MARANGONI INSTABILITY DURING ABSORPTION ACCOMPANIED BY CHEMICAL REACTION

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Abstract

Based on an extended model of Marangoni convection during absorption accompanied by chemical reaction certain characteristics of the process are studied. Thus, the probability of oscillatory modes occurring in the system is analysed, the dimensions of the convective cells are evaluated and the gas–liquid contact time necessary for the instability to appear is determined. The quantitative conclusions are compared with the reliant experimental data concerning the absorption of CO_2 into monoethanolamine in both wetted-wall and packed columns.

Keywords: absorption of CO_2 into monoethanolamine, Marangoni convection, Marangoni instability.

1. The Model

Cellular convection induced by the gradients of surface tension (Marangoni instability) may accompany a number of processes in which mass or heat are transferred between phases. A typical example is the absorption of carbon dioxide in the aqueous solutions of monoethanolamine (MEA), where the convection may lead to two- or threefold increase in the rate of mass transfer [1, 2].

A general model of the phenomenon taking place in a two-phase system represented schematically in *Fig. 1* has been proposed in [3, 4]:

$$\left[p - Sc \left(D^2 - \alpha^2 \right) \right] \left(D^2 - \alpha^2 \right) f(\eta) = 0 , \tag{1}$$

$$\left[p - \left(D^2 - a^2 \right) \right] g_1(\eta) = -f(\eta) , \tag{2}$$

$$\left[p - \left(D^2 - \alpha^2 \right) \right] h_1(\eta) = -\Psi f(\eta) + b g_1(\eta) , \tag{3}$$

$$\left[p - \left(D^2 - a^2 \right) \right] g_2(\eta) = 0 , \tag{4}$$

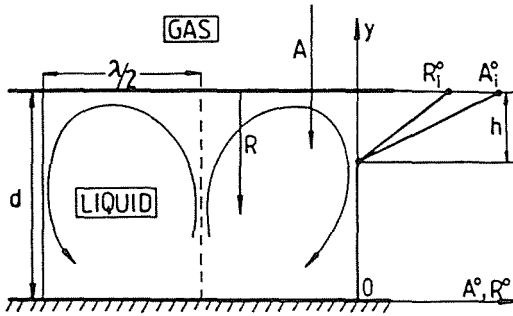$$\left[p - \left(D^2 - \alpha^2 \right) \right] h_2(\eta) = b g_2(\eta) . \tag{5}$$

Fig. 1. Schematic representation of cellular convection in a liquid layer of finite depth and the idealized unperturbed concentration profiles

The boundary conditions are:

$\eta = 0$:

$$f(0) = f'(0) = g_2'(0) = h_2'(0) = 0. \qquad (6)$$

$\eta = 1 - \varepsilon$:

$$g_1(1 - \varepsilon) = g_2(1 - \varepsilon), \qquad (7)$$

$$g_1'(1 - \varepsilon) = g_2'(1 - \varepsilon), \qquad (8)$$

$$h_1(1 - \varepsilon) = h_2(1 - \varepsilon), \qquad (9)$$

$$h_1'(1 - \varepsilon) = h_2'(1 - \varepsilon). \qquad (10)$$

$\eta = 1$:

$$f(1) = 0, \qquad (11)$$

$$f''(1) = Ma - \alpha^2 \left[g_1(1) + s - h_1(1) \right], \qquad (12)$$

$$g_1'(1) = - \left[Sh - \frac{\Phi}{\varepsilon}(p + b) \right] g_1(1) - \Phi f'(1), \qquad (13)$$

$$h_1'(1) = - \left(\frac{b - \Phi}{\varepsilon} \right) g_1(1) + p \left(\frac{\Phi - s}{\varepsilon} \right) h_1(1) - (s - \Psi - \Phi) f'(1). \qquad (14)$$

Eqs. (1)–(5) lead to a strongly non-linear characteristic equation

$$Ma = \frac{f''(1)}{\alpha^2 \left[g_1(1) + s - h_1(1) \right]}$$

in which the right-hand side is a function of α, p and the dimensionless parameters of the model: Sc, s, ε, b, Φ, Sh and Ψ (a complete form of this

equation is given in [3]). Relation (15) gives a condition for the existence of non-zero solutions to *Eqs.* (1)–(5) with respect to perturbations of velocity and concentrations, subject to boundary conditions (6)–(14). It therefore enables us to determine a set of such values of the dimensionless parameters which correspond to the onset of instability in the system analysed.

