.55\left(\frac{\Pr}{7}\right) + 0.45\left(\frac{\Pr}{7}\right)^3 \tag{15}$$



(a) (b)

Figure 2: Critical time functions (a) of the Lewis number and (b) of the Prandtl number. Results of the calculations. $Z_1 = Z_2 = 10/Le^{1/2}$

Calculations of the critical time, performed in the range 2 < Pr < 12, 20 < Le < 200 at the same initial perturbation intensities, showed that the function

$$f(Le, \Pr) = \frac{\tau_{cr}(Le, \Pr, P)}{\tau_{cr}(80, 7, P)} \tag{16}$$

weakly depends on the initial intensity of the perturbations. To calculate it, we can use the following approximate formula:

$$\begin{aligned} &f(\Pr, Le) = f_{Le}(Le) * f_{\Pr}(\Pr)[1 + \alpha(x-1) + \beta(y-1) + \gamma(x-1)(y-1)] \\ &\alpha = 0.05, \quad \beta = 0.17, \quad \gamma = 0.29; \quad x = \frac{80}{Le} \quad y = \frac{\Pr}{7} \end{aligned} \tag{17}$$

5. Comparison with known experimental data

Table 1 presents the known experimental data of the critical time and the results of calculations for the nonlinear model. For the case of CO_2 absorption by water at a temperature of 24.5 ^{0}C, we take the experimental value of the critical time of 100 s. Theoretical estimates for other systems were performed using Eq(17).

Table 1: Theoretical estimates and known experimental data

Solvent	t^*, s	Le	Pr	t_{cr}, s, experimental data		t_{cr}, s, Eq(17)
				value	reference	
water, 24.5 ^{0}C	0.0171	76.6	6.19	100	Plevan, 1966, Dil'man,1998, Tan, 1992	100
water, 18 ^{0}C	0.0155	88	7.45	120	Tan, 1992	115
toluen, 25 ^{0}C	2.06×10^{-4}	20.2	6.88	10.75	Sun, 2002	6.9
methanol, 25 ^{0}C	1.09×10^{-4}	27.6	6.80	9.13	Sun, 2002	2.4

The theoretical estimates are in agreement with the experimental data on the absorption of carbon dioxide in water and toluene. The underestimation of the critical time for the absorption of carbon dioxide in methanol is due the following factors. The solvent density changes during the absorption. Dissolution of carbon dioxide at a constant temperature leads to an increase in density. The released heat of absorption leads to an increase in the temperature of the solvent, and reduces the density. In this case, the density change caused by heating the liquid is greater than when the solute concentration is changed. Reducing the density in the upper layers of the solvent generates forces that impede surface convection. Due to the high equilibrium concentration of carbon dioxide and the high coefficient of thermal expansion of methanol, this effect becomes significant and delays the critical time.

6. Conclusions

The development of perturbations in the transient process of gas absorption is determined by two sharply differing time scales. The first is the time of the stationary point of the perturbation amplitudes, when the perturbations of the concentration cease to decay and begin to grow. The second is the critical time for the transition of the absorption process to the convective regime. Such a strong difference in time scales is due to the strong effect of the viscosity of the liquid on the critical time. Calculations using the simplified nonlinear model lead to approximate estimates of the critical time. For more accurate estimates, it is expected that more terms should be taken into account in the Fourier series of the concentration for the coordinate along the interface.

Reference

Ahmad M.Z., Hashim H., Yunus N.A., Lim J.C., Ho W.C., Ho C.S., 2017, A physical absorption assessment of a new alternative solvent for carbon capture, Chemical Engineering transactions, 56, 625-630.

Dil’man V.V., Kulov N.N., Lotkhov V.A., Kaminskii V.A., Naidenov V.I., 1998, On the difference in rates of absorption and desorption of gases, Theoretical Foundations of Chemical Engineering, 32, 337-346.

Homsy G.M., 1973, Global stability of time-dependent flows: impulsively heated or cooled fluid layers, J.Fluid Mech., 60, 129-139.

Lick W., 1965, The instability of a fluid layer with time-dependant heating, J. Fluid Mech., 21, 565-576.

Molder E., Tenno T., Mashirin A., 2002, The effect of surfactants on oxygenmass-transfer through the air-water interface, Environ. Sci. Pollut. Res., 9, 39–42.

Nepomnyashchy A., Velarde M.G., Colinet.P, 2002, Interfacial phenomena and convection, Chapman&Hall/CRC, New York, USA.

Phang F.A., Wong W.Y., Ho C. S., Musa A.N., 2017, Achieving low carbon society through primary school ecolife challenge in iscandar Malaysia, Chemical Engineering Transactions, 56, 415-420.

Plevan R.E., Quin J.A., 1966, The effect of monomolercular films on the rate of gas absorption into a quiescent liquid, AIChE Journal, 12, 894-902.

Poroiko T.A., Skurygin E.F., 2013, Effect of Thickness of Liquid Layer on Instability of absorption, Theoretical Foundations of Chemical Engineering, 47, 682-686.

Poroyko T.A., Skurygin E.F., 2014, On the Marangoni Instability in Gas Absorption, Journal of Physics: Conference Series, 495, 012033.

Scriven L.E., Sternling C.V., 1959, Interfacial turbulence: Hydrodynamic instability and the Marangoni effect, AIChE Journal, 5, 514-523.

Skurygin E.F., Poroyko T.A., 2016, A simplified nonlinear model of the Marangoni Instability in Gas Absorption, Journal of Physics: Conference Series, 710, 012036

Sun Z.F., Yu K.T., Wang S.Y., Miao Y.Z., 2002, Absorption and desorption of carbon dioxide into and from organic solvents: effects of Rayleigh and Marangoni instability, Industrial & Engineering Chemistry Research, 41, 1905-1913.

Tan K.K., Thorpe R.B., 1992, Gas diffusion into viscous and non-Newtonian liquids, Chemical Engineering Science, 47, 3565-3572.

Trouette B., Chenier E, Doumenc F, Declarte C, Guerrier B, 2012, Transient Rayleigh-Bernard – Marangoni solutal convection, Physics of Fluids, American Institute of Physics (AIP), 24, 074108.