2. Oscillatory Instabilities

The possibility of oscillatory instabilities appearing during absorption of CO_2 into aqueous solutions of MEA was analysed based on the experimental data obtained in a wetted-wall column [1, 4].

The calculations were carried out using the characteristic *Eq.* (15). For the given experimental values of Sc, s, ε, b, Φ, Sh and Ψ the values of α and $\hat{p}$ were assumed, and then the Marangoni number was calculated for a series of values of $\tilde{p}$.

Complex values of p yield, in general, complex values of the right-hand side of *Eq.* (15): $Ma = \hat{M}a + i\tilde{M}a$. Only real values of Ma have, however, any physical significance. Thus, if $\tilde{M}a = 0$ only when $\tilde{p} = 0$, we deal with a stationary pattern of instability. If, on the other hand, meaningful values of Ma are found for $\tilde{p} -= 0$, cellular convection appearing in the system develops via oscillatory modes.
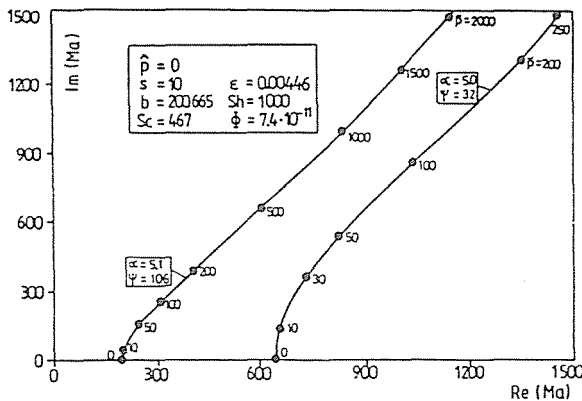

Fig. 2. Illustration of the stationary character of cellular convection accompanying the absorption of CO_2 in MEA

Fig. 2 shows the results obtained for Run 52 [1, 4]. The curves are typical of all the sets of the experimental data analysed: the only physically

justified values of Ma correspond to $\tilde{p} = 0$, and therefore, to the purely stationary nature of the phenomenon.

3. The Morphology of the Convection

For a given set of the dimensionless parameters Sc, s, ε, b, Φ, Sh and Ψ, the relation between α and Ma for $\tilde{p} = 0$ and the various values of $\hat{p}$ is shown in *Fig. 3* (the values of the dimensionless parameters are identical with those for the curve on the right-hand side of *Fig. 2*).
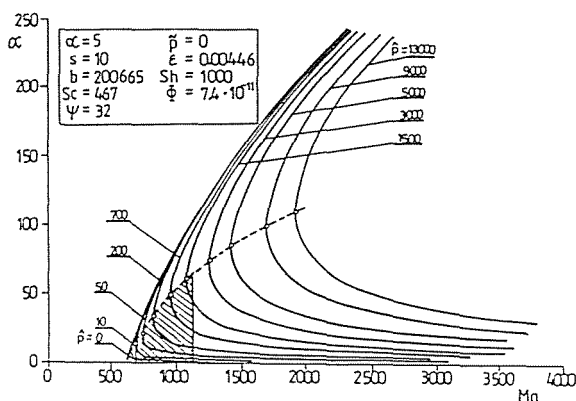

Fig. 3. Stability conditions and the size of the dominant convective cells (broken line) for the system CO_2-MEA. The shaded area denotes the values of Ma corresponding to the cell widths observed in [6] at the onset of convection ($\alpha = 13 - 63$)

This figure provides the most comprehensive description of the system within the framework of the linearized theory since, apart from indicating the onset of cellular convection (this moment corresponds to a minimum value of Ma at $\hat{p} = 0$), it enables us to follow the way the phenomenon develops as we move deeper into the region of instability. In particular, this graph makes it possible to analyse the changing morphology of the phenomenon with the progress of the absorption

According to ref. [6], concerning the absorption of CO_2 in the aqueous solutions of monoethanolamine on a flat wetted wall, a recognizable pattern was already apparent about $0.02\,s$ after CO_2 had been brought into contact with MEA. At this point the cell width was $\lambda = (0.1 - 0.5)d$, that is, the experimental wave number $\alpha = 2\pi d/\lambda$ was 13–63 and roughly agreed with the values predicted by the model in the region close to the onset of the

convection in the experiments presented in [1] (the shaded area in *Fig. 3*). As the solution flows farther down the wall, that is, as the concentration of MEA decreases, the convection gradually disappears and, obviously, its effect on the mass transfer rate becomes weaker [1, 2]. The experiments performed in [6] reveal that after about 0.1 s the value of α decreases to 3–6. A similar value is predicted by the model: the progressing depletion of the amine moves the system out of the instability region towards its boundary ($\hat{p} = 0$), where $\alpha \equiv 5$ (i.e., $\lambda = 0.3\,\mathrm{mm}$).

As may be seen from *Fig. 3*, an increase in Ma produces a dramatic decrease in the cell size; $Ma = 1250$ ($\hat{p} = 3000$) the dominant cell becomes as low as 0.02 mm.

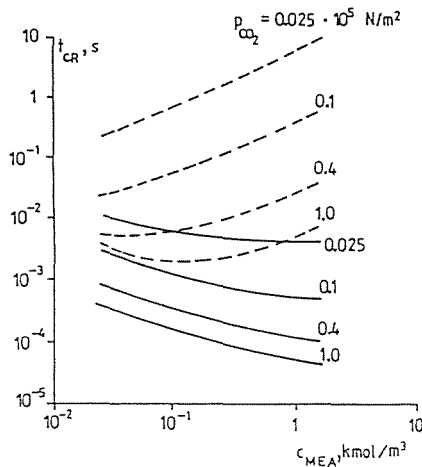## 4. The Gas–liquid Contact Time Necessary to Initiate the Convection

Fig. 4. Theoretical time necessary for the inception of instability in the CO_2-MEA absorption system. The broken lines show the maximum gas–liquid contact times for which the reaction may still be regarded as pseudo-first-order

The model developed makes it possible to determine the minimum theoretical time required for the Marangoni instability to manifest itself. The analysis of packed absorbers requires, however, a modification of the model, allowing for the possibility of the product of the reaction, R, appearing in the bulk liquid. Formally, the modification consists in substituting a new dimensionless number $\overline{\Psi}$ for Ψ in *Eq. (3)*. This new parameter is simply

a ratio of unperturbed concentration profiles of the product and of the reacting gas (CO_2).

Typical numerical results are presented in *Fig. 4*. As may be seen, for all the MEA concentrations analysed the duration of unsteady absorption required for the initiation of the phenomenon is very short (less than $0.01\,s$). This time decreases with increasing initial partial pressure of CO_2. It should be stressed that the maximum values of t_{CR}, predicted by the present model in [2], are of the same order of magnitude as those found experimentally in [6], where cellular convection was already apparent after about $0.02\,s$. Most probably, it started even earlier, but extremely small dimensions of the cells (below $0.02\,mm$) made direct visualization of the phenomenon impossible.

Notation

A, R	small perturbations of concentration of components A (carbon dioxide) and R (carbonated amine), $kmol/m^3$
A^0, R^0	unperturbed concentrations of A and R, $kmol/m^3$
$a = \overline{\alpha^2 + b^2}$	
$B_A = \dfrac{A^0_\infty - A^0_i}{h}$, $kmol/m^4$	
$D - \dfrac{d}{d\eta}$	
D_C	diffusion coefficient, m^2/s
d	liquid layer depth, m
$f(\eta), g(\eta), h(\eta)$	functions representing variation of v, A and R with η
H	Henry's law constant
h	penetration depth, m
$i = \overline{-1}$	
k	reaction rate constant, $1/s$
k_g	gas-phase mass transfer coefficient, m/s
$p = \widehat{p} + \tilde{p}i$	growth rate constant for disturbances
$R_g = 8314.4$	gas constant, $J/(kmol\ K)$
T	temperature, K
t	time, s
v	small velocity component in y direction, m/s
y	position coordinate normal to interface, m
$\alpha = \dfrac{2\pi}{\lambda}d$	wave number

$$\Gamma_A^0 = \frac{A_i^0 \sigma_A}{R_g T}$$

unperturbed surface concentration of A,

kmol/m^2

λ wavelength of disturbance, m

μ liquid viscosity, kg/(m s)

$v = \dfrac{\mu}{\rho}$ liquid kinematic viscosity, m^2/s

$\eta = \dfrac{y}{d}$

ρ liquid density, kg/m^3

σ_A, σ_R negative of slopes of curves of surface tension vs. concentration of A and R, (kg m^3)/(kmol s^2)

Dimensionless parameters of the model

$b = \dfrac{kd^2}{D_C}$ reaction rate constant

$Ma = \dfrac{\sigma_A B_A d^2}{\mu D_C}$ $\left(= -\dfrac{\sigma_A A_i^0 d}{\varepsilon \mu D_C} \text{ for } A_\infty^0 = 0 \right)$, Marangoni number

$s = \dfrac{\sigma_R}{\sigma_A}$

$Sc = \dfrac{v}{D_C}$ Schmidt number

$Sh = \dfrac{H k_g d}{D_C}$ liquid-to-gas phase resistance ratio

$\varepsilon = \dfrac{h}{d}$ penetration depth

$\Phi = \dfrac{\Gamma_A^0}{B_A d^2}$ $\left(= -\dfrac{\sigma_A \varepsilon}{R_g T d} \text{ for } A_\infty^0 = 0 \right)$, adsorption number

$\Psi = \dfrac{R_i^0}{A_i^0}$

$\overline{\Psi} = \dfrac{R_\infty^0 - R_i^0}{A_\infty^0 - A_i^0}$

Subscripts

CR   critical

i gas–liquid interface

—   bulk liquid

1 region of variable unperturbed concentrations of A and R
  $(1 - \varepsilon < \eta < 1)$
2 region of uniform unperturbed concentrations of A and R
  $(0 < \eta \leq 1 - \varepsilon)$

References

1. BUZEK, J.: Cellular Convection During Absorption with Chemical Reaction, *Zesz. Nauk. Politech. Śl.,* No. 90, Silesian Tech. Univ., 1979, p. 109 (in Polish).
2. PODKAŃSKI, J.: Effect of Cellular Convection on the Process of Chemical Absorption in Packed Columns. Ph. D. Thesis, Inst. Chem. Eng., Polish Acad. of Sci., Gliwice, 1990 (in Polish).
3. WARMUZIŃSKI, K. – TAŃCZYK, M.: Oscillatory Marangoni Instability during Absorption Accompanied by Chemical Reaction, *Chem. Eng. Sci.,* Vol. 46, p. 2031 (1991).
4. WARMUZIŃSKI, K. – TAŃCZYK, M.: Marangoni Instability during the Absorption of Carbon Dioxide into Aqueous solutions of Monoethanolamine, *Chem. Eng. Process.,* Vol. 30, p. 113 (1991).
5. WARMUZIŃSKI, K. – BUZEK, J.: A Model of Cellular Convection during Absorption Accompanied by Chemical Reaction, *Chem. Eng. Sci.,* Vol. 45, p. 243 (1990).
6. IMAISHI, N.– FUJINAWA, K.: An Optical Study of Interfacial Turbulence Accompanying Chemical Absorption, *Int. Chem. Eng.,* Vol. 20, p. 226 (1980